UNIVERSITÉ DE SHERBROOKE
Faculté de génie
Département de génie mécanique

ÉLABORATION DE PHOTOCONDUCTEURS D'InGaAsP PAR IMPLANTATION D'IONS DE FER POUR DES APPLICATIONS EN IMAGERIE PROCHE-INFRAROUGE ET SPECTROSCOPIE TÉRAHERTZ

Thèse de doctorat
Spécialité : génie mécanique

André FEKECS

Jury : Richard ARÈS (directeur)
Paul G. CHARETTE (co-directeur)
Andreas RUEDIGER
Simon FAFARD
Nadi BRADY

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"Le cristal est sujet à plusieurs défauts: une
sorte de soudure raboteuse, des taches en
forme de nébulosité, quelque dépôt intérieur
qu'on n'y saurait soupçonner, quelque centre
ou noyau très dur et très cassant,
et ce qu'on appelle des grains de sel."

Pline L'Ancien, Histoire Naturelle,
Livre XXXVII, ch. X

RÉSUMÉ

Cette thèse décrit l'incorporation de fer dans l'hétérostructure InGaAsP/InP par implantation ionique à haute énergie (MeV) suivi d'un recuit thermique rapide. L'alliage quaternaire InGaAsP est tout indiqué pour fabriquer des couches photoconductrices qui peuvent absorber dans le proche-infrarouge, à 1.3 μm ou 1.55 μm. Ce procédé vise à développer de nouveaux matériaux de forte résistivité pour l'holographie photoréfractive et la spectroscopie térahertz pulsée. À notre connaissance, cette investigation représente les premiers essais détaillés de l'implantation de fer dans le matériau InGaAsP/InP. Les principaux paramètres de fabrication, tels la fluence d'ions de fer, la température d'implantation et la température de recuit ont été explorés. Les propriétés physiques des matériaux produits ont été étudiées avec des mesures électriques (résistivité et effet Hall avec l'analyse de Van der Pauw), optiques (photoluminescence, absorption et réflectivité différentielle résolue en temps) et structurales (diffraction de rayons X, canalisation de la rétrodiffusion Rutherford et microscopie électronique en transmission). Pour fabriquer des couches à forte résistivité pour des applications holographiques à 1.3 μm, nos résultats ont montré qu'il est préférable d'éviter l'amorce de l'amorphisation lors de l'implantation du quaternaire pour maintenir une bonne qualité cristalline après recuit. Ceci favoriserait une compensation par l'activation du fer comme impureté profonde. Une résistivité de l'ordre de 10^4 Ω·cm est mesurée après recuit. Pour fabriquer des couches à forte résistivité pour des applications de spectroscopie térahertz pulsée à 1.55 μm, nous privilégions l'amorphisation par implantation froide et la recristallisation, ce qui réduit le temps de recombinaison des photoporteurs sous la picoseconde. L'émission d'ondes térahertz par ce matériau est démontrée sur une largeur de bande de 2 THz. L'évidence expérimentale montre la formation d'une microstructure polycrystalline dans la couche d'InGaAsP, ayant une forte densité de fautes planaires et une taille de grains nanométrique qui varient avec la température de recuit, ce qui suggère une connexion avec les propriétés optoélectroniques du matériau.

Mots-clés : Photoconducteur, InGaAsP, implantation ionique, recuit rapide, défauts résiduels, effet Hall, temps de recombinaison, microstructure.

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CHAPITRE 1 Introduction

Tous les jours, nous tirons parti d'une grande variété de dispositifs photoniques qui opèrent dans le proche infrarouge, aux longueurs d'ondes de faibles pertes de la fibre optique. Ceci se produit, par exemple, lors d'un téléchargement de données à large bande sur notre téléphone ou notre ordinateur. Pour en arriver là, plusieurs matériaux photoniques ont dû être habilement perfectionnés. C'est ainsi que le composé semi-conducteur InGaAsP fut rapidement identifié à la fin des années '70 pour élaborer des transmetteurs lasers et des récepteurs opérant à 1.3 μm et 1.55 μm ou que le verre de silice dopé à l'erbium fut étudié, à la fin des années '80, pour développer les amplificateurs optiques à 1.55 μm. Le développement de ces deux matériaux s'appuient sur d'intenses recherches qui ont permis de bien comprendre leurs propriétés optiques, électroniques et structurales en relation avec leurs procédés de synthèse et de fabrication. Ces matériaux sont désormais omniprésents et font partie de la boîte à outils de l'ingénieur en optoélectronique.

Durant mes travaux de thèse, mon intérêt s'est porté particulièrement sur le composé quaternaire $In_{1-x}Ga_xAs_yP_{1-y}$ pour l'élaboration de nouveaux dispositifs photoniques. C'est un semi-conducteur à transition de bande directe où les porteurs libres ont une mobilité relativement forte due à une faible masse effective [Katz, 1991]. Une grande plage d'ajustement de l'énergie de la bande interdite (ou énergie de gap) est possible en contrôlant la fraction molaire (x et y) des éléments III et V du composé. La figure 1.1 montre la plage d'ajustement de l'énergie de gap de l'InGaAsP lorsque cet alliage est en accord de maille avec l'InP (a = 5.87 Å). La courbe en noir, tracée selon la loi de Vegard, montre l'énergie de gap qui varie linéairement, de 0.74 eV à 1.35 eV, en fonction de y, la fraction molaire de l'As [Mei, 2007]. Un résultat plus exact, tenant compte du « bowing », est tracé en vert selon l'expression donnée par Vurgaftman *et al.* (2001).

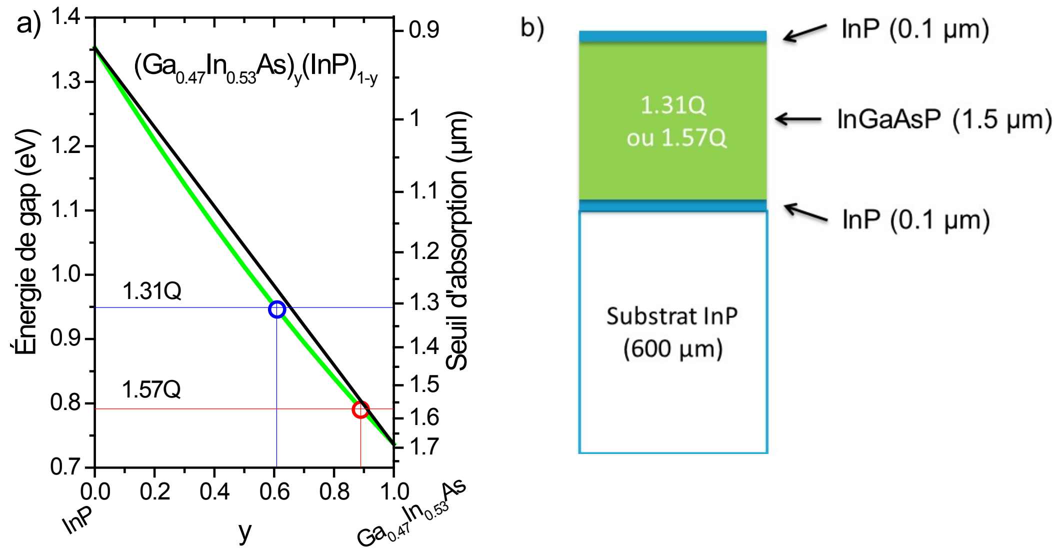

Figure 1.1 a) Énergie de gap E_g de l'alliage quaternaire InGaAsP, en accord de maille avec l'InP, calculée selon la loi de Vegard (en noir) et tracée en tenant compte du « bowing » (en vert). Les lignes verticales indiquent les compositions de l'alliage qui correspondent aux énergies de gap de 0.95 eV et 0.79 eV. En pratique, ces compositions sont dénotées 1.31Q et 1.57Q. Le nombre en suffixe est la longueur d'onde du seuil d'absorption optique de l'alliage, donné en µm. b) Une structure en couches minces d'InGaAsP/InP fabriquée au cours de cette thèse.

Le contrôle sur le seuil d'absorption optique ainsi que la bonne mobilité des porteurs rendent le composé InGaAsP attrayant pour élaborer des dispositifs photoconducteurs, car le principe de la photoconduction est basé sur l'excitation optique de porteurs de charges mobiles. Un exemple de couches minces photoconductrices produites par croissance épitaxiale est donné à la figure 1.1b). Dans la cadre de mes travaux, j'identifie deux nouvelles opportunités concernant le développement d'applications photoconductrices en couches minces qui opèrent à 1.3 µm et 1.55 µm. Celles-ci sont décrites brièvement ci-après.

1.1 Opportunité à 1.3 µm en imagerie en faible cohérence optique

L'imagerie en cohérence optique (*optical coherence imaging* - OCI) est une modalité d'imagerie des tissus biologiques [Nolte, 2012]. Cette modalité produit des images résolues en profondeur, *i.e.*, un plan situé à une certaine profondeur dans le tissu sous observation, grâce à une interférence en faible cohérence optique. Un bon contraste peut être obtenu malgré la diffusion multiple de la lumière car cette technique tire avantage d'une interférence

holographique en champ complet qui filtre la cohérence du signal rétrodiffusé par le tissu. Ce filtrage holographique, qui élimine les composantes diffuses indésirables, est obtenu dans un film photoconducteur spécialement conçu pour exploiter un effet photoréfractif rapide. Un tel dispositif est montré à la figure 1.2. Pour l'instant, les systèmes d'OCI opèrent dans le proche infrarouge avec des caméras CCD basées sur le silicium et des matériaux photoréfractifs développés pour une fenêtre spectrale centrée à 0.8 µm. Ces systèmes offrent des profondeurs d'imageries de l'ordre de 1 millimètre.

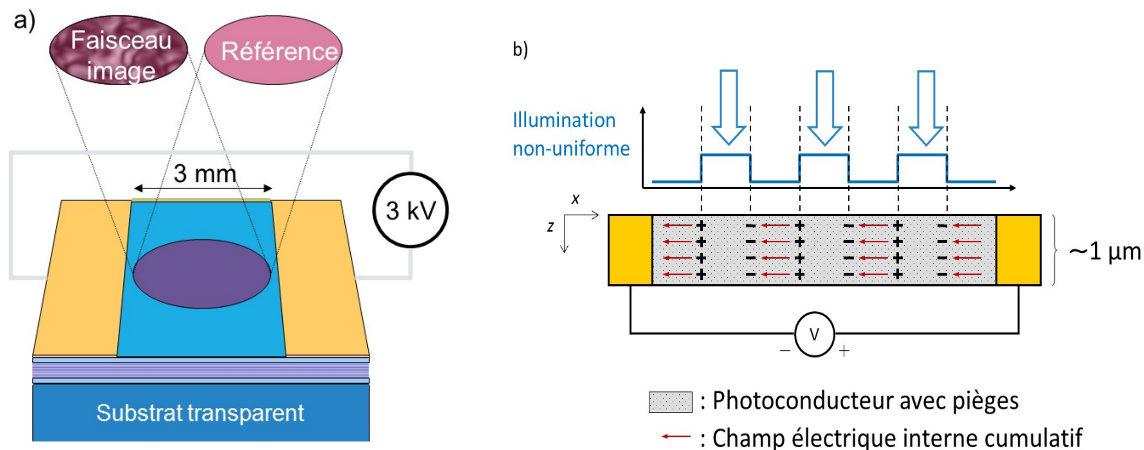

Figure 1.2 a) Dispositif photoréfractif utilisé pour l'écriture d'hologrammes dynamique en OCI. Le film photoréfractif a une épaisseur typique d'environ 1 µm et est installé sur un substrat transparent. b) En écriture, une illumination non uniforme génère une charge d'espace dans les pièges de la couche photoréfractive. L'hologramme est formé par l'entremise du champ électrique interne et de l'électro-réfraction du semi-conducteur.

L'imagerie en temps réel est possible en OCI [Dunsby *et al.*, 2003] et elle pourrait s'avérer fort utile pour fournir des données dynamiques à haute résolution sur la déformation mécanique de tissus mous. Déjà, des travaux ont montré qu'une mesure directe de la déformation est possible lorsque l'imagerie photoréfractive est couplée avec des techniques de shearographie [Rosso *et al.*, 2008]. Ainsi, avec des mesures dynamiques de déformation faites à haute résolution sur le muscle du myocarde chez de petits animaux, il serait possible d'améliorer les modèles biomécaniques de cet organe très complexe. Cependant, la profondeur d'imagerie requise pour un animal comme la souris demeure un problème majeur. Pour cet animal, le mur ventriculaire a une épaisseur de 1 mm à 1.2 mm et cette partie du muscle est située à une profondeur de quelques millimètres sous la peau [Zhou *et al.*, 2003].

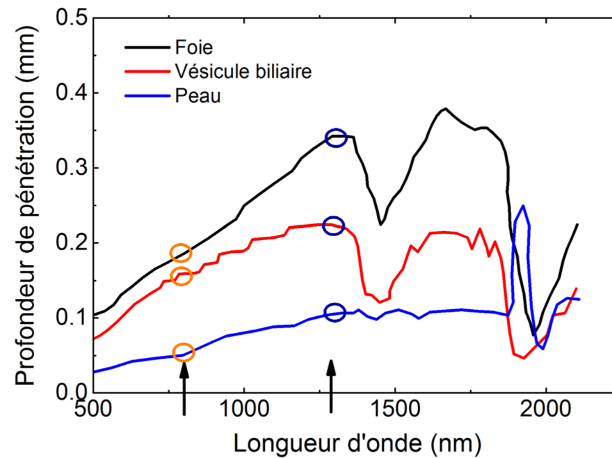

Figure 1.3 Calcul de la profondeur de pénétration de la lumière dans quelques tissus mous. Les longueurs d'ondes de 0.8 μm et 1.3 μm sont indiquées par des flèches. Données tirées de Sainter *et al.* (2004).

Un indicateur de la profondeur d'imagerie optique dans un milieu diffusant est la distance de libre parcours moyen de la lumière. Celle-ci varie en fonction de la longueur d'onde, selon les coefficients de diffusion et d'absorption du milieu. Pour la plupart des tissus mous, le libre parcours moyen de la lumière présente 3 fenêtres spectrales utiles (0.8 μm, 1.3 μm et 1.7 μm) séparées par quelques bandes d'absorption de l'eau. Comme le montre la figure 1.3, le libre parcours moyen augmente généralement avec la longueur d'onde. Cette tendance est due à une moindre diffusion optique quand la longueur d'onde augmente et est exploitée par d'autres techniques d'imagerie en faible cohérence optique [Kodach *et al.*, 2010].

La figure 1.3 suggère que différentes fenêtres spectrales sont disponibles pour obtenir des systèmes d'OCI potentiellement plus performants. Il s'avère donc pertinent d'élaborer de nouveaux photoconducteurs à effet photoréfractif rapide, centrés à 1.3 μm, pour que les systèmes d'OCI puissent opérer dans une deuxième fenêtre d'imagerie.

1.2 Opportunité à 1.55 μm en spectroscopie térahertz

Les ondes térahertz correspondent à une région du spectre électromagnétique étalée sur une plage de fréquences allant de 0.1 THz à 30 THz. L'exploitation de cette plage de fréquences par plusieurs méthodes de spectroscopie et d'imagerie offre de nouvelles perspectives d'applications, comme le contrôle de qualité de la production industrielle (pâtes et papier,

médicaments, puces microélectroniques) ou l'identification de différentes formes de cancers de la peau [Tonouchi, 2007]. Pour développer ces applications, nous nous intéressons de près à la spectroscopie « THz-TDS » (*terahertz time-domain spectroscopy*). Cette méthode optique utilise un laser infrarouge à impulsions ultracourtes d'une durée d'une centaine de femtosecondes environ, pour générer des transitoires de densité de photoporteurs dans un photoconducteur. Pour un émetteur photoconducteur, le champ térahertz, est produit par l'accélération de photoporteurs lorsqu'ils sont soumis à un champ électrique externe, comme l'illustre la figure 1.4.

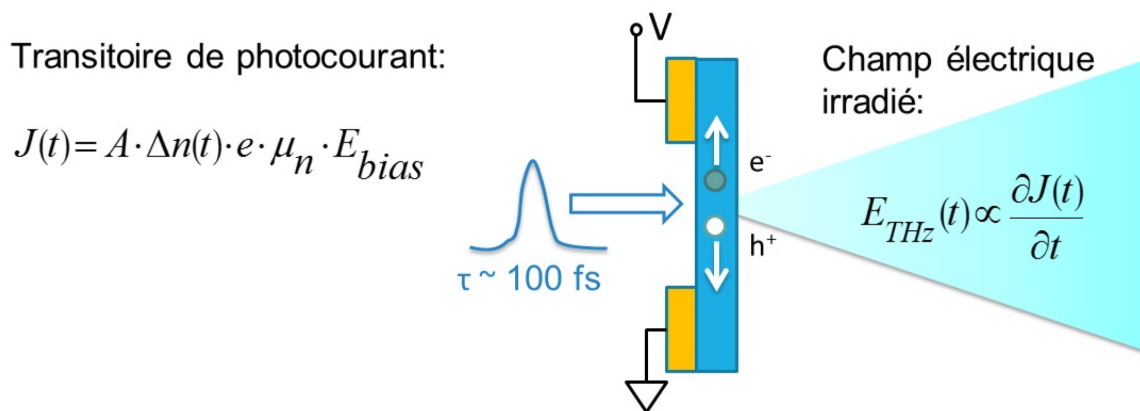

Figure 1.4 Principe de fonctionnement des émetteurs photoconducteurs pour la spectroscopie térahertz pulsée. Une impulsion optique d'une durée τ excite des paires électron-trou dans une couche photoconductrice (en bleu), d'une épaisseur de 1-2 μm. La production d'un photocourant $J(t)$ dépend de la densité des photoporteurs $\Delta n(t)$ excités, leur mobilité μ_n et du champ $E_{\text{bias}} = V/d$, appliqué sur les électrodes du dispositif. Les électrodes sont espacées d'une distance d, soit quelques dizaines de micromètres, pour appliquer des champs électriques élevés. L'amplitude du champ électrique émis $E_{\text{THz}}(t)$ dépend de la variation temporelle du photocourant dipolaire $J(t)$.

Il s'avère nécessaire que les montages de THz-TDS demeurent compacts, portables et très robustes aux perturbations de l'environnement. En ce sens, l'utilisation de lasers à fibre et de composantes optiques externes fibrées offre de bonnes perspectives d'intégration. Ces oscillateurs lasers utilisent une cavité formée par une fibre optique dopée à l'erbium pour émettre des impulsions ultracourtes à haut taux de répétition avec un spectre centré à 1.55 μm. Avec ces nouveaux montages, l'émission et la détection d'ondes térahertz requiert des photoconducteurs ultrarapides qui peuvent absorber à 1.55 μm. Depuis une dizaine d'années,

plusieurs groupes de recherche ont proposé des photoconducteurs ultrarapides pouvant opérer à cette longueur d'onde [Chimot *et al.*, 2005; Driscoll *et al.*, 2005; Kuenzel *et al.*, 2008; Suzuki et Tonouchi, 2005a; Takazato *et al.*, 2007; Wood *et al.*, 2010; Zhang 2015]. Ils sont généralement basés sur le composé ternaire $In_{0.53}Ga_{0.47}As$. Cependant, peu de solutions sont offertes commercialement. Les structures multicouches $In_{0.53}Ga_{0.57}As/In_{0.52}Al_{0.48}As$ sur substrat d'InP sont performantes, mais demandent une recette de croissance épitaxiale assez complexe avec alternance de basse et haute températures de croissance [Dietz *et al.*, 2011; Kostakis *et al.*, 2012]. D'autre part, les monocouches $In_{0.53}Ga_{0.57}As$ fabriquées par croissance épitaxiale à basse température sont plus simples à réaliser mais souffrent de faible résistivité [Kunzel *et al.*, 1992]. Une forte résistivité est nécessaire afin de réduire l'échauffement par effet Joule lorsqu'une polarisation externe est employée pour maximiser l'émission térahertz. Notons aussi qu'une forte résistivité favorise aussi une réduction de bruit en détection.

Puisque le gap de l'InGaAsP peut être ajusté pour absorber à 1.55 µm, nous proposons d'utiliser une monocouche d'InGaAsP sur substrat d'InP comme point de départ pour la réalisation d'émetteurs photoconducteurs ultrarapides et résistifs pour la spectroscopie térahertz.

1.3 Problématique

Les semi-conducteurs semi-isolants sont des matériaux prisés pour leur grande résistivité, leur forte densité de défauts ainsi que leur court temps de vie de porteurs. Ces matériaux constituent fréquemment la couche active d'un élément photoréfractif pour l'holographie dynamique ou d'un émetteur photoconducteur ultrarapide pour la spectroscopie THz pulsée [Nolte, 1999]. On retrouvera à l'annexe A1 un tableau montrant les similitudes entre ces deux dispositifs et les caractéristiques des couches semi-isolantes qui les composent.

Pour développer ces dispositifs, notre problématique consiste à produire un alliage quaternaire InGaAsP ayant un caractère semi-isolant. Cependant, ce caractère n'est pas présent lorsque le composé est fabriqué dans des conditions normales de croissance épitaxiale. En effet, une couche cristalline d'InGaAsP sans dopage intentionnel offre une densité de porteurs libres, de type n, de l'ordre de 10^{15} à 10^{16} cm^{-3}. Puisque la mobilité des électrons est de l'ordre de

10^3 cm^{2}V^{-1}s^{-1}, sa résistivité est faible (0.1-1 Ω·cm). Le temps de vie des porteurs est aussi généralement long, de l'ordre de quelques centaines de nanosecondes, due à une faible densité de centres de recombinaison.

1.3.1 InGaAsP semi-isolant et ingénierie des défauts

Un semi-conducteur devient semi-isolant si les porteurs libres majoritaires sont compensés de telle manière que le niveau de Fermi se positionne vers le milieu de la bande interdite [Nolte, 1999]. La compensation des impuretés non intentionnelles de type n par l'ajout d'impuretés de type p est possible mais elle est difficile à contrôler et elle n'aurait que peu d'effet sur le temps de vie des porteurs. Généralement, une compensation contrôlée est obtenue en présence de défauts qui forment des niveaux profonds dans la bande interdite. Ces défauts profonds agissent efficacement pour piéger les porteurs libres (ce qui résulte aussi à des temps de vie réduits) et bloquent le niveau de Fermi vers le milieu de la bande comme l'illustre la figure 1.5.

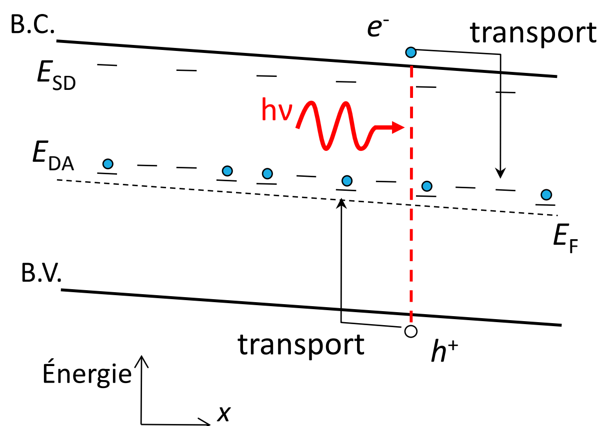

Figure 1.5 Diagramme de bande d'un matériau photoconducteur basé sur un semi-conducteur semi-isolant pouvant absorber efficacement à l'énergie $E = h\nu$. Ce diagramme illustre la compensation de donneurs peu profonds ionisés, situés à l'énergie E_{SD}, en présence de niveaux accepteurs profonds, situés à l'énergie d'ionisation E_{DA}. Le niveau de Fermi E_F est bloqué vers le milieu de la bande, légèrement sous E_{DA}. Ce diagramme illustre aussi le mécanisme génération de photoporteurs, leur transport et leur recombinaison dans les pièges.

L'ingénierie des défauts se fait en introduisant des défauts cristallins ou des défauts chimiques dans le cristal semi-conducteur. Pour l'InP et les composés semi-conducteurs à petits gap

apparentés à l'InP, tels que $In_{0.53}Ga_{0.47}As$ et $In_{1-x}Ga_xAs_yP_{1-y}$, les niveaux d'énergie des défauts ponctuels (*i.e.* des lacunes, des antisites, *etc.*) sont situés assez près de la bande de conduction et tendent à ressembler à des donneurs [Pearton et Chakrabarti, 1991]. Ceci peut être expliqué par l'énergie de stabilisation du niveau de Fermi E_{FS}, une propriété intrinsèque de plusieurs matériaux semi-conducteurs. Lorsqu'un semi-conducteur est fortement endommagé, par irradiation ou implantation, le niveau de Fermi tend à se stabiliser à l'énergie moyenne des états associés aux liaisons pendantes. [Nolte, 1999].

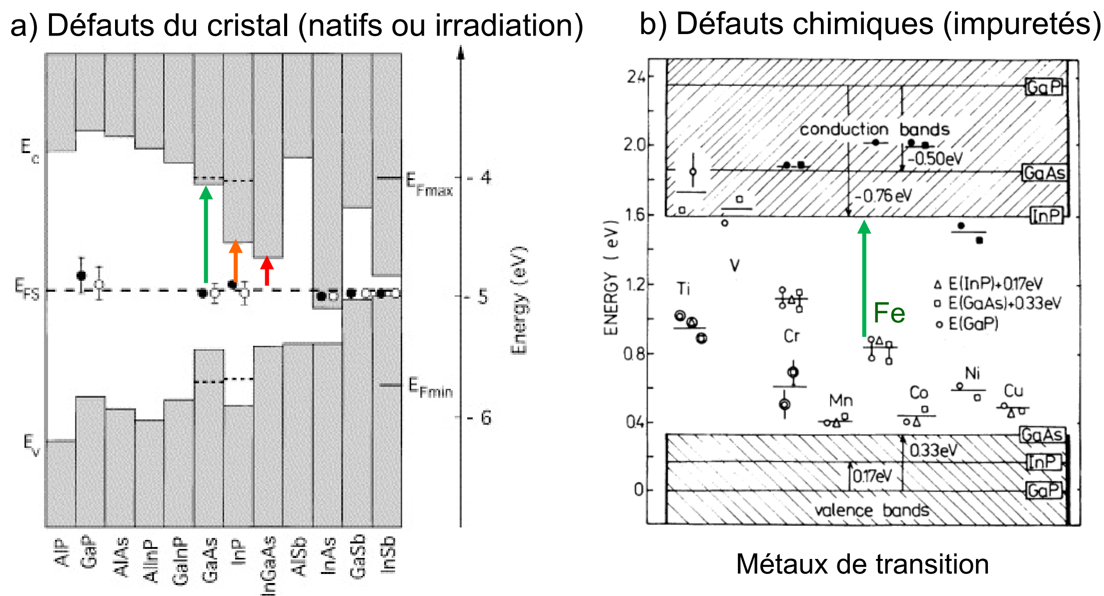

Figure 1.6 a) Alignement de bande et énergie de stabilisation du niveau de Fermi E_{FS} (symboles pleins) pour divers composés semi-conducteurs III-V. Des flèches indiquent E_{FS} pour le GaAs, l'InP et l'$In_{0.53}Ga_{0.47}As$. Figure reproduite de Walukiewicz (2001). « Copyright 2001, with permission from Elsevier » b) Énergie d'ionisation des niveaux profonds produits dans le GaP, l'InP et le GaAs par des métaux de transition de la période 4 du tableau périodique. Les symboles ouverts indiquent un niveau accepteur, les symboles pleins indiquent un niveau double accepteur et les symboles encerclés indiquent un niveau donneur. Figure reproduite avec permission de Langer *et al.* (1988), « Copyright 1988 by The American Physical Society ».

Pour l'$In_{0.53}Ga_{0.47}As$, la figure 1.6(a) montre qu'à 300 K, E_{FS} est située assez près de la bande de conduction, environ à E_C-0.26 eV. Pour l'InP, E_F se situe environ à E_C-0.4 eV. Ces valeurs sont donc de l'ordre de E_C-E_g/3. On peut s'attendre à des valeurs semblables pour l'alliage quaternaire InGaAsP, ce qui signifie une difficulté pour compenser cet alliage de petit gap

avec des défauts cristallins natifs ou obtenus par bombardement ionique. Néanmoins, il est possible d'obtenir un meilleur caractère semi-isolant en optant pour des défauts « chimiques » plus profonds et fortement localisés. La méthode la plus répandue consiste à doper les semi-conducteurs avec des métaux de transition afin de former des niveaux profonds, des accepteurs ou donneurs, selon l'atome choisi [Langer *et al.*, 1988]. Ainsi, lorsque le fer est substitutionnel sur un site de groupe III dans un composé III-V, la transition Fe^{3+}/Fe^{2+} forme un niveau accepteur profond, tel que montré à la figure 1.6(b).

Plusieurs travaux portant sur la croissance épitaxiale d'InGaAsP sur InP ont montré qu'il est possible d'obtenir des couches semi-isolantes par dopage avec des impuretés de fer en utilisant des sources élémentaires ou organométallique [Knight *et al.*, 1992; Kondo *et al.*, 1988; Pagnod-Rossiaux *et al.*, 1993]. Toutefois, avec la croissance d'InGaAsP:Fe, une accumulation de composés de Fe sur les murs et les lignes du bâtit pourrait causer des « effets de mémoire » entre les séquences de croissance. C'est le cas pour la croissance de GaN:Fe où certains effets de mémoire ont été documentés [Heikman *et al.* 2002]. Il ne serait donc pas toujours souhaitable d'opérer une source de Fe, par exemple lorsqu'un seul bâtit d'épitaxie est disponible.

1.3.2 Fabrication en post-croissance par implantation et recuit

Il est possible, cependant, d'incorporer les impuretés de fer dans l'InGaAsP avec l'implantation ionique. L'implantation est un procédé en post-croissance qui comporte de nombreux avantages sur toute autre technique d'introduction d'impuretés. La distribution en profondeur des impuretés est bien contrôlée par l'énergie des ions du faisceau. La quantité totale d'impureté introduite peut être facilement mesurée par le courant du faisceau d'ion. De plus, l'implantation permet de dépasser la limite de solubilité solide des impuretés introduites [Favennec, 1993].

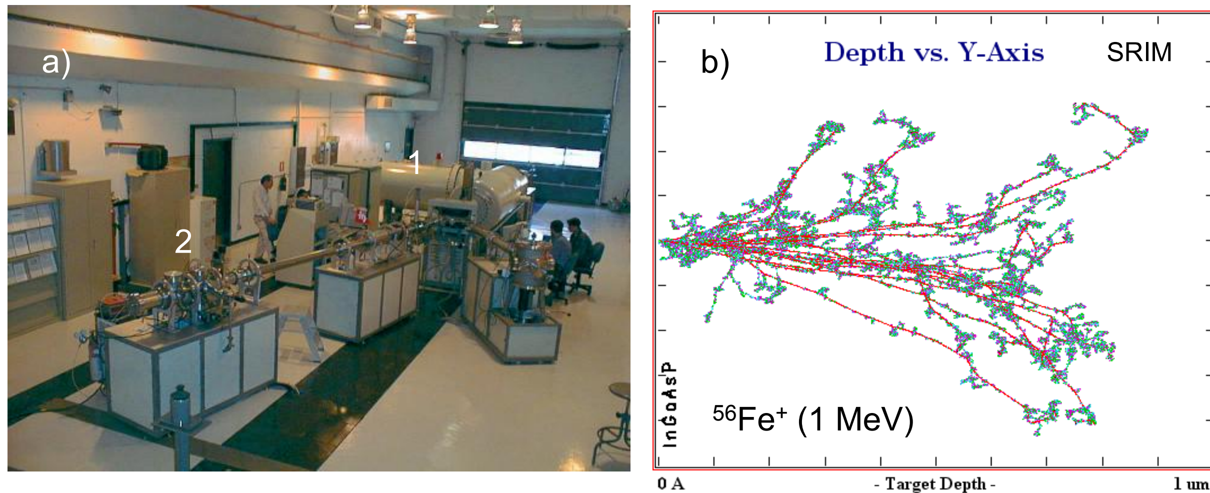

Figure 1.7 a) Photographie de l'accélérateur Tandetron 1.7 MV (HVEE) de l'Université de Montréal indiquant l'accélérateur tandem (1) et la chambre d'implantation (2). b) Simulations SRIM de trajectoires d'ions de Fe de 1 MeV et du dommage causé par le bombardement dans une couche d'InGaAsP [Ziegler *et al.*, 1985].

Pour doper au ^{56}Fe des couches d'InGaAsP ayant des épaisseurs de 1 à 1.5 μm, des énergies de quelques MeV sont requises. Celles-ci peuvent être produites avec un accélérateur à haute énergie de type tandem, tel qu'illustré à la figure 1.7(a). Cependant, l'incorporation d'impuretés est toujours accompagnée par une production de défauts structuraux. Lorsqu'un atome de masse élevée comme le ^{56}Fe entre en collision avec les atomes du cristal hôte, la cascade de reculs atomiques qui s'en suit peut résulter en amas de défauts et en poches amorphes ou en amas de défauts ponctuels, selon que la température d'implantation soit basse ou élevée [Wendler *et al.*, 1997; Wendler, 2009]. La simulation de la figure 1.7(b) illustre bien l'importance du dommage causé par quelques ions de Fe qui bombardent une couche mince d'InGaAsP. Puisque ces défauts nuisent à la mobilité des porteurs libres et nuisent à la compensation du matériau s'ils ne sont pas assez profonds, une méthode de guérison de défauts est nécessaire. Pour notre étude, nous appliquons la technique du recuit thermique rapide (RTA - *rapid thermal annealing*) [Timans 1998]. Les recuits rapides servent à guérir les défauts primaires d'implantation, à activer électriquement les impuretés tout en minimisant leur redistribution dans l'hétérostructure. Si le dommage d'implantation est assez sévère pour induire l'amorphisation du matériau, le recuit rapide sert aussi à le recristalliser. Une description du montage de recuit thermique rapide que nous avons utilisé est donnée à l'Annexe A2.

1.4 Objectifs de l'étude

Mon travail de thèse a pour thème la modification du composé semi-conducteur InGaAsP. Le composé est modifié avec un procédé en post-croissance basé sur l'implantation d'ions de Fe à haute énergie suivie d'un recuit rapide, tel que schématisé à la figure 1.8.

Figure 1.8 Ma question de recherche : « Avec ce procédé, peut-on établir des conditions de fabrication qui produisent des couches d'InGaAsP photoconductrices, résistives et potentiellement ultrarapides ? » Les astérisques (*) correspondent à des étapes de caractérisations optiques, électriques et structurales et de microfabrication.

Malgré la popularité de l'implantation ionique, très peu de résultats ont été rapportés en regard de l'implantation de Fe dans l'InGaAsP [Kong *et al.*, 2004]. Je propose donc de conduire l'étude exhaustive de ce procédé avec deux compositions populaires de l'alliage quaternaire, dont les énergies de gap sont 0.95 eV et 0.79 eV. Les hétérostructures InGaAsP/InP nécessaires à l'étude sont produites selon mes spécifications par le Centre canadien de fabrication de dispositifs photoniques du CNRC, avec la contribution de CMC Microsystems. L'objectif principal de mon travail consiste à élaborer, avec ce procédé, des couches photoconductrices pour des applications en imagerie optique et en spectroscopie térahertz.

Le premier volet de mon travail de thèse porte sur la fabrication d'une couche d'InGaAsP semi-isolante de bonne qualité cristalline. Puisqu'une certaine densité de niveaux profonds est requise pour compenser les donneurs non-intentionnels de cette couche, nous conduisons l'étude détaillée des effets de la fluence d'implantation de Fe. Nous portons notre attention sur les propriétés structurales, électriques et optiques qui sont mesurées avant et après le recuit à haute température. Notre but est de valider ce procédé d'isolation, dans un premier temps, sur une monocouche d'InGaAsP ayant un seuil d'absorption à 1.3 µm. Cette validation est une étape importante avant de produire un dispositif photoréfractif complet destiné à l'imagerie

holographique. Ce dispositif, qui n'a pas été réalisé dans le cadre de mon travail de thèse, comportera éventuellement une structure multicouche à puits quantiques afin de maximiser l'effet électro-optique requis à 1.3 µm.

Le second volet de mon travail traite de l'élaboration d'un matériau photoconducteur ultrarapide. Le photoconducteur doit pouvoir être couplé avec des sources lasers qui émettent à 1.55 µm pour la réalisation de dispositifs térahertz pulsés. Le procédé de fabrication est également basé sur l'implantation de Fe dans l'InGaAsP. Dans ce cas-ci, l'implantation se fait à très forte fluence de Fe afin de produire une couche photoconductrice de grande résistivité contenant une grande densité de centres de recombinaison. Nous menons l'étude détaillée des effets des températures d'implantation et de recuit rapide sur les propriétés structurales, électriques et optiques du matériau. Afin de préciser l'effet des impuretés de Fe, nous comparons l'implantation de Ga, un constituent de l'alliage, à l'implantation de Fe. Le matériau ayant les caractéristiques les plus prometteuses est sélectionné pour fabriquer un émetteur térahertz. L'émission térahertz de ce dispositif est validée pour une excitation à 1.55 µm.

Au cours du développement des procédés, les propriétés des matériaux sont mesurées après chaque étape de fabrication : la croissance, l'implantation et le recuit des couches d'InGaAsP. Les propriétés électriques sont caractérisées par des mesures de l'effet Hall sur des dispositifs van der Pauw. Les propriétés optiques sont observées près de l'énergie de gap par mesures spectrales de transmission optique et de spectroscopie de la photoluminescence. La dynamique des photoporteurs est sondée par des mesures de réflectivité optique résolue temporellement. Les propriétés structurales sont étudiées avec l'analyse par faisceau d'ions en rétrodiffusion de Rutherford, la diffraction de rayons X et la microscopie électronique en transmission. Ces étapes de caractérisation s'avèrent très importantes afin de vérifier ou d'établir des mécanismes liés à la formation du matériau et de prévoir les impacts sur les performances du dispositif final.

1.5 Organisation du document

La présentation de nos travaux est donnée sous le format de la thèse par articles. Ce chapitre d'introduction a permis de faire un survol des motivations principales et des questions de recherches. Les détails essentiels concernant l'état de l'art, le matériel et les méthodes sont intégrés aux quatre articles (rédigés en anglais) qui constituent les chapitres 2, 4, 5, et 6. Des avant-propos précèdent chaque article et apportent des précisions supplémentaires. La thèse est divisée en deux parties.

La première partie cette thèse concerne le développement du procédé de fabrication d'un photoconducteur InGaAsP/InP semi-isolant ayant un seuil d'absorption à 1.3 µm. Le procédé est basé sur l'implantation à faible fluence de fer. Le chapitre 2 traite de la qualité cristalline de l'InGaAsP lorsque le dommage d'implantation n'excède pas l'amorphisation complète. Nous étudions les propriétés électriques et optiques du photoconducteur en fonction de la fluence de fer et identifions la plage d'intérêt. Nous appuyons notre étude avec un modèle électrique et concluons avec quelques perpectives au sujet de la suite des travaux.

La seconde partie de cette thèse concerne le développement d'un photoconducteur InGaAsP/InP résistif et ultrarapide pour une application térahertz pulsée à 1.55 µm. Elle regroupe les résultats d'implantation quand la fluence est forte et peut même induire l'amorphisation complète du matériau quaternaire. Le chapitre 3 précise l'intérêt de l'implantation à forte fluence pour réduire le temps de recombinaison des photoporteurs. Dans le chapitre 4, nous précisons le besoin de développer de nouveaux matériaux photoconducteurs ultrarapides opérant dans le proche-infrarouge. Nous proposons l'implantation de fer à 83 K dans l'InGaAsP, suivi d'un recuit rapide, comme nouvelle piste de recherche. Les matériaux obtenus avec ce procédé montrent des caractéristiques recherchées : forte résistivité, absorption à 1.55 µm et dynamique ultrarapide des photoporteurs. Nous rapportons, pour la première fois, le fonctionnement d'un émetteur térahertz basé sur une hétérostructure InGaAsP/InP implantée au fer. Au chapitre 5, nous explorons les paramètres du procédé. Nous mesurons les effets de la température d'implantation sur les propriétés structurales et électriques de l'InGaAsP selon deux compositions de l'alliage. Nous comparons l'implantation de Fe à 83 K avec l'implantation de

Ga à 83 K. Au chapitre 6, nous décrivons la microstructure des photoconducteurs InGaAsP/InP produits par le procédé d'implantation de Fe à 83 K. Nous mettons en évidence l'évolution de la microstructure à l'échelle nanométrique en fonction de la température de recuit. Enfin, nous concluons l'ensemble du travail au chapitre 7.

CHAPITRE 2 Implantation ionique de l'InGaAsP à faible fluence

Avant-propos

Dans ce chapitre, nous développons un procédé de fabrication en post-croissance capable de produire des propriétés semi-isolantes dans une hétérostructure InGaAsP/InP de type-n. Le procédé est basé sur l'implantation à haute énergie d'ions de Fe et l'activation de l'impureté par recuit thermique rapide. Le but du procédé consiste à compenser cette hétérostructure avec l'activation du fer pour former un niveau accepteur profond. En se basant sur les données obtenues lors de croissance d'InGaAsP:Fe par Sugawara *et al.* (1987), Knight *et al.* (1992) donnent l'expression suivante pour E_{da}, l'énergie de l'accepteur profond, en fonction de la fraction molaire de l'arsenic y dans le composé $(In_{0.53}Ga_{0.47}As)_y(InP)_{1-y}$: E_c-E_{da} = 0.63-0.26y (eV), où E_c est l'énergie au minimum de la bande de conduction. Pour ce travail, le seuil d'absorption de l'hétérostructure se situe à 1.31 µm (E_g = 0.95 eV), et selon la figure 1.1a), y = 0.61. Le niveau E_{da} associé au Fe est situé au milieu du gap, à 0.47 eV sous la bande de conduction de l'InGaAsP, donc idéal pour obtenir des propriétés semi-isolantes.

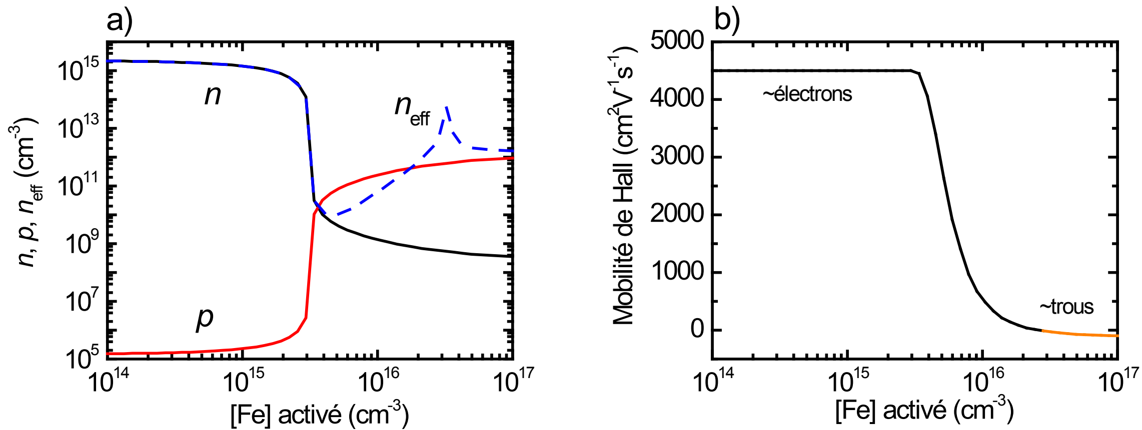

Figure 2.0 a) Calcul de la densité de porteurs libres n (électrons) et p (trous) pour une couche d'InGaAsP type-n en fonction du dopage au Fe. La conduction mixte a une forte influence sur les résultats : la courbe en pointillés bleu correspond à la mesure par effet Hall de la densité de porteurs, n_{eff}. b) Tracé de la mobilité par effet Hall lorsqu'il y a conduction mixte. Alliage InGaAsP avec y=0.61 et E_g=0.95 eV. $N_{sd} = 3\times10^{15}$ cm^{-3}. Les valeurs de mobilité sont fixée à μ_n=4500 cm^{2}V^{-1}s^{-1} et μ_p=100 cm^{2}V^{-1}s^{-1}.

La qualité de la compensation électrique de l'hétérostructure d'InGaAsP/InP dépend de la densité de fer qui est introduite par implantation et du dopage non-intentionnel à la croissance. Connaissant la position du niveau E_{da} dans le gap de l'InGaAsP, nous pouvons calculer l'effet de la densité de Fe substitutionnel sur les populations de porteurs libres n (électrons) et p (trous). Le résultat est montré à la figure 2.0(a). Les détails du modèle sont donnés à l'Annexe A3. Si la densité active de Fe est moindre que le dopage type-n non-intentionnel (3×10^{15} cm^{-3}), une petite fraction seulement des porteurs libres est piégée et pratiquement aucun changement n'est observé pour n et p. Le modèle prédit une baisse soudaine de la densité de porteurs libres majoritaires quand la densité de Fe activé excède 3×10^{15} cm^{-3}. Au point de croisement de n et p, la densité des porteurs libres est estimée à 2×10^{10} cm^{-3}, ce qui est proche du niveau intrinsèque à 300 K. Au-delà du point de croisement, le type des porteurs majoritaires change. Même surcompensé, la densité des porteurs libres demeure faible.

L'effet Hall est une des méthodes des plus communes pour mesurer la densité des porteurs majoritaires dans un semi-conducteur [Look, 1989]. Pour bien comprendre les mesures Hall faite sur un matériau semi-isolant, l'interprétation doit tenir compte de la conduction mixte car les densités n et p sont comparables [Groves 1985]. À la figure 2.0a), la courbe en pointillés bleu donne la densité effective des porteurs n_{eff} qui serait mesurée par effet Hall en fonction de la densité de Fe activé dans l'InGaAsP. La baisse soudaine de n_{eff} se produit encore à 3×10^{15} cm^{-3} mais le changement de signe de n_{eff} se produit seulement vers 3×10^{16} cm^{-3} quand les trous dominent la conduction. La mobilité mixte μ_{Hall} qui serait mesurée est calculée à la figure 2.0(b). À faible densité de Fe, on observe une valeur proche de la mobilité des électrons. Une forte chute de la mobilité survient quand p excède n. Quand l'InGaAsP est surcompensé au-delà de 3×10^{16} cm^{-3}, le transport est dominé par les trous.

En résumé, des variations abruptes affectent les propriétés électriques de l'InGaAsP selon la densité des impuretés Fe actives. Il semble donc possible d'optimiser le procédé d'implantation/recuit en fonction de la fluence d'ions de Fe afin d'obtenir des propriétés semi-isolantes. C'est le sujet de la présente étude.

Auteurs et affiliation

André Fekecs : candidat au doctorat, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

Martin Chicoine : professionnel de recherche, Université de Montréal. Département de physique.

Bouraoui Ilahi : professeur visiteur, Université de Sherbrooke. Institut Interdisciplinaire d'Innovation Technologique (3IT).

François Schiettekatte : professeur, Université de Montréal. Département de physique.

Paul Charette : professeur, Université de Sherbrooke. Faculté de génie. Département de génie électrique et de génie informatique.

Richard Arès : professeur, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

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Titre français : Vers des couches InGaAsP/InP semi-isolantes par procédés en post-croissance basés sur l'implantation ionique de Fe et le recuit rapide.

Contribution au document : Cet article contribue à la thèse en détaillant un procédé de fabrication en post-croissance, appliqué sur un alliage quaternaire InGaAsP, afin de produire de nouveaux films photoconducteurs de forte résistivité pouvant absorber dans le proche infrarouge à 1.3 µm. Le procédé utilise l'implantation ionique et des recuits thermiques rapides pour le dopage au fer, l'activation de niveaux profonds et la guérison des défauts d'implantation. Cet article traite d'aspects fondamentaux reliés à l'introduction d'impuretés et de défauts qu'on retrouve généralement dans les matériaux semi-conducteurs qui sont

modifiés par ce procédé de post-croissance. Ce papier étudie l'implantation à faible fluence afin d'introduire suffisamment d'impuretés profondes actives dans le matériau tout en guérissant les défauts d'implantation par recuit thermique. Ce papier montre que la fluence d'implantation affecte les propriétés électriques, structurales et optiques du matériau et qu'elle peut être ajustée pour produire des couches d'InGaAsP dopée au fer de forte résistivité. Ce procédé est destiné à fabriquer, éventuellement, des matériaux photoréfractifs pouvant opérer à 1.3 µm pour une application en imagerie holographique.

Résumé en français : Dans ce papier, nous rapportons une technique de procédé de post-croissance qui est efficace pour le développement de couches minces semi-isolantes et photo-absorbantes à 1.3 µm. À cet effet, nous avons examiné une couche épitaxiale d'$In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$ (énergie de gap de 0.95 eV) d'une épaisseur de 1 µm, dopée type n non-intentionnellement, qui a été modifiée par implantation d'ions de Fe à multiples énergies (MeV). Le fer est une impureté qui forme des niveaux d'énergie profonds. Son incorporation par implantation ionique a été effectuée à la température de la pièce. Cette étape est suivie de recuits rapides à 800 °C d'une durée de 15 s. Nous avons investigué l'impact de la fluence des ions sur les propriétés électriques en effectuant des mesures de l'effet Hall. Des mesures de spectrométrie de la rétrodiffusion Rutherford en canalisation, de la diffraction de rayons-X et de la photoluminescence ont été menées pour évaluer la qualité cristalline suivant chaque étape de fabrication. Au-delà de l'amorce de l'amorphisation, quand la fluence totale de Fe excède 4.8×10^{13} cm^{-2}, le recuit de la couche d'InGaAsP implantée a produit une recristallisation de mauvaise qualité, ce qui affecte son isolation électrique. Les valeurs de résistivité maximales ont été obtenues avec une fluence en deçà de l'amorce de l'amorphisation, alors que le recuit peut réduire la décanalisation des ions et la contrainte induite par le dommage. Avec une fluence totale de Fe de 1.6×10^{13} cm^{-2}, la résistivité électrique et la mobilité Hall a atteint des valeurs de 1.4×10^{4} $\Omega\cdot cm$ et 4×10^{2} $cm^{2}V^{-1}s^{-1}$. Ces résultats amènent des précisions importantes au sujet de l'optimisation de ce procédé pour le développement de films photoconducteurs semi-isolants basés sur l'InP.

Towards semi-insulating InGaAsP/InP layers by postgrowth processing using Fe ion implantation and rapid thermal annealing

A. Fekecs, M. Chicoine, B. Ilahi, F. Schiettekatte, P. Charette, R. Arès

Abstract In this paper, we report on an effective postgrowth processing technique for developing semi-insulating (SI) photonic thin films absorbing in 1.3 μm. For that purpose, we examined a 1-μm thick unintentionally n-doped $In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$ epilayer (0.95 eV bandgap) modified by multiple-energy MeV Fe ion implantation. Fe was chosen as a deep level impurity. The ion beam processing was performed at room temperature, followed by rapid thermal annealing (RTA) at 800 °C for 15 s. We investigated the impact of ion fluence on electrical properties by Hall effect measurements. Channelling Rutherford backscattering spectrometry, X-ray diffraction and photoluminescence measurements were carried out to evaluate crystal quality after each fabrication step. Beyond the onset of amorphization, when the total Fe fluence was more than 4.8×10^{13} cm^{-2}, the implanted InGaAsP layer showed evidence of a poor recrystallization after RTA, and its isolation was impaired. Maximum resistivity values were achieved below the onset of amorphization where annealing reduced ion de-channeling and recovered damage-induced strain. With a total Fe fluence of 1.6×10^{13} cm^{-2}, the electrical resistivity and Hall mobility reached values of 1.4×10^{4} Ω·cm and 4×10^{2} $cm^{2}V^{-1}s^{-1}$. These results add important insights on the optimization of this process for the development of InP-based SI photoconductive films.

2.1 Introduction

Photoconductive devices made of semi-insulating (SI) GaAs/AlGaAs multilayers proved to be of value in developing real-time photorefractive imaging systems working around 0.8 μm [Dunsby *et al.*, 2003]. Such holographic systems can be used for depth-resolved imaging through about a millimeter of biological tissues and provide high resolution images with minimal electronic signal processing [Nolte, 2012]. To produce these devices, the removal of

the opaque GaAs substrate is often necessary and photorefractive films are transferred to a transparent substrate, which may create unwanted scattering optical defects [Dunsby *et al.*, 2003]. A second optical window suitable for deep imaging in biological soft tissue is available around 1.3 μm [Smith *et al.*, 2009]. Weaker optical diffusion and a local minimum in water absorption are found at that operating wavelength which is also well adapted to the InP material system. In this material system, the InP substrate (1.35 eV) is not the lowest bandgap (E_g) material. Thick layers of ternary ($In_{0.53}Ga_{0.47}As$) and quaternary alloys ($In_{1-x}Ga_xAs_yP_{1-y}$), with lower energy gap, can be grown under lattice-matched conditions. Their optical absorption band edge lies in a broad energy range, from 1.35 eV to 0.74 eV (i.e., from 0.92 μm to 1.68 μm), depending on x and y. Therefore, the InP substrate is transparent and can be left with the photorefractive film on. Nevertheless, developing novel photorefractive films working at 1.3 μm using InP-based semiconductors presents two main challenges. In order to record interferograms as space-charge fields, those films made with lower gap materials must trap photocarriers at deep levels and must be resistive for sensitive recordings. Those films must also have strong electro-refraction/absorption coefficients to produce holograms. Both requirements are usually met in SI multiple-quantum well structures, usually of around 100 layers, with band edge energy close to the operating wavelength [Nolte, 1999]. In this work, we address the first problem of demonstrating near-intrinsic resistivity by deep level compensation, but in a simpler semiconductor device structure. A single bulk layer of InGaAsP grown on InP was chosen, with a band edge energy located close to 1.3 μm (0.95eV). At this band gap, the resistivity of fully compensated InGaAsP is about 1×10^5 Ω·cm at room temperature and constitutes a representative benchmark. The resistivity was derived by estimating the intrinsic carrier density of the semiconductor [Sze et Ng, 2007].

Fully compensated semiconductors can be achieved when deep trapping levels are able to pin the Fermi level at about the mid-gap [Nolte, 1999]. This can be done by chemical doping with transition metals [Langer *et al.*, 1988]. Near-intrinsic electrical resistivity was reported over the full compositional range in Fe-doped InGaAsP alloys fabricated by a variety of epitaxial growth methods [Pagnod-Rossiaux *et al.*, 1993]. Nevertheless, the utilization of elemental and organometallic Fe sources in a controlled chamber is not always practical to the crystal

grower, it may raise concerns about reactor contamination and require to use a dedicated equipment for the production of SI InGaAsP layers.

A postgrowth process able to produce SI InGaAsP layers by avoiding Fe sources for growth is therefore very desirable. Accordingly, many groups have developed isolation processes based on ion implantation. Implantation damage obtained with light ions, such as $^{1}H^{+}$, $^{4}He^{+}$, $^{11}B^{+}$, $^{14}N^{+}$, $^{16}O^{+}$, or $^{19}F^{+}$, has been shown to increase the resistivity of n-type InGaAsP (E_g = 0.95 eV) up to 1.8×10^{3} Ω·cm [Ahmed *et al.*, 2007; Akano *et al.*, 1993; Comedi *et al.*, 1994; Pearton *et al.*, 1993]. However, this resistivity value would cause significant dark currents in a photorefractive film and compromise the sensitivity of holographic recording [Nolte, 1999]. In principle, deep-level chemical doping with Fe atoms can be achieved via ion implantation and is expected to allow for better compensation if the implantation damage is well annealed. However, despite a substantial body of work published on Fe-implanted InP and $In_{0.53}Ga_{0.47}As$ about their morphology and their electrical properties [Carmody *et al.*, 2003b; Carnera *et al.*, 1994; Donnelly et Hurwitz, 1978; Gasparotto *et al.*, 1999b; Pearton *et al.*, 1989; Rao *et al.*, 1989; Schwarz *et al.*, 1985; Too *et al.*, 2004], very limited data have been communicated on Fe-implanted InGaAsP [Fekecs *et al.*, 2011; Kong *et al.*, 2004].

In this paper, we report on a post-growth isolation process of InGaAsP, successfully developed with multiple-energy ion implantation carried out at room temperature and rapid thermal annealing (RTA). We study in details the effects of the Fe ion fluence on electrical and structural properties of unintentionally n-doped InGaAsP layers (E_g = 0.95 eV). Our work adds important insights on the optimization of this process that can be used potentially to produce photorefractive layers of high dark resistivity for novel uses in the second window of optical soft tissue imaging.

2.2 Experimental study

2.2.1 Fabrication details of Fe-implanted InGaAsP layers

A layer of $In_{1-x}Ga_xAs_yP_{1-y}$ with a thickness of 1 μm, which is a typical value of normal incidence photonic devices, was used for this study. The undoped structure was grown on a 75 mm SI InP wafer via organometallic vapor phase epitaxy. The quaternary layer was capped by InP (10 nm) and grown over an InP buffer (100 nm). Substrate lattice-matching was

confirmed by high resolution x-ray diffraction. The wafer average photoluminescence (PL) peak wavelength was 1311 nm at room temperature (figure 1), corresponding to a band gap energy of about 0.95 eV. For this gap energy, the layer composition (x = 0.28 and y = 0.61) was estimated using the expression given by Kuphal [Swaminathan, 1991]. Hall effect measurements on this structure gave a resistivity of 0.5 Ω·cm, a free electron density of 3.0×10^{15} cm^{-3} and a Hall mobility of 4500 cm^{2}V^{-1}s^{-1}.

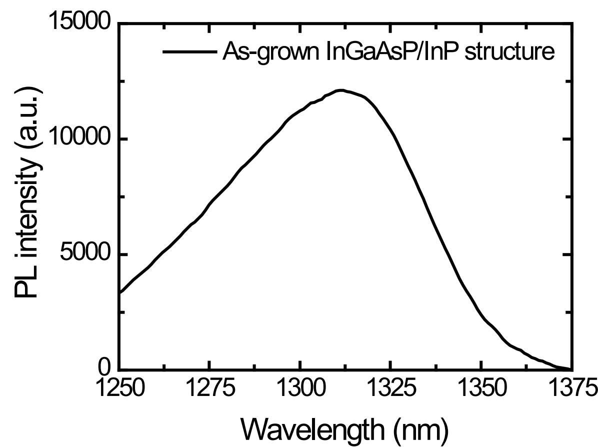

Figure 2.1. Photoluminescence spectra of the InP/InGaAsP/InP layer structure taken at room temperature.

Electrical compensation of the quaternary layer requires a density of Fe-related deep levels greater than the free electrons density. Therefore, the experiment was devised to identify the minimum implantation fluence that is required to achieve this. A simulation of ion implantation through the quaternary and the buffer layers was conducted in SRIM-2006 (Stopping Range of Ions in Matter) using the Kinchin-Pease solution for target damage [Ziegler *et al.*, 1985]. In the calculations, displacement energies of In, Ga, As, and P were set to 10 eV. In figure 2, we plot the calculated damage and Fe profiles. The implantation damage profile was uniform for a 4-energy fluence of (0.12, 0.25, 0.11 and 1.12) $\times10^{12}$ cm^{-2} at (250, 500, 1000 and 1800) keV, respectively. A total fluence of 1.6×10^{12} cm^{-2} corresponds to an average Fe density of 9×10^{15} cm^{-3} throughout the layer.

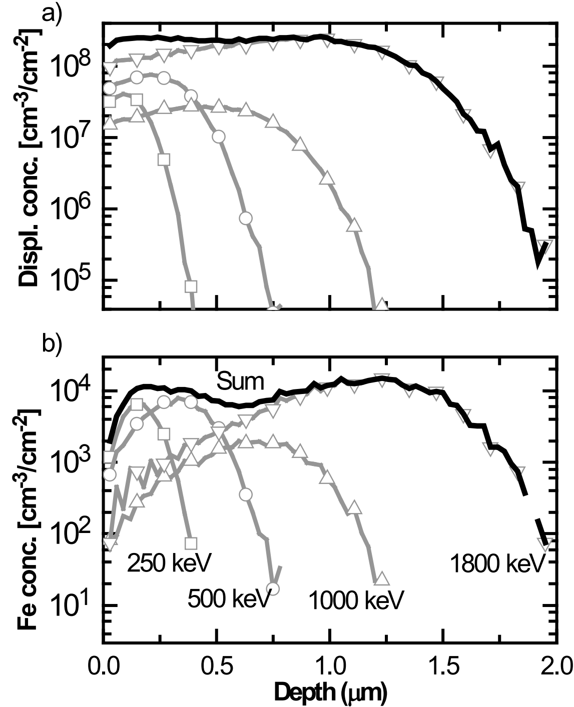

Figure 2.2. Simulation of multiple-energy Fe ion implantation in a InP/InGaAsP/InP layer structure (thicknesses of 10 nm, 1000 nm and 100 nm, respectively) grown over an InP substrate. (a) Sum of atomic displacement density (lattice damage) from four weighted fluences. (b) Sum of Fe atomic density implanted with the same four weighted fluences.

The multiple-energy ion implantation was performed at room temperature on a series of 12 mm × 12 mm InGaAsP structures. $^{56}Fe^{+}$ ions were generated by a 1.7 MV Tandetron accelerator (High Voltage Engineering Europa). The ion fluence rate from the beam line was always below 2×10^{10} $cm^{-2}\cdot s^{-1}$. Five total fluences in the range of $1.6\times10^{12} - 1.6\times10^{14}$ cm^{-2} were used. The pressure in the implant chamber was kept below 1×10^{-6} Torr and samples were tilted at 7° with respect to the ion beam to reduce channelling effects. Subsequently, the implanted samples were cleaved into 6 mm × 6 mm pieces and cleaned in organic solvents.

In order to achieve high resistivity with compensation by Fe-related deep levels, the primary implantation damage has to be annealed out. Due to its atomic mass, the primary damage is likely to consist of heavily damaged and amorphous nanoscale clusters as they appear in InP implanted by Fe [Wendler *et al.*, 1997]. For that purpose, we used RTA. The implanted pieces were processed at 800 ºC for 15 s in a nitrogen atmosphere using a JetFirst RTA chamber

(Jipelec). They were placed with their epilayer face down on a silicon wafer susceptor and their backside was protected by a piece of silicon.

2.2.2 Sample characterization methodology

The structural quality of InGaAsP samples was verified before and after annealing. We checked the degree of crystal recovery after annealing by channelling Rutherford backscattering spectrometry (RBS). RBS is sensitive to amorphous, heavily damaged areas and points defects [Wendler, 2009]. The probe beam was generated by the Tandetron accelerator and carried $^{4}He^{+}$ primary ions at 2.042 MeV. The samples were located in a separate analysis chamber where backscattered ions were detected at an angle of 170° by a surface barrier detector connected to a multichannel energy analyzer. We also used high resolution x-ray diffraction (HRXRD), which is very sensitive to lattice parameter changes. Rocking curves (ω-2θ coupled scan) were acquired by an MRD system (Panalytical) equipped with a 4-bounce Ge (2 2 0) Bartels monochromator at the source and without a slit at the detector. We extracted the diffraction angle of the quaternary layer relative to the substrate peak angle and used it to estimate changes in lattice strain.

Electrical properties of the Fe-implanted InGaAsP thin films were investigated by resistivity and Hall effect measurements at 300 K. These were done in the Van der Pauw geometry. Ohmic contacts were fabricated by alloying indium at 300 °C during 240 s under forming gas in the RTA chamber. The measurements were carried out in the dark and in vacuum, using a commercial Hall system (MMR Technologies, model H-50) and a 0.37 T permanent magnet. For the calculations, the Hall scattering factor was set to 1, a single carrier was considered, and the majority of the conduction was assumed to happen within the quaternary layer.

The optical quality of the fabricated materials was monitored with PL spectra measurements taken at room temperature by a PL mapping instrument (PLM 150, Philips) under a 25-mW laser excitation at 532 nm. The grating was centered at 1310 nm and swept over 120 nm spans.

2.3 Results and discussion

2.3.1 Implantation damage and recovery

The channeling RBS and HRXRD and experiments were used to quantifying implant-induced primary damage and secondary damage from annealing. Channeling RBS results are presented first in figure 3. Two groups of spectra were taken on a series of as-implanted samples and a series of annealed samples. The shape of the RBS spectrum is typical of a quaternary alloy signature. As shown in figure 3(b), a simulation with RUMP software [Doolittle, 1985] agreed very well with the backscattered random signal (i.e. misaligned) of the $In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$ layer (its thickness was set to 995 nm in the simulation).

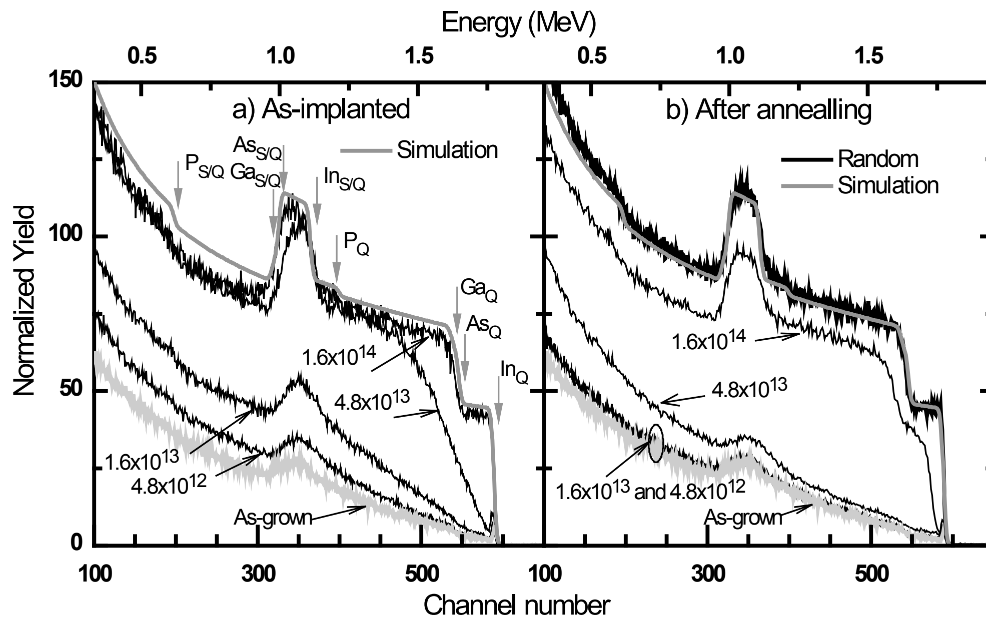

Figure 2.3. Rutherford backscattering (RBS) random and channelling spectra of the InGaAsP/InP structure measured at different steps of the fabrication process. (a) Group of samples implanted to various total Fe fluences (indicated in cm^{-2}), and (b) group of annealed samples. A simulated random RBS spectrum is shown for comparison and clarity. Vertical arrows locate signal contributions from atoms of the quaternary at interfaces.

With low ion implantation fluences (up to 1.6×10^{13} cm^{-2}), dechannelling was observed over the full backscattered energy range but no amorphous layer was detected. At these low fluences, only a small difference in the backscattered yield with respect to an unprocessed sample could be distinguished upon an RTA treatment. At an intermediary ion fluence

(4.8×10^{13} cm^{-2}), the RBS curves show a transition. The layer was heavily damaged in depth and recovers only partially with annealing. Finally, the layer implanted at the highest fluence (1.6×10^{14} cm^{-2}) appears to be heavily damaged over its entire thickness. Likely, it was partially amorphized which is consistent with the average density of displacements given by SRIM-2006 (2.4×10^{22} cm^{-3}) in figure 2(a). Using a density of 5.2 g/cm^3 for InGaAsP (i.e. an atomic density of 3.9×10^{22} cm^{-3}), the average number of displacements per atom due to collisions can be estimated as 0.6. After the annealing step, the disorder observed by RBS remained high and rather uniform.

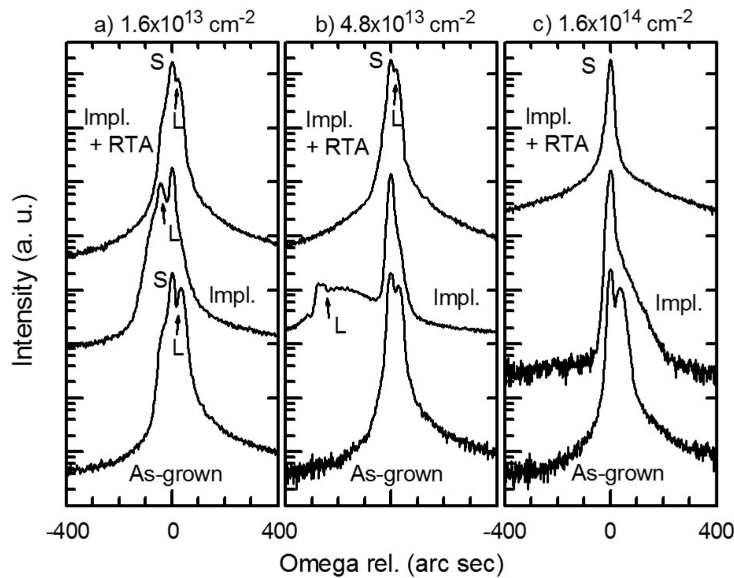

Figure 2.4 HRXRD spectra showing the diffraction peak of the InGaAsP layer (L) relative to the (004) InP substrate peak (S). Data is shown for 3 as-grown layers, after Fe implantation with a) 1.6×10^{13} cm^{-2}, b) 4.8×10^{13} cm^{-2}, c) 1.6×10^{14} cm^{-2}, and after annealing them at 800 °C for 15 s. Spectra are scaled $10^2\times$ and $10^4\times$ for better view.

The effects of the ion fluence and the annealing on the quaternary layer structure were also detectable by x-ray diffraction. Figure 4 shows HRXRD rocking curves taken around the (0 0 4) substrate's Bragg angle ($\theta_B = 31.7$º) at each significant step of the post-growth process. Three ion fluences were examined. Upon Fe implantation at 1.6×10^{13} cm^{-2} (figure 4(a)), the quaternary lattice expanded, as shown by a negative shift ($\Delta\theta = -0.021°$, or -76 arcsec) in the reflection angle of the layer's peak. At that fluence, the out-of-plane lattice strain added by implantation was estimated, by taking a derivative of Bragg's law, as $\Delta d/d = -\Delta\theta/\tan(\theta_B) \approx$

6×10^{-4}. A lattice expansion of comparable magnitude has been observed in room temperature Fe-implanted InP [Bocchi *et al.*, 1994] and InGaAs [Too *et al.*, 2005] and was attributed to implant-induced defects. After the RTA treatment, the diffraction peak of the quaternary layer went back close to its initial angle. A small implant-induced residual strain of only $\Delta d/d \approx 9\times10^{-5}$ was found. The small value of residual strain (about 15 % of the implant-induced lattice expansion) on this sample indicates an almost complete annealing of the implantation damage. This residual strain may well originate from defects liberated when damage clusters were annihilated with the RTA. Upon a higher fluence, (i.e., 4.8×10^{13} cm^{-2}, figure 4b), the layer diffraction peak was broadened, strongly attenuated and shifted towards even lower angles (centered at -190 arcsec). The diffracted intensity appears to originate from a thin crystalline region close to the sample surface, as suggested by the channelling RBS results (figure 3(a)). The asymmetry can be associated with a strain gradient of that region where x-ray interference caused small ripple and overshooting at -260 arcsec [Zeimer et Nebauer, 2000]. Still, its diffraction peak recovered upon annealing and the implant-induced residual strain was $\Delta d/d \approx 7\times10^{-5}$, thus comparable to what was observed for a fluence of 1.6×10^{13} cm^{-2}. Finally, at a fluence of 1.6×10^{14} cm^{-2} (figure 4(c)), HRXRD detected only the substrate peak, over the measurement range (±800 arcsec). After the RTA treatment, diffraction from the InGaAsP layer was still not detected but the InP substrate peak showed a more symmetrical line shape. We believe that this is caused by bad structural quality resulting from the recrystallization of a heavily damaged layer.

2.3.2 Onset of amorphization

Our HRXRD and RBS analyses suggest that the onset of amorphization of the layer, due to primary damage, occurs around a fluence of 4.8×10^{13} cm^{-2}. HRXRD analyses are also suggesting that rapid thermal annealing (800 °C for 15 s) could restore, to good extent, long-range crystalline order in layers implanted at fluences up to the onset of amorphization. RBS analyses were also sensitive and indicated that samples implanted at the onset fluence are producing some dechannelling after annealing. That suggests that some amorphous pockets are not completely recovered with annealing and produced secondary defects. Observations made on InP implanted with 2 MeV Fe^{+} [Gasparotto *et al.*, 1999a] located the onset of amorphization at fluences around 3×10^{13} cm^{-2} and extended defects formed after annealing.

These defects tend to form where crystalline zones and amorphous areas coexist after the implantation. In that work, complete amorphization occurred with a 2×10^{14} cm^{-2} fluence, then annealing produced a poorly regrown crystal which is also consistent with our observations.

2.3.3 The effect of ion fluence on electrical properties

Hall measurements were carried out on the implanted/annealed InGaAsP layers. Values of resistivity, carrier density, and carrier mobility are plotted against ion fluence in figure 5. Data taken on as-grown material is also shown. The sign of the Hall coefficient was negative for all fluences. The magnitude of Hall coefficient was also stable (within 7% of the value taken with the 0.37 T magnet) when other magnetic fields were checked (0.18 and 0.78 T).

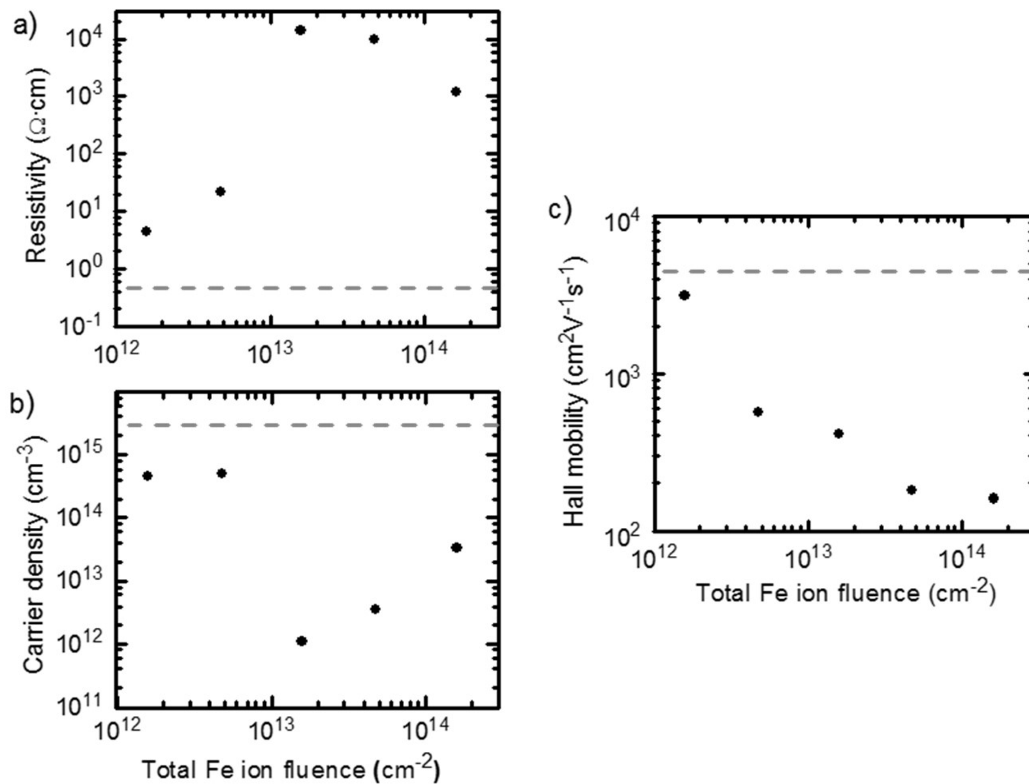

Figure 2.5. Hall measurements on Fe-implanted InGaAsP/InP structures after annealing. (a) Electrical resistivity, (b) carrier density and (c) Hall mobility at room temperature against ion fluence. Dashed lines indicate the measured levels for the as-grown material.

Signs of decaying persistent photoconductivity were noticed in samples implanted at 1.6×10^{13} and 4.8×10^{13} cm^{-2}. These had to be pre-heated at 400 K on the probing stage in order to stabilize the resistivity which otherwise tended to increase slowly during the measurement (up to a factor of 2–3 after several minutes). By handling the samples in ambient light between the measurements, a small fraction of excited photocarriers were recombining slowly. Layers with the highest resistivity appeared sensitive to that effect at room temperature. The persistent photoconductivity is a possible indication of compositional inhomogeneities of the quaternary layer after annealing or is possibly linked to residual defects that our structural analysis has suggested, causing small spatial fluctuations of the bandgap [Theodorou et Symeonidis, 1988].

The Hall mobility of the material followed a downward trend with increasing ion fluence (figure 5(c)). A drop to 570 cm^{2}V^{-1}s^{-1} occurred at 4.8×10^{12} cm^{-2} and a second drop to 180 cm^{2}V^{-1}s^{-1} occurred at the onset of amorphization (4.8×10^{13} cm^{-2}) .Qualitatively, this trend could be attributed to carrier scattering from Fe impurities and residual defects. Our data also show a significant increase in electrical resistivity (figure 5(a)) compared to the reference material. Overall, most of the resistivity variations were driven by the carrier density (figure 5(b)). As the ion fluence was increased to 1.6×10^{13} cm^{-2}, the carrier density dropped sharply to 1×10^{12} cm^{-3} which produced a sample with the highest dark resistivity (i.e. 1.4×10^{4} $\Omega\cdot$cm). The temperature-dependent resistivity $\rho(T)$ of that sample, recorded between 300 and 400 K, had a thermal activation energy E_a of about 0.48 eV, which was given by fitting the data with $\rho\sim\exp(E_a/k_BT)$. This suggests pinning of the Fermi level close to mid-gap by deep levels. At that fluence, densities of Fe-related deep levels and of deep impurity-defect complexes that likely formed within the implanted/annealed InGaAsP layer appeared sufficient to compensate for shallow donors (i.e, grown-in impurities, native defects or residual donor-like defects). Above the onset of amorphization fluence (4.8×10^{13} cm^{-2}), even though more Fe was implanted, the resistivity dropped gradually and the carrier density increased. At these higher fluences, the interplay between Fe, other impurities, defects, and the probable extended defect structure that forms with annealing could be responsible for the observed behavior. Details on these semi-insulating characteristics, which were dependent on the Fe fluence, needed further investigations and will be published elsewhere.

When processed at room temperature by Fe implantation, the Hall mobility of resistive InGaAsP was comparable to that obtained in the case of resistive He-implanted n-InGaAsP [Comedi *et al.*, 1994]. Moreover the peak resistivity achieved with Fe implantation was closer to intrinsic resistivity by one order of magnitude compared to values reported for implantation of He and other light ion [Ahmed *et al.*, 2007; Comedi *et al.*, 1994]. To compensate n-type InGaAsP with Fe implantation done at room temperature and subsequent RTA, our data showed that when working with nominally undoped material, it is important to keep the Fe fluence below the onset of amorphization. The onset of amorphization can be shifted by ion implantation done at higher temperature [Wendler *et al.*, 1997; Wendler *et al.*, 1999]. Higher incorporation of Fe and reduced interactions with secondary defects were confirmed in InP after long annealing [Gasparotto *et al.*, 1999a; Gasparotto *et al.*, 1999b]. However, our preliminary investigations with multiple-energy Fe implantation done at 473 K coupled with RTA did not yield resistive InGaAsP layers. In order to take full advantage of the post-growth isolation approach, it would be practical to increase the offset between the optimal Fe fluence and the onset of amorphization and to reduce persistent photoconductivity. Longer thermal annealing done at lower temperatures should be considered in future experiments for room temperature and high temperature Fe-implanted InGaAsP.

Regarding optical properties, we show and discuss hereafter the PL of Fe-implanted InGaAsP material which was monitored through the fabrication process. An as-grown InGaAsP layer and its SI InP:Fe substrate (i.e. its polished backside surface) were also characterized. The comparison is shown in figure 6.

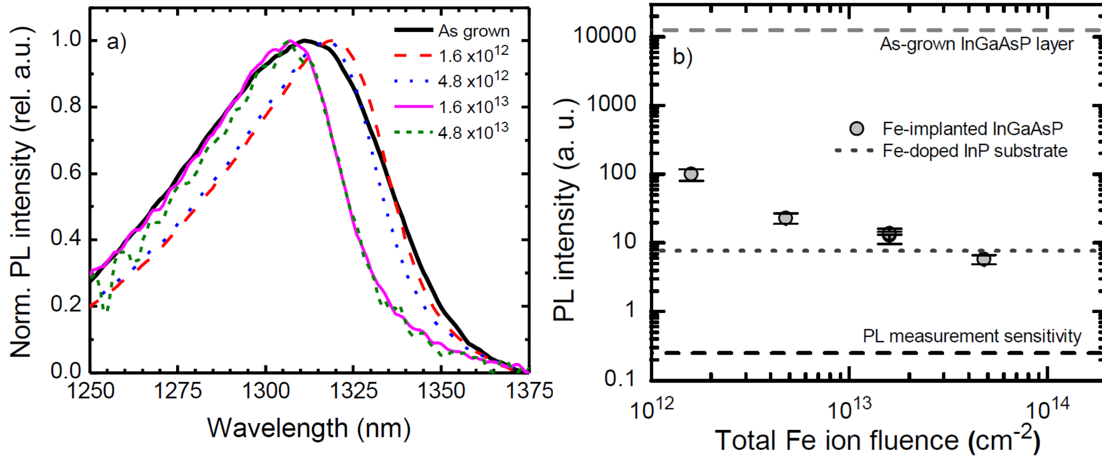

Figure 2.6 Photoluminescence of Fe-implanted InGaAsP/InP structures, after annealing. (a) Normalized PL intensity spectra. (b) PL peak intensity against Fe ion fluence. Measurements were taken at room temperature.

Upon Fe implantation, all InGaAsP samples had a fully extinct PL, regardless of fluence. After annealing, PL spectra could be detected again (figure 6(a)), which indicated a significant recovery of damage-related recombination centers. Sample-to-sample variations of the peak wavelength were due to small compositional non-uniformity that occurred at growth. We found that the PL intensity decreased with the implantation fluence (figure 6(b)). The detected levels were much lower than the as-grown material, but were comparable to PL emitted by crystalline InP:Fe (a standard semi-insulating material which do not suffer from implantation damage) up to an implantation fluence of 4.8×10^{13} cm^{-2}. However, at 1.6×10^{14} cm^{-2}, no PL signal was detectable. The decrease of the PL intensity, connected with the decrease observed in Hall mobility (figure 5(c)), would be consistent with higher Fe incorporation and accumulation of residual defects as shown in RBS-C (figure 3). More importantly, figures 6(a) and (b) are showing that relatively good optical properties could be maintained up to an implantation fluence of 4.8×10^{13} cm^{-2} with respect to crystalline Fe compensated InP. By keeping an optical band edge, the post-growth isolation process looks promising for developing semi-insulating layers exploiting a photorefractive effect in the near infrared [Nolte, 1999]

2.4 Summary and Conclusion

In this study, unintentionally doped n-InGaAsP layers with bandgap around 0.95 eV were implanted at room temperature by multiple-energy MeV Fe ions. Their electrical properties

were investigated after rapid thermal annealing, as a function of ion fluence. Layers with better carrier mobility and crystalline quality were produced when the total Fe fluence was kept below the onset of amorphization, which was observed at 4.8×10^{13} cm^{-2}. As a consequence, high resistivity up to 1.4×10^{4} $\Omega\cdot cm$ and carrier density down to 1×10^{12} cm^{-3} were achieved with an implantation fluence of 1.6×10^{13} cm^{-2}. Our results indicate that ion implantation with Fe gives supplementary isolation in InGaAsP in comparison to implantation with light ions and there is still room for improvement to match intrinsic levels achieved by epitaxial growth methods. In conclusion, the Fe implantation postgrowth process produces resistive InP-based crystalline layer with band edge wavelength around 1.3 µm by avoiding the use of Fe sources during their growth.

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2.5 Conclusion du Chapitre 2

Le dopage de l'InGaAsP par implantation ionique de Fe suivi de recuits rapides est prometteur pour produire des couches avec des caractéristiques semi-isolantes et pouvant absorber à 1.3 μm. L'incorporation d'une densité de Fe de 9×10^{16} cm^{-3} permet de compenser une couche d'InGaAsP dopée non-intentionnellement à la croissance (n = 3×10^{15} cm^{-3}) et produire une résistivité de 1.4×10^{4} $\Omega\cdot$cm. Ce procédé de post-croissance évite l'utilisation *in-situ* de sources de Fe durant la fabrication des couches par épitaxie.

Éventuellement, ce procédé devra être validé pour fabriquer des couches ayant des propriétés photoréfractives utiles à 1.3 μm. La résistivité d'obscurité est un facteur déterminant qui influence la sensibilité de l'holographie à faible cohérence, car le courant d'obscurité affectent le contraste de l'écriture holographique. Des mesures Hall complémentaires, faites en fonction de la température sur l'échantillon implanté au fer avec une fluence totale de 1.6×10^{13} cm^{-2}, nous ont montré qu'il est possible d'augmenter la résistivité d'un ordre de grandeur en le refroidissant à 273 K. L'exploitation de ce phénomène pour améliorer la sensibilité d'écriture holographique pourrait impliquer un montage optique refroidi.

Bien que des effets électro-optiques et photoréfractifs sont possibles théoriquement dans une couche épaisse semi-isolante, une structure à multiples puits quantiques est généralement plus efficace car elle exploite un effet de résonnance de l'absorption optique due au confinement des porteurs [Nolte *et al.*, 1990; Wang *et al.*, 1992]. Nous envisageons quelques problématiques qui pourraient se poser lors de l'ajustement des propriétés photoréfractives d'une telle structure multi-couches avec notre procédé d'implantation/recuit. Par exemple, la quantité de défauts résiduels devra affecter le moins possible le facteur de qualité de la résonance de l'absorption optique. De plus, la conception des couches devra tenir compte d'un décalage possible vers le bleu de la position de cette résonance, causé par l'interdiffusion des puits qui survient généralement au recuit [Charbonneau *et al.*, 1995]. On voudra aussi vérifier si les effets de photoconductivité persistante que nous avons observés dans notre étude de l'implantation de l'InGaAsP se reproduisent et s'ils influencent l'écriture holographique de la structure multi-couches.

CHAPITRE 3 Implantation ionique de l'InGaAsP à forte fluence

3.1 Introduction

Dans la suite de cette thèse, nous investiguons le procédé d'implantation de Fe à forte fluence pour élaborer des dispositifs photoconducteurs à base de couches d'InGaAsP ayant une dynamique de photoporteurs ultrarapide, une forte résistivité et qui sont absorbantes à 1550 nm. Ce sont là trois caractéristiques recherchées des sources et des détecteurs photoconducteurs utilisés dans les spectromètres térahertz pulsés.

3.2 Vers des caractéristiques ultrarapides

Dans une couche semi-conductrice sans défaut, le temps de vie dépend du taux de recombinaison directe de paires électron-trou. On estime ce temps avec la relation $1/\tau = Bn$. Pour l'InGaAsP, le coefficient de recombinaison radiative $B \sim 1.2\times10^{-10}$ cm^{-3}/s [Agrawal et Dutta, 1993] . Dans une couche non-intentionnellement dopée (avec $n = 3\times10^{15}$ cm^{-3}), on estime un temps de vie de $\tau \sim 3$ μs en faible injection de porteurs. L'implantation de Fe et le recuit ajoutent dans la couche des niveaux profonds et des défauts résiduels qui agissent comme des centres de recombinaison non-radiatifs [Orton et Blood, 1990]. Nous avons constaté au chapitre 2, à la figure 2.6b, une diminution de l'intensité de la photoluminescence de l'InGaAsP lorsque nous augmentons la fluence de l'implantation de fer. Cette diminution est reliée à une hausse de la densité de pièges (*i.e.*, des centres de recombinaison associés aux impuretés de fer et aux défauts résiduels) qui s'associe, en principe, à une baisse du temps de vie des porteurs. En régime de faible injection, le temps de vie est donné par la théorie Schokley-Read-Hall selon $1/\tau = \sigma_c N_{trap} v_{th}$, où v_{th} est la vitesse thermique des porteurs, σ_c est la section efficace de capture et N_{trap}, la densité de pièges [Coutaz, 2002]. Certains des échantillons étudiés au chapitre 2 ont été caractérisés par réflectivité différentielle résolue en temps. La figure 3.1 montre la dynamique des photoporteurs mesurée pour l'échantillon d'InGaAsP implanté avec une fluence de Fe égale à 1.6×10^{13} cm^{-2}.

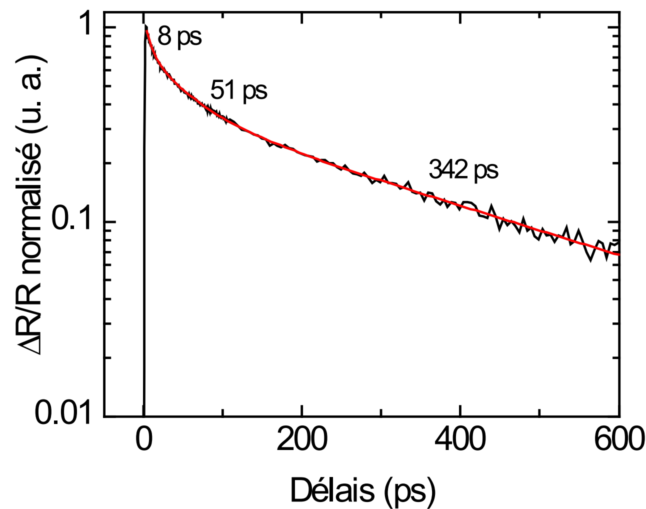

Figure 3.1 Mesure de réflectivité différentielle résolue en temps d'une hétérostructure InGaAsP/InP (énergie de gap de 0.95 eV) implantée Fe à 300 K (fluence de Fe égale à 1.6×10^{13} cm^{-2}) après un recuit (800 °C pendant 15 s). La mesure (courbe en noir) est réalisée avec un laser femtoseconde Ti:saphir émettant à 0.8 μm.

L'allure de la courbe de réflectivité $\Delta R/R$ suggère une dynamique de photoporteurs complexe. L'analyse de la courbe avec un lissage à 3 exponentielles donne 3 temps de décroissance s'étalant sur 3 ordres de grandeur, d'amplitudes sensiblement égales. Les recombinaisons de surface pourraient expliquer la descente initiale rapide. Les deux autres temps pourraient être associés aux recombinaisons par les défauts résiduels et le Fe. Si l'on considère simplement la valeur de réflectivité à 1/e, la dynamique de recombinaison dans ce matériau résistif est de l'ordre de 10^2 ps. Or, un temps de recombinaison de photoporteurs beaucoup moindre est requis, moins de 1 ps, pour qu'un système de spectroscopie THz-TDS utilisant des sources et des détecteurs photoconducteurs puisse offrir une largeur de bande excédant 1 THz.

Peut-on réduire suffisamment le temps de vie dans une couche d'InGaAsP par implantation et recuit? Cela semble possible avec un procédé d'implantation Fe à forte fluence. D'une part, une plus grande densité de Fe s'incorpore dans la couche implantée lorsque la fluence est augmentée. Par exemple, des densités de fer jusqu'à $\sim 2 \times 10^{18}$ cm^{-3} peuvent être activée dans l'InP fortement dopé si l'implantation à forte fluence (10^{15} cm^{-2}) est réalisée à 473 K et suivie de recuits de longue durée sous atmosphère de phosphore [Fraboni *et al.*, 2001]. Pour ce matériau, une forte résistivité est obtenue mais le temps de vie des porteurs n'est pas connu. D'autre part, l'étude du chapitre 2 indique que les défauts résiduels se forment en plus grande

quantité dans l'InGaAsP quand l'implantation à 300 K est faite à plus forte fluence (par exemple à 1.6×10^{14} cm^{-2}, au-delà du seuil d'amorphisation du matériau). De plus, lorsque des structures ternaires $In_{0.53}Ga_{0.47}As$/InP sont implantées à 300 K avec des fluences de Fe de l'ordre de 10^{15} cm^{-2}, elles présentent des dynamiques de photoporteurs ayant des temps caractéristiques de moins de 1 ps [Carmody *et al.*, 2003b; Shin *et al.*, 2011].

3.3 Présentation du travail

Nous présentons notre travail avec 3 articles. Dans le premier article, nous avons développé un nouveau matériau photoconducteur résistif et ultrarapide opérant à 1550 nm avec un alliage InGaAsP/InP de faible gap (0.79 eV). Le procédé de fabrication est basé sur l'implantation à 83 K à forte fluence avec des ions de Fe suivi d'un recuit thermique rapide. Nous avons étudié les propriétés électriques, optiques et ultrarapides de l'InGaAsP implanté à froid. Des sources térahertz ont été fabriquées avec ce matériau et peuvent émettre au-delà de 2 THz lorsque qu'elles sont photoexcitées à 1550 nm avec des impulsions ultracourtes.

Dans le second article, nous avons exploré les limites du procédé de fabrication. Nous nous sommes intéressés aux effets de la température d'implantation et de la température du RTA sur les paramètres électriques et structuraux de la couche d'InGaAsP implantée au Fe. C'est une étude comparative sur deux compositions de l'alliage quaternaire et deux espèces implantée, le fer et le gallium. Nous discutons de l'évolution de la mobilité de porteurs et de la résistivité du matériau, vers des valeurs hautement sollicitées par l'application térahertz. Les comparaisons entre l'implantation Fe et l'implantation Ga nous aident à préciser les rôles des défauts résiduels et du dopage.

Le troisième article est une étude microstructurale du matériau InGaAsP/InP obtenu avec le procédé d'implantation de fer à 83 K et le recuit rapide. Avec la diffraction de rayons X et la microscopie électronique, nous investiguons les processus de transformation qui opèrent durant la fabrication, soit l'amorphisation et la recristallisation, afin d'identifier les éléments microstructuraux qui sont responsables des propriétés optoélectroniques observées.

CHAPITRE 4 Fabrication de photoconducteurs pour des dispositifs térahertz pulsés

Avant-propos

Dans cet article, notre intention est de décrire le procédé de fabrication d'un nouveau matériau photoconducteur résistif et ultrarapide basé sur l'InGaAsP/InP qui peut être employé pour l'émission d'ondes térahertz.

Auteurs et affiliation

André Fekecs : candidat au doctorat, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

Maxime Bernier : stagiaire postdoctoral, Université de Sherbrooke. Faculté des sciences. Département de physique.

Denis Morris : professeur, Université de Sherbrooke. Faculté des sciences. Département de physique.

Martin Chicoine : Professionnel de recherche, Université de Montréal. Département de physique.

François Schiettekatte : professeur, Université de Montréal. Département de physique.

Paul Charette : professeur, Université de Sherbrooke. Faculté de génie. Département de génie électrique et de génie informatique.

Richard Arès : professeur, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

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Titre français : Fabrication de photoconducteurs d'InGaAsP de forte résistivité, implantés à froid, pour des dispositifs térahertz pulsés efficaces.

Contribution au document : Cet article met en contexte notre travail en décrivant le fort potentiel des technologies térahertz. Pour la spectroscopie THz, nous présentons le besoin de nouveaux matériaux photoconducteur compatibles avec des solutions compactes et robustes basées sur les sources lasers fibrées du proche infra-rouge, notamment à 1550 nm. Nous décrivons brièvement les principaux matériaux existants et présentons nos motivations et les détails du développement d'un procédé d'implantation de Fe dans l'InGaAsP pour la fabrication de photoconducteurs ultrarapides. Notre article montre les effets surprenants de l'implantation de fer à 83 K et de la température du recuit rapide sur les propriétés optoélectroniques (mesures Hall, absorption optique, réflectivité différentielle résolue en temps) quand l'InGaAsP est modifié par un tel procédé. Nous montrons qu'il est possible d'optimiser la résistivité du matériau implanté avec un recuit à température modérée (entre 500 °C et 600 °C) tout en conservant une dynamique de photoporteurs ultrarapide, ce qui est prometteur pour la fabrication de sources et de détecteurs THz pulsés. Nous avons microfabriqué et testé une source THz basée sur une couche d'InGaAsP modifiée par notre procédé de fabrication et les résultats établissent la possibilité d'émettre au-delà de 2 THz. Un tel émetteur est montré à la figure 4.0.

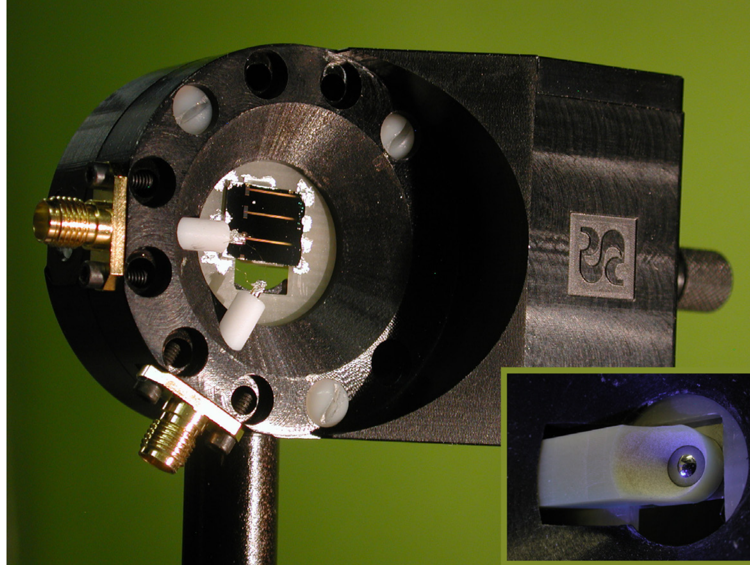

Figure 4.0 Assemblage d'un émetteur térahertz à électrodes colinéaires basé sur un photoconducteur d'InGaAsP/InP implanté au fer. L'insertion montre la lentille de collimation de l'émission térahertz qui est installée au dos du dispositif.

Résumé en français : Un procédé d'implantation ionique de Fe, comportant de multiples énergies MeV et fait à haute fluence, a été appliqué à 83 K pour endommager fortement une couche épitaxiale d'InGaAsP de faible énergie de gap de 0.79 eV. Des conditions optimales de recuit rapide ont été trouvées et ont produit un photoconducteur de forte résistivité, jusqu'à 2500 Ωcm, avec une mobilité de 400 $cm^2V^{-1}s^{-1}$. De très courts temps de piégeage de photoporteurs, 0.3 ps – 3 ps, ont été observés en réflectivité différentielle résolue en temps. De plus, des dispositifs photoconducteurs térahertz, munis d'électrodes colinéaires, ont été fabriqués avec ce matériau et leur fonctionnement validé. Sous excitation pulsée à 1550 nm avec une source laser femtoseconde fibrée, des antennes basées sur l'InGaAsP implanté Fe peuvent émettre une radiation à large bande qui excède 2 THz. Avec de telles spécifications, ce nouveau matériau est un candidat qui mérite d'être considéré pour l'élaboration de dispositifs pouvant être intégrés aux designs de spectromètres térahertz.

Fabrication of high resistivity cold-implanted InGaAsP photoconductors for efficient pulsed terahertz devices

A. Fekecs, M. Bernier, D. Morris, M. Chicoine, F. Schiettekatte, P. Charette et R. Arès

Abstract A multiple-energy, high fluence, MeV Fe ion implantation process was applied at 83 K to heavily damage a low band gap (0.79 eV) epitaxial InGaAsP layer. Optimal rapid thermal annealing conditions were found and produced a fast photoconductor with high resistivity (up to 2500 Ωcm) and Hall mobility around 400 $cm^2V^{-1}s^{-1}$. Short photocarrier trapping times (0.3 ps – 3 ps) were observed via transient differential reflectivity measurements. Furthermore, photoconductive terahertz devices with coplanar electrodes were fabricated and validated. Under pulsed excitation with a 1550 nm femtosecond fiber laser source, antennas based on Fe-implanted InGaAsP are able to emit broadband radiation exceeding 2 THz. Given such specifications, this new material qualifies as a worthy candidate for an integration into optical terahertz spectrometer designs.

OCIS Codes: (160.5140) Photoconductive materials; (160.6000) Semiconductor materials; (320.7080) Ultrafast devices; (320.7100) Ultrafast measurements; (300.6495) Spectroscopy, terahertz.

4.1 Introduction

Terahertz waves have significant potential for varied applications. They are efficient for the safe detection of prohibited substances like drugs [Kawase *et al.*, 2003], explosives [Leahy-Hoppa *et al.*, 2007], and lethal gases [Saleck *et al.*, 1995]. They are ideal for security and environmental applications. THz waves have also been shown to be very sensitive to polymorphic structures [Allard *et al.*, 2011] making them particularly interesting to the pharmacological industry. High contrast imaging systems, based either on continuous-wave or

pulsed THz sources, offer major advantages in security [Kemp *et al.*, 2003], microelectronic [Hu et Nuss, 1995] and medical domains The THz band is also becoming increasingly popular in wireless ultrafast communication systems [Piesiewicz *et al.*, 2007] and proving promising for tracking/authentication/identification systems [Perret *et al.*, 2011]. With continued efforts towards the development of compact, cost-effective, robust and reliable tabletop THz sources and detectors, exciting developments in the THz technology can be expected. In many terahertz time-domain spectroscopy (THz-TDS) systems, pulsed THz waves are radiated from photoconductive antennas [Dragoman et Dragoman, 2004] that are generally made of GaAs-based semiconductor materials and triggered by femtosecond pulses from a Ti:sapphire laser at about 800 nm. Such a THz setup is sensitive to vibrations and small changes in ambient temperature and relative humidity. Using instead high power femtosecond fiber laser sources emitting at 1030, 1300 and 1550 nm (based on Yb-, Pr- and Er-doped fiber gain media, respectively) it is now possible to build environmentally robust and compact THz spectroscopy and imaging systems. However, when shifting to long wavelengths, different materials have to be considered in order to replace GaAs-based photoconductors now turned transparent. Interesting results have been reported by many research teams at 1550 nm on using efficient terahertz devices made with InGaAs ternary compounds, which were produced via various fabrication approaches [Chimot *et al.*, 2005; Driscoll *et al.*, 2005; Kuenzel *et al.*, 2008; Suzuki et Tonouchi, 2005a; Takazato *et al.*, 2007; Wood *et al.*, 2010]. These approaches are briefly described in the next section. In light of these works, we propose to investigate the use of quaternary III-V photoconductive materials (*i.e.*, InGaAsP) modified by a post-growth fabrication process based on high fluence Fe ion implantation at low temperature (83 K) and optimized by thermal annealing treatments. We are presenting characterization results of the material optimization and conclude the work by showing results on optical generation of broadband (2 THz) electrical pulses at 1550 nm from Fe-implanted InGaAsP photoconductive antennas.

4.2 Rationale and fabrication of Fe-implanted InGaAsP

Band-to-band photocarrier generation with femtosecond Er-doped fiber lasers is efficient when the photoconductor band gap energy E_g is smaller than 0.80 eV (*i.e.*, the photon energy at 1550 nm). The ternary alloy $In_{0.53}Ga_{0.47}As$ meets this criteria (E_g = 0.74 eV) and has been

the subject of many developments in recent years. Its fabrication by low-temperature (LT) growth was studied first and led to short carrier lifetimes [Kunzel *et al.*, 1992]. However, it was found to electrically underperform LT grown GaAs. The dominant traps, assigned to point defects, are too shallow for adequate electrical isolation. As a result, extra processing has to be performed in order to increase the material resistivity after annealing. Carrier compensation with berylium doping does not allow for a sufficient increase of the resistivity. Some authors suggest to reduce slightly the gallium content (thus increasing the material band gap) for superior results [Takazato *et al.*, 2007]. Other epitaxy-based approaches were tested recently and photoconductors exhibiting suitable properties for making THz devices have been obtained by i) incorporating ErAs metallic precipitates in Be-doped $In_{0.53}Ga_{0.47}As$ [Driscoll *et al.*, 2005], ii) incorporating iron impurities that act as mid-gap states in $In_{0.53}Ga_{0.47}As$ [Wood *et al.*, 2010], or iii) using an especially designed InGaAs/InAlAs multilayer structure for which absorption and photocarrier trapping occur in different layers of the structure [Kuenzel *et al.*, 2008]. Be-doped plasma-assisted epitaxy has also been used to fabricate ultrafast III–V compounds [Qian *et al.*, 1997] but such materials have not yet been exploited for optical THz emission. Despite the high level of material control that can be achieved by all these epitaxial growth techniques, the development of new structures and growth recipes may be particularly time consuming (*i.e.*, requires numerous wafer pieces and growth hours) depending on the number of parameters to be optimized. Standard epitaxial $In_{0.53}Ga_{0.47}As$ layers can also be damaged by ion beam processing, which is a popular post-growth fabrication technique that reduces the carrier lifetime [Doany *et al.*, 1987]. For instance, ultrafast ternary layers were produced after damaging them with heavy ions (*i.e.*, by irradiation [Chimot *et al.*, 2005] or implantation [Carmody *et al.*, 2003b; Suzuki et Tonouchi, 2005a]). It was found that energetic atomic recoils from the collision cascade triggers the formation of a high number of small defect clusters which further evolve into defect complexes after subsequent thermal annealing treatments. These complexes, unlike point defects, are believed to increase the ternary's electrical resistivity through forming deep carrier traps and efficient carrier recombination centers. When iron is the implanted species, it appears to combine with defect complexes and contribute to raise the resistivity. This is probably due to its capacity for producing extra mid-gap states [Carmody *et al.*, 2003b]. However, resistivity levels discussed in the literature in

relationship to ultrafast irradiated or Fe-implanted $In_{0.53}Ga_{0.47}As$ are typically lower than those pertaining to materials fabricated by epitaxial growth only [Driscoll *et al.*, 2005; Kuenzel *et al.*, 2008; Takazato *et al.*, 2007; Wood *et al.*, 2010]. High resistivity is desirable since Joule heating becomes a problem when operating photoconductive emitters under high DC electric fields. Overall, the resistivity of most ultrafast materials based on $In_{0.53}Ga_{0.47}As$ struggles to exceed 500 Ωcm, sometimes with low Hall mobility of less than 100 $cm^2V^{-1}s^{-1}$, a situation which prompts to look for alternatives.

InGaAsP quaternary alloys offer some extra design flexibility over $In_{0.53}Ga_{0.47}As$. Lattice-matching with InP is met by adjusting the molar fraction y in $(In_{0.53}Ga_{0.47}As)_y(InP)_{1-y}$. Its bandgap can be tuned from 0.74 eV up to 1.35 eV. It becomes possible to tailor the absorption band edge of the quaternary photoconductor close to any of the aformentioned rare-earth fiber laser wavelengths. This could prove useful for avoiding intervalley carrier scattering [Ralph *et al.*, 1996], particularly with the use of Yb-doped fiber sources. As a rule of thumb, semiconductors with higher bandgaps show larger intrinsic resistivity. For use with Er-doped fiber lasers, band-to-band absorption at 1550 nm is allowed for molar fractions of about $y = 0.9$ or greater. Relative to $In_{0.53}Ga_{0.47}As$, a small increase in the band gap is possible ($E_g = 0.79$ eV) which corresponds to a factor of about 2 or 3 in higher intrinsic resistivity. Amongst the fabrication techniques listed here, we select the Fe implantation post-growth process, given that the epitaxy of quaternary alloys is based on already rigorous calibrations.

In this context, undoped InGaAsP layers (1.5 μm thick) were grown on semi-insulating InP wafers (75 mm diameter) by metal-organic chemical vapor deposition. The quaternary layer was sandwiched between thin (100 nm) undoped InP buffer and capping layers. Two wafers were selected to assess the end-to-end reproducibility of the material processing. Their room-temperature photoluminescence (PL) peak wavelengths were 1565 nm (wafer 1) and 1575 nm (wafer 2). Offsets of −240 arc sec (wafer 1) and −380 arc sec (wafer 2) in the high resolution X-ray diffraction rocking curve were observed for the (004) reflection, revealing a small lattice mismatch. Thus the starting material was $In_{1-x}Ga_xAs_yP_{1-y}$, with $x = 0.39$ and $y = 0.865$ for wafer 1 and with $x = 0.38$ and $y = 0.86$ for wafer 2. The level of compressive strain (0.1% and 0.15%) was acceptable and layer coherence was maintained.

Using a Tandetron 1.7 MV accelerator (High Voltage Engineering Europa), one quarter of each wafer was implanted with an incident beam of Fe ions, impacting the surface at a 7 degree angle. The ion fluence level was set around 10^{15} cm^{-2} which produced better overall results in previous Fe-implanted $In_{0.53}Ga_{0.47}As$ studies [Carmody *et al.*, 2003b]. Five energies (0.25, 0.5, 1, 1.8, 2.5) MeV and respective fluences (0.11, 0.22, 0.33, 0.44, 1) × 10^{15} cm^{-2} were determined by SRIM software simulations [Ziegler *et al.*, 1985] and optimized for flat damage and uniform iron profiles through the whole quaternary layer. Summing for all energies, a total fluence of 2.1 × 10^{15} cm^{-2} was implanted, resulting in an average Fe concentration of 1.1 × 10^{19} cm^{-3} in the InGaAsP layer. At these high Fe fluences, the quaternary layer is heavily damaged, if not amorphized [Suzuki et Tonouchi, 2005a]. SRIM software simulations predicted 6.5 atomic displacements per atom (using 10 eV as the displacement energy for In, Ga, As, and P atoms). According to [Too *et al.*, 2003], [Marcinkevicius *et al.*, 2004] and [Subramaniam et Rezazadeh, 2006], the implantation temperature can also affect significantly the electrical properties of Fe-implanted $In_{0.53}Ga_{0.47}As$ at high fluences. The InGaAsP samples were implanted at 83 K for that very reason. The cold implantation suppresses detrimental dynamic defect annealing that may otherwise occur during room temperature implantations [Wendler, 2009].

The damaged quaternary layers were then processed by rapid thermal annealing (RTA) in order to modify and optimize their electrical and optical properties. For each wafer, a series of cleaved samples were maintained for 30 s at distinct temperatures between 400 °C to 800 °C in a nitrogen filled thermal processing chamber (Jipelec, Jetfirst). A 100 mm silicon wafer (which served as a susceptor) and a silicon proximity cap protected both top and bottom surfaces from phosphorous desorption. Prior to characterization, the InP capping layer was removed by selective wet chemical etching.

4.3 Effects of Fe ion implantation and RTA on critical properties for THz emission

4.3.1 Electrical Hall measurements

The carrier transport in Fe-implanted InGaAsP layers was investigated by Hall measurements (at 300 K, in dark ambient conditions). Resistivity, carrier density and Hall mobility were

estimated assuming a uniform layer, a single carrier type and a unity scattering factor. Measurements were made in the van der Pauw geometry on 6 mm×6 mm samples with indium contacts alloyed at 300 °C for 60 s. Hall coefficients were recorded at 0.36 T. Measurements on Fe-implanted InGaAsP samples reported in Fig. 1 pertain to two wafers. Properties of the as-grown InGaAsP epilayers are also tabulated in the inset of this figure. Hall coefficients values are negative in all cases, the electrons being the majority carrier in the as-grown material.

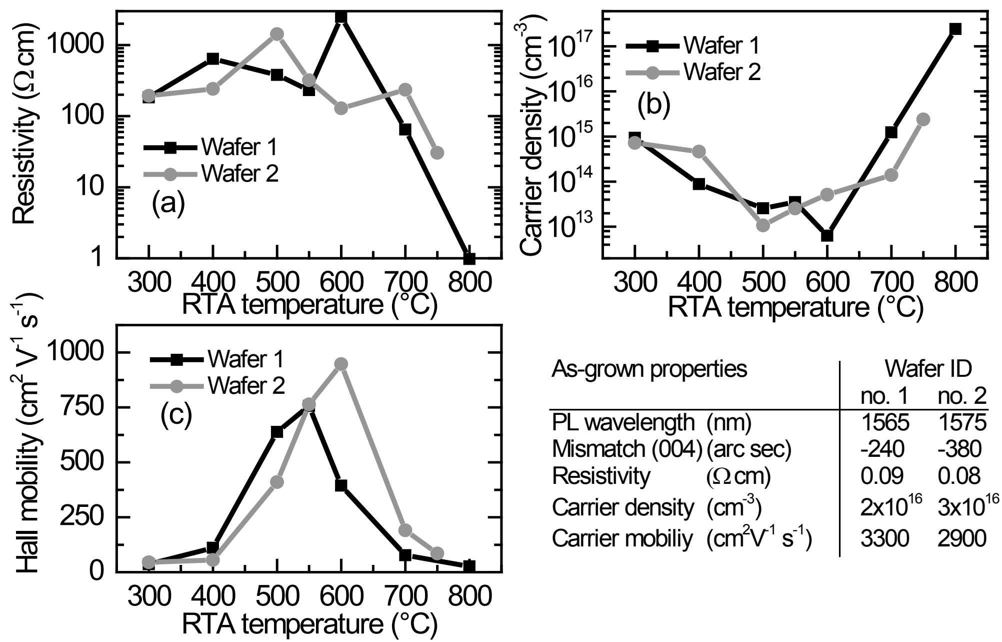

Figure 4.1 Effects of a 30 s RTA (400 °C to 800 °C) on (a) resistivity, (b) free carrier density and (c) Hall mobility of implanted InGaAsP with an Fe fluence of 2.1×10^{15} cm^{-2} at 83 K. Data for as-implanted samples are indicated at 300 °C, which was the In alloying temperature. Two wafers were used and their as-grown parameters are tabulated here. The solid lines are only guides for the eye.

For both wafers, the Hall transport results show similar influence of the Fe implantation and RTA processes. At the lowest annealing temperature (300 °C), necessary for In alloying, we find that ion implantation at high fluences causes a drastic reduction of the Hall mobility, compared to the as-grown material. By increasing the RTA temperature up to 500 °C, we observe an important decline of the free carrier density (Fig. 1b) along with a progressive recovery of the Hall mobility (Fig. 1c). Then, maximum resistivity values of 2500 Ωcm and

1400 Ωcm and minimal carrier density values of about 10^{13} cm^{-3} were achieved at 600 °C and 500 °C for wafer 1 and wafer 2, respectively (Figs. 1a and 1b). The resistivity increases by more than a 10^4 factor with respect to the as-grown material. The Hall mobility peaks at slightly different RTA temperatures. Still, the highest resistivity sample of both series show a reasonable mobility, of about 400 $cm^2V^{-1}s^{-1}$. By further increasing the RTA temperature beyond 600 °C, our results show a rapid reduction of the material resistivity associated with a strong increase of the carrier density and a gradual decrease of the carrier mobility.

Low mobility hopping conduction is expected to be the actual carrier transport mechanism in an amorphized quaternary layer [Carmody *et al.*, 2003b]. Accordingly, our implanted samples annealed at the lowest temperature do show a 100-fold reduction in mobility with respect to as-grown layers. As the annealing temperature increases, mobile defects can diffuse, annihilate or agglomerate to form complexes along with the implanted Fe that act as deep level carrier traps. Because the thermal annealing reduces the number of defects and restores to some extent the crystalline quality of the layer, carrier mobility tends to increase, especially between 400 °C and 550 °C (i.e., channels of conductive paths gradually open as the temperature increases). At RTA temperatures above 600 °C, the upturn in free carrier density follows a carrier release mechanism.

Either shallow donor defects are forming, such as As or P antisites [Carmody *et al.*, 2003b], or donor impurities intrinsic to the material are re-activated. Other possible mechanisms might be related to the dissociation of Fe defect complexes, or related to the in-diffusion of interface contaminants such as C or Si, or else the out-diffusion of Fe at high annealing temperatures, as it typically does [Too *et al.*, 2003]. Detailed analysis of impurity depth profiles with secondary ion mass spectrometry and advanced capacitance-voltage measurements would be required for a proper assignment. These shallow levels are probably ionized which explains the gradual decrease of carrier mobility with temperature. The activation of Fe, which is expected at high temperatures, did not cause the resistivity to re-increase, as observed by Carmody *et al.* with Fe-implanted $In_{0.53}Ga_{0.47}As$[Carmody *et al.*, 2003b].

4.3.2 Optical absorption

The optical transmission spectra of the samples were measured with an arc lamp source (Oriel, model 66881) and a spectrum analyzer (Ando, model AQ6317). The samples were illuminated at normal incidence with a collimated beam (0.7 mm spot size). The power spectral density was kept below −65 dBm/nm. A 1 nm resolution bandwidth gave an adequate dynamic range. At this resolution, the Fabry-Perot interferences, caused by multiple reflections from the facets of the 600 μm thick InP substrate, are partially smoothed out. Signals transmitted through and without the sample were recorded subsequently, at each wavelength position.

Room-temperature transmission loss spectra of the as-grown, implanted and annealed samples are shown in Fig. 2. The inset shows the fraction of the light absorbed by the samples around 1550 nm obtained after subtracting the amount of light reflected by the sample's facets.

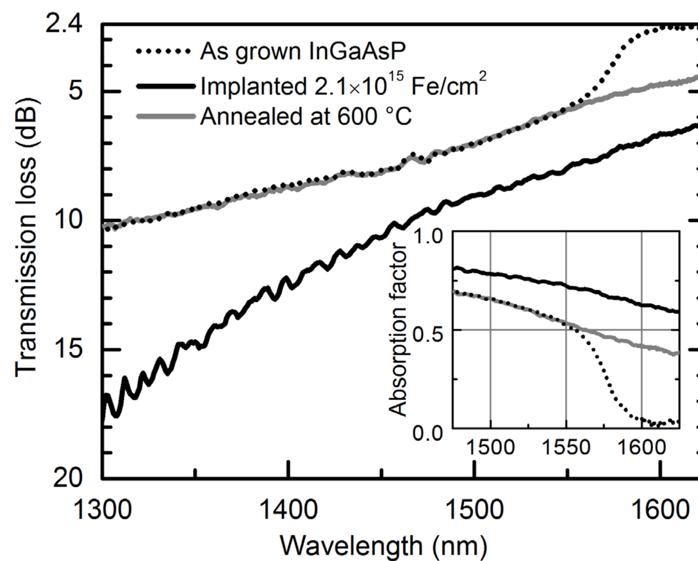

Figure 4.2 White light transmission loss spectra of as-grown, implanted and annealed InGaAsP/InP samples from wafer 1. The spectrum analyzer resolution bandwidth = 1 nm, the scanning step = 1 nm, and a 10-point Savitsky-Golay smoothing was applied. The y-axis reference level is located at 2.4 dB, it is the average transmission loss from a cavity with facet reflection of 27 %. The figure inset shows the optical absorption factor within the 1.5 μm-thick quaternary layer around 1550 nm

For the as-grown quaternary layer, we observe a step-like transmission enhancement at 1575 nm which corresponds to the absorption band edge of this material. For wavelengths

longer than the band edge wavelength, the small 2.4 dB transmission loss is caused by 27% facet reflections. After the implantation of Fe at a fluence of 2.1×10^{15} cm^{-2}, the band edge signature is no longer visible and the transmission loss becomes larger by more than 3 dB at 1550 nm. The increased absorption factor at short wavelengths might be caused by strong scattering of light on large defects present in the amorphized layer. The absence of a sharp transmission feature at 1575 nm, on the other hand, can be explained by extra optical transitions involving trap states that are distributed within the band gap of the material. Annealing the sample at 600 °C reduces the transmission loss to the level of the as-grown material and extra absorption is still observed for wavelengths longer than 1550 nm due to the remaining energy-distributed trap states. The total absorption of the laser light at 1550 nm by this 1.5 μm thick InGaAsP photoconductive layer is only 0.5. This corresponds to an optical attenuation coefficient of 4700 cm^{-1}. By contrast, $In_{0.53}Ga_{0.47}As$ has an absorption coefficient of about 7500 cm^{-1} at 1550 nm [Bacher *et al.*, 1988]. A ternary layer of the same thickness would absorb about 0.75 of an incoming light. These relatively small factors need to be taken into account when coupling these photoconductors to Er-doped fiber laser sources.

4.3.3 Photocarrier trapping time measurements

Experimental setup

A schematic of the transient differential reflectivity setup used to estimate the carrier trapping time of Fe-implanted InGaAsP layers is shown in Fig. 3. An Er-doped fiber laser source developed by the Institut National d'Optique was used for these measurements. This source delivers 250 fs pulses at a repetition rate of 20 MHz, and with an average power of 1 W. The linearly polarized output beam, centered at 1550 nm, is split into cross-polarized pump and probe beams. Their power ratio is set by the rotation of a half-wave plate placed before the polarizing beam splitter. In the context of our study, the pump and probe powers are set to 10 mW and 300 μW, respectively. The pump and probe beams are focused on the sample and the overlapping spots have full widths at half maximum of 20 μm and 10 μm, respectively.

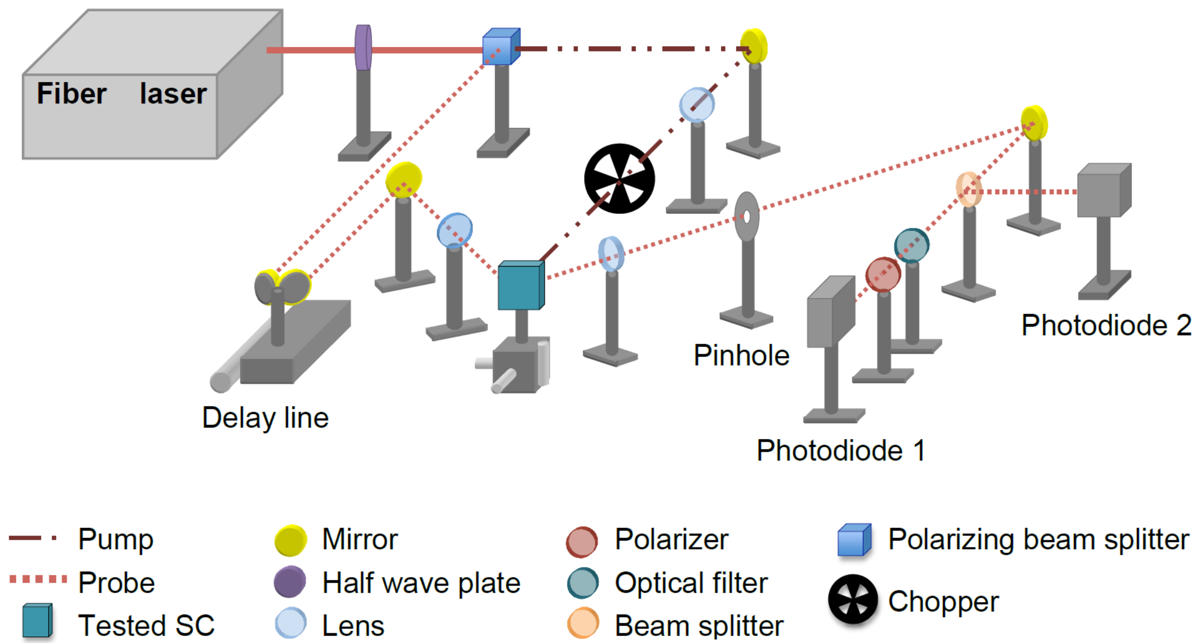

Figure 4.3. Schematic of the transient differential reflectivity setup configured for testing semiconductor chips (SC) at 1550 nm.

The pump beam illuminates the sample surface at normal incidence and its intensity is modulated at 1 kHz with a mechanical chopper. The probe beam is reflected by the sample surface and then collected and redirected on two separate photodiodes. The output of photodiode 1 is sent to a lock-in amplifier for a measurement of the pump-induced reflectivity (ΔR) signal. The output of photodiode 2 is low-pass filtered (the cut-off frequency being much lower than the chopper frequency) giving rise to the average reflectivity signal. A pinhole is inserted into the detection path and spatially filters the reflected probe beam such that the detected signal mainly originates from a 1 µm spot size on the sample. The pinhole also reduces significantly the level of pump scattering from the semiconductor surface. A high-pass optical filter and a polarizer are placed in front of photodiode 1 in order to cut photoluminescence at 1565 nm and the remaining pump intensity, respectively. Under these experimental conditions, the noise level is low enough to detect relative changes of reflectivity as small as 0.001%. Finally, a variable delay line is used to record ΔR/R signals at different time delays between the pump and probe pulses hitting the sample surface.

Differential reflectivity measurements were made with wafer 2 sample series, which was annealed at temperatures between 400 °C and 750 °C. We chose this sample series because of better overall surface quality (as compared to wafer 1 series). We found out that small particles tend to appear on the silicon susceptor after many RTA cycles. This influences the quality of the InGaAsP top surface, which is facing the susceptor during the RTA process. The wafer 2 sample series was processed just after replacing the susceptor with a new one.

Results and analysis

Figure 4 shows the differential reflectivity signals (circles in Fig. 4a) which are plotted on a semi-log graph as a function of the pump-probe time delay. The experimental curves exhibit exponential decay behaviours. The reflectivity signal from the sample annealed at 400 °C decays very rapidly with a single exponential. As the annealing temperature increases, the decay time becomes longer and a second exponential decay has to be taken into account, in order to describe the experimental data at longer pump-probe time delays.

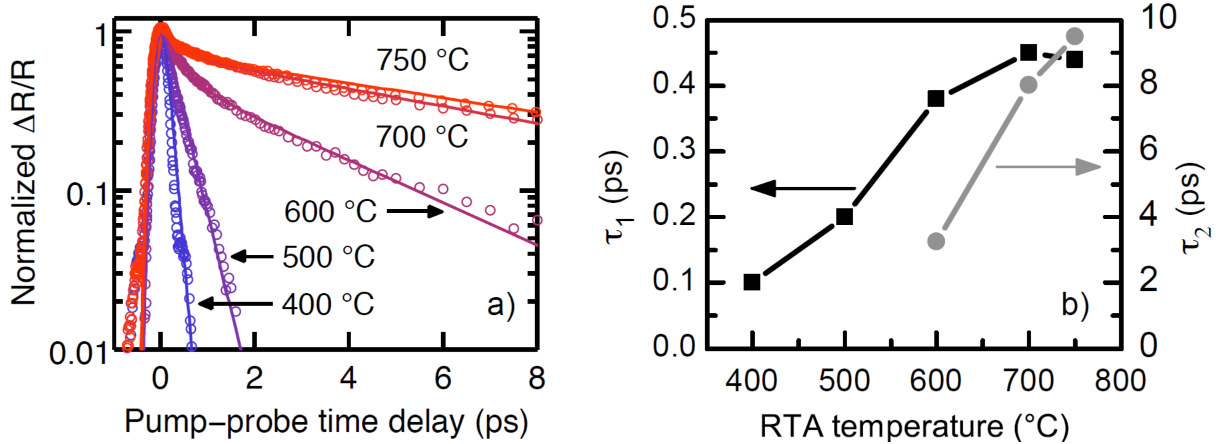

Figure 4.4 (a) Normalized differential reflectivity measurements (circles) and fitted curves (solid lines) for InGaAsP (wafer 2) implanted with Fe at a fluence of 2.1×10^{15} cm^{-2} at 83 K, after 30 s RTA at various temperature. (b) Amplitude ratio A_1/A_2 and (c) decay times τ_1 and τ_2 are plotted against the RTA temperature, after their extraction from curve fitting.

Those differential reflectivity signals could be modeled by two convolution products involving the laser probe pulse, the pump pulse, and the impulse response of the sample:

$$\Delta R/R \propto I_{probe}(t) * [I_{pump}(t) * U(t)] \quad (1)$$

where I_{probe} (t) and I_{pump} (t) are the temporal intensity profiles of the probe and pump, respectively. $U(t)$ is an impulse response function describing the return to equilibrium of the photoexcited semiconductor. $U(t)$ is given by:

$$U(t) = H(t)\left[A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp(-\frac{t}{\tau_2})\right] \quad (2)$$

with $H(t)$ being the unit step function. Parameters A_1 and A_2 are the amplitudes of the two exponential functions with decay times of τ_1 and τ_2, respectively. The solid lines plotted in Fig. 4a correspond to the fitted curves calculated using Eqs. (1) and (2), and considering a Gaussian temporal profile for the probe and pump laser pulses (with a full width at half maximum of 250 fs). This model can fit properly the rising edge of the differential reflectivity measurements which is also essential for extracting decay times of comparable or smaller duration than the excitation pulse width. Relative pump-induced variations of the Fresnel reflection coefficient $\Delta R/R$ are generally small enough (no more than a few percent) to be considered linearly dependent on the excess electron-hole pair density [Korn *et al.*, 2002]. The analysis, however, is often complicated by contributions of several mechanisms that affect the total absorption change $\Delta\alpha(t)$ and its related real refractive index change $\Delta n(t)$ [Ortiz *et al.*, 2007; Prabhu et Vengurlekar, 2004]. Since the maximum of the $\Delta R/R$ signal varies almost linearly with the excitation pump power (from 1 mW to 10 mW), the hypothesis we made was that the transient differential reflectivity is more or less proportional to $N_{ph}(t)$ (which is either the number of photo-created electron-hole pairs due to band-to-band absorption or the number of free electrons in the conduction band due to absorption from deep levels).

Figures 4c and 4b show the photocarrier population decay times and amplitude ratio extracted from the fitting procedure applied to each sample. The shortness in decay times observed with all samples is somehow related to capture and recombination mechanisms associated with traps located directly at the surface of the semiconductor and within the photoexcited region. After a 400 °C anneal, intrinsic and implantation-induced surface defect densities remain so high that photocarriers are captured very efficiently by surface traps ($\tau_1 < 0.2$ ps). For samples annealed at temperatures of 500 °C and above, a slower second exponential decay time τ_2 is observed. The relative amplitude of this second recombination channel increases with the

RTA temperature. This behavior might be explained by the back-diffusion of deep photocarriers towards the surface since this transport channel opens up once carriers initially photoexcited near the surface partially fill surface traps. Fig. 4c shows that both decay times (τ_1 and τ_2) become longer as the annealing temperature increases, although τ_1 seems to saturate at about 0.45 ps. These trends are related to the thermal annealing process which reduces the density of ion implantation induced defects at the surface and within the 1.5 μm thick epilayer. The upper value of 0.45 ps for τ_1 is most likely related to remaining intrinsic surface defects that cannot restored by thermal annealing. Explanations presented here might not be unique. For instance, the contribution of two independent populations of carriers also give rise to a double exponential decay. In order to validate these working hypotheses, further experiments are planned. The influence of the laser pump power on the transient differential reflectivity curves is going to be studied over a wide range of pump powers.

In summary, optimal electrical properties for making a photoconductive THz antenna device are produced for RTA temperatures ranging from 500 °C to 600 °C (see Fig. 1). In this range, the fast decay time in transient reflectivity measurements is subpicosecond. The presence of implantation-induced defects throughout the InGaAsP layer limits the second decay time to a few ps. With such small decay times ($\leqslant$ 3 ps), a THz-TDS system made with Fe-implanted InGaAsP THz photoconductive antennas is expected to show more than 1 THz of usable bandwidth.

4.4 Antenna fabrication and THz emission with Fe-implanted InGaAsP

THz emitters were developed using dipolar antennas fabricated on InGaAsP samples taken from wafer 1 which were cold-implanted with Fe ions. The samples were annealed for 30 s at 600 °C. Ohmic contacts were formed by e-beam deposition of a 285 nm thick layer of a standard mixture of Ni/AuGe/Au, followed by a 30 s anneal at 410 °C. Coplanar electrodes (10 μm wide, 8 mm long and spaced by a 120 μm gap) were patterned by standard lift-off photolithography. A current-voltage curve was recorded for this device and a dark current value of 8.4 μA was found at 1 V bias. With this particular electrode geometry, it corresponds to a layer sheet resistivity of 7.9 MΩ/sq and a material resistivity of 1200 Ωcm. The THz emitter was mounted on a holder and its electrodes were wire-bonded to a coaxial connector pair. A hemispherical high resistivity silicon lens was placed in contact with the back side of the device for an efficient collection of the THz radiation.

The broadband emission of the photoconductive antennas was recorded using a THz time-domain spectroscopy setup coupled to the Er-doped fiber laser source described previously. The excitation laser power was about 80 mW and the pump beam intensity was modulated at 1 kHz using a mechanical chopper. The antenna was operated at 50 V, well below thermal runaway. The 1550 nm excitation beam was focused into a spot size diameter of about 20 μm (using the 1/e intensity fall criteria). We did observe an enhancement of the emitted THz radiation by exciting near the anode of the antenna (the radiation was measured using a bolometer). This behavior might be related to the ionization of traps that enhances locally the electric field (as reported by [Ralph et Grischkowsky, 1991]) but contrary to trap-enhanced-field THz sources made on GaAs, we observed a similar enhancement by exciting near the antenna's cathode. Experiments are ongoing in order to better understand this behavior. The radiation emitted by the antenna was collimated and refocused on the THz detector using a combination of the silicon lens followed by four off-axis parabolic mirrors. This mirror configuration was chosen because our setup is also designed to perform absorption measurement and visible-pump –THz-probe experiments. The electric field of the THz pulses was measured with electro-optic sampling detection and a 10 mW probing beam in a 0.5 mm

thick < 110 > ZnTe crystal. The THz signal was retrieved using a Pockels cell setup with two balanced photodiodes and a lock-in amplifier. THz traces were recorded point by point using a delay line. The spectra of these traces were then produced using numerical Fourier transforms.

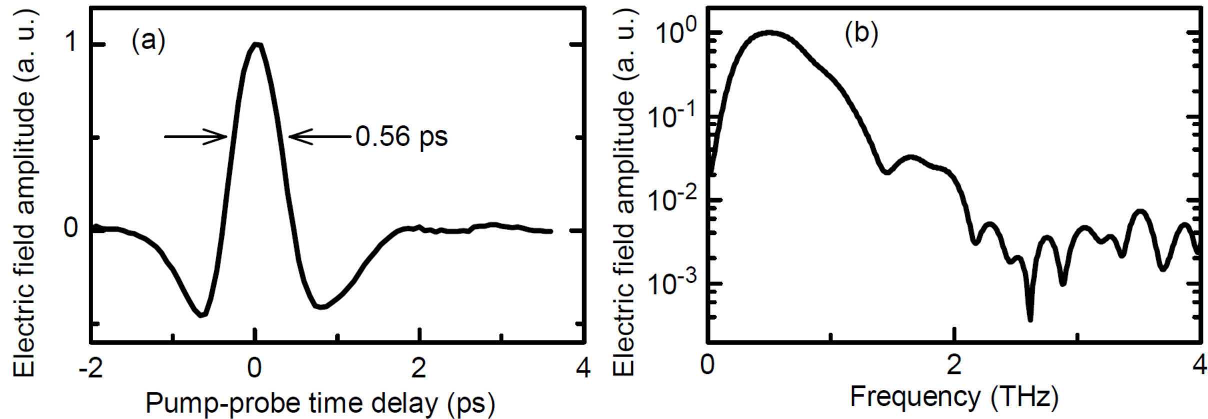

Figure 4.5 (a) Time-domain signal emitted from a photoconductive antenna made of Fe-implanted InGaAsP annealed at 600 °C, excited by 250 fs pulses from an Er-doped fiber laser (P_{pump} = 80 mW) at V_{bias} = 50 V (4.2 kV/cm) and detected using a 0.5 mm thick ZnTe electro-optic crystal. (b) Amplitude spectrum obtained by fast Fourier transform of the temporal signal.

Figure 5 shows the temporal trace of the THz pulses (emitted by the InGaAsP-based antenna) and its corresponding spectrum. The Fourier-transformed THz spectrum peaks at 500 GHz. It exhibits a usable spectral range of 2 THz, and a maximum amplitude signal-to-noise ratio of 25 dB. The spectral bandwidth is likely limited by the detector since a large mismatch exists between the group velocity of the 1550 nm probing pulse and the phase velocity of the THz pulse in ZnTe [Nagai *et al.*, 2004; Wood *et al.*, 2010]. Further measurements using a thin GaP electro-optic crystal are underway to confirm this. It is also known that the antenna's geometry can have significant effect on the bandwidth. Results shown in the context of this study were obtained on the very first antennas made with already existing lithographic masks. Nevertheless, their overall characteristics are comparable to the best ones made on $In_{0.47}Ga_{0.53}As$:Fe photoconductive materials [Wood *et al.*, 2010]. The complete spectral investigation of the InGaAsP emitter against bias voltage and pump power will be the subject of a separate publication.

4.5 Discussion

For use with Er-doped femtosecond lasers, thermally annealed Fe-implanted InGaAsP compares favorably to many of the materials proposed up to now (see Table 1). In fact, 20- to 30-fold improvements in resistivity over ultrafast Fe-implanted $In_{0.53}Ga_{0.47}As$ reported by [Carmody *et al.*, 2003b] is quite remarkable. Both were implanted with MeV Fe ions at similar fluence and annealed at similar temperatures

Table 4.1 Summary of Results Reported for Ultrafast Photoconductive Layers Grown on Semi-Insulating InP Which Were Used for THz Emission.

Material description	Dark resistivity (Ωcm)	Hall mobility ($cm^2V^{-1}s^{-1}$)	Carrier trapping time (ps)
Be-doped LT $In_{0.45}Ga_{0.55}As$ [Takazato *et al.*, 2007]	760	26	-
Fe-doped $In_{0.47}Ga_{0.53}As$ [Wood *et al.*, 2010]	2100	-	-
Be-doped $In_{0.47}Ga_{0.53}As$ with ErAs islands [Driscoll *et al.*, 2005]	343	202	< 0.22
Be-doped LT InGaAs/InAlAs multilayer [Kuenzel *et al.*, 2008]	100 – 200	500 – 1500	0.23 – 1.5
Br-irradiated $In_{0.47}Ga_{0.53}As$ [Chimot *et al.*, 2005]	3	490	0.2
Fe-implanted (300 K) $In_{0.47}Ga_{0.53}As$ [Carmody *et al.*, 2003b]	~ 80	100	0.3
Fe-implanted (83 K) $In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$	1200 – 2500	400	0.3 – 3

The quaternary band gap energy E_g is only larger by 0.04 eV compared to the ternary value, which rules out any large band gap-related intrinsic resistivity enhancement with respect to Fe-implanted $In_{0.47}Ga_{0.53}As$. It is not clear whether the phosphorous present in the quaternary plays a critical role in forming Fe defect complexes. The multiple-energy cold implantation process is likely responsible for the improvement and clearly shows free carrier compensation as low as the 10^{13} cm^{-3} level. In a previous annealing study on n-doped $In_{0.47}Ga_{0.53}As$ implanted with Fe at 77 K by [Subramaniam et Rezazadeh, 2006], the resistivity reached 950 Ωcm with very similar fabrication parameters. The ion beam damage from high fluence MeV Fe implantation takes about a day to complete on a 75 mm wafer quarter, due to nA ion current levels of the Fe^+ source. The 1/e absorption length (at 1550 nm) of the Fe-implanted

quaternary is 2.1 μm. Therefore, the existing layer thickness could be increased for photoconductive efficiency improvements, but at the cost of lengthened implantation and lower resistance between the electrodes. Strong band tails, resulting from cold implantation with high Fe^+ fluence, are helping to absorb the spectral content of femtosecond pulses beyond the primary InGaAsP band edge wavelength. It may indicate that similar physics found in highly disordered and amorphous semiconductors is indeed happening (*i.e.*, multiple conduction involving extended states, tail states and hopping transport) [Madan et Shaw, 1988]. Additional work has to be undertaken in order to better understand the origin of the material tail states and defect states along with their influences on carrier transport, carrier lifetime, and on THz emission.

4.6 Conclusion

We investigated the use of quaternary InGaAsP alloys in fabricating photoconductive THz emitters. Epitaxial InGaAsP layers (with PL wavelengths at 1565 and 1575 nm) underwent high fluence Fe ion implantation at 83 K. They were then processed by rapid thermal annealing and characterized. Interesting optoelectronic properties occurred at annealing temperatures between 500 °C and 600 °C. We report a high resistivity of about (1200 – 2500) Ωcm, a Hall mobility of 400 $cm^2V^{-1}s^{-1}$, and a photocarrier trapping time of (0.3 – 3) ps. At 1550 nm, the optical absorption coefficient is 4700 cm^{-1}. Fe-implanted InGaAsP dipole antennas were fabricated for a THz-TDS validation. They were excited at 1550 nm with 250 fs pulses. The emitted spectral range exceeded 2 THz and had 25 dB of peak-to-noise ratio. Post-growth processing with cold, high fluence, Fe implantation was key to produce InGaAsP-based THz devices with good emitter characteristics.

Quaternary alloys allow to adjust the offset of their optical absorption edge to the laser emission wavelength. Implantation damage makes femtosecond pulse absorption possible beyond the primary PL wavelength. Besides 1.55 μm, other wavelengths can be exploited for THz technologies. Work is in progress to characterize the MeV Fe implantation process on a quaternary with E_g = 0.95 eV, which could be used as a photoconductive material for Pr-doped fiber lasers sources operating at 1.3 μm or Yb-doped fiber lasers sources operating around 1.0 μm.

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CHAPITRE 5 Températures critiques de fabrication

Avant-propos

Dans cet article, notre intention est d'explorer les limites du procédé d'implantation à forte fluence en variant la température d'implantation, la température de recuit, la composition de l'alliage d'InGaAsP et l'espèce implantée.

Auteurs et affiliation

André Fekecs : candidat au doctorat, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

Martin Chicoine : professionnel de recherche, Université de Montréal. Département de physique.

Bouraoui Ilahi : professeur visiteur, Université de Sherbrooke. Institut Interdisciplinaire d'Innovation Technologique (3IT).

Anthony SpringThorpe : agent de recherche principal, Canadian Photonics Fabrication Centre (CPFC), CNRC.

François Schiettekatte : professeur, Université de Montréal. Département de physique.

Denis Morris : professeur, Université de Sherbrooke. Faculté des sciences. Département de physique.

Paul Charette : professeur, Université de Sherbrooke. Faculté de génie. Département de génie électrique et de génie informatique.

Richard Arès : professeur, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

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Revue : Nuclear Instruments and Methods in Physics Research Section B

Titre français : Températures critiques pour fabriquer des hétérostructures d'InGaAsP/InP résistives par forte implantation d'ions de Fe ou de Ga.

Contribution au document : Nous présentons une étude exhaustive de l'implantation d'ions lourds (^{56}Fe et ^{69}Ga) à hautes énergies et à forte fluence dans l'alliage InGaAsP/InP dans le but de former des couches résistives. La présente étude illustre le rôle important joué par la température d'implantation dans réalisation de notre objectif. Pour obtenir des structures résistives, l'InGaAsP/InP peut être implanté à 83 K et 300 K avec des caractéristiques électriques et structurales semblables. Nous interprétons ce résultat avec la température critique d'implantation (T_c) propre à l'InGaAsP et l'InP. Notre discussion des résultats s'appuie sur des simulations des séquences d'implantation et des mesures de diffraction de rayons X.

Résumé en français : Nous rapportons des températures d'implantation et des températures de recuit rapide qui produisent des hétérostructures InGaAsP/InP de forte résistivité. Quatre gaufres comportant des hétérostructures InGaAsP/InP ont été modifiées avec des séquences d'implantation de Fe ou de Ga faites à multiples énergies MeV et à fluence élevée (10^{15} cm^{-2}). L'étude est faite sur deux compositions d'InGaAsP, qui correspondent aux longueurs d'onde de bande interdite de 1.3 µm et 1.57 µm. L'étude révèle que la résistance des hétérostructures est fortement reliée à la température d'implantation, laquelle influence le type de défauts induits par implantation. Avec une implantation chaude, à 373 K et 473 K, la diffraction de rayons X a établi qu'un recuit dynamique empêche l'amorphisation des couches d'InGaAsP. Les couches implantées à chaud étaient moins résistives et une forte résistivité n'est pas obtenue systématiquement après le recuit. Avec une implantation froide à 83 K, et même à 300 K, le recuit dynamique est minime. Le dommage de l'implantation peut s'accumuler et produit des structures amorphes et résistives. Après un recuit rapide, toutes les couches implantées à froid avec le Fe ou le Ga présentent des signatures polycristallines en diffraction de rayons X. Leurs paramètres électriques évoluent similairement en fonction de la température de recuit et des couches résistives sont formées près de 500 °C. Cependant, une meilleure isolation est obtenue avec l'implantation Fe. Les différences de résistivité obtenues entre les deux compositions de l'alliage sont moindres qu'un effet associé à l'énergie de bande

interdite. Les observations que nous faisons sont reliées aux mécanismes d'accumulation et de guérison du dommage d'implantation. Elles ont d'importantes implications pour la réalisation de couches résistives pouvant être excitées par des impulsions laser pour des applications d'optoélectronique ultrarapide dans l'infrarouge.

Critical process temperatures for resistive InGaAsP/InP heterostructures heavily implanted by Fe or Ga ions

A. Fekecs, M. Chicoine, B. Ilahi, A. SpringThorpe, F. Schiettekatte, D. Morris,
P. Charette et R. Arès

Abstract We report on critical ion implantation and rapid thermal annealing (RTA) process temperatures that produce resistive Fe- or Ga-implanted InGaAsP/InP heterostructures. Two InGaAsP/InP heterostructure compositions, with band gap wavelengths of 1.3 µm and 1.57 µm, were processed by ion implantation sequences done at multiple MeV energies and high fluence (10^{15} cm^{-2}). The optimization of the fabrication process was closely related to the implantation temperature which influences the type of implant-induced defect structures. With hot implantation temperatures, at 373 K and 473 K, X-ray diffraction (XRD) revealed that dynamic defect annealing was strong and prevented the amorphization of the InGaAsP layers. These hot-implanted layers were less resistive and RTA could not optimize them systematically in favour of high resistivity. With cold implantation temperatures, at 83 K, and even at 300 K, dynamic annealing was minimized. Damage clusters could form and accumulate to produce resistive amorphous-like structures. After recrystallization by RTA, polycrystalline signatures were found on every cold Fe- and Ga-implanted structures. For both ion species, electrical parameters evolved similarly against annealing temperatures, and resistive structures were produced near 500 °C. However, better isolation was obtained with Fe implantation. Differences in sheet resistivities between the two alloy compositions were less than band gap-related effects. These observations, related to damage accumulation and recovery mechanisms, have important implications for the realization ion-implanted resistive layers that can be triggered with near infrared laser pulses and suitable for ultrafast optoelectronics.

Keywords: III-V semiconductors, ion implantation, rapid thermal annealing, crystal defects, Hall effect, X-ray diffraction.

5.1 Introduction

It was demonstrated that ultrafast photoconductive materials based on bulk ternary $In_{0.53}Ga_{0.47}As$ layers can be obtained after Fe ion.[Carmody *et al.*, 2003b; Shin *et al.*, 2011] Such materials have found their use in novel terahertz spectrometers as photoconductive terahertz sources and detectors working at 1550 nm.[Suzuki et Tonouchi, 2005a; Suzuki et Tonouchi, 2005b] The process involves Fe ion implantation done at room temperature with a high ion fluence, close to 10^{15} cm^{-2} usually followed by rapid thermal annealing (RTA). RTA is aiming at maximizing the on-chip resistivity to enable high external bias for maximum terahertz emission or to minimize thermal noise for sensitive detection. This process was able to achieve apparent electrical resistivity levels up to 80 Ω·cm in Fe-implanted $In_{0.53}Ga_{0.47}As$ layers. [Carmody *et al.*, 2003b; Shin *et al.*, 2011] Obtaining high resistivity in low band gap InP-related semiconductor compounds (*i.e.*, with $E_g < 1$ eV), using primary ion implantation damage or in presence of secondary damage after annealing, was pointed out to be rather difficult.[Pearton et Chakrabarti, 1991] In these compounds, defects created by implantation tend to pin the Fermi level in the upper half of the band gap. Even though a mid-gap chemical impurity (Fe) was incorporated in these ultrafast materials, their apparent resistivity was much less than what one expects for fully compensated semiconductors. Such "intrinsic" resistivity is strongly dependent on the band gap energy E_g and is about 10^3 Ω·cm at room temperarure for the $In_{0.53}Ga_{0.47}As$ alloy ($E_g = 0.74$ eV).[Subramaniam et Rezazadeh, 2006]

Damage-related isolation studies on the ternary compound $In_{0.53}Ga_{0.47}As$ using Kr^+ and on the quaternary compound InGaAsP using N^+ or He^+ revealed that better resistivity can often be achieved with low implantation temperatures.[Comedi *et al.*, 1994; Too *et al.*, 2004] Comedi *et al.* [1994] remarked that amorphization of InGaAsP led to high resistivity and stability after annealing/recrystallization. Similar behaviour was also noted in the case of high fluence Fe implantation studies in $In_{0.53}Ga_{0.47}As$.[Marcinkevicius *et al.*, 2004; Subramaniam et Rezazadeh, 2006; Too *et al.*, 2003] These observations motivated our use of cold Fe-implantation, done at 83 K, to produce an ultrafast photoconductive material working at 1550 nm which is based instead an InGaAsP alloy with E_g=0.79 eV. Apparent resistivity levels exceeding 10^3 Ω·cm were achieved.[Fekecs *et al.*, 2011]

In this work, we report on a wide range of implantation temperatures (83 K to 473 K) that we investigated in order to obtain resistive Fe-implanted InGaAsP-based materials. We made these investigations by Hall effect measurements. For better insight, we accomplish this with two quaternary alloy compositions lattice-matched to InP (*i.e.*, 1.3Q and 1.57Q). The Q notation represents band gap wavelengths of 1.3 μm and 1.57 μm, respectively. Assuming that intrinsic resistivity levels could be achieved, an increase of the resistivity by a factor of 2-3 was expected with 1.57Q layers over $In_{0.53}Ga_{0.47}As$. A factor of about 50 was expected with 1.3Q layers. These factors take into account the energy gap difference $\Delta E = E_{gQ} - E_{gT}$ between the quaternary and the ternary alloys and are approximated by $e^{\Delta E/0.052}$ (in eV) at room temperature. In order to separate Fe-related deep level contributions from secondary damage contributions, we compare cold implantations made with Fe and Ga ions. We support the interpretations of the results by structural X-ray verifications done after ion implantation and after rapid thermal annealing. Fabrication conditions capable of producing high resistivity levels are then discussed, which gives important insights for developing novel photoconductive InGaAsP-based ultrafast devices.

5.2 Experimental study

5.2.1 Fabrication details on ion implanted InGaAsP

InGaAsP/InP heterostructures were grown on 75 mm semi-insulating single crystal (100) InP wafers. They were unintentionally n-doped. This was done by organometallic vapor phase epitaxy (OMVPE) in a multi-wafer reactor (Aixtron). They comprise a quaternary layer of InGaAsP (1.5 μm) capped by InP (0.1 μm) and grown over an InP buffer layer (0.1 μm), as shown by figure 1.

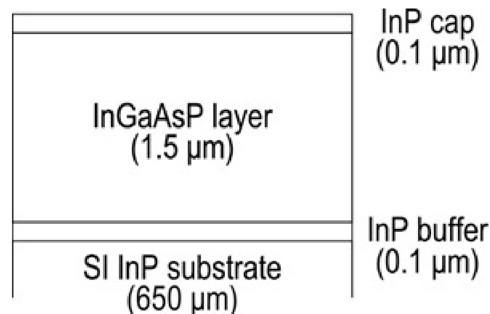

Figure 5.1 Layer diagram of InGaAsP/InP epitaxial heterostructures used in this work. Nominal thicknesses are indicated for each layer.

A total of four wafers were used, two were grown with a band gap wavelength of 1.57 µm (1.57Q) and the other two had a band gap wavelength around 1.3 µm (1.3Q). Growth temperatures were 625 °C for 1.57Q and 650 °C for 1.3Q. Their properties are reported in Table I. Photoluminescence (PL) average peak wavelength, substrate lattice mismatch (monitored by X-ray diffraction), as well as molar compositions (x, y) are tabulated for each wafer along with electrical properties determined by Hall effect measurements.

Table 5.1 List of basic properties of OMVPE grown $In_{1-x}Ga_xAs_yP_{1-y}$/InP structures used in this work. Ion implantation conditions – ion species and implantation temperatures (T_{impl}) – specific to each wafer quarter are also indicated for reference.

Basic properties and implantation conditions	Wafer identification no. 1 E972	 no. 2 F697	 no. 3 E971	 no. 4 F695
PL wavelength (nm)	1565	1575	1309	1341
Mismatch to (004) InP (arc sec)	-240	-380	-220	-320
Composition (x, y)	(0.39, 0.87)	(0.38, 0.86)	(0.27, 0.60)	(0.27, 0.62)
Carrier density (cm^{-3})	2×10^{16}	3×10^{16}	2.4×10^{16}	1.8×10^{16}
Hall mobility ($cm^2V^{-1}s^{-1}$)	3300	2900	2060	1250
Resistivity (Ω cm)	0.09	0.08	0.13	0.28
T_{impl} for ^{56}Fe ions (K)	83, 473	83, 300	83, 373,473	-
T_{impl} for ^{69}Ga ions (K)	-	83	-	83

High fluence, multiple-energy ion implantation was performed at various temperatures (T_{impl}) on InGaAsP wafer quarters (see Table 1). The temperature of the sample holder, a copper block, was controlled by liquid nitrogen and a resistive heater. The pressure in the implant chamber was kept below 1×10^{-6} Torr and samples were tilted at 7° with respect to the ion beam to reduce channelling effects. High energy ions were supplied by a 1.7 MV Tandetron accelerator (High Voltage Engineering Europa). Ion currents from the beam line were of the order of 30 nA. We ran SRIM simulations [Ziegler *et al.*, 1985] to develop multiple-energy implantation sequences. Five energies were used and a relative fluence weight was assigned to each in order to produce uniform implant damage and uniform implanted ion density profiles across the InGaAsP layer. The implantation sequence for ^{56}Fe was determined first. The implantation sequence for ^{69}Ga was determined after. Ga is a group III metal already present in the quaternary structure but heavier than Fe, therefore its implantation parameters had to be adjusted to obtain a damage level similar to that of Fe. Other simulation details were given

previously.[Fekecs *et al.*, 2011] Energies, fluences and profile averages are summarized in Table 2 for both Fe and Ga implantation sequences. Simulated implantation profiles are plotted in figure 2.

Table 5.2 List of implantation parameters used for high fluence Fe and Ga implantation based on 5-energy profiles SRIM simulations. Averages are calculated over the InGaAsP layer thickness.

Parameters	^{56}Fe implantation sequence	^{69}Ga implantation sequence
Energy (MeV)	(0.25, 0.50, 1.0, 1.8, 2.5)	(0.33, 0.63, 1.15, 2.03, 3.3)
Fluence ($\times 10^{15}$ cm^{-2})	(0.11, 0.22, 0.33, 0.44, 1)	(0.07, 0.12, 0.24, 0.29, 0.74)
Total fluence (cm^{-2})	2.1×10^{15}	1.46×10^{15}
Average density (cm^{-3})	1.1×10^{19}	7.3×10^{18}
Displacements per atom (n_{dpa})	6.5	5.8

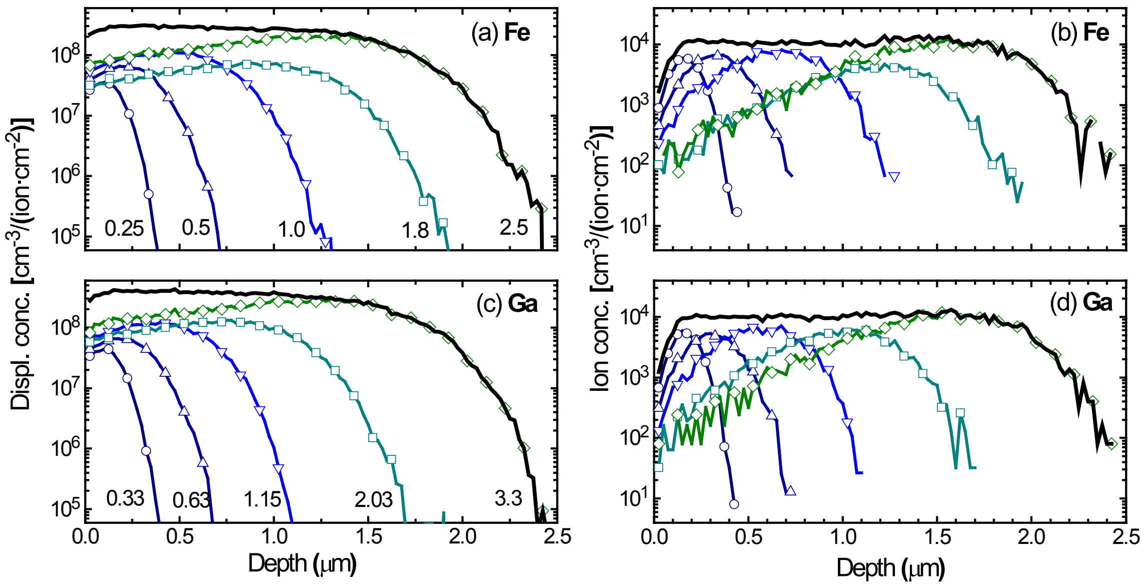

Figure 5.2 Multiple-energy implantation profiles of the displacement density and the implanted ion density, and their sums, in the InGaAsP/InP structure simulated by SRIM for two heavy ions. (a,b) Fe implantation and (c,d) Ga implantation. Ion energies are indicated in MeV on damage profiles. Details can be found in Table 2.

After implantation, surfaces were protected by a resin layer baked at 115 °C. As required, the implanted material was cleaved in 8 mm × 8 mm pieces and the resin was removed in solvents prior to rapid thermal annealing (RTA). The optimization of the annealing temperature was

undertaken in steps of 100 °C and sometimes of 50 °C. Each piece was processed at a distinct plateau temperature between 400 °C and 800 °C for 30 s in a dry nitrogen atmosphere using a lamp-based RTA chamber (Jipelec JetFirst). In one instance (Fe-implanted 1.57Q at 300 K) a different RTA apparatus (AG Associates Heatpulse AG610) was employed. Their thermocouple temperature profiles were equivalent. The pieces were placed with their epilayers face down on a clean silicon wafer susceptor. Back chip surfaces were also protected by 10 mm × 10 mm Si proximity caps. Proximity capping with silicon has been described as efficient for protecting InP surfaces from desorption of phosphorous atoms.[Quemerais *et al.*, 1990] Each annealed piece was scribed and cleaved down to 6 mm × 6 mm to remove its edges. The final sample was dipped in a solution of HCl to etch selectively the InP cap layer.

5.2.3 Sample characterization methodology

The structural quality of InGaAsP samples was verified before and after annealing by X-ray diffraction (XRD). High resolution (HRXRD) rocking curves were acquired by an MRD system (PANalytical) equipped with a 4-bounce Ge (220) Bartels monochromator at the source. Edge effects of the line source when surveying small samples were avoided by inserting a square aperture (0.2° × 0.2°) in front of the detector. Rocking curves were also acquired for wide angle scans on an X'pert Pro MRD powder diffractometer (PANalytical) in the Bragg-Brentano geometry equipped with a Xe-filled proportional detector. Electrical properties of the ion implanted InGaAsP thin films were investigated by resistivity and Hall effect measurements at 300 K. Measurements were made in the Van der Pauw geometry on 6 mm × 6 mm samples with indium contacts alloyed at 300 °C for about 75 s. Non-annealed ohmic contacts were formed on as-implanted samples with liquid In-Ga applied at room temperature. The measurements were carried out in the dark and in vacuum, using a commercial Hall system (MMR Technologies, model H-50). Hall voltages were recorded at 0.37 T. The calculations assumed a single carrier type and a unity scattering factor.

5.3 Ion beam damage

High resolution X-ray diffraction spectra (HRXRD) were taken on as-grown and 1.3Q structures implanted at 3 temperatures (83 K, 373 K and 474 K) with the Fe implantation sequence. Results are shown on Figure 3. The as-grown 1.3Q structure had a double peak

signature assigned to the InP substrate (S) and to a quaternary layer (Q). At growth, we aimed for a peak separation of -250 arc sec in order to detect and follow unambiguously the diffraction peak of the modified quaternary layer relative to the (004) reflection peak of the InP substrate. Here, the peak separation (*i.e.,* lattice mismatch) of the as-grown layer corresponded to a slight compressive strain (~0.1 %). A modulation, visible in the tails of the spectrum was produced by interference from the 100 nm InP cap layer.

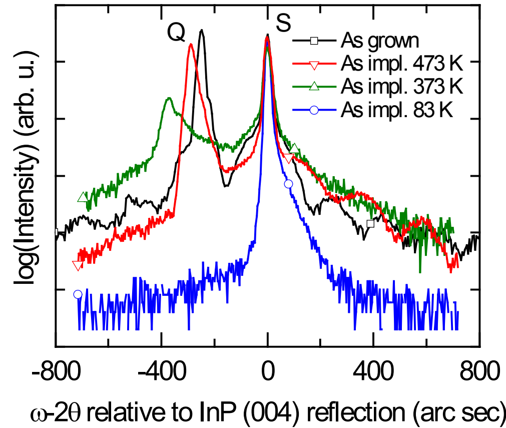

Figure 5.3 HRXRD ω-2θ coupled scans taken on a virgin sample of wafer no. 3 (1.3Q) and on samples implanted with the Fe ion sequence at 83 K, 373 K and 473 K. For these measurements, the InP cap layer was still on top of the structure. S=substrate peak, Q=quaternary layer peak.

After cold implantation at 83 K, the diffraction peak of the InGaAsP layer was completely suppressed, leaving out a single diffraction peak assigned to the InP wafer. As a result, long range crystalline order was lost in the quaternary layer. For heavy ions, the nuclear stopping process and the recoil collision cascade produces atom displacements that are clustered in heavily damaged pockets.[Wendler, 2009] Multiple-energy implantation distributes them across the quaternary layer. At high enough fluence these pockets accumulate, overlap, and form small amorphous regions. Our work on ion implantation of 1.3Q layers at room temperature has located this onset of amorphization for Fe ions when the average number of displacements par lattice atom (n_{dpa}), simulated by SRIM, was about 0.3. It corresponded to a total fluence of about 4.8×10^{13} cm^{-2}.[Fekecs *et al.*, 2013] Here, with the Fe implantation sequence, the simulated n_{dpa} was 6.5 (see figure 2 and Table 2) and one reasonably considers the InGaAsP layers as amorphous-like. The simulation showed that n_{dpa} was greater than unity to a depth of 2 µm. Therefore, according to simulations, the top part of the original InP

substrate was also amorphized. For greater depths, the total ion damage decayed rapidly; n_{dpa} was less than 0.01 to a depth of about 2.4 μm according to simulations.

We now return to figure 3. Increasing the implantation temperature to 373 K clearly influences the HRXRD spectra; a weak diffraction peak of the quaternary was found to persist. Then at 473 K, the signal from the quaternary layer was almost as strong as in the as-grown material and the modulation from the InP cap layer remained. This lasting effect of the diffracted intensity at 373 K and 473 K was caused by "dynamic defect annealing". The defect annealing occurs during ion implantation and is caused by mobile defects, therefore depends strongly on T_{impl}, the implantation temperature.[Wendler, 2009] Dynamic annealing happens on very short time scales and prevents primary heavy ions and recoiling atoms to form heavily damaged pockets and limits damage accumulation. At a critical implantation temperature T_c, the amorphization fluence is, by definition, infinite.[Wendler, 2009] T_c is specific to each material and depends on ion species, ion energy and ion flux. At 473 K, the Fe ion implantation of the InGaAsP layer was made close to the critical temperature. Around that temperature, dynamic defect annealing leaves a crystalline material bearing point defects and clusters of point defects.[Wesch *et al.*, 2012]

5.4 Critical implantation and RTA temperatures

To obtain resistive InGaAsP/InP heterostructures, we optimized the fabrication process by varying both implantation and RTA temperatures. The efficacy of this optimization was verified against two fabrication parameters: alloy composition (1.3Q and 1.57Q), implantation species (Fe and Ga). Consequently, over 60 samples were produced for this study. To guide our interpretation, structural measurements are presented first.

5.4.1 Structural verification

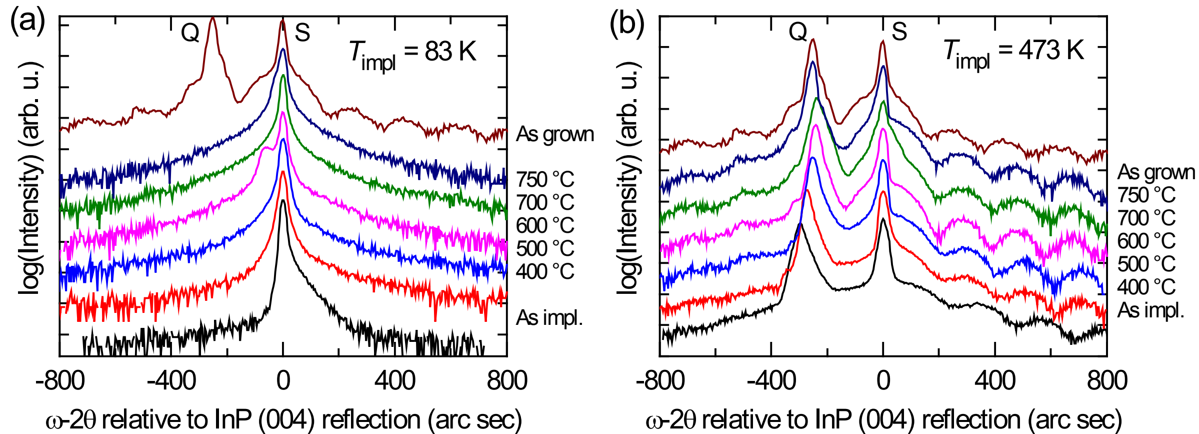

Figure 5.4 Effect of the RTA temperature on ω-2θ coupled scans. HRXRD spectra taken on a virgin sample from wafer no.3 (1.3Q) and on samples implanted with the Fe ion sequence at a) 83 K and b) 473 K. S=substrate peak,Q=quaternary layer peak.

HRXRD measurements were taken after RTA for both cold and hot Fe-implanted 1.3Q samples. For samples implanted at 473 K, the RTA temperature had some effects on the shape of the diffraction spectrum shown on figure 4(b). Two narrow peaks were assigned to single-crystal substrate (S) and quaternary layer (Q), respectively. The quaternary layer diffracting angle varied with the RTA temperature which could be the result of the interplay upon annealing between implanted Fe impurities and primary implantation defects. This will be briefly discussed next along with electrical characterization.

For samples implanted at 83 K, the original quaternary layer diffraction signal cannot be recovered for any RTA temperature, as shown by figure 4(a). A secondary defect structure was preventing the detection of a coherent quaternary signal by HRXRD. However, a low angle shoulder was found on one sample, processed with RTA at 600 °C, which could mean that some quaternary domains recrystallized with an orientation that could be detected. Such suppressed diffraction after RTA was observed before with HRXRD studies of cold MeV Fe-implanted $In_{0.53}Ga_{0.47}As$ with a fluence of 5×10^{14} cm^2.[Too *et al.*, 2005]

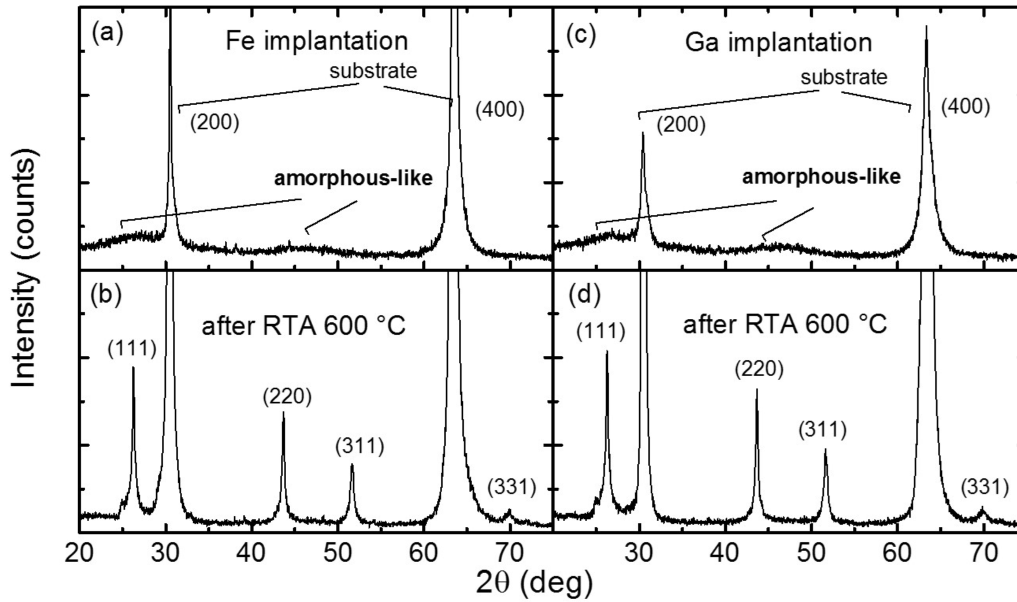

Figure 5.5 Wide angle XRD ω-2θ coupled scans of cold Fe-implanted and Ga-implanted InGaAsP/InP structures. These comparisons are made for 1.3Q layers implanted at 83 K. Insets (a) and (c) show diffracted signals from amorphous phases induced by the ion implantation damage. Insets (b) and (d) show diffracted signals from polycrystalline phases obtained after recrystallization by RTA at 600 °C. Strong diffraction peaks from the (001)-oriented InP substrate are also detected, as indicated.

Additional XRD measurements were made at lower resolution using a powder diffraction instrument. Typical wide angle scans recorded for cold as-implanted samples are shown on figure 5(a) and figure 5(c). A weak signal with broad maxima located at 27° and 47° was detected, which corresponds to the signature of a damage-induced amorphous-like phase, as predicted by SRIM simulations in Section 3. The amorphous-like signature was detected in all Fe- and Ga-implanted quaternary materials at $T_{\text{impl}} = 83$ K and 300 K. Several diffraction peaks associated to a cubic zincblende InGaAsP/InP phase were observed on these materials after RTA. This can be seen in figure 5(b) and figure 5(d), which implies the transformation of the amorphous structure into a polycrystalline structure. A polycrystalline structure developed in all quaternary materials Fe- and Ga-implanted at $T_{\text{impl}} = 83$ K and 300 K. The microstructure of this recrystallization have been investigated by XRD line profile analysis and electron microscopy, and details are published elsewhere.[Fekecs *et al.*, 2015] The findings confirm the full amorphization of the InGaAsP/InP structure up to 1.9 μm below the sample surface. After RTA, multiple structural layers are found. The InGaAsP layer becomes polycrystalline with highly defective submicron grains, a band of planar faults grows at the

former amorphous/crystalline interface and a band of secondary extended defects is found at the end-of-range.

5.4.2 Effects on electrical properties

The optimization of the fabrication process was studied by Hall effect measurements at 300 K. Although great care was taken to obtain uniform ion incorporation and damage density profiles within the InGaAsP layer (figure 2), simulations are predicting profile gradients in the underlying InP substrate and, for cold implantation, an amorphous/crystalline interface. For both hot and cold implantations, distribution of primary and secondary defects may therefore affect a number of layers with different conductivity. Consequently, the Hall measurements most likely consist in a combination of the electrical properties of these layers, not necessarily properties for the implanted InGaAsP layer alone. For that reason, it is better to report about the resistance of these films in terms of sheet resistivity.

Electrical properties produced by Fe implantation in 1.3Q and 1.57Q structures are presented first. These are compared for various implantation temperatures. Data series for dark sheet resistivity, Hall sheet carrier density and effective Hall mobility are plotted against RTA temperatures on figure 6. Data of each sample in the series are shown at its maximum process temperature. Therefore, as-implanted samples equipped with non-annealed In-Ga contacts and equipped with indium contacts are shown at temperature values of 115 °C and 300 °C, respectively. We also show a series of non-implanted 1.3Q reference samples, which had stable electrical parameters upon the whole RTA temperature range, establishing that sample preparation did not create obvious electrical deterioration problems.

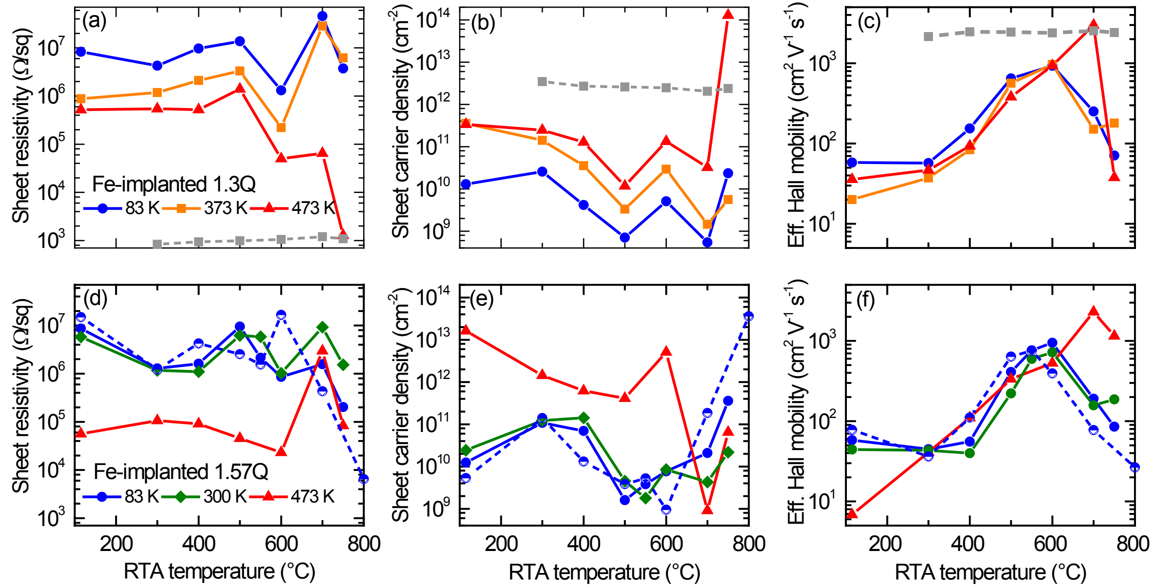

Figure 5.6 Hall measurements of 1.3Q and 1.57Q structures implanted with the Fe ion sequence showing the effects of the implantation temperature and of the RTA temperature. Insets (a,d), (b,e) and (c,f) show, respectively, dark sheet resistivity, sheet carrier density (n-type) and effective Hall mobility. Dashed grey lines correspond to non-implanted 1.3Q reference samples. Data regarding 1.57Q implanted by Fe at 83 K were published previously and are shown for wafer 1 as a dashed line and for wafer 2 as a solid line. [Fekecs *et al.*, 2011]

Compared to cold implantation, hot implantation at 373 K or 473 K resulted in poorer sheet resistivity in 1.3Q and 1.57Q structures. This can be seen in figure 6(a) and 6(d) right after ion implantation and even after annealing, up to 600 °C. A similar trend can be seen also in the sheet carrier density data in figure 6(b) and 6(e). As discussed with the HRXRD data, temperature-driven dynamic defect annealing leaves a crystalline heterostructure bearing Fe impurities and point defects after ion implantation. Such damaged-related centres in ion-implanted InP compounds tend to produce donor levels relatively close to the conduction band.[Carmody *et al.*, 2003a; Pearton et Chakrabarti, 1991] It is also known that, after hot implantation in InP, a large fraction of Fe is activated substitutionally.[Bharuth-Ram *et al.*, 2012; Cesca *et al.*, 2006] Therefore, InGaAsP/InP hot-implanted at high ion fluence probably contains a large density of shallow level defects and these appear more abundant than activated Fe-related deep levels and other defect-related deep acceptors. The inspection of carrier density data after RTA suggests that these shallow defects were not annealed efficiently with RTA up to temperatures of 600 °C, probably due to too short annealing times. Kick-out of Fe atoms from substitutional sites due to annealing is another factor that may

come into play, as it is the case for long anneals in InP.[Cesca *et al.*, 2006] This interplay of point defect and substitutional Fe densities probably drove the relative peak location of the InGaAsP layer seen in the HRXRD measurements on figure 4(b). At RTA temperatures around 700 °C, we noticed high resistivity or high effective mobility, but not consistently. This may correspond to an annealing condition where deep Fe-related levels were able to compensate shallow donor defects but confirmation of the interpretation requires further investigation.

With ion implantation done at lower temperatures, *i.e.*, 83 K and 300 K, as-implanted materials had much higher sheet resistivity than with hot implantation. About 10^7 Ω/sq was recorded for both 1.3Q and 1.57Q structures, as shown in figure 6(a) and 6(c). Dependencies to RTA temperature were also comparable for both compositions. Annealing at 300 °C resulted in a small decrease of the resistivity. From 300 °C to 500 °C, a general decline of the sheet carrier density is observed in figure 6(b) and 6(e). A progressive recovery of the effective Hall mobility is observed in figure 6(c) and 6(f), from 300 °C to 600 °C. Maximum resistivity values and minimum carrier densities were achieved between 500 °C and 600 °C. The sheet resistivity increased by more than a 10^4 factor with respect to the as-grown material. The effective Hall mobility peaked generally around 600 °C, close to 10^3 $cm^2V^{-1}s^{-1}$. For RTA temperatures above 600 °C, our results showed a gradual decrease of the mobility. At such temperatures, the carrier compensation process appeared more variable across data series. Some divergences were observed at 700 °C when in some instances the annealed material exhibited high resistivity, a behaviour also reported previously for $In_{0.53}Ga_{0.47}As$ implanted by Fe at at 300 K [Carmody *et al.*, 2003b] and at 77 K [Too *et al.*, 2004].

To help in discriminating possible defect-related effects from Fe-related compensation effects, electrical properties of cold Fe-implanted InGaAsP are compared to Ga-implanted InGaAsP in figure 7. Properties found in as-implanted InGaAsP are discussed first and then, against the RTA temperature.

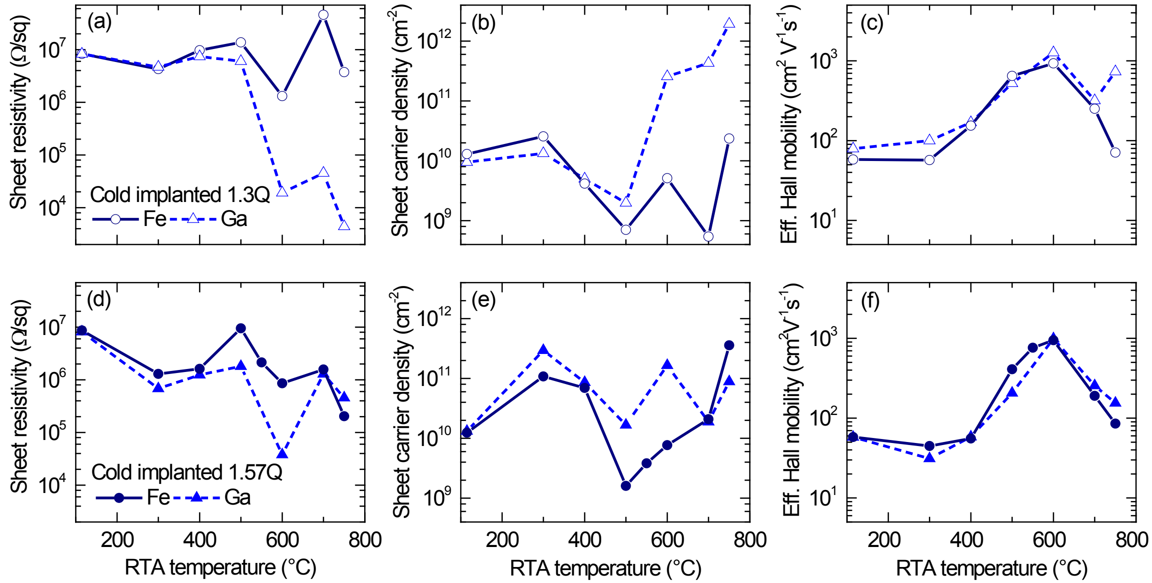

Figure 5.7 Hall measurements of cold Fe-implanted and Ga-implanted InGaAsP/InP structures after the RTA process. Comparisons for both 1.3Q and 1.57Q implanted at 83 K. Insets (a,d), (b,e), and (c,f) show, respectively, dark sheet resistivity, sheet carrier density (n-type) and effective Hall mobility.

Just after implantation, the Ga ion sequence produced almost identical electrical properties to the Fe ion sequence. We found that InGaAsP/InP structures modified with either cold Fe or Ga implantation have rather high dark resistivity ($\sim 8\times10^6$ Ω/sq) and show similar effective carrier density ($\sim 1\times10^{10}$ cm^{-3}). Deep level electrical contributions of Fe did not stand out. We relate this to the same level of primary damage expected from both implantations, which made these materials amorphous-like. It was suggested that amorphous solids can accommodate a locally varying number of covalent bonds, therefore doping impurities are difficult to activate. The carrier compensation effect would rather come from dangling bonds, always present in amorphous semiconductors, which can create deep localized states that usually govern the Fermi level energy.[Mott et Davis, 1979] In all cases, effective Hall mobility levels were close to 70 $cm^2V^{-1}s^{-1}$. We suspect that part of conduction within the amorphized layer could be done by carriers thermally excited in extended states rather than by hopping conduction only, since hopping Hall mobility levels are usually much lower.[Betko *et al.*, 1996] Non-negligible conduction in extended states may be occurring also within the buried layer of the semi-insulating InP substrate that was also ion damaged. This could explain the near-equal resistivity of as-implanted 1.3Q and 1.57Q structures.

After RTA-driven recrystallization, figure 7 shows that above 400 °C cold Fe implantation can produce higher sheet resistivity and lower sheet carrier densities than cold Ga implantation. This suggests a non-negligible contribution to carrier compensation from Fe within at least one of the defective InGaAsP or InP structural layers of the heterostructure.[Fekecs *et al.*, 2015] However, this contribution occurs at RTA temperatures much lower than those found, and known to be related to Fe activation, using lower, non-amorphizing, Fe implantation fluences in $In_{0.57}Ga0_{.47}As$.[Gulwadi *et al.*, 1991] On figure 7, sheet carrier density minima are observed around 500 °C and similar effective Hall mobilities are recorded for the whole RTA temperature range up to 700 °C. This common evolution of Hall effect parameters for both Fe and Ga implantation against the RTA temperature may be suggesting the contributions of common post-annealing microstructures or defects. For both Fe and Ga implantation, cold implanted 1.3Q structures were more resistive than 1.57Q structures for annealing temperatures up to 500 °C. However, such difference was not as strong as the bandgap-related effect predicted in the Introduction. Then, for 600 °C anneals, minor differences are observed on the resistivity of both alloy compositions, along with mobility levels which would be exceedingly high for single conduction in a polycrystalline layer. These points, which could be associated to multiple conduction layers or channels, need further investigation.

5.5 Discussion

The optimization of the fabrication process for high sheet resistivity was closely related to the critical implantation temperature T_c of Fe ions into the InGaAsP layer (Section 3). At T_{impl} = 473 K, strong dynamic defect annealing reduced damage accumulation and prevented amorphization, even if n_{dpa} was ~ 6.5. For implantation temperature of 373 K, the level of dynamic annealing hinted by HRXRD remained significantly large. We conclude that 373 K < T_c < 473 K for MeV Fe ion implantation in InGaAsP. When T_{impl} is close to T_c, the point defect densities left behind by dynamic annealing appeared difficult to remove with RTA. Previous studies made on hot Fe-implanted InP have shown that hour-long high temperature furnace annealing done in phosphorous atmospheres can be more effective to permit high resistivity. [Cesca *et al.*, 2006]

For InGaAsP/InP implantated at 300 K, Hall measurements taken before and after RTA behaved as if the structure was cold-implanted. From these Hall measurements and the wide

angle XRD results, we conclude that InGaAsP/InP heterostructures are robust to dynamic annealing at 300 K using our ion implantation process parameters and profiles. According to previous implant damage studies made on binary III-V compounds, the critical implantation temperature T_c is higher in phosphides (for InP and GaP : $T_c \sim 410$ K) than in arsenides (for InAs: $T_c \sim 300$ K, and for GaAs $T_c \sim 340$ K). [Wendler *et al.*, 1999] Since both alloys of the heterostructure (InGaAsP and InP) had high T_c, the Fe ion fluence needed for amorphization would have been similar at 83 K and at 300 K, therefore depths at which crystalline regions are left into the material must be also similar at both temperatures. These depths are dependent to the design of the implantation damage profile (see figure 2 and Section 3).

Compared to previous reports on Fe-implanted $In_{0.53}Ga_{0.47}As$/InP at 300K, experimental resistivity improvement obtained here with the $In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$/InP heterostructure were about 13 and 33,[Carmody *et al.*, 2003b; Shin *et al.*, 2011] which is significant and stronger than what can be expected from a band-gap related effect (*i.e.*, a factor of 2-3 with respect to $In_{0.53}Ga_{0.47}As$, see Introduction). Part of that improvement could be linked to a lower T_c for $In_{0.53}Ga_{0.47}As$, based on data available on InAs and GaAs. [Wendler *et al.*, 1999] Finally, regarding Fe implantation done at 83 K, experimental resistivity improvement factors are smaller, about 4 and 10.[Subramaniam et Rezazadeh, 2006; Too *et al.*, 2003] In this case, T_{impl} is well below T_c for both alloys. For proper interpretation of this comparison, one will need to investigate further the microstructural effects of the annealing/recrystallization process peculiar to each Fe-implanted heterostructure.

5.6 Summary and conclusion

We investigated the fabrication of thin structures made from quaternary InGaAsP alloys grown on InP substrates in order to obtain resistive photoconductive devices that can be triggered with near infrared laser pulses. Critical fabrication process temperatures were found when epitaxial InGaAsP layers underwent high fluence Fe or Ga ion implantation and were subsequently processed by rapid thermal annealing. With hot implantation temperatures, at 373 K and 473 K, dynamic defect annealing prevented the amorphization of the InGaAsP layers. These hot-implanted layers were less resistive and we suspect that the RTA process had difficulty to anneal out implantation induced shallow defects, especially below 700 °C. With cold implantation temperatures, at 83 K and even at 300 K, due to the high T_c of the

InGaAsP/InP heterostructure, dynamic annealing was minimized and damage clusters could form and accumulate to produce amorphous-like InGaAsP/InP layers. After RTA-driven recrystallization, the use of the Fe ion implantation sequence was better at achieving high sheet resistivity and sheet carrier compensation compared to the Ga ion implantation sequence. Since RTA temperatures near 500 °C were necessary to produce resistive Fe-implanted InGaAsP/InP structures, the material is believed compatible with standard photolithographic and metal deposition process temperatures, which are usually lower, in order to fabricate photoconductive devices for ultrafast optoelectronic applications.

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CHAPITRE 6 Évolution microstructurale d'une hétérostructure InGaAsP/InP recristallisée

Avant-propos

Dans cet article, notre intention est de décrire la microstructure d'une hétérostructure d'InGaAsP/InP après l'implantation à forte fluence d'ions de fer à 83 K et le recuit rapide.

Auteurs et affiliation

André Fekecs : candidat au doctorat, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

Andreas Korinek: professionnel de recherche, McMaster University. Canadian Centre for Electron Microscopy (CCEM).

Martin Chicoine : Professionnel de recherche, Université de Montréal. Département de physique.

Bouraoui Ilahi : Professeur visiteur, Université de Sherbrooke. Institut Interdisciplinaire d'Innovation Technologique (3IT).

François Schiettekatte : professeur, Université de Montréal. Département de physique.

Denis Morris : professeur, Université de Sherbrooke. Faculté des sciences. Département de physique.

Richard Arès : professeur, Université de Sherbrooke. Faculté de génie. Département de génie mécanique.

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Titre français : Évolution microstructurale d'une hétérostructure InGaAsP/InP implantée Fe et recristallisée.

Contribution au document : Notre article présente de nouvelles perspectives structurales, essentielles pour l'interprétation des diverses caractéristiques mesurées sur ce matériau. D'une part, notre article met en lumière la nature complexe de la recristallisation d'une hétérostructure amorphe, un alliage quaternaire InGaAsP/InP comportant un excès d'impuretés Fe. La recristallisation est étudiée pour la premièrement fois par microcopie électronique en association avec l'analyse de la diffraction de rayons X. D'autre part, notre article met en évidence des changements de la structure de défauts étendus de la couche photoconductrice d'InGaAsP. La couche d'InGaAsP, qui est poly-cristalline avec des grains submicroniques, comporte une forte densité de fautes planaires qui forment des sous-structures nanométriques. Pour la première fois, il est montré que la température du recuit de recristallisation modifie la densité de fautes planaires et la taille moyenne des grains, ce qui suggère une connexion structurale avec la dynamique ultrarapide des photoporteurs dans le matériau. Cependant, l'identification précise des mécanismes de relaxation ultrarapide des photoporteurs est au-delà de la portée de la présente étude.

Résumé en français : Avec la recristallisation d'une hétérostructure amorphe, obtenue par implantation d'ions Fe à haute énergie (MeV), nous pouvons modifier un matériau semi-conducteur standard, une couche épitaxiale de l'alliage InGaAsP/InP, pour obtenir un photoconducteur adéquat pour l'optoélectronique térahertz. Nous rapportons ici les changements microstructuraux qui surviennent dans le matériau sur une plage étendue de température de recuit rapide, avec l'analyse du profil des pics de diffraction de rayons X et la microscopie électronique en transmission. Les résultats montrent une transition amorphe complète de l'hétérostructure après implantation multi-énergies à 83 K. Suite au recuit rapide, plusieurs couches structurales se développent par épitaxie et recristallisation en phase solide. La couche photoconductrice d'InGaAsP devient poly-cristalline avec une structure de grain submicronique, une forte fraction volumique cristalline et une texture apparente ⟨110⟩.

Plusieurs grains sont allongés et comportent des fautes internes, dont une forte densité de fautes planaires dans la séquence d'empilement des plans (111). L'élargissement des pics de diffraction de rayons X est anisotrope et évolue avec la température de recuit. À 500 °C, la taille des domaines cohérents aux rayons X est estimée à 10 nm en moyenne et s'aligne bien avec les observations en microscopie électronique des régions de fautes planaires. Au-delà de 500 °C, une diminution significative de la densité des fautes planaires est détectée. Nous discutons de l'influence de ces changements microstructuraux reliés à la température de recristallisation sur la réponse photoconductrice ultrarapide de l'InGaAsP/InP implanté Fe.

Microstructural evolution of a recrystallized Fe-implanted InGaAsP/InP heterostructure

A. Fekecs, A. Korinek, M. Chicoine, B. Ilahi, F. Schiettekatte, D. Morris et R. Arès

Abstract Through the recrystallization of an amorphous heterostructure, obtained by MeV Fe ion implantation, we are able to tailor a standard epitaxial semiconductor material, a small gap InGaAsP/InP alloy, for photoconductive terahertz optoelectronics. Here, we report on microstructural changes occurring in the material over a broad range of rapid thermal annealing temperatures, using X-ray diffraction line profile analysis and transmission electron microscopy. Results show a complete amorphous transition of the heterostructure after multiple-energy implantations done at 83 K. Upon thermal annealing, multiple structural layers develops *via* solid phase epitaxy and solid phase recrystallization. The photoconductive InGaAsP layer becomes polycrystalline and submicron-grained, with high crystalline volume fraction and apparent ⟨110⟩ texture. Many grains are elongated and internally faulted, with high densities of planar faults occurring on closed-packed (111) planes. The X-ray diffraction line broadening is anisotropic and evolves with RTA temperatures. At 500 °C, the X-ray coherent domain size estimate of 10 nm is aligned reasonably with electron microscopy made in faulted areas. Above 500 °C, a significant decrease of the planar fault density is detected. We discuss the influence of these microstructural changes happening with recrystallization temperatures on the ultrafast photoconductive response of Fe-implanted InGaAsP/InP.

Keywords: heterostructures; InGaAsP; ion implantation; recrystallization; transmission electron microscopy; X-ray diffraction

6.1 Introduction

Under specific processing conditions, ultrafast photoconductive properties are achieved in bulk semiconductor materials, such as ternary $In_{0.53}Ga_{0.47}As$/InP and quaternary $In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$/InP heterostructures, following ion implantation with Fe ions and rapid thermal annealing (RTA) [Carmody *et al.*, 2003b; Fekecs *et al.*, 2011; Shin *et al.*, 2011]. These Fe-implanted small gap materials were developed to build photoconductive emitters and detectors for novel terahertz spectrometer systems working at 1550 nm, the operating wavelength of practical designs integrating an erbium-doped femtosecond fiber laser [Fekecs *et al.*, 2011; Lloyd-Hughes *et al.*, 2006; Shin *et al.*, 2009; Suzuki et Tonouchi, 2005a; Suzuki et Tonouchi, 2005b]. For emitter devices, broadband terahertz emission can be produced at the picosecond timescale *via* photo-induced conductivity transients when a region of the heterostructure, located between externally biased electrodes, is illuminated by short pulses. Achieving high dark sheet resistivity is very important for allowing substantial external bias [Tani *et al.*, 2012]. If the resistivity of the material is too low, emitter devices may suffer from Joule heating. In particular, Joule heating is known to limit the performance of interdigitated large area devices made for 1550 nm operation [Xu *et al.*, 2013]. When done at room temperature in $In_{0.53}Ga_{0.47}As$ materials, MeV Fe ion implantation has produced sheet resistivities of 0.24 MΩ/sq and 0.5 MΩ/sq [Carmody *et al.*, 2003; Shin *et al.*, 2011]. However, with $In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$/InP layers implanted at 83 K, we reported much higher sheet resistivity, of more than 10 MΩ/sq [Fekecs *et al.*, 2011].

These “macroscopic” optoelectronic properties, *i.e.*, dark resistivity and photocarrier decay times, are strongly influenced by the evolution of material microstructures throughout the fabrication process. Microstructural effects were thoroughly discussed for ultrafast GaAs devices made by As ion implantation by Tan *et al.* [1999] who stress that different types of post-annealing defects, such as point defects, clusters, dislocation loops or polycrystalline grain boundaries, are strongly dependent on the primary damage profile and directly influence carrier dynamics. With cold Fe-implanted InGaAsP, our previous work showed that the primary implantation damage from high Fe ion fluence is causing strong optical absorption tails beyond the original band edge wavelength of the quaternary alloy.[Fekecs *et al.*, 2011] The effect is consistent with an amorphization of the InGaAsP layer, which is also predicted

by the simulation of atomic displacements of the implantation damage. [Fekecs *et al.*, 2011] Thermal annealing can in principle allow the recrystallization of these amorphous regions. After RTA, we have observed negligible changes in the tails of the optical absorption spectra of our implanted samples but a significant improvement of the effective Hall mobility.[Fekecs *et al.*, 2011] These observations suggest a crystalline recovery taking place but leaving secondary disorder, such as a residual amorphous phase and/or structural defects into the heterostructure. Such imperfections could lead to a high density of energy-distributed traps which are believed to be responsible for the subpicosecond photocarrier dynamics of this material.[Fekecs *et al.*, 2011; Martin *et al.*, 2012] It is worth noticing that high defect densities, able to capture free carriers, are typically associated to high field breakdown.[Coutaz, 2002] For this material, fields up to 50 kV/cm have been applied on illuminated devices without catastrophic breakdown.

In this context, this structural study provides evidence for defective microstructures formed during the recrystallization of amorphous Fe-implanted InGaAsP/InP heterostructures. Since the photocarrier dynamics of the material slows down gradually as a function of the RTA temperature, [Fekecs *et al.*, 2011] we are specifically looking for RTA-dependent structural changes responsible for a possible coexistence of crystalline phases and regions containing defects acting as efficient traps. In this work, quantitative structural estimates are made based on peak analysis of powder X-ray diffraction data. The results are correlated to electron diffraction patterns and images obtained with transmission electron microscopy (TEM). Our findings support the idea that nanoscale structural defects produced by the recrystallization process are at the origin of desirable optoelectronic properties found in cold Fe-implanted InGaAsP.

6.2 Experimental

6.2.1 Material and sample preparation

Specific details on epitaxial InGaAsP/InP growth, simulation of optimized implantation and damage profiles, multiple high-energy Fe ion implantation, and on rapid thermal annealing were given previously [Fekecs *et al.*, 2011]. They are summarized here. A sequence of not intentionally doped layers of InP (0.1 μm), $In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$ (1.5 μm), and InP (0.1 μm) were grown epitaxially on semi-insulating (001) InP substrates. The absorption band edge wavelength was 1.57 μm. These heterostructures were implanted by a 5-energy Fe ion sequence (up to 2.5 MeV), which was designed to obtain uniform implantation damage and Fe incorporation into the whole InGaAsP layer. Samples were held cold, at 83 K, during the implantation, which avoided dynamical defect annealing and favored implant damage accumulation. The implantation sequence had a total ion fluence of 1.9×10^{15} cm^2 which created, from simulations, an average of 6.5 atomic displacements per atoms, and incorporated Fe at about 0.03 at%. Next, the implanted samples were processed in a lamp-based rapid thermal annealer at various temperatures between 400 °C and 750 °C. The linear temperature ramp up was completed in 20 s and the RTA temperature plateau was held for 30 s. One sample was annealed at 300 °C, which corresponds to the temperature used for sintering indium contacts for about 75 s. These electrical contacts were easily scraped off before structural measurements. For many samples of this study, the thin InP cap layer was removed by means of selective chemical etching before structural measurements.

6.2.2 XRD measurements

X-ray diffraction (XRD) measurements were made on an X'pert Pro MRD powder diffractometer (PANalytical) in the Bragg-Brentano geometry equipped with a Xe-filled proportional detector. The X-ray wavelength was 1.54 Å (Cu_α lines). The source divergence slit opening was set to 0.25°. The powder XRD instrument was able to detect weak signals over wide ω-2θ coupled scans (up to $2\theta = 100°$). Contrary to a high resolution XRD machine, it does not allow for fine adjustment of the tilt angle (ψ) of the sample. Therefore, symmetrical peaks signals from the InP single crystal substrate may not always give accurate intensity and width. Diffractograms were taken on samples of identical size (6 mm × 6 mm). Since the implant-damaged and recrystallized layers had similar thicknesses, their diffractograms

(number of counts as a function of 2θ) could be compared directly without geometrical corrections. The instrument's broadening function was determined by measuring a LaB_6 powder standard (SRM 660) from the National Institute of Standards and Technology (NIST). Details of the peak shape analysis is given in the Supporting Information.

Using peak shape parameters, we calculated crystalline fractions X_c with the following expression: $X_c = I_c/(I_a+I_c)$, where I_c and I_a are integrated intensities of signals scattered from crystalline and amorphous phases. For the crystalline phase, three main reflections contribute to the integrated intensity ($I_c = I_{111}+I_{220}+I_{311}$). I_{hkl} includes also contributions from all subreflection assigned to planar faults (PFs). According to the InP diffraction powder standard, the summation of those 3 reflections accounts for 89 % of the total integrated intensity up to $2\theta = 60°$; therefore omitting weaker reflections in the analysis was acceptable. For the amorphous phase, the first two halos centered at 27° and 47° were summed as $I_a = I_{27°}+I_{47°}$. This approach has been applied before on microcrystalline silicon samples with XRD data taken in grazing incidence [Houben *et al.*, 1998; Schicho *et al.*, 2012] and in the Bragg-Brentano configuration [Schicho, 2011]. For the analysis of texture, integrated peak intensities were compared to each other, relative to the zincblende InP powder diffraction standard (ICDD 04-004-1833). Intensity ratios of a reflection I_{hkl} to the sum $\Sigma I = I_{111}+I_{220}+I_{311}$ were calculated. I_{hkl} includes also contributions from all subreflection ascribed to planar faults. These $I_{hkl}/\Sigma I$ ratios were normalized to what is expected from the random orientation given by the powder standard (*i.e.*, $I_{111}/\Sigma I = 0.54$, $I_{220}/\Sigma I = 0.27$, $I_{311}/\Sigma I = 0.20$).

6.2.3 Electron microscopy

Conventional cross-sections were prepared by mechanical polishing followed by argon-ion milling at low-angle (Gatan PIPS). Specimens are thinned down to approximately 100 nanometers thickness. For as-implanted material and material annealed at 700 °C, transmission electron microscopy (TEM) was carried out with an electron microscope (JEOL JEM-2010) equipped with a 200 kV field emission gun. For material annealed at 500 °C, the electron microscopy data acquisition was performed using a FEI Titan microscope (FEI Company, Eindhoven, The Netherlands), equipped with a CEOS image corrector (CEOS GmbH, Heidelberg, Germany), operated at 300 kV. For HR-TEM micrograph acquisition, the

information limit of the microscope was tuned to 0.8 Angstrom. For nano-beam electron diffraction measurements, the microscope was operated in STEM mode with a probe convergence angle of 1 mrad, resulting in an approximate beam size of 2-3 nm. Diffraction patterns were recorded in an array of points; each pattern was recorded with an exposure time of 100 ms with a beam current of <30 pA.

6.3 Results and discussion

6.3.1 An amorphous-to-crystalline transformation

Figure 6.1(a) shows a typical X-ray diffractogram recorded on InGaAsP/InP heterostructures after implantation with Fe ions. Two strong diffraction peaks are assigned to symmetrical (200) and (400) reflections from the single-crystal InP substrate. Two broad shapes, centered at $2\theta = 27°$ and 47° and a weaker and broader feature centered at 75°-80°, are also detected. Their angular location corresponds to reciprocal lengths of 0.30 $Å^{-1}$, 0.52 $Å^{-1}$, and 0.79 $Å^{-1}$. These shapes are ascribed to an implant-amorphized InGaAsP/InP layer, as X-ray diffraction from amorphous materials produces a series of broad diffuse halos [Guinier, 1994; Klug et Alexander, 1974]. The diffraction angles corresponding to these halos locations are consistent with published values of similar amorphous semiconductors.[Brodsky *et al.*, 1970; Moss et Graczyk, 1969] With careful analysis of the shape of the scattered X-ray intensity, one can estimate the radial distribution of nearest atom neighbors of the amorphous solid [Guinier, 1994; Klug et Alexander, 1974]. The formation of a thick amorphous layer extending through the heterostructure is confirmed by TEM imaging (see **Figure S1** in the Supporting Information, online at: www.pss-a.com).

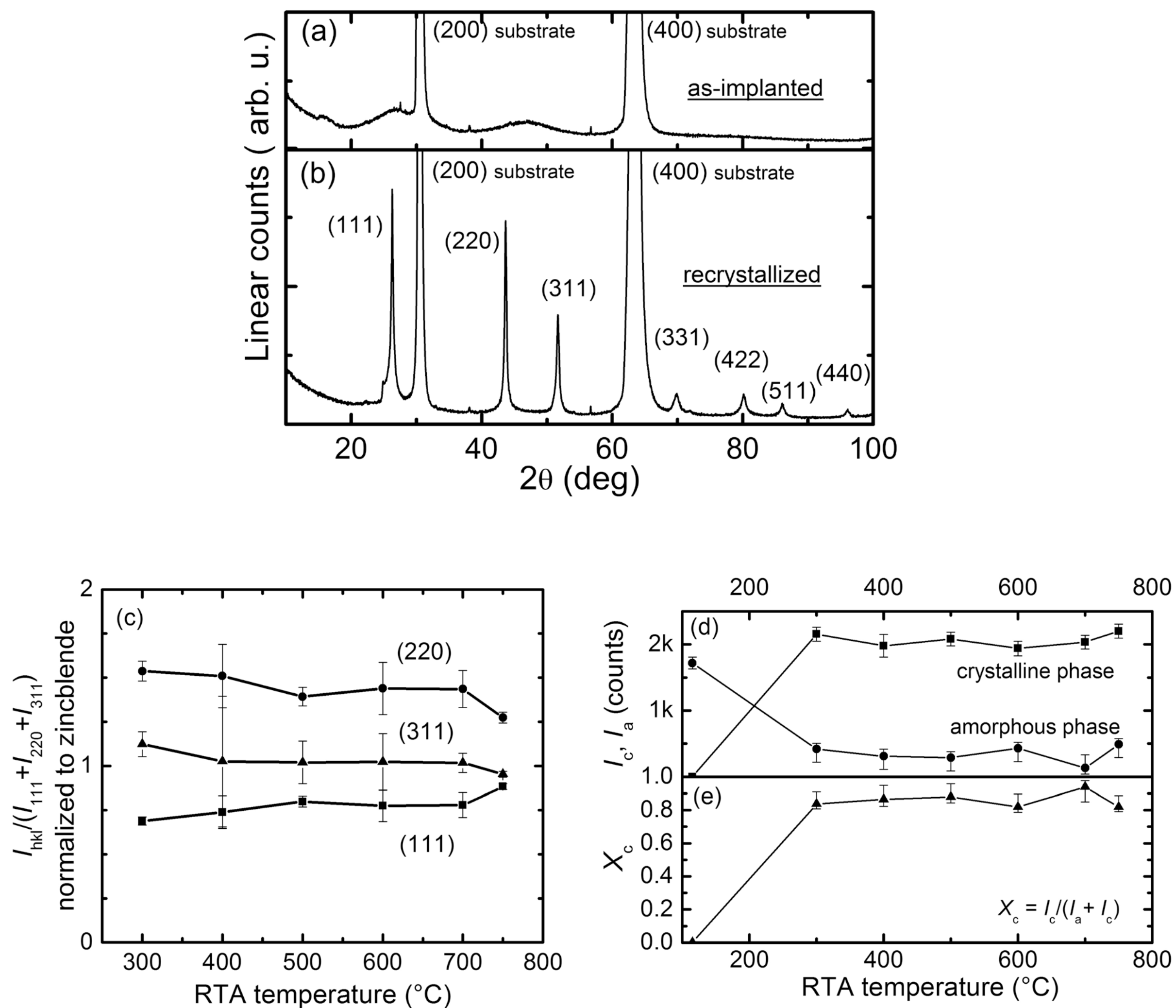

Figure 6.1 X-ray diffraction spectra from wide ω-2θ coupled scans of (a) Fe-implanted InGaAsP and then (b) annealed at 550 °C for 30 s. Each scan was ~10-hour long for better detection of weak reflections beyond 70°. (c) Preferential orientation showing the relative contribution of each *hkl* reflection normalized to random zincblende powder standard. These values are obtained for different annealing temperatures of the recrystallized Fe-implanted InGaAsP material. (d) Peak analysis of the amorphous-to-crystalline transformation showing integrated scattered intensities of the amorphous phase I_a and the crystalline phase I_c. (e) Evolution of the crystalline volume fraction X_c.

Figure 1(b) shows a typical diffraction spectrum after further processing with RTA. The broad halos related to the implanted amorphous layer (at 27°, 47° and 75°) are suppressed while the (200) and (400) substrate peaks are still present. In addition, a series of new peaks from a polycrystalline phase appear, these being located at diffracting angles corresponding to

those of the cubic zincblende structure with the InP lattice parameter (5.87 Å). All reflections of the zincblende phase were observed. Signals related to (222) and (420) reflections are barely distinguishable from the background as they are the weakest peaks found in the InP powder diffraction standard. Symmetrical reflections (200) and (400) are hidden by substrate peaks.

The amorphous-to-crystalline transformation was studied by collecting XRD spectra taken for amorphous-like material and for material recrystallized with various RTA temperatures (see **Figure S2**, Supporting Information). These XRD spectra were then reproduced by curve fitting. [Wojdyr, 2010] Details of the fitting are given in Supporting Information. Structural parameters were extracted from the fitting results and are reviewed over the course of this paper. By analyzing integrated peak intensities we can demonstrate that the polycrystalline InGaAsP/InP structure developed a small ⟨110⟩ preferential orientation of its coherent domains with diffracting planes perpendicular to the surface normal. This result is shown in Figure **1(c)**. The preferential orientation does not vary much over the range of RTA temperatures. We also worked under the assumption that scattered intensities from both a residual amorphous phase (I_a) and a crystalline phase (I_c) can be present in the signal. **Figure 1(d)** shows I_a and I_c as a function of the RTA process temperature. According to Figure 1(d) and **Figure 1(e)**, the crystalline volume fraction (X_c) in the InGaAsP/InP layers is significant. At an annealing temperature of 300 °C, X_c was ~ 0.84. The crystalline volume fraction appears unaffected by higher RTA temperatures which may suggest a mostly complete transformation. These observations are consistent with amorphous-to-crystalline transformations that are known to occur at even lower temperatures for InP: the onset of the transformation is observed at ~ 220 °C after few hour-long isochronal annealing cycles.[de M. Azevedo *et al.*, 2003] The exact fraction of the small residual amorphous phase signature remains difficult to quantify as our estimates likely include unassigned contributions from peak tails of symmetrical reflections and from other sources of diffuse scattering related to alloy imperfections.

6.3.2 A multilayered microstructure after recrystallization

TEM techniques can provide precise information on the spatial distribution and defects of the recrystallized phase found in Fe-implanted InGaAsP/InP after RTA. **Figure 2(a)** shows a cross-section view obtained with annular dark field scanning TEM (ADF-STEM) of material

annealed at 500 °C. **Figure 2(b)** shows a cross-section view obtained with conventional TEM of material annealed at 700 °C.

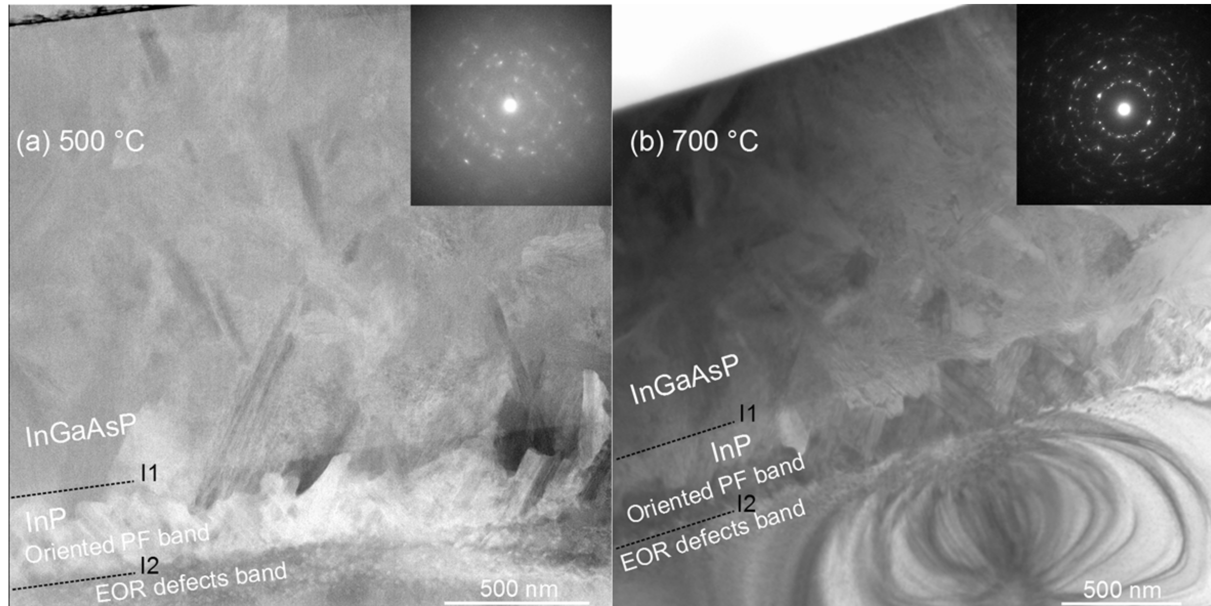

Figure 6.2 (a) ADF STEM micrograph taken on a cold Fe-implanted InGaAsP/InP heterostructure annealed at 500 °C. (b) TEM micrograph taken on another heterostructure annealed at 700 °C. The electron beam is at the [011] zone axis of the substrate, showing bend contours. For both micrographs, dotted lines I1 indicates the interface between InGaAsP and InP materials. Dense bundles of oriented planar faults (PF) and EOR defects can be observed near dotted lines I2, the former a/c interface. Insets are showing typical SAED patterns taken across the polycrystalline InGaAsP layers.

Image contrast in both specimens of Figure 2 shows multiple and distinct structural layers which are described next, from top to bottom. Large crystalline regions, sometimes extending over hundreds of nanometers, are found distributed throughout the InGaAsP layers. Many regions have an apparent (projected) elongation along one axis. Selected area electron diffraction (SAED) patterns taken across these InGaAsP layers indicate the presence of crystalline grains with large misorientation, as diffracted spots and streaks appear within discontinuous rings. The radial positions of these rings correspond to the interplanar *d*-spacings of a cubic zincblende structure lattice-matched to InP, consistent with X-ray diffraction data. Distinct intensity maxima, observed on SAED rings, indicate some amount of preferred orientation of the recrystallization. Variations in the local grain structure are also found when sampling multiple SAED patterns on smaller adjacent areas of these

polycrystalline InGaAsP layers. We detail such effects in **Figure S4** of the Supporting Information for the specimen recrystallized at 700 °C.

Two characteristic bands, although much thinner than the polycrystalline InGaAsP layer, are also clearly visible on Figure 2. Just underneath the InGaAsP layer below I1, a defective band, finely streaked, cause intense diffuse scattering on the STEM micrograph (Figure 2a) and show as a dark band of streaked InP regions on the conventional TEM image (Figure 2b). The orientation of the diffuse streaking associated to this structural band was determined with SAED and with nano-beam electron diffraction (NBED) mapping (see **Figure S5** and **Figure S6**, of the Supporting Information). Diffraction patterns taken from this band are streaked along <111> and correspond to planar fault (PF) bundles growing epitaxially from I2, the former amorphous/crystalline (a/c) interface. Such observation of solid phase epitaxy with strong {111} planar disorder has been reported before. [Auvray *et al.*, 1982; Belay *et al.*, 1996; Frigeri *et al.*, 1997; Jasinski *et al.*, 1997; Licoppe *et al.*, 1987; Mueller *et al.*, 1993; Ridgway *et al.*, 1991] Along with imaging and NBED, many oriented PF bundles remain confined to the InP, extending for less than 0.3 µm above the former a/c interface. Some twins are detected in the transition of the InP oriented PF band to the polycrystalline InGaAsP layer. A second band scattered with small contrasting dots is also visible on Figure 2, below the PF band. This band encloses secondary defects associated to the “end-of-range” (EOR) damage, and extends for about 0.15 µm deeper into the substrate. These defects correspond to amorphous and defective clusters, formed by primary Fe ion damage at the EOR of the most energetic ions. For InP-related materials, these clusters typically produce dislocation loops as they annealed out. [Gasparotto *et al.*, 1999a] One EOR defect has been imaged by HR-TEM on the 700 °C specimen. A coffee-bean shape of its TEM contrast was detected, typical of dislocation loops and coherent precipitates. [Williams et Carter, 2009]

6.3.3 The nanoscale substructure of the polycrystalline InGaAsP layer

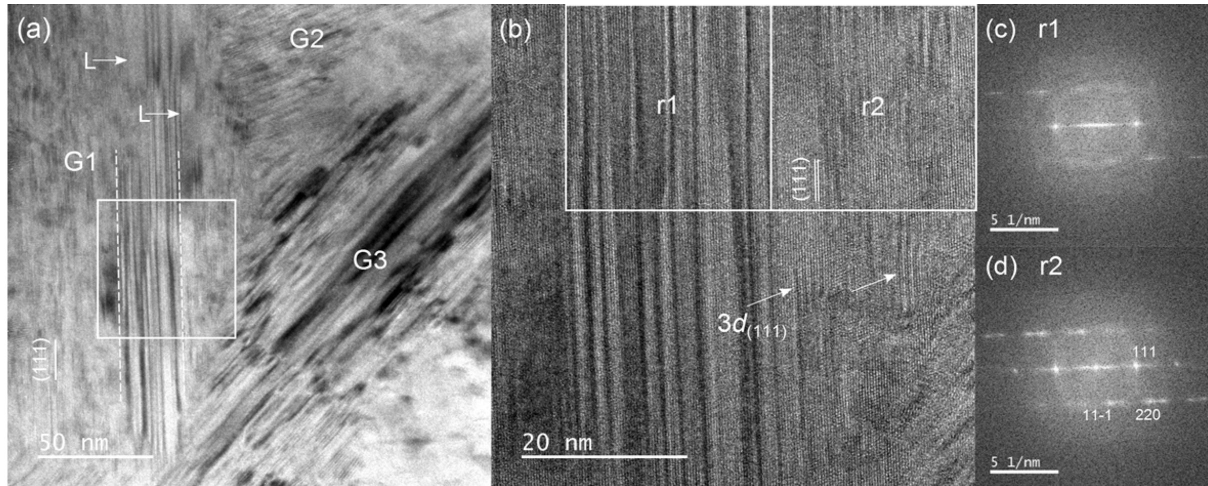

Figure 6.3 (a) TEM cross section image from the top part of the InGaAsP layer recrystallized at 500 °C. The image contrast of grains, labelled G1, G2 and G3, make striations running at different angles. In a band in the middle of G1, delimited by 2 dashed lines, the contrast is coarser and runs rather continuously. In G1, thin lamellae (L) extending vertically are indicated by arrows. In G3, the contrast is stronger and complex, sometimes stopping abruptly. (b) HR-TEM close-up corresponding to a region delimited by a square in (a). (111) lattice fringes are observed. Fine details of the contrast are highlighted in regions labelled r1 (coarser bands) and r2 (finer bands) for which Fourier transforms are given in (c) and (d) and showing diffuse scattering and streaking. Below r2, arrows indicate local variation of the contrast as a modulation of the (111) lattices fringes with a period of $3d_{(111)}$.

The TEM specimen shown in Figure 2(a) was thinned further to produce detailed microstructural images of the polycrystalline InGaAsP layer. We selected this specimen because desirable optoelectronic properties, such as ultrafast photocarrier dynamics and high dark resistivity, are achieved after recrystallization at 500 °C. At lower TEM magnification, the image of **Figure 3a** shows the streaked substructure of 3 InGaAsP grains. At high resolution in **Figure 3b**, (111) lattice fringes are clearly visible. Their real-space average d-spacing are 0.341(5) nm. The (111) fringe contrast of G1 is often striated, finer at grain periphery, and runs parallel (or almost parallel) to (111) planes. Such intra-grain contrast reveals a high density of (111) planar defects, local strain from dislocations, and crystallographic texture. Grain G1 contains oriented lamellar regions in its interior, some are

designated by L on the image. They are bounded at (111) planes and their widest thicknesses are about 5 nm to 8 nm. The lamellar elongation is directed towards <211>. For solid phase recrystallization, exaggerated growth along this axis is consistent with faulting on (111) planes in case of twinning.[Spinella *et al.*, 1998] At the periphery of grain G1, a modulation of the (111) lattice contrast at a triple-period is observed in small regions, 7 nm to 10 nm wide, below r2 on Figure 3(b). This irregularity may correspond to Moiré patterns resulting from the superposition of small coherent (111) twin subdomains. [Haji *et al.*, 1994] A fine striated contrast is also observed in region r2, however it is not as clear and periodic, perhaps due to local strain fields or mutual misorientation. A small anisotropy of d-spacings can be detected on the Fourier transformed (FT) image of r2 (**Figure 3d**). One set (-111) appear expanded by about 5 % compared to the other one (111) which is closer to an unstrained lattice. Since microscope astigmatism is removed in the alignment procedure, such possibility can be ruled out. This anisotropy of the FT/HR-TEM pattern remains not satisfactorily explained and requires further investigation.

6.3.4 Correlating TEM results and XRD peak shape analysis

XRD peak shapes correlate in many ways to the nanoscale substructure of the InGaAsP submicron grains. In **Figure 4(a)**, we show the evolution of the (111) Bragg reflection with various RTA temperatures. The base of the (111) reflections are made of a broad composite peak. The shoulder at the low angle side can be attributed to the dilatation of (111) interplane spacings at coherent domain boundaries.[Veprek *et al.*, 1987] This typical peak shape is often found in face-centered cubic, diamond and zincblende crystals that are structurally faulted along close-packed {111} lattice planes. [Balogh *et al.*, 2006; Houben *et al.*, 2003; Kohler *et al.*, 2012] Since planar faults modify the order of the atom stacking sequence, structurally faulted cubic crystals can locally appear as a polytypic hexagonal phase in the XRD diffractogram.[Schicho *et al.*, 2012]

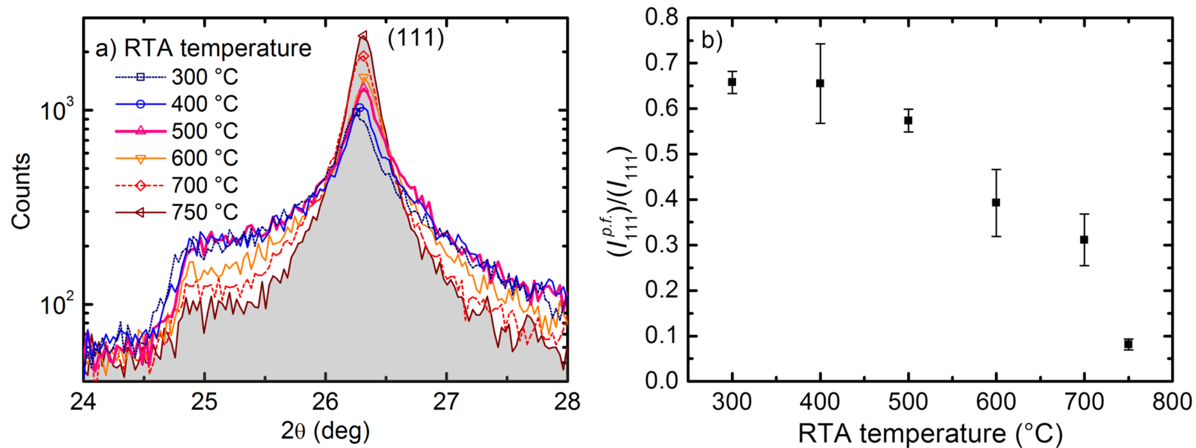

Figure 6.4 (a) Details of the (111) XRD reflection of Fe-implanted InGaAsP/InP samples recrystallized at different RTA temperatures. (b) Intensity of the (111) signal associated to planar faults relative to the total diffracted intensity at different RTA plateau temperatures

The diffraction angle of the peak needed to reproduce the low-angle shoulder of the (111) reflection in our recrystallized InGaAsP samples is compatible with the strongest diffraction peak calculated for wurtzite InP.[Gaiduk *et al.*, 2000] Such closed-packed $(10\bar{1}0)$ planes, with interplanar spacings of 3.578 Å, diffract at a Bragg angle of $2\theta = 24.9°$. This agreement can be seen in **Figure S3b** (see Supporting Information). Also noticeable on Figure S3b are the XRD peak shapes corresponding to 'Super-Lorentzian' line profiles, *i.e.,* with tails falling off more slowly than for a Lorentzian. These peaks are rather symmetric. 'Super-Lorentzian' profiles are often observed with faulted structures, in which cases twin faults happen to cause symmetric tails [Balogh *et al.*, 2006; Estevez-Rams *et al.*, 2005]. Using fit parameters found for the (111) reflection, the ratio of the intensity of the broad composite peak attributed to planar faults $(I_{111}^{p.f.})$ relative to the total peak intensity (I_{111}) was calculated.[Köhler *et al.*, 2013] The result is shown in **Figure 4(b)** at various RTA temperatures. The ratio is maximum and almost constant for RTA plateau temperatures below 500 °C. This suggests that planar faults are formed at low temperatures with a high fault probability in the polycrystalline phase, including temperatures corresponding to the heating up of the sample. The ratio then decreases appreciably at higher temperatures. Apparently, a minimum RTA plateau temperature is necessary to significantly anneal out planar faults.

XRD peak shapes are also influenced by the size and shape of regions over which diffraction is coherent. Grain boundaries and planar defects limit such coherent lengths and cause peak broadening. From the full-with at half maximum (B_{hkl}) of each diffraction peak, we made estimates of the apparent size of the coherent domain population (*i.e.*, a volume-weighted mean size). We use the set of sharp lines (as described in the Supporting Information) which contains information on domain sizes. For Lorentzian line profiles the experimental peak width (reproduced by fitting) can be written as follow: $B_{\mathrm{exp}} = B_{hkl} + B_{\mathrm{ins}}$, where B_{ins} is the instrument's broadening function. We show *hkl* peak broadening in a Williamson-Hall (W-H) representation. Peak widths in the reciprocal space $B^*_{hkl} = B_{hkl}(2\theta) \cdot cos(\theta)/\lambda$ are plotted against $d^* = 2\sin\theta/\lambda$, the inverse lattice plane spacing at the Bragg angle. In a W-H representation, B^*_{hkl} is constant with d^* for isotropic size effects only (*i.e.*, the Scherrer equation). A slope often implies microscopic strain gradients. In general cases, size is given by the intercept.[Cullity et Stock, 2001] Peak widths collected in the course of this work at $d^* >$ 6 nm^{-1} were also taken into account for a meaningful W-H analysis, shown in **Figure 5**.

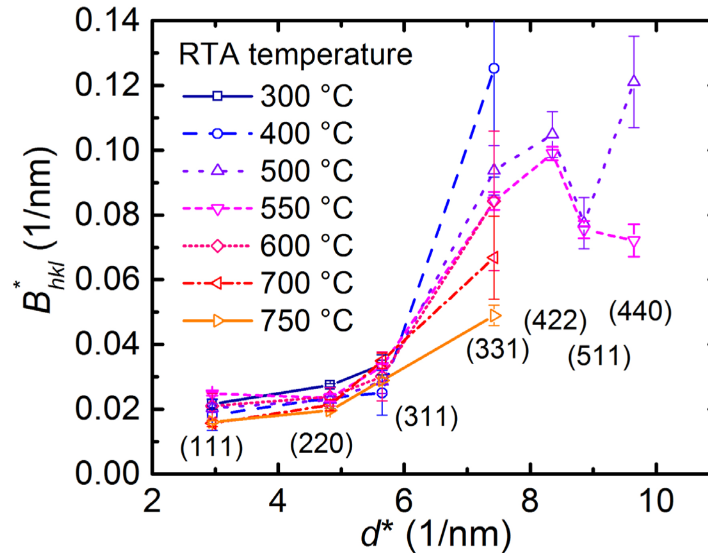

Figure 6.5 W-H representation of the *hkl* broadening from XRD peaks. Peak widths (in reciprocal space) are obtained for different annealing temperatures of the recrystallized Fe-implanted InGaAsP material.

The W-H plot shows a general increasing trend of B^*_{hkl} with d^*. However, this trend is not linear and not monotonous. Linear fitting of pair of data points that are related to higher order reflections (*i.e.,* (220) and (440) for material annealed at 500 °C and 550 °C) yields to a small

negative intercepts. In that case, anisotropic microstrain-like broadening due to dislocations, anisotropic domain shapes or effects resulting from the interference between mutually coherent diffracting domains have to be considered.[Mittemeijer et Welzel, 2008] A strong local preferred orientation is prerequisite for visible partial mutual coherence effects on diffraction line broadening of nanocrystalline materials.[Gelisio et Scardi, 2012; Rafaja *et al.*, 2004] For low d^*, nanoscale regions of the recrystallized grains could diffract coherently, giving rise to a narrowing of the diffraction peaks in Figure 5. As d^* increases, a gradual loss of partial coherence between nanoscale regions explains the upward curvature of the line broadening. An abrupt and plateau-like change in B^*_{hkl} is observed above d^* = 6 nm^{-1} for two sample annealed at 500 °C and 550 °C and corresponds to an incoherent diffraction regime. This plateau-like broadening corresponds to a mean apparent size $K/\langle B^*_{hkl}\rangle$ of 10±0.5 nm. A default value of the Scherrer constant K = 0.9 was used as a first approximation.[Langford et Wilson, 1978] One cannot forget that such basic size estimate associated to XRD peak broadening is a sum of size and shape effects from a very heterogeneous material. Some regions have faults, small grains, others do not. However, when taking into account a partial coherence effect, the XRD size estimate is in relatively good agreement with our TEM observations of internally faulted grain substructures, showing TEM contrasted regions of comparable sizes. Furthermore, one will notice on Figure 5 that the peak broadening of (331) is particularly influenced by the RTA temperature. According to the interpretation of the W-H plot discussed hereabove, diffracted signals are adding up incoherently for (331). The RTA temperature appear then to have an influence on the sizes and shapes of nanoscale regions or, in other terms, on the intragrain defect distributions.

6.4 Discussion on recrystallization and 'macroscopic' optoelectronic properties

The present work introduced XRD techniques, paired with electron microscopy, to study structural defects developing at various RTA conditions of the recrystallization of Fe-implanted InGaAsP/InP heterostructures. The cumulative damage of the cold Fe ion implantation sequence induced an amorphous transition through the thick InGaAsP layer and the top part of the InP wafer. This created particular initial conditions to the recrystallization,

in addition to the incorporation of excess Fe impurities at about 1×10^{19} cm^{-3}, much greater than the normally believed solid solubility limit of Fe in InP-related alloys (10^{17} to 10^{18} cm^{-3}). [Gasparotto *et al.*, 1999a; Vellanki *et al.*, 1993] Some of the complexity of the RTA-induced recrystallization resulted from the interplay of two growth mechanisms: solid phase epitaxy occurring from the a/c interface and solid phase recrystallization happening into the InGaAsP layer, the latter being responsible for the polycrystalline structure. Clustering of excess Fe impurities appears probable, however our attempts to detect Fe-rich nanoscale clusters by EELS were not successful, due to small Fe concentration levels and the thickness of our cross-section specimens. In addition, substantial faulting and associated dislocations are suspected to help accommodating for Fe impurities above their solid solubility limit in the recrystallized InGaAsP layer.[Sadana, 1985] Polycrystalline recrystallizations of binary III-V compounds had previously been identified by TEM in MeV ion implantation works. Auvray *et al.* [1982] found a thin polycrystalline phase close to sample surfaces after 800 keV Se implantation done at room temperature in InP. Polycrystalline layers formed in the central part between two a/c interfaces were also reported by Narayanan and Spitzer [1978] for 2.7 MeV P implantation in GaAs, by Xiong *et al.* [1989] for 15 MeV N implantation in InP, and by Jasinski *et al.* [1997] for 2 MeV As or Ga ion implantation in GaAs.

In the context of pulsed photoconductive terahertz applications, control over the recrystallization of the amorphous InGaAsP/InP heterostructure, and its outcomes, is essential for refining macroscopic optoelectronic properties of the material. For instance, a maximization of the on-chip dark resistivity is obtained in heterostructures recrystallized at moderate RTA temperatures, around 500 °C. [Fekecs *et al.*, 2011] Since carrier transport properties may vary within the defective layers of the InGaAsP/InP microstructure, possibilities for parallel conduction need to be examined further to better explain the workings of this optimization. Concerning photocarrier dynamics, the material demonstrates fast exponentially decaying signals in pump-probe photoreflection and phototransmission measurements.[Fekecs *et al.*, 2011; Martin *et al.*, 2012] Subpicosecond decay times, less than 0.7 ps, are observed when the RTA temperature is moderate (500 °C or below). Above 500 °C, significantly longer decays are measured in the photoreflection response. [Fekecs *et al.*, 2011]. Structurally, the relative diffracted intensity ascribed to planar faults decreases

significantly above 500 °C in Figure 3. Progressive increases in the apparent size of XRD-coherent domains are also observed with RTA temperatures in Figure 5. This appears consistent with previous observations made on microcrystalline Si by time-resolved terahertz spectroscopy, linking rapid photocarrier dynamics to the nanoscale size of crystalline domains and the nature of their boundaries.[Fekete *et al.*, 2009] Typically, submicron polycrystalline columnar growth and nanoscale twinning are found in microcrystalline Si layers. [Houben *et al.*, 1998; Houben *et al.*, 2003] The defect structures of the submicron grained polycrystalline InGaAsP:Fe layers are, however, more complex and heterogeneous. Planar faults are generally considered as electronically inactive,[Mahajan, 2000] but electronic states associated to dangling bonds found at their edges, at partial dislocation cores, or associated to Fe impurity atoms "contaminating" partial dislocations or fault planes may influence the photocarrier capture rates.[Chen *et al.*, 2009; Xu *et al.*, 2005] As the occurrence of planar faults in the (111) stacking sequence of zincblende crystals happens to form small band alignment discontinuities,[Belabbes *et al.*, 2012] further examinations are also needed to determine whether microscopic carrier scattering effects at small intra-grain potential barriers are significant to the material's photocarrier dynamics.

6.5 Conclusion

With a postgrowth process such as Fe ion implantation and rapid thermal annealing, one can modify a single layer bulk InGaAsP/InP heterostructure into a complex nanostructured material that is promising for the development of ultrafast optoelectronic switching and photomixing devices. This paper brings forward additional connections to be made between microstructural parameters and functional properties of this material that are RTA-temperature dependent. Given the probable importance of Fe atom redistribution, crystalline domain sizes, and planar fault configurations on photoconductive properties of Fe-implanted InGaAsP layers, a finer control of the recrystallization's temperature-time profile can be envisioned to refine device performances, a work that can be assisted by non-destructive XRD characterization and verified by electron microcopy techniques.

Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's website.

Acknowledgements

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Supporting Information to

Microstructural evolution of a recrystallized Fe-implanted InGaAsP/InP heterostructure

A. Fekecs, A. Korinek, M. Chicoine, B. Ilahi, F. Schiettekatte, D. Morris, R. Arès

- TEM Thin Section View of the Fe-Implanted InGaAsP/InP Heterostructure
- XRD Data of Fe-Implanted InGaAsP/InP and Reference Materials
- Details of the XRD Profile Analysis
- SAED Patterns of 2 Adjacent Regions on the Recrystallized InGaAsP Layer
- SAED Patterns Taken Across the InP Planar Faulted Band
- NBED Patterns of the Recrystallized InGaAsP/InP Heterostructure

6.6 TEM Thin Section View of the Fe-Implanted InGaAsP/InP Heterostructure

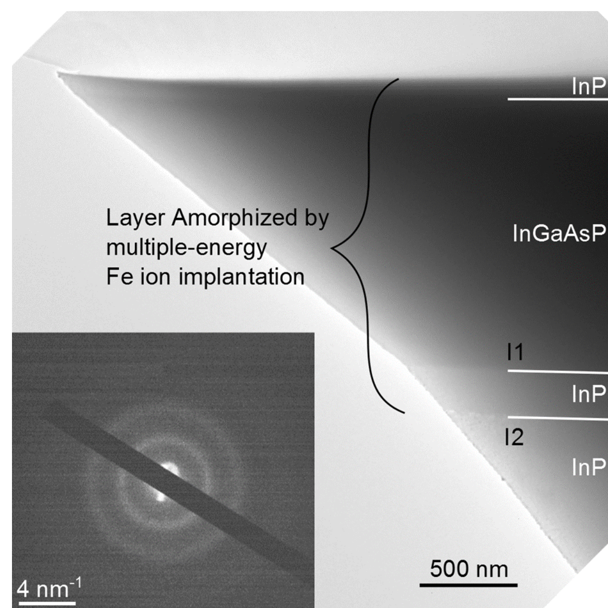

Figure 6.S1 TEM micrograph of the as-implanted InGaAsP/InP heterostructure obtained by Fe ion implantation at 83 K. Differences in the contrast of InP and InGaAsP layers are detected. Inset shows a selected area electron diffraction pattern taken close to the sample surface. Concentric halos of decreasing intensity are visible and diffraction spots are absent. At peak intensity, the halos radii are 0.30 $Å^{-1}$, 0.51 $Å^{-1}$, matching those found by X-ray diffraction according to Bragg's law. From imaging, and further selected area diffraction, the observations reveal the formation of an amorphous InP/InGaAsP/InP heterostructure extending from the surface to the amorphous/crystalline interface located within the InP substrate, marked as I2.

6.7 XRD Data of Fe-Implanted InGaAsP/InP and Reference Materials

Figure S2 shows X-ray diffraction (XRD) spectra for amorphous Fe-implanted InGaAsP/InP heterostructures and material recrystallized at various rapid thermal annealing (RTA) temperatures. These spectra are used in the peak profile analysis. For material annealed at 300 °C (blue line in Figure S2), the InP substrate (200) reflection was distorted due inadvertent tilt misalignment. Corresponding small angular span was omitted in curve fitting. For material annealed at 750 °C (red line in Figure S2), a narrow peak of low intensity was observed at 33.0°. It is ascribed to the (101) reflection of In. Small In balls were found on

unprotected edges of the sample. They formed by P atom desorption at this elevated temperature. The figure also show XRD signal baselines estimated from the diffuse background produced by a LaB_6 powder reference, a (001) Si crystal (data shown by a blue-green line) and the as-grown InGaAsP/InP epitaxial heterostructure (data is shown by a green line).

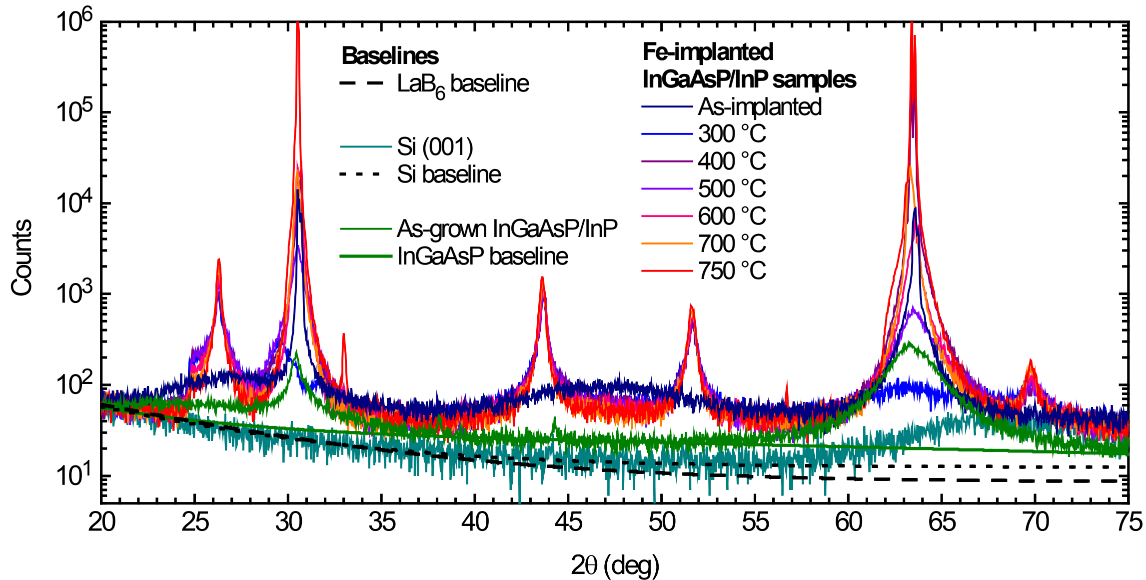

Figure 6.S2 X-ray diffraction spectra from ω-2θ coupled scans of 6 mm × 6 mm cold Fe-implanted InGaAsP/InP samples and then annealed at various RTA temperatures. Additional to the spectra, the figure also displays baseline averages for a LaB_6 powder standard, a (100) Si reference and the as-grown InGaAsP/InP material

6.8 Details of the XRD Profile Analysis

XRD spectra for amorphous-like material and material recrystallized at various RTA temperatures (shown in **Figure S2**) were reproduced using a curve fitting program called Fityk v0.9.8.[Wojdyr, 2010] The fitting was done by minimization of the χ^2 using the Levenberg-Marquardt method. The signal's standard deviation was set to $\sigma_i = \sqrt{I(2\theta_i)}$ to account for random fluctuations of a counting process. The measurement's background level was determined using the LaB_6 powder standard and a baseline was estimated (dashed black line in Figure S2). It was very close to what was given by a single crystal of silicon (dotted black line in Figure S2). Extra diffuse scattering was observed for the as-grown InGaAsP material. Some can be attributed to displacement disorder from microscopic atom size variations of the alloy

(see 8.3.3 in [Guinier, 1994]) and produces a hump around 27° which happens to mirror an amorphous signature. The InGaAsP baseline (solid green line in Figure S2) without the hump was included into each peak analysis. The XRD spectrum of as-implanted material was reproduced first. This step is shown in **Figure S3a**.

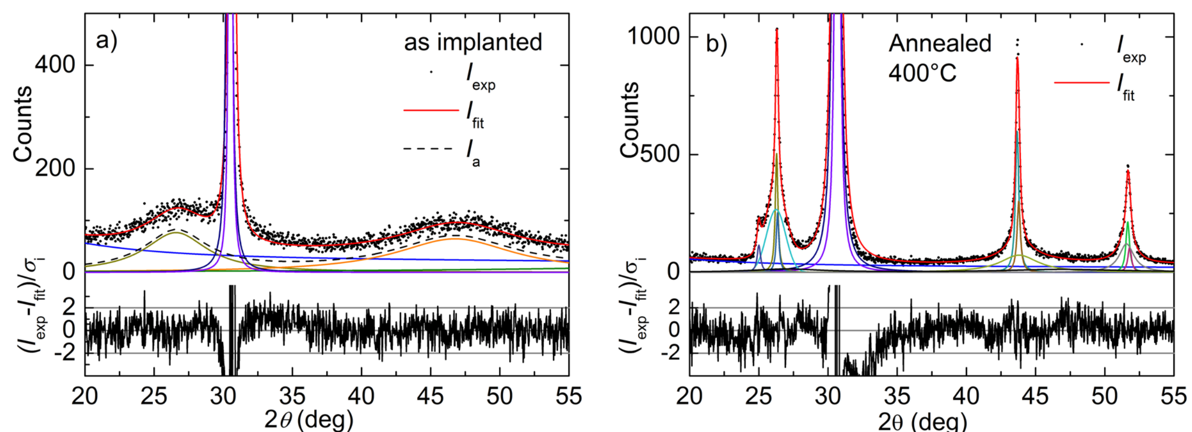

Figure 6.S3 XRD spectra (I_{exp}) for (a) as-implanted InGaAsP/InP and (b) taken after annealing at 400 °C, and reproduced by curve fitting (I_{fit}). Quality of the fit (residual error weighted by the standard deviation) is displayed for both curves.

Broad peaks centered at $2\theta = 27°$, 47° and 75°, related the amorphous region, were modeled as a sum of Lorentzian functions (dashed line I_a). The shape of I_a is then fed into the analysis of the recrystallized material in order to estimate the reflected intensity from a residual amorphous fraction that may be present along with the crystalline phase. An example is given in **Figure S3b** for material recrystallized at 400 °C. Lorentzian functions were used to reproduce the sharp (111), (220) and (311) reflections. Two peaks accounted for the $K\alpha_{1,}\alpha_2$ doublet line for accurate estimation of peak broadening. A second set of broader lineshapes were used to reproduce tails of those peaks. Lorentzian tails were used for (220) and (311). For (111), however, tails were better reproduced by a Gaussian shape which was combined with an additional Lorentzian peak at $2\theta = 25.0°$ in order to adequately reproduce the low-angle shoulder of the (111) reflection. For stability of the fit, extra peaks were needed to reproduce symmetrical reflections for as-implanted and recrystallized materials. Peak parameters that resulted of this fitting procedure were used in subsequent structural analyses. For peak broadening analyses, additional peaks at higher *hkl* were reproduced using Lorentzian doublet lines and the aforementioned background baseline. Residual errors shown

in Figure S3 show that amorphous peaks for as-implanted InGaAsP/InP and new peaks arising from the recrystallization are reproduced reasonably well relative to the measurement noise.

6.9 SAED Patterns of 2 Adjacent Regions of the Recrystallized InGaAsP Layer

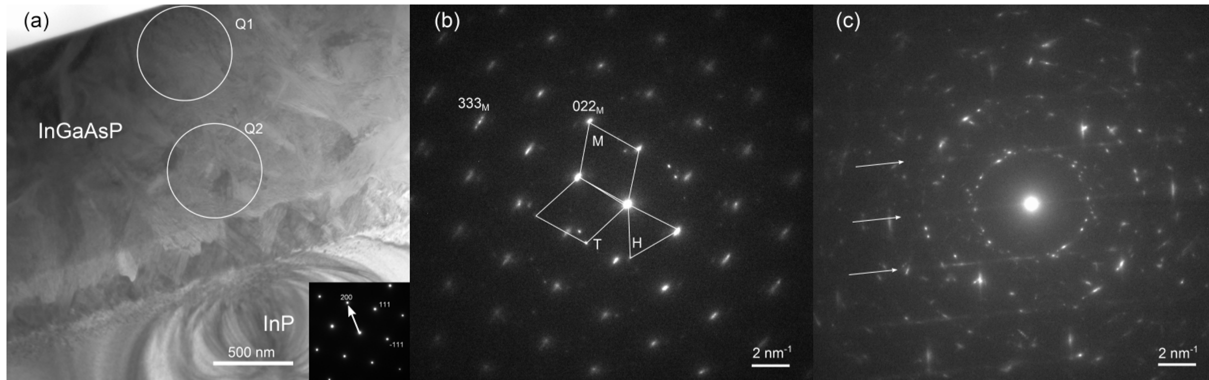

Figure 6.S4 SAED patterns taken in (b) top half, and (c) bottom half of the InGaAsP layer, as specified in (a) the TEM image of a cold Fe-implanted InGaAsP/InP heterostructure annealed at 700 °C. The InP substrate zone axis pattern is shown in the inset of the TEM image and an arrow indicates the surface normal.

Variations in the local grain structure of the InGaAsP layer annealed at 700 °C are found by looking at adjacent selected area electron diffraction (SAED) patterns. In **Figure S4**, SAED patterns from nearby regions of the InGaAsP layer are quite different. For the top region, the SAED pattern of **Figure S4b** can be indexed with three main sets of reflections, marked as M, T and H. The region giving rise to M produces strong, elliptically broadened diffraction spots. The $(022)_M$ reflection is indicated on the pattern and its orientation is close to the sample's surface normal, given by the vector in the inset of **Figure S4a**. Such orientation appears connected to the ⟨110⟩ texture found by XRD (see Figure 1c). A second set of reflections, identified as T, has an imperfect (111) twin relationship with M. We observe a small tilt of 1.8° relative to the zone axis of M. A third pattern (H) has hexagonal symmetry with *d*-spacings of 0.357 nm. This pattern can arise from a hexagonal polytypic inclusion with the electron beam aligned on its [1010] axis, or from a heavily faulted cubic grain diffracting with the electron beam along its [121] zone axis.[Walter et Gerthsen, 2000] These 3 sets of reflections produce composite diffraction spots, one being particularly visible close to $(333)_M$. For the bottom region, the SAED pattern of **Figure S4c** shows discontinuous rings made of a

large number of diffracting spots arising from many smaller diffracting grains. Fine streaks due to (111) stacking disorder are also detected and indicated by arrows. Many diffracting spots are streaked, or appear elliptical or are split, often azimuthally. These shape effects are associated with extended defects and elastic lattice distortions.

6.10 SAED Patterns Taken Across the InP Planar Faulted Band

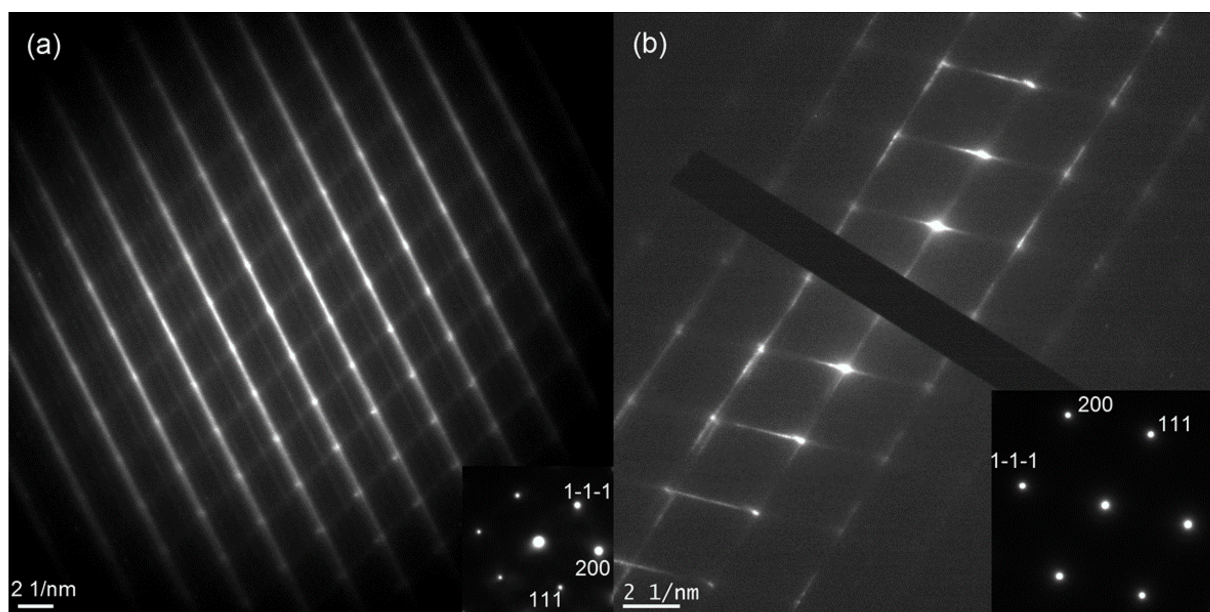

Figure 6.S5 SAED patterns taken across the InP planar faulted (PF) band showing fine streaks associated to strong {111} planar disorder of the crystalline re-growth occurring at the former amorphous-crystalline interface. Patterns were taken on cold Fe-implanted InGaAsP/InP heterostructures (a) annealed at 500 °C and (b) annealed at 700 °C. SAED diffraction patterns of the InP substrate are inset. They confirm the epitaxial relationship of the defective re-growth.

6.11 Nano-beam Electron Diffraction Patterns of the Recrystallized InGaAsP/InP Heterostructure

To provide further insight into the local structural evolution and orientation development, the whole heterostructure annealed at 500 °C was mapped by nano-beam electron diffraction (NBED) with a small-convergence electron probe (diameter of about 2 to 3 nm) so that

overlap of the diffracting disks with most reflections can be minimized. We recorded 1000 diffraction patterns some of which are sampled in **Figure S6**.

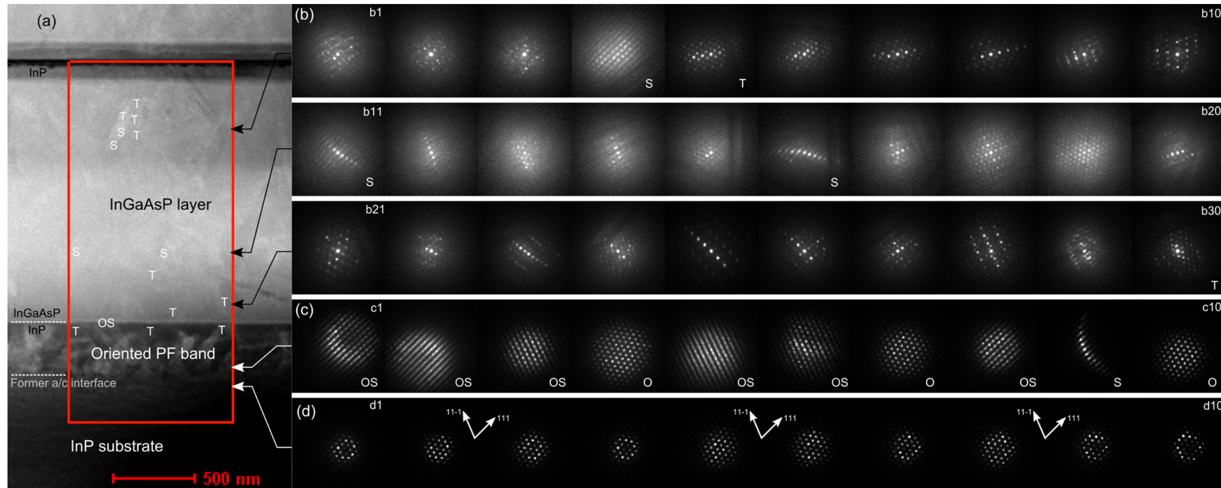

Figure 6.S6 NBED diffraction patterns taken on cold Fe-implanted InGaAsP/InP annealed at 500 °C. Image (a) shows the overall survey area. Groups of diffraction patterns are sampled at (b) various depths across the polycrystalline InGaAsP layer, (c) the planar faulted (PF) InP band, and (d) the InP substrate. The lateral mapping step size is 100 nm. Each pattern has a label. Marks are put on some patterns as follows: epitaxially oriented (O), oriented and streaked (OS), twinned (T), streaked (S). Regions in space where these effects are present are marked on the image.

Diffraction patterns pertaining to the InP substrate are detected below the former a/c interface, and are illustrated in **Figure S6d**. Just above the former interface, most diffraction patterns of **Figure S6c** are streaked in spite of the very small electron beam diameter used to record the patterns. Streaks extend along <111> directions of the substrate. Streak-less patterns corresponding to regrown regions with epitaxial relationship to the InP substrate are also detected. (111) twins are detected in the transition region between the planar faulted InP band and the InGaAsP layer and are marked in the image space. Diffraction patterns recorded in the InGaAsP layer, some of which are sampled in **Figure S6b**, reveal a polycrystalline structure with abrupt changes of the crystal orientation. Streaked patterns are observed at some locations, corresponding to b4, b11 and b16. Few patterns can be indexed as (111) twins with respect to the substrate, such as patterns b5 and b30.

CHAPITRE 7 CONCLUSION

7.1 Sommaire

Nous avons utilisé des procédés de fabrication en post-croissance, basés sur l'implantation ionique à haute énergie (MeV) et le recuit thermique rapide, pour modifier les propriétés d'une hétérostructure d'InGaAsP/InP. En variant la composition de cet alliage quaternaire, il est possible d'ajuster la longueur d'onde de son seuil d'absorption dans le proche infrarouge. L'implantation à haute énergie nous a permis d'incorporer des espèces relativement lourdes (^{56}Fe et ^{69}Ga) sur toute l'épaisseur des couches d'InGaAsP en employant des séquences d'implantation à plusieurs énergies. Cette technique permet un contrôle facile sur le niveau d'incorporation de l'espèce implantée avec un ajustement de la fluence. Par contre elle produit un endommagement du cristal, ce que le recuit rapide tend à réduire. Notre objectif était d'étudier cette technique de fabrication pour obtenir, avec l'implantation d'ion de fer, des couches d'InGaAsP semi-isolantes ayant un seuil d'absorption à 1.3 μm et des couches photoconductrices résistives et ultrarapides d'InGaAsP fonctionnant à 1.55 μm.

7.1.1 Fabrication de couches quaternaires semi-isolantes

Tout d'abord, nous avons étudié l'effet de la fluence d'implantation de Fe sur l'endommagement d'une hétérostructure d'InGaAsP/InP avec des techniques de diffraction de rayons X et de spectroscopie de la rétrodiffusion Rutherford. Cette hétérostructure avait un seuil d'absorption à 1.3 μm. Cette étude nous a permis de déterminer la fluence correspondant au début de la transition cristalline/amorphe qui se produit avec l'accumulation du dommage d'implantation. Avec une fluence en deçà de cette amorce, les résultats montrent que les recuits RTA de 15 s à 800 °C peuvent guérir la structure de défaut primaire de l'implantation et conserver une structure monocristalline de bonne qualité. Ceci est important pour maintenir un seuil d'absorption abrupt dans le matériau. Malgré la possibilité de défauts résiduels, nous avons produit des couches de grande résistivité après recuit, de l'ordre de 10^4 Ω·cm, avec une fluence totale de 1.6×10^{13} cm^{-3}. Selon les profils d'implantation simulés, le procédé a

incorporé une densité de Fe d'environ 9×10^{16} cm^{-3} à la couche d'InGaAsP alors que celle-ci étaient initialement dopée type n à 3×10^{15} cm^{-3}. La résistivité qui est obtenue avec l'implantation de Fe excède les niveaux généralement obtenus avec des procédés d'implantation d'ions légers. Nous entrevoyons l'utilisation éventuelle de ce procédé pour la fabrication de couches semi-isolantes à puits quantiques multiples pour permettre le développement d'applications photoréfractives autour de 1.3 µm, une région spectrale relativement transparente des tissus mous biologiques.

7.1.2 Fabrication de couches quaternaires ultrarapides

Exploration du procédé

Pour le développement d'un photoconducteur ultrarapide, nous avons utilisé l'implantation ionique faite à haute fluence pour modifier des hétérostructures d'InGaAsP/InP. Les ions $^{56}Fe^{+}$ et de $^{69}Ga^{+}$ ont été implantés avec des séquences à multiples énergies (allant jusqu'à 3.3 MeV) et des fluences totales autour de 10^{15} cm^{-2}. Dans le cadre général de cette étude, nous avons comparé deux compositions du quaternaire, avec des seuils d'absorption autour de 1.3 µm et 1.57 µm et que nous notons 1.3Q et 1.57Q, respectivement.

Nous avons tout d'abord étudié l'effet de la température d'implantation sur la nature du dommage d'implantation en utilisant des méthodes de diffraction de rayons X. Cette étude structurale nous a permis de constater qu'un recuit dynamique de l'hétérostructure se produit durant l'implantation à 373 K et 473 K. Ces résultats nous ont permis d'estimer la température critique d'implantation T_c de l'InGaAsP. Avec des implantations bien en dessous de T_c, à 83 K et 300 K, l'accumulation du dommage entraine l'amorphisation de la couche d'InGaAsP, un résultat aussi confirmé par microscopie électronique. Le recuit rapide des couches amorphes entraîne une recristallisation polycrystalline du matériau, telle qu'identifiée avec la diffraction de rayons X.

Selon leur température d'implantation, les propriétés électriques des hétérostructures InGaAsP/InP évoluent différemment avec la température du recuit rapide. Pour des températures de recuit de moins de 700 °C, les mesures électriques en configuration Van der Pauw ont montré une plus forte résistivité avec l'implantation « froide », c'est-à-dire avec des conditions produisant une recristallisation polycrystalline. Une résistivité maximale est atteinte

avec un recuit autour de 500 °C, elle est de l'ordre de 10 MΩ/□ pour les hétérostructures 1.57Q implantées au Fe. Un tel niveau de résistivité est hautement sollicité pour une couche photoconductrice opérant à 1550 nm.

Vérification et démonstration

La caractérisation optique des couches résistives d'InGaAsP 1.57Q implantées à froid nous a permis d'évaluer leur potentiel comme photoconducteur ultrarapide et absorbant à 1550 nm. Des mesures du spectre de transmission optique ont montré les effets de l'amorphisation et de la recristallisation sur l'absorption optique autour de 1550 nm. De fortes queues dans le flanc de bande de l'absorption indiquent une forte densité de défauts reliés à la recristallisation qui agiraient comme des pièges distribués en énergie La dynamique des photoporteurs a été étudiée avec la réflectivité différentielle. Cette mesure a confirmé une dynamique ultrarapide, avec des temps caractéristiques de moins de 0.7 ps, quand la température de recuit est en dessous de 600 °C. C'est une aussi une valeur hautement sollicitée pour développer des dispositifs térahertz.

Suite à ces résultats très encourageants, nous avons fabriqué sur ce matériau des dispositifs térahertz comportant des électrodes colinéaires en utilisant un procédé standard de photolithographie. Avec un montage de spectroscopie térahertz comportant une détection électro-optique, lorsque les dispositifs opèrent à 4.2 kV/cm et qu'ils sont photoexcités à 80 mW avec des impulsions courtes à 1550 nm, nous avons noté une émission THz allant au-delà de 2 THz et un rapport signal-à-bruit de 25 dB de l'amplitude THz. Ce résultat montre que le procédé d'implantation de Fe et de recuit dans un matériau à faible gap comme l'InGaAsP est capable produire des dispositifs térahertz avec de bonnes caractéristiques en émission.

Caractérisation microstructurale

Nous avons étudié la microstructure du matériau térahertz à l'aide de la diffraction de rayons X et de la microscopie électronique en transmission (TEM). Nous avons constaté que l'implantation multi-énergie à 83 K a produit une hétérostructure amorphe InGaAsP/InP. Une seule interface amorphe/cristalline (a/c) est présente. Elle est localisée dans le substrat d'InP, à une profondeur de 1.8-1.9 µm sous la surface de l'échantillon implanté. Après recuit, de nouvelles couches structurales ont été observées. Nous avons noté une bande de défauts *end-of-range* sous l'ancienne interface a/c. Juste au-dessus, une bande de faisceaux de fautes planaires orientés et largement confinés dans l'InP s'est formée par épitaxie en phase solide. La microstructure de la couche photoconductrice d'InGaAsP est différente. La couche possède une phase polycrystalline après recristallisation. Pour cette couche, nous avons rapporté des changements microstructuraux qui surviennent sur une plage étendue de températures de recuit rapide avec l'analyse du profil des pics de diffraction de rayons X. Les images TEM ont montré une structure hétérogène de grains submicroniques, souvent allongés et comportant de nombreux défauts étendus. L'évidence expérimentale suggère que les grains comportent une grande densité de fautes planaires dans les plans (111), produisant ainsi une sous-structure nanométrique. Dans le tracé de Williamson-Hall, l'élargissement des pics de diffraction de rayons X est anisotropique et évolue avec la température de recuit. La taille apparente moyenne des domaines cristallins est de 10 nm pour un recuit à 500 °C. Au-delà de 500 °C, la densité de fautes planaires diminue avec la température de recuit.

Cette évolution structurale semble correspondre avec la variation de la dynamique de photoporteurs, mesurée à diverses températures de recuit. Tel qu'illustré à la figure 7.1, la dynamique des porteurs est d'autant plus rapide dans l'InGaAsP polycristallin que la taille apparente des domaines cohérents est petite et que la densité de fautes planaires est grande, un résultat qui soulève de nouvelles questions de recherche.

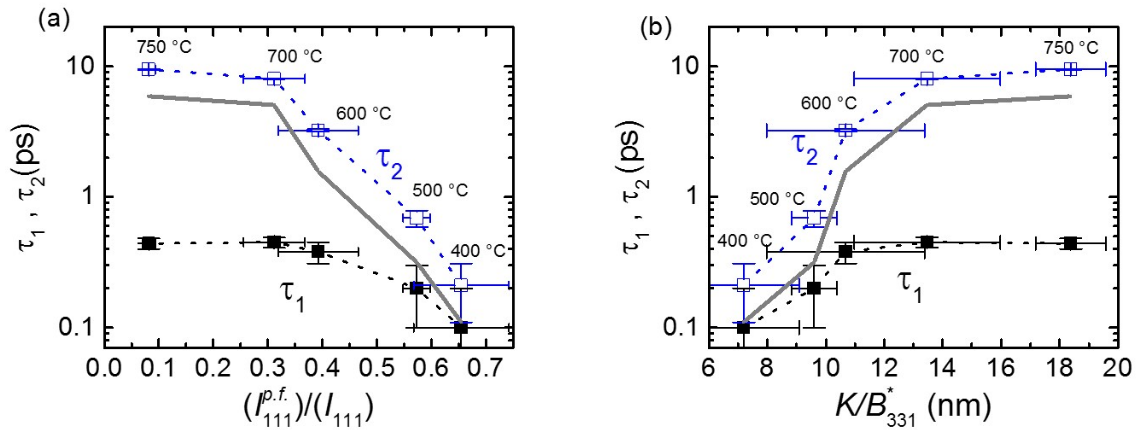

Figure 7.1. Temps de décroissance bi-exponentielle τ_1 et τ_2 mesurés en réflectivité différentielle. Ils sont tracés en fonction de (a) l'intensité relative de diffraction assignée aux fautes planaires, et (b) de la taille apparente des domaines cohérents. Les échantillons recuits à diverses températures de RTA sont identiques pour les 2 mesures. Les données sont tirées des figures 4.4(b), 6.4(b) et 6.5. La dynamique globale est donnée par le temps pondéré $\tau = (A_1\tau_1+A_2\tau_2)/(A_1+A_2)$, tracé en gris, qui tient compte des coefficients d'amplitude A_1 et A_2 de la double décroissance.

La compréhension des propriétés microstructurales, mises en évidence dans ce travail, s'avère essentielle pour l'interprétation adéquate et la modélisation des propriétés optoélectroniques du matériau. Cette connaissance est aussi nécessaire pour modifier judicieusement le procédé de fabrication du matériau photoconducteur en vue d'améliorer les performances d'un spectromètre térahertz.

7.2 Contributions originales des travaux

Le tableau présenté ci-après résume et décrit les contributions originales des travaux.

#	Contribution	Indicateur/Justification/Pertinence
1	L'implantation ionique avec des ions lourds d'énergies MeV dans l'alliage quaternaire InGaAsP/InP et les applications de cette technique.	Insuffisance de littérature spécifiquement sur ce sujet pour l'InGaAsP malgré l'ample littérature existante pour InP, InGaP, InGaAs, InAlAs, etc. Nous avons été invités à présenter nos résultats à 4 conférences internationales : sur les semi-conducteurs (CSTC 2009, Hamilton, ON), l'implantation ionique (IBMM 2010, Montréal, QC), la technologie THz (Optical Sensors 2011, Toronto, ON) et les semi-conducteurs nanocristallins (ICANS 2013, Toronto, ON).
2	L'implantation ionique de ^{56}Fe à 300 K pour fabriquer une couche d'InGaAsP semi-isolante avec un seuil d'absorption à 1.3 µm	L'isolation électrique par implantation est une méthode bien connue dans la technologie des semi-conducteurs III-V. Nous rapportons ce procédé pour la première fois pour isoler une couche InGaAsP/InP (1.3Q) avec le fer [Fekecs *et al.* 2013]. Une forte résistivité a été obtenue (10^4 Ω·cm), ce qui est plus élevé que ce qui a été rapporté jusqu'à maintenant avec l'implantation ionique dans l'InGaAsP (1.3Q).
3	L'étude de l'effet de la fluence de ^{56}Fe sur le dommage d'implantation primaire de l'InGaAsP et le dommage résiduel après recuit rapide.	Première étude publiée [Fekecs *et al.* 2013]. Elle est basée sur les mesures HRXRD et RBS-C. Localisation de l'amorce de la transition cristalline/amorphe pour l'implantation de Fe dans l'InGaAsP. Elle se produit lorsque la fluence est de 4.8×10^{13} cm^{-2}.
4	L'implantation ionique de ^{56}Fe dans l'InGaAsP pour fabriquer une couche photoconductrice résistive, ultrarapide et absorbante à 1.55 µm.	L'endommagement par implantation est une méthode bien connue dans la technologie des semi-conducteurs pour réduire le temps de vie. Le Fe a déjà été implanté dans l'InP et l'$In_{0.53}Ga_{0.47}As$ à cet effet. Nous rendons une couche d'$In_{0.61}Ga_{0.39}As_{0.87}P_{0.13}$/InP ultrarapide et résistive pour la première fois avec ce procédé [Fekecs *et al.* 2011]. Nos résultats ont été validés par le groupe du Pr. Elliott Brown à Wright State University, ce qui a mené à une étude comparative de plusieurs matériaux [Martin *et al.*, 2012].

5	L'optimisation de la température d'implantation de ^{56}Fe et ^{69}Ga dans l'InGaAsP/InP et de la température de recuit.	Première étude d'implantation de ^{69}Ga dans l'InGaAsP. Premier estimé de la température critique d'implantation pour le ^{56}Fe dans l'InGaAsP: 373 K < T_c < 473 K. L'amorphisation est donc possible avec une température d'implantation de 300 K (sous T_c) et de fortes résistivités sont mesurées après recristallisation.
6	Démonstration de l'émission THz pulsée avec des antennes photoconductrices basées sur l'InGaAsP implanté au Fe à 83 K.	Premiers résultats publiés [Fekecs *et al.* 2011]. Le développement du matériau, de dispositifs et de spectromètres térahertz se poursuivent avec plusieurs collaborateurs. Un spectromètre équipé d'une source et d'un détecteur incorporant une couche d'InGaAsP implanté Fe a été démontré par B. Petrov au laboratoire du Pr. D. Morris.
7	La fabrication d'une hétérostructure amorphe InGaAsP/InP obtenue par implantation d'ions lourds.	C'est un matériau absent dans la littérature.
8	L'étude microstructurale de la recristallisation d'une hétérostructure amorphe InGaAsP/InP.	Étude originale combinant la mesure de la diffraction de rayons X et la microscopie électronique [Fekecs *et al.* 2015]. Nous avons identifié plusieurs couches structurales et étudié la microstructure de la couche photoconductrice d'InGaAsP. Cette étude est d'une grande utilité pour l'interprétation des résultats de caractérisation optique et électrique et l'amélioration du procédé de fabrication.

7.3 Nouvelles perspectives de recherche

Le champ d'étude de l'implantation ionique des matériaux semi-conducteurs est très vaste. Nous espérons que notre apport contribuera à l'avancement de cette technique et au développement des applications basées sur les alliages III-V. Le travail présenté dans cette thèse mène vers plusieurs perspectives de recherche concernant les méthodes d'analyses, les procédés et le développement de dispositifs et d'applications. Nous pouvons en énumérer quelques une ici :

1) Concernant l'étude de la fabrication d'une couche d'InGaAsP (1.3Q) semi-isolante, l'activation électrique des impuretés et des complexes de Fe pourrait être démontrée avec des techniques de mesures spectroscopiques de type *photo deep-level transient*

spectroscopy, *photo-induced current transient spectroscopy* ou bien estimée avec des mesures Hall en température. Avec la limitation causée par l'amorce de l'amorphisation durant l'implantation à 300 K, il y a peu de marge de manœuvre pour ajuster la concentration du Fe relativement à la concentration de donneurs qui pourraient être présents dans la couche. L'implantation à haute température pourrait être considérée, cependant il semble falloir allonger le temps de recuit et le faire sous atmosphère de phosphore, pour mieux guérir les défauts ponctuels formés durant l'implantation.

2) Le travail d'optimisation des dispositifs térahertz obtenus avec le matériau InGaAsP/InP (1.57Q) implanté à froid et recuit à 500 °C est déjà en cours avec nos collaborateurs. La gravure d'un mésa et l'optimisation des designs d'électrodes spécifiques à l'émission et à la détection sont considérées, de même que l'ajout d'une couche diélectrique comme antireflet. Il serait aussi très utile de réduire la taille des puces pour permettre un usage plus efficace du matériau.

3) Selon nos observations, l'InGaAsP implanté à forte fluence et recristallisé peut se présenter en couches structurales multiples. Si une couche est, ne serait-ce que légèrement, plus conductrice qu'une autre, elle influence les mesures électriques en configuration Van der Pauw. Des mesures électriques pouvant profiler séparément les diverses couches structurales seraient utiles pour mieux caractériser les propriétés du transport électrique.

4) La présence d'amas riches en Fe et l'activation du Fe dans l'InGaAsP polycristallin reste à démontrer. Des mesures en spectroscopie FT-IR (*Fourrier transform infrared*) pourraient confirmer des signatures de nano-amas métalliques ou la transition électronique du fer activé. Nous suggérons aussi de pousser un peu plus l'étude TEM avec la préparation de spécimens ultraminces (~10 nm) pour permettre la détection du fer et sa distribution dans la microstructure avec la technique EELS (*electron energy loss spectroscopy*). Un spécimen ultramince pourrait servir pour des analyses plus détaillées de l'orientation des domaines cristallins et de la configuration des défauts planaires.

5) Concernant l'étude microstructurale non-destructive avec la diffraction de rayons X, une configuration de mesure en incidence rasante serait utile pour s'affranchir des pics de substrat, afin d'améliorer l'analyse de Williamson-Hall et l'estimation de la fraction de

volume cristalline. Cet estimé pourrait être corroboré avec une étude en spectroscopie Raman. Il serait intéressant de coupler ce travail avec une nouvelle étude de la dynamique des porteurs basée, par exemple, sur une technique de spectroscopie résolue temporellement avec une pompe infrarouge et sonde térahertz en transmission, pour mieux cerner l'interdépendance entre la micro/nanostructure et la dynamique de porteurs.

6) Il nous semble aussi important d'étudier la formation de la microstructure dans les premiers stades de la recristallisation, quand la température du profil de recuit se situe entre 200 °C et 300 °C et de mieux comprendre les transformations qui surviennent au-delà de 500 °C.

7) Il serait utile de quantifier l'impact de la qualité cristalline sur l'efficacité de l'émission térahertz. Il serait probablement très judicieux d'optimiser le procédé de fabrication du matériau en se basant sur les performances des dispositifs térahertz, sans passer par des mesures intermédiaires. Afin de faciliter les tests, l'intégration sur un même substrat de plusieurs recettes d'implantation ou de recuit est souhaitable. Le recuit laser, qui peut être appliqué localement, pourrait être employé à cette fin.

ANNEXE A Informations supplémentaires

A1. Similarité des dispositifs photoconducteurs

Tableau A.1 Comparaisons entre un dispositif photoréfractif et un émetteur térahertz [Coutaz, 2002; Nolte, 1999; Wang *et al.*, 1992].

	Photoconducteurs photoréfractifs à 1.3 µm	**Photoconducteurs térahertz à 1.55 µm**
Configuration	Éclairement à incidence normale. Épaisseur de la couche mince de 1–2 µm. Électrodes planaires espacées de quelques mm.	Éclairement à incidence normale. Épaisseur de la couche mince de 1–2 µm. Électrodes planaires espacées de quelques dizaines de µm.
Surface active	Quelques dizaines de mm^2	Quelques centaines de μm^2
Principe de fonctionnement	Illumination non-uniforme et accumulation des charges photo-générées par des défauts profonds. Ce qui permet l'écriture d'un interférogramme sous forme d'une charge d'espace qui module un champ électrique local. Un effet électro-optique est requis pour former un hologramme.	Illumination intense ultracourte et génération de photoporteurs. Il y a séparation et accélération des photoporteurs avec l'application d'un champ externe. Les photoporteurs recombinent rapidement aux défauts. Le transitoire de photocourant ultrarapide irradie un champ électromagnétique THz.
Matériau visé	Semi-isolant compensé avec des défauts (des pièges profonds d'un métal de transition, le fer dans notre cas).	Semi-isolant obtenu avec des défauts d'implantation. Dans notre cas, on implante le fer.
Une forte **absorbance**	Pour une bonne photoconductivité. Effet électro-optique requis à 1.3 µm.	Pour une bonne photoconductivité autour de 1.55 µm.
Bonne **mobilité** des porteurs (μ)	Le produit mu-tau bipolaire <μ τ> influence la longueur de diffusion, donc le pas du réseau holographique. Il influence aussi le courant de photoconduction, donc la dynamique d'écriture.	La mobilité influence le courant de photoconduction.
Un court **temps de vie** des porteurs (τ)		Pour une variation rapide du courant de photoconduction. *Moins de 1 ps dans le cas d'un détecteur.*
Résistivité élevée en obscurité	Reliée à l'effacement de la charge d'espace et à l'intensité de saturation d'écriture. Minimise l'échauffement par effet Joule.	Pour réduire l'échauffement par effet Joule sous haut champ électrique. *Pour réduire le bruit thermique dans un détecteur.*

A2. Recuit thermique rapide

La figure A.2a) donne la configuration de la chambre de recuit thermique rapide (RTA) utilisée à l'Université de Sherbrooke pour la fabrication de couches photoconductrices d'InGaAsP ultrarapide. La chambre Jetfirst (Jipelec) contient un système de lampes infrarouges (IR) capable d'irradier de la chaleur vers un suscepteur, un substrat de silicium de 100 mm, supporté par trois tiges de quartz biseautées. Une boucle d'asservissement permet d'ajuster le niveau de la puissance thermique délivrée par les lampes, afin de contrôler les températures qui sont déterminées avec un thermocouple (TC) placé en contact mécanique avec la face arrière du suscepteur. La chambre est pompée et ensuite purgée avec de l'azote sec avant le recuit. L'échantillon est placé face vers le bas en contact avec le suscepteur. Un capot de silicium protège la face arrière de l'échantillon. Le tableau A.2 donne les caractéristiques du suscepteur et des capots utilisés. Le graphique A.2b) montre des profils de température enregistrés par le TC pour plusieurs températures de plateau, entre 400 °C and 750 °C. Les temps de montés et de descente nominaux demandés sont de 20 s et la durée du plateau de recuit est de 30 s. Le gradient radial de la température du suscepteur est estimé à ~0.8 K/mm à 725 °C [Neng Liu, communication privée, 2012].

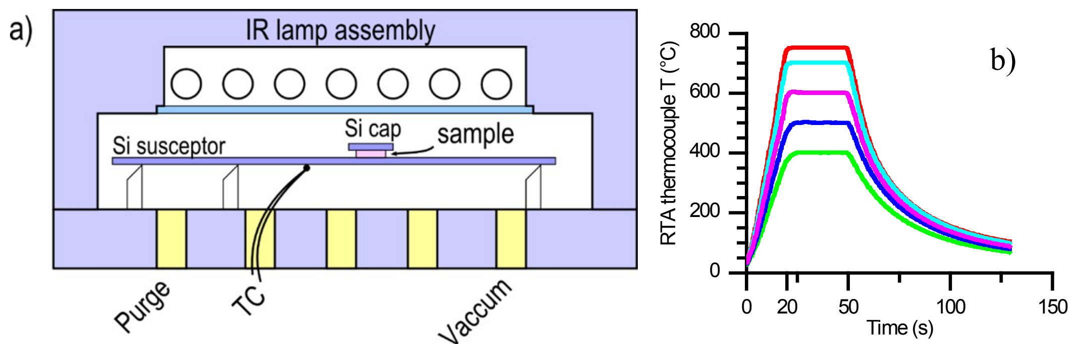

Figure A.2 Configuration de la chambre de recuit rapide et profils de température utilisés pour développer les couches photoconductrices d'InGaAsP ultrarapides.

Tableau A.2 Spécifications des substrats de silicium utilisés comme suscepteur et capot de proximité pour le recuit thermique rapide.

Description	Dopage	Résistivité (Ω cm)	Épaisseur (mm)	Notes/No. SSE
Suscepteur de Si	type-*p* (B)		0.27	Face polie vers le haut
Capot de Si	type-*p*	1 – 100	0.47	D020
	type-*p* (B)	20 – 30	0.51	F1083

A3. Modèle électrique à un niveau profond

Il est possible de modéliser la compensation électrique de l'InGaAsP type-n par dopage au fer. Nous employons pour cela un modèle dérivé des statistiques de Fermi-Dirac, les équations (A.1) à (A.5), qui tient compte d'un seul niveau accepteur profond. Ce modèle est parfois appelé un diagramme de Schockley quand il est résolu graphiquement. Ce modèle électrique est fréquemment utilisé pour décrire les populations de porteurs libres n (électrons) et p (trous), la fraction ionisée des accepteurs profonds N_{da}, des accepteurs peu profonds N_{sa} et des donneurs peu profonds N_{sd} [Lourdudoss *et al.*, 2000; Söderström, 2001].

$$N_{\mathrm{da}}^{-} = \frac{N_{\mathrm{da}}}{1 + g_{\mathrm{da}} \exp\left[(E_{\mathrm{da}} - E_{\mathrm{F}})/(k_{\mathrm{B}}T)\right]} \tag{A.1}$$

$$N_{\mathrm{sa}}^{-} = \frac{N_{\mathrm{sa}}}{1 + g_{\mathrm{sa}} \exp\left[(E_{\mathrm{sa}} - E_{\mathrm{F}})/(k_{\mathrm{B}}T)\right]} \tag{A.2}$$

$$N_{\mathrm{sd}}^{+} = \frac{N_{\mathrm{sd}}}{1 + g_{\mathrm{sd}} \exp\left[-(E_{\mathrm{sd}} - E_{\mathrm{F}})/(k_{\mathrm{B}}T)\right]} \tag{A.3}$$

$$p = \frac{N_{\mathrm{V}}}{1 + \exp\left[-(E_{\mathrm{V}} - E_{\mathrm{F}})/(k_{\mathrm{B}}T)\right]} \tag{A.4}$$

$$n = \frac{N_{\mathrm{C}}}{1 + \exp\left[(E_{\mathrm{C}} - E_{\mathrm{F}})/(k_{\mathrm{B}}T)\right]} \tag{A.5}$$

$$N_{da}^{-} + N_{sa}^{-} + n = N_{\mathrm{sd}}^{+} + p \tag{A.6}$$

Ici, E_{V} et E_{C} sont les énergies du bas de la bande de valence et du bas de la bande de conduction et E_{da} est l'énergie de l'accepteur profond. N_{V} et N_{C} sont les densités d'états des bandes de valence et de conduction, respectivement. Les facteurs de dégénérescence g_{da}, g_{sa} and g_{sd} correspondent aux accepteurs profonds, accepteurs peu profonds et donneurs peu profonds. Ils valent 0.45, 4 et 2, respectivement [Lourdudoss *et al.*, 2000]. La valeur de N_{sd} utilisée est la densité de porteurs qui est mesurée par effet Hall après la croissance de l'hétérostructure (*i.e.*, 3×10^{15} cm^{-3}). N_{sa} est fixé à 1×10^{14} cm^{-3} puisque des impuretés de type-p sont présentes, mais en moindre quantité. Pour que les équations (A.1)-(A.3) soient valides, les

énergies des niveaux peu profonds E_{sd} et E_{sa} sont fixées avec un écart de $3k_BT$ des bandes de conduction et de valence. k_B est la constante de Boltzmann et le calcul est fait à une température T de 300 K. Le modèle est résolu en solutionnant l'équation d'équilibre des charges donnée par l'équation (A.6). Le calcul permet d'estimer l'énergie du niveau de Fermi E_F en fonction de N_{da}, la densité de l'accepteur profond. La figure A.3 montre que le niveau de Fermi de l'InGaAsP est bloqué près du milieu du gap quand la densité de fer activé N_{da} excède N_{sd}, la densité du dopage type-n. Une flèche indique le point de croisement quand $n = p$.

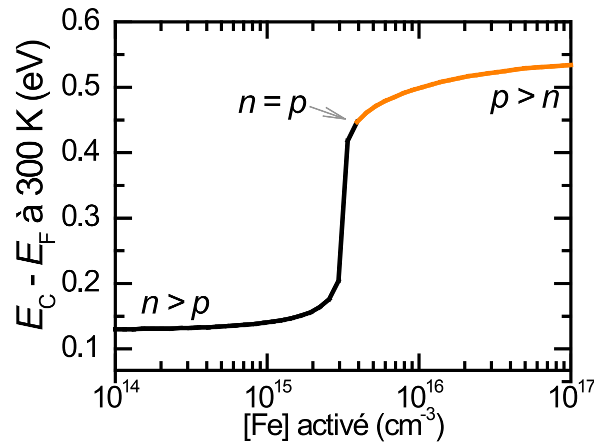

Figure A.3 Position du niveau de Fermi E_F en fonction de N_{da}, la densité de fer activé dans la couche d'InGaAsP type-n. $E_g=E_C–E_V = 0.95$ eV, $E_C–E_{da} = 0.47$ eV et $N_{sd}=3\times10^{15}$ cm^{-3}.

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