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INFLUENCE OF PROCESSING TECHNIQUES ON COPPER DEEP LEVELS FORMATION AND ON PHOTOCONDUCTIVITY IN SILICON DOPED GALLIUM ARSENIDE

by

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ABSTRACT

INFLUENCE OF PROCESSING TECHNIQUES ON COPPER DEEP LEVELS FORMATION AND PHOTOCONDUCTIVITY IN SILICON DOPED GALLIUM ARSENIDE SWITCHES

Lucy M. Thomas

Old Dominion University, 1993

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Diffusion of copper in silicon doped gallium arsenide under different diffusion conditions is studied. Copper compensated silicon doped gallium arsenide (GaAs:Si:Cu) is used as switch material for bulk optically controlled semiconductor switch, and on-state photoconductivity of the switch is primarily due to the properties of the copper deep levels introduced in the material during diffusion. Gallium arsenide being a compound semiconductor, presence of vacancies and defects make the study of diffusion a complex process. The objective of the current research is twofold: a) to study the influence of diffusion conditions and processing techniques on copper deep level formation in silicon doped gallium arsenide (GaAs:Si) and b) to fabricate a switch material with high photoconductive gain so that low power semiconductor lasers can be used as the excitation source for closing the switch. Influence of different diffusion parameters, in particular, arsenic vapor pressure on the diffusion of copper and copper deep level formation in GaAs:Si is studied. Three different diffusion techniques, namely, closed tube diffusion, semi-closed tube diffusion, and leaky tube diffusion are used to diffuse copper in GaAs:Si. The diffusion of copper in GaAs is studied for the first time in the present work using the leaky tube diffusion technique, and the results show that it is the best among the three techniques studied, to diffuse copper to obtain high efficiency switch material.

Photoinduced current transient spectroscopy (PICTS) and van der Pauw-Hall measurements are used to characterize the diffused samples. Various deep levels present in the diffused samples are identified and the variation of the characteristics of these levels with diffusion conditions is analyzed. PICTS spectra of GaAs:Si:Cu samples processed using different techniques are found to be strikingly different. Deep level structure at different depths from the surface of the GaAs:Si:Cu crystal annealed using the closed tube diffusion technique has been studied using the PICTS, and the results indicated the presence of a gradient in the copper related levels in the material. In leaky tube diffusion, the gradient effect is minimized by providing a source of copper on both surfaces of the sample and protecting the surfaces by silicon dioxide coating. Based on the characterization results, models for different copper related complexes have been identified, V_{As} Cu_{Ga} V_{As} (arsenic vacancy is denoted as V_{As} and copper in gallium site is denoted as Cu_{Ga}) and Cu_{Ga} for Cu_B and Cu_A respectively. Photoconductivity of the GaAs:Si:Cu switches fabricated using the three different techniques is measured and found that switches fabricated using the leaky tube diffusion technique are the most efficient among the three. The efficiency of the leaky tube samples is high enough to use low power semiconductor laser diode as the excitation source.

DEDICATION

To my brother Tom Thomas
for whom words are not enough to express my gratitude...

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CHAPTER 1

INTRODUCTION

The study of the physics of various processes in semiconductor devices is of extreme importance for the continuous development of semiconductor industry. Since the dawn of modern semiconductor technology during the 1950's, the effort to study the physics of various processes and the vast amount of literature published in this area show the stature of this field. The physics of semiconductors is the basis of semiconductor technology, on which the whole field of microelectronics and hence the modern information technology depends. The quest for the miniaturization of the semiconductor devices has led the integrated circuit fabrication (silicon) technology from SSI in the 60's, through LSI, and VLSI to ULSI by the late 80's. The technological importance of GaAs has gained much attention among researchers because of many desirable properties the material possess such as high carrier mobilities, light emitting properties, and the ability to produce superconducting films [1]. In particular, GaAs has found application for high-frequency electronic devices, especially since the introduction of modulation doping in 1978 [2]. In modulation doping, the band edge discontinuity in the heterostructure (e.g., GaAs/$Al_xGa_{1-x}As$) from their parent donors (acceptors) is utilized to separate the electrons (holes), and this leads to record carrier mobilities for both electrons and holes.

Among various processes to fabricate VLSI devices, diffusion is an important step. Diffusion of various impurities in silicon has been thoroughly studied and well understood. However, diffusion studies in GaAs have not been matured enough yet to understand the physics clearly. GaAs is a compound semiconductor, and hence many factors such as Fermi level effect, non-equilibrium point defects, vapor-phase pressure effect etc., make it more difficult to elucidate the diffusion mechanisms compared to silicon which is an elemental semiconductor. Diffusion of zinc (Zn), copper (Cu), and tin (Sn) in GaAs has been extensively studied compared to other metals. Among these, Zn is the most studied metal, and most of the existing theories and mechanisms are derived based on the results obtained from the study of Zn diffusion. Since melting point of Zn is below 500^{0}C, and decomposition of GaAs is congruent below 637^{0}C, a systematic study of diffusion of Zn in GaAs is feasible without changing the surface stoichiometry of GaAs.

For the fabrication of high-frequency electronic devices, the quality of the GaAs crystal must be sufficiently controlled, if possible, as much as in case of silicon and germanium. In practice, GaAs grown using vapor phase or liquid phase epitaxy is found to be of high quality, whereas the melt-grown crystals, which are easily obtainable but are usually impure, and far from the requirements of device fabrication. Since Cu diffuses rapidly in GaAs even at relatively low temperatures (below 600^{0}C), contamination by this impurity during semiconductor device processing is very likely. Copper introduces various deep acceptor levels in GaAs, of which the levels Cu_A (activation energy, E_T = 0.14 eV) and Cu_B (E_T = 0.44 eV) are the prominent levels. The study of deep levels in GaAs is important due to many reasons: the effect they have on a) the carrier concentration from shallow doping; b) mobility because of ionized impurity scattering; c) trapping effects that can influence transport, frequency and switching performances of devices; and d) the recombination diffusion lengths and generation in bipolar structures (such as solar cells and other optical sensing devices). In the fabrication of many devices such as, laser diodes, field effect devices, light emitting diodes etc., Cu is considered an undesired impurity, since it is detrimental to the properties of the substrate material (semi-insulating GaAs) by forming non-radiative recombination centers and also by compromising the high resistive nature of the substrate. The present study, however, is motivated by the novel photoconductive switching properties of copper compensated, silicon doped GaAs (GaAs:Si:Cu) contributed by the Cu deep levels (Cu_A and Cu_B etc.) introduced in the material by copper diffusion.

The photoconductivity of GaAs has been studied by many researchers [3-5] since the 1950's, however its application in pulse power switching has been investigated only in the 1970's [6-8]. Among the semiconductors which are being investigated for pulse power switching applications, GaAs has been gaining more attention among researchers due its high speed, jitter-free, and high rep-rate operation. The material, GaAs:Si:Cu has been demonstrated as a bulk optically controlled semiconductor switch (BOSS), which can be turned on and off on command. The BOSS concept has been developed by Schoenbach *et al.* [9-11] in 1988, which utilizes the below band gap excitation of the electrons and holes from the deep impurity centers in wide band gap semiconductors. The characteristics of the BOSS are primarily due to the properties of the Cu deep levels. The large capture cross section of Cu_B level for holes in GaAs:Si:Cu allows some of the electrons reaching the conduction band during illumination to remain there even after the cessation of the laser light, and thus the switch remains on for longer time compared to other semiconductor switches (See Fig. 1.1). The switch can be opened on command by using a second laser light of longer wavelength to excite the holes from the Cu_B level to stimulate recombination. The Cu_B level, in general, is primarily responsible for the switch conductivity, and hence higher concentration of the Cu_B states is desired to obtain high on-state conductivity.

The existence of the Cu entering GaAs as Cu_A or Cu_B (and other complexes) is influenced by the processing conditions. The Cu deep levels are introduced by the diffusion process and hence the study of the mechanism and the physics of the process becomes important. The major thrust of the present work was to concentrate on developing procedures to improve the quality of the BOSS switch material. It was targeted to fabricate switch materials (with greater concentration of the Cu_B states in the semiconductor) to improve the quantum efficiency or the photoconductive gain, so that higher on-state photoconductivity for low power laser excitation of the switch can be achieved. The influence of the diffusion technique used to anneal the samples and the diffusion conditions, specifically the arsenic vapor pressure during diffusion, on Cu deep levels formation and on the switch on-state photoconductivity is studied in the present work. Three different diffusion techniques, namely, semi-closed tube diffusion, closed tube diffusion, and leaky tube diffusion are used to introduce Cu into GaAs. The switch samples have been fabricated in our laboratory using the semi-closed tube technique, and the closed tube technique is commonly used technique for the diffusion of impurities in semiconductors. Copper diffusion in GaAs:Si has been studied for the first time using

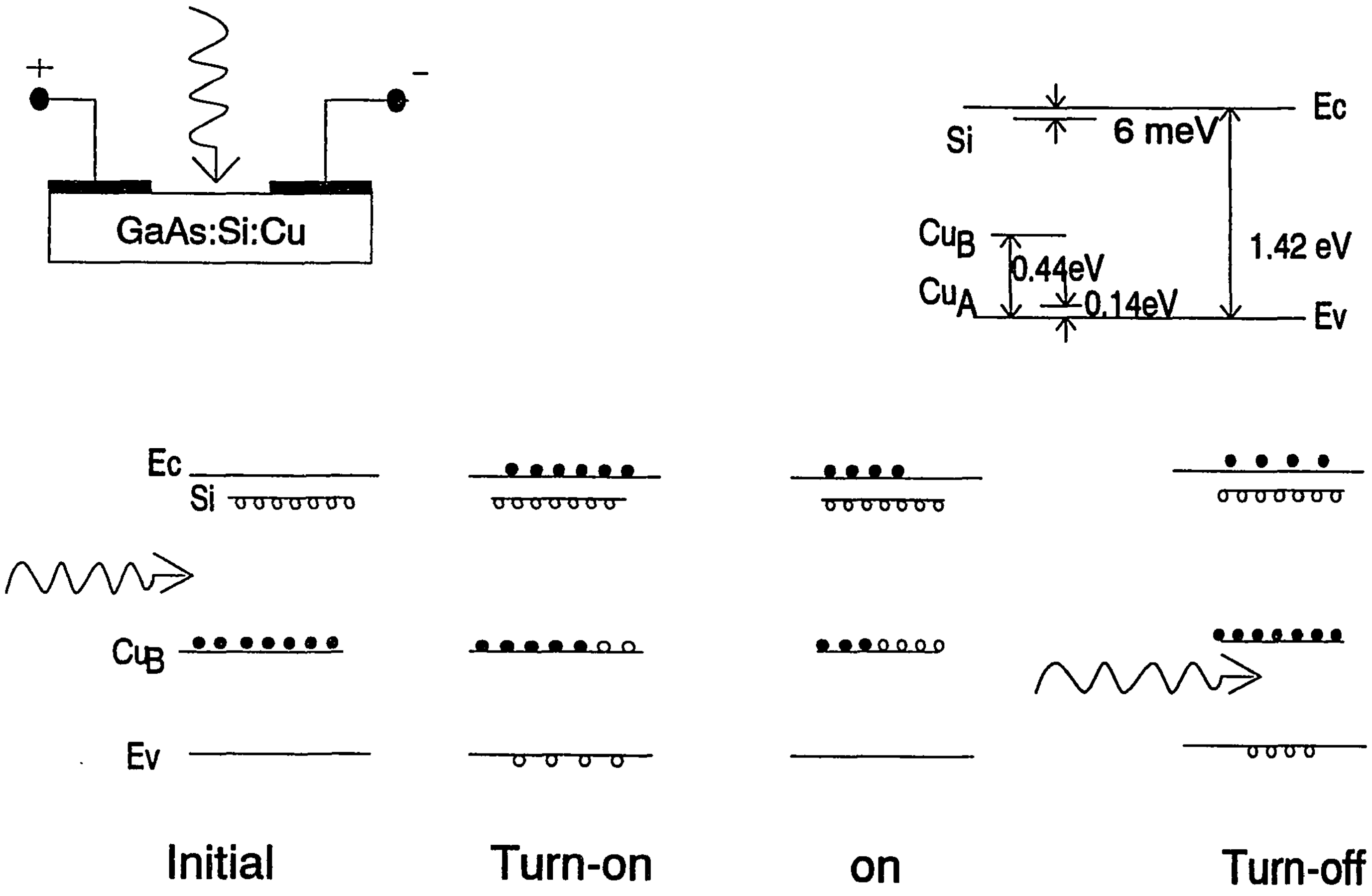


Fig. 1.1. Schematic diagram depicting the BOSS Switch Concept

the leaky tube diffusion technique in the present study. Photoinduced current transient spectroscopy (PICTS), room temperature Hall, and DC I - V measurements are used to characterize the copper compensated silicon doped GaAs (GaAs:Si:Cu). The results are analyzed to study the microstructure of the deep levels formed and the mechanism of copper compensation in GaAs:Si. In summary, the objective of the current research is two-fold: (1) to fabricate a switch material with high photoconductive gain so that low power semiconductor lasers can be used as excitation source for closing the switch; and (2) to study the microstructure of the deep levels in the GaAs:Si:Cu and thus to elucidate the compensation mechanism in GaAs:Si.

1.1 Previous Work

BOSS research has been ongoing at Old Dominion University for the past six years and a number of excellent references [9-13] are available. Hence, the literature survey will be limited mainly to the following topics: a) BOSS switches, b) diffusion of Cu in GaAs, and c) Cu deep levels in GaAs:Si:Cu and d) the study of the microstructure of the deep levels and the compensation mechanism.

Since the introduction of the BOSS concept in 1988, the Physical Electronics Research group at Old Dominion University as well as various other research groups have investigated various research issues in this area. The BOSS concept has been demonstrated using an Nd:YAG laser pulse (wavelength, λ_1 = 1064 nm for closing and λ_2 = 1620 nm for opening) at low and high electric fields [13]. Multi-megawatt power level (up to 10 MW) operation of GaAs switches has been demonstrated using low power laser diode array as well as Nd:YAG laser as a light source [14,15] for closing. Zutavern *et al.* [16] have reported the "Lock-on" effect in GaAs switches, where permanent current flow is observed above a threshold voltage (several kV/cm). Very recently, the research effort at Old Dominion University has been directed towards the demonstration of the BOSS concept using low power laser diodes as optical control elements by processing more efficient GaAs:Si:Cu switch material using modified processing techniques, and the study of temporal development of the electric field during switching [17-20].

Copper diffusion in GaAs has been studied by many researchers [2,21-26] since the 1960's, however, there is no consensus among researchers on the actual mechanism and the various levels introduced. Many researchers suggested an interstitialcy mechanism, where the Cu atoms enter the GaAs surface interstitially and then change over to occupy substitutional lattice sites displacing Ga or As atoms. The Cu atoms in substitutional lattice form complexes with the neighboring vacancies and these complexes are mostly immobile and slow down further diffusion. Because of this, the observed diffusion constant is lower than that for interstitial diffusion; the value is an average of both interstitial and substitutional diffusion. The present study is on the diffusion of Cu in GaAs:Si, which makes the study even more complicated due to the presence of additional donor impurities. The presence of donor impurities can introduce additional levels due to the complex formation of these centers and Cu. One of the earliest work on diffusion of Cu in GaAs is by Fuller *et al.* [21], and they have determined the solubility of Cu in GaAs from 700^0C to 1160^0C by means of ^{64}Cu. Blanc *et al.* [2] have studied the Cu compensation of GaAs:Si in detail, and have identified five acceptor levels. In their studies, diffusion was carried out at higher temperatures (>800^{0}C). The effect of heat treatment, doping level, and diffusion of Cu on the defect structure of Si-doped GaAs has been studied by Hutchinson *et al.* [25]. The results of their study show that at high doping levels (>10^{18} cm^{-3}) small, perfect and faulted loops were present in GaAs:Si crystal. The concentration and size of the faulted loops varied depending on the annealing temperature. It is known that As vapor pressure during crystal growth determines the crystal stoichiometry, and the native defect chemistry has been studied by annealing GaAs under different As vapor pressure by van de Ven *et al.* [26]. They have conducted photoluminescence studies of GaAs:Si annealed under different As vapor pressure, and found that Si and Cu atoms occupying Ga substitutional sites (Si_{Ga}, Cu_{Ga} respectively) can form complexes.

The electrical properties of the crystal depend on the impurities and the defects present in the crystal and are, therefore, considered as the quality parameters of the material. Earlier studies (27,28) on diffusion of Cu in doped GaAs have shown that the compensation of shallow donor levels in n-type GaAs is mainly due to Cu, but many processes can contribute towards this. At higher diffusion temperatures (>900^{0}C), Cu deep acceptors as well as shallow acceptors (Si) can be responsible for the compensation, whereas at lower diffusion temperatures (<870^{0}C) copper is mainly responsible for the compensation, as reported by Hwang [27]. The thermal conversion of the conductivity type of GaAs by high temperature annealing was found to initiate at the surface of the crystal and then to proceed into the interior [28]. It is reported that the compensation mechanism in undoped, semi-insulating (SI) GaAs is due to the partial compensation of midgap donor EL2 by shallow carbon acceptor [29].

1.2 Organization

The theory and mechanism of diffusion, the switch concept, and the photoconductivity of GaAs:Si:Cu are discussed in Chapter 2. The experimental procedure which includes fabrication of the switch devices, the techniques used to characterize the samples, and the experimental set up used to test the switches is discussed in Chapter 3. Chapter 4 discusses the results of the characterization studies, and the results of the testing of the switch devices. The discussion of the results, the conclusions derived from the study, and the suggestions for future work are given in Chapter 5.

CHAPTER 2

THEORETICAL BACKGROUND

The basic principles and the theory related to the optically controlled switching in semiconductors, and the diffusion of Cu in GaAs are discussed in this chapter. The present research effort is primarily directed to the development of processing conditions to fabricate a switch device which can be turned on using a low energy semiconductor laser diode. To achieve this, diffusion of Cu in GaAs and the mechanism of compensation in GaAs have been studied. The Cu compensated samples were characterized using the PICTS technique. The physics behind the photoconductivity and the switching property of GaAs:Si:Cu, the theory and mechanism of Cu diffusion in GaAs, and the basic principles of the PICTS technique will be discussed.

2.1 Band structure and Impurity and Defect levels

The electronic states of a perfect crystalline solid satisfy the periodic boundary conditions depending on the crystal symmetry (E(**k**) periodicity), and the states can be labelled by a reduced vector (**k**) and by a band index. The band structure of GaAs is shown in Fig 2.1, which is a result of extensive computer-aided calculations [30]. The equation used in the computation of the band structure is given below:

$$E_k=\frac{h^2}{8\pi^2 m}(k+G)^2 \qquad (2.1)$$

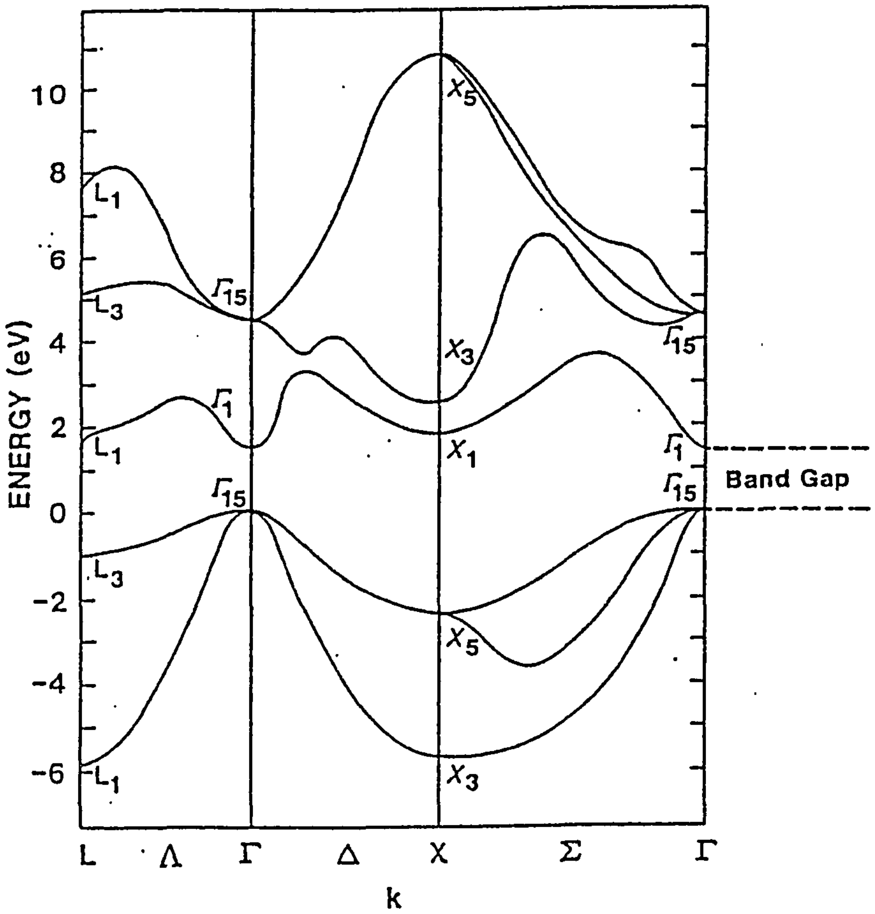


Fig. 2.1 Calculated energy band structure of GaAs. Adapted from reference 30.

where **G** is the translation vector. GaAs is a direct band gap material, i.e., the maxima of the valence band and the minima of the conduction band occur at the same **k** value (Γ, the origin in Fig. 2.1). The occupied states in the valence band are separated from the empty states in the conduction band by the forbidden energy gap, which results from the interaction of the conduction electron waves with the ion cores of the crystal.

The potential distribution of a crystalline solid where the atoms are arranged in the periodic lattice can be best approximated by the periodic repetition of the potential wells of length **a** and potential barriers of width **b** and height V_0 as shown in Fig. 2.2a. However, this simplified model does not consider the overlapping of the individual potential from each lattice site, and the fact that the inner electrons are more strongly bound to the core, i.e., the 1/r dependence of the potential function of a point charge. When these two factors are considered, the potential distribution of a crystal can be represented as shown in Fig. 2.2b, which is referred as the muffin tin potential. The potential energy of the conduction electron in the field of the crystal lattice is shown in Fig. 2.2c, and the charge density corresponding to the standing waves, $\psi(+)$ and $\psi(-)$, and to a travelling wave is shown in Fig. 2.2d.

$$\psi(+) = 2\cos\,(\pi x \,/\, a) \tag{2.2}$$

$$\psi(-) = 2i\,\sin\,(\pi x \,/\, a) \tag{2.3}$$

$$\rho(+) = \psi(+)^2; \quad \rho(-) = \psi(-)^2; \tag{2.4}$$

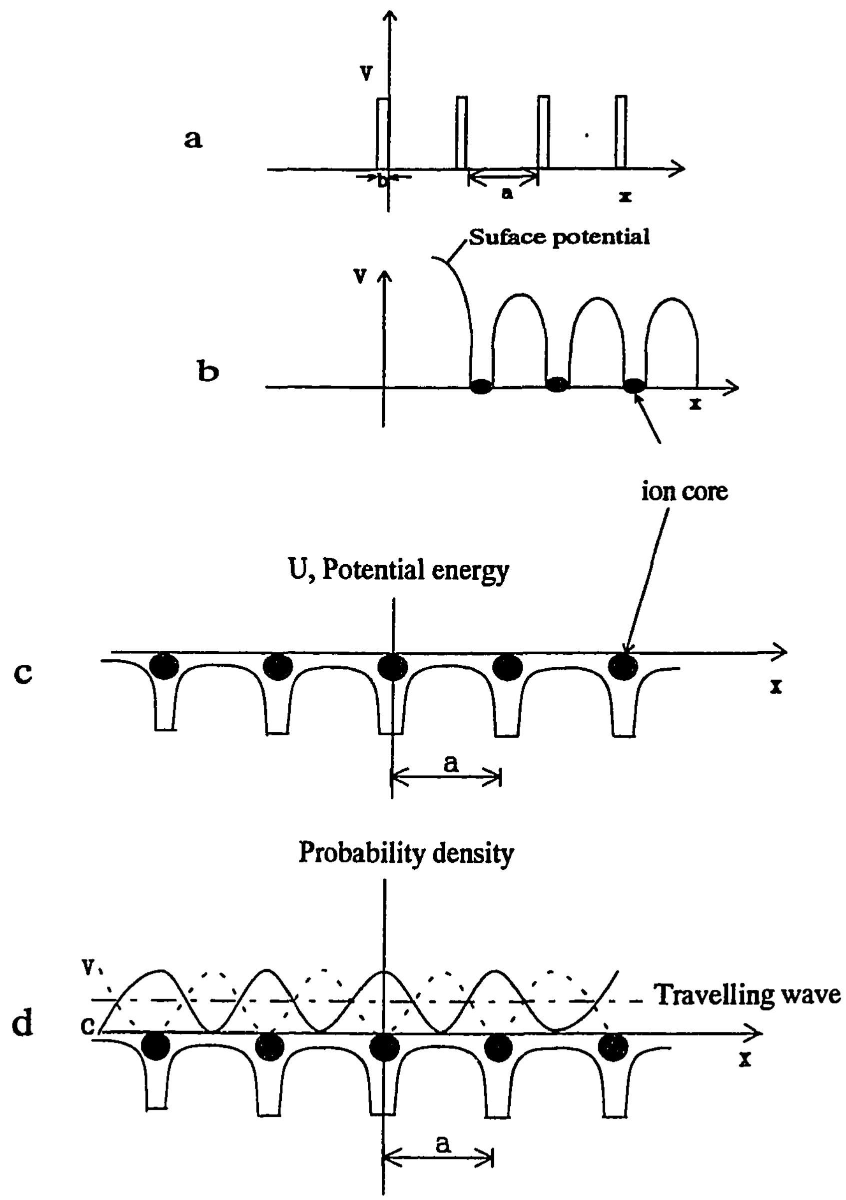


Fig. 2.2 a) Simplified model of one-dimensional periodic potential distribution for a crystal b) muffin tin potential model c) variation of potential energy of a conduction electron in the field of the ion cores of a crystal lattice d) distribution of probability density corresponding to the standing waves and to a travelling wave. 'a' is the lattice separation

For the travelling wave (e^{ikx}), the charge density ρ is constant ($\rho = 1$). The charge density of $\psi(+)$ is the maximum at the lattice, where the positive ion is located, whereas the maximum of $\psi(-)$ is midway between ion cores. The average value of the potential energy of $\rho(+)$ is lower than that of the travelling wave, and $\rho(-)$ is higher than that of the travelling wave. The band gap is a measure of the difference in energy of $\rho(+)$ and ρ (-). In general, the energy band structure is simplified and only the valence band and the conduction band near the **k** value where the maximum and the minimum of the bands are occurring is utilized. The bands are represented as the continuums with a gap between them, equal to the band gap energy, and this simplified band structure is used for the discussion of the GaAs:Si:Cu system which is studied.

When the translational symmetry of a perfect crystal is broken, localized states (states with decaying wavefunctions) can appear in the band gap. Imperfections in the crystal can be due to the presence of a chemical impurity or a lattice vacancy, and play a major role in affecting the material characteristics. Despite a striking variety in the chemical nature of imperfections, and in their relationship with the host metal, they all possess (except the isoelectronic systems such as GaP:As) the ability to form localized states in the forbidden gap. However, if the entire charge of an impurity electron is localized in the atomic volume of the impurity, the binding energy would vary on a scale greatly exceeding the magnitude of the band gap, and only a few impurity states could fall into the gap. Localization of these bound states is possible only when a substantial portion of the electronic charge lies well outside the range of the short-range, deep atomic potential associated with the impurity. In such cases, the energy of the states can be found by solving the Schrodinger equation:

$$H\psi = E\psi \tag{2.5}$$

where,

$$H = H_0 + V \tag{2.6}$$

H_0 represents the perfect crystal Hamiltonian and V is the effective impurity potential centered at the site of the defect. It is to be pointed out that the short-range potential may be very strong within the effective radius of the defect and even a small portion of the electronic charge localized there might give rise to a substantial contribution to the binding. This could be the reason for the variation of the experimental binding energy from defect to defect.

When the amount of localized charge remaining in the region of the short-range potential is too small, the Schrodinger equation (2.5) can be reduced to its hydrogenic form which leads to the well known effective mass theory [31]. The impurity electron is bound by the attractive force of the long-range (coulomb) part of the potential (V) which behaves as ~ $(\varepsilon r)^{-1}$, where ε is the static dielectric constant of the host semiconductor. The wavefunctions can be shown as the product of a slowly varying envelope function F(r) and a periodic function derived from the nearest band minimum. Near the band edge, the crystal Hamiltonian can be expressed using the effective mass parameter (m^*). Equation (2.5) for the radial function R(r) = rF(r) in an isotropic semiconductor reduces to:

$$\left(\frac{d^2}{dr^2}+\frac{8\pi^2 m^*}{h^2}(E\frac{Ze^2}{\epsilon r})-\frac{l(l+1)}{r^2}\right)R(r) = 0 \tag{2.7}$$

where l is the angular momentum. The solutions of equation (2.7) resemble the spectrum of a hydrogen atom immersed in a uniform dielectric medium.

Impurity levels in the band gap can be of two types: shallow levels which are very near to the bands (< 3kT eV below the conduction band or above the valence band) and deep levels which exist deeper into the band gap. The effects associated with the shallow donor and acceptor levels, where the potential (V) is dominated by its long range Coulomb term, can be explained using the hydrogenic model. In the case of deep levels, where the short range interactions become important and a contraction of the impurity wavefunction leads to the breakdown of the hydrogenic theory. Lacking an analytical solution of equation (2.5) for the deep level problem, the solutions can be represented in terms of a suitable complete set of functions as shown below:

$$\psi = \sum A_{n,k}\phi_{n,k} \tag{2.8}$$

The wavefunction Ψ of a localized state in the gap can be expanded in terms of the eigen functions $\phi_{n,k}$ of the perfect crystal Hamiltonian H_0. $A_{n,k}$ denote the coefficients.

GaAs being a compound semiconductor, Ga and As vacancies play a major role in the diffusion of impurities in the crystal. Therefore, a discussion of the possible defects is included here to understand the diffusion mechanism of impurity atoms in GaAs. It is known that GaAs grown by various techniques such as LEC (liquid encapsulated Czochralski), Bridgeman, VPE (vapor-phase epitaxy), MOVPE (metalorganic VPE), MBE (molecular beam epitaxy), and LPE (liquid phase epitaxy) have different properties in terms of the energy levels within the band gap due to the differences in defect levels, trace impurities, and impurity complexes [32]. Therefore, in addition to the characterization of the crystal in terms of mobility and carrier concentration, characterization of the deep levels in the energy band is also necessary.

Table 2.1 lists the number of possible native defects in GaAs and there are large number of defects possible. So far, none of these have been identified with any confidence. Even the simple Ga and As vacancies have not been able to be related to particular energy levels. Experiments to identify these defects tend to be too uncontrolled due to the changes in the electrical properties of the crystals after heating under various conditions of Ga and As overpressure, and due to the difficulties in performing heating operations under conditions of comparable cleanliness. The impurity atoms can form complexes with the native defects present in the crystal, and more details of these complexes are discussed in the following sections.

2.2 Diffusion of Cu in GaAs

The diffusion process in semiconductors, and also in other solids, is critically dependent on the structural defects and imperfections of various kinds (impurities, dislocations, color centers etc.) which are always present in real crystals. Copper is a fast interstitial diffuser in GaAs. The common grade of fused silica is a source of Cu during processing. The diffusion of Cu in GaAs is quite complicated since Cu may be incorporated interstitially as a single donor, substitutionally as a double acceptor, or in a

Table 2.1 Possible Defects in gallium arsenide [33]

Gallium vacancies involved	Arsenic vacancies involved	Antisite defects	Interstitials involved	Three component defects
V_{Ga}	V_{As}	Ga_{As}	Ga_i	
$V_{Ga}V_{Ga}$	$V_{As}V_{As}$	As_{Ga}	As_i	
$V_{Ga}V_{As}$	$V_{Ga}V_{As}$		Ga_iAs_i	
		$Ga_{As}As_{Ga}$		
Ga_iV_{Ga}			Ga_iV_{Ga}	
	As_iV_{As}		As_iV_{As}	
$Ga_{As}V_{As}$		$Ga_{As}V_{As}$		
	$Ga_{As}V_{As}$	$Ga_{As}V_{As}$		
$As_{Ga}V_{Ga}$		$As_{Ga}V_{Ga}$		
	$As_{Ga}V_{As}$	$As_{Ga}V_{As}$		
	Ga_iV_{As}		Ga_iV_{As}	
As_iV_{Ga}			As_iV_{Ga}	
				$V_{Ga}V_{As}V_{Ga}$
				$V_{Ga}As_{Ga}V_{Ga}$
				$V_{As}G_{Ga}V_{As}$

Subscript "i" denotes interstitial

"V" denotes vacancy

variety of complexes with other impurities and/or native defects. A wealth of experimental data (some conflicting in nature) on the diffusion of impurities is available, however, the fundamental mechanisms have not been firmly established at the present time. In GaAs, the theory and mechanism of diffusion is derived mainly from the studies of zinc (Zn) diffusion, which is the most studied metal and many of the results have been extrapolated to other impurities. Characteristics of Zn make it easy to carry out diffusion studies, whereas, high melting point and unintentional contamination from various sources makes it difficult to control the study of Cu diffusion in GaAs. In the present study, the base material chosen is Si-doped GaAs, and the presence of the donor atoms increases the complexity of the study.

Diffusion describes the process by which atoms move in a crystal lattice, and it provides an important means of introducing controlled amounts of impurities in crystals. Diffusion is the transport, due to thermal motion, of atoms of an impurity or of a major constituent. In presence of a concentration gradient, a directed diffusional flow arises, and the diffusion current J due to the flow is given by the differential equation:

$$J = -D\nabla N \tag{2.9}$$

For one-dimensional case, the above equation becomes:

$$J_x = -D\frac{\partial N}{\partial x} \tag{2.10}$$

where N is the concentration of the diffusing species, and D is the diffusion coefficient. In case of solid state diffusion, a second differential equation is often used:

$$\frac{\partial N}{\partial t}=D\frac{\partial^2 N}{\partial x^2} \tag{2.11}$$

The above equation describes the spatial distribution of the diffusing species as a function of time for a given diffusion coefficient. Equations (2.10) and (2.11) are known as Fick's first and second diffusion laws. The diffusion coefficient is a material parameter which characterizes the rate of diffusion. In general, the diffusion coefficient is expressed in Arrhenius form as shown below:

$$D(T) = D_0\, e^{-E_0/kT} \tag{2.12}$$

where k is the Boltzmann constant, T is the absolute temperature, E_0 is the activation energy, and D_0 is the frequency factor. The values of D_0 and E_0 for various impurities are listed in Table 2.2.

In general, the diffusion process in crystals occurs via interstitial, substitutional, interstitial-substitutional, or interstitialcy method. In interstitial diffusion, the impurity atoms jump from one interstitial site to another adjacent interstitial site, whereas in substitutional diffusion, the impurity atoms jump from one substitutional site to an adjacent substitutional site (Fig. 2.3). In interstitial-substitutional mechanism, diffusion takes place by the combined motion of the interstitial and substitutional atoms. In interstitialcy diffusion, the impurity atoms enters the crystal interstitially, and change over to a substitutional site, by pushing one of its nearest substitutional neighbors into an adjacent interstitial site. For substitutional diffusion, there should be neighboring vacant substitutional sites to promote the diffusion. Since equilibrium concentration of vacancies is quite low, the rate of substitutional diffusion is much lower compared to that of

Table 2.2 Diffusion constant and activation energies of diffusion for impurities in GaAs [34]

Impurity	D_0 (cm^2/s)	E_0 (eV)
Au	2.9×10^{1}	2.64
Be	7.3×10^{-6}	1.2
Cr	4.3×10^{3}	3.4
Cu	3×10^{-2}	0.53
Li	5.3×10^{-1}	1.0
Mg	2.6×10^{-2}	2.7
Mn	6.5×10^{-1}	2.49
O	2×10^{-3}	1.1
S	1.85×10^{-2}	2.6
Se	3.0×10^{3}	4.16
Sn	3.8×10^{-2}	2.7
Hg	$D = 5 \times 10^{-14}$ at 1000^0C	
Te	$D = 10^{-13}$ at 1000^0C	
	$= 2 \times 10^{-12}$ at 1100^0C	

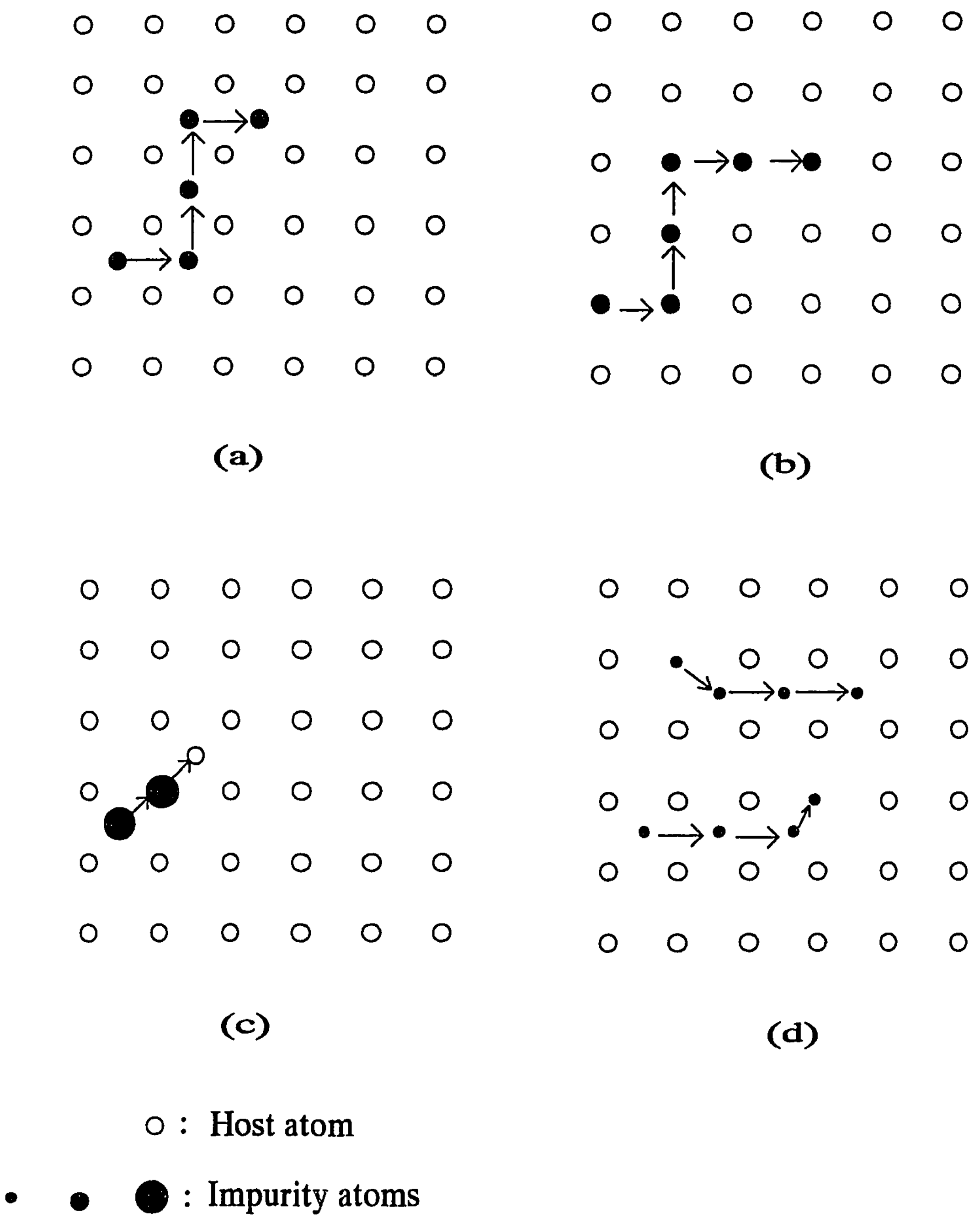


Fig. 2.3 Diffusion processess (a) Interstitial (b) Substitutional (c) Interstitialcy (d) Interstitial-substitutional

interstitial diffusion. Combinations of the above four mechanisms can occur in crystals, and some of the diffusing atoms may finally end up in substitutional sites, with the others in interstitial sites. In such cases, the diffusion rate will be an average of all different mechanisms. Furthermore, diffusion also occurs by movement along dislocations and grain boundaries. However, it has been established that these processes are anisotropic, and the atom movement is three or four orders of magnitude faster than that obtained by the lattice diffusion processes. The frequency, f, with which the atoms can jump in a zinc blend lattice from interstitial site to another adjacent one, assuming that all sites are vacant and the possible jumps are uncorrelated, is given by:

$$f = 4 f_0 \, e^{-E_m / kT} \tag{2.13}$$

where,

E_m = interaction energy involved, in eV

T = temperature of lattice, in K

f_0 = frequency of lattice vibrations, about 10^{13} - 10^{14} s^{-1}

Typical values for E_m are about 0.6-1.2 eV, which gives a frequency of one jump per minute at room temperature. Substitutional diffusion requires the presence of vacant sites, breakage of certain covalent bonds, and the making of yet others. The vacant sites are Schottky defects, with an energy of formation E_s. The process of breaking or making of a covalent bond is associated with a potential barrier E_n. The frequency with which the atoms can jump from one substitutional site to an adjacent one is given by:

$$f = 4f_0 e^{-(E_n+E_s)/kT} \tag{2.14}$$

The binding energy between an impurity atom and its neighboring atom is less than that between two adjacent atoms in the lattice, and consequently, the energy of formation of a vacancy next to an impurity atom is less than that of forming a vacancy at any other site. The experimental values of $E_n + E_s$ range from 3 to 4 eV for substitutional impurities in silicon, and thus the jump rate of a substitutional impurity at room temperature is once in every 10^{45} years. In case of interstitial-substitutional diffusion, the substitutional solubility, N_s is much higher than interstitial solubility, N_i. However, the rates of movements of these species through the lattice are very different, with the impurity comparatively immobile when it is in substitutional site, but is free to move rapidly when it is in interstitia site. If we assume independent motion of these species, the impurity will spend $N_i/(N_i + N_s)$ of its time in an interstitial site, and $N_s/(N_i + N_s)$ in a substitutional site. Then the effective jump frequency, f_{eff}, is given by:

$$f_{eff} = \frac{f_s N_s}{N_i+N_s} + \frac{f_i N_i}{N_i+N_s} \tag{2.15}$$

where f_s and f_i are the substitutional and interstitial jump frequencies, respectively. If the crystal contains many defects, the vacancy concentration readily attains its equilibrium value, and the impurity spends $N_i/(N_i + N_s)$ of its time in an interstitial site, and f_{eff} becomes:

$$f_{eff} \approx \frac{f_i N_i}{N_i+N_s} \tag{2.16}$$

The diffusion coefficients of Ga and As in GaAs are given below:

$$D_{Ga} = 0.1e^{-3.2/kT} \tag{2.17}$$

$$D_{As} = 0.7e^{-5.6/kT} \tag{2.18}$$

The diffusion coefficients are very different which shows that the movement of the Ga and As atoms occurs along separate sublattices, with each atom moving on its own sublattice. The impurities are also considered to diffuse by movement in their sublattices. Typically, group II impurities (beryllium, cadmium, magnesium, mercury, and zinc) are shallow, p-type, and move along the Ga sublattice. Since each Ga site has four As sites as nearest neighbors, the movement of these impurities are considered as a combination of interstitial and substitutional mechanism. Group VI impurities (selenium, sulfur, and tellurium) are shallow n-type, and moves along the As sublattice with a divacancy mechanism and are very slow diffusers. The group IV impurities (carbon, germanium, silicon, and tin) are amphoteric (acts as a donor as well as an acceptor), depending on the sublattice on which they are preferentially located. These impurities are very slow diffusers, and assumed that they move on both sublattices. Most other impurities introduce deep levels, and no conclusive information is available on their mechanism of diffusion.

As seen in the Table 2.1, in GaAs, there are large number of possible defects which involves As and Ga vacancies. The As vapor pressure (P_{As4}) alters the concentration of the Ga and As vacancies in a crystal. The law of mass action shows that:

$$[V_{Ga}] = K_1 P_{As_4}^{1/4} \qquad (2.19)$$

$$[V_{As}] = K_2 P_{As_4}^{-1/4} \qquad (2.20)$$

where K_1 and K_2 are the equlibrium constants. The concentration of the As vacancies is decreased by an increase in the As vapor pressure, whereas, the concentration of the Ga vacancies is increased.

2.3 Diffusion of Copper in Silicon-doped GaAs

Silicon (Si) is an amphoteric impurity in GaAs. Silicon behaves as a donor when it occupies a Ga site (Si_{Ga}^+), and an acceptor when it occupies an As site (Si_{As}^-). However, Si prefers to occupy a Ga site compared to an As site, because the covalent radius of Si is closer to that of Ga (Si: 1.17 Å, Ga: 1.58 Å, and As: 0.96 Å). Silicon atoms occupying neighboring Ga and As sites exist as a neutral complex ($Si_{Ga}Si_{As}$). When Cu is introduced in Si-doped GaAs, it can occupy an interstitial site or a substitutional site. Copper, a group I element of the periodic table, preferably occupies an interstitial site. However, due to the presence of vacancies and comparable covalent radii of Ga and Cu (Cu: 1.35 Å), Cu atoms occupy Ga sites (Cu_{Ga}) also.

Copper introduces various levels in Si-doped GaAs which can be attributed to the complexes formed by Ga and As vacancies (V_{Ga}, V_{As} respectively), substitutional Si atom on an As site or Ga site and substitutional Cu atom on a Ga site. The complexes formed can be of different types such as: V_{Ga} V_{As}, Cu_{Ga} V_{As}, V_{As} Cu_{Ga} V_{As}, Cu_{Ga} V_{As} Cu_{Ga}, V_{Ga} Si_{As}, and Cu_{Ga} Si_{As}. The formation of these complexes can be represented using simple crystallochemical reactions. For example, the formation of Cu_{Ga} V_{As} and Cu_{Ga} V_{As} Cu_{Ga} complexes can be shown by the following equations:

$$3V_{Ga}+3V_{As} \rightarrow 3V_{Ga}V_{As} \tag{2.21}$$

$$2Cu_i + 2V_{Ga}V_{As} \rightarrow Cu_{Ga}V_{As}Cu_{Ga} + V_{As} \tag{2.22}$$

$$Cu_i + V_{Ga}V_{As} \rightarrow Cu_{Ga}V_{As} \tag{2.23}$$

The Si atoms in As site can occupy the Ga lattice sites according to the reaction:

$$Si_{As} + V_{Ga} \rightarrow Si_{Ga} + V_{As} \tag{2.24}$$

By adding reactions (2.21) through (2.24) we obtain,

$$4V_{Ga} + V_{As} + 3Cu_i + Si_{As} \rightarrow Cu_{Ga}V_{As}Cu_{Ga} + Cu_{Ga}V_{As} + Si_{Ga} \tag{2.25}$$

The equilibrium constant of this total reaction is:

$$K_1 = \frac{[V_{Ga}]^4[V_{As}][Cu_i]^3[Si_{As}]}{[Cu_{Ga}V_{As}Cu_{Ga}][Cu_{Ga}V_{As}][Si_{Ga}]} \tag{2.26}$$

Since $[V_{Ga}][V_{As}]$ = constant, the product $[V_{Ga}]^4[V_{As}]$ in the above equation should increase with a deviation from stoichiometry towards excess As, which leads to an increase in the concentration of Ga vacancies. Under these conditions, the reaction of equation 2.26 is shifted to the right, which leads to an increase in the concentration of the complexes, Cu_{Ga}

V_{As} Cu_{Ga} and Cu_{Ga} V_{As}. In presence of excess Ga (heating in vacuum), the reaction of equation 2.24 shifts in the reverse direction,

$$Si_{Ga} + V_{As} \rightarrow Si_{As} + V_{Ga} \tag{2.27}$$

The complete reaction will be of the form,

$$2V_{Ga} + 3V_{As} + 3Cu_{i} + Si_{Ga} \rightarrow Cu_{Ga}V_{As}Cu_{Ga} + Cu_{Ga}V_{As} + Si_{As} \tag{2.28}$$

The equilibrium constant of the reaction is:

$$K_2 = \frac{[V_{Ga}]^2[V_{As}]^3[Cu_i]^3[Si_{Ga}]}{[Cu_{Ga}V_{As}Cu_{Ga}][Cu_{Ga}V_{As}][Si_{As}]} \tag{2.29}$$

In this case, an increase in the concentration of As vacancies shifts reaction (2.26) to the right, resulting in an increase in the concentration of the complexes. Comparing equations (2.23) and (2.29), it follows that heating in As vapor at an excess, as opposed to an equilibrium, pressure must have greater effect on the change in the concentration of the complexes than heating in the vacuum. Since the complex formation is favored by the vacancies, an outflow of Cu from the volume of the crystal towards the surface occurs, i.e., the region of the crystal close to the surface and characterized by the presence of higher concentration of vacancies acts as a getter. The depth of the layer enriched by Cu is determined, in a given case, by the rate at which the vacancies penetrate from the surface. The vacancies are the less mobile component in the reaction compared with the interstitial Cu which is diffusing rapidly from the volume.

2.4 Compensation Mechanism

If an acceptor impurity is added to an n-type semiconductor, or a donor impurity to a p-type semiconductor, a redistribution of the charge carriers which populate the energy levels must takes place, and the magnitude and type of the electrical conductivity changes. This process is called compensation of impurities, and by this process we can decrease the concentration of the mobile current carriers until the resistivity of a given impurity semiconductor approaches that of the intrinsic, and to higher values. Compensation mechanism in GaAs has been studied by many researchers due to its importance in preparing semi-insulating (SI) GaAs, the substrate material for the fabrication of GaAs ICs. In SI-GaAs, shallow energy levels in the band gap are compensated by deep levels. The steps in compensation process can be explained as follows. When a deep acceptor level is available, the electron in the shallow donor levels will prefer to make a transition to the deep acceptor level and combine with a hole there. Similarly, the hole in a shallow acceptor level prefer to make a transition to the deep donor levels and combine with an electron there. Consider an n-type semiconductor where the concentration N_A of acceptor is lower than that of the concentration N_D of the donor level ($N_A < N_D$) and the acceptor levels are located just above the valence band. At absolute zero, all the available acceptor levels will be occupied by electrons from the donor levels leaving only N_D - N_A donor levels occupied. Thus at temperatures just sufficient to excite electrons from the donor levels to the conduction band, the number of available conduction electrons is less than the number of impurity centers, and the material is referred as *compensated.* Fig. 2.4 is the energy band diagram of a compensated n-type semiconductor.

The material under investigation in the present study, GaAs:Si:Cu, the two Cu acceptor levels as well as some electron traps and recombination centers are present. The Cu_A level ($E_T = 0.14$ eV) is filled by the electrons from the shallow donor level first, the remaining electrons will go to Cu_B level ($E_T = 0.44$ eV). When several kinds of traps are present in compensated semiconductors, determination of the compensation by conventional mobility analysis is impractical. Temperature dependent Hall-effect measurements can in principle be analyzed to obtain the compensation, but the analysis would be complicated when more than two acceptor levels are simultaneously present. Hwang [27] has studied the compensation process in GaAs using photoluminescence measurements. He reported that at higher temperatures (>900^{0}C), Cu deep levels as well as shallow acceptors can be responsible for the compensation, whereas at lower temperatures (<870^{0}C) Cu is mainly responsible for the compensation.

2.5 Photoconductive Switching in GaAs

When a semiconductor material is excited with external optical energy, different optoelectronic processes takes place, including photoconductivity, trapping, detrapping, retrapping, recombination, emission, etc. The increase in the conductivity of the crystal, by the illumination of light is referred to as photoconductivity of the material. In case of a pure crystal, i.e.., without any impurities, the photoconductivity increases during illumination due to electron pair generation, and drops to zero due to recombination of

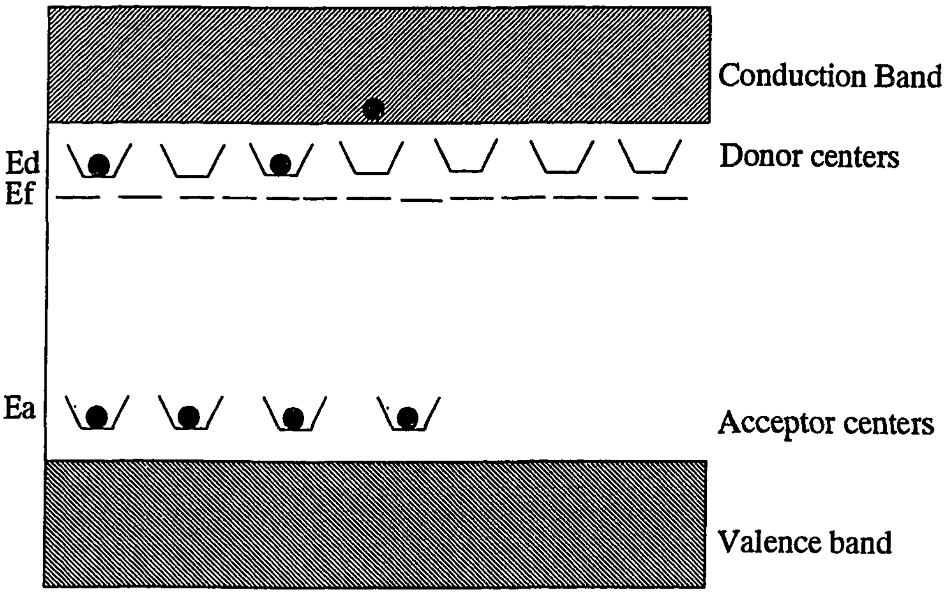


Figure 2.4 Energy band diagram of compensated n-type semiconductor

trap centers and recombination centers play a role, and the conductivity does not always drop to zero even after the laser light is off. This is the basis of using GaAs:Si:Cu as a switching material. During illumination, holes are trapped by the Cu deep levels and since the Cu_B level has a very large capture cross section for holes compared to that for electrons which causes some of the electrons which reached the conduction band remain there even after the laser pulse is turned off. Thus the switch remains on for a long duration compared to the laser pulse duration, and is controlled by the temperature dependent detrapping of the holes which is of the order of tens of microseconds at room temperature. Figure 1.1 in Chapter 1 shows a schematic of this switching mechanism. The energy band diagram of the GaAs:Si:Cu system is simplified showing only the Cu acceptor levels and the Si donor level. Silicon introduces a shallow donor level, and Cu introduces two primary deep acceptor levels (Cu_A and Cu_B) in GaAs. In the model of the GaAs:Si:Cu system used for the simulation studies, three other levels, EL2, EL5, and a recombination center, RC are also included [12,35]. The defect levels EL2 and EL5 are native electron traps and affect the on-state performance of the switch by capturing free electrons at the traps.

A below-band gap laser pulse is used to induce conductivity in the switch. The switch conductivity remains high during the laser pulse excitation, and decays after the cessation of the laser pulse. The generation of photoconductivity can be due to one-photon absorption through defect levels or two-photon absorption (TPA). As the pulse duration decreases, the absorption by two-photon created excess carriers becomes important. In GaAs, the experimentally measured values of TPA coefficient (β) vary from 20 - 5600 cm/GW at a laser wavelength of 1.06 μm [36]. A value of 26 cm/GW [37] is chosen in the modelling studies of the GaAs:Si:Cu system. The magnitude of the coefficient differs between semiconductors by a factor of $(E_g n_p)^{-1}$, where n_p is the refractive index and E_g is the band gap. The TPA coefficient calculated for nonparabolic bands is larger than for parabolic bands, and this difference increases as the photon energy increases, and this could be one of the reasons for the wide disparity of the measured values.

The conductivity decays initially due to direct recombination of the carriers via fast recombination centers, after the laser pulse is turned off. The Cu_B state has a much larger capture cross section (about 10^6 times) for free holes compared to that for free electrons. Due to this property, a sufficient density of holes generated during illumination can be re-trapped back into Cu_B allowing a large free electron density to remain in the conduction band. After the initial decay, the recombination of free electrons is mainly controlled by the thermally emitted holes from Cu_B. The rate equations used in the modeling of the system are shown below:

$$\frac{dn}{dt} = \frac{\beta h\nu\Phi^2}{2} + \sum e_{ni} n_{Ti} - k_d np - \sum c_{ni} n (N_{Ti} - n_{Ti}) - k_a n^2 p \tag{2.30}$$

$$\frac{dp}{dt} = \frac{\beta h\nu\Phi^2}{2} + \sum e_{pi} (N_{Ti} - n_{Ti}) - k_d np - \sum c_{pi} p n_{Ti} - k_a n^2 p \tag{2.31}$$

$$\frac{dn_{Ti}}{dt} = c_{ni}n(N_{Ti}-n_{Ti})+e_{pi}(N_{Ti}-n_{Ti})-e_{ni}n_{Ti}-c_{pi}pn_{Ti}$$

where the subscript i denotes the i^{th} trap, n, p are the free electron, and free hole density respectively, N_T is the total trap density, n_T is the density of traps occupied by electrons, Φ is the photon flux, $c_{n,p}$ is the electron-hole capture parameter, $e_{n,p}$ is the electron-hole emission parameter, k_a is the Auger recombination coefficient, and k_d is the direct band-to-band recombination coefficient.

The on-state photoconductivity of the switch depends on various parameters such as photon flux, concentration of the Cu deep levels, laser pulse width etc. As photon flux increases, more traps are filled during laser pulse illumination and results in a higher on-state conductivity, and at a certain photon flux, saturation of trap filling occurs and the conductivity does not increase any further. In case of picosecond switching, this saturation should occur at a higher photon flux than for nanosecond switching, if the pulse energy is kept constant. As the pulse width decreases, the rise time and fall time of the laser decreases which leads to better switch turn-on and turn-off characteristics. The photoconductivity decay depends on many factors such as, Auger recombination, direct band to band recombination, band to impurity recombination, etc. Auger recombination is dominant near the peak of the laser pulse, but decreases after the laser pulse is turned off. When the laser pulse is off, the dominant recombination is due to impurities . As photon flux increases, the peak conductivity as well as the on-state conductivity increases, but the switch requires less time to reach the steady state. The characterization technique, photoinduced current transient spectroscopy (PICTS), used to characterize the GaAs:Si:Cu samples, also utilizes the current transient generated by illuminating the sample using a laser light. The details of the technique will be discussed in Chapter 3.

In summary, the theory related to the topics relevant to the current research is discussed in this chapter. The topics include the band structure, the impurity and defect levels, the diffusion of Cu in GaAs and GaAs:Si, the compensation of GaAs:Si, and the photoconductive switching in GaAs:Si:Cu.

CHAPTER 3

EXPERIMENTAL PROCEDURES

The fabrication of the BOSS switch and PICTS samples, the characterization techniques, and the switching experiments are discussed in this chapter. The processing steps involved in the fabrication of the devices, with particular emphasis on the different diffusion techniques, are described. The characterization techniques used to study the GaAs:Si:Cu samples are PICTS, I-V measurements, and Hall measurements. The basic principles and the theory of these techniques are included in the discussion. The experimental setups to test the photoconductivity of the GaAs:Si:Cu switches are discussed.

3.1 Device Fabrication

Silicon doped GaAs (Horizontal Bridgeman (HB)-grown, $N_{Si} = 1.2 \times 10^{16}$ cm^{-3} as specified by the manufacturer) wafers are used as the starting material to fabricate the samples for the switching experiments and for the characterization studies. The two-inch diameter GaAs:Si wafers with one side polished are manufactured at Bertram Labs (38). For diffusion of Cu into GaAs, a deposited layer of Cu or Cu-doped SiO_2 coating is used as the Cu source and is deposited only on one surface (polished source). The GaAs:Si samples are then subjected to the following processing steps: Cu diffusion by thermal annealing, polishing, Au-Ge ohmic contact deposition, contact annealing, and epoxy

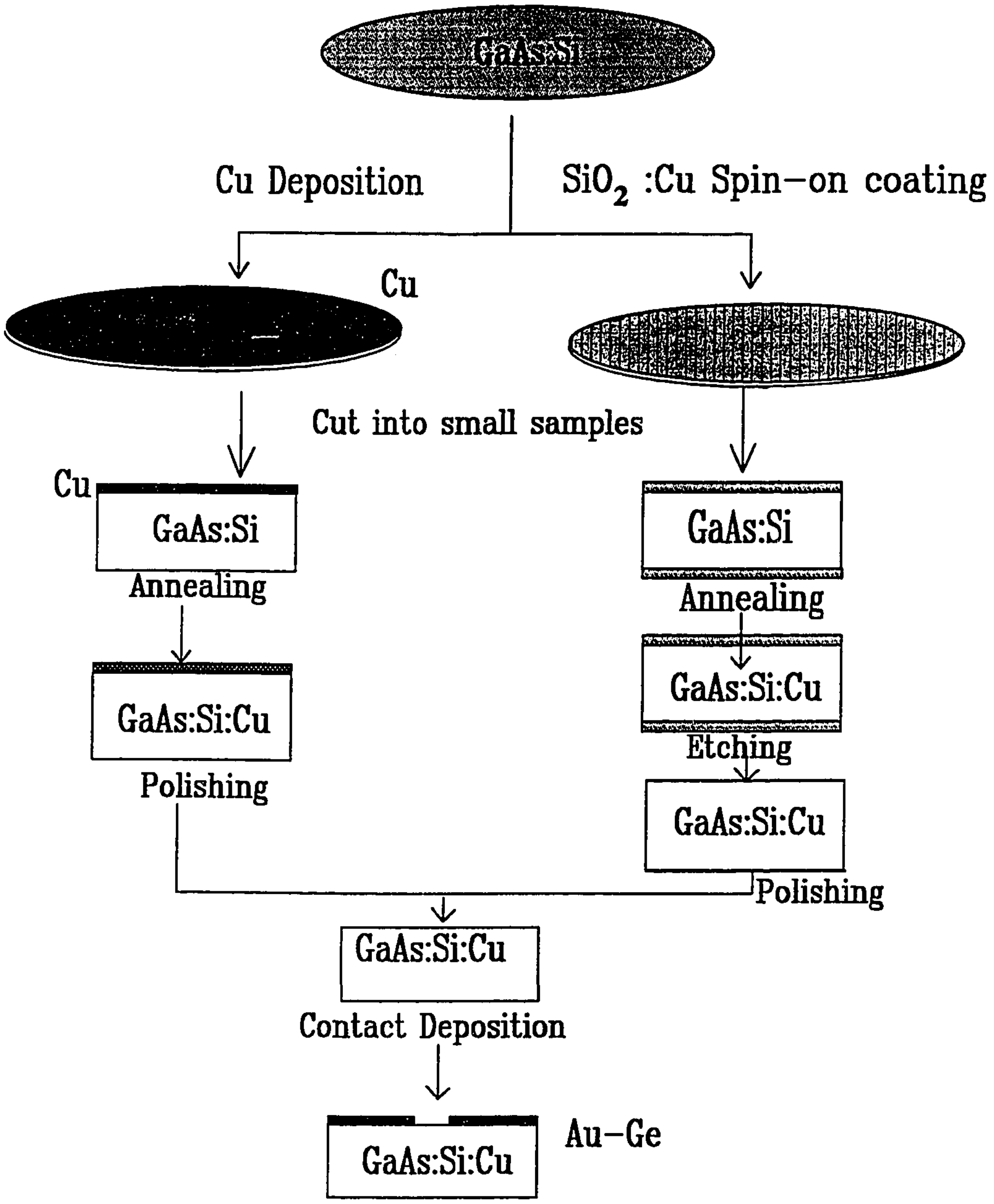


Fig. 3.1 GaAs:Si:Cu switch/PICTS sample fabrication steps

contacts. The processing steps are shown in Fig. 3.1. Among the processing steps listed in Fig. 3.1, the diffusion of Cu is of much importance in the fabrication of the BOSS switches. The process of Cu diffusion compensates the low resistivity n-GaAs and hence the resistivity of the material increases, i.e., from 10^{-2} Ω cm up to MΩ cm.

3.1.1 Diffusion of Cu in GaAs:Si

The basic requirements for any diffusion system are that a means should be provided for bringing the diffusing impurity in contact with the surface of the sample, and this process be maintained for a specific time and at a specific temperature. Diffusion system can be of either sealed tube (closed tube) or open tube type. The dopant atoms can be brought in contact with the samples by various means, either in gas phase, or as deposited thin films, or as spin-on coating. Thus the diffusion techniques vary depending upon the type of system used as well as the method of providing the source. In the present study, three different diffusion techniques, namely, closed tube diffusion, semi-closed tube diffusion, and leaky tube diffusion, are used to diffuse Cu into GaAs:Si. For the closed tube and the semi-closed tube diffusion systems (discussed in detail in the following section), source is provided by a film of Cu about 1 μm thick, vacuum deposited on one surface (polished) of the wafer. The GaAs sample with the deposited Cu film along with a small amount of weighed As is placed in the inner reaction tube of the system and evacuated before pushed to the hot zone. For the closed tube diffusion system, the sample with the deposited Cu film and a small piece of weighed As are enclosed in a clean, evacuated quartz tube prior to heat treatment. In the semi-closed tube diffusion system also, the inner tube is closed, however, the volume of the tube is much larger compared to that of the ampoule used in the closed tube diffusion. Also, only a small part of this volume is in the hot zone. These are the main differences between the closed tube and semi-closed tube systems. After diffusion the samples are removed by breaking the tube. Closed tube diffusion system can be easily maintained free from contamination, however, once impurities are trapped inside the ampoule, it is not easy to remove them.

The Cu-GaAs system exhibits a eutectic point below the diffusion temperature, so that an alloy interface results and the diffusion takes place from the dopant source (i.e., constant concentration). The deposited Cu film is 1 μm thick and the dopant source can be considered as an infinite source. The surface concentration is set at the solid solubility limit of Cu in GaAs at the diffusion temperature.

For the leaky tube diffusion, spin-on dopant source is used. Spin-on techniques are versatile, and almost any impurity source is available in the form of spin-on coating for GaAs and Si processing. However, their degree of control is poor by modern microcircuit standards and hence the spin-on dopants are used only where dopant control is not crucial. In this technique, the sample is held in a vacuum chuck and a few drops of the dopant mixture is added to the surface and rotated at high speed (2500-5000 rpm). A thin uniform layer of SiO_2 can be formed across the sample by a balance between centrifugal driving force and viscous resisting force. In general, the dopant mixture consists of the dopant source and an inert oxide in polyvinyl alcohol and is commonly referred as spin-on glass. Cu-doped SiO_2 (39) is used as the dopant source in the present study. The concentration of the dopant can be controlled by adjusting the dopant-to-binder ratio, and the diffusion results in a surface concentration which is controlled by the concentration of the dopant in the oxide and not by the solid-solubility limit in the semiconductor as in case where deposited Cu film is used as the source. By decreasing the spinning speed, the thickness of the spin-on coating can be increased and is a means to provide more Cu for diffusion.

3.1.2 Diffusion Systems

Two diffusion systems are setup in our Semiconductor Processing Laboratory, one with a single zone furnace and temperature control unit and the other with a three zone furnace with programmable control console unit, both manufactured by Lindberg (model 55342 and 58434-P-B respectively). The single zone unit is set up as the semi-closed tube diffusion system, and the three zone is set up as a the leaky tube diffusion system. For the closed tube diffusion either one of these systems can be used. The semi-closed tube diffusion system consists of one outer diffusion tube and an inner reaction tube. The inner reaction tube is a quartz tube of volume about 300 cm^3 with quartz stopper with a long quarter inch diameter access tube which is sealed against the ground glass joint of the reaction tube. The end of the access tube is attached to a vacuum hose which is connected to a vacuum pump. The outer tube is equipped with inlet and outlet for purging with nitrogen, to keep the inner tube in a pure environment during diffusion and also for protection against accidental As leak. The diffusion system assembly is shown in Fig. 3.2, and the details of the systems is given in Ref. 13.

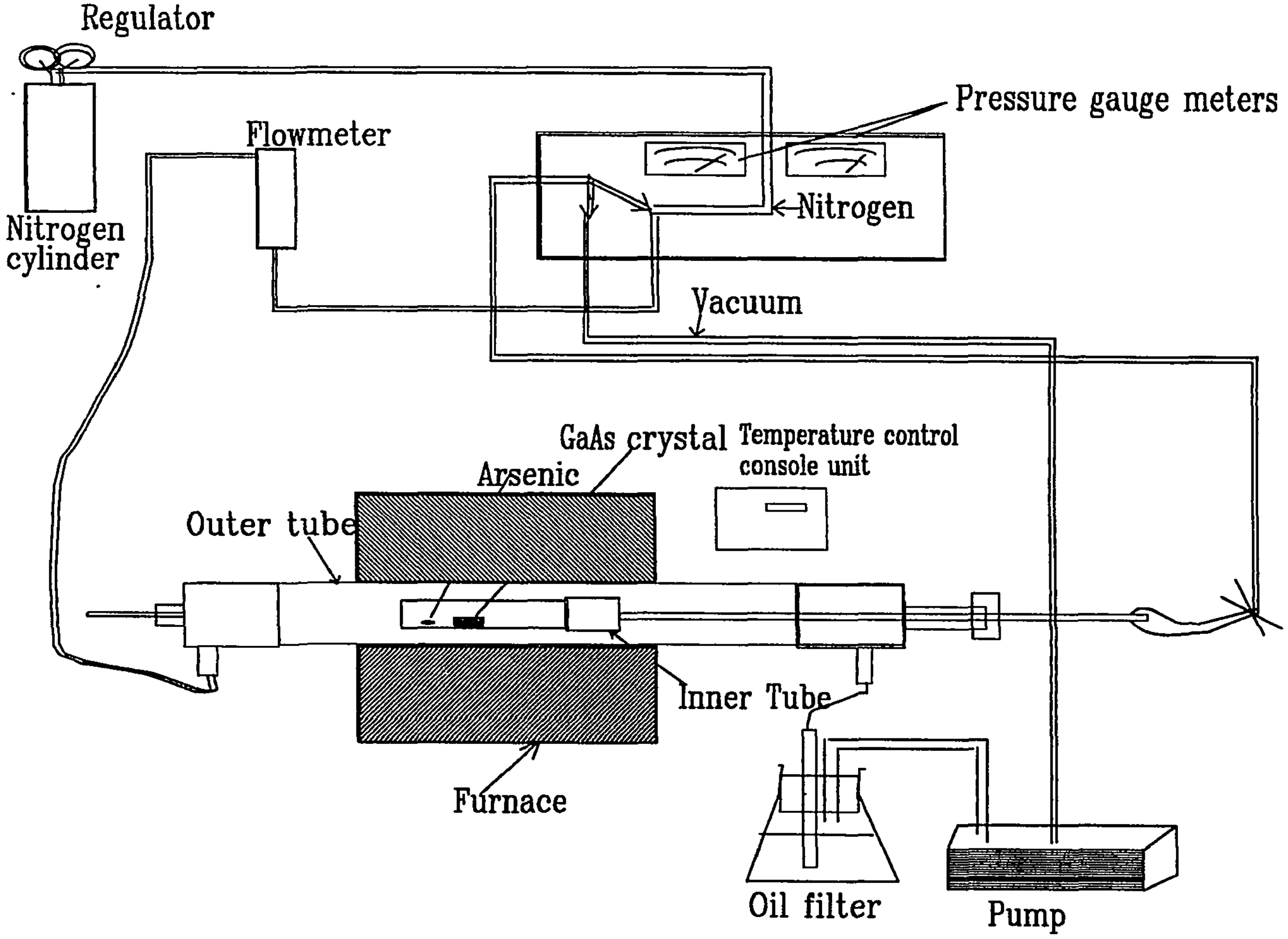


Fig. 3.2 Schematic of the semi-closed tube diffusion system

The GaAs:Si sample with the deposited Cu film along with a small piece of weighed As is loaded in the inner reaction tube of the diffusion system, which is cleaned using various solvents (acetone, methanol, and trichloroethylene), to remove any As deposits from previous diffusions and to degrease. The access tube is then attached to the reaction tube and placed at the cool end of the furnace. The tube is evacuated to a pressure of no less than few hundred millitorr, and sealed from the outside environment by closing the valve on the pump side of the vacuum hose. Then the tube is moved to the hot zone of the furnace to start the diffusion process. The temperature profile of the furnace is taken before each diffusion to determine the position in the hot zone for placing the sample to anneal the sample at the desired temperature. When the sample is annealed for the specified time, the reaction tube is quickly pulled from the hot zone to the cold zone of the furnace and allowed to cool.

When the inner reaction tube loaded with the sample and As is pushed to the hot zone, As vaporizes and the As vapor pressure increases in the reaction tube. The ground glass joint of the reaction tube should be sealed and should prevent any leakage of the As from the reaction tube. In case of any failure in sealing, it is possible for the As vapor to escape from the reaction tube to the outer tube. The outer reaction tube is filled with nitrogen and the nitrogen flow is led to an oil filter where any As vapor present in the flow condenses and therefore the exhaust gas is not hazardous. The As vapor inside the reaction tube condenses when the tube is pulled to the cold zone. Then the tube is flushed with nitrogen and evacuated, and the process is repeated three or four times to remove all traces of As vapor from tube so that it will be safe to the operator to break the vacuum in the inner reaction tube.

The safety measures discussed above are necessary for the semi-closed tube diffusion due to the presence of As vapor. As vapor pressure (provided by the As pieces placed in the inner reaction tube) is to prevent the escape of As from the surface of the sample which is exposed to the ambient. For the closed tube diffusion, the GaAs:Si sample with the deposited Cu film, along with weighed amount of As is placed in the quartz ampoule of volume six cm^3, and evacuated to 5×10^{-3} millitorr and sealed. The ampoules are then placed in the diffusion furnace and annealed for about 17 hours. In case of the leaky tube diffusion system, samples are coated with Cu doped SiO_2 which will prevent the escape of As from the surface and therefore the addition of As is not required. Also, using the leaky tube system the diffusion takes place in an atmosphere of UHP grade He which ensures a purer environment.

The leaky tube diffusion system consists of two quartz tubes, the outer one which is open at both ends with Al end caps, and the inner one which is closed at one end. It can be considered as a quasi-closed system which encompasses the properties of both the open tube and closed tube diffusion systems. The leaky tube system assembly is shown in Fig. 3.3. The closed end of the inner tube is placed near to the carrier gas input, and the open end of both tubes are lined up. The end caps have a fixed part and a removable part, and the removable part has openings for a purge tube and a push rod. The purge tube lies in the inner tube and extends to the closed end of the tube. The sample is placed in a boat and push rod is hooked to the end of the push rod. After the sample is

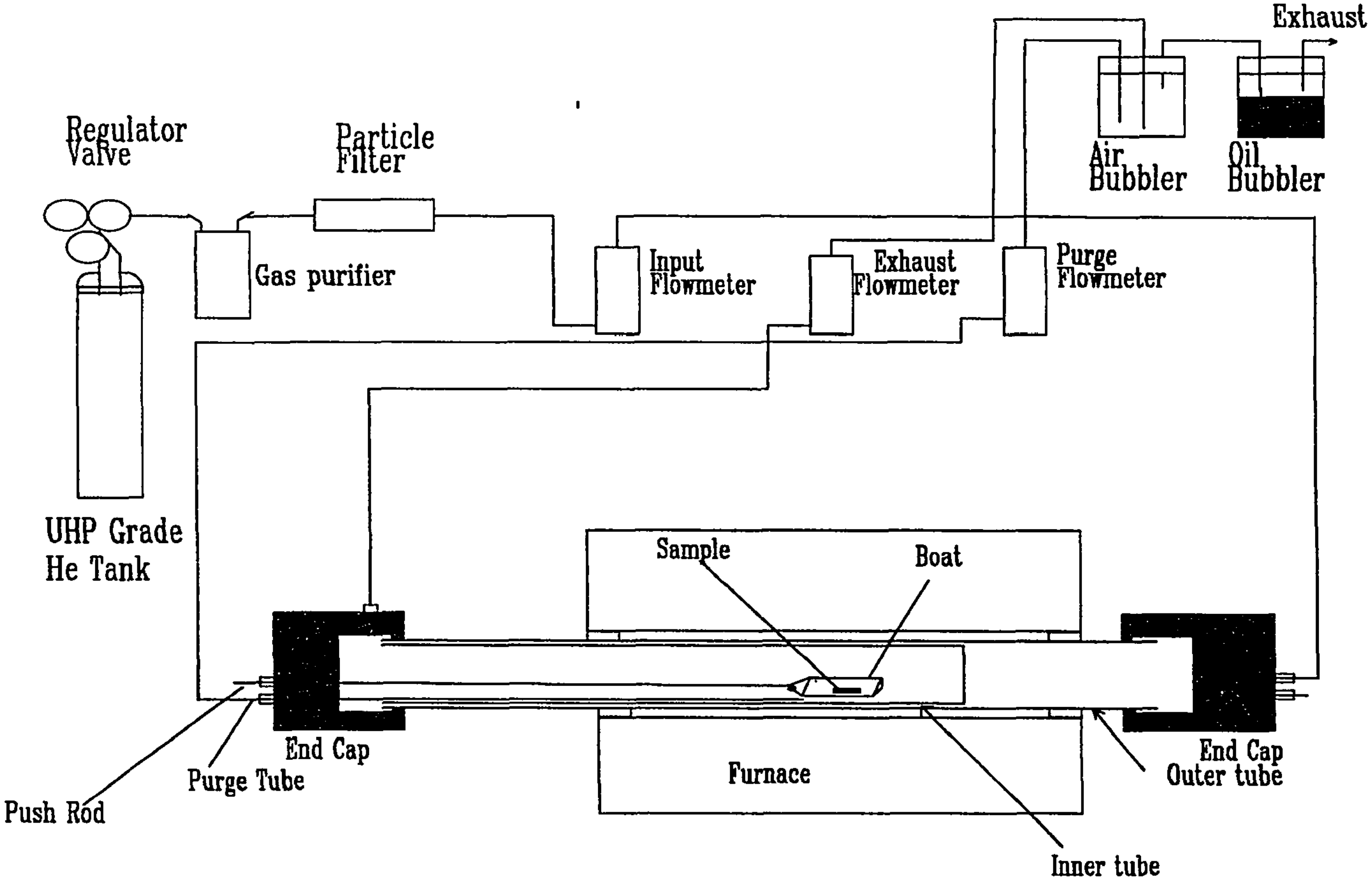


Fig. 3.3 Schematic of the leaky tube diffusion system

helium gas for about two hours. The leaky tube diffusion procedure was first demonstrated by Roedel et al [40] and we have set up a similar system in our laboratory with the guidance of Dr. H. Erkaya from the same research group. The details of the diffusion procedure includingcleaning procedure of the system, and the samples is discussed below.

The experimental procedure for the leaky tube diffusion consists of mainly three parts: 1) furnace preparation, 2) sample preparation, and 3) diffusion. The furnace preparation includes temperature profiling to setup the diffusion temperature and cleaning of the quartzware. The quartzware of the system includes the outer tube, inner tube, purge tube, push rod and boat. The outer tube is cleaned before installation and the inner tube, purge tube, and push rod are cleaned after every six to seven runs. The boat is cleaned after every run. The cleaning procedure for the quartzware is as follows:

1. Rinse with deionized (DI) water to remove loose impurities
2. Etch with HNO_3:HF:H_2O (1:1:10)
3. Rinse with DI-water
4. Etch with HF:H_2O (1:10)
5. Rinse with DI-water 3-4 times
6. Rinse with methanol
7. Blow dry with N_2

The boat is cleaned after every run with methanol and acetone and after every six to seven runs using the above cleaning procedure.

Sample preparation: HB-grown GaAs doped with Si with carrier concentration and resistivity specified from the manufacture is used as the starting material. The material properties (carrier concentration, resistivity, and mobility) are determined by Hall measurements. The samples (cleaned and vacuum packed by the manufacturer) were coated with Cu-doped SiO_2. The spin-on glass used contained 1.7 % wt. of Cu in the binder. The coating procedure is as follows:

1. The spin-on glass is dropped on the surface of the wafer covering 3/4th of the wafer.
2. Spin (2000 rpm, 20 sec)
3. Bake (100^0C, 20 min)
4. Coat the other surface with spin-on glass (spin - 2000 rpm, 20 sec; bake - 120^0C, 20 min)

The spin-coating time, speed, and annealing temperature shown above are chosen for the diffusions conducted in the present study. The process outline provided by the Silica Source Technology for highly doped semiconductor is given in appendix A. When spin-coating a wafer with a dopant, polished surfaces are preferred to obtain a good surface contact. In the present study, the GaAs:Si wafers used for closed tube and semi-closed tube diffusion are polished only on one side, and the wafers from the same batch are used for the leaky tube diffusion also. While spin-coating the wafer, extra care is taken to obtain a uniform coating to provide uniform source of Cu on all areas of the wafer for diffusion. The wafers coated with the spin-on glass is then cleaved into desired dimensions (1 - 2 cm x 5 mm) for diffusion. The samples are then loaded to the cold end of the diffusion furnace and the system is purged with UHP He for two hours. The input flowmeter setting during purging is about 470 cc/min (pyrex ball at 108), and the exhaust and the purge set at full scale (note: extra care should be taken to ensure that the exhaust and the purge flowmeters are kept at full scale to avoid pressure buildup inside the tube which can lead to an explosion). After purging, the input flowmeter reading is set to 30 cc/min (pyrex ball at 12). The exhaust flowmeter is kept at full scale and the purge flowmeter is reduced to zero to create a stagnant atmosphere. After diffusion time is over, the sample is pulled to the cold zone slowly (to avoid thermal shock to sample) and allowed to cool. GaAs:Si samples coated with Cu-doped SiO_2 were annealed for different time, ranging from 1 hour to 17 hours, to study the effect of annealing time on diffusion of Cu by the leaky tube technique.

The annealed samples are then treated with buffered HF to etch SiO_2 coating, and polished using lapping film of various thicknesses, and etched using Br_2 - methanol mixture using a laminar flow method. The chemical etching using Br_2 - methanol mixture ensures a fine polished surface, by removing the outer nonuniform surface layers remained after the manual lapping. The samples are cleaned using standard cleaning procedure shown below, before contact deposition are deposited. Small beakers containing the sample and the chemical for cleaning are placed in ultrasonic bath (model 450 from E/MC Corp.) for the specified time shown below:

1.	5 min.	Acetone
2.	5 min.	Methanol/Isopropyl alcohol
3.	5 min.	50% methanol-DI H_2O

4.	10 min.	DI-H_2O
5.	10 min.	15% H_2O_2 + 85% DI-H_2O
6.	10 min.	DI-H_2O
7.	2 min.	Conc. NH_4OH (Hand agitate; use fume hood)
8.	3 min.	DI-H_2O
9.	Dry the sample using N_2 blow	

3.1.3 Ohmic contact deposition

The technology of the ohmic contact on GaAs is not fully understood as is in the case of Si and can be considered more as a technical art rather as a science. The quality of the ohmic contact is one of the most significant factors affecting the performance of GaAs devices. In practice, ohmicity of a contact is considered satisfactory if the contact does not perturb the device performance, i.e, the contact metal/semiconductor barrier height should be almost transparent to carrier flow and if the contact is stable electrically and mechanically. The most common method of making an ohmic contact is to place a metal layer in contact with a highly doped region, to enhance field-emission-enhanced conduction. Methods to obtain highly doped region include: alloy regrowth, in-diffusion of a dopant contained in the contact material, epitaxial regrowth, ion implantation, and shallow diffusion. For the samples fabricated in the present work, Au-Ge alloy (88% Au and 12% Ge) is used to obtain a highly doped region. In the alloy regrowth technique the metal will dissolve some of the semiconductor during heating which come out of the solution during cooling and regrow on the underlying crystal. The metal content in the regrown region will be substantially high and can be considered as a dopant. By adding another dopant impurity (e.g., Au-Ge, Au-Zn) in the contact metal, lower alloying temperatures and higher doping levels can be obtained. "Balling up" of the contact material can result in a heterogeneous ohmic contact. It arises due to the low wetting action of metallic compounds on GaAs, and this difficulty can be alleviated by incorporating a catalytic metal in the contact material (e.g., Au-Ge-Ni) which acts as wetting agent. Ni is an extremely fast diffuser in GaAs and it greatly enhances the diffusivity of Ge in GaAs by reducing the chemical free energy. The native oxide which can form on GaAs surface also creates some difficulty in forming reliable and reproducible ohmic contacts. It is known that 20 A^0 gallium oxide can form on an exposed GaAs in one hour. To ensure an oxide free GaAs surface, the samples are cleaned as described above and immediately loaded to the vacuum deposition system. More details on ohmic contacts on III-V compounds can be found in literature [41-44].

The Au-Ge contacts are vacuum deposited on the GaAs:Si:Cu samples used in the present study. Other methods commonly used for contact deposition are sputtering, preformed contacts, pressure contacts, plating, and soldering. The Au-Ge contacts are annealed at 400^0 C for three - four minutes in an atmosphere of N_2 flow.

3.2 Device Characterization

Several semiconductor characterization techniques, optical as well as electrical, have been developed during the past couple of decades, as the researchers recognized the paramount importance of the characterization of the semiconductor materials in VLSI processing technology. To name a few: deep level transient spectroscopy (DLTS), photoinduced current transient spectroscopy (PICTS), thermally stimulated current transient spectroscopy (TSC), temperature dependent Hall (TDH) measurements, and Hall effect transient spectroscopy (HETS). The characterization of high resistivity GaAs, attracted the attention of many researchers recently because semi-insulating GaAs is used as the substrate material for many devices such as light emitting diodes, field effect transistors etc. To characterize the high resistive GaAs:Si:Cu samples studied here, we have used I-V measurements, Hall measurements and PICTS technique. The theory and the basic principle behind these measurements will be discussed in following sections.

3.2.1 I - V Measurements

As discussed in Section 3.1 of this Chapter, Au-Ge contacts (88% Au and 12% Ge alloy) are deposited on the GaAs:Si:Cu switch samples to obtain ohmic contacts. I - V characteristics are measured to test the ohmic nature of the Au-Ge contacts deposited on the GaAs:Si:Cu samples. The space-charge region associated with the metal-semiconductor contact results in nonlinear I -V characteristics as the voltage increases, but if the contact resistance of the space charge layer is negligible compared to the bulk or spreading resistance of the semiconductor, the contact is considered as an ideal ohmic contact. In practice, the contact is considered acceptable if it can provide the required current density with a voltage drop that is sufficiently small compared to the voltage drop across the active region of the device, even if the I -V curve is not strictly linear. The devices fabricated in the present work, have shown acceptable linear I - V behavior.

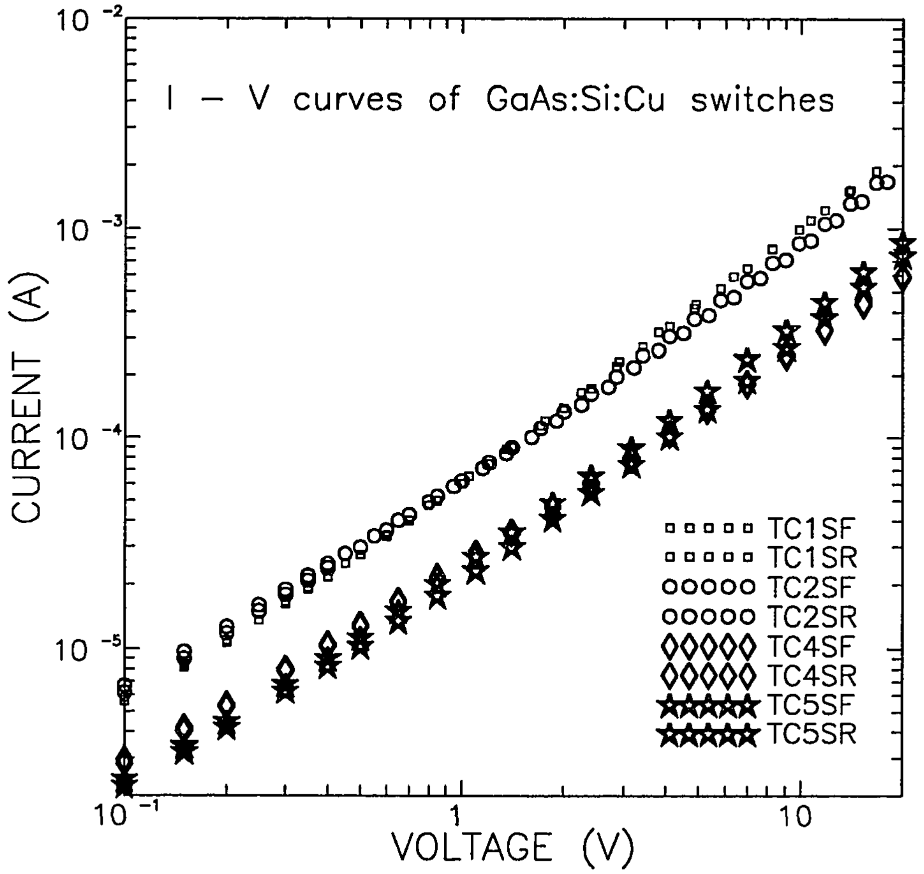


Fig. 3.4. I - V curves of GaAs:Si:Cu switches (closed tube diffusion under various As vapor pressure).

Figure 3.4 shows I - V characteristics of some of the devices. The I - V curves are used to test the ohmic nature of the contacts as well as to calculate the resistivity of the samples.

3.2.2 van der Pauw-Hall Measurement Technique

Developed in 1879 by E. T. Hall, Hall measurements has proved to be a powerful characterization technique to study semiconductor materials. Even though the theory of conductivity was not well understood when Hall effect was introduced, over the years the theory behind Hall effect has been well explained. About 100 years after Hall's original work, quantum Hall effect was discovered in 1980 by von Klitzing, Dorda, and Peppe. Hall measurements give information on semiconductor resistivity, mobility, carrier concentration, and conductivity type. Test structures for Hall measurements require specific geometry and the preparation of these structures is not an easy task. Also, need of material for making test structures during each processing step poses problems in VLSI processing, where it is preferred to use as small area as possible for characterization. Thus, need for a method to characterize arbitrary shaped samples led van der Pauw to develop a technique which is based on the conformal mapping. The van der Pauw technique was first introduced in 1958 and has been widely used since then. This measurement technique allows measurements of resistivity and mobility which are virtually independent of sample geometry.

Test Structures: According to van der Pauw, test structures of arbitrary shape can be used to measure resistivity, mobility, and carrier concentration when the following conditions are met:

a) The surface should be perfectly flat

b) The contacts must be point shaped and placed along the periphery

c) The sample is uniformly thick

d) the surface of the sample is singly connected

Among these conditions, the second one is difficult to meet in practice, and corrections should be added to the measurements for the sample with finite size contacts.

Resistivity measurements: To measure the resistivity of the sample, current source is connected to two contacts and the voltage difference between the remaining two contacts is measured. The polarity of the meters is shown in Fig. 3.5. The measurements can be repeated such as to allow each lead to serve as a current supply lead and as a voltage measurement lead in combination with each of the other leads. The permutations of the current and voltage leads allow the user to eliminate the effect of thermoelectric emfs and other sources of measurement error. When the measurements are taken for two different contact connections, the resistances are defined as:

$$R_{12,34} = V_{34} / I_{12} \tag{3.1}$$

$$R_{23,41} = V_{41} / I_{23} \tag{3.2}$$

The resistivity is defined as:

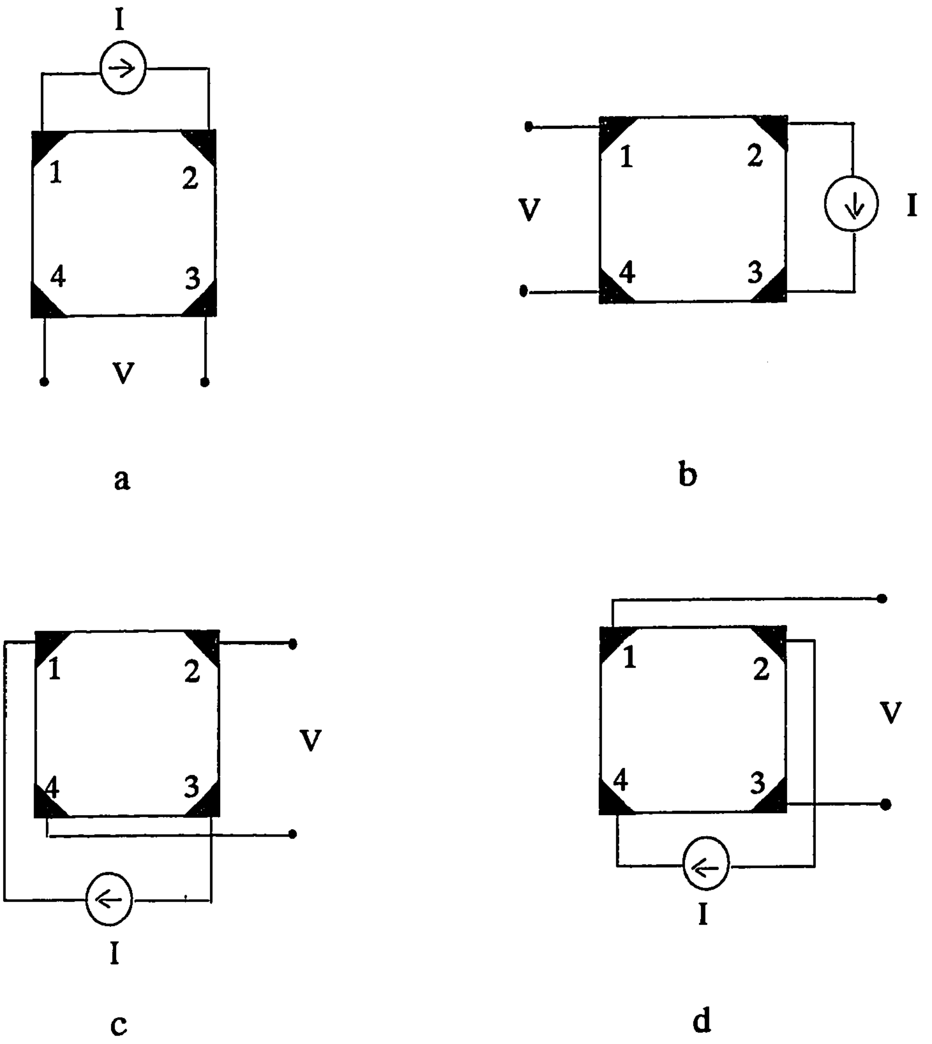


Fig. 3.5 Van der Pauw measurement configurations for resistivity (a and b) and Hall (c and d) measurements

$$\rho = \frac{\pi t}{\ln(2)} \frac{R_{12,34} + R_{23,41}}{2} F \qquad (3.3)$$

where F is a function only of the ratio of the resistances measured, $R_r = R_{12,34} / R_{23,41}$, and satisfy the following relation:

$$\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln(2)} \cosh^{-1}\left[\frac{\exp(\ln 2 / F)}{2}\right] \qquad (3.4)$$

For symmetrical samples, $R_r = 1$ and $F = 1$. For samples with out symmetrical geometry, value of F can be found from the graph of the above equation, F vs R_r (Fig. 1.7 in Ref. 45).

Mobility and carrier concentration measurements: Mobility of a semiconductor material can be determined by measuring the Hall voltage and then calculating the Hall coefficient using van der Pauw test structures. For Hall voltage measurements, current source should be connected to alternate contacts instead of adjacent contacts (Fig. 3.5). In the present study, the Hall measurements are done in a magnetic field of strength 2.4 Tesla. The measurements are repeated by changing the direction of the magnetic field as well as interchanging the contacts for voltage and current measurements, to eliminate the magnetoresistance effect and the effect due to the asymmetry of the sample. Hall coefficient can be calculated using the equation:

$$R_H = \frac{t\,\Delta V_{24}}{2BI} \tag{3.5}$$

where ΔV_{24} is the difference in voltage due to the uniform magnetic field applied. Knowing the Hall coefficient, mobility can be calculated using the equation:

$$\mu_H = \frac{|R_H|}{\rho} \tag{3.6}$$

Carrier concentration can be calculated using the equation:

$$n = \frac{1}{\mu e \rho} \tag{3.7}$$

The carrier concentration calculated from the Hall method is the free carrier concentration. In case of compensated sample, which is the material (GaAs:Si:Cu) of interest in the present study, carrier concentration calculated will give information on amount of compensation of the donor levels by the Cu acceptor levels achieved. $N_D - N_A$, for $N_A < N_D$ and $N_A - N_D$ for $N_A > N_D$, when the temperature is high enough for complete ionization. In the present study, Hall measurements are done at room temperature. However, a temperature dependent Hall (TDH) measurement can give information on the various impurity levels present in the material including deep levels. When many levels are present, the level with E ~ kT will dominate contribution to the carrier concentration.

3.2.3 Photoinduced Current Transient Spectroscopy (PICTS)

To study high resistivity semiconductor materials, most of the available characterization techniques have limitations due to the requirements of specific sample geometry and cumbersome sample preparation techniques. The DLTS is commonly used to characterize deep levels in highly conductive semiconductor materials. In the DLTS technique, bias voltage is applied to a reverse biased p-n junction and the change in the capacitance transient as a function of temperature is analyzed to obtain the trap parameters. In high resistivity materials, since carrier injection by electrical means is not easy due to difficulty in forming junctions, optical excitation is required for carrier generation. The PICTS technique, first introduced by Hurtes *et al.* [46] has proved to be a powerful technique to characterize high resistivity semiconductors. In this technique, a below or above band gap laser light is used to excite the semiconductor material and the decay of the photocurrent generated as a function of temperature is studied to obtain information on the deep levels present in the material. The free carrier and trap density in a semiconductor subjected to an extrinsic excitation can be represented by the rate equations (2.30, 2.31, and 2.32) given in Chapter 2. The set of equations does not have any analytical solutions and in the PICTS analysis, several assumptions are made to simplify the analysis. The PICTS analysis is discussed in detail by many authors [47-51].

The PICTS experimental setup in our laboratory is shown in Fig. 3.6, which consists of mainly three sections: temperature control system, optical control system, and electronics and data acquisition system. The liquid nitrogen cryostat is capable of cooling the system upto -188^{0}C. He-Ne laser (hv = 2 eV) with set exposure and delay time is

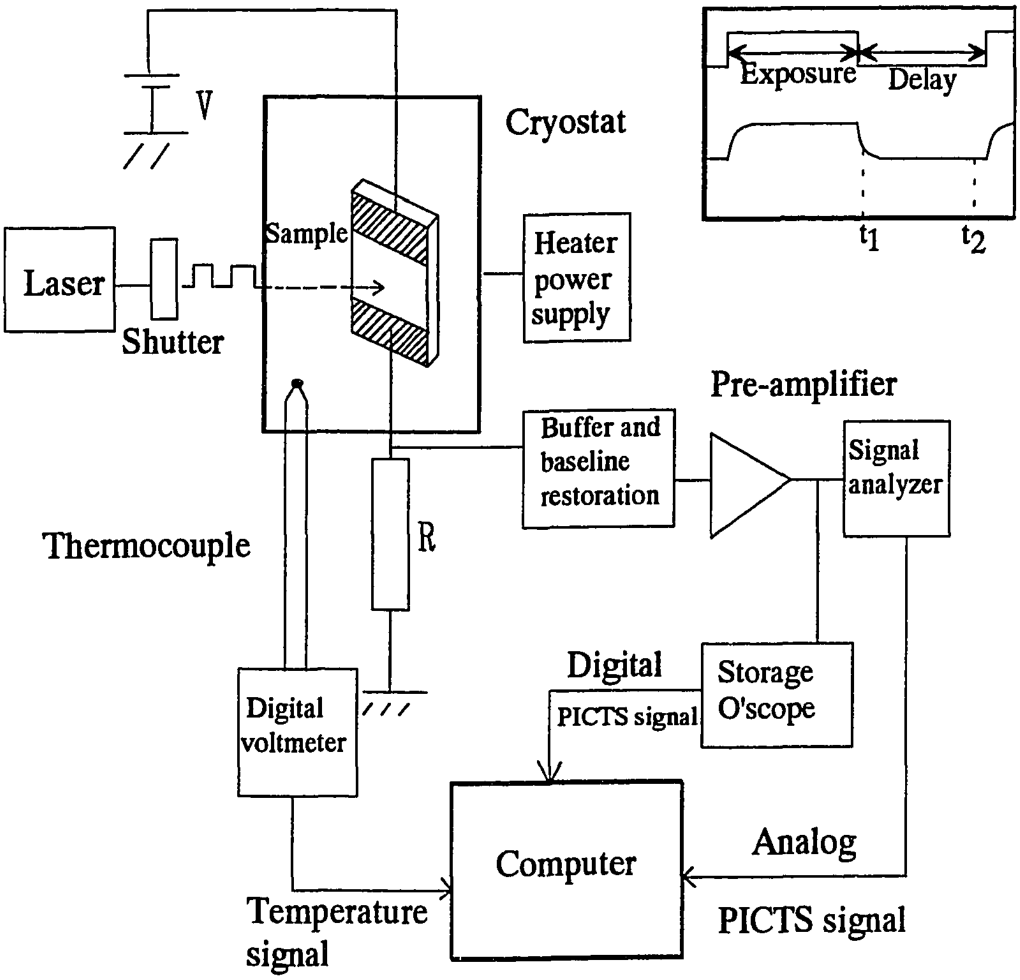


Fig. 3.6 Schematic of experimental setup for PICTS measurements

used to excite the sample, and the resulting photoinduced current decay for selected rate windows is scanned as a function of temperature. The current transient can be stored in a storage oscilloscope or can be measured for a specified rate window. Along with the conventional two gate rate window method, other modifications of the PICTS technique (four gate rate window method, and curve fitting method) have been in use currently [32, 47, 52]. The two gate rate window technique is based upon the assumption that only one trap species is active at a time for the temperature interval specified. If more than one trap species are active simultaneously, this method will not provide accurate values. The inaccuracy depends on how many levels are present within a range of ± 4kT (~0.1 eV) of the trap of interest. When multiple traps are occurring closer together, the current transient will no longer be exponential, and in this case a curve fitting technique is more appropriate to calculate the trap parameters. The PICTS technique is useful for the characterization of high resistivity material, however, the type of the carriers released from the traps can not be easily identified using this technique. The PICTS together with the TDH measurements will provide complete information on the trap parameters. A combination of the two methods, Hall effect transient spectroscopy (HETS) has been developed by Kachwalla *et al.* [53] in 1987. In this technique, the carrier concentration after excitation is measured by observing the decay in the Hall voltage of the material.

Assuming that the retrapping of the carriers is negligible (valid assumption in case of high resistivity materials) and there is only one trap species active at the specified temperature, the photoinduced transient current generated $\delta i(t)$ is given by the following equation:

$$\delta i(t) = \frac{CN_T}{\tau_T} e^{-t/\tau_T} \tag{3.8}$$

where C is a constant which depends on the geometrical parameters and material properties of the sample, applied voltage, and the penetration depth of the laser, N_T is the trap concentration of the active trap and τ_T is the trap relaxation time. Equation 3.8 represents the transient current due to emptying of a trap completely filled at t = 0 and emptied at t = ∞. Differentiating equation 3.8 with respect to temperature results in the following:

$$\frac{d\delta i(t)}{dT} = CN_T\,(1-\tau_T^{-1})\; e^{-t/\tau_T}\,\frac{d\tau_T^{-1}}{dT} \tag{3.9}$$

The condition for maximum current (i.e. maximum emission from the trap levels) can be expressed using the equation given below:

$$\frac{1}{t_1}=\frac{1}{\tau_T} = \sigma\gamma T_{\max}^{2} e^{-E_T/k\,T_{\max}} \tag{3.10}$$

where t_1 is one of the rate window settings of t_1 and t_2 ($t_2 >> t_1$), σ is the capture cross section of the trap, and γ is a numerical constant depending on the effective density of states in the conduction or valence band and the effective mass of the charge carriers. The trap parameters, activation energy and capture cross section, are respectively obtained from the slope and intercept of the Arrhenius plot, which is a plot of ln $\tau_T T^2$ vs 1/T or 1000/T. Figure 3.7 shows the PICTS spectra of GaAs:Si:Cu sample for various rate windows and the Arrhenius plots for the traps identified. The photoinduced current for the selected rate window is stored in the computer to obtain the spectra shown in Fig. 3.7.

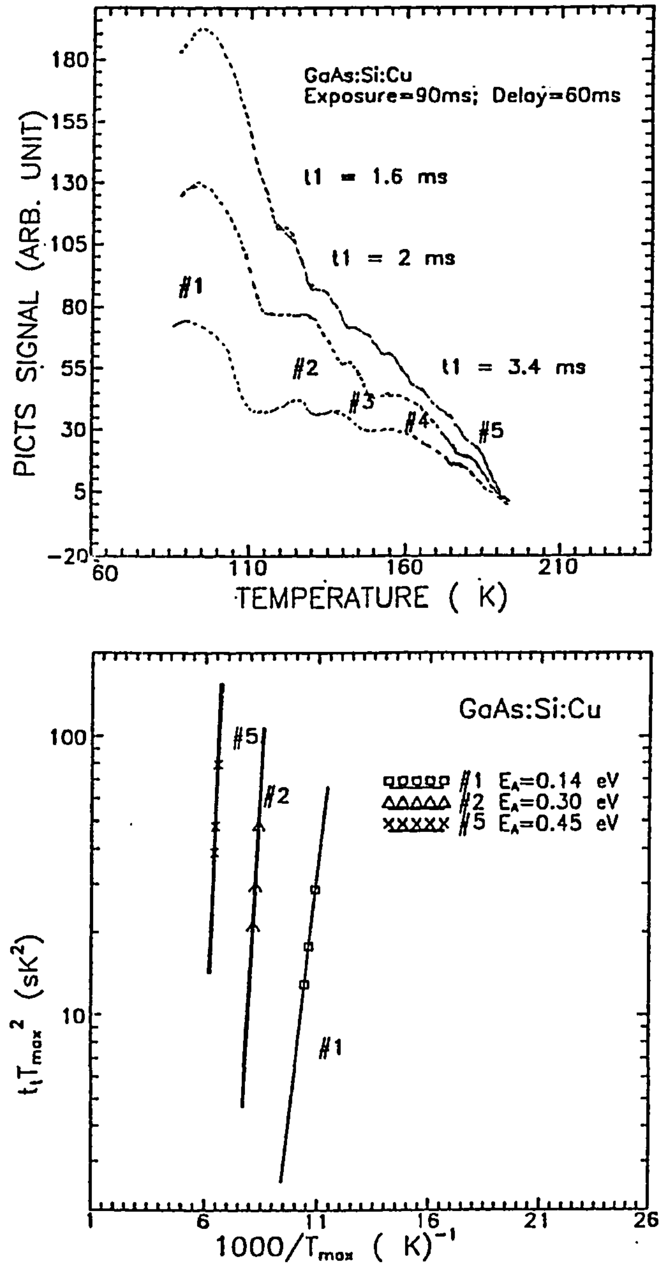


Fig. 3.7 a) The PICTS spectra of GaAs:Si:Cu sample (semi-closed tube diffusion) for different rate window and b) Arrhenius plot for three peaks shown in a.

The experiments are repeated for three different rate windows since the transients are not stored. Equation 3.8 enables one to calculate the trap concentration, provided the value of the constant C is known.

3.3 Device Testing: Switching Experiments

The GaAs:Si:Cu samples fabricated using the three different diffusion techniques are tested to study the turn-on photoconductivity. The switching experiments are conducted using a semiconductor laser (60 watt, full width half maximum (FWHM) = 30 ns, wavelength, $\lambda = 906$ nm) and also a Q-switched Nd:YAG laser (DCR-11 from Spectra Physics, $\lambda = 1064$ nm, FWHM = 7 ns) to irradiate the samples. Typical energy per pulse of the Q-switched Nd:YAG laser is about 40 mJ and a beam splitter is used to incident only 10% of the energy on the samples. The laser beam from the beam splitter is focussed through a lens and the focussed beam is passed through a homogenizer and then incident on the sample (Fig. 3.8a). The circuit diagram for the DC experimental setup can be shown as in Fig. 3.9, where the capacitor shown is charged with a DC voltage and is applied to the sample and maintains a steady voltage across the switch sample for the duration of switching. The current, i(t) through the sample is measured using a 50 Ω current viewing resistor (CVR), and knowing the DC voltage applied, conductance of the sample as a function of time can be calculated using the following equation:

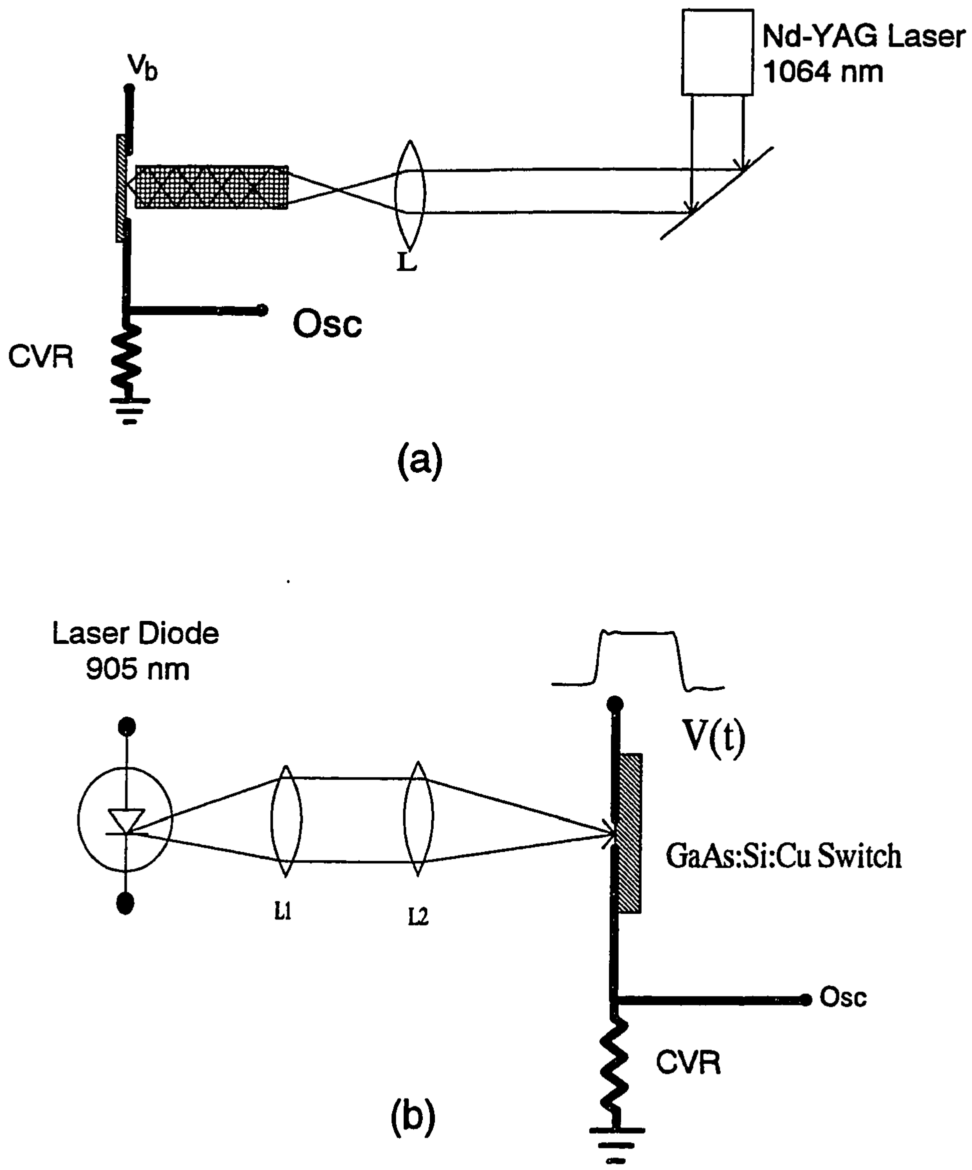


Fig. 3.8. Setup for the low power switching experiment
(a) using Nd:YAG laser
(b) using semiconductor laser diode

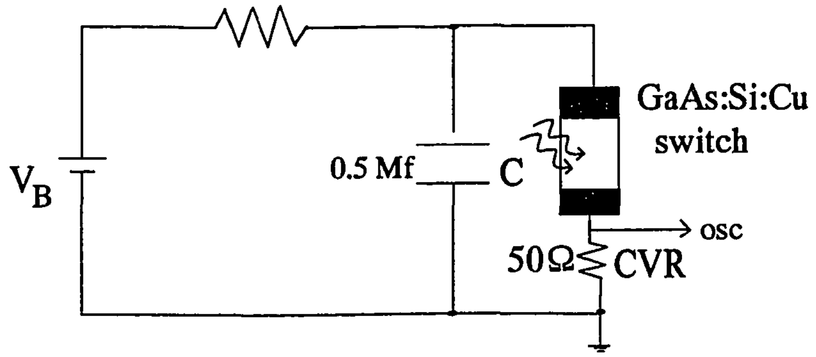


Fig. 3.9 Circuit diagram for the low power switching experiments

$$G(t) = \frac{i(t)}{V_B - R\,i(t)} \tag{3.11}$$

The laser beam from the semiconductor laser is passed through lenses and then incident on the sample (Fig. 3.8b). The sample is charged with a voltage pulse before the laser pulse is turned on. The current through the sample is stored in the oscilloscope and the time dependent conductance of the sample is calculated from these waveforms. Conductivity of the sample can be calculated, knowing the geometric parameters of the sample using the equation:

$$\sigma(t) = G(t)\,\frac{l}{A} \tag{3.12}$$

where A is cross sectional area of illumination and l is the gap between the contacts.

The switching experiments are conducted for various laser intensities and bias voltages. The intensity of the laser is reduced by using neutral density filters, and photon fluxes ranging from 10^{22} to 10^{25} cm^{-2} s^{-1} have been used. The sample is pulse charged to the desired voltage (ranging from 60 V to 500 V) before the application of the laser pulse. The voltage pulse applied to the sample is stored in the oscilloscope and the current waveform is stored in the digitizer.

In summary, various experimental procedures utilized for the present study are discussed in this chapter including the switch fabrication, the characterization techniques, and the switching experiments to test the device performance .

CHAPTER 4

EXPERIMENTAL RESULTS

The results of the characterization and the switching experiments of the GaAs:Si:Cu samples processed using the different fabrication techniques are included in this chapter. The results are organized in the order in which the present research study is developed. The switch photoconductivity has been simulated using a picosecond laser pulse as the excitation source to study the variation of switch photoconductivity as a function of the ratio of the concentration of the Cu_A and Cu_B levels, known as partition ratio ($P = N_{CuA}/N_{CuB}$). The influence of As vapor pressure during diffusion on the switch photoconductivity is studied using the semi-closed tube diffusion system. Then the closed tube diffusion system is used to study systematically the influence of the As vapor pressure, i.e., the samples are annealed at four different As vapor pressures. The results of the study indicated the presence of a gradient in the concentration of various deep levels in the GaAs:Si:Cu samples. In order to reduce this gradient effect, samples are diffused with Cu using a third diffusion technique, called the leaky tube diffusion technique, and the results are presented.

4.1 Simulation of GaAs:Si:Cu Switch Photoconductivity

The switching performance of the GaAs:Si:Cu switches depends on various factors such as the laser energy, the concentration of deep levels (including Cu levels) present in the material etc. Simulation studies have been performed to study the influence of these parameters on turn-on photoconductivity of the switch using the source code developed by Ko [12] wherein a nanosecond laser was used as the excitation source. The rate equations used for the modelling of the GaAs:Si:Cu switch are given in Chapter 2 (equations 2.30 to 2.32). The required modifications are included for the present study where a ps laser pulse is used as the excitation source, and more details of the simulation study are given in reference 35 .

Figure 4.1a shows the variation of the photoconductivity of the switch with photon flux for a 300 ps (FWHM) laser pulse. The temporal shape of the laser pulse is assumed to be Gaussian. As the photon flux increases, the peak conductivity as well as the on-state conductivity increases. The photoconductive transients of the switch for various incident photon flux are shown in Fig. 4.1b. The photoconductive transient is normalized with respect to the on-state photoconductivity at 40 ns, to show the decay more clearly. The ratio of the peak conductivity to the on-state conductivity decreases with the increasing photon flux. As the photon flux increases, more carriers are excited and consequently more carriers will remain in the conduction band which leads to higher on-state conductivity. It can be seen that the switch requires less time to reach the steady state conductivity at higher photon fluxes.

The introduction of various deep levels in GaAs:Si:Cu depends on the processing conditions. As discussed in Chapter 1, Cu introduces many deep levels in GaAs, among which Cu_A and Cu_B levels are the prominent ones. The partition ratio is used as a variable parameter in the simulation of the switch to study the effect of the concentration

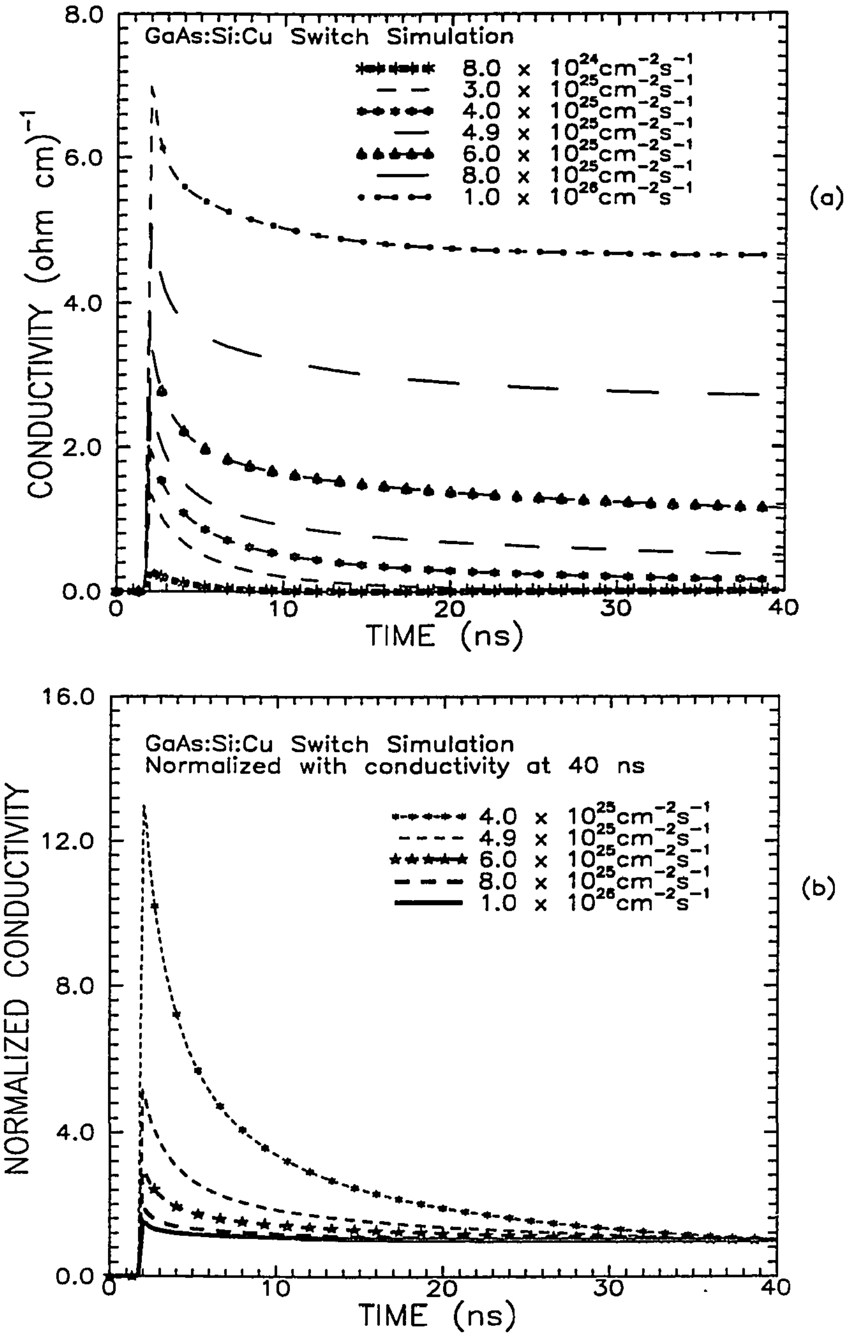


Fig. 4.1 a) Photoconductivity and b) normalized photoconductivity (normalized with respect to the on-state photoconductivity at 40 ns) of GaAs:Si:Cu switch using a 300 ps laser pulse excitation for various photon fluxes.

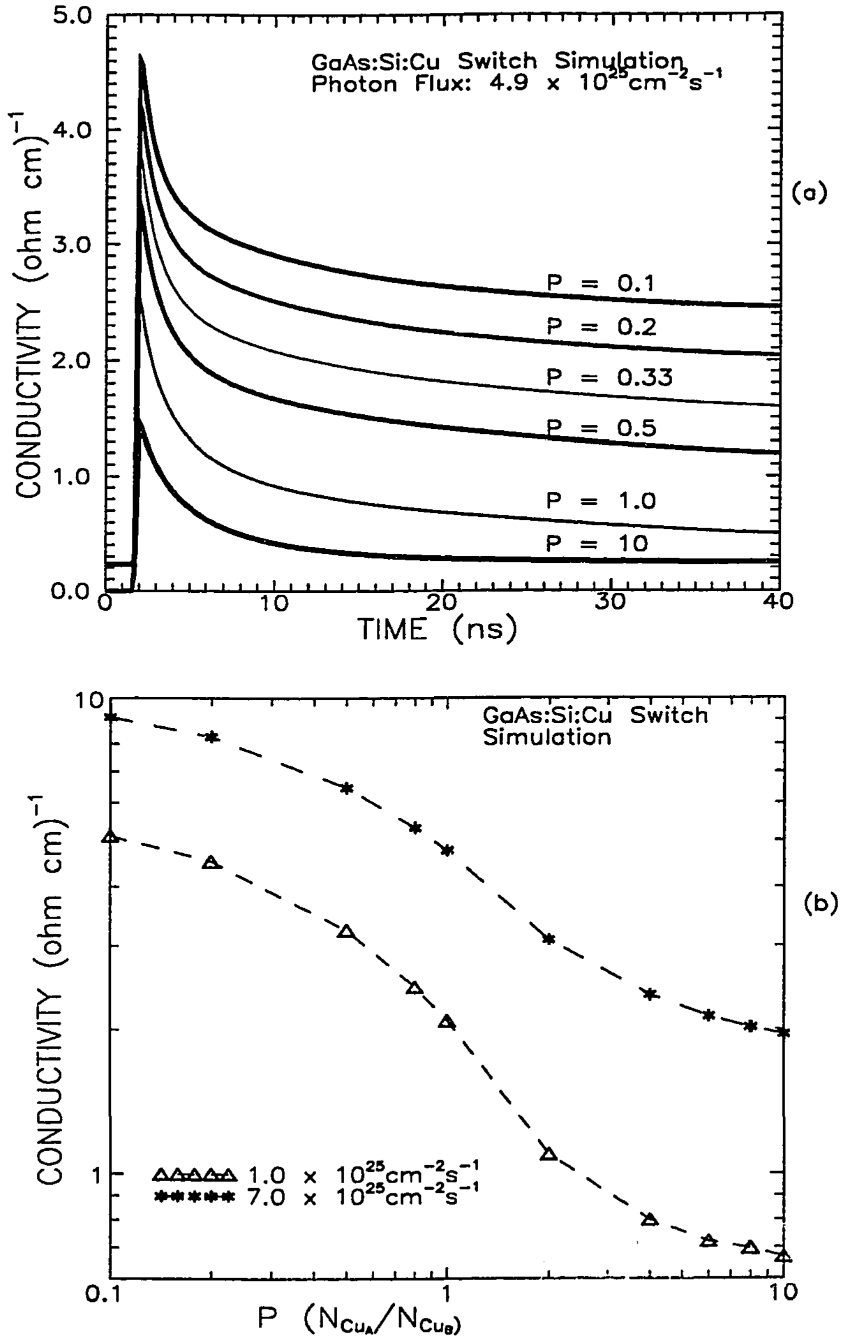


Fig. 4.2 a) GaAs:Si:Cu switch photoconductivity for various partition ($P = N_{CuA}/N_{CuB}$) values and b) GaAs:Si:Cu switch photoconductivity at 20 ns as a function of P using a 300 ps laser pulse excitation.

of the Cu deep levels on the switch photoconductivity. Figure 4.2a shows the photoconductive transients of the switch as a function of P values, ranging from 0.1 to 10 for a fixed photon flux of 4.9 x 10^{25} cm^{-2} s^{-1}. It is seen that as the partition ratio decreases, i.e., the concentration of Cu_B state increases, the switch on-state conductivity increases. The effect is clearly shown in Fig. 4.2b, which is a plot of the on-state conductivity of the switch (at 20 ns) as a function of P.

4.2 Diffusion of Cu using Semi-closed Tube Diffusion Technique

Using the semi-closed tube diffusion system, GaAs:Si samples with the deposited Cu are annealed under different As vapor pressure in the ambient, keeping all the other diffusion parameters such as time and temperature constant. The base material, i.e., GaAs:Si, before Cu diffusion, has been characterized earlier [12] and three deep levels, EL6 (peak #1), EL3 (peak #2), and EL2 (peak #3) with activation energies, 0.36 eV, 0.61 eV, and 0.76 eV respectively have been identified (Fig. 4.3). A typical PICTS spectrum for a GaAs:Si:Cu sample (diffused under an As vapor pressure of about 0.1 atm) is shown in Fig. 4.4, which shows various peaks associated with different deep levels. Three peaks, #1 (E_T = 0.14 eV; σ_T = 7.0 x 10^{-16} cm^2), #2 (E_T = 0.32 eV; σ_T = 6.0 x 10^{-11} cm^2), and #5 (E_T = 0.45 eV; σ_T = 3.0 x 10^{-10} cm^2) have been identified (see Fig. 3.7a and 3.7b). As can be seen, these peaks are at different energy levels than those observed in DLTS of GaAs:Si and hence can be attributed to the Cu related levels introduced during diffusion. The levels at 0.14 eV and 0.45 eV are referred as Cu_A and Cu_B respectively

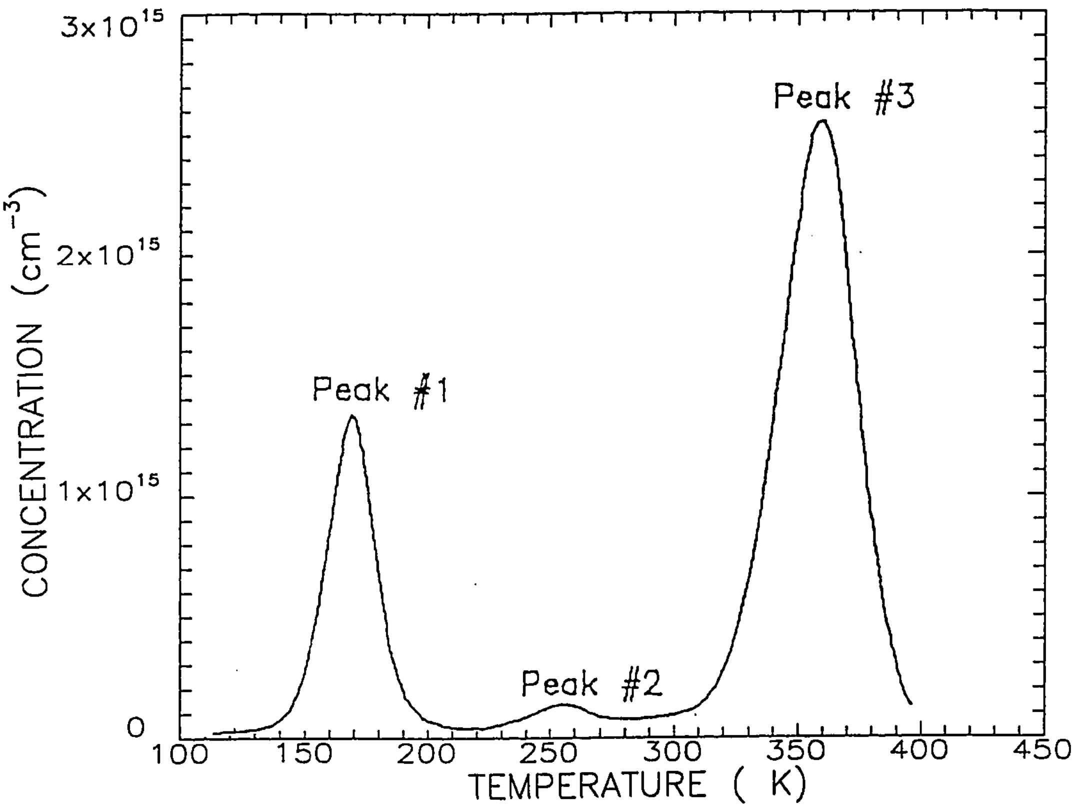


Fig. 4.3 The DLTS spectrum of GaAs:Si before Cu diffusion [12]

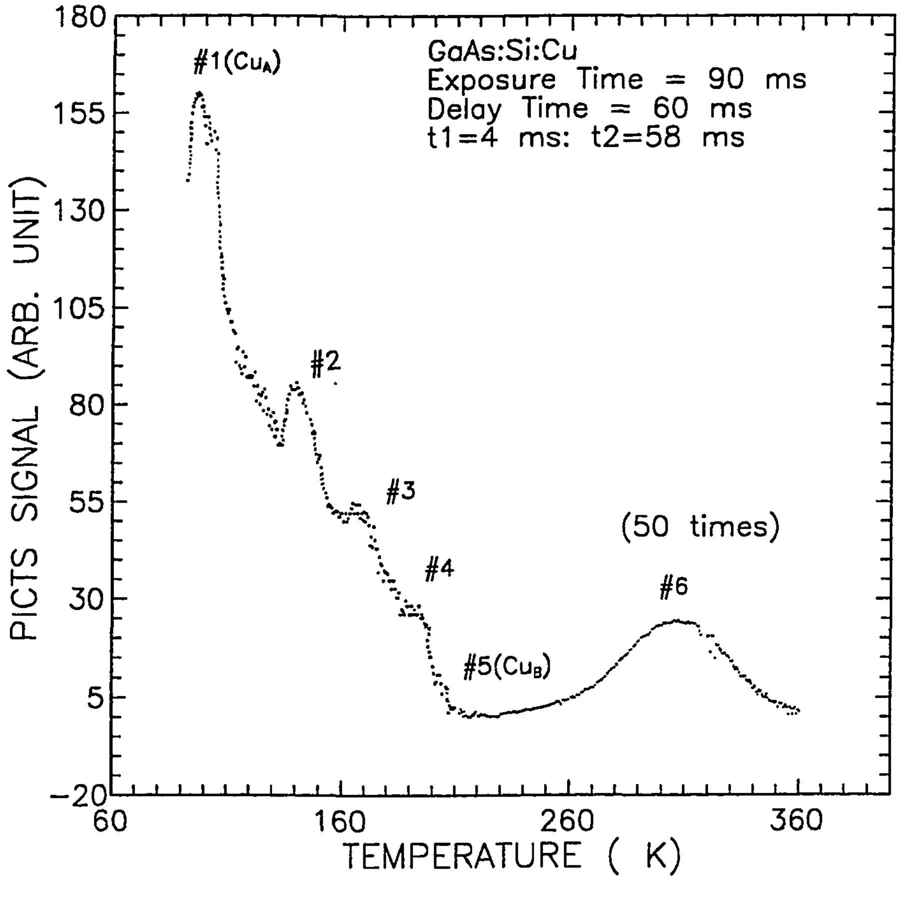


Fig. 4.4 A typical PICTS spectrum of GaAs:Si:Cu sample annealed using semi-closed tube diffusion technique at an As vapor pressure of 0.1 atm.

(after Ref 54). The capture cross section obtained for Cu_B level is higher than the value obtained using the DLTS technique ($\sigma_T = 3 \times 10^{-14}$ cm^2) by Lang *et al.* [50]. Other peaks, #3, and #6 (peak #6 is magnified 50 times, which indicates very small relative concentration) can also be seen in the spectrum.

Figure 4.5 shows PICTS spectra for samples diffused with two different As vapor pressure in the diffusion tube, while keeping other experimental parameters for the PICTS such as the applied voltage, the CVR, the sample geometry etc., constant. The samples are fabricated under identical processing conditions except the As vapor pressure during diffusion. The PICTS spectra in Fig. 4.5 show that peak #1 and peak #2 are well resolved. However, other peaks (peaks #3, #4, and #5) are broader in nature, indicating probably the presence of many traps clustered together. A new PICTS data analysis technique called curve fitting technique [32] is more useful than the conventional rate window technique, when the trap levels are clustered together, however, the current transient has to be stored for the analysis. The PICTS spectra shown in Fig. 4.5 show the dependence of Cu peaks on As vapor pressure. By qualitatively comparing the PICTS spectra of the samples in Fig. 4.5, it is observed that the relative concentration of Cu_A level (peak #1) with respect to Cu_B level (peak #5) is higher in the samples diffused in the absence of As. The amplitude of peak #2 ($E_T = 0.32$ eV; 6.0×10^{-11} cm^2) decreases for the sample diffused with increased As vapor pressure.

For the above studies, GaAs:Si samples were annealed with deposited Cu only on one surface (surface A) of the GaAs:Si samples; the other surface (surface B) was exposed to the ambient during annealing (see Fig. 4.6). To study the capping effect of

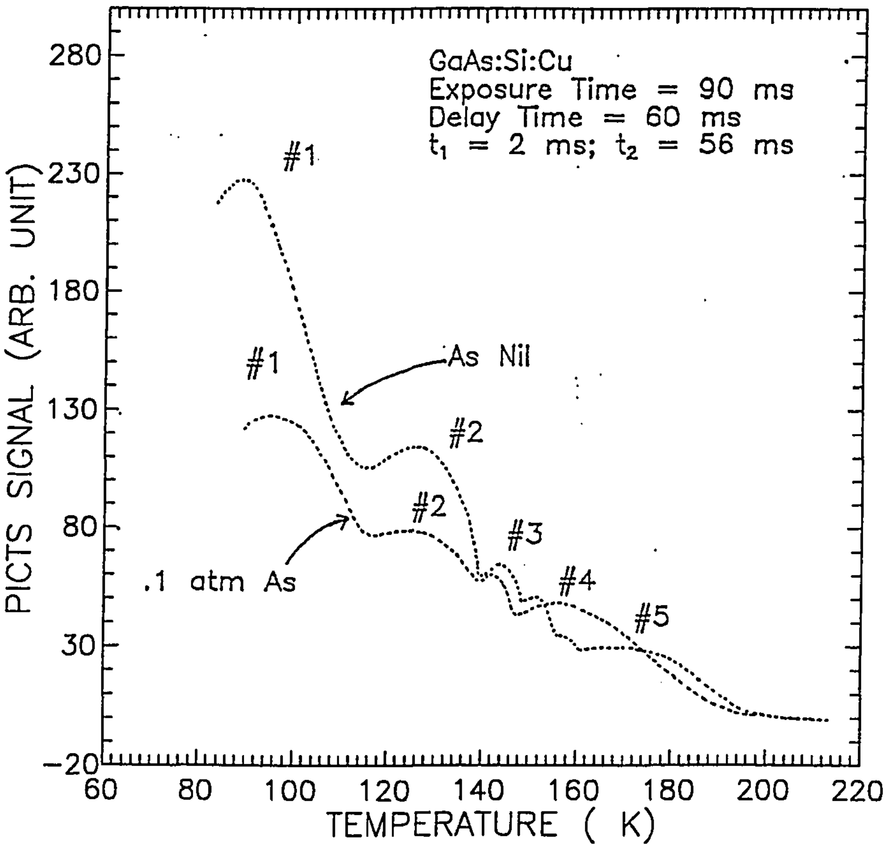


Fig. 4.5 The PICTS spectra of GaAs:Si:Cu samples annealed under different As vapor pressure (semi-closed tube diffusion technique).

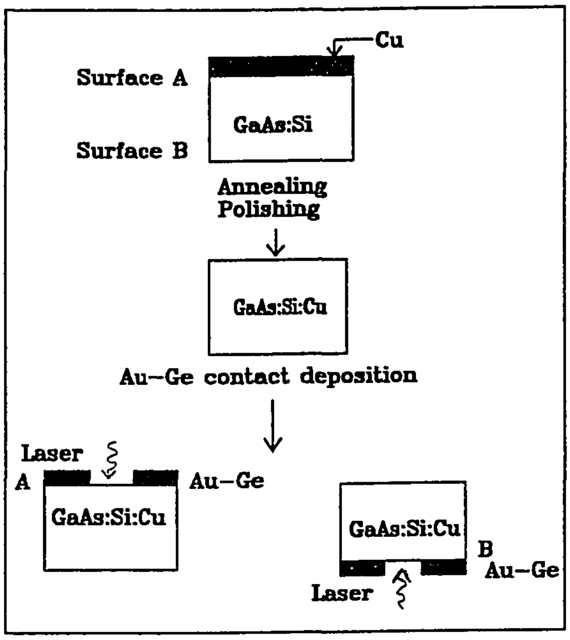


Fig. 4.6 Steps involved in the fabrication of PICTS samples to obtain the spectra from both surfaces, shown in Fig. 4.7.

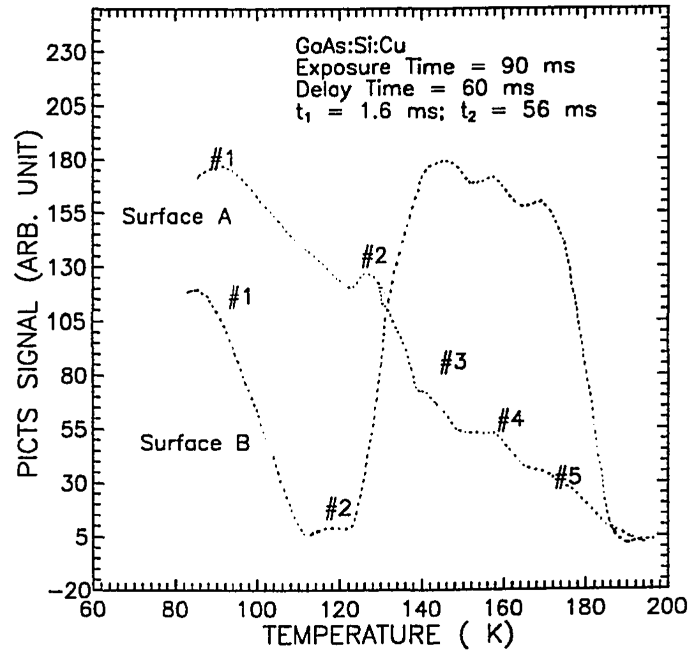


Fig. 4.7 The PICTS spectra from surface A and B of GaAs:Si:Cu sample (semi-closed tube diffusion)

the deposited Cu layer, two samples are prepared for the PICTS characterization: one with Au-Ge contacts on the surface A and the other with Au-Ge contacts on the surface B. The steps involved in the fabrication of the samples are shown in Fig. 4.6. The penetration depth of the probing laser pulse (He-Ne laser with hv = 2 eV) is about 1 μm. Hence, the information on the deep levels obtained from the PICTS spectra is predominantly for the surface of the material. The PICTS spectra are distinctly different depending on the surface on which the laser is incident (as seen in Fig. 4.7). It is observed that amplitude of the peaks due to the Cu-related deep levels (#3, #4, and #5) is much higher in the PICTS spectrum from the surface B compared to that from the surface A. The results indicate the presence of a gradient in the concentration of the deep levels due to the Cu-related deep levels.

To study the influence of As vapor pressure on the deep levels formation, we have annealed four set of samples, one set with out any As, and three sets with varying amount of weighed As (10 mg, 20 mg, and 60 mg respectively) in the diffusion tube. All the samples are characterized using the PICTS technique. The PICTS spectra of the samples are shown in Fig. 4.8, and all of them are taken for the same rate window settings and identical experimental conditions and sample geometry. The results clearly indicated that the Cu related deep levels formation is influenced by the amount of As added; the amplitude of peak #1 and peak #2 is decreased as the As vapor pressure is increased. However, because of the uncertainty in the vapor pressure during diffusion (due to the semi-closed nature of the diffusion system used), experiments are repeated using the closed tube diffusion technique.

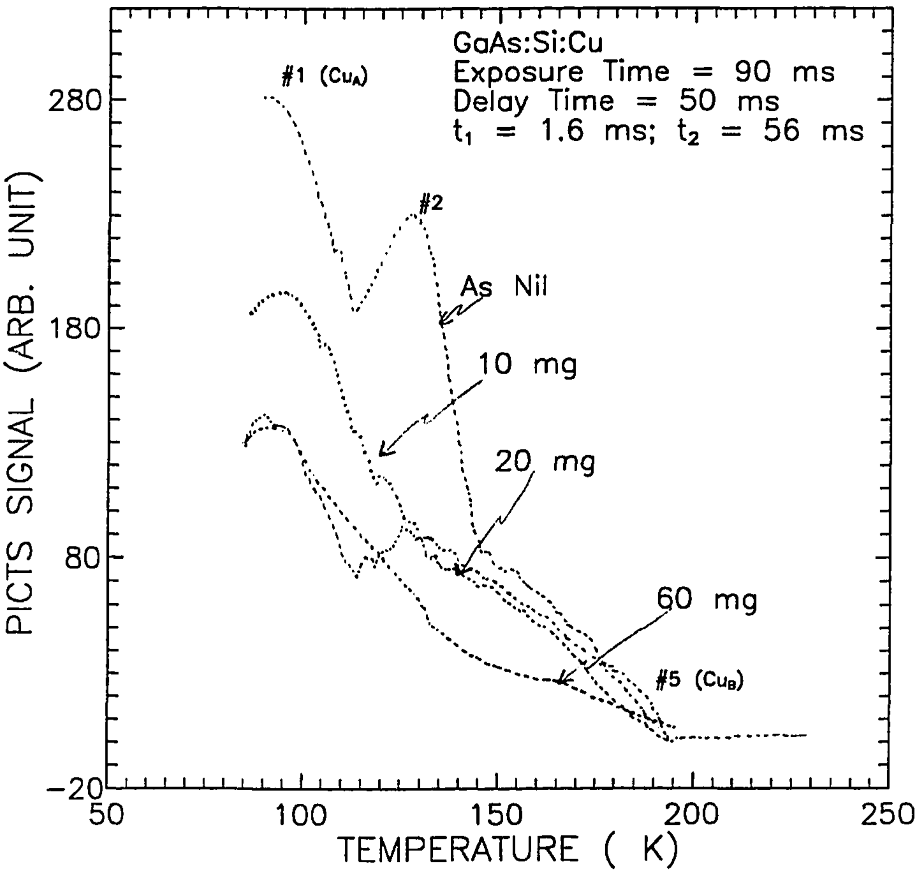


Fig. 4.8 The PICTS spectra of GaAs:Si:Cu samples annealed under various amounts of As in the diffusion tube (semi-closed tube diffusion).

Switch samples of sandwich geometry (see inset in Fig. 4.9) are fabricated from the GaAs:Si:Cu samples annealed at different As vapor pressure. Three samples (annealed with 10 mg, 30 mg, and 60 mg respectively) were tested using an Nd:YAG laser of 7 ns duration and with the experimental setup shown in Fig. 3.6a. Figure 4.9 shows that the photo-current transients of the switch sample annealed with 60 mg As resulted in higher on-state photo-current. Photo-current transients of the GaAs:Si:Cu switch of planar geometry sample annealed using the semi-closed tube diffusion system (60 mg As) is shown in Fig. 4.10. The experiments are conducted using various laser energies (from 0.23 mJ to 0.56 mJ). It is seen in Fig. 4.10 that as the laser energy increases the on-state conductivity as well as the peak conductivity increases. Also, the switch reaches the steady state value faster. These results are in good agreement with the simulation results presented earlier in section 4.1 (see Fig. 4.1a and 4.1b).

4.3 Diffusion of Cu using Closed Tube Diffusion Technique

Having established the presence of the gradient in the concentration of the deep levels due to the Cu-related complexes in the switch material (GaAs:Si:Cu) studied in the present work, the experiments are repeated using the closed tube diffusion technique, where the As vapor pressure could be controlled more accurately. The GaAs:Si samples with the deposited Cu layer are annealed at different As vapor pressures, 0.08, 1.0, and 7.8 atm respectively. One set of samples is annealed without any added As in the quartz ampoule. Also, a set of GaAs:Si samples without any deposited Cu was annealed with 1.0 atm As vapor pressure in the ampoule. These samples are used as control samples

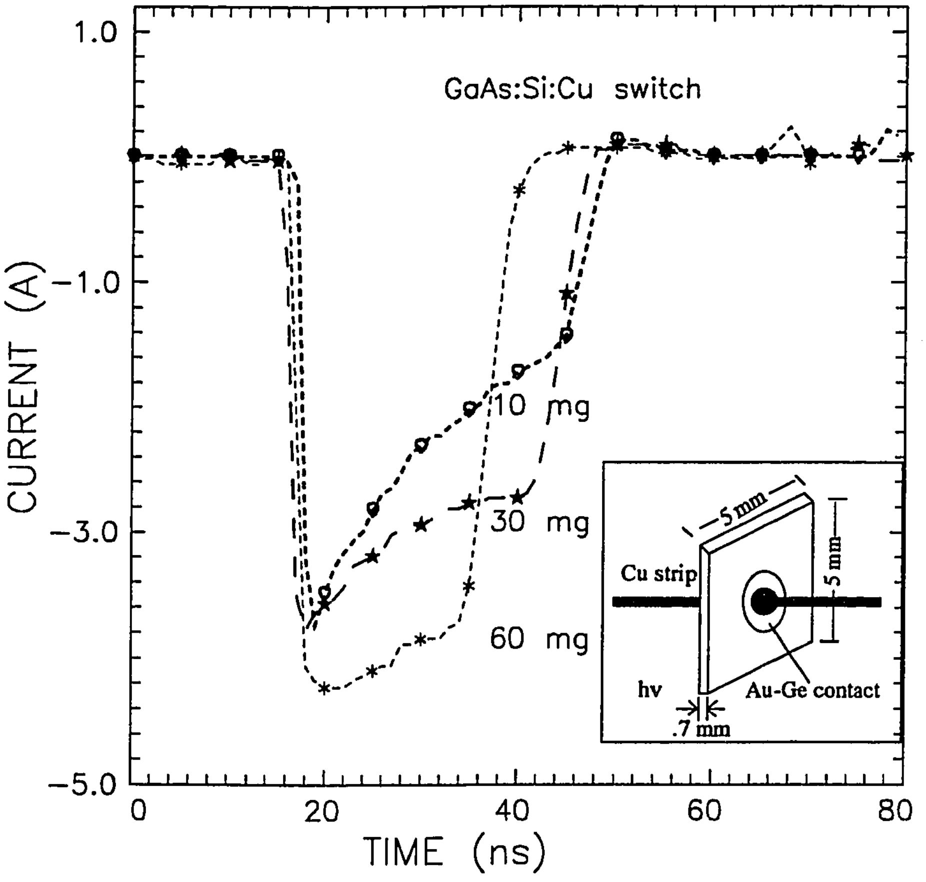


Fig. 4.9 Photocurrent transients of GaAs:Si:Cu switches processed under different As vapor pressure using Nd:YAG laser pulse excitation (semi-closed tube diffusion; sandwich geometry).

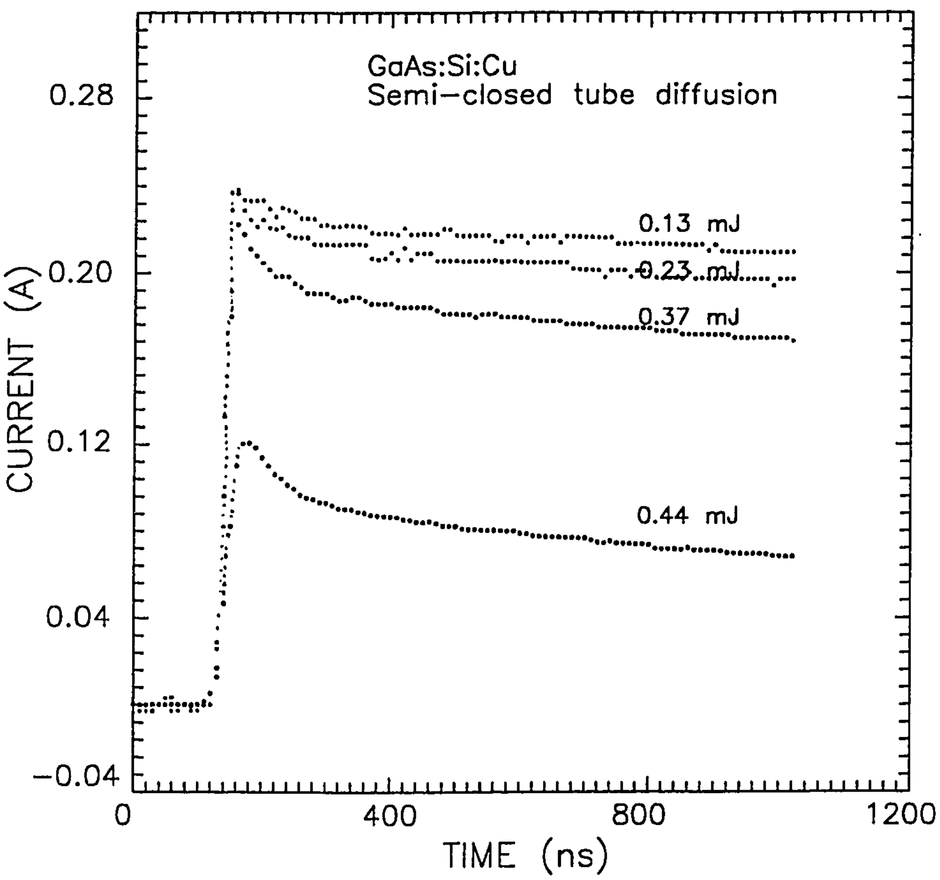


Fig. 4.10 Photocurrent transients of GaAs:Si:Cu switch using Nd:YAG laser pulse excitation for various laser energies (semi-closed tube diffusion; planar geometry).

and are prepared to study the effect of Cu in the compensation process in GaAs:Si. The samples with the deposited Cu layer resulted in high resistivity (kΩ cm range), whereas the control samples resulted in low resistivity (Ω cm range) after annealing. This indicated that at the annealing temperature used in the present study (550^0C), Cu is solely responsible for the compensation of the GaAs:Si samples.

The ohmic nature of the Au-Ge contacts on the GaAs:Si:Cu is confirmed from the I - V curves of the samples. Room temperature Hall measurements are done to determine the resistivity and the carrier concentration of the GaAs:Si:Cu samples. The results of the Hall measurements on the samples (named TC1, TC2, TC4, and TC5) annealed with various amounts of As vapor pressure in the diffusion tube is tabulated in Table 4.1. Figure 4.11 is the PICTS spectrum of a GaAs:Si:Cu sample annealed using the closed tube diffusion system at an As pressure of one atm. Six peaks are observed in the spectrum as in case of the PICTS spectrum of the semi-closed tube sample, and the peaks, #1 (E_T= 0.14 eV) due to Cu_A and #5 (E_T = 0.45 eV) due Cu_B are of significance to the present study. The amplitude of the Cu_A peak is smaller than that of the Cu_B peak in the PICTS spectrum of the closed tube sample. It can be seen the amplitude of the various peaks are strikingly different compared to that of the semi-closed tube sample.

The PICTS spectra of the samples annealed under various As vapor pressure is shown in Fig. 4.12. Three peaks are observed in the PICTS of the samples annealed with no As (Fig. 4.12a) and 0.08 atm As vapor pressure (Fig. 4.12b). The PICTS spectra of the samples annealed at one atm (Fig. 4.12c) and 7.8 atm (Fig. 4.12d) contains six peaks,

Table 4.1 Hall data on GaAs:Si:Cu samples annealed at different As vapor pressure (Closed tube diffusion)

Sample	As vapor pressure (atm)	R_H (x 10^7)	μ_H (cm^2/V.s)	n, p (cm^{-3})
TC1	Nil	1.257	1637	4.97 x 10^{11}
TC2	0.08	0.068	541	9.19 x 10^{12}
TC4	1.00	0.155	259	4.03 x 10^{12}
TC5	7.80	0.083	427	7.58 x 10^{12}

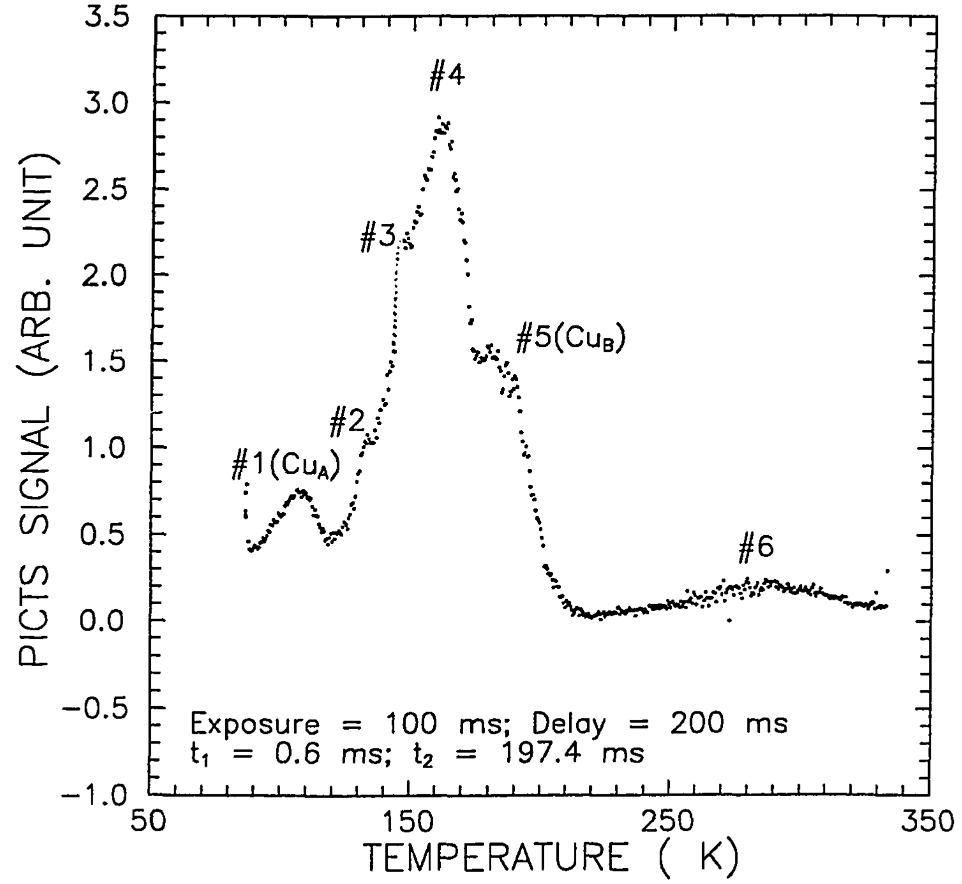


Fig. 4.11 The PICTS spectrum of GaAs:Si:Cu sample annealed using closed tube diffusion technique (1.0 atm As vapor pressure).

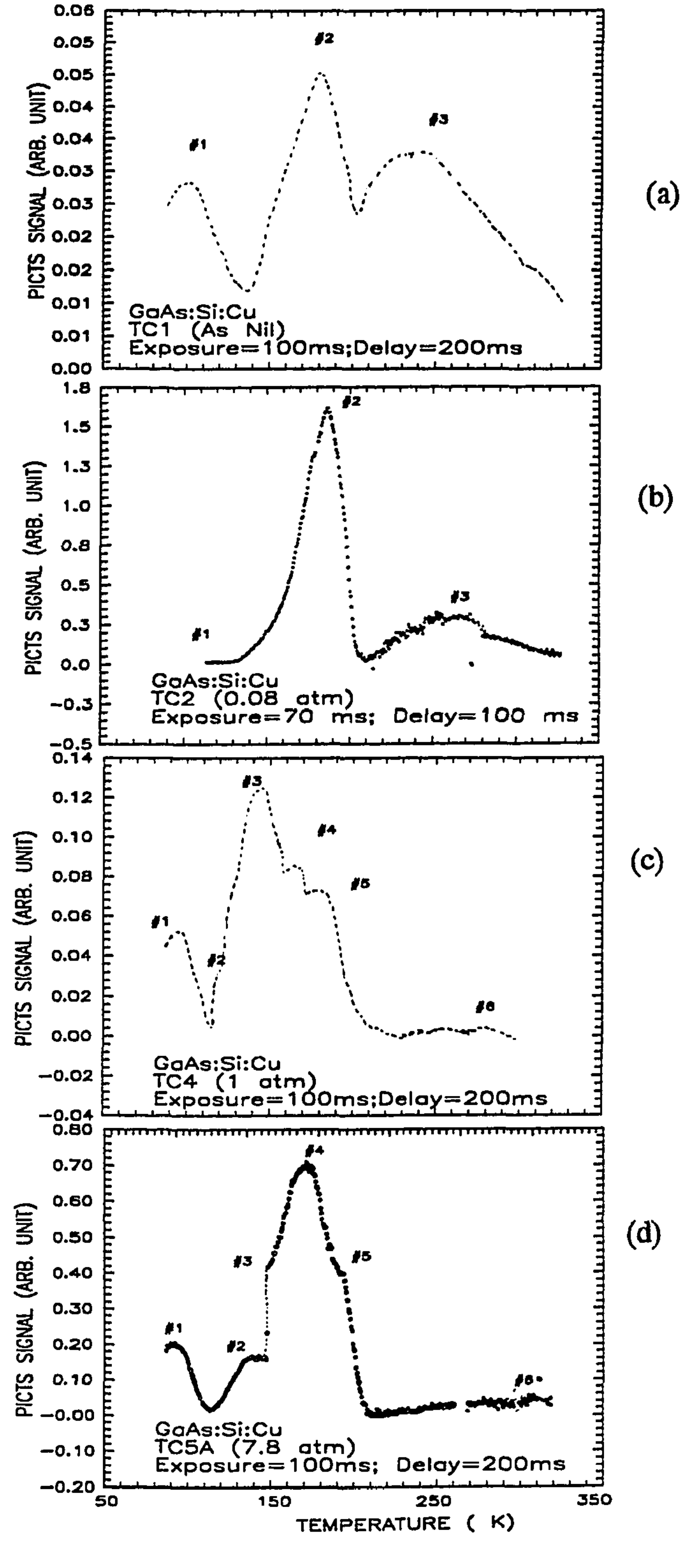


Fig. 4.12 The PICTS spectra of GaAs:Si:Cu samples annealed under various As vapor pressure (closed tube diffusion).

as in the case of the semi-closed tube annealed sample. The amplitude of the Cu_B peak (#2 in Fig. 4.12a and 4.12b, and #5 in Fig. 4.12c and 4.12d) decreased as the As vapor pressure increased. For the semi-closed tube annealed samples, the amplitude of the CuB states at the surface A remained almost same as the As vapor pressure increased (refer Fig. 4.5). It is possible that due to the semi-closed nature of the diffusion system, the capping effect of the deposited Cu layer is dominant for the semi-closed tube samples.

To study the deep level structure as a function of depth from the surface of the sample, the samples are etched to different depth and the PICTS spectra are taken (Fig. 4.13). The samples are annealed with an As vapor pressure of 7.8 atm in the ampoule. The annealed sample is cut into four 2 mm x 5 mm pieces (see inset in Fig. 4.13). On one piece Au-Ge contact on the surface (surface A) where the copper film has been deposited, and Curve 1 in Fig. 4.13 is for this sample. Two pieces are etched to different depths (0.35 mm and 0.20 mm) from the surface A, and curves 2 and 3 are for these samples. Curve 4 is the PICTS spectrum from the surface (surface B) where no Cu has been deposited. Six peaks are observed in the spectrum for all the four samples, where the peak #1 ($E_T = 0.14$ eV) is due to the Cu_A level and the peak #5 ($E_T = 0.44$ eV) is due to the Cu_B level.

The PICTS spectra at different depths from the surface of the GaAs:Si:Cu material show the influence of As vapor pressure during diffusion. Figure 4.14 shows the PICTS spectra of samples annealed at 1.0 atm and 7.8 atm As pressures, and these spectra are taken at a depth of about 0.35 mm from the surface of the sample. For the sample annealed at 7.8 atm As vapor pressure, the amplitude of the Cu_A peak (#1) is higher than

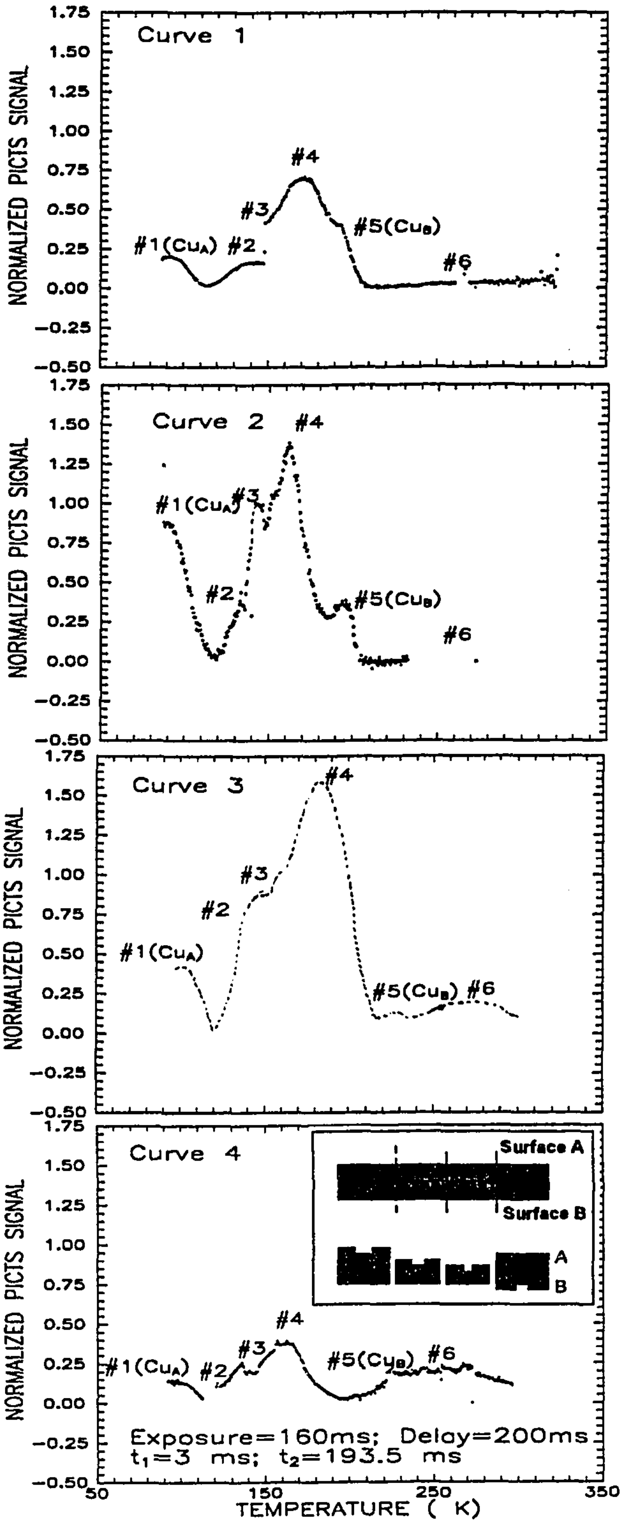


Fig. 4.13 The PICTS spectra at different depths from the surface of GaAs:Si:Cu sample (Closed tube diffusion; 7.8 atm As pressure)

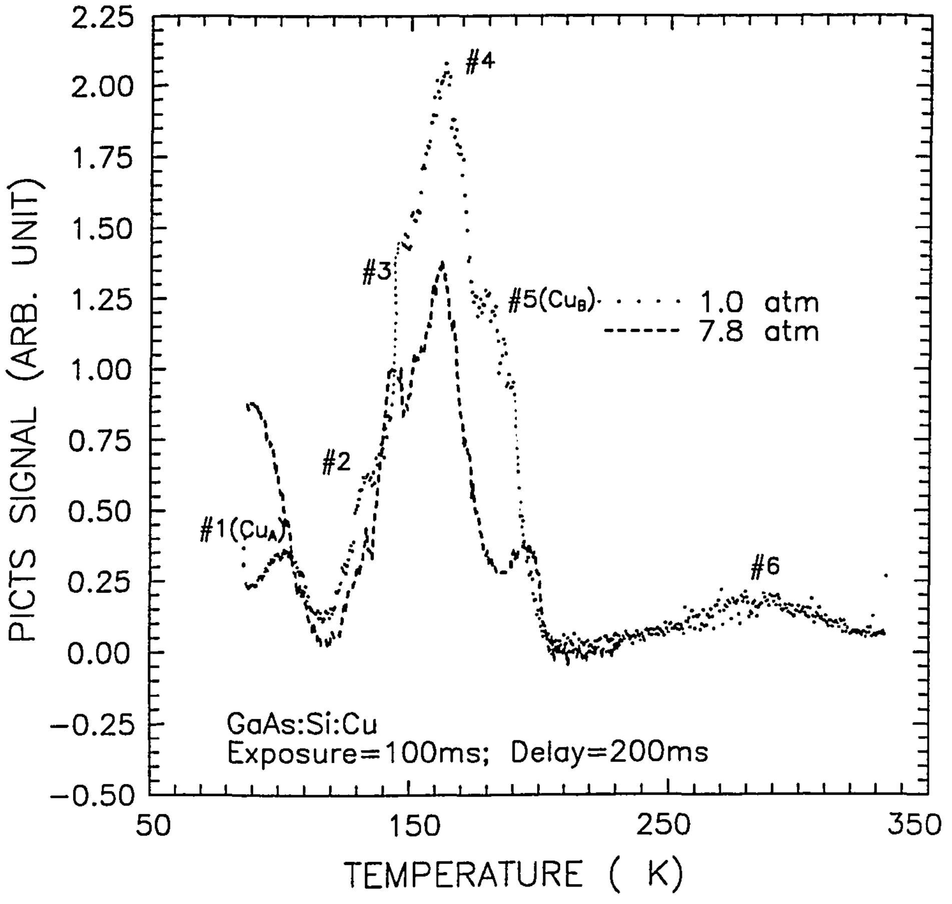


Fig. 4.14 The PICTS spectra of GaAs:Si:Cu samples annealed at 1.0 atm and 7.8 atm As vapor pressure (closed tube diffusion; spectra taken at 0.35 mm from the surface)

that of the Cu_B peak (#5), whereas for the sample annealed at 1.0 atm, the amplitude of the Cu_A peak (#1) is smaller than that of the Cu_B peak (#5).

The PICTS spectra at different depth from the surface of the GaAs:Si:Cu sample annealed at an As vapor pressure of 0.08 atm are shown in Fig. 4.15a and b. Curve 1 (at surface A) and curve 3 (at 0.35 mm) are plotted together in Fig. 4.15a. Curve 2 (at surface B), curve 3 (at 0.35 mm), and curve 4 (at 0.2 mm) are plotted in Fig. 4.15b. An important result to be noticed in case of these curves is the presence of a negative peak which is clearly seen in the curves 2, 3, and 4. In case of the curve 1, the negative peak is very small. In our laboratory, among all the GaAs:Si:Cu and SI-GaAs samples characterized using the PICTS technique, the negative peak has been observed in the PICTS spectra of these four samples only.

The switches fabricated from the four sets of samples annealed at different As vapor pressure, are tested using the experimental setup shown in Fig. 3.6a. The photocurrent transients of the switches is shown in Fig. 4.16. The low power switching experiments are conducted using a Q-switched Nd:YAG laser with a pulse width of about 7 ns, and results for two different laser energies, 0.23 mJ ($\Phi = 1.6 \times 10^{24}$ cm^{-2} s^{-1}) and 0.56 mJ ($\Phi = 4.0 \times 10^{24}$ cm^{-2} s^{-1}) are shown in Fig. 4.16a and Fig. 4.16b respectively. It can be seen that as the photon flux increases, the peak value as well as the on-state value of the photocurrent increases. The TC4S (annealed at one atm As vapor pressure) has the lowest peak as well as the on-state photocurrent. From the Hall data (Table 4.1), it is seen that TC4S has the lowest mobility value which indicated a higher level of compensation compared to the other three samples. Photoconductivity measurements

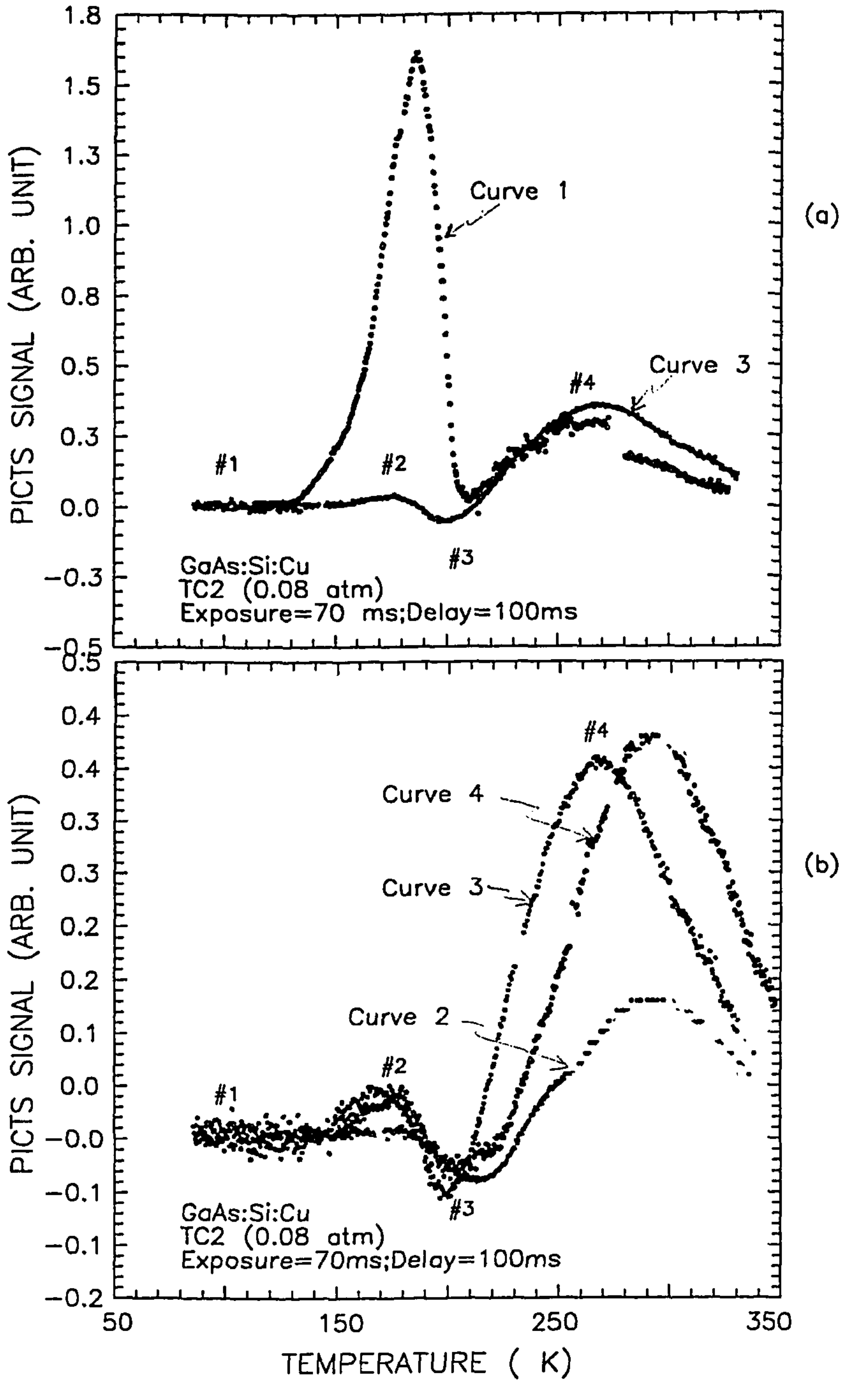
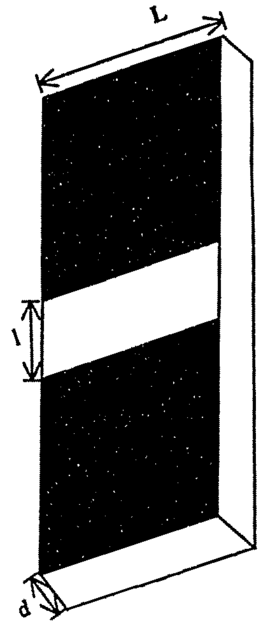


Fig. 4.15 The PICTS spectra of GaAs:Si:Cu sample (closed tube diffusion) at different depths from the surface: a) at surface A (curve 1) and at .35 mm (curve 3) b) at surface B (curve 2), at .35 mm (curve 3), and .20 mm (curve 4).



Switch/PICTS sample with planar geometry

Table 4.2 Geometrical parameters of the switch samples

Sample	As vapor (atm)	d (mm)	*l* (mm)	L x d (mm^2)	*l*/(Lxd) (mm^{-1})
TC1S	As Nil	0.7	1.15	3.61	0.319
TC2S	0.08	0.7	1.0	2.77	0.362
TC4S	1.04	0.7	1.1	2.80	0.393
TC5S	7.40	0.7	1.1	2.00	0.551

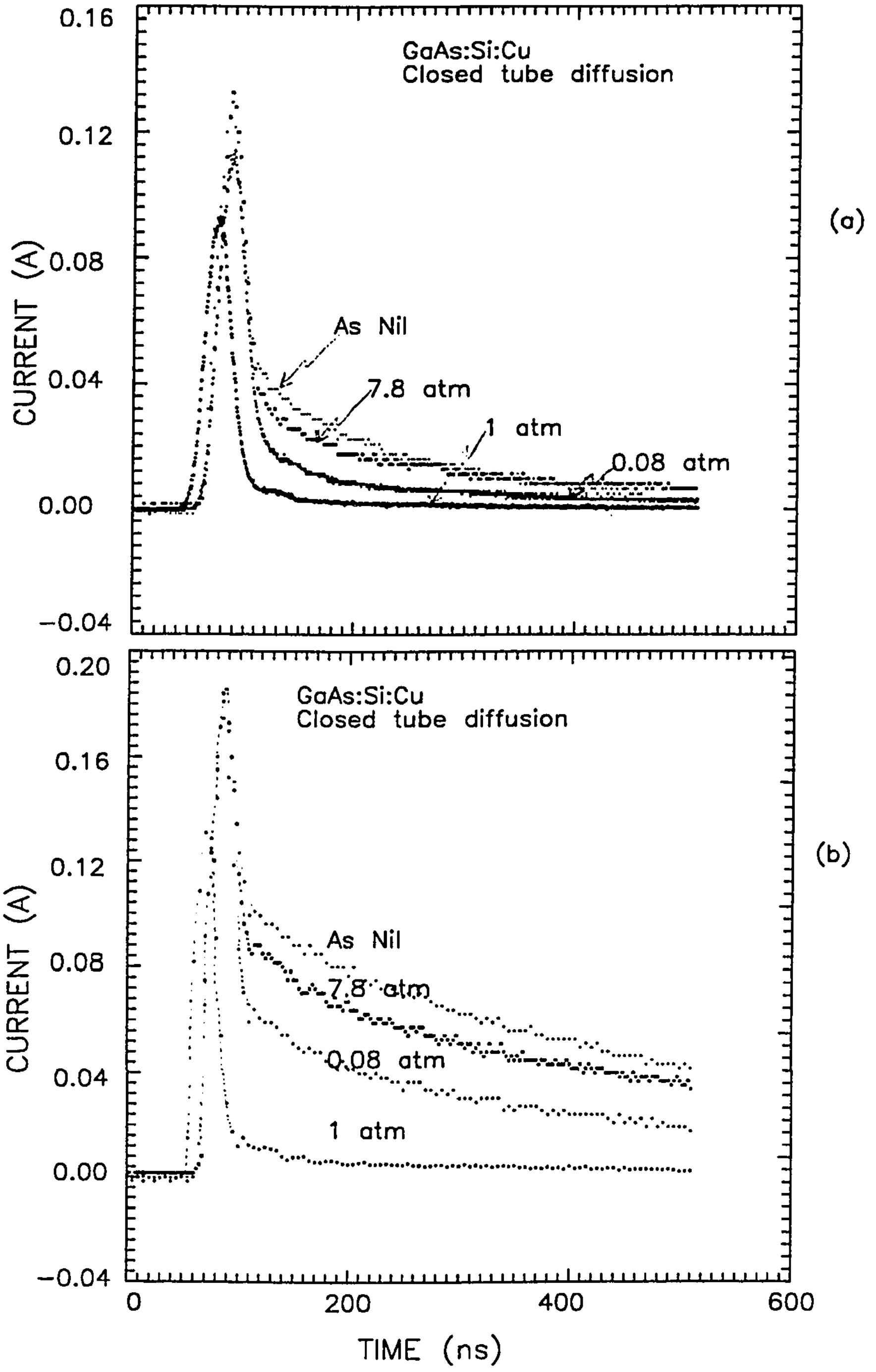


Fig. 4.16 Photocurrent transients of GaAs:Si:Cu switches processed under various As pressure during diffusion (closed tube diffusion) using Nd:YAG laser pulse excitation for two different laser energies. a) for 0.23 mJ and b) 0.56 mJ

are done on these switch samples using the low semiconductor laser diode as the excitation source and the results are shown later in this section (Fig. 4.21a and 4.21b) and a detailed discussion of the results are included.

4.4 Diffusion of Cu using Leaky Tube Diffusion Technique

The PICTS characterization and the testing of the switching performance of the closed tube and the semi-closed tube GaAs:Si:Cu samples confirmed the presence of the concentration gradient of the deep levels due to the Cu-related complexes in the switch material. The subsequent research efforts were directed to modify the fabrication techniques to reduce this gradient effect and also to increase the concentration of the Cu in the diffused material so as to obtain increased on-state photoconductivity for the switches. For this purpose, the leaky tube diffusion technique is used to diffuse Cu into the GaAs:Si samples. Using this technique, both surfaces of the samples are coated with Cu-doped spin-on glass, which acts as a capping layer during the diffusion process and prevents the escape of As from the surface. Also, the presence of the Cu source on both the surfaces increases the amount of Cu diffused into the material. Figure 4.17 shows the PICTS spectrum of the GaAs:Si:Cu sample diffused using the leaky tube diffusion system. The sample is annealed for 10 hours. Six peaks are observed in the spectrum also, as in the PICTS spectra of the closed tube and the semi-closed tube samples, among which the peak #1 is due to the Cu_A level and the peak #5 is due to the Cu_B level. It is seen that the characteristics of the PICTS spectra of the leaky tube sample is more similar to that of the semi-closed tube sample (Fig. 4.4) than to that of closed tube sample (Fig. 4.11).

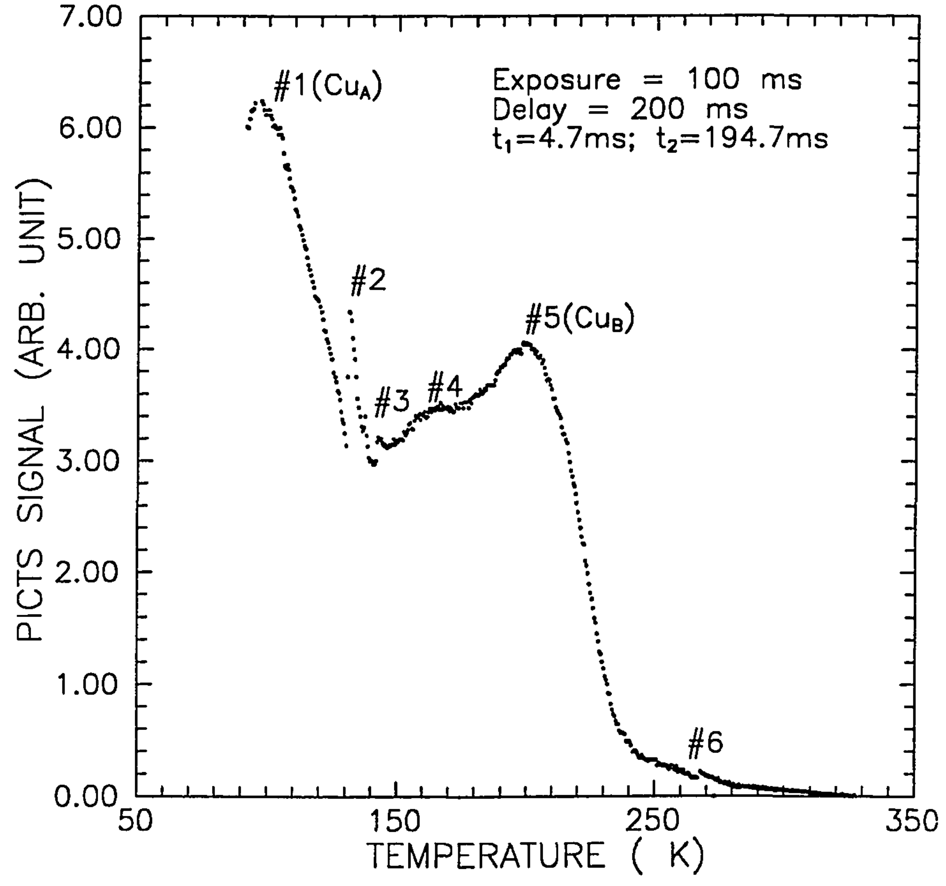


Fig. 4.17 The PICTS spectrum of GaAs:Si:Cu sample annealed (10 hours) using leaky tube diffusion technique.

The amplitude of the peak #1 is highest among all the peaks for the leaky tube and the semi-closed tube samples, whereas for the closed tube sample, the amplitude of the peak #1 is smaller than the peaks in the spectrum. The relative amplitude of the Cu_A to Cu_B is lower for the leaky tube sample than that of the semi-closed tube sample, i.e., the partition ratio is lower for the leaky tube sample and therefore, should result in a better BOSS switch material.

Using the leaky tube diffusion technique, samples are diffused for three different diffusion times (2, 10, and 17 hours). Figure 4.18 shows the PICTS spectra of the samples annealed for 2 hr, 10 hr, and 17 hr respectively. In the PICTS spectra of the sample annealed for 2 hr, the ratio of the peak #1 (Cu_A) to that of peak #5 (Cu_B)is larger compared to similar ratios for the 10 hr and 17 hr annealed samples, i.e., the partition ratio is highest for the 2 hr sample. As the annealing time is increased, the amplitude of the peak #5 as well as that of the other peaks, #2, #3, and #5, increases. It is pointed out that the PICTS spectra shown in Fig. 18 are taken at surface A of the sample. The change in the amplitude of the Cu_A and Cu_B peak in the PICTS spectra of the samples annealed for different time indicates that the concentration of these levels at surface A changes as a function of diffusion time.

The switch samples are tested using the experimental set shown in Fig. 3.6. The experiments are conducted using both the Nd:YAG laser and the low power semiconductor laser to turn the switch on and the results are shown in Fig. 4.19a. Using the Nd:YAG laser, a DC bias of 15 V and a laser energy of 0.23 mJ are used. The on-state photoconductivity is highest for the 2 hr annealed sample among the three samples

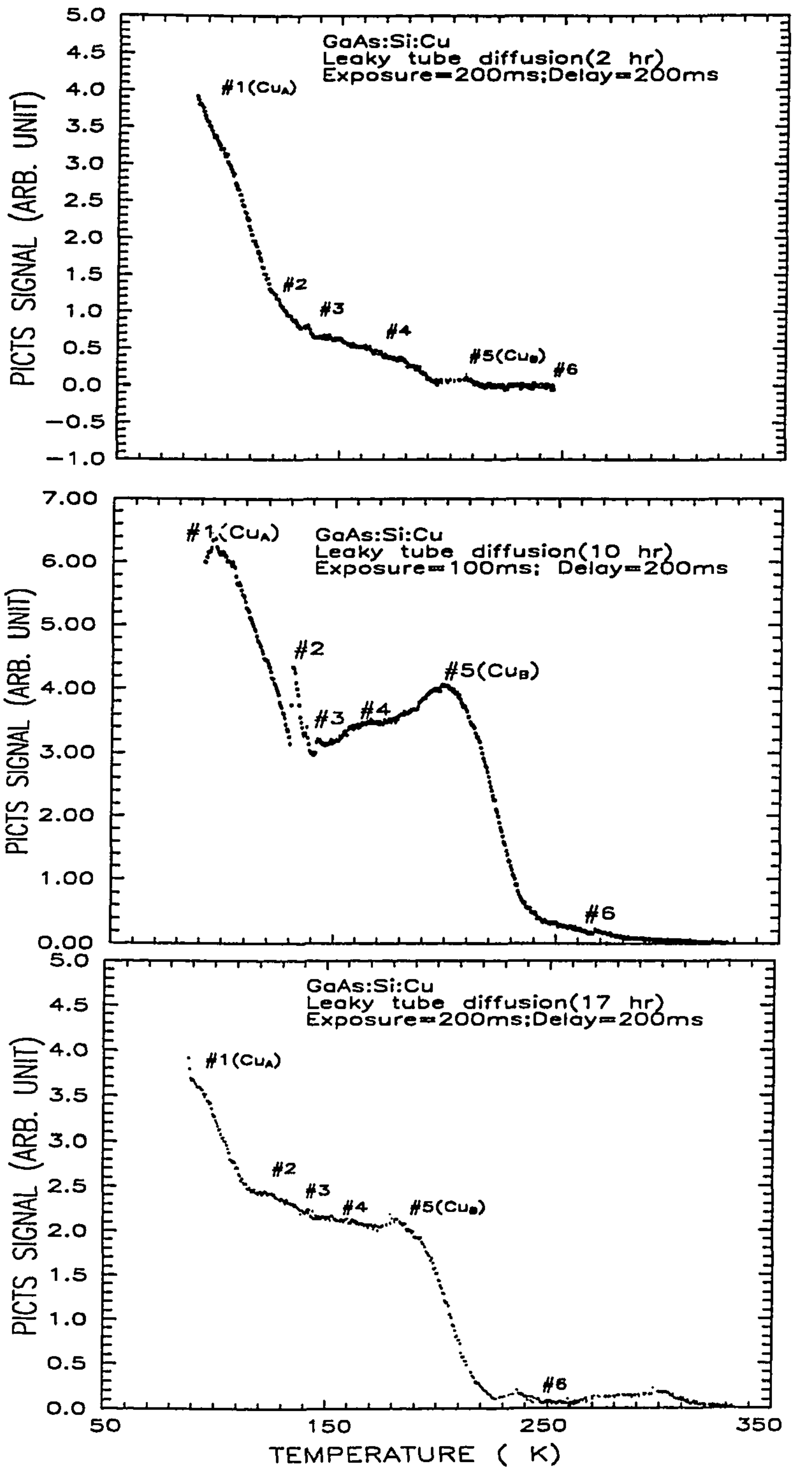


Fig. 4.18 The PICTS spectra of GaAs:Si:Cu samples annealed for different times (leaky tube diffusion).

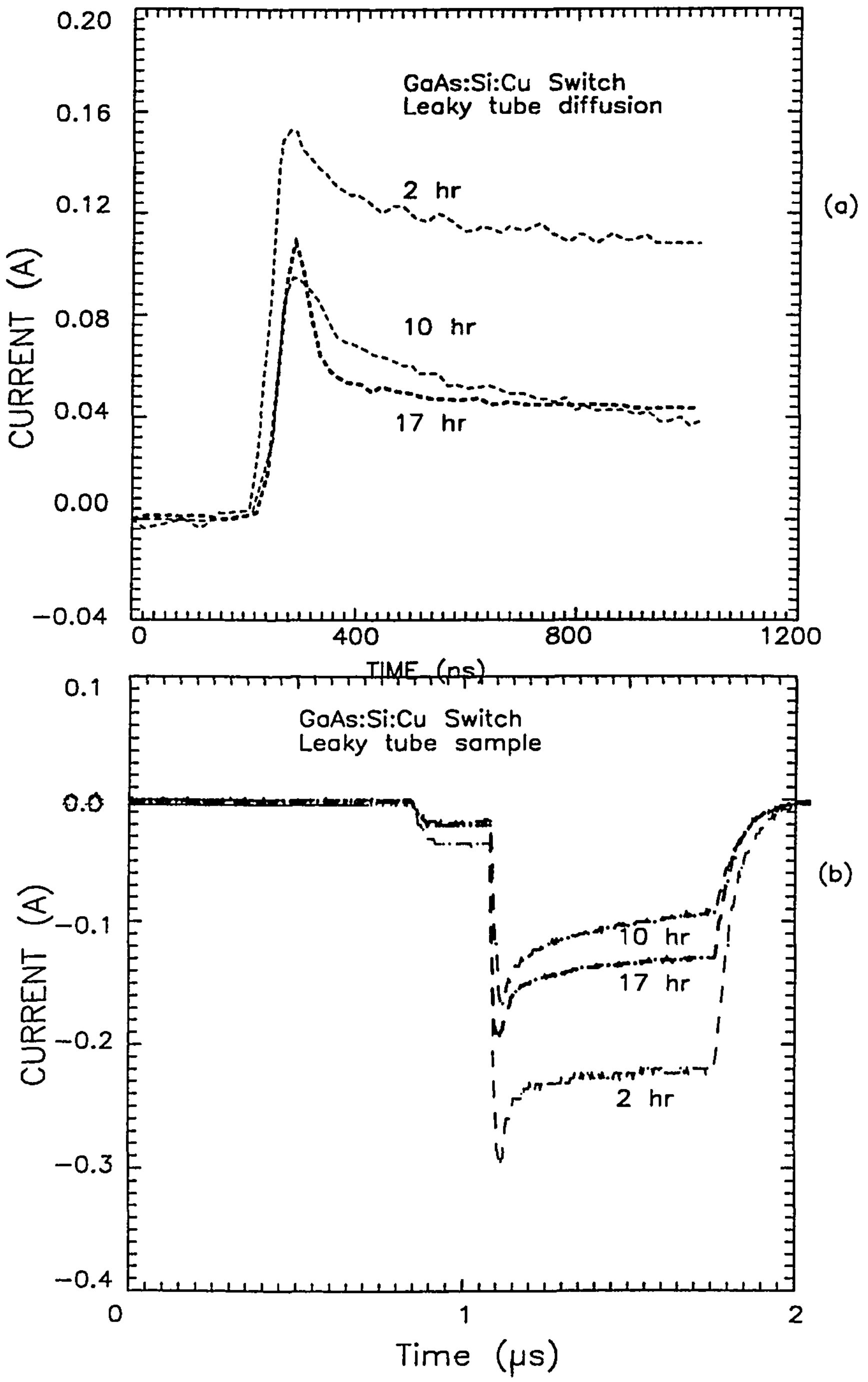


Fig. 4.19 Photocurrent transients of GaAs:Si:Cu switches annealed (leaky tube diffusion) for different times using a) Nd:YAG laser excitation and b) semiconductor laser excitation.

annealed for 2, 10, and 17 hr respectively. It is seen that the 17 hr sample reached steady state faster compared to the 10 hr sample. The on-state photocurrent of all the three samples is much larger compared to that of the closed tube and the semi-closed tube annealed samples. The switching experiments are conducted using the semiconductor laser diode to turn the switch on using the experimental setup shown in Fig. 3.6b, and the results are shown in Fig. 4.19b. All the three samples show on-state photocurrent which clearly indicates that the leaky tube material is efficient enough to use the low power semiconductor laser diode as the excitation source. The 17 hr and the 10 hr samples have almost the same on-state current whereas in Fig. 19b, the 17 hr sample has higher on-state current than that of 10 hr sample. This is due to the difference in the voltages applied to the sample. For the experiments using the Nd:YAG laser excitation, 15 V is applied to all the samples, whereas for the semiconductor laser diode excitation, the voltage pulses applied to the three samples are not of the same amplitude(120 V for the 2 hr and the 10 hr and 100 V for the 17 hr sample).

4.5 Photoconductivity of GaAs:Si:Cu switches fabricated using different processing techniques

The switching experiments for the GaAs:Si:Cu samples are conducted using the Nd:YAG laser as well as the semiconductor laser diode as the excitation source, and the results are shown in the previous sections of this chapter. The energy of the semiconductor laser is much less than that of the Nd:YAG laser (400 mJ maximum for Nd:YAG and about 40 μJ for the semiconductor laser). It is observed that the efficiency of the switch samples processed using the leaky tube diffusion technique is high enough to use the low power semiconductor laser as the excitation source. To compare the photoconductive transients of the samples processed using the three different diffusion techniques, the transients are normalized with respect to the peak conductivity and are shown in Fig. 4.20. The on-state photoconductivity of the GaAs:Si:Cu switch processed using the leaky tube diffusion technique is much larger compared to that of the samples annealed using the closed tube and semi-closed tube technique, 12 times compared to the closed tube and 3 times compared to the semi-closed tube sample.

The low power switching results of the GaAs:Si:Cu samples processed using the closed tube (annealed at 7.8 atm As vapor pressure for 17 hours) and the leaky tube diffusion (annealed for 2 hours) techniques are shown in Fig. 4.21 a and 4.21 b respectively. The photoconductivity measurements are done using the low power semiconductor laser diode to turn the switch on. The leaky tube sample is pulse charged to 20 V and the closed tube sample to 50 V before the application of the laser pulse and the voltage (V_1) at the 50 Ω terminating resistance at the oscilloscope input is plotted along with the voltage pulse (V_2) applied. The photon flux of the incident laser beam calculated from the values given by the manufacturer is in the order of 10^{22} cm^{-2} s^{-1}. Even with this low photon flux, the on-state photoconductivity measured ($1.32 \times 10^{-2}\,\Omega^{-1}$ cm^{-1} at 200 ns) is higher than the dark conductivity ($1.11 \times 10^{-3}\,\Omega^{-1}cm^{-1}$) for the leaky tube sample whereas for the closed tube sample, on-state photoconductivity ($2.8 \times 10^{-4}\,\Omega^{-1}cm^{-1}$) is very close to the dark conductivity ($2.58 \times 10^{-4}\,\Omega^{-1}cm^{-1}$). The resistivity of the closed tube sample is an order of magnitude higher than that of the leaky tube sample.

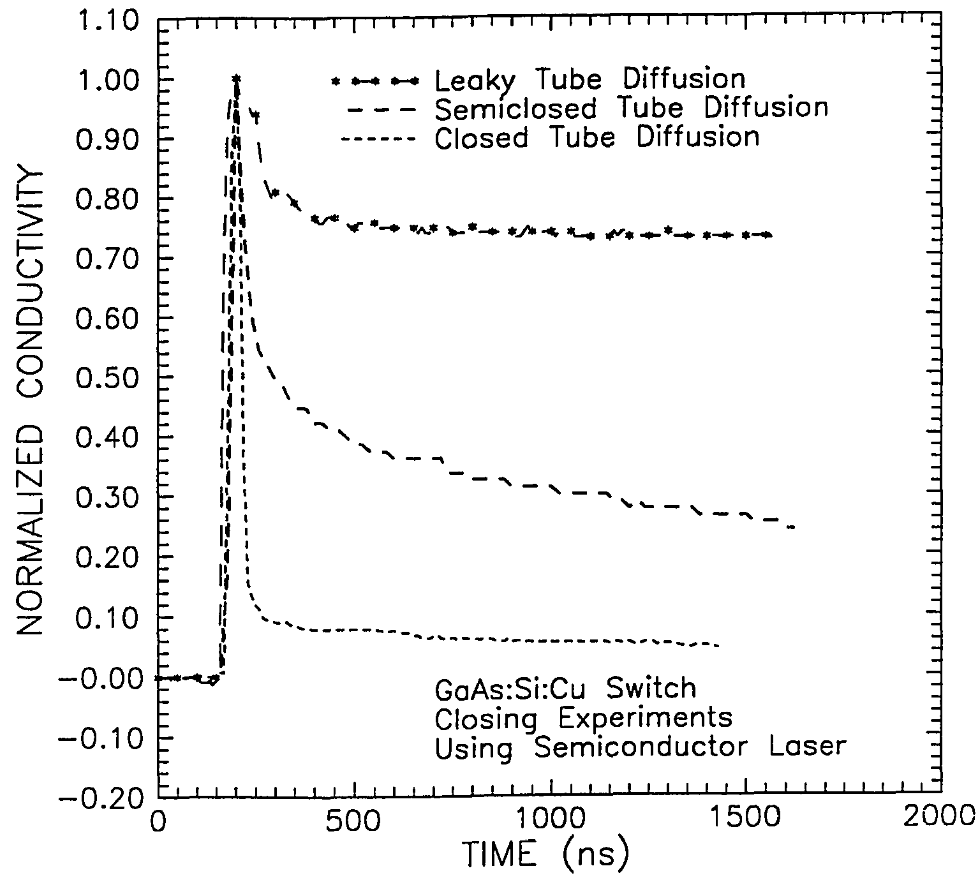


Fig. 4.20 Normalized photoconductivity of GaAs:Si:Cu switches fabricated using three different processing techniques.

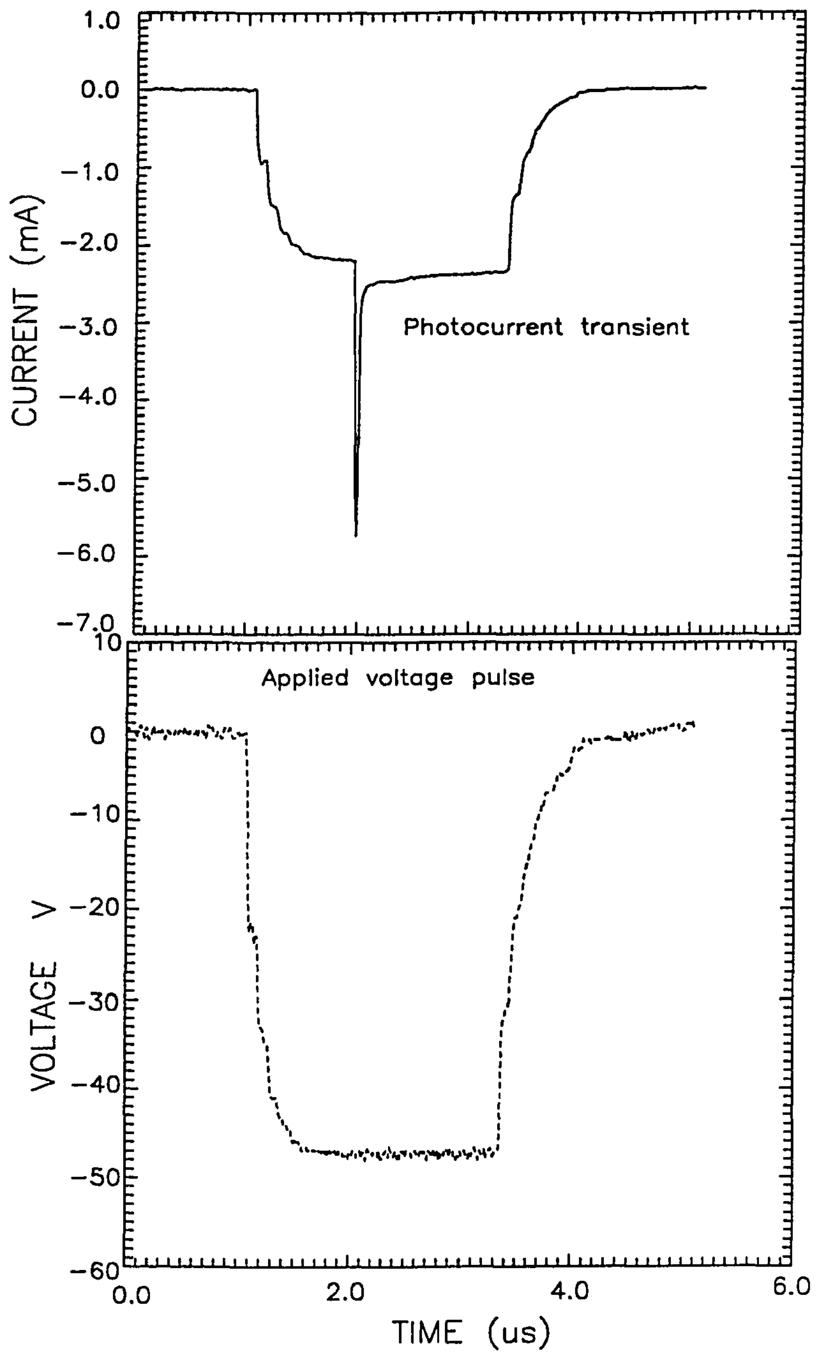


Fig. 4.21a Photoconductive response of GaAs:Si:Cu switches (closed tube diffusion) for semiconductor laser excitation

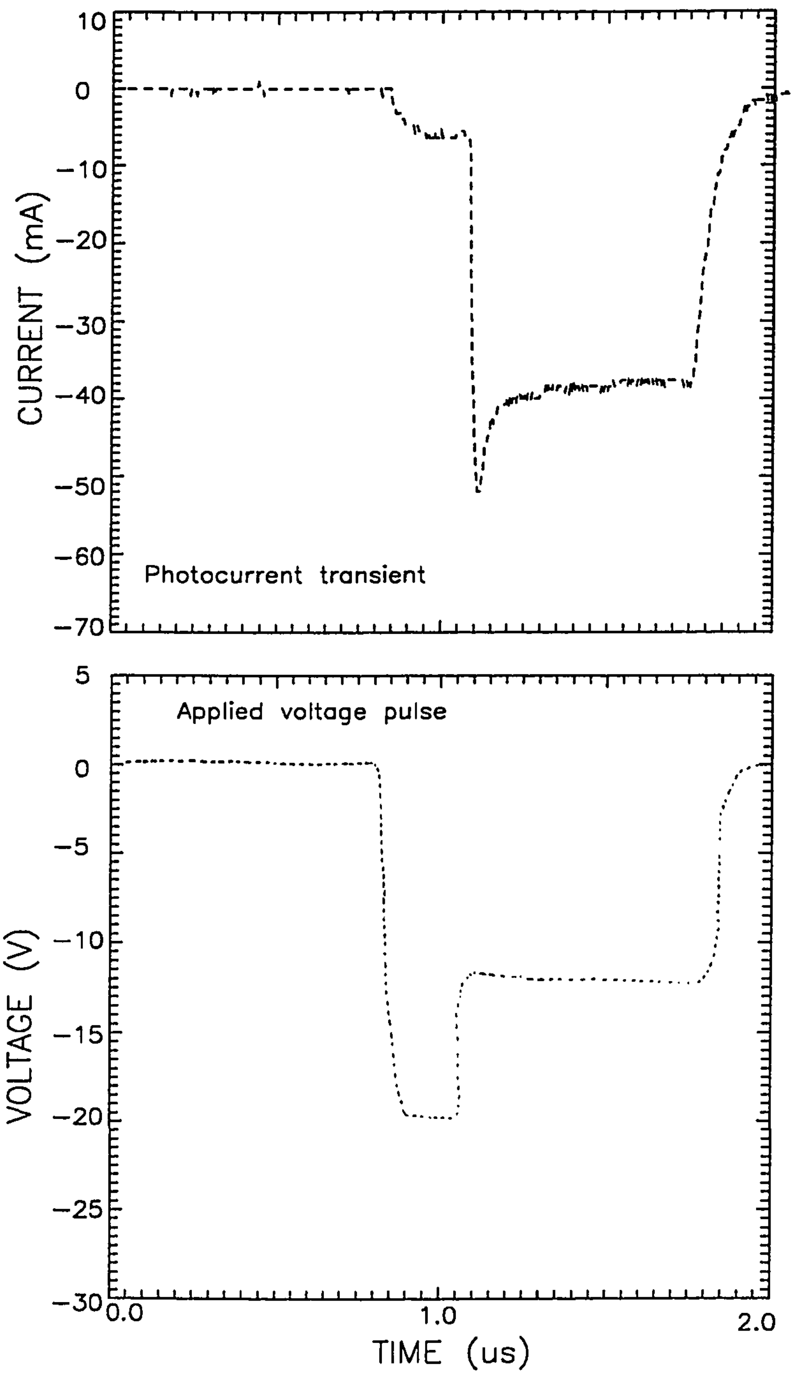


Fig. 4.21b Photoconductive response of GaAs:Si:Cu switches (leaky tube diffusion) for semiconductor laser excitation

The energy of the Nd:YAG used for the switching experiments is measured using the thermal detector and the power meter (made by Scientech). However, the energy of the semiconductor laser is too low to measure using the available detector and the power meter. Therefore, to get an estimate of the energy of the semiconductor laser diode, the switch on-state photoconductivity is measured as a function of laser energy. The photoconductivity measurements are repeated using the high power Nd:YAG laser to turn the switch on and by applying a DC voltage of 15 V across the sample. Fig. 4.22a shows the results of the switching experiments on closed tube sample, the laser energy is set at 185 μJ (1.32×10^{24} cm^{-2} s^{-1}) and the neutral density filter combinations are used to vary the energy of the incident laser beam down to 8 μJ (5.72×10^{22} cm^{-2} s^{-1}). It is seen that the peak conductivity increases as the laser energy increases, however, even at high laser energy, the observed on-state photoconductivity is not much higher than the dark conductivity. Fig. 4.22b shows the photocurrent transients of the leaky tube sample. As the energy of the incident laser increases, the peak as well as the on-state photoconductivity increases. Even at low laser energy, on-state photoconductivity can be clearly seen.

The switching experiments are conducted for all the leaky tube annealed samples, where the current transient is stored in a digitizer (Tektronix 7912) and the voltage transients are stored in the storage oscilloscope. The energy of the incident laser is varied from 0.04 mJ to 9.5 mJ and the amplitude of the applied voltage pulses is varied from 60 V to 1000 V. The turn-on transient of the switch (2 hr sample) as function a laser

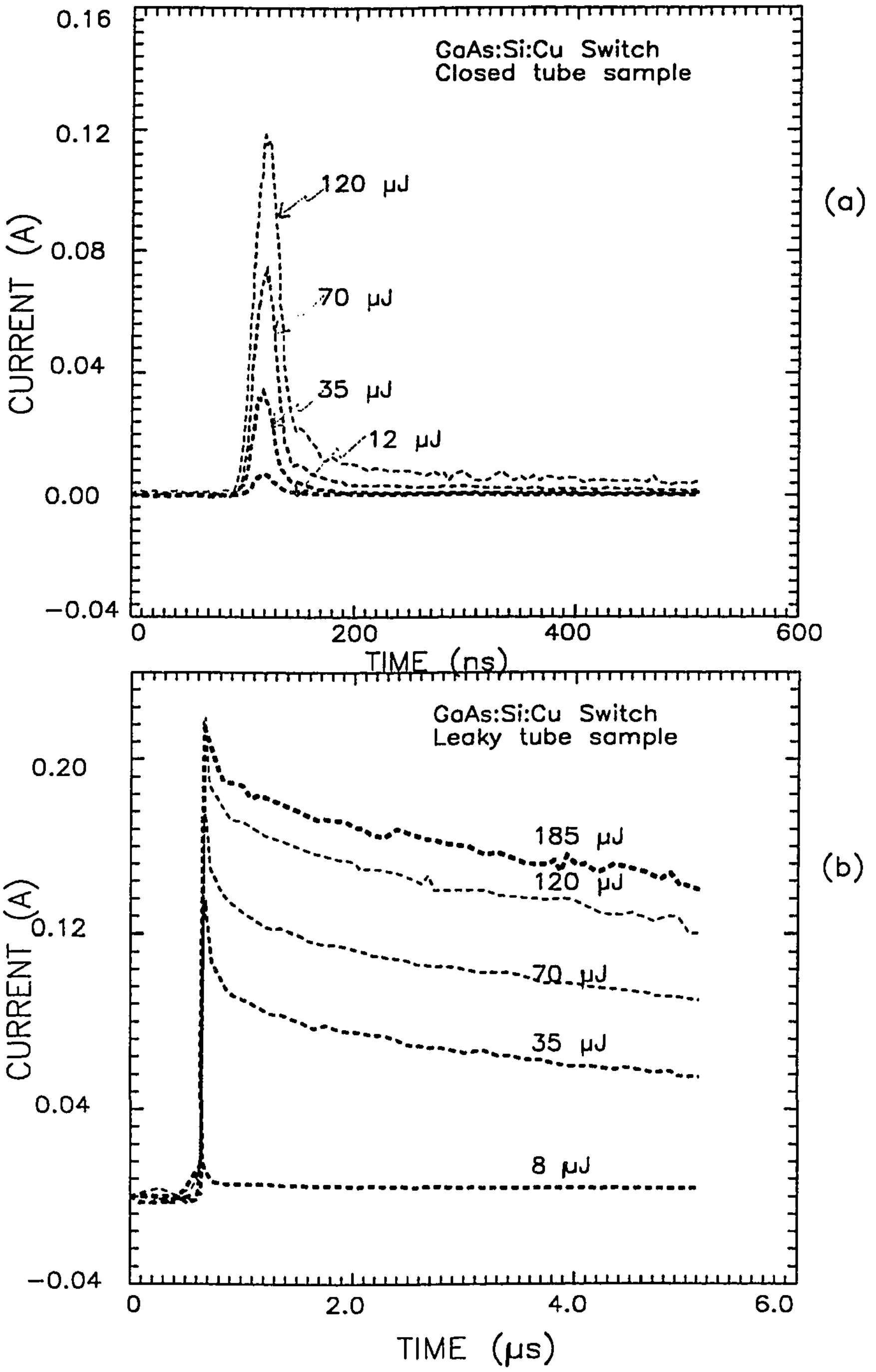


Fig. 4.22 Photocurrent transients of GaAs:Si:Cu switches as a function of laser energies, a) closed tube annealed switch and b) leaky tube annealed switch.

energy is plotted in Fig. 4.23a. A voltage pulse of 60 V and 4 μs duration and 60 V is used. The voltage pulse of 4 μs is used. The laser power is varied using different filters and the power incident on the sample is measured using the power meter and the detector. The photocurrent transients of the switch (2 hr sample) as a function of the applied voltage is shown in Fig. 23b. It is observed from Fig. 4.23a that the on-state photoconductivity saturates as the laser energy increased to about 0.4 mJ, and therefore it is possible that the photoconductive transients of the leaky tube annealed samples shown in the previous sections are above the on-set of saturation.

In summary, the results of the characterization studies and the photoconductivity measurements of the GaAs:Si:Cu switch material fabricated using different processing techniques are presented. A detailed discussion of the presented in this Chapter is included in Chapter 5.

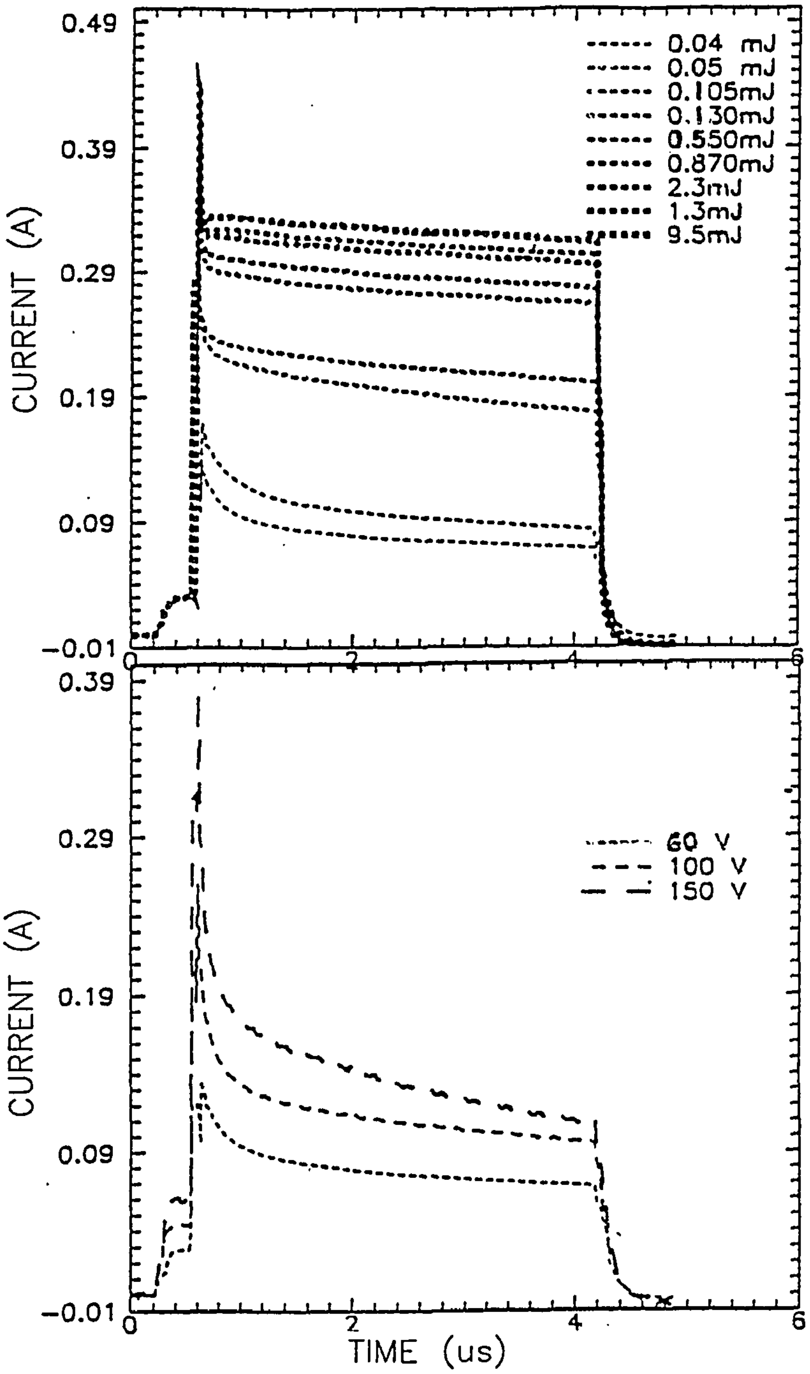


Fig. 4.23 Photocurrent transients of GaAs:Si:Cu switch (leaky tube diffusion, 2 hr) a) as a function of laser (Nd:YAG) energy and b) as a function of voltage applied.

CHAPTER 5

DISCUSSION OF RESULTS AND CONCLUSIONS

The results of the PICTS characterization and the photoconductivity studies on the switch material, GaAs:Si:Cu, presented in Chapter 4 are discussed in this chapter. The objectives of the current research, the fabrication of high efficiency GaAs:Si:Cu switches and the study of the influence of processing techniques on the deep levels formation and on the photoconductivity of the switches are realized. The PICTS characterization results showed that the GaAs:Si:Cu samples annealed using the leaky tube diffusion technique have the highest Cu_B concentration compared to the samples annealed using the semi-closed tube and the closed tube samples. Based on this finding, we expected the highest on-state photoconductivity for the leaky tube samples, and the switching results showed this. For the discussion, the results in Chapter 4 are grouped into four sections: identification of the deep levels due to Cu, influence of processing techniques on Cu deep levels formation and photoconductivity, influence of As vapor pressure on Cu deep levels formation and phtotoconductivity, and capping effect of the deposited Cu film. Also, a discussion of the repeatability of the experiments and the lifetime of the samples is included. The conclusions derived from the results of the current research and the suggestions for future research are included in this chapter.

5.1 Discussion

5.1.1 The levels are due to Cu?

GaAs:Si:Cu, the switch material, has been processed using three different techniques in the present study. The source of Cu was provided by different means and the samples after the Cu diffusion were compensated resulting in high resistivity materials. However, since compensation can be due to many sources, it was necessary to confirm that the deep levels seen in the PICTS spectra of the GaAs:Si:Cu samples were indeed due to the Cu introduced during diffusion. Copper is well known as a fast interstitial diffuser in GaAs, and occupies both interstitial and substitutional lattice sites. Copper introduces many acceptor levels and a donor level ($E_T = 0.07$ eV [54]) in GaAs. The thermal conversion of n-type GaAs to p-type or less n-type GaAs by high temperature heat treatment has been reported earlier [27,55]. It is concluded that thermal conversion at lower temperatures ($<870^0$C) is solely due to Cu, whereas at higher temperatures ($>900^0$C), both Cu acceptors and shallow acceptors (Si) are responsible. In the present study, the GaAs:Si:Cu samples were annealed (semi-closed tube and closed tube) at 550^0C for 17 hours, and therefore, the compensation is due to the Cu deep levels introduced during annealing. Experiments were conducted to confirm that the compensation is indeed due to the Cu deep levels. Two samples, one with Cu source (deposited Cu layer) and one without any Cu source were annealed under the same diffusion conditions of temperature, time and As vapor pressure. The sample with deposited Cu resulted in a high resistivity material ($>$kΩ cm) after annealing. The resistivity of the sample annealed without any Cu was too low (~ Ω cm) to characterize using the PICTS technique. Therefore, a direct comparison of the PICTS spectra of these samples was not possible. Also, Au-Ge contacts were deposited on all samples and were not suitable for DLTS characterization which requires ohmic and Schottky contacts. However, a comparison of the DLTS spectrum of the GaAs:Si shown in Fig. 4.3, and the PICTS spectrum of the GaAs:Si:Cu in Fig. 4.4 clearly shows the change in the deep level structure caused by the Cu diffusion.

The DLTS technique yields complete information on trap parameters including the conductivity type of the trap, but the type determination is not easy using the conventional PICTS technique. The conductivity type has been determined by obtaining the PICTS spectrum by reversing the polarity of the contacts of a sample with sandwich geometry, where one contact is semitransparent for laser excitation [56]. In the PICTS technique, laser pulse is used to irradiate the sample which causes lattice vibrations and leads to a shift of the trap energy levels (Frank-Condon shift). Therefore the trap activation energy calculated by the PICTS technique usually differs from the thermal activation energy. In general, a deviation of ±0.03 eV is included to the calculated trap energy. In the current research, the deep levels of interest are the Cu levels. It is shown in the earlier part of the study that these levels are introduced in the GaAs:Si:Cu samples by the Cu diffusion. In the PICTS characterization of the samples processed under different conditions, the main interest is on the concentration of the Cu deep levels. To calculate the trap concentration, the PICTS technique is not a very reliable method, however, for the characterization of high resistivity materials the PICTS is one of the few techniques available currently. The trap concentration is estimated from the amplitude of the peaks which is dependent on many factors such as the sample geometrical parameters, applied voltage, load resistance, variation of $\mu\tau$ product with the temperature and the time etc. By keeping the experimental conditions and geometrical parameters same, the amplitude of the peaks in the PICTS spectra of different samples can be compared, which gives information on the influence of processing conditions on the concentration of Cu deep levels. Thus, a qualitative study of the trap concentration as a function of processing conditions is possible using the PICTS technique.

5.1.2 Influence of processing techniques on deep levels formation and photoconductivity

The amplitude of the peak in a PICTS spectrum indicates the concentration of the trap level corresponding to the peak. The PICTS spectrum in Fig. 4.4 shows that the amplitude of the Cu_B peak is smaller than that of the Cu_A, i.e., the relative concentration of the Cu_A states is higher than that of the Cu_B states. For the GaAs:Si:Cu samples fabricated using the closed tube diffusion technique (Fig. 4.12), the concentration of the Cu_B states is higher than that of the Cu_A states. For samples annealed using the leaky tube diffusion technique, the amplitude of the Cu_A peak is higher than that of the Cu_B peak as in case of the semi-closed tube samples. The partition ratios ($P = N_{CuA} / N_{CuB}$), for the semi-closed tube, leaky tube and closed tube samples are 16, 1.5, and 0.5 respectively as calculated from the PICTS spectra of the samples (see Fig. 4.4, 4.11, and 4.17). If these partition values are representative of the bulk of the material, the closed tube sample should result in the highest on-state photoconductivity and the semi-closed tube sample, the lowest. However, the switching results showed that the on-state photoconductivity of the closed tube samples is the lowest and that of the leaky tube sample is the highest among the samples diffused using the three different diffusion techniques. The observed on-state photoconductivity of the closed tube sample can be explained, if the peak #4 in Fig. 4.11, is due to an electron trap. The turn-on transient of the closed tube samples is similar to that of a semi-insulating GaAs, i.e., the switch is conducting only while the external laser source is on. The electron trap level can capture the conduction electron, which otherwise could contribute to the persistent photoconductivity of the switch. From the Hall measurements, it is known that two of the samples (TC1, TC2) were n-type and the other two (TC4,TC5) were p-type. The possible origin of this trap is discussed in the following paragraph. However, the interest in the current research effort is the development of the BOSS switch technology and therefore the preceding discussion has been limited to the Cu_A and Cu_B levels.

The closed tube diffusions were conducted primarily to study the influence of As vapor pressure on the Cu diffusion systematically, and the method is chosen because the As vapor pressure could be controlled more accurately compared to the semi-closed tube technique. Even though, the GaAs:Si:Cu switches fabricated were not the best as the photoconductivity results show (lowest efficiency) , this batch of experiments provided information on the Cu diffusion in GaAs, specifically, on the influence of As vapor pressure on the Cu deep levels formation. Ampouling of the samples for the closed tube diffusion was done at the Chemistry Laboratory at the University of Virginia at Charlottesville, Virginia. The possibility of contamination during the cleaning of the quartzware and the ampouling procedure can not be ruled out. In practice, it is not easy to conduct diffusion of Cu using the closed tube technique in a research environment, because for each experiment the samples need to be ampouled separately.

The PICTS spectrum of the GaAs:Si:Cu sample annealed in the leaky tube diffusion system shown in Fig. 4.17 is similar in characteristics to the PICTS spectrum obtained for the semi-closed tube sample (see Fig. 4.4). For both the samples, the concentration of the Cu_A is higher than that of Cu_B. For the semi-closed tube sample the amplitude of the Cu_B peak is much smaller compared to the remaining peaks whereas for the leaky tube sample, the Cu_B peak is one of the prominent peaks among the remaining peaks. For the leaky tube sample, Cu doped glass (Cu source) was present on both the surfaces of the sample which acted as a capping layer. The prominent peak in the PICTS spectrum of the closed tube sample is in the temperature region of 143 - 200 K, whereas for the leaky tube sample, peaks in this region are smaller in amplitude than the Cu_B peak. The PICTS spectra of the samples annealed using the leaky tube diffusion technique do not vary much as a function of annealing time. The PICTS spectra of all the three samples (annealed for 2, 10, and 17 hours), show same number of peaks and the Cu_A peak (#1) has the highest amplitude.

In the present study, diffusion of Cu using the semi-closed and closed tube diffusion technique was carried out with a thin film of Cu deposited only on one surface (surface A) of the GaAs:Si. The opposite surface (surface B) was exposed to the ambient. The PICTS spectra shown in Chapter 4 are taken from the surface A of the sample (unless otherwise stated). The penetration depth of the probing laser pulse for PICTS spectra was about 1 μm. Hence, the information on the deep level data obtained from these spectra is predominantly for the surface of the sample. Therefore, a high concentration of the Cu deep levels as indicated by the large amplitude of the peaks in the PICTS spectra may not always results in a large on-state photoconductivity for the switch samples, since the on-state photoconductivity is a property of the bulk material.

5.1.3 Influence of As vapor pressure on Cu deep levels formation and photoconductivity

Gallium arsenide, being a compound semiconductor decomposes when heated to give a Ga-rich liquid phase and As_2 and As_4 in the vapor. Above 637°C, the evaporation is not congruent and the surface becomes non-stoichiometric. At lower temperatures (< 637°C), evaporation will be congruent and the vapor will have the same composition as the solid phase. When external As source is provided in the diffusion chamber, arsenic vapor pressure influences the diffusion process in GaAs by changing the concentration of Ga and As vacancies, and the concentration of Cu available for diffusion. The decrease in Cu solubility in GaAs with an increase in the As vapor pressure increased has been reported earlier [22,57], and the reason for the decrease is attributed to the dilution of Cu in the liquid phase due to the added As. If peak #1 and #2 (Fig. 4.5) are due to Cu_{Ga} and Cu_{Ga} Si_{Ga} respectively, a decrease in the available Cu leads to a decrease in the substitutional Cu and thus can explain the decrease in the amplitudes of these peaks as a function of As vapor pressure. In previous studies, Cu_A and Cu_B levels were attributed to various complexes such as: Cu_{Ga} and Cu_{Ga} V_{As}, Cu_{Ga} V_{As} and V_{As} Cu_{Ga} V_{As}, Cu_{Ga} V_{As}

and Cu_{Ga} V_{As} Cu_{Ga}, and V_{As} Cu_{Ga} V_{As} and Cu_{Ga} V_{As} respectively (Ref. 58 and references therein). Copper entering a Ga site can form a complex with one V_{As} (As vacancy) to form Cu_{Ga} V_{As} first, and then react with one more V_{As} to form V_{As} Cu_{Ga} V_{As}. But the formation of V_{As} Cu_{Ga} V_{As} is a slow process. However, since all of our samples (semi-closed tube diffusion) were annealed for 17 hours, the formation of this complex is possible.

The concentration of Cu_B on surface A does not change significantly with As pressure (Fig. 4.5). If Cu_B level is due to the complex, V_{As} Cu_{Ga} V_{As}, a change in the available Cu for diffusion should lead to a decrease in the amplitude of the peak corresponding to this level. However, two As vacancies are involved in the formation of V_{As} Cu_{Ga} V_{As}, and a change in the concentration of V_{As} results in a higher concentration of the complex. In the present study, the deposited Cu capping layer on the surface A prevents the escape of As from that surface, and the concentration of V_{As} remains constant. Cu_{Ga} forms a complex with the available V_{As}, and any change in the available Cu is reflected only in the concentration of Cu_{Ga}, and the complex Si_{Ga} Cu_{Ga}. This point is made clearer when the PICTS spectrum from surface B, where no Cu layer is present, is discussed later in this chapter. van de Ven *et al.* [26] have studied diffusion of Cu in doped and undoped GaAs under different As vapor pressure, where the source of Cu was the quartz ampoule used. In their study, since both the surfaces of the sample were exposed to the ambient, the concentration of vacancies varied with the As vapor pressure. It is known that the concentration of Ga and As vacancies in GaAs is influenced by the

As vapor pressure, however, in the present study, the concentration of V_{As} and V_{Ga} will not change significantly at the surface A due to the presence of Cu layer.

The photoconductive transients of the switch samples annealed using the semi-closed tube system (Fig. 4.9) show that the photoconductivity of the sample, annealed at the highest As vapor pressure, reached the saturation conductivity. For the samples annealed at lower As vapor pressures, the conductivity decays and the decay rate is faster compared to the samples annealed at the higher As vapor pressure. The PICTS spectra of the semi-closed samples (Fig. 4.4) showed that the concentration of the Cu_A states is decreased as the As vapor pressure is increased, whereas, the concentration of the Cu_B states remained almost the same at the surface A, i.e., the partition ratio decreased as the As vapor pressure is increased. As the partition ratio decreases, the switch photoconductivity should increase, as is observed in Fig. 4.9 (experimental) and Fig. 4.2 (simulation results). Thus the characterization results of the semi-closed tube samples are in agreement with the photoconductivity measurements.

For the samples annealed using the closed tube diffusion technique at higher As vapor pressure, the PICTS spectra (Fig. 4.12) show more peaks compared to those annealed at lower As vapor pressure. At higher As pressure, the concentration of As vacancies is low compared to the concentration of Ga vacancies, and consequently, concentration of the deep levels involving V_{As} will be lower. The GaAs:Si:Cu samples annealed at low As vapor pressure (closed tube diffusion) has the highest mobility value (Table 4.1) which indicated the lowest compensation. Since the efficiency of the GaAs:Si:Cu switches processed using the closed tube diffusion technique was very low, the influence of As vapor pressure on the on-state photoconductivity of these samples could not be studied in detail. The sample annealed at one atm As vapor pressure reached the steady state faster and has the lowest on-state photoconductivity compared to all the other samples (Fig. 4.16a and 4.16b).

5.1.4 Photoconductivity of GaAs:Si:Cu switches processed using leaky tube and closed tube technique

The photoconductivity measurements on the switch fabricated using the three different techniques show that the leaky tube sample resulted in high on-state photoconductivity (Fig. 4.20 and 4.21). It is to be pointed out that the annealing time for the samples used to compare the switching results (Fig. 21a and 4.21b) are different (17 hours for the closed tube and 2 hr for the leaky tube sample). However, the photocurrent transients in Fig. 19 show that the on-state photoconductivity is not varied much as the annealing time varied from 2 hr to 17 hr. Experiments conducted on the closed tube sample by applying higher voltages (upto 200 V) using Nd:YAG laser as the excitation source, did not result in any considerable increase in the on-state conductivity. The absence of the on-state conductivity for the closed tube sample is indeed the material property, i.e., the amount of Cu_B states introduced in the material by this technique is not sufficient to result in an on-state conductivity. For the leaky tube sample, even with a very low applied voltage (20 V) and photon flux (~ 10^{22} cm^{-2} s^{-1}), the on-state conductivity is an order of magnitude higher than that of the dark conductivity. At higher photon flux values, on-state conductivity is higher. The quantum efficiency (η - the number of electrons generated per incident photon) of the leaky tube samples is found to be 0.015 which is larger than that of the closed tube sample by two orders of magnitude. Even though the η values are low, the relative improvement is striking which is due to the fact that the right Cu levels in greater concentration can be introduced in GaAs:Si by the leaky tube diffusion. However, these values are approximate since the mobility values used are assumed values.

The closed tube GaAs:Si:Cu switch sample, for which the photocurrent transients are shown in Fig. 21a, is p-type as indicated from the Hall measurements data ($\mu_H = 427$ cm^2 / V s). For the leaky tube samples used in this study Hall measurement data is not available and hence the information on the compensation level of the material can not be given. However, switch samples were fabricated for different annealing times and all of the samples showed on-state conductivity as is seen in Fig. 19. Compensation process in semiconductors depends on many parameters such as temperature, impurity levels present in the material etc. It is seen that the amount of compensation is almost same for the samples annealed for different times. We have fabricated the switches using the closed tube technique and the leaky tube technique, keeping the diffusion parameters, time and temperature constant. However, the results shown in the present study for the leaky tube sample are for only one diffusion temperature. Since temperature is a critical parameter which determines the compensation process in semiconductors, resistivity and conductivity type of the switch material, samples annealed at various diffusion temperatures need to be studied. As pointed out earlier these techniques differ in many aspects such as the source of copper and the diffusion system, and our aim was to compare the on-state photoconductivity of the samples fabricated using the two techniques. Using the leaky tube technique, it is seen that we have successfully introduced more Cu into the GaAs:Si.

5.1.4 Repeatability of the experiments and lifetime of the samples

The PICTS experiments on all the samples studied in the present work have been repeated. The PICTS spectra which were taken after a period of about one month, showed the same characteristics which indicated that the material properties did not change within the period of time of the experiments. The photoconductivity measurements on the samples were repeated four to five times under different experimental conditions. The switching experiments on the leaky tube samples were repeated over a period of eight months, using both the semiconductor laser diode and the Nd:YAG laser excitation. The results indicated that the switch material properties were maintained. However, during the last set of experiments, the switches were exposed to high laser intensities (up to 9.5 mJ) as well as high electric fields (up to 20 kV/cm). The low switching experiments repeated on one of the leaky tube sample (10 hr) after 16 months period, did not result in the previously observed on-state photocurrent. The actual reason for the degradation of the switch properties is not clear at this time, though, many factors can contribute toward this. Aging of the samples could be one reason. In the present case, in addition, it is also probable that the exposure of the sample to the high electric and high laser intensity made the aging of the sample faster. It is well known that Cu levels in GaAs change their structural property over a long period of time (e.g., two years). This behavior needs more investigation since it is beyond the scope of the current work.

5.1.5 Capping Effect of the deposited Cu layer

To study the possible capping effect of the deposited Cu layer on the formation of the deep traps, separate PICTS measurements were made with laser radiation incident on either surfaces A and B of the switch, for the same sample. The PICTS spectra show different characteristics depending upon which surface the laser is incident (see Fig. 4.6). The spectra are for a sample diffused with As vapor pressure in the diffusion chamber, which is cut into two, on one Au-Ge contacts are deposited on the surface A and on the other the contacts are on surface B. It is seen that the amplitude of peaks #3, #4, and #5 (corresponding to the Cu complexes) is much higher when the PICTS spectrum is taken from surface B. It is therefore possible that the deposited copper on the surface A acts as a capping layer during diffusion, and thereby preventing As to escape from the surface A. Since As can escape more readily from the surface B during diffusion, the concentration of As vacancies will be much higher near this surface compared to the surface A and subsequently favors the formation of Cu complexes with these vacancies. Tin *et al.* [58] have studied the capping effect of the deposited Cu film during diffusion in LEC SI GaAs by annealing the samples at 550°C for 12 hours (our samples were annealed at 550°C for 17 hours). Based on the results of their study, they have proposed that one of the Cu-related levels ($E_T = 0.52$ eV) is due to V_{As} Cu_{Ga} V_{As}. They found that the amplitude of the peak due to this level is maximum in the PICTS spectrum from surface A and is minimum in that from surface B. In the present study, three peaks are observed whose amplitudes are much higher in the PICTS spectrum from surface B compared to that from surface A. Hence, these peaks are probably due to Cu complexes involving As vacancies.

In case of samples annealed using the closed tube diffusion system, the characteristics of the PICTS spectra taken at different depths from the surface A are *strikingly* different from that of semi-closed tube sample. The amplitude of peak #5 is larger than peak #1 near the surface A (curves 1 and 2 in Fig. 4.13), whereas near the surface B (curves 3 and 4) the amplitude of peak #5 is very small. A collection of small peaks appear in the temperature region 220 - 320 K for the spectrum taken at the surface B. For the surface A spectrum also, a broad peak of very small amplitude appears but is shifted more towards the high temperature.

The amplitude of the peak #1 (Cu_A) appears to be almost same at the surface A. However at greater depths in the crystal, the amplitude of the peak #1 increases first, then decreases and has the lowest amplitude at the surface B. This indicates the presence of a gradient in the concentration of the Cu_A states which is attributed to Cu_{Ga}. The concentration of vacancies are higher at the surfaces of the crystal compared to the bulk, and therefore, the formation of deep levels involving As vacancies are favored at the surface. In the bulk of the material, Cu occupies the substitutional sites. Thus the concentration of the Cu_{Ga} is expected to be low at the surfaces and high in the bulk which supports our findings from the PICTS spectra. At surface B, the concentration of As vacancies is higher than that at surface A for our samples because of the capping effect of the deposited Cu film, and the formation of Cu deep levels involving vacancies is favored. This explains the smallest amplitude for the Cu_A peak at the surface B compared to that at surface A.

The variation in the amplitude of the various peaks in the PICTS curves of Fig. 4.13, clearly indicates the presence of the concentration gradient of various deep levels across the cross section of the GaAs:Si:Cu crystal. As in case of the semi-closed tube samples, at surface B (curve 4 in Fig. 4.13) a number of peaks appear in the temperature range 200 - 300 K whose amplitude is higher than that of the peak #1. The amplitude of these peaks is smallest in curve 1 and largest in curve 4. These results confirm the findings from the semi-closed tube samples. Due to the capping effect of the deposited Cu layer, the concentration of the vacancies near the surface A did not change considerably. Hence, the Cu_{Ga} forms complexes with the available V_{As}.

From the results of the characterization study of the semi-closed tube GaAs:Si:Cu samples, it is seen that the concentration of Cu_B level (N_{CuB}) is higher where the concentration of As vacancies (V_{As}) is higher in the crystal. Also, it is seen that due to the capping effect of deposited Cu layer, the concentration of V_{As} on surface A is not altered. Thus, the N_{CuB} appears to have a gradient along the cross section of the material. However, since Si doping is expected to be uniform throughout the sample, a gradient in N_{CuB} leads to a gradient in Cu compensation. Hence, regions where compensation is higher could be less n-type (or p-type in case of overcompensated samples). As discussed earlier, the main objective of the present study was to establish processing conditions to fabricate GaAs:Si:Cu switches with high on-state conductivity. A homogeneous distribution and increased concentration of Cu_B level in the Cu diffused GaAs:Si are desired to obtain an increased photoconductivity. From these results it is concluded that by providing an external Cu source and exposing both the surfaces to the ambient will lead to a more homogeneous, Cu_B rich GaAs:Si:Cu.

For the leaky tube annealed samples, Cu-doped glass is present on both the surfaces as the protective layer to prevent the As escape, and as the Cu source. Therefore, the PICTS spectra from both the surfaces should be of the same characteristics, and the gradient in the Cu deep levels should be observed in the PICTS spectra at different depths from the surface. However, it is to be pointed out that only one surface of the GaAs wafers used for the study were polished and this can lead to some differences in the PICTS spectra from both surfaces.

GaAs:Si wafers polished only on one surface is used to diffuse Cu using the leaky tube technique, to have the same starting material for all three different diffusion techniques used. Characterization studies of the semi-closed tube and closed tube annealed GaAs:Si:Cu samples showed that a higher concentration of V_{As} leads to higher concentration of Cu_B. This was another reason for using the wafers with one side polished because the unpolished side with a higher concentration of vacancies can act as a gettering agent for the formation of the Cu_B states.

5.2 Conclusions

Diffusion of Cu in GaAs:Si using the leaky tube technique with spin-on coating source has been investigated for the first time in the present research. It is well known that the formation of deep levels in GaAs is dependent on the growth technique and the diffusion conditions. From the results of the present study, it is found that the deep level structure of the compensated GaAs:Si samples is different depending on the techniques used for Cu diffusion. The GaAs:Si:Cu switches were fabricated using the three different processing techniques and the photoconductivity of the samples was studied. Samples for which Cu diffusion was done using the leaky tube technique with Cu doped spin-on coating on both the surfaces of the sample were, the most efficient among the switches studied.

Diffusion of Cu in GaAs is a complex process. We have studied the influence of As vapor pressure during diffusion on the formation of various Cu related complexes. Capping effect of the deposited Cu layer has been investigated, and the results indicated the existence of a gradient in the concentration of the Cu deep levels in the switch material. The concentration of Cu related complexes on the surface with out the capping layer is found to be much higher compared to that with the capping layer and it is proposed that the levels are due to Cu related complexes involving As vacancies. The Cu_B level is attributed to the complex, $V_{As}\ Cu_{Ga}\ V_{As}$ and the Cu_A level is attributed to Cu_{Ga}. Also, a level with activation energy 0.32 eV has been identified which is attributed to $Si_{Ga}\ Cu_{Ga}$ complex. The variation in the Cu compensation at different depths from the surface of the GaAs:Si:Cu samples can be eliminated by providing an external Cu source and exposing both surfaces to the ambient.

The presence of the gradient in the concentration of Cu deep levels in the GaAs:Si:Cu switch material is clearly established from the results of the present research.

The concentration gradient can result in some undesirable effect for switching applications depending on the switch geometry. In a semiconductor material with trap levels, the traps can be filled by providing external excitation. The I-V curve of such materials shows that when all the traps are filled the increase in the current is not a linear function of voltage. When the concentration of the Cu_B states is higher at one surface, rate of trap filling is higher in that region and this consequently can provide a conductive path when the traps are filled in that region. The high current regions (or filamentation) observed in the material for switching experiments conducted in our laboratory can probably be due to the concentration gradient of the Cu deep levels in the material. It is to be pointed out that the switch geometry plays a role in the formation of the high current regions. To study this aspect in detail, switching experiments need to be conducted with samples of both sandwich as well as planar geometry, fabricated under identical processing techniques.

The processing conditions influence the formation of various Cu deep levels in GaAs:Si. It is found that for the GaAs:Si samples annealed by providing an external source of Cu (quartz) to eliminate the capping effect, the Cu compensation is not high enough (resulting in low resistivity samples) for our switching applications. The better turn-on performance of the leaky tube samples is indeed due to a higher concentration of the Cu_B states compared to that of the closed tube and semi-closed tube sample.

In summary, diffusion of Cu in GaAs:Si is studied using the three different diffusion techniques. Using the closed tube and the semi-closed tube diffusion techniques, influence of As vapor pressure on the Cu deep levels formation and switch photoconductivity is investigated. Using the leaky tube technique, the effect of diffusion time on switch photoconductivity is studied. Five sets of samples were fabricated using each technique, and the characterization studies (PICTS and Hall measurements) and low power photoconductivity measurements yielded a wealth of information on the deep level structure in the GaAs:Si:Cu switch material. Polishing of the GaAs:Si:Cu after the diffusion process is found to be a very critical step in obtaining good samples. If the surface finish is not good, it can result in high dark current and poor switch samples. Among the five sets of samples fabricated using the leaky tube technique, two sets of samples had high dark current and the switching response (with respect to persistent photoconductivity) was negligible. The surfaces of these samples were not smooth after polishing and this damaged surfaces lead to the high leakage current.

From the results of the switching experiments on the GaAs:Si:Cu samples processed using the three different techniques, it is clearly established that the leaky tube diffusion technique is a better choice for the diffusion of Cu in GaAs. This conclusion is primarily based on the efficiency of the switches, however, it is strongly supported by two other factors, the relative ease to conduct the diffusion using the system as well as the safety of operation of the system. The semi-closed technique is the next best choice when we compare the efficiency of the switches, however, when considering the safety aspects, this technique is least preferred. One of our research goals was to successfully demonstrate the turn-on switching experiments using the low power semiconductor laser diode as the excitation source, and the GaAs:Si:Cu samples fabricated using the leaky tube diffusion technique are found to be the best candidate for this purpose. This is one step closer to the target of replacing the large, space consuming solid state lasers by the table top semiconductor lasers for switching purposes.

5.3 Future Research

The leaky tube diffusion technique has been applied for the diffusion of Cu in GaAs, to the best of our knowledge, for the first time in the present study. The influence of diffusion time on the diffusion of Cu using this technique is investigated here. The diffusion temperature is kept at 550°C which is the temperature used for the closed tube and semi-closed tube diffusion. An earlier experiments using the semi-closed diffusion, indicated that diffusion at 550°C results in compensated samples. Influence of other diffusion parameters, such as diffusion temperature, thickness of the spin-on coating, dopant concentration in spin-on coating etc. on GaAs:Si:Cu switch material properties need to be studied using the leaky tube system.

For switching applications, the aim is to introduce more Cu_B states in the material. GaAs:Si wafer polished only on one surface is used to fabricate the samples studied to have the same starting material for all three different diffusion techniques used. The characterization studies of the semi-closed tube and closed tube annealed GaAs:Si:Cu samples showed that a higher concentration of V_{As} leads to higher concentration of Cu_B. This was another reason for using the wafers with one side polished surface in current investigation, because the unpolished surface side with a higher concentration of vacancies can act as a gettering agent for the formation of the Cu_B states. Experiments could be conducted with wafers polished on both sides and one side polished to study the gettering effect of the unpolished surface. To study the effect of the concentration gradient and switch geometry on the switch performance, experiments could be conducted with samples of planar as well as sandwich geometry, fabricated under identical processing conditions. The results may enable us to explain the occurrence of high current regions and filamentation during switching.

As discussed earlier in this chapter, spin-on dopant source is a limited source and is used in semiconductor processes where accurate control of the concentration of the dopant is not critical. Theoretical analysis of the diffusion process using this technique is not studied in detail and therefore is considered as an avenue for future research.

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