Abstract

This review paper discusses different synthesis methods and characterization techniques of gallium Phosphide for its application in various fields.

Keywords: Gallium phosphide; Band gap; Thin film; Thick films; nanocomposite; EMI Shielding; III-V semiconductors; photo thermal deflection spectroscopy; molecular beam epitaxy.

1. Introduction

III-V-based alloys and heterostructures have been attracting much interest because of their great device applications as well as their fundamental importance. A major issue of composing III-V-based systems is the miscibility gap in solids by Stringfellow GB (1982). It is known that the mixing enthalpy of the systems, such as GaAs-GaSb and GaP-GaSb, is proportional to the square of the difference in lattice constant of the two end binary components of the system by Stringfellow GB (1974). This reason prohibits the epitaxial growth of most alloys at ordinary growth temperatures by Pessetto JR and Stringfellow GB (1983).
Therefore, the epitaxial growth of these systems was not achieved until the first growth of GaAs-GaSb was done in 1979 by carrying out the growth under a high-supersaturation condition, such as molecular beam epitaxy (MBE) by Waho T et al. (1977). The ternary alloy gallium phosphide antimonide (GaP1−xSbx) was grown on GaAs for the first time using the organometallic vapor-phase epitaxy method by Jou MJ et al. (1988). Since then, there has been a lack of work on gallium phosphide antimonide as well as on the transport behavior in such material.

Among all the III-V semiconductors, gallium phosphide (GaP) is an excellent candidate to be part of a high band gap solar cell in a multijunction system, due to its band gap (2.26 eV) and well developed grown technology by epitaxial techniques by X. Lu et al. (2009). It has usually been grown in crystalline form by using epitaxial techniques, mainly for applications in optical devices, light-emitting diodes (LEDs), photo cells, and it is one of the most promising materials for development of solar cells by J. Gao et al. (2011). Moreover, GaP-based ternary and quaternary compound semiconductors, such as InGaP and AlInGaP, provide several interesting properties which are suitable for multijunction solar cell applications by M. Yamaguchi et al. (2005). In contrast with a-Si, amorphous GaP (a-GaP) has a variety of localized states, like wrong bonds or dangling bonds with respect to the individual elements (III and V elements) of its composition and coordination. For that reason, a-GaP has been used in applications, such as LEDs and high-temperature transistors by N. Elgun et al. (1994). The flexibility of its energy gap should be useful for tuning wide area tandem solar cells in the near future. In the photovoltaic field, a-GaP has the advantages of being relatively cheap, low temperature deposition and the possibility of growth on a variety of substrates, including glass, metal and plastic, with diverse commercial applications by J. Nelson (2003) being its visible light absorption higher than that reported for crystalline structure by J.E. Davey and T. Pankey (1969). As mentioned above, epitaxial techniques have mainly been used to obtain crystalline GaP thin films; however, several deposition methods have also been used for the preparation of amorphous and crystalline GaP thin films, like plasma enhanced chemical transport deposition (PECTD) by J.H. Xu et al. (1991), evaporation by J.E. Davey and T. Pankey (1969), D.F. Barbe and N.S. Saks (1973), plasma deposition by J.C. Knights and R.A. Lujan (1978), liquid phase epitaxy (LPE) by X. Lu et al. (2009), S.R. Huang et al. (2009), ion beam assisted deposition and sputtering by J. Gao et al. (2011), N. Elgun and E.A. Davis (2003), N. Elgun et al. (1992), K. Starosta, J. et al. (1979), A.P. Mora et al. (2005), Y.P. Li, Z.T. Liu (2010). Among these deposition techniques, radio frequency (rf) sputtering is known to be suitable for large-scale applications in device fabrication at a relatively low cost by A.P. Mora et al. (2005). Compared with other deposition techniques, rf sputtering does not involve high temperature deposition, in both source material and substrate, which is particularly advantageous as it is known that the atomic bond between Ga and P dissociates at high temperatures, resulting in the volatilization of the phosphorous by J. Gao et al. (2011).

2. Synthesis and characterisation

Zhanjun Gu et al. (2008) synthesized Gallium phosphide (GaP) nanowires in a high yield by vapor-phase reaction of gallium vapor and phosphorus vapor at 1150 °C in a tube furnace system. The nanowires have diameters in the range of 25-100 nm and lengths of up to tens of micrometers. Twinning growth occurs in GaP nanowires, and as a result most nanowires contain a high density of twinning faults. Novel necklace like GaP nanostructures that were formed by stringing tens of amorphous Ga-P-O microbeads upon one crystalline GaP nanowires were also found in some synthesis runs. This simple vapor-phase approach may be applied to synthesize other important group III-V compound nanowires. The growth was conducted inside a tube furnace system, as that shown in Figure 1.
V.A. Krasno et al. (2008) developed the technique of obtaining of p+-n-type gallium phosphide diode epitaxial structures from liquid phase as well as pilot samples of diode temperature sensors were fabricated based on them. Thermometric and current-voltage characteristics of the test diodes were measured in the temperature range of 80÷520K and their basic technical characteristics were determined. The purpose of the work in this paper is to work out and to test the technology of fabricating of GaP-based diodes of p+-n-type with design and technological parameters that ensure their application in high-temperature thermometry. An availability of application of the structures developed as sensing elements of high-temperature heat sensors are also discussed.

Alexander Dobrovolsky et al. (2013) studied recombination processes in GaP/GaNP core/shell nanowires (NWs) grown on Si by employing temperature-dependent continuous wave and time-resolved photoluminescence (PL) spectroscopies. The NWs exhibit bright PL emissions due to radiative carrier recombination in the GaNP shell. Though the radiative efficiency of the NWs is found to decrease with increasing temperature, the PL emission remains intense even at room temperature. Two thermal quenching processes of the PL emission are found to be responsible for the degradation of the PL intensity at elevated temperatures: (a) thermal activation of the localized excitons from the N-related localized states and (b) activation of a competing non-radiative recombination (NRR) process. The activation energy of the latter process is determined as being around 180 meV. NRR is also found to cause a significant decrease of carrier lifetime.

J. C. Knights and R. A. Lujan (1978) reported the preparation of thin films of gallium phosphide and gallium nitride by deposition from low pressure rf-excited plasmas in mixtures of trimethylgallium with ammonia and phosphine respectively. With the deposition conditions used, the gallium phosphide is found to be amorphous, while the gallium nitride is polycrystalline. We present preliminary measurements of optical and electrical properties.

Yangping Li and Zhengtang Liu (2010) employed Radio-frequency (RF) magnetron sputtering to prepare gallium phosphide (GaP) thick films on zinc sulfide (ZnS) substrates by sputtering a single crystalline GaP target in an Ar atmosphere. The infrared (IR) transmission properties, structure, morphology, composition and hardness of the film were studied. Results show that both amorphous and zinc-blende crystalline phases existed in the GaP film in almost stoichiometric amounts. The GaP film exhibited good IR transmission properties, though the relatively rough surface and loose microstructure caused a small loss of IR transmission due to scattering. The GaP film also showed a much higher hardness than the ZnS substrate, thereby providing good protection to ZnS.

D. Pastor et al. (2009) investigated the pulse laser melting (PLM) effects on single crystal GaP. The samples have been studied by means of Raman spectroscopy, glancing incidence X-ray diffraction (GIRXD), van der Pauw and Hall effect measurements. After PLM process, the Raman spectra of samples annealed with the highest energy density show a forbidden TO vibrational mode of GaP. This suggests the formation of crystalline domains with a different orientation in the GaP PLM region regarding to the GaP unannealed region. This behavior has been corroborated by glancing incidence x-ray diffraction measurements. A slightly increase in the sheet resistivity and a suppression of the mobility in PLM samples have been observed in all the measured temperature range. Such annealing effects are a cause of great concern for intermediate band (IB) materials formation where PLM processes are required first, to recovery the lattice crystallinity after high dose ion implantation processes and second, to avoid impurities outdiffusion when the solid solubility limit is exceeded.

Frank J. P. Schuurmans et al. (1999) developed a photo-assisted electrochemical etching technique to fabricate macropores in single-crystalline gallium phosphide (GaP) with variable porosity. Scanning electron microscopy and x-ray diffraction experiments confirm that the material consists of three-dimensional, interconnected random networks with pore sizes of about 150 nanometers. Optical transmission measurements demonstrate that the nonabsorbing disordered structures strongly scatter light. The photonic strength is controlled by filling the pores with liquids of different refractive indices. Macroporous gallium phosphide filled with air has the highest scattering efficiency for visible light.

Janik Wolters et al. (2013) studied thermo-optical effects in gallium phosphate photonic crystal cavities in the visible. By measuring the shift of narrow resonances we derive the temperature dependency of the local refractive index of gallium phosphide in attoliter volumina over a temperature range between 5 K and 300 K at a wavelength...
of about 605 nm. Additionally, the potential of photonic crystal cavities for thermooptical switching of visible light is investigated.

John e. davey and Titus pankey (1969) observed optical absorption-edge shifts of up to 1.5 eV for GaP films deposited in textured polycrystalline states and in the amorphous state. The amorphous-crystalline transition occurs for a substrate temperature \( T_s \) of about 240°C. The films deposited at 240°C \( \leq T_s \leq 270°C \) exhibiting the large optical absorption-edge shift are nontransparent, metallic-appearing, and exhibit a strong [110] texture. The amorphous films deposited at just below 240°C exhibit the same optical properties. With increasing \( T_s \), the films exhibit decreasing optical absorption-edge shifts, becoming transparent-yellow for \( T_s \geq 425°C \). However, a bulk optical behavior is achieved only by annealing the films at temperatures up to 600°C. The principal textures found by x-ray diffraction are [110] for 240°C \( \leq T_s \leq 270°C \), and [111 J for \( T_s > 350°C \). Reflection-electron-diffraction (RED) observations agree substantially with those obtained by x-ray, but also indicate some mixed textures. A weak (1010) reflection is observed by both x rays and RED, indicating an incipient hcp phase; it is shown that this is not causally related to the optical-edge shift. X-ray lattice-constant measurements over the range of \( T_s \) from 250°C-425°C indicate no observable systematic deviation from bulk values; these observations rule out any causal relationship between changes in lattice constant and the optical absorption-edge shift. Extinction bands or bounded-plasma resonance effects do not seem to be able to explain the experimental behavior; the shifts are most probably due to large concentrations of self-compensated natural defects. It is emphasized that these as-deposited and annealed GaP films cover the entire absorption spectrum of all III-V compounds (except InAs and InSh) plus Ge and Si.

D.A. Mota et al. (2013) deposited gallium phosphide thin films on glass substrates by radio frequency (RF) magnetron sputtering technique under different depositions conditions. The X-ray diffraction analysis showed a diversity of states: from amorphous in the films deposited at 175°C to a nearly stoichiometric and polycrystalline films, exhibiting cubic phase with preferred orientation along (220), in the films deposited at temperatures higher than 250°C. Scanning electron microscopy images revealed that all films were uniform with a smooth surface, while the energy-dispersive spectroscopy (EDS) analysis showed that there was a visible dependence on the Ga/P ratio in the deposition conditions and confirmed that a residual Ga metallic phase was presented in the surface of all the films. The Raman analysis showed the structural evolution of the GaP films was strongly dependent on the deposition conditions. The conductivity of the films was slightly dependent on the argon pressure and the rf power, but strongly dependent on the deposition temperature, mainly above 200°C. The optical transmission and absorption analyses of the GaP films revealed an indirect band gap of ~1.70 eV in the films deposited at temperatures less than 200°C, which transited to a band gap of 2.26 eV as the deposition temperature was close to 300°C. Fig. 2(a) shows a representative energy-dispersive spectroscopy (EDS) analysis pattern of the GaP films deposited at 0.4 Pa, keeping the rf source power at 80 W and substrate temperature at 175°C. Fig. 2(b) shows the variation of elemental atomic percentages of Ga and P as a function of the argon pressure. Fig. 2(c) shows the variation of elemental atomic percentages Ga and P as a function of the rf power.

![Figure 2](image-url)

**Figure 2** (a) Representative EDX spectra of GaP thin film deposited under different conditions, (b) variation of Ga and P atomic percentages as a function of the argon deposition pressure, (c) variation of Ga and P atomic percentages as a function of the rf deposition power (D.A. Mota et.al, (2013) cited in the list below)

The main challenge for light-emitting diodes is to increase the efficiency in the green part of the spectrum. Gallium
phosphide (GaP) with the normal cubic crystal structure has an indirect band gap, which severely limits the green emission efficiency. Band structure calculations have predicted a direct band gap for wurtzite GaP. S. Assali et al. (2013) reported the fabrication of GaP nanowires with pure hexagonal crystal structure and demonstrated the direct nature of the band gap. We observe strong photoluminescence at a wavelength of 594 nm with short lifetime, typical for a direct band gap. Furthermore, by incorporation of aluminum or arsenic in the GaP nanowires, the emitted wavelength is tuned across an important range of the visible light spectrum (555–690 nm). This approach of crystal structure engineering enables new pathways to tailor materials properties enhancing the functionality. For this study, GaP nanowires are grown on (111) oriented zinc blende GaP substrates using the VLS mechanism and patterned gold islands as catalysts at a temperature of 750 °C and low V/III ratio to promote the formation of the wurtzite crystalline structure by Algra, R. E. et al. (2008), Caroff, P. et al. (2009), Shtrikman, H. et al. (2009), Joyce, H. J. et al. (2010), Dick, K. A. et al. (2010), Algra, R. E. et al. (2011). In order to control the nanowire position two lithography techniques are used; electron beam lithography to fabricate small arrays with varying pitch and diameter, and nanoimprint to pattern large-scale areas with a constant pitch and diameter. The cross sectional scanning electron microscopy (SEM) image in Figure 3a shows a uniform array of 6.6 ± 0.2 μm long non-tapered nanowires with almost 100% yield defined by nanoimprint. Radial growth, which leads to tapered nanowires, has been totally suppressed by using HCl during growth by Borgström, M. T. et al. (2010). The optical photograph image in Figure 3b shows the large-scale uniformity of a typical sample. The periodicity of the nanoimprint pattern is clearly visible in Figure 3c.

D. F. Barbe and N. S. Saks (1972) studied conduction processes in 50 amorphous GaP films over the temperature range 77 ≤ T ≤ 400° K, for sample thicknesses from 0.1 to 2 μ, for electric fields up to 10⁶ V/cm, and for frequencies up to 10⁸ Hz. Contact effects were shown to be negligible; therefore, all conduction processes reported here are bulk limited. ac and dc conduction is Ohmic for fields up to 10⁴ V/cm. The dc activation energy at 300° K is 0.55 eV which is approximately half the optical band gap. Above 10⁵ Hz, the ac conductivity at 300 °K increases as ω⁰.⁹, indicating hopping conduction. Dc conduction at fields greater than 10⁴ V/cm exhibits Poole-Frenkel behavior. Calculation of the dielectric constant by means of the Poole-Frenkel constant yields K = 9.84, in agreement with the optically determined dielectric constant.

Shun-Tsung Lo et al. (2012) performed transport measurements on a gallium phosphide antimonide (GaPSb) film grown on GaAs. At low temperatures (T), transport is governed by three-dimensional Mott variable range hopping (VRH) due to strong localization. Therefore, electron–electron interactions are not significant in GaPSb. With increasing T, the coexistence of VRH conduction and the activated behavior with a gap of 20 meV is found. The fact that the measured gap is comparable to the thermal broadening at room temperature (approximately 25 meV) demonstrates that electrons can be thermally activated in an intrinsic GaPSb film. Moreover, the observed carrier...
density dependence on temperature also supports the coexistence of VRH and the activated behavior. It is shown that the carriers are delocalized either with increasing temperature or magnetic field in GaPSe. Their new experimental results provide important information regarding GaPSe-based device applications such as in high electron- mobility transistor and heterojunction bipolar transistors.

Paul Klocek et al. (1994) the platforms they perform on, and their missions continue to place increasing requirements on the infrared windows and domes associated with Electro-optical (EO) systems. Supersonic flight, observability, EMI shielding, sensor range, multispectral sensors, environmental degradation resistance (sand and rain erosion resistance), and affordability are some of the requirements that are rendering most current IR window and dome technologies inadequate. Texas Instruments (TI), through both IR&D and DoD contract work, has been developing enabling IR materials technology to address these critical needs. Specifically, work on CVD diamond, gallium arsenide (GaAs), gallium phosphide (GaP), and polymers is described and compared with other IR window and dome materials. Trade studies involving thermal shock, transmission, absorption, emission, strength, durability, protective coatings, EMI shielding, transmitted wavefront distortion, and material status are presented. High-speed IR domes for use with 8- to 12 micrometers sensors on Mach 3 or greater missiles will generally require diamond; slower missiles could use ZnS, GaAs, and possibly GaP. For Mach 3 or greater missile systems with IR sensors operating in the 3- to 5-micrometers range, GaP is the most promising material, its higher thermal shock resistance and lower absorption and, therefore, lower emission at elevated temperatures at 3 to 5 micrometers than sapphire, spinel, yttria, ALON, Si or ZnS. For multispectral use (3 to 5 and 8 to 12 micrometers) at supersonic speeds, GaP and multispectral ZnS are the candidates; low supersonic use could include GaAs; and subsonic use could include ZnSe. For IR windows and domes where EMI shielding is required, GaAs offers the highest shielding of any window with or without metal grids. Si, Ge, and GaP offer bulk electrical conductivity like GaAs, but, because of the intrinsic behavior of the carriers, cannot offer the same level of shielding. Durability is a growing concern on all IR windows and domes. Various coatings for rain and sand erosion including diamond, BP, and TI GaP, amorphous carbon and novel Ti IR polymers are discussed.

N. Elgun et al. (2003) prepared hydrogenated amorphous GaP films by reactive rf sputtering. Infrared spectroscopy, optical transmission and reflection, photothermal deflection spectroscopy and dc conductivity have been studied to investigate the local bonding configurations, the optical absorption edges and the temperature dependence of the conductivity as a function of hydrogen content. The results are discussed and compared with the effects of hydrogenation on amorphous Si.

Wu Q et al. (2005) synthesized gallium phosphide nanotubes with zinc blende structure for the first time. The as-prepared GaP nanotubes are polycrystalline with diameters of 30-120 nm and occasionally partially filled. The growth has been reasonably proposed to follow vapor-liquid-solid (VLS) mechanism. The integration of the nanotubular structure with the unique intrinsic semiconducting properties of GaP might bring GaP nanotubes some novel optical and electronic properties and applications.

H.B. Pogge et al. (1977) grown heteroepitaxial GaP films on (100) silicon substrates with a dual deposition process which consisted of a pyrolytically deposited GaP surface primer and a halide-transport-deposited bulk film. Their electrical, optical, and structural characteristics were compared with simultaneously grown homoepitaxial GaP/GaP films. Except for some cracking in the GaP/Si films, these two types of films exhibited nearly identical properties. Hall mobilities at 77 K for GaP/Si were up to 1730 cm²/V-sec for carrier concentrations of 7.7×10¹³ atoms/cm³. These films were doped with tellurium and nitrogen.

Han-Chang Tsai (2007) Electromagnetic Interference (EMI) has a detrimental effect upon the performance of Optical-Fiber Communication (OFC) systems. The present study considers the case where EMI is induced in a conducting wire (CW), and derives equations to establish the influence of the induced EMI on GaP and GaAsP Light-Emitting Diodes (LEDs). These equations are then verified experimentally. The results indicate that the degree of influence of the EMI upon both LED devices depends upon the interference power, the interference frequency, the induced power, the input resistance of the device, the inverse saturation current, and the ideal factor of the LED. Moreover, it is found that the induced interference current increases with an increasing interference frequency and that the EMI has a greater influence on devices with a lower input impedance. The theoretical results...
are found to be in good agreement with the experimental data.

N Elgun and E A Davis (1994) investigated the electronic properties of a series of nearly stoichiometric sputtered a-GaP films as a function of increasing deposition and annealing temperatures up to 270 degrees C. The optical absorption coefficient \( 10^{4} \text{ cm}^{-1} < \alpha < 10^{5} \text{ cm}^{-1} \) as a function of photon energy, deduced both from transmission (T) and reflection (R) measurements and from photothermal deflection spectroscopy (PDS), shows a very large shift of the edge towards lower energies relative to that of c-GaP. The electrical conductivity data have an activation energy that varies continuously with temperature.

**Conclusion**

The synthesis of gallium phosphide has been pursued, with improvements in technique, product quality and efficiency. Several alternate synthesis method and characterization technique are explored in this review. Further improvement in the synthesis and characterization of gallium phosphide is still required for its use in different applications.

**References**


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