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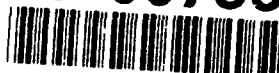
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SUMMARY

This is the Final Report of a research project "Laser Induced Chemical Vapor Phase Epitaxial Growth of III-V Semiconductor Films" sponsored by the Office of Naval Research and Strategic Defense Initiative Organization under contract numbers N00014-90-C-0032-P00003 and SDIO84-89-C-0024. The objective of this project is to investigate the homoepitaxial and heteroepitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth at temperatures considerably below the temperature required in the conventional epitaxial growth process.

The use of high power ultraviolet radiation and tunable wavelength free electron laser (FEL) offers a novel approach to the preparation of device-quality semiconductor films of controlled electrical and structural properties. The excitation of reaction species to higher electronic states by the FEL will enable the use of considerably lower temperatures for the preparation and crystal growth of semiconductors. During the first phase of this program at Southern Methodist University, the epitaxial growth of GaAs by laser induced metalorganic vapor phase epitaxy (MOVPE) was carried out using the reaction between trimethylgallium and arsine in a hydrogen atmosphere. An ArF excimer laser (193nm) was used since FEL is not yet available.

The major concern to the use of MOVPE in both research laboratories and manufacturing facilities is the high toxicity of arsine gas used as a source material. Efforts during this period have been focused on the homoepitaxial growth of GaAs using TMGa or TEGa and elemental arsenic to eliminate the use of toxic arsine gas.

Prior to the homoepitaxial growth of GaAs films by the laser enhanced MOVPE using TMGa or TEGa and elemental arsenic, the growth of GaAs films was carried out by the conventional substrate heating method under atmospheric and reduced pressures to establish the films properties and process parameters. Good quality epitaxial GaAs films with specular surface have been prepared reproducibly for the first time using this process. Without intentional doping, the epitaxial GaAs films are p-type with a net hole concentration of $(2-3) \times 10^{15} \text{ cm}^{-3}$ from TMGa and As and the films are n-type with net electron concentration of $(2-7) \times 10^{15} \text{ cm}^{-3}$ from TEGa and As. In an n-type GaAs film deposited from TEGa and As with an net 77K electron concentration of $2 \times 10^{15} \text{ cm}^{-3}$, the electron mobilities are 7×10^3 and $2.3 \times 10^4 \text{ cm}^2/\text{Vs}$ at 300K and 77K, respectively. The

carbon concentration estimated from the 4.2K photoluminescence and Hall mobility data is on the order of $5 \times 10^{15} \text{ cm}^{-3}$. The device quality of the GaAs films was also demonstrated by the p-n junction properties. This process eliminates the use of highly toxic arsine and is suitable for the epitaxial growth of GaAs and other binary and ternary arsenic containing alloys for many applications.

The laser enhanced MOVPE of GaAs from TEGa and elemental As was carried out using an ArF excimer laser. The use of ArF excimer laser has been found to enhance the epitaxial growth of GaAs from As and TEGa. The extent of enhancement depends strongly on the laser fluence. The grown films are usually n-type with a room temperature net carrier concentration of $(1-6) \times 10^{15} \text{ cm}^{-3}$; however, mobility measurements indicated a high degree of compensation, particularly in films grown under high fluences.

The fabrication of InP based devices on Si substrates is an attractive technology in combining the optoelectronic and high mobility characteristics of III-V compounds with the high integration capabilities of Si. Due to large lattice mismatch between InP and Si, the use of a GaAs interlayer is advantageous in reducing the defect densities in heteroepitaxial InP on Si. As an initial step for the growth of InP on Si, the heteroepitaxial growth of InP on GaAs substrates was investigated using tertiarybutylphosphine (TBP) and ethyldimethylindium (EDMIn) to eliminate the highly toxic phosphine gas source commonly used for the epitaxial growth of InP. The growth process was carried out in a hydrogen flow under atmospheric pressure. Heteroepitaxial InP layers with mirror smooth surfaces were deposited on GaAs substrates using a two temperature growth process under atmospheric pressure: a buffer layer was deposited at 400°C followed by the deposition of an epitaxial layer at $500^\circ - 550^\circ\text{C}$. InP layers deposited without intentional doping are n-type with a net electron concentration of $(2-3) \times 10^{16} \text{ cm}^{-3}$. The FWHM of the excitonic peak of the 4.2K photoluminescence of an InP layer of $1.1 \mu\text{m}$ thickness is 5.2 meV.

Section 1.0

INTRODUCTION

This is the Final Report of a research project "Laser Induced Chemical Vapor Phase Epitaxial Growth of III-V Semiconductor Films" sponsored by the Office of Naval Research and Strategic Defense Initiative Organization under contract numbers N00014-90-C-0032-P00003 and SDIO84-89-C-0024. The objective of this project is to investigate the homoepitaxial and heteroepitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth at temperatures considerably below the temperature required in the conventional epitaxial growth process.

III-V compound semiconductors, gallium arsenide (GaAs), indium phosphide (InP), and many III-V ternary and quaternary alloys, have become increasingly important in electronic device applications. The homo- and hetero- epitaxial films of device-quality III-V compounds and their alloys are used for the majority of the devices. Metalorganic vapor phase epitaxy (MOVPE) has been demonstrated to be the most versatile epitaxial technique which can be used to grow essentially all III-V compounds and alloys containing Al, Ga, and In of group III elements and P, As, and Sb of group V elements.

The typical source materials for the growth of III-V semiconductors by MOVPE technique are volatile organometallic compounds of group III elements and hydrides of group V elements (with the exception of Sb due to the instability of antimony hydride, SbH_3). The commonly used group III organometallic compounds are trimethylgallium (TMGa), triethylgallium (TEGa), trimethylaluminum (TMAI), trimethylindium (TMIn), etc. These compounds are volatile liquids or solids and are kept in stainless steel bubblers at constant temperatures. A controlled amount of the compound can be transported to the

reactor by passing a carrier gas, usually hydrogen, through the bubblers. The group V hydrides, arsine (AsH_3) and phosphine (PH_3) are introduced as dilute (usually 10%) mixtures in H_2 .

The properties of GaAs, InP, and other III-V semiconductors grown by MOVPE are comparable or better than those obtained by other techniques. For example, electron mobilities of $210,000 \text{ cm}^2/\text{V-s}$ at 77K for GaAs [1] and $200,000 \text{ cm}^2/\text{V-s}$ at 50K for InP [2] have been reported for MOVPE grown films. The MOVPE technique is capable of producing atomically abrupt interfaces in multi-layer structures with different compositions. Device structures such as high efficiency solar cells, field effect transistors, quantum well lasers, multiple quantum wells, and superlattices have been prepared by the MOVPE technique [3-18]. Furthermore, large capacity reactors are available for commercial applications.

In the conventional MOVPE process, the deposition temperatures are usually in the range of $600^\circ\text{-}800^\circ\text{C}$. The advantages of the epitaxial growth of GaAs and other III-V compounds at lower temperatures by the MOVPE technique are well recognized. The contamination and interdiffusion can be minimized in multilayer device structures, the process-induced defects due to thermal stress can be reduced, and the processing flexibility, such as the epitaxial growth of GaAs and InP on silicon (Si) substrates can open up many avenues in device fabrication. The major advantage of this technology is the possibility to merge the high electron mobility and optoelectronic devices of GaAs and InP with the high-level integration capabilities of Si. A new breed of integrated circuits combining Si-based digital circuits with GaAs optoelectronics can be achieved for light-based interconnections.

The use of high power density ultraviolet radiation and tunable wavelength free electron laser (FEL) offers a novel approach to the preparation of device-quality

semiconductor films of controlled electrical and structural properties. The excitation of reaction species to higher electronic states or the dissociation of reaction species to radicals by the FEL will enable the use of considerably lower temperatures for the preparation and crystal growth of semiconductors. The vapors of essentially all metalorganic compounds and group V hydrides are colorless and show strong absorption bands in the 200 nm region [19]. The effects of the laser can be photothermal or photochemical, depending on the wavelength and fluences of the laser. For example, using an Ar ion laser at low fluences, multi-photon absorption has low probabilities. One would expect the epitaxial growth of GaAs to be enhanced photothermally, since the laser radiation is essentially transparent to TMGa and AsH₃ and is strongly absorbed by the GaAs substrate. By impinging the argon ion laser radiation upon the selected areas of a GaAs substrate, local heating of the substrate over the beam area occurs, and patterned GaAs growth has been achieved [20,21]. However, a surface-catalyzed photochemical effect has also been postulated in the enhancement of MOVPE growth of GaAs from TMGa and AsH₃ by CW argon ion laser irradiation [22]. Using a laser power of 774 mW focused to a 350 μ m diameter area of the substrate, the growth rate has been found to increase with decreasing substrate temperature, and large enhancement factors have been observed at low substrate temperatures, 530° - 550°C. The properties of GaAs have been found to be modified by laser irradiation. For example, the photoluminescence from GaAs grown by laser enhancement has considerably higher intensity than that in conventionally grown material.

Excimer lasers have been used more extensively to enhance the MOVPE growth of compound semiconductors. The enhancement process is mainly photochemical in nature. In a single or multi-photon process, the metalorganic and the hydride molecules are excited to higher electronic states or are dissociated into radicals which then react on the substrate

surface, permitting epitaxial growth at lower temperatures than those required for the thermal growth process. The MOVPE growth of InP [23], GaAs [24-26], GaP [27], ZnSe[28], $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ [29], CdTe [30], etc. by excimer laser enhancement has been reported. Thin films of InP have been deposited on InP substrates by ArF laser (193 nm) enhanced photochemical reaction of a trimethylindium, $(\text{CH}_3)_3\text{In}$, and trimethylphosphorous, $\text{P}(\text{CH}_3)_3$, mixture [23]. Films range from amorphous to epitaxial, depending mainly on laser fluence incident on the substrate. The best film deposited at 0.1 J/cm^2 at 320°C is similar to the substrate in backscattering spectrum. However, GaAs films grown on GaAs substrates by ArF laser enhanced MOVPE process from a TMGa - TMAs mixture were polycrystalline with grain sizes of 20-2000 Å [24]. Deposited films were found to contain 1-3 at % carbon which could have interfered with the epitaxial growth process. Annealing was not sufficient to promote epitaxial growth at fluences as high as 70 mJ/cm^2 at average substrate temperatures of up to 400°C . Homoepitaxial GaAs films have been grown at temperatures as low as 425°C by an ArF laser enhanced process from a TMGa-AsH₃ mixture during the first phase of this program at Southern Methodist University [25,33]. The growth of GaAs from TMGa-AsH₃ can also be enhanced by a KrF laser (248 nm) but not by XeF laser (351 nm), since TMGa and AsH₃ show no significant absorption at 351 nm [26]. However, information on the properties of laser enhanced epitaxial GaAs relevant to device operation is very limited.

During the first phase of this program at Southern Methodist University [25,31,33], the epitaxial growth of GaAs by Laser-induced metalorganic vapor phase epitaxy (LIMOVPE) was carried out by a computer-controlled MOVPE system using TMGa and AsH₃ in hydrogen. The growth process was performed under reduced pressure to minimize the gas phase nucleation. An ArF excimer laser emitting at 193 nm was used since FEL is

not yet available. Homoepitaxial GaAs films of good structural perfection and electrical properties have been grown successfully at 425°-500°C for the first time. The deposited films are p-type when the AsH₃/TMGa molar ratio was less than 30, and a laser pulse energy of 95 mJ and a pulse rate of 70 Hz were used. At a given temperature, the hole concentration decreases with increasing AsH₃/TMGa molar ratio in the reactant mixture. The hole concentration varies from $(1-2) \times 10^{18} \text{ cm}^{-3}$ to $(3-4) \times 10^{16} \text{ cm}^{-3}$ as the AsH₃/TMGa molar ratio increased from 10 to 30 at a substrate temperature of 500°C. Furthermore, the hole concentration depends on substrate temperature, it varied from $5 \times 10^{16} \text{ cm}^{-3}$ at 425°C to $(2-3) \times 10^{17} \text{ cm}^{-3}$ at 500°C using a fixed AsH₃/TMGa molar ratio of 20. The room temperature hole mobilities are in the range of $(150-200) \text{ cm}^2/\text{Vs}$.

The heteroepitaxial growth of GaAs films on Si substrates was also carried out by the ArF laser enhanced process. GaAs films of about 0.2 μm thickness deposited on Si substrates was essentially free of threading dislocations at the interface as shown by transmission electron microscopy. The heteroepitaxial GaAs films on Si were deposited at 450° - 500°C using similar laser parameters as those for the homoepitaxial growth [34].

The major concern to the use of MOVPE in both research laboratories and manufacturing facilities is the high toxicity of the gaseous AsH₃ and PH₃ source materials. Furthermore, a large V/III molar ratio is required to grow device quality III-V compounds, particularly at low substrate temperatures and reduced pressure growth conditions due to the thermal stability of the hydrides. Many research and manufacturing facilities are extremely interested to substitute these hydride by less hazardous arsenic and phosphorus sources either in liquid or solid form. The alternate sources are organoarsenic and organophosphorus compounds and elemental arsenic and phosphorous. The organoarsenic and organophosphorus compounds have been under development as the alternate sources

during the past several years [35,36]. The organoarsenic compounds studied for the MOVPE of GaAs include trimethylarsenic (TMAs) [37], triethylarsenic (TEAs) [38,39], diethylarsine (DEAs) [40], and tertiarybutylarsine (TBAs) [41-45]. Tertiarybutylphosphine (TBP) [46,47] has been used as the source material for the MOVPE growth of InP. However, the organoarsenic and organophosphorus compounds are very expensive although TBAs and TBP have shown to be promising in producing device quality GaAs and InP films [37-39]. For example, when purchasing in kilogram quantities, the cost of TBAs is about \$30 per gram of arsenic as compared with \$1.20 for an equivalent amount of arsine and \$0.25 per gram for 7N (99.99999%) purity of elemental arsenic.

Very limited information is available on the use of elemental arsenic as the alternate source for the growth of GaAs films. Either hazy surface morphologies or high background carrier concentrations have been reported [48,49]. The available information on the use of non-hydride arsenic and phosphorus sources will be reviewed in Section 2.0. The homoepitaxial growth of GaAs by MOVPE using TMGa or TEGa and elemental arsenic has been investigated in this program to eliminate the use of toxic AsH₃ gas.

Prior to the homoepitaxial growth of GaAs films by the LIMOVPE using TMGa or TEGa and elemental arsenic, the epitaxial growth of GaAs films was carried out by the conventional thermal process under atmospheric and reduced pressures to establish the film properties and process parameters. Good quality epitaxial GaAs films with specular surface have been prepared reproducibly for the first time using these processes. Elemental phosphorus is unsuitable for the growth of InP by MOVPE due to the transformation of red phosphorus to the white modification and the reactivity of phosphorus toward quartz at elevated temperatures. The heteroepitaxial growth of InP films on GaAs substrates was carried out using ethyldimethylindium (EDMIn) and TBP. These processes eliminate the

use of highly toxic arsine and phosphine and are suitable for the epitaxial growth of GaAs, InP and other binary and ternary III-V alloys for many applications. The experimental procedures and results carried out in this program are discussed in the following sections.

Section 2.0

NON-HYDRIDE ARSENIC AND PHOSPHORUS SOURCES IN THE MOVPE GROWTH OF GaAs AND InP

As discussed in Section 1.0, the typical arsenic and phosphorus source materials in the epitaxial growth of GaAs and InP by the MOVPE technique are AsH_3 and PH_3 , respectively. Arsine and phosphine are extremely toxic gases. The use of arsine and phosphine is a major safety concern in university laboratories and industrial facilities. This is particularly true in large scale production since the general public has become increasingly aware of the use of toxic material in metropolitan areas. The development of less toxic arsenic and phosphorus source materials for the growth of GaAs, InP, and other III-V compounds is highly desirable. During the past few years, less toxic organoarsenic and organophosphorus compounds have been under development. The use of organoarsenic compounds as well as solid elemental arsenic have been investigated in the MOVPE growth of GaAs and organophosphorus compounds in the MOVPE growth of InP [35].

2.1 Organoarsenic Compounds

The organoarsenic compounds available for the MOVPE growth of gallium arsenide are liquids and their physical properties are listed in Table 1. These compounds have been used successfully for the epitaxial growth of GaAs films, and the properties of the grown films characterized.

Table 1. Vapor Pressure of Organoarsenic Compounds

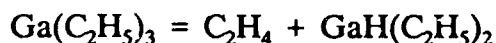
Compound	Formula	Melting Point, °C	Vapor Pressure, Torr	
Trimethylarsenic (TMAs)	$(\text{CH}_3)_3\text{As}$	-87	97	at 0°C
Triethylarsenic (TEAs)	$(\text{C}_2\text{H}_5)_3\text{As}$	-91	15.5	at 37°C
Diethylarsine (DEAs)	$(\text{C}_2\text{H}_5)_2\text{AsH}$	-	~0.6	at 18°C
Tertiarybutylarsine (TBAs)	$(\text{C}_4\text{H}_9)\text{AsH}_2$	-	81	at 10°C

2.1.1 Trimethylarsenic (TMAs)

The use of trimethylarsenic as an arsenic source has been studied by several investigators [37,50]. The pyrolysis temperature of TMAs was found to be significantly higher than that of arsine (AsH_3), thus higher growth temperature is required. The epitaxial GaAs layers grown by using TMAs have high impurity concentrations with carbon incorporation of $\sim 5 \times 10^{16} \text{ cm}^{-3}$. By using a thermal precracking of TMAs [50], the net background doping was changed from p-type to n-type and the doping concentration was reduced from $N_a \sim 5 \times 10^{16} \text{ cm}^{-3}$ to $N_d \sim 1 \times 10^{16} \text{ cm}^{-3}$. The carbon incorporation was reduced below the SIMS detection level of $5 \times 10^{16} \text{ cm}^{-3}$. However, the electron mobility of about $7000 \text{ cm}^2/\text{V-s}$ at 77K indicated severe compensation in the grown layer.

2.1.2 Triethylarsenic (TEAs)

Since the methyl group from TMAs is a major source of carbon incorporation in the deposited films, TEAs has been investigated as the arsenic precursor. It has been demonstrated that the substitution of TEGa for TMGa as the gallium source in MOVPE growth results in a substantial reduction of carbon incorporation in the epitaxial GaAs layers [51]. This result has been attributed to the difference in the mechanisms of the thermal decomposition of TEGa and TMGa. TMGa appeared to decompose via homolysis of the Ga- CH_3 bonds to produce reactive methyl radicals which leads to carbon incorporation during MOVPE growth. TEGa pyrolyzes unimolecularly by beta-hydride elimination with the formation of ethylene, without the production of reactive carbon-containing species, as shown by:



It was anticipated that TEAs would decomposes with the similar mechanism as that of

TEGa, thus reducing the carbon incorporation.

The GaAs growth experiments have been carried out under atmospheric pressure using TEAs and TMGa over a wide range of substrate temperatures (550 - 750°C), and V/III molar ratios (2-13) [38,39]. GaAs films with good surface morphology, background doping levels of $< 10^{15} \text{ cm}^{-3}$, and 77K mobilities of $13,000 \text{ cm}^2/\text{Vs}$ have been prepared [39]. However, the carbon content is greater than 10^{17} cm^{-3} . Thus unlike the case for gallium, the substitution of ethyl for methyl groups in organoarsenic compounds does not appear to inhibit carbon incorporation in GaAs films.

2.1.3 Diethylarsine (DEAs)

Diethylarsine, with only two of the hydrogen atoms in AsH_3 replaced by alkyl groups, has been investigated for the growth of GaAs to determine the effect of the remaining hydrogen on carbon incorporation. Although DEAs has a very low vapor pressure at room temperature, high quality epitaxial GaAs films have been prepared at growth temperatures of 500 - 580°C. The deposited films are n-type with a lowest background net carrier concentration of $3 \times 10^{14} \text{ cm}^{-3}$ and a highest 77K mobility of $64,600 \text{ cm}^2/\text{Vs}$. The low-temperature (2K) photoluminescence spectrum has well-resolved excitonic peaks, confirming the high quality of the material [40]. The predominant donor has been identified as germanium (Ge) from DEAs and carbon is the major acceptor. The carbon concentration in epitaxial layers is still higher than that in GaAs prepared from AsH_3 . One advantage of using DEAs is that lower temperature and lower V/III ratio (~ 1) can be used as compared with the AsH_3 process, presumably due to the lower pyrolysis temperature of DEAs. However, the major difficulty is that the vapor pressure of DEAs is too low to be utilized conveniently.

2.1.4 Tertiarybutylarsine (TBAs)

Tertiarybutylarsine (TBAs), in which two hydrogen atoms bonded to As, has been used as an arsenic source for the epitaxial growth of GaAs. The initial studies have shown that GaAs epitaxial layers with good morphology, background doping level of $5 \times 10^{15} \text{ cm}^{-3}$, and room temperature mobilities of $4,000 \text{ cm}^2/\text{Vs}$ can be grown with TBAs [41,42]. Using an improved synthesis process for TBAs, GaAs films with net background carrier concentrations of $(2-3) \times 10^{14} \text{ cm}^{-3}$, room temperature mobilities of $7,600 \text{ cm}^2/\text{Vs}$, 77K mobilities of $80,000 \text{ cm}^2/\text{Vs}$, and 4K photoluminescence spectra with sharp excitonic transitions have been obtained [43]. When TBAs and TEGa were used as the source materials, GaAs films with 77K electron mobility of up to $116,000 \text{ cm}^2/\text{Vs}$ have been grown at 580°C at a rate of $1.6 \mu\text{m/hr}$ by using a TBAs/TEGa molar ratio of 10 [44]. TBAs also pyrolyzes at lower temperatures with approximately 50% pyrolyzed at 425°C . For arsine, about 675°C is required to have a 50% pyrolysis. Concentrator GaAs solar cells with good characteristics have been demonstrated by using TBAs as an arsenic source [52]. It appears that TBAs is the most promising alternate source material at present time; however, the cost is too high, $\sim \$30$ per gram of As, for the manufacturing of GaAs devices.

2.2 Elemental Arsenic

Elemental arsenic is a solid at room temperature with a melting point of 814°C . As shown by the vapor pressure-temperature relationship in Fig. 2.1, the vapor pressure of arsenic at room temperature is too low to be practical for MOVPE. It is necessary to maintain the arsenic at a higher temperature during the growth of GaAs. Limited studies have been carried out on the use of elemental arsenic for the epitaxial growth of GaAs films by MOVPE. The growth of GaAs under atmospheric pressure was demonstrated by using

TMGa and arsenic vapor which was introduced to the deposition zone by passing hydrogen over the elemental arsenic at 425°-475°C [48]. The growth was carried out at substrate temperatures of 625°-750°C; however, the deposited films with hazy surface morphologies were always obtained. When grown at 625°-700°C, the epitaxial layers were p-type with a carrier concentration of $7 \times 10^{14} - 1.5 \times 10^{16} \text{ cm}^{-3}$. The layers grown at 750°C were n-type with a carrier concentration of $(2-3) \times 10^{15} \text{ cm}^{-3}$. High carbon incorporation was observed due presumably to the lack of atomic hydrogen which has been postulated to be formed during the dissociation of arsine. The use of solid arsenic source was also investigated by low pressure MOVPE. Defect free GaAs epitaxial layers with mirror-like surface morphology was obtained using TEGa and elemental arsenic as the source materials in a low pressure MOVPE reactor [49]. The epitaxial GaAs layers are n-type with a net

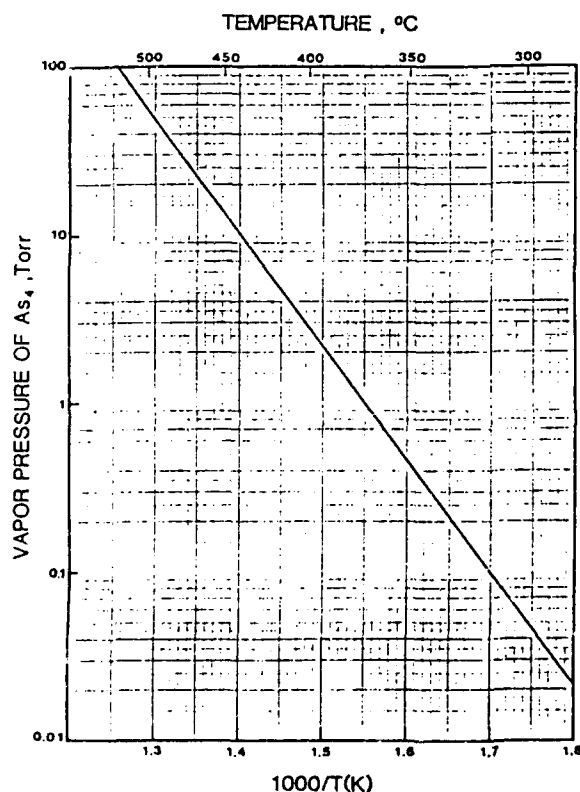


Figure 2.1 Vapor pressure of elemental arsenic in the temperature range of 300° - 500°C.

carrier concentration of $5 \times 10^{16} \text{ cm}^{-3}$ and room temperature mobilities of about $4500 \text{ cm}^2/\text{Vs}$. The growth rate is in the range of $1\text{-}14 \text{ }\mu\text{m/hr}$ and is a function of the hydrogen flow rate through TEGa and is independent of temperature at growth temperatures above 650°C . The electrical properties were dominated by residual impurities in the arsenic and by silicon in the TEGa.

2.3 Organophosphorus Compounds

Two organophosphorus compounds, tertiarybutylphosphine (TBP) and isobutylphosphine (IBP), have been used successfully as the phosphorus source for the MOVPE growth of InP. Other organophosphorus compounds, such as trimethyl- and triethyl-phosphorus, cannot be used since they do not pyrolyze readily and instead form adducts with the group III sources. The melting points of IBP and TBP are -20°C and 4°C , respectively, and the vapor pressure of IBP is 57 Torr at 10°C and that of TBP is 192 Torr at 17°C . Epitaxial InP film has been deposited from TMIn and IBP at 610°C by using a V/III ratio of 140. The layers have a smooth mirror appearance and the 4.2 K photoluminescence measurements indicated that the InP layers grown from IBP have higher total impurity concentration than those grown from phosphine [46]. Tertiarybutylphosphine has been investigated more extensively as the phosphorus source for the MOVPE growth of InP and $\text{GaAs}_x\text{P}_{1-x}$ [47,53-54]. Excellent morphologies have been obtained for the growth of InP between 560 and 630°C using TMIn and TBP. The electron mobility increases and the electron concentration decreases as the temperature is increased. A room temperature mobility of $3800 \text{ cm}^2/\text{Vs}$ and electron concentration of $3 \times 10^{15} \text{ cm}^{-3}$ were obtained at 630°C . The V/III ratios higher than 10 are necessary to obtain good morphologies although a V/III ratio of 3 has been used to grow InP epilayers with featureless morphologies at 600°C [47].

With continued improvements in the production and purification of TBP, the 77K mobilities of greater than $100,000 \text{ cm}^2/\text{Vs}$ have been achieved. When the growth was carried out under reduced pressure using TMIn and TBP, InP epilayers with the best characteristics were obtained at a growth temperature of 560°C . The electron concentration has been found to remain at $2 \times 10^{14} \text{ cm}^{-3}$ over a range of V/III ratios of 13 to 50. The peak 77K mobility of $132,000 \text{ cm}^2/\text{Vs}$ was obtained at a V/III ratio of 50 [54].

Section 3.0

HOMOEPITAXIAL GROWTH OF GaAs FILMS FROM ELEMENTAL ARSENIC

The homoepitaxial growth of GaAs by MOVPE using TMGa or TEGa and elemental arsenic (As) has been investigated in this program to eliminate the use of toxic arsine gas. Prior to the homoepitaxial growth of GaAs film by laser-enhanced MOVPE using TMGa or TEGa and elemental As, the growth of GaAs films was carried out by the conventional inductive heating of the substrate under atmospheric and reduced pressures to establish the film properties and process parameters. The experimental procedures and results are discussed in this section.

3.1 Reaction Chamber Design

The reaction chamber for the conventional MOVPE using TMGa or TEGa and arsine is made of fused silica, either in horizontal or vertical configuration. The substrates are usually placed on a silicon carbide coated graphite susceptor in a fused silica reaction tube, and the susceptor heated externally by rf induction. The susceptor is usually tilted at 5 - 10° angle in horizontal reactor to improve the uniformity of the deposited layer. The reactant gas mixture is introduced into the reaction chamber, and the reaction between TMGa or TEGa and arsine takes place on the heated substrate surface depositing GaAs. The schematic diagram of a typical horizontal reactor is shown in Figure 3.1.

When elemental As is used as the alternate As source, the source must be heated to provide sufficient vapor pressure of arsenic (Figure 2.1). For example, the vapor pressure of As is about 3 Torr at 400°C. Figure 3.2 shows the design of the reaction chamber used in this program, where the arsenic container is an integral part of the deposition system. The reaction tube was made of fused silicon of 5.5 cm ID. The As source is heated

independently by quartz halogen lamps. A thermocouple inserted into the As container is used to monitor and control the temperature of the As. The inlet tube for the reactant gases, such as TMGa (or TEGa) and dopants, is located in between the As container and the susceptor so that the metalorganic compounds are not subjected to the heated As zone. When silicon carbide susceptor of 2" x 4" size is used, the reaction chamber is capable of providing uniform GaAs epitaxial layer over two 1" diameter substrates.

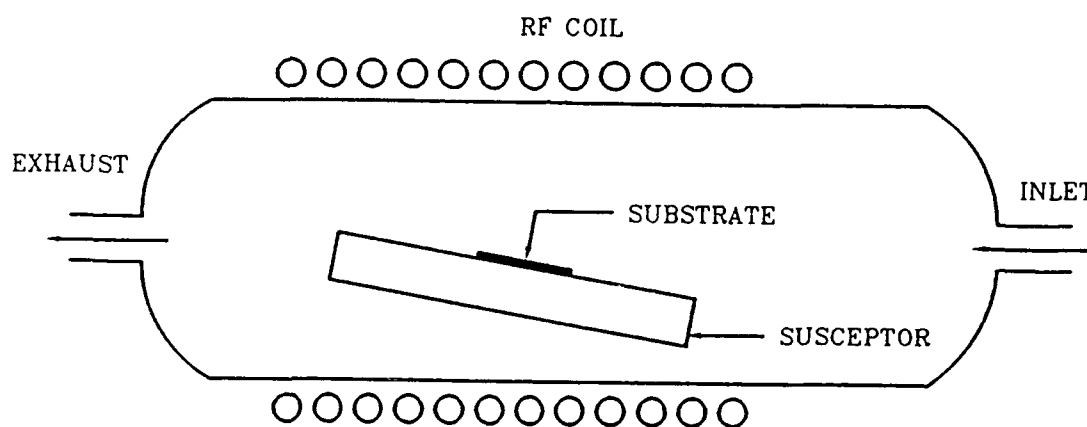


Figure 3.1 A typical horizontal reactor for the MOVPE growth of GaAs.

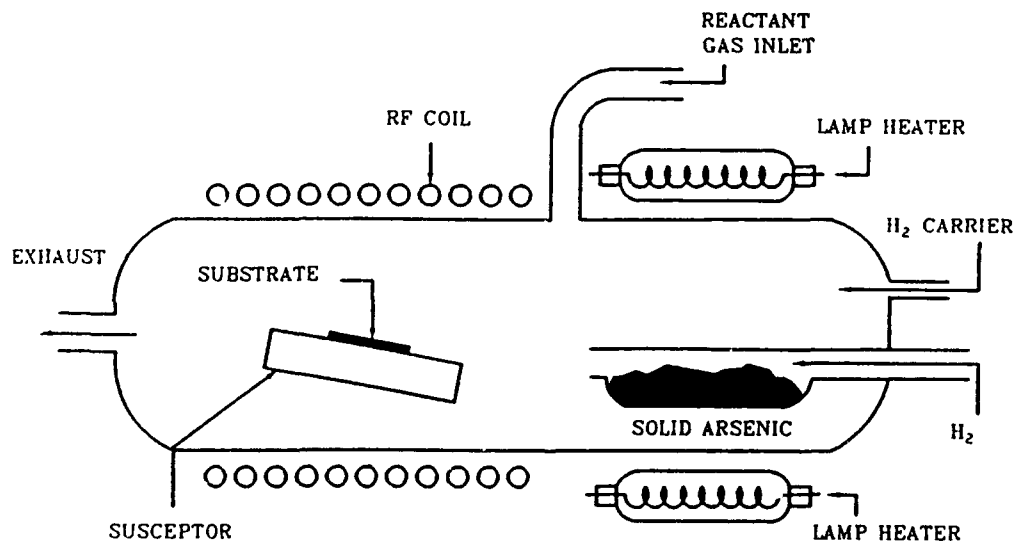


Figure 3.2 The horizontal reactor for the MOVPE growth of GaAs using elemental arsenic.

3.2 The Growth Process

The homoepitaxial growth of GaAs using elemental As source was carried out in hydrogen using the reaction chamber described in Section 3.1. Arsenic of 7N purity and electronic grade TMGa and TEGa were used. The growth was carried out under atmospheric pressure for the TMGa + As process and under reduced pressure for the TEGa + As process. The use of reduced pressure is essential in the TEGa + As process to eliminate gas phase nucleation. GaAs substrates of (100) orientation, semi-insulating or Si-doped at a concentration of about 10^{18} cm^{-3} , were etched with a 6:1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ mixture and rinsed with DI water in the usual manner. They were supported on a silicon carbide coated graphite susceptor in the reaction tube, and the susceptor was heated inductively. Alternately, the substrates may also be heated radiatively by using a 2 kW quartz lamp. The substrate temperature was monitored by using a thermocouple inserted inside the susceptor; the susceptor temperature was about 25°C higher than the substrate temperature.

The As container was usually maintained at $360^\circ - 470^\circ\text{C}$, depending on the pressure in the reaction tube, and the partial pressure of As in the reaction mixture was controlled by the temperature of As and the flow rate of hydrogen through the container. The measured weight loss of As was in agreement with the ideal gas law. TMGa and TEGa bubblers were maintained at 0°C and 17°C , respectively, and the amount of TMGa (or TEGa) are introduced into the reaction chamber by controlling the flow rate of hydrogen through the bubbler. Prior to the growth process, the GaAs substrates were heated in-situ at 650°C in a H_2 atmosphere containing several ppm of As to provide a clean substrate surface. Vapors of TMGa or TEGa and As were then carried by H_2 to the substrate surface where they react to deposit GaAs. The growth has been carried out over a wide range of

deposition parameters under atmospheric and reduced pressures.

The homoepitaxial growth of GaAs films from TMGa and As was carried out under atmospheric pressure in the temperature range of 600°-700°C, TMGa flow rate of $(1.6 - 9.6) \times 10^{-5}$ moles/min, As/TMGa molar ratios of 5-30, and a fixed hydrogen flow rate of 10 ℓ /min. It has been found that the minimum As/TMGa molar ratio required to obtain specular epitaxial layers at 600°C is approximately 7. At lower As/TMGa molar ratios, the grown surface appears hazy due presumably to As deficiency. At a fixed As/TMGa molar ratio, the growth rate of GaAs varies linearly with the TMGa concentration and is independent of the substrate temperature. For example, when the deposition was carried out at a substrate temperature of 600°C and an As/TMGa molar ratio of 10, the growth rates are 6 and 4 $\mu\text{m/hr}$ at TMGa flow rates of 9.8×10^{-5} and 5.0×10^{-5} mole/min., respectively.

The epitaxial growth of GaAs films was also carried out under a reduced pressure of 20-60 Torr from TEGa and elemental As, at substrate temperature in the range of 425°C - 525°C. The flow rate of TEGa, the As/TEGa molar ratio, and the hydrogen carrier flow rate were in the range of $(1-3) \times 10^{-5}$ mole/min, 5-30, and 1-3 ℓ /min, respectively. Epitaxial GaAs films with specular surfaces, examined under scanning electron microscopy (SEM), have been grown at substrate temperatures above 450°C and at As/TEGa ratios above 10. The growth rate increases linearly with increasing TEGa concentration in the reaction mixture and is a function of the substrate temperature. Figure 3.3 shows the temperature dependence of growth rate obtained by using a TEGa flow rate of 1.2×10^{-5} mole/min, an As/TEGa molar ratio of 20, a H_2 flow rate of 1.5 ℓ /min, and a reactor pressure of 60 Torr. The growth rate is about 240 $\text{\AA}/\text{min}$ at 450°C and is increased to 410 $\text{\AA}/\text{min}$ at 525°C. The activation energy is 0.35 eV, indicating that the growth mechanism is not controlled by the

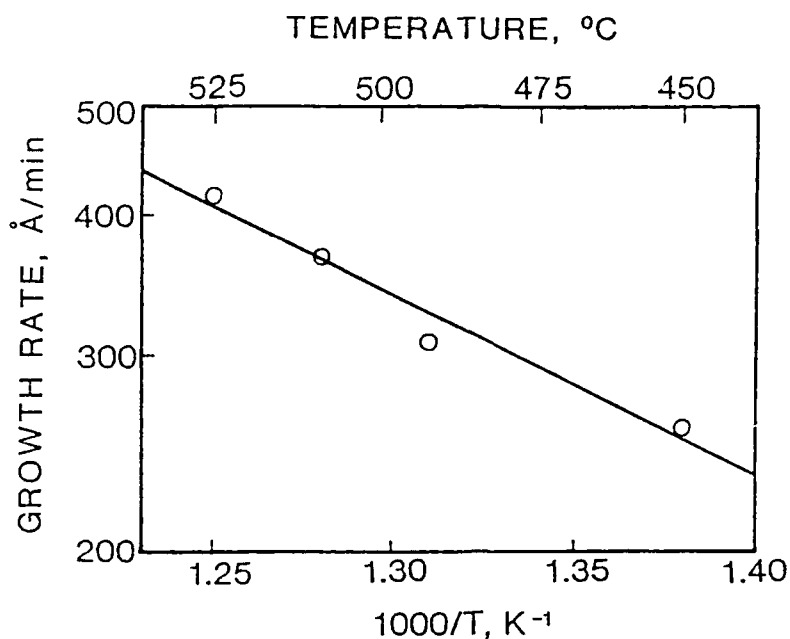


Figure 3.3 Average growth rate of epitaxial GaAs as a function of substrate temperature grown from TEGa and As.

surface reaction. As a comparison, the minimum temperature required for the MOVPE growth of GaAs by the TEGa and AsH₃ process is 510°C [55]. The use of lower substrate temperature is an additional advantage of using elemental As as the source material.

3.3 Characterization

The structural and electrical properties of deposited GaAs films have been characterized by chemical etching and SEM, carrier concentration profiling, secondary-ion mass spectrometry (SIMS), photoluminescence, Hall measurement and p-n junction properties. The deposited films from either TMGa or TEGa and As showed no structural features under SEM. The dislocation density in the film revealed by using a FeCl₃-HCl etch [56] was very similar to that in the substrate. The deposited films from TMGa and As are always p-type, and the hole concentration was determined by the electrochemical carrier concentration profiling and Hall measurements. At high growth rates, 6 μm/hr for example,

the hole concentration decreases with increasing As/TMGa molar ratio, $(1-2) \times 10^{15} \text{ cm}^{-3}$ at an As/TMGa ratio of 30 and $2 \times 10^{16} \text{ cm}^{-3}$ at an As/TMGa ratio of 10. When the growth rate is reduced to $4 \text{ } \mu\text{m/hr}$, the hole concentration is essentially independent of the As/TMGa ratio and is in the range of $(4-6) \times 10^{15} \text{ cm}^{-3}$. The p-type conductivity of GaAs films from TMGa and As is due primarily to carbon incorporation, and the carbon incorporation is reduced by either using a high As/TMGa ratio or lower growth rate. The carbon concentration in the GaAs films, determined by SIMS analysis is in the range of $5 \times 10^{16} - 1 \times 10^{17} \text{ cm}^{-3}$, just above the SIMS detection limit of $5 \times 10^{16} \text{ cm}^{-3}$. The doping of the GaAs films deposited from TMGa and As was carried out by using 100 ppm disilane (Si_2H_6) in hydrogen as the dopant. N-type GaAs films with net electron concentrations in the range of $4.5 \times 10^{17} \text{ cm}^{-3}$ to $1.5 \times 10^{18} \text{ cm}^{-3}$ were obtained by using Si_2H_6 /TMGa molar ratios of 6×10^{-5} to 2.4×10^{-4} as shown in Fig. 3.4.

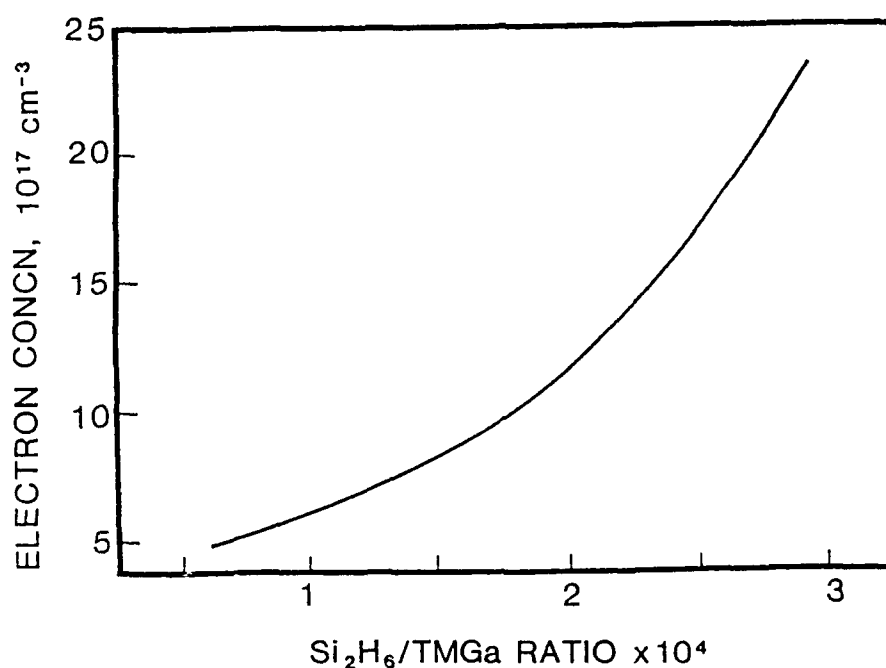


Figure 3.4 The electron concentration in GaAs films as a function of Si_2H_6 /TMGa ratio in the reaction mixture.

When TEGa and As are used as the source materials, the deposited GaAs films are always n-type. The ethyl radical is known to undergo beta-hydride elimination [51], thus minimizing the carbon incorporation in the deposited films. The electron concentration is essentially independent of the substrate temperature at 450° - 525°C and is in the range of $(2-7) \times 10^{15} \text{ cm}^{-3}$ depending on the As/TEGa molar ratio. The electron concentration is $2 \times 10^{15} \text{ cm}^{-3}$ at an As/TEGa molar ratio of 20 and is increased to $7 \times 10^{15} \text{ cm}^{-3}$ at a ratio of 50. The carrier concentration is uniform in the depth direction of the epitaxial layer as shown in Fig. 3.5 by using the Bio-rad PN4200 Polaron depth profiler.

The Hall mobilities in GaAs films deposited on semi-insulating substrates were determined by the van der Pauw technique using In-Sn or In-Ga contacts. The hole mobilities in a p-type GaAs film deposited from TMGa and As with a hole concentration of $2 \times 10^{16} \text{ cm}^{-3}$ are 300 and 3,530 cm^2/Vs at 300 K and 77 K, respectively. In an n-type GaAs film deposited from TEGa and As with an net 77K electron concentration of 2×10^{15}

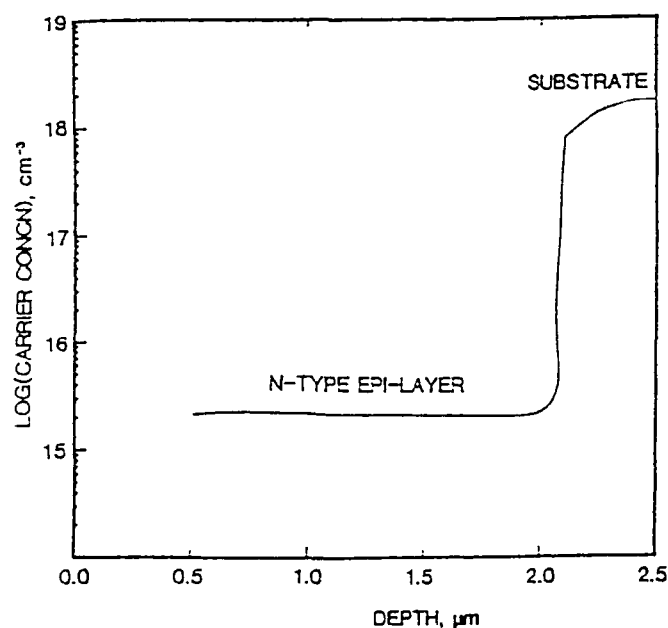


Figure 3.5 The electron concentration profile of a n-type homoepitaxial GaAs film deposited from TEGa and As on a n-type substrate at 495°C at an As/TEGa molar ratio of 20.

cm^{-3} , the electron mobilities are 7×10^3 and $2.3 \times 10^4 \text{ cm}^2/\text{Vs}$ at 300 K and 77 K, respectively.

The quality of epitaxial GaAs films was also evaluated by photoluminescence measurements at 4.2K. The sample was supported on a copper holder immersed in liquid helium in a Janis Cryogenic Dewar, and its temperature was monitored by a silicon diode. Excitation was provided by a mechanically chopped (1 kHz) radiation from an argon ion laser with a 484 nm interference filter. Luminescence from the sample was optically focused onto the slit of a Spex Model 1704 spectrometer, and the slit width of the spectrometer was selected to yield energy resolution of 0.5 mV or better in the luminescence spectra. The signal was detected with an EG and G germanium p-i-n detector maintained at 77 K and processed with a lock-in amplifier. The spectrometer and the detector were interfaced with a data acquisition system. The photoluminescence of GaAs films deposited from TEGa + As and TMGa + As with an excitation power density of $65 \text{ W}/\text{cm}^2$ are shown in Fig. 3.6 and 3.7, respectively. The transitions arising from the excitons and carbon states are indicated. The carbon concentration in the film deposited from TEGa and As were estimated from the intensity of the carbon band and from Hall mobility data to be on the order of $5 \times 10^{15} \text{ cm}^{-3}$ [57,58]. The carbon concentration in GaAs films from TEGa and As is at least one order of magnitude lower than that deposited from TMGa and As, as shown by the photoluminescence and SIMS data. The oxygen concentration in GaAs films was found to be below the SIMS detection limit of about $5 \times 10^{17} \text{ cm}^{-3}$.

The junction properties of an epitaxial GaAs mesa diode was determined to further evaluate the device quality of GaAs films deposited from elemental arsenic. The junction is of the $n^+/p/p^+$ configuration and was prepared from TMGa and As by the in-situ deposition of a p-GaAs layer of 4 - 5 μm thickness and of an n^+ -GaAs layer of 1-2 μm

thickness on a p^+ -GaAs substrate. The p -layer with a carrier concentration of $(1-2) \times 10^{16} \text{ cm}^{-3}$ was deposited from TMGa and As without intentional doping using an As/TMGa molar ratio of 7. The n^+ -layer with a carrier concentration of $2.5 \times 10^{18} \text{ cm}^{-3}$ was deposited by using disilane as the dopant, and the Si_2H_6 /TMGa molar ratio in the reaction mixture was 2.9×10^{-4} . The $n^+/p/p^+$ mesa diodes of 3 mm diameter were isolated by the usual

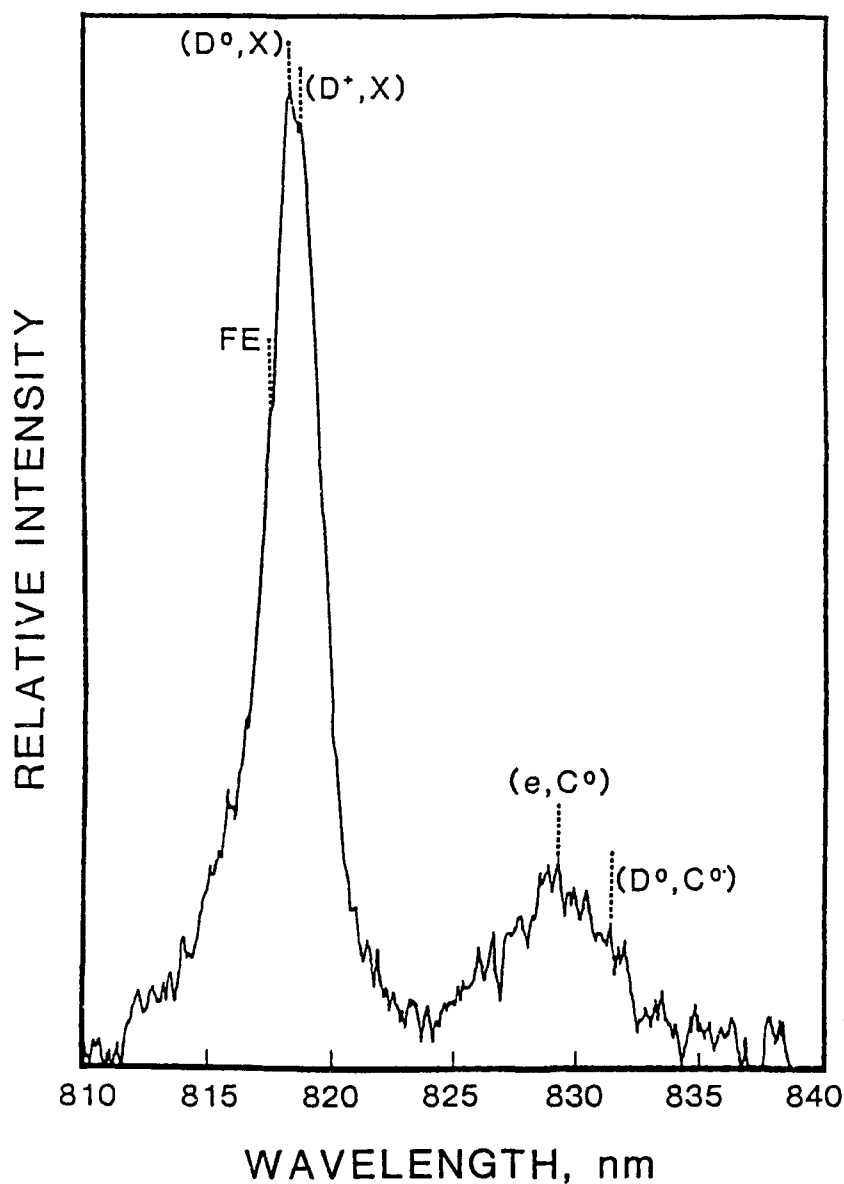


Figure 3.6 4.2K Photoluminescence of a homoepitaxial GaAs film grown from TEGa and As.

photolithographic and chemical etching techniques. Gold contact were applied to n^+ - and p^+ -GaAs by using a gold plating solution. Figure 3.8 shows the dark current-voltage characteristics of a typical $n^+/p/p^+$ diode prepared in this manner. The saturation current density and diode factor are 10^{-12}A/cm^2 and 1.2, respectively, indicating the good device quality of the GaAs films deposited from elemental arsenic.

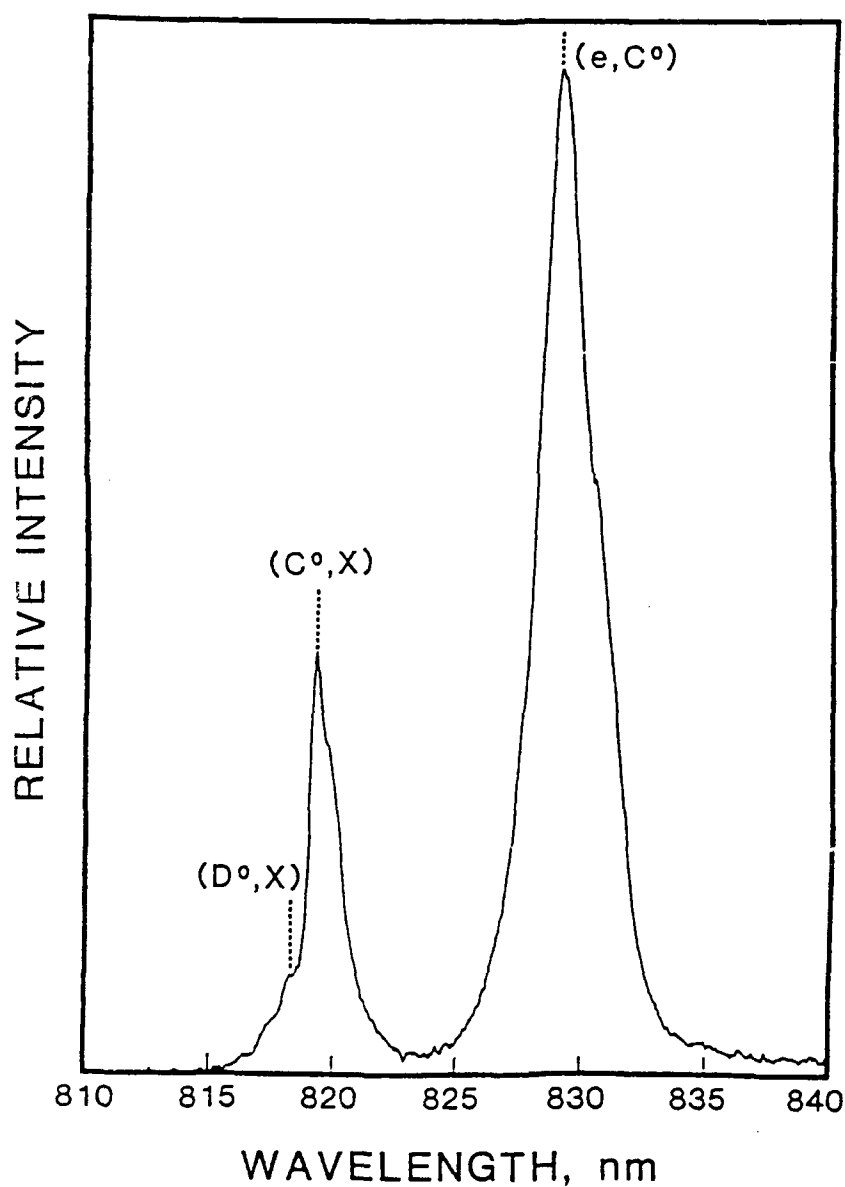


Figure 3.7 4.2 K Photoluminescence of a homoepitaxial GaAs film grown from TMGa and As.

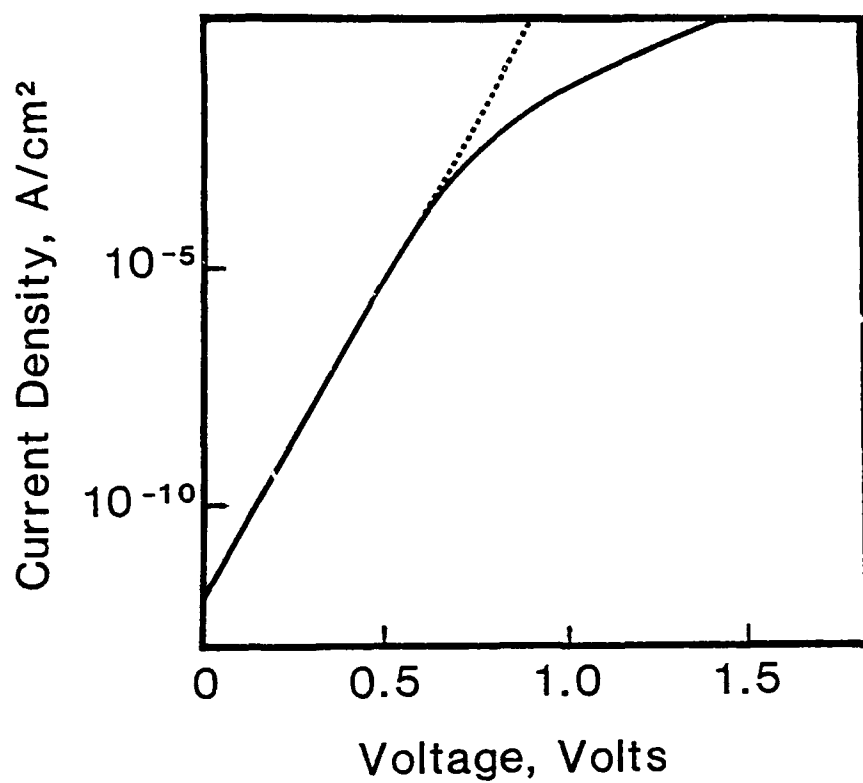


Figure 3.8 The dark current-voltage characteristics of a GaAs $n^+/p/p^+$ mesa diode deposited from TMGa and As.

Section 4.0

LASER ENHANCED HOMOEPITAXIAL GROWTH OF GaAs FILMS FROM ELEMENTAL ARSENIC

During the first phase of this program at Southern Methodist University, the laser enhanced MOVPE growth of GaAs films was carried out from TMGa and AsH₃ in hydrogen using a 193 nm ArF excimer laser [25,31]. To eliminate the use of toxic AsH₃, the ArF excimer laser enhanced homoepitaxial growth of GaAs films using TEGa and elemental arsenic was investigated and the film properties characterized. The growth process and the characteristics of the deposited films are summarized in this section.

4.1 Reaction Chamber Design

The reaction chamber used for the laser enhanced epitaxial growth of GaAs [25] was modified to accommodate the elemental As source material, as shown in Fig. 4.1. The reaction chamber is made of fused silica with a 2" diameter Suprasil II window. The substrate was mounted on the flat face of a fused silica tube. A quartz lamp inserted into the silica tube was used for substrate heating, and the substrate temperature was controlled by a thermocouple on the substrate surface. The As container, inserted into the reaction chamber through a demountable seal, is also heated radiatively, and its temperature controlled by a thermocouple inside As, not shown in Fig. 4.1. Arsenic was introduced into the reaction chamber by passing hydrogen through the container. The concentration of arsenic in the reaction mixture is then determined by the As temperature and the flow rate of hydrogen through the As container. The vaporization rate of As calculated from the ideal gas law was in good agreement with the weight loss of the As container.

The reaction chamber also has gas inlet tubes for TEGa and window purging. TEGa was maintained at 18°C (vapor pressure: 4 Torr) in a constant temperature bath and

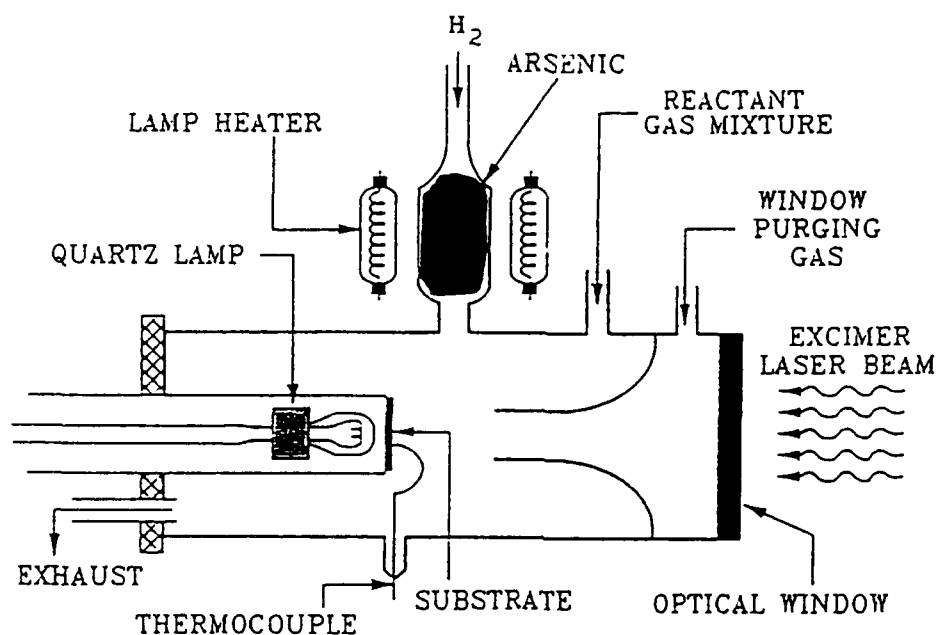


Figure 4.1 Schematic diagram of the reaction chamber for the laser enhanced epitaxial growth of GaAs.

introduced into the reaction chamber by passing hydrogen of a measured flow rate through the liquid. The pressure in the reaction chamber was controlled by using a microprocessor operated throttle valve, a Baratron gauge, and a vacuum pump. The exhaust gas from the reaction chamber was passed through a cracking furnace and a liquid nitrogen trap to ensure the complete decomposition and removal of unreacted species before entering the throttle valve.

4.2 Growth Process

An ArF excimer laser (193 nm) of 25 W maximum average power was used to enhance the growth process. The laser can be pulsed at rates of up to 80 Hz with a pulse duration of 10-12 ns, and a maximum pulse energy of 400 mJ. It is capable of constant power operation by using a microprocessor control. The laser beam, 8 mm x 33 mm in cross section, was perpendicular to the substrate surface. The flow of hydrogen over the surface of Suprasil window in the reaction chamber prevented any deposition on the window.

Single crystalline GaAs substrates of (100) orientation, usually n-type with a carrier concentration of about 10^{18} cm^{-3} and semi-insulating for Hall samples, were used. They were etched in a 6:1:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ solution, cleaned in the usual manner, and placed in the reaction chamber. The reaction chamber was maintained at 20 Torr throughout the deposition process with a hydrogen flow of about 1.5 ℓ/min . When substrate reached the deposition temperature, $425^\circ - 525^\circ\text{C}$, the substrate was etched in-situ to remove 1-2 μm GaAs from the surface by irradiation with laser at fluences below the damage threshold, about $50 \text{ mJ}/\text{cm}^2$. The irradiation of the substrate with laser provides a convenient means for the in-situ etching process.

The important process parameters of the laser-enhanced MOVPE of GaAs are (1) the composition and flow rate of the reaction mixture, (2) the substrate temperature and surface cleanliness, (3) the pressure in the reaction chamber, and (4) the repetition rate and fluence of the ArF laser. Many of these parameters are interrelated. To simplify the optimization of growth parameters, the flow rates of hydrogen and TEGa were fixed at 0.065 and 2×10^{-5} moles/min, respectively, the As/TEGa molar ratio was varied in the range of 10 to 30, and the substrate temperature was varied in the range of $425^\circ - 525^\circ\text{C}$. The laser repetition rate was 40 Hz at fluences of $15\text{-}40 \text{ mJ}/\text{cm}^2$. The average photon flux at the substrate surface was significantly higher than that of TEGa. For example, using a pulse rate of 40 Hz at a fluence of $20 \text{ mJ}/\text{cm}^2$, the average photon density is about ten times of the density of TEGa molecules in the reaction chamber.

Specular epitaxial GaAs films have been grown reproducibly by using the TEGa flow rate, substrate temperature, and laser fluence described above; the temperature required for the epitaxial growth process has been reduced by laser-irradiation. The crystallinity and defect density in the epitaxial films are similar to those in the substrate, as indicated by

using a preferential etch, such as a 0.2 M solution of FeCl_3 in 6 M HCl [56]. The As/TEGa molar ratio in the reaction mixture has been found to affect the quality of the GaAs films, depending on the substrate temperature. At low temperatures, 425°C for example, films grown with As/TEGa ratios of lower than about 16 were hazy, particular after etching, due to arsenic deficiency in the films. The As/TEGa ratio required for the growth of specular films decreases with increasing substrate temperature; an As/TEGa ratio of about 10 is suitable for the growth process at 500°C. This dependence is presumably related to the temperature dependence of the dissociation of As_4 into As_2 . To compare the growth rate versus temperature, an As/TEGa ratio of 20 was used in all experiments. Figure 4.2 shows the average growth rate of epitaxial GaAs films, enhanced by laser fluences of 20.8 and 29.5 mJ/cm^2 , as a function of temperature, where a linear scale was used because of the small variation of the growth rate with temperature. The rates of the thermal process are also

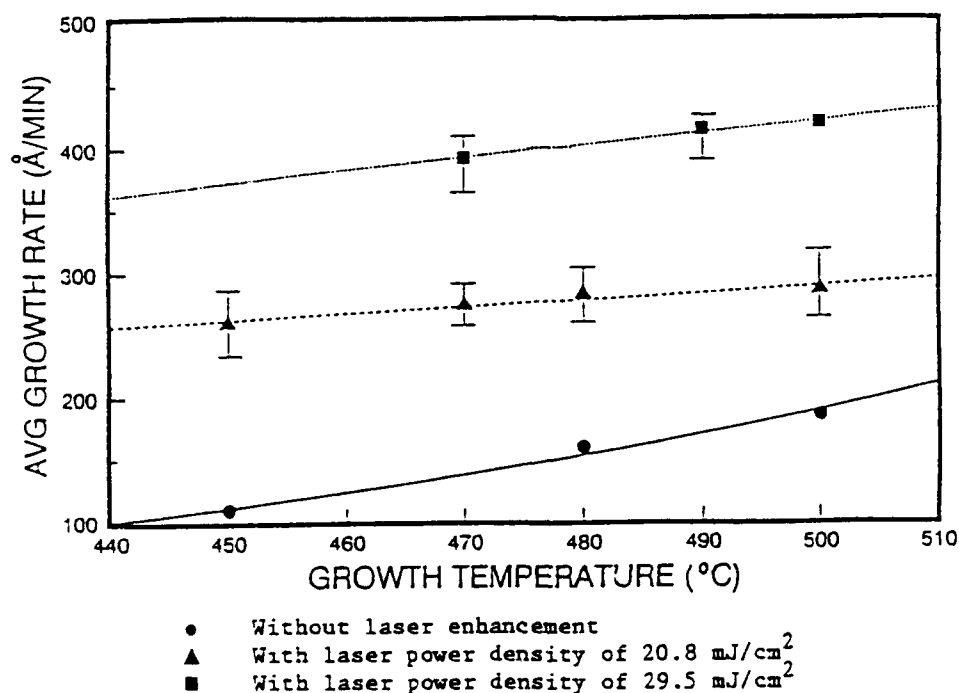


Figure 4.2 Average growth rate of epitaxial GaAs films as a function of temperature by laser enhanced (laser fluences of 20.8 and 29.5 mJ/cm^2) and thermal processes.

shown in Fig. 4.2 for comparison. The thickness of grown films and the growth rate were determined from the carrier concentration profile in the thickness direction by the electrochemical technique, and the results were confirmed in selected cases by direct measurement of angle-polished and etched cross-sectional surfaces. At a given temperature, the growth rate of epitaxial GaAs films is significantly enhanced by laser irradiation, and the extent of enhancement increases essentially linearly with increasing laser fluence, as shown in Fig. 4.3. The activation energy of the laser enhanced growth process is very small, 0.1 to 0.12 eV at the laser fluences used, indicating that the growth process is not limited by the surface process.

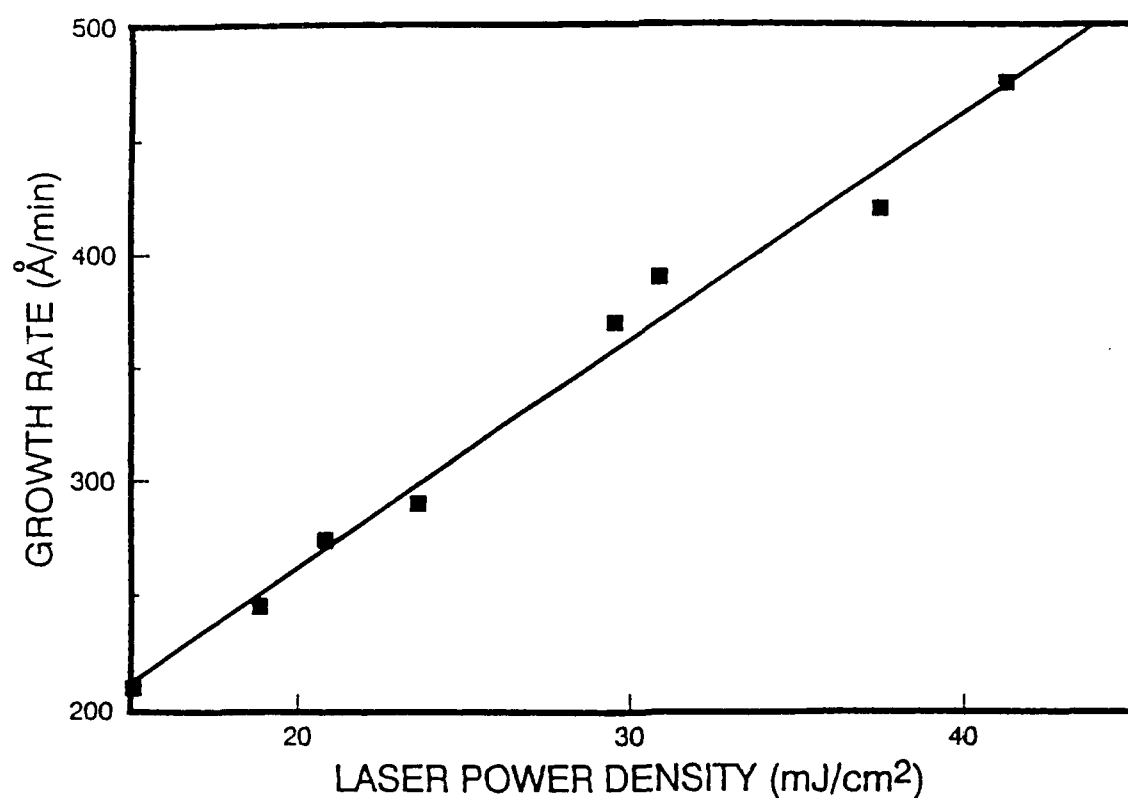


Figure 4.3 Average growth rate of epitaxial GaAs films at 450°C as a function of laser fluence.

4.3 Characterization

Epitaxial GaAs films grown by the laser-enhanced process are usually n-type with net carrier concentrations in the range of $(1-6) \times 10^{15} \text{ cm}^{-3}$, depending on the substrate temperature and laser fluence. Figure 4.4 shows the carrier concentration depth profile, measured by the electrochemical technique, in a typical GaAs films grown on an n^+ -substrate at 450°C by the laser enhanced process. Hall mobilities in several GaAs films grown on semi-insulating substrates at laser fluences greater than about 25 mJ/cm^2 at 40 Hz were measured by the van der Pauw technique using In-Sn alloy contacts. They were in the range of $3,000 - 4,000 \text{ cm}^2/\text{Vs}$ at room temperature and less than $9,000 \text{ cm}^2/\text{Vs}$ at 77K. The low mobility of the laser-enhanced grown GaAs is most likely to be associated with a high degree of compensation.

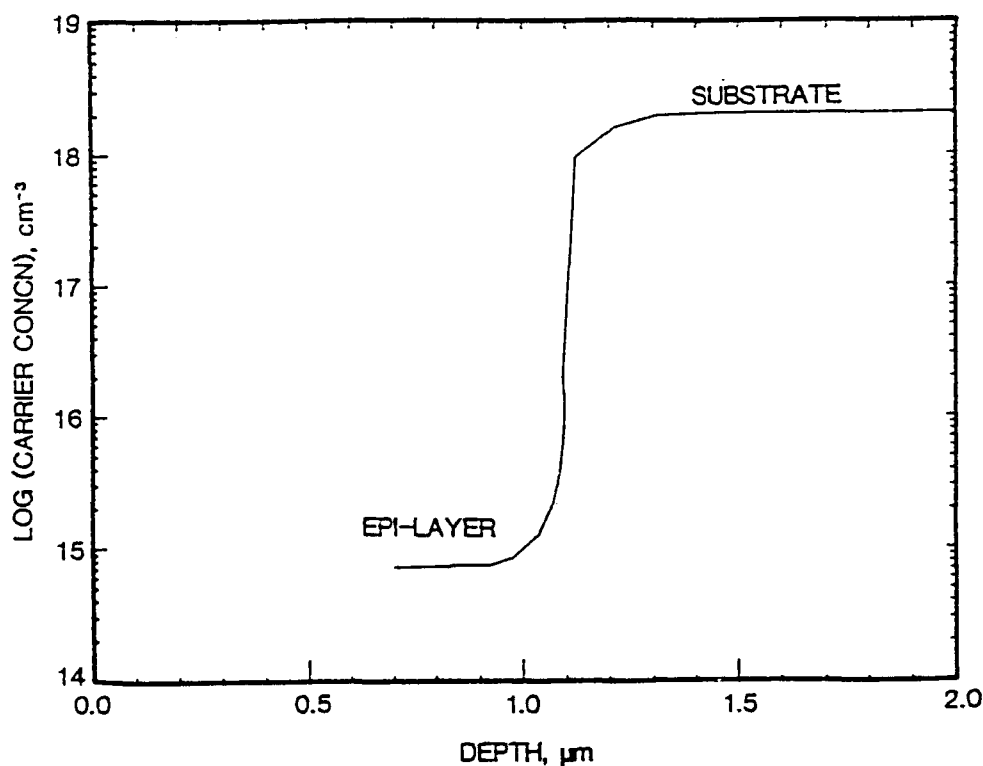


Figure 4.4 Carrier concentration profile in an epitaxial GaAs films grown at 450°C by the laser enhanced process.

The photoluminescence spectra of epitaxial GaAs films grown by laser enhancement were measured at 4.2K. Figure 4.5 shows the luminescence spectra of two epitaxial GaAs films grown at laser fluences of 20.8 and 23.6 mJ/cm², and the various transitions are designated. The bands at 818 nm are associated with the free exciton, exciton-donor, exciton-donor ion, and exciton-carbon transitions. The bands at 829 nm are characteristic of carbon. The relative intensity of the two bands in conjunction with the mobility data may be used to estimate the carbon concentration in GaAs. The film deposited at a laser fluence of 20.8 mJ/cm² is estimated to have a carbon concentration of about 10¹⁶ cm⁻³, and the carbon concentration in the film deposited at 23.6 mJ/cm² approaches 5 x 10¹⁶ cm⁻³. As a comparison, the carbon concentration in thermally grown GaAs is less than 5 x 10¹⁵ cm⁻³. It is thus likely that the use of ArF laser irradiation has resulted in the dissociation of C-C, C-H, and C-Ga bonds in TEGa since the photon energy, 6.5 eV, is considerably higher than these bond energies, 3-4 eV. Carbon is known to be an acceptor in GaAs, compensating the donors from TEGa. Several epitaxial GaAs samples grown from TMGa and As were found to be all p-type, similar to those deposited from TMGa and arsine [25], due apparently to the higher degree of carbon incorporation. The lower carbon concentration in GaAs films grown from TEGa could be related to the β -elimination mechanism of its decomposition [51]. The relative high carbon concentration in laser-enhanced MOVPE GaAs may limit its application in certain minority carrier devices.

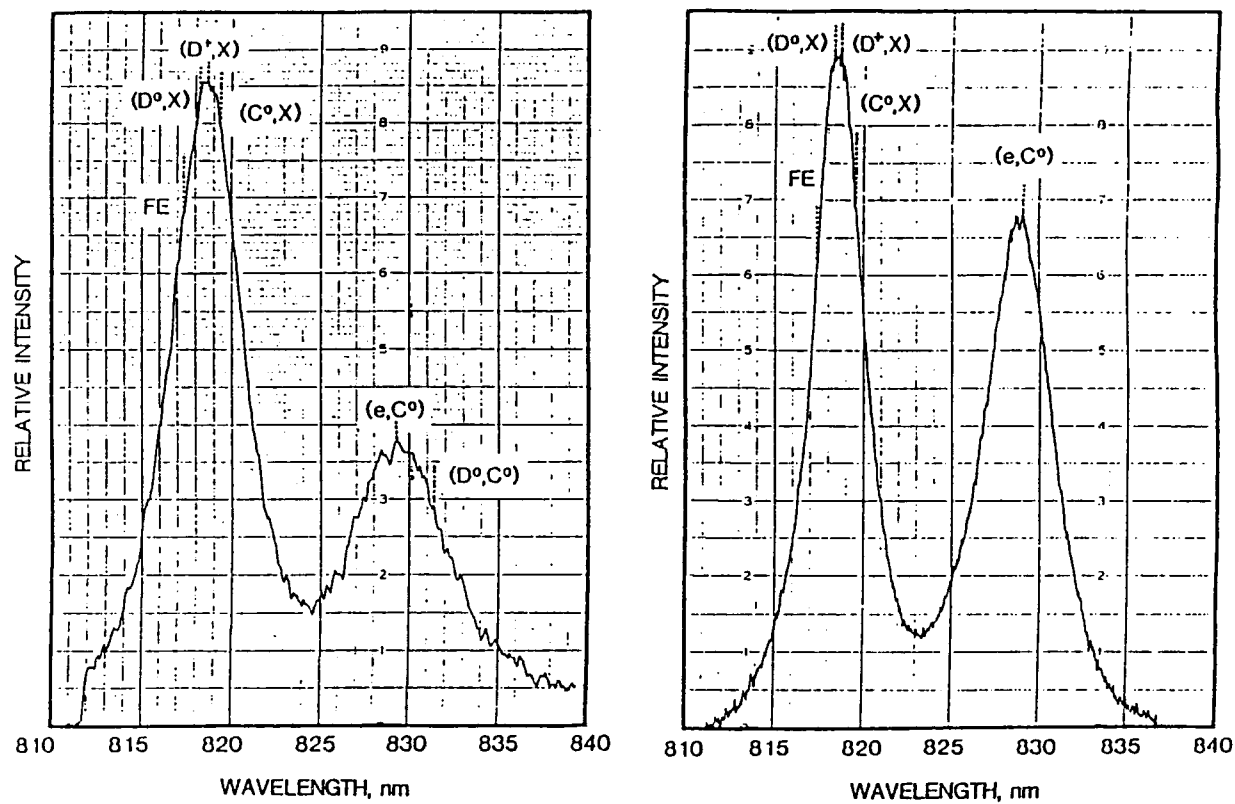


Figure 4.5 4.2 K Photoluminescence spectra of epitaxial GaAs films grown by laser-enhancement at fluences of 20.8 (left) and 23.6 (right) mJ/cm².

Section 5.0

HETEROEPITAXIAL GROWTH OF InP ON GaAs SUBSTRATES FROM NONHYDRIDE SOURCES

Indium phosphide (InP) and lattice matched to InP alloys, $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ and $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ ($0 < x < 0.47$, $y \approx 2.2x$), are useful for many optoelectronic devices. The high cost of bulk InP wafers in addition to the small size (2 to 3" diameter) and high defect density, the epitaxial growth of device quality InP on Si is an attractive technology, particularly in the integration of III-V and Si devices. The heteroepitaxial growth of InP on Si substrates by MOVPE from TMI_n and phosphine has been under investigation during recent years [59-62]. A GaAs interlayer is usually utilized for the heteroepitaxial growth of InP on Si due to the large lattice mismatch between InP and Si as shown in Table 2. Since

Table 2. Physical Properties of Si, GaAs, and InP

	Si	GaAs	InP
Lattice Constant (Å)	5.431	5.653	5.868
Thermal Expansion Coeff (K ⁻¹)	2.6×10^{-6}	6.8×10^{-6}	4.56×10^{-6}
Thermal Conductivity (W/cm-K)	0.21	0.07	0.10
Critical Resolved Shear Stress (MPa)	1.85	0.40	0.36
Melting Point (°C)	1420	1238	1070

the heteroepitaxial growth of GaAs on Si technology has been established, the growth of InP on GaAs substrates by MOVPE was investigated in this program using TBP as the phosphorus source to eliminate the hazard associated with phosphine. Further, ethyldimethylindium (EDMIn), a relative new organoindium compound, was selected as the In source on account that EDMIn is a liquid at room temperature instead of TMI_n which is a solid at room temperature. The vapor pressure of EDMIn is 0.85 Torr at 17°C and is similar to that of TMI_n. The growth process and results are discussed in this section.

5.1 Growth Process

The heteroepitaxial growth of InP on GaAs substrates has been carried out under atmospheric pressure using the reaction of EDMIn and TBP in a hydrogen flow in a horizontal fused silica reactor of 55 mm ID as shown in Fig. 3.1. The EDMIn, TMGa, TBP, and TBAs containers were kept at 17°, 0°, 10° and 10°C, respectively. These compounds were introduced into the reactor by passing hydrogen of measured flow rates through each container. The total flow rate of H₂ through the reactor was 4 - 7 ℓ/min. Silicon doped or undoped GaAs wafers of 2 - 3° off the {100} orientation toward a [100] direction were used as substrates. The substrates were cleaned ultrasonically in organic solvents and etched in a 8:1:1 H₂SO₄:H₂O₂:H₂O solution. They were placed on the silicon carbide-coated graphite support in the reactor after thorough rinsing with deionized water and drying with a filtered N₂ jet. Prior to the deposition of InP on GaAs, the GaAs substrates were heated at 650°C in H₂-TBAs ambient for 15 min. to remove the surface oxide followed by the deposition of a thin GaAs buffer layer at 600°C from TMGa and TBAs.

The heteroepitaxial growth of InP on GaAs substrates was carried out under atmospheric pressure by using a two temperature growth process. This process involves the growth of an initial nucleation layer at low temperature followed by the deposition of epitaxial layer at a higher temperature. Since the crystallinity of the epitaxial layer is determined by growth parameters of the nucleation layer, the deposition of the nucleation layer was investigated over a wide range of conditions. The flow rate of EDMIn was fixed at 3.2×10^{-6} mole/min. The TBP/EDMIn molar ratio, the growth temperature, and the duration of growth were varied from 30-75, 400°-450°C, and 5-20 min, respectively. The deposited layers were evaluated by x-ray diffraction, SEM, and photoluminescence. When a TBP/EDMIn molar ratio of 30 was used, the deposited layer was discontinuous in the

growth temperature range studied. The layer became continuous when the TBP/EDMIn ratio was increased to 75. A high TBP/EDMIn ratio is required because of the instability of EDMIn compared to TBP. The deposition rate was about $100 \text{ \AA/min}$ and the surface of the InP films of $0.2 \text{ }\mu\text{m}$ thickness deposited at $400^\circ\text{--}420^\circ\text{C}$ was mirror smooth under visual observation and showed orange peel appearance under SEM. The nucleation layer grown at 400°C was found to be single crystalline from x-ray diffraction as shown in Fig. 5.1. The annealing of the nucleation layer at 600°C for 10 min improved the crystallinity as demonstrated by the decrease in FWHM of the x-ray diffraction peak.

Following the deposition of InP nucleation layer at $400^\circ\text{--}420^\circ\text{C}$ for 10-20 min and the subsequent annealing, the epitaxial layer was deposited at $500^\circ\text{--}550^\circ\text{C}$ using a fixed flow rate of EDMIn of $3.2 \times 10^{-6} \text{ mole/min}$ and a TBP/EDMIn ratio of 30-75. The deposited layer was mirror smooth and nearly featureless under SEM. The deposition rate was about

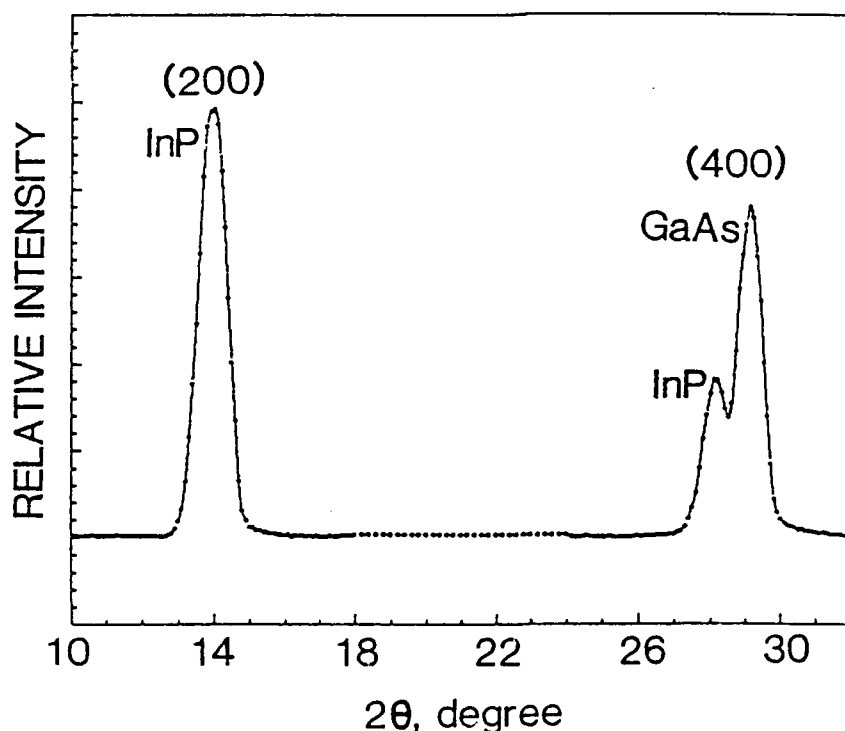


Figure 5.1 X-Ray diffraction spectrum of an InP buffer layer deposited at 400°C without annealing.

1 $\mu\text{m/hr}$ in the temperature range of 500°-550°C. Thus, by using EDMIn and TBP as the source materials, epitaxial InP layers can be grown at temperatures considerably below those deposited from trimethylindium (TMIn) and phosphine.

5.2 Characterization

The InP films deposited on GaAs substrates were characterized by electrochemical carrier concentration profile, photoluminescence, and Hall mobility measurements. Without intentional doping, the deposited InP films are n-type, and the net electron concentration depends on the TBP/EDMIn molar ratio in the reactant mixture and is essentially independent of growth temperature. At a growth temperature of 400°-550°C, the net electron concentration in InP is in the range of $8 \times 10^{16} - 1 \times 10^{17} \text{ cm}^{-3}$ at a TBP/EDMIn molar ratio of 75 and is reduced to $(2-3) \times 10^{16} \text{ cm}^{-3}$ when the TBP/EDMIn ratio is decreased to 30. These results indicated that the donors in deposited InP films are most likely to be associated with impurities in TBP. Figure 5.2 shows the electron concentration profile of an InP layer deposited on an n-type GaAs substrate with a buffer layer deposited at 420°C and a TBP/EDMIn ratio of 75 and an epitaxial layer deposited at 550°C and a TBP/EDMIn ratio of 30. The carrier concentration is uniform through the thickness of the epitaxial layer.

The photoluminescence spectra of InP buffer layers and InP epitaxial layers were measured at 77 K using an argon ion laser of 65 W/cm² power density as the excitation source. Typical results are shown in Fig. 5.3. The excitonic transition of 1.413 eV is clearly shown in the spectrum of the InP epitaxial layer. A broad band with energy of 1.35-1.37 eV is observed in the spectrum of the buffer layer; this band is associated with impurity and defect transitions. The intense photoluminescence of the buffer layer further demonstrates the reasonably good crystallinity of the InP buffer layer deposited at 400°-420°C without

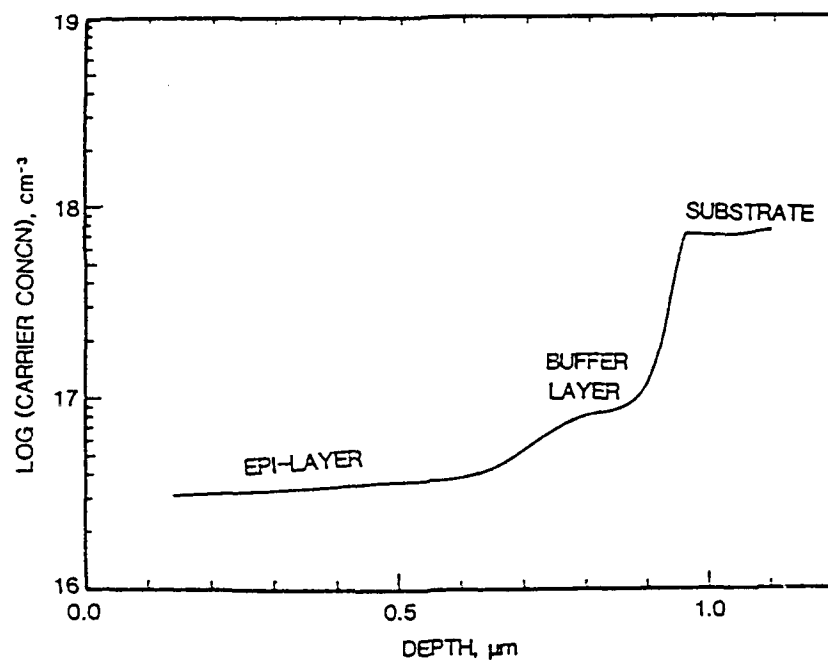


Figure 5.2 Carrier concentration depth profile of an InP epitaxial layer deposited on GaAs at 550°C (TBP/EDMIn = 30) with an InP buffer layer deposited at 420°C (TBP/EDMIn = 75).

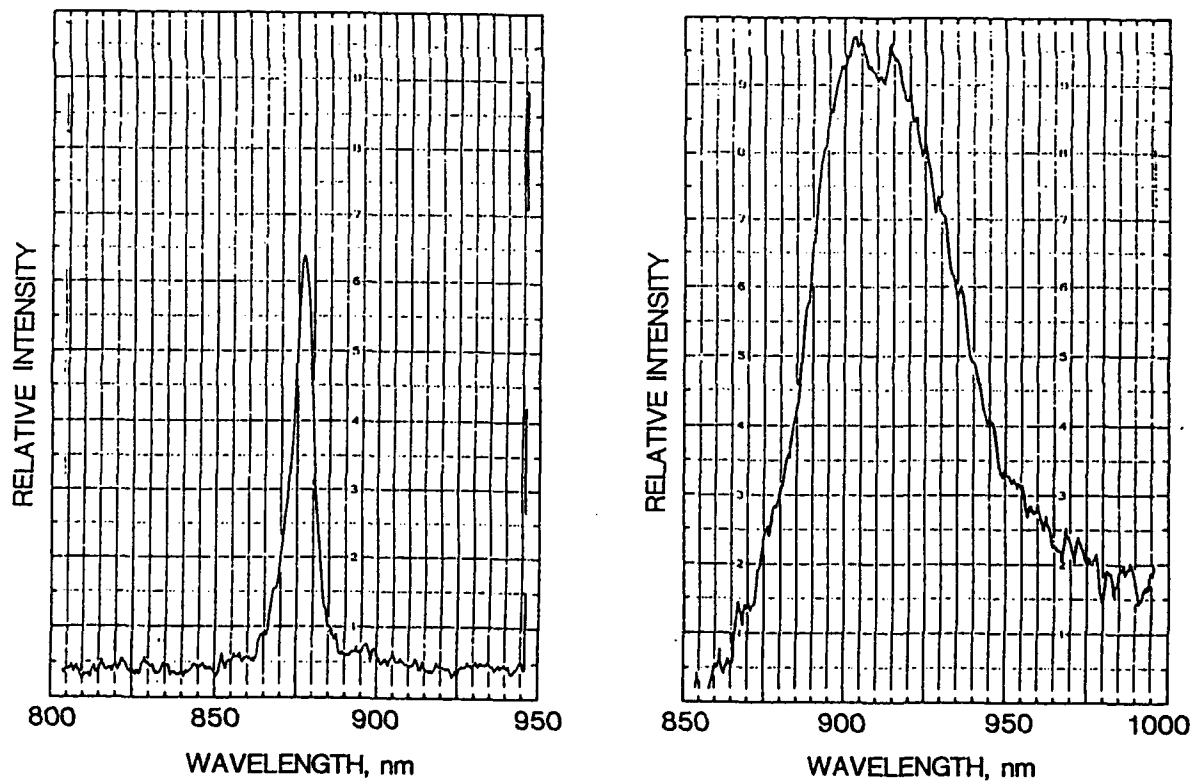


Figure 5.3 The 77 K photoluminescence spectra of an InP epitaxial layer (left) and buffer layer (right).

subsequent annealing. The 4.4 K photoluminescence of an InP layer of $1.1\ \mu\text{m}$ thickness with an excitation energy of $64\ \text{W}/\text{cm}^2$ is shown in Fig. 5.4. The high energy peak at 1.420 eV is associated with the excitonic transition, and the broad band at 1.381 eV is due to the impurities associated with acceptors [63], similar to that observed in the buffer layer. The FWHM of the excitonic peak is 5.2 meV, indicating the relative good quality of the InP films on GaAs. As a comparison, the 2.9 K FWHM is 4 meV in a homoepitaxial InP film deposited by using TMIn and phosphine at 600°C [64] and the 10 K FWHM is 11 meV and 6 meV in a homoepitaxial InP layer deposited from TMIn and TBP at 580°C and 600°C , respectively [47].

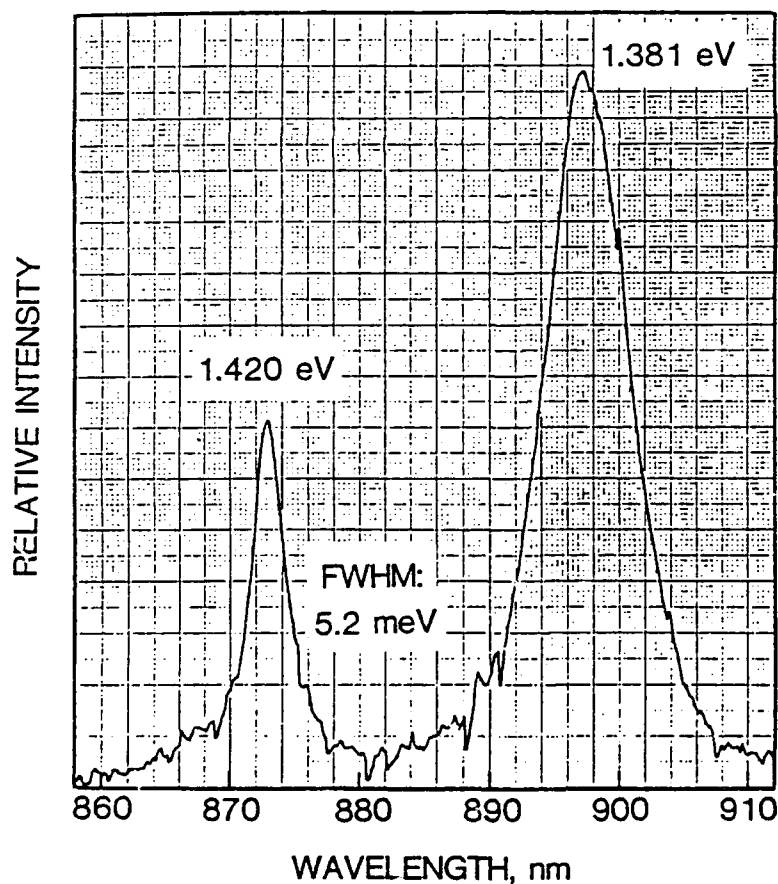


Figure 5.4 The 4.4 K photoluminescence spectrum of an InP layer of $1.1\ \mu\text{m}$ thickness.

Section 6.0

CONCLUSION

The epitaxial growth of GaAs films has been carried out from TEGa (or TMGa) and elemental As. The epitaxial temperature in the TEGa + As process is considerably lower than that required in the TEGa + AsH₃ process. The results have demonstrated for the first time that epitaxial GaAs films of good structural perfection and controlled carrier concentration can be prepared from elemental As. Although the GaAs films deposited from organoarsenic compounds have shown good electrical characteristics, it is unlikely that they will be used for epitaxial GaAs production due to their extremely high cost. The epitaxial GaAs films grown from elemental As are suitable for many GaAs based devices. The arsenic-process is particularly suited for large area devices, such as solar cells. Significant cost reduction and less stringent safety requirements are major advantages.

The process parameters for the epitaxial growth of GaAs films from TEGa and As by ArF laser enhancement, including the substrate temperature, the composition and flow rate of the reaction mixture, and the repetition rate and fluence of the laser, have been investigated. The epitaxial temperature is reduced, and the growth rate is increased. However, a relatively high concentration of carbon, $(1-5) \times 10^{16}$ depending on the laser fluence, has been found to be incorporated into GaAs. The carbon incorporation has not been reported in the GaAs films grown by argon ion laser enhancement where the photon energy is appreciably lower than the bond energies. Thus, the use of high photon energy laser for the MOVPE growth process has the disadvantage of breaking the C-containing bonds leading to the incorporation of carbon in the epitaxial films.

The heteroepitaxial growth of InP films on GaAs substrates have been carried out by using EDMIn, TBP as source materials. The two temperature growth process was used

for the deposition of InP. The InP nucleation layer deposited at 400° - 420°C by the reaction of EDMin and TBP without subsequent annealing was found to be single crystalline, epitaxial to the GaAs substrate. The epitaxial layer was deposited at 500° - 550°C, which is considerably lower than the temperature required by the phosphine process. The good structural perfection of an InP layer of 1.1 μm thickness was shown by the 5.2 meV FWHM of the excitonic peak in the 4.4 K photoluminescence spectrum.

Section 7.0

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Section 8.0

PUBLICATIONS AND PRESENTATIONS

8.1 Publications

Shirley S. Chu, "ArF Excimer Laser-Induced Epitaxial Growth of Gallium Arsenide Films", Proceedings of the International Society for Optical Engineering on Photochemistry in Thin Films, **1056**, 188 (1989).

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"Laser Assisted MOCVD Growth of Compound Semiconductors", Florida Chapter of American Vacuum Society, Clearwater, Fl., February 8, 1989.

"Epitaxial Growth of Gallium Arsenide Using Solid Arsenic Source", 176th Electrochemical Society Meeting, Hollywood, Fl., October 15-20, 1989.

"Heteroepitaxial Growth of InP and GaInAs on GaAs Substrates Using Tertiarybutylarsine and Tertiarybutylphosphine", Materials Research Society Meeting, San Francisco, CA., April 16-20, 1990.

"ArF Laser Induced Epitaxial Growth of GaAs Films on GaAs and Si Substrates Using Elemental Arsenic", Electronic Materials Conference, Santa Barbara, CA., June 27-29, 1990.

"Homoepitaxial Growth of GaAs Using Elemental Arsenic With and Without Laser Enhancement", Second International Conference on Electronic Materials, Materials Research Society, Newark, NJ, September 17-19, 1990.

"Epitaxial Growth of Gallium Arsenide from Elemental Arsenic", SPIE's International Conference on Physical Concepts of Materials for Novel Optoelectronic Device Applications, Aachen, Germany, October 27 - November 2, 1990.

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