Characterization of III-V Semiconductor Materials by Surface-Sensitive Analytical Techniques

A Review

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Applications of surface-sensitive analytical techniques to research and development of III-V semiconductor materials are illustrated. The studies reviewed are related to the understanding of various aspects of material processing such as epitaxial growth by molecular beam epitaxy, diffusion of group II elements in InP, ion implantation of n- and p-type dopant species, and dry etching in chlorine-containing discharges. In addition, impurity-induced layer disordering of quantum well heterostructures and superlattices will be discussed. Examples are drawn from a number of analytical techniques sensitive to the surface and to the interface. Special emphasis is given to GaAs and InP which are currently under study most extensively.

Keywords III-V semiconductors, epitaxial growth, molecular beam epitaxy, quantum well heterostructures, impurity diffusion, ion implantation, dry etching, superlattice disordering, reflection high energy electron diffraction, cathodeluminescence, secondary ion mass spectrometry, Auger electron spectroscopy, depth profiling, transmission electron microscope, ion backscattering, ion channeling, Raman scattering, modulated molecular beam mass spectrometry, X-ray photoelectron spectroscopy

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1 Introduction

A variety of surface analysis techniques have now become indispensable implements to develop electronic materials and devices. Among various kinds of electronic materials, III-V semiconductors have several prominent properties:^{1,2}

(1) Most of them have a higher electron mobility than do elemental semiconductors such as Si and Ge.

(2) Most of them belong to the direct band-gap semiconductors in which the lowest conduction band minimum and the highest valence band maximum are at the same wave vector in the Brillouin zone. On the other hand, Si is an indirect band-gap semiconductor in which the extrema are at different wave vectors. Since the momentum is automatically conserved in the optical transition in a direct band-gap semiconductor, the optical gain is expected to be high. The optical

transition in an indirect band-gap semiconductor, however, involves phonons and other scattering processes to conserve the momentum and energy; thus the radiative transitions are weaker, and the available gain is smaller.

(3) The band-gap energy can be varied by the use of crystalline solid solutions in which some of the host atoms are replaced by other atoms in the same period of the periodic table. For example, a ternary III-V solid solution may consist of atoms of group III elements A and B which are randomly mixed at group III lattice sites, and atoms of group V element C on all of the group V lattice sites. This solid solution is designated as $\text{A}_x\text{B}_{1-x}\text{C}$ and x may vary between zero and unity.

Recent progress in the understanding and preparation of III-V semiconductor materials has made possible optoelectronic and high-speed devices with unique properties. This paper will outline how we are making

use of the surface analysis techniques in the research and development of III-V semiconductor materials and devices.

2 Epitaxial Growth

Modern semiconductor injection lasers have a structure in which a layer of a semiconductor with a relatively narrow band-gap is sandwiched between two layers of a wider band-gap semiconductor. A junction of two such dissimilar semiconductors is called a heterojunction. The lattice-matched crystalline growth of one semiconductor over another is called epitaxy. The development of sophisticated epitaxial techniques has been of major significance in the development not only of semiconductor lasers but also of other III-V semiconductor devices. Among epitaxial growth techniques, molecular beam epitaxy (MBE) is capable of producing ultra-thin epitaxial layers with a precision of one monolayer and also capable of doing characterization measurements of the growing layers *in situ*.

2.1 Reflection high energy electron diffraction intensity oscillations

In 1981, Harris and coworkers reported that there are oscillations in the intensity of the specular beam, that is, the central diffraction line, in the reflection high energy electron diffraction (RHEED) pattern during the growth of GaAs by MBE.³ It was originally thought that the oscillations occurred as the result of the complex incorporation behavior of Sn which was

being used as a dopant.³ It was subsequently pointed out that for certain growth conditions weak oscillations could be observed even without any dopant present.⁴ It was shown, however, that the period of the oscillation corresponded exactly to the monolayer growth rate on a (001) oriented GaAs substrate^{3,4}, where a monolayer is defined as one complete layer of Ga, plus one complete layer of As, or also defined as a thickness equivalent to a half of the lattice constant. An example of RHEED intensity oscillations is shown in Fig. 1; this has been observed during the MBE growth of InP using trimethylindium and PH_3 .⁵ The 25 keV electron beam was aligned along the [001] azimuth. Although rapid damping is observed immediately after initiation of growth, the oscillations continued more than 700 cycles with a constant period of 4.3 s. In the past few years, intensity oscillations have been observed not only in GaAs and InP but also in AlGaAs, InGaAs, Si and SiGe.⁶⁻¹⁰

A growth model has recently been constructed which accounts for the RHEED intensity oscillations on the basis of two-dimensional nucleation and a single-scattering (kinematical) diffraction process, as is illustrated in Fig. 2.¹¹ If we equate changes in specular beam intensity with changes in surface roughness, we can assume that the equilibrium surface is smooth, corresponding to high intensity ($\theta=0$ in Fig. 2). When growth starts, two-dimensional nuclei are formed at random positions on the crystal surface, resulting in a decrease in diffracted intensity. In a kinematical approximation this is the expected result, since the de Broglie wavelength of electrons is typically 0.1 Å (the

Fig. 1 RHEED intensity oscillations observed during the growth of InP by MBE using trimethylindium (TMI) and PH_3 .⁵ Upper figures represent the number of oscillations after the start of growth. $T_g=490^\circ\text{C}$; TMI, 0.5 ccm; PH_3 , 3.0 ccm.

Fig. 2 A growth model (two monolayers) in relation to the RHEED intensity behavior.¹¹ θ =number of monolayers deposited.

RHEED diffraction patterns are usually observed at glancing incidence, $1-4^\circ$, using electron beam energy of 10–30 keV, while the step height for GaAs is 2.83 Å, so that the wavelength is over a decade smaller than the size of the scatterer, resulting in diffuse scattering. Diffuse scattering will be a maximum at half-layer coverage ($\theta=0.5$) and a minimum at the start of each layer ($\theta=1$). In this model, damping occurs because a second layer can start to grow before the first is complete and the growth front eventually becomes statistically distributed over several incomplete layers. More sophisticated studies to interpret the RHEED oscillations are being continued by taking dynamical (multiple-scattering) effects into consideration.¹²

The RHEED intensity oscillation technique is now widely used for monitoring morphology and disorder, molecular beam flux calibration, growth rate control and quantum well thickness determination, in addition to the studies of MBE growth dynamics. Quite recently, similar oscillatory behavior during MBE growth of GaAs and AlAs have also been observed in secondary electron emission¹³, in the energy-integrated near-threshold photoemission¹⁴, and in optical reflectance signals.¹⁵ These observations are also attributed to

Fig. 3 SIMS depth profiles of alternating superlattice layers of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(950 \text{ \AA})/\text{InP}(650 \text{ \AA})$ grown on a (100) InP substrate.¹⁶

the periodic changes in the nature of the surface and they are expected to provide information complementary to that from RHEED.

2.2 Abruptness of heterointerfaces

The atomic configuration of heterojunction interfaces has decisive influence on the optical and electronic properties of semiconductor multilayered structures. Therefore, the accurate characterization of the abruptness in composition, crystal integrity and strain at these interfaces is indispensable.

In the study of the abruptness of heterojunctions, the most popular technique for depth profiling is the use of ion bombardment associated with secondary ion mass spectrometry (SIMS) or Auger electron spectroscopy (AES). Figure 3 shows a typical SIMS depth profile of alternating superlattice layers of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}(950 \text{ \AA})/\text{InP}(650 \text{ \AA})$ grown on a (100) InP substrate.¹⁶ On the top of the superlattice, an additional InP layer (2.2 μm thick) was grown. The analyses were performed using Cs^+ ions at 10 keV and electronegative secondary ions at -4.5 keV were extracted for detection. This configuration was adopted to optimize sensitivity to the principal material constituents (In, Ga, As and P) and to permit enhanced primary beam stability for the desired beam intensity. An approximately 20-nA primary beam focused to a 50-μm-diameter spot was rastered to cover a calibrated 400×400 μm square area. The signal from an approximately 60-μm-diameter area

in the center of the crater bottom was detected in order to minimize the signal resulting from material sputtered from the crater walls.

As is well known, the depth resolution of the techniques which rely on ion bombardment will be degraded due to the presence of the primary recoils, to the large difference between the sputtering yields of the constituent elements, and to the cascade mixing. An interesting alternative to conventional ion bombardment depth profiling combined with Auger analysis is the use of the beveling usually performed with diamond or alumina paste. Bisaro *et al.* proposed chemical beveling instead of mechanical beveling.¹⁷ The apparatus¹⁸ used for the chemical bevel formation consists of two cylindrical tanks linkable by taps. The first (A) is filled with methanol while the other (B) is filled with the etchant (bromine-methanol solution). A piston which is driven by a motor set into tank B is used to push the etchant from tank B to tank A at a constant speed. The sample is glued on a glass plate, which is held vertically with the sample immersed in methanol from tank A. Next, the tap between tanks A and B is opened. As a consequence, an interface is formed when the two liquids are in contact. When the motor is started, this interface goes up along the sample surface. The bevel formation is a result of the linear motion of this interface. The primary electrons are scanned in a scanning Auger machine along the bevel and the data associated with every Auger energy specified are collected. Figure 4 shows a schematic representation of the bevel.¹⁹ This method has been applied to evaluate the concentration distribution of an InP/GaAs heterostructure and to discuss the transition region formation due to the differences between the atomic diffusions of III- and V-type elements. The ultimate width which could be checked by this method lies between 10 and 15 Å and is of the order of magnitude of the escape depth of the Auger electrons selected.¹⁷

High-resolution transmission electron microscope (HRTEM) represents a tool extensively employed in the investigation of semiconductor/semiconductor interfaces. The interface is usually studied in cross section, with the electron beam parallel to the $\langle 110 \rangle$ direction. The position of the interface is deduced from the change in background intensity of the lattice image as one proceeds from one semiconductor material to the

other. However, the background intensity can be strongly modulated by a variety of causes, such as surface contamination and ion-milling damage, and in any case it does not change appreciably across the interface in the thinner regions of a sample. Since no structural change takes place across semiconductor/semiconductor interfaces, the question of their atomic configuration is chemical rather than structural in nature.

The majority of reflections in the zinc-blende structures, to which III-V semiconductors belong, are only mildly sensitive to chemical changes in the material. In the zinc-blende structure, the two sublattices are occupied by different atomic species and the (200) reflections become kinematically allowed because of the difference in the atomic form factors of the different species. Consequently, these reflections are extremely sensitive to the chemical nature of the occupants of the sublattices in III-V semiconductors. In the $\langle 110 \rangle$ projection, two (200) reflections contribute to the lattice image. They are, however, dominated by the four strong and chemically insensitive (111) reflections. In the $\langle 100 \rangle$ projection, four (200) reflections can contribute to the lattice image, thus leading to increased chemical sensitivity.²¹

The advantage of forming lattice images in the $\langle 100 \rangle$ projection has recently been discussed.²⁰⁻²² Ourmazd *et al.*²² have shown that an interface normally considered to be atomically smooth and abrupt can possess significant roughness on an atomic scale; they proved this by imaging the same area of an interface between $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and InP along $[110]$ and $[100]$.

Superlattices are produced by the epitaxial growth of alternating layers of two different semiconductor materials.²³ When thin layers are lattice-mismatched, the mismatch is often accommodated by tetragonal distortions along the growth direction. These structures are known as strained layer superlattices (SLS).²⁴ It is important to be able to quantify the strain in this type of material; it has been shown^{25,26} that ion backscattering and channeling can provide this information. Cole *et al.*²⁷ have reported strain measurements performed for a series of lattice mismatched $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{InP}$ structures (lattice matched for $x=0.47$). Single $\text{In}_{1-x}\text{Ga}_x\text{As}$ layers were grown on (001) InP substrates by metal organic chemical vapor deposition (MOCVD). Layer thicknesses were close to 3000 Å and x values spanned the compositional range $0.34 < x < 0.53$. Helium ions at 2 MeV were used to perform ion backscattering and channeling measurements, with an angular resolution of 0.01° and an ion beam divergence of $< 0.04^\circ$. They found that the dechanneling is enhanced in the $\langle 110 \rangle$ direction compared to that obtained for the $\langle 001 \rangle$ alignment. A schematic diagram is illustrated in Fig. 5 showing the accommodation of lattice mismatch by layer strains and the angular separation of the substrate and surface $\langle 110 \rangle$ channeling directions for an epitaxial $\text{In}_{1-x}\text{Ga}_x\text{As}$ layer lattice

Fig. 4 Schematic representation of the bevel of the InP/GaAs structure showing how a surface analysis along the bevel is converted into depth analysis.¹⁹

Fig. 5 A schematic diagram showing the accommodation of lattice mismatch by layer strains and the angular separation of the substrate and surface $\langle 110 \rangle$ channeling directions for an epitaxial $\text{In}_{1-x}\text{Ga}_x\text{As}$ layer lattice mismatched to an InP substrate.²⁷

mismatched to an InP substrate.²⁷ As the tetragonal distortions occur along the $\langle 001 \rangle$ growth direction, they are unobservable by channeling along this axis. However, channeling along the inclined $\langle 110 \rangle$ axis will reveal the strain, since ions channeled in the surface layer will be dechanneled on reaching the substrate.

To obtain a quantitative estimate of the layer strains, the angular separation ($\Delta\phi$) (Fig. 5) of the surface and substrate $\langle 110 \rangle$ channeling directions can be measured directly.²⁸ Assuming the single in-plane lattice constant (b_1) to be that of unstrained InP, a value for the strained lattice constant (b_3) can be determined using $\Delta\phi = \tan^{-1}(b_3/b_1)$ and a value of $(b_3 - b_1)/b_1$ can be calculated for the strain. Based on this method, Cole *et al.* have obtained a compression (negative) strain of 0.0152 ± 0.0008 for a lattice-mismatched $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ epitaxial layer on an InP substrate and an expansion (positive) strain of 0.0126 ± 0.0010 for a lattice-mismatched $\text{In}_{0.58}\text{Ga}_{0.42}\text{As}$ layer structure.²⁷

The study of RHEED oscillations on III-V compounds has been focused mainly on the growth of lattice-matched materials such as AlGaAs on GaAs substrates and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ on InP substrates. Lievin and Fonstad²⁹ have recently observed the RHEED oscillations during the growth of strained $\text{In}_{1-x}\text{Al}_x\text{As}$ layers on InP substrates by MBE. Long-lasting oscilla-

Fig. 6 RHEED oscillation behavior on AlInAs as a function of positive or negative mismatch $\Delta a/a$. (a) -1.6×10^{-2} ; (b) -6.6×10^{-3} ; (c) ≈ 0 , i.e., lattice matched; (d) 1.7×10^{-2} ; (e) 2.5×10^{-2} .²⁹

tions (over 100) were recorded on $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ growing lattice matched on InP. Figure 6 shows the oscillation recordings on $\text{In}_{1-x}\text{Al}_x\text{As}$ for varying positive ($x < 0.48$) and negative ($x > 0.48$) lattice mismatches. The lattice mismatch variations were achieved by lowering the aluminum cell temperature for positive mismatch and lowering the indium cell temperature for negative mismatch, so that the growth rates were comparable for layers with the same magnitude of mismatch. They proposed a method to deduce the lattice mismatch by the use of the oscillation period. They also showed that the threshold thickness above which monolayer by monolayer growth no longer occurs can be determined by counting the number of well-defined oscillations. This threshold thickness has been shown to be smaller by a factor of 5 than the critical thickness at which dislocations are generated.

Many studies have been focused on the characterization and the determination of the origin of macroscopic surface defects observed on epilayers grown by MBE. The presence of such defects with density and size as high as 10^4 cm^{-2} and $10^2 \mu\text{m}$, respectively, is a serious problem for the realization of integrated circuits. These defects are usually called "oval defects", in relation to their oval shape. This large variety of surface defects is also related to their different origins: impurities from the Ga source (oxide) or the As cell, impurity contamination of the substrate surface, localized excess of Ga, and adherence of particulates to the wafer surface. Papadopoulos *et al.*⁵⁵ studied oval defects in Si-doped $\text{Ga}_{0.7}\text{Al}_{0.3}\text{As}$ MBE grown layers by filtered

cathodoluminescence (CL) at low temperatures (10 K) in a scanning electron microscope. The spectra obtained inside and outside the same kinds of oval defects exhibited very different main emission lines; this result can be explained by an important variation of the Al/Ga ratio at the center of the defects, which was confirmed by AES.

3 Diffusion of Impurities

The diffusion of group II elements, Zn or Cd (p-type dopants), into the III-V semiconductors is a technologically important process, and a good deal of research has been carried out on the subject in order to form high quality p-n junctions. In principle, the shape of the diffusion profile should give a lot of information on the diffusion mechanism. If, for example, the diffusion coefficient is a constant, the diffusion profile would be an error function complement (erfc) curve. Diffusion in the III-V semiconductors is rarely simple, however, and it is more usual for the diffusion coefficient to depend in some way on the concentration of diffusant.^{30,31}

3-1 Diffusion of zinc

It is well known that the diffusion profiles of Zn in GaAs and InP can not be described by a complementary error function. It is widely accepted that Zn diffuses in these materials by an interstitial-substitutional (I-S) mechanism. In this mechanism, a small fraction of the total dissolved Zn is present interstitially. Interstitial Zn is considered to be a singly or doubly ionized donor (Zn_i^+ or Zn_i^{++}). This interstitial Zn diffuses rapidly and combines with a group II vacancy to form a substitutional Zn acceptor. A typical diffusion profile of Zn measured by SIMS is shown in Fig. 7³², which was obtained for an undoped GaAs substrate. In this particular sample, a vapor phase diffusion method was employed using diethylzinc and trimethylarsenic (TMAs). TMAs was used to prevent GaAs surface decomposition at elevated temperatures. Two diffusion fronts are seen around the depths of 0.3 and 0.6 μm . It has also been reported that when Zn or Cd was diffused into substrates of electron concentration $n < 5 \times 10^{16} \text{ cm}^{-3}$, two diffusion fronts were observed by stain etching.^{31,33,34} The I-S model successfully predicts the high Zn concentration surface region, but does not predict the complex double profiles.

Reynolds *et al.*³² have closely examined the variation of the diffusion profile of Zn in GaAs with time and temperature by SIMS. They proposed a new model to explain the two observed diffusion fronts. In their model, Zn can exist as either a singly ionized interstitial (Zn_i^+) or a doubly ionized interstitial (Zn_i^{++}), in addition to being a substitutional acceptor. Zn_i^{++} is assumed to be a deep donor level, within a few tenths of an eV from the valence band edge. Zn_i^+ would also be a deep donor, but near the center of the band gap. The Zn_i^{++} would be formed at the surface and dominate the

Fig. 7 A SIMS depth profile of Zn (open circle) and a fitted computer simulation (solid line).³²

diffusion process in the heavily doped surface region. In less heavily p-type regions near the diffusion front, the Fermi level would move away from the valence-band edge. The more mobile Zn_i^+ would then be favored. The solid line in Fig. 7 is a profile calculated under these assumptions. Kazmierski *et al.*³⁵ studied the Zn diffusion in InP by SIMS and suggested that the shallower diffusion front can be properly explained by assuming the diffusing species to be doubly ionized interstitial donors.

A sealed evacuated quartz ampoule is commonly used to contain the sample, P or As source, and diffusant. However, this approach is inappropriate for mass production, because it is both expensive and restricted in wafer size. Another approach is to use a vapor phase diffusion method already described, which may enable us to use larger wafers. Recently, an open tube diffusion using evaporated Zn_3P_2 as the diffusion source of Zn has been reported.⁴² A layer of 2000 Å Zn_3P_2 was deposited using a thermal evaporator on the Fe-doped semi-insulating InP substrate and the Fe-doped InP epilayer (4.5 μm) grown by MOCVD. After deposition, 100 nm SiO_2 was deposited to prevent Zn_3P_2 evaporation during the diffusion. Diffusion was performed with a rapid thermal annealer which utilizes radiation heating.

Figure 8⁴² shows the carrier concentration profiles for both the InP substrate and the MOCVD Fe-InP epilayer annealed at 850°C for 15 s prior to diffusion. The diffusion time and temperature were 20 s and 520°C, respectively. Open circles in Fig. 8 shows the results obtained for InP substrate without preannealing.

Fig. 8 Comparison of the Zn_3P_2 diffusion into nonannealed semi-insulating InP substrate with high temperature (850°C) annealed semi-insulating InP substrate and MOCVD Fe-doped epilayer. The diffusion time and temperature were 20 s and 520°C , respectively.⁴²

Diffusion has been enhanced by the preannealing performed at 850°C for 15 s, and the second diffusion fronts are observed in both cases. The first diffusion fronts are 0.8 and $0.6\ \mu\text{m}$ for the substrate and epilayer, respectively. The second diffusion depths are 2.4 and $2.8\ \mu\text{m}$ for the substrate and epilayer, respectively.

Figure 9⁴² shows results of SIMS analysis for Zn_3P_2 diffusion on the annealed InP substrate. Three regions of Zn are identified; (1) a surface Zn accumulation, $\text{Zn } 2 \times 10^{20}/\text{cm}^3$, within a region nearly $0.2\ \mu\text{m}$; (2) an error-function-like diffusion region at $0.2\text{--}0.6\ \mu\text{m}$ underlying; (3) a deep diffusion region with Zn $(5\text{--}10) \times 10^{16}/\text{cm}^3$. The Zn profile in Fig. 9 is close to the electrical profiles shown in Fig. 8. Fe is redistributed into a surface Fe accumulation region and is depleted up to the depth of $2\text{--}3\ \mu\text{m}$. The concentration of Fe recovers to the background level at $2\text{--}3\ \mu\text{m}$ which corresponds to the Zn diffusion front. This depleted region behaved as a group of Ga vacancies. The depletion depth was found to be a function of annealing time and temperature. The zinc will diffuse into this region, causing a second diffusion front. All these results suggest that in order to form a shallow layer neither high temperature treatment nor any source for the redistribution of the dopant, e.g., Fe, should be applied prior to the diffusion.

Fig. 9 SIMS analysis for Zn_3P_2 diffusion into $850^\circ\text{C}/15\text{ s}$ preannealed semi-insulating InP substrate.⁴²

3.2 Diffusion of gold

It has been suggested by several groups that gold migration from the contacts in the InP layers may cause degradations on devices such as light-emitting diodes, laser diodes, or field-effect transistors. Gold migration occurs during thermal aging or during contact-annealing processes. Auger³⁶, Rutherford backscattering³⁷ and SIMS³⁸ analyses have suggested that gold was migrating in the bulk substrate up to several micrometers. Parguel *et al.*³⁹ studied gold diffusion by SIMS with a metallic layer deposited on InP substrates as a diffusion source. Sample A: a 20-nm-thick gold layer was deposited and the sample was annealed at 550°C for 1 h with a 100-nm-thick Si_3N_4 layer deposited in order to reduce phosphorus exodiffusion and hence to avoid the crystal decomposition. The Si_3N_4 and gold layers were then removed by chemical etching. B samples were prepared like A samples, but were turned over, glued on a silicon substrate, and polished down to a thickness of about $25\ \mu\text{m}$. Depth profiles were measured by directing the primary Cs^+ ion beam onto the deposited surface for A samples (forward erosion direction) and on the polished surface for B samples (backward), respectively. The SIMS detection limit of gold was less than $3 \times 10^{13}\ \text{atoms}/\text{cm}^3$. The comparison of the two depth profiles, which are given in Fig. 10, shows that forward sputtering induces an artifact. The forward sample-A profile is masked up to a depth of several micrometers. The profile obtained from B samples exhibits a rather flat level equal to $6 \times 10^{14}\ \text{atoms}/\text{cm}^3$ and then an abrupt decreasing slope. The researchers also found that the penetration depth

Fig. 10 Gold depth profiles measured by SIMS, compared between the two SIMS analyzing processes (forward and backward erosion directions) for 1 h at 550°C anneal.³⁹

increases with increasing annealing time and that profiles at other annealing temperatures always exhibit a maximum concentration equal to 6×10^{14} atoms/cm³. The diffusion coefficient of gold in InP was shown to be smaller than those already published.^{40,41} They concluded that the thermal migration of gold from the contact is not a mechanism responsible for the device degradation.

4 Ion Implantation

The development of ion implantation technology for III-V semiconductors is very important because of its potential use in the fabrication of optoelectronic and microwave devices. Implantation offers the advantages of planar fabrication and precise dopant control. Post-implant annealing of the implanted material to remove the unwanted damage introduced during ion implantation and to activate the implanted dopants is the most important step in the entire process. Such heat treatments, however, may modify both the surface and bulk properties of the samples.

Rothmund and Fritzsche⁴³ studied radiation damage introduced during implantation in InP by monitoring the change of absorbed electron current in a scanning electron microscope when the electron beam crosses the boundary between an implanted and an unimplanted part of a wafer surface. This method supplies information on radiation damage mainly within a distance up to about 100 Å from the surface. Their results indicated that 150 keV Ar⁺ ions produced an amorphous layer during a room-temperature implant at fluences of 10^{14} ions/cm² or greater and that amor-

phization can be avoided by heating the target to 150°C during implantation. They also found that noticeable residual damage was left after annealing an amorphous layer at 500°C.

Gamo *et al.*⁴⁴ studied the ordering of thick implanted amorphous layers in GaAs by Rutherford backscattering (RBS) and found that the reordering was not a simple epitaxial regrowth process as is the case for implanted Si and Ge. Ion implantation in compound semiconductors differs from implantation in elemental semiconductors such as Si and Ge because of different scattering cross sections of the primary implants and two substrate species. As a result, the number and range of atoms that are displaced by collisions are different for the two constituent species. They speculated that the different behavior of GaAs is due to the local variations of its stoichiometry in the implanted region and proposed that similar reordering phenomena would be found in other compound semiconductors. Christel and Gibbons⁴⁵ studied this uneven displacement of the constituent elements theoretically and found that an excess concentration of the heavier element develops near the surface, while an excess concentration of the lighter element appears deeper in the substrate. The transition point, where the substrate remains stoichiometric, is located approximately at the peak of the distribution of the implanted ions.

Kennedy⁴⁶ reported channeling effect measurements of the distribution of crystalline disorder in InP following the Si⁺ ion implantation and the results of annealing experiments to reorder the damaged layers. The InP substrates were Zn doped (1×10^{17} /cm³) and had surface normals about 3° from the <100> axis. These samples were implanted with 200 keV with different fluences. Annealing of samples up to 450°C was carried out in a vacuum furnace at 2×10^{-6} Torr or less. Channeling-effect measurements were made along the <100> direction with 1 MeV He⁺ ions with the detector mounted at 170° to the incident beam direction.

Figure 11 shows random and <100> aligned backscattering spectra for a sample with a completely disordered layer before and after vacuum furnace annealing. The small difference between the as-implanted spectrum and the random spectrum near the high-energy edge indicates that there was a thin layer near the surface of the as-implanted sample, which was not completely disordered. Following a 1 h annealing at 250°C the sample had epitaxially regrown but was left with a highly disordered region centered about 1500 Å below the surface, a depth which is approximately the projected range of the implanted Si atoms. An additional hour's annealing at 350°C further reduced the damage and one more hour at 450°C caused a large reduction in the remaining disorder. The sample annealed in a PH₃ ambient at 650°C for one more hour was still left with some disorder. He also found that the backscattering spectrum for the sample which was subjected to implantation at 180°C was

Fig. 11 Random and $\langle 100 \rangle$ aligned backscattering spectra for an InP crystal which had an amorphous layer following 200 keV Si implantation. The spectra were recorded before annealing and following 1 h annealing at the indicated temperatures. Also shown for reference is the aligned spectrum for a virgin sample.⁴⁶

remarkably similar to the spectrum for the sample which was isochronally annealed from 250 to 650°C.

Some studies^{47,48} have been conducted on the effects of implantation temperature on the postannealed electrical mobility of InP implanted with Si. A significant improvement, by a factor of 2, was reported to occur on implanting at 200°C rather than at room temperature. Dislocations found after the room-temperature implants but not after the 200°C ones may account for the mobility differences.

Numerous published results on InP have shown that a high peak carrier concentration of $10^{19}/\text{cm}^3$ is achievable in n-type implants. For p-type implants, electrical activation is usually less than 50% and the maximum achievable hole concentration is about $10^{18}/\text{cm}^3$. In this connection, GaAs implantation behaves differently from InP implantation e.g., in general, acceptor implants behave better than donor implants in GaAs. A broadening of the implant profile as well as an in-diffusion of p-type dopant in InP is observed in an elevated temperature activation process. To reduce the in-diffusion of Be in InP caused by stoichiometric disturbance or bulk impurity redistribution, Wang⁴⁹ implanted a group V element, phosphorus, with Be. A phosphorus-rich surface is formed as a result of this implant. The Be implantation was performed at 20 keV with a dose of $6 \times 10^{13}/\text{cm}^2$ on Fe-doped semi-insulating (100) InP substrates. The co-implant wafer was preimplanted with phosphorus at 200°C with an energy of 100 keV at a dose of $6 \times 10^{13}/\text{cm}^2$. The implanted samples were annealed at 850°C or 950°C for 15 s. Figure 12 shows the carrier concentration profiles for P/Be co-implants. Theoretical predictions, Lindhard-Scharff-Schiott (LSS), of

Fig. 12 Electrical carrier profiles for a P/Be co-implant in InP annealed at 850°C for 15 s (■) and at 900°C for 5 s (○). The hole concentration profile for a Be implant annealed at 850°C for 15 s (Δ) and LSS profiles for Be (20 keV, $6 \times 10^{13}/\text{cm}^2$) (—), P (100 keV, $6 \times 10^{13}/\text{cm}^2$) (---) are also shown.⁴⁹

the implanted Be and phosphorus atomic distributions are both shown. The electrical carrier profile of a Be implant is also included in the figure. It is clearly shown in the figure that the Be in-diffusion was eliminated by using a phosphorus co-implant.

Raman scattering spectrometry is a powerful tool for local and nondestructive investigation of the perturbations such as mechanical alteration⁵⁰, incorporation of impurities⁵¹, alloying⁵² and ion implantation.⁵³ Bedel *et al.*⁵⁴ investigated Zn-implanted InP by Raman scattering in order to determine critical fluences needed for a complete disturbance of the lattice and recovery temperature during thermal annealing. Disorder-activated first-order acoustical scattering and second-order optical scattering have been shown to be highly sensitive probes.

5 Dry Etching

Dry etching techniques, by now familiar to the silicon integrated circuit community, are finding applications to patterning of III-V semiconductors for optoelectronic and integrated optical devices. For example, many applications of integrated optoelectronics require the fabrication of laser diodes with other optical and electronic components on the same chip. One of the

key technical problems is, therefore, the development of a method of forming inside laser mirrors so that laser performance is not seriously compromised. It has been demonstrated that various III-V compounds can be etched in chlorine-containing discharges. Most dry etching processes rely on formation of chemical compounds of the material to be etched, which are then removed from the surface by thermal or ion-assisted desorption processes. It has been shown that transport of reagents to the surface and of products from the surface can be the limiting factors in the rate of etching.

The III-V compounds have the added complication of the greatly different volatility of the group III and group V halides. This raises the possibility that etching can be inhibited by the low volatility of the group III halides, or that the group V element will be selectively removed from the surface, leaving a surface layer enriched in the group III element. For example, III-V compounds will not etch in CF_4 discharges due to formation of an involatile group III fluoride, which passivates the surface. In spite of the technological advances, understanding of the etching process on a fundamental level is rudimentary. This is mainly due to the fact that practical etching involves a combination of chemical phenomena and physical sputtering or damage production.

Substrate temperature during etching influences etching in many ways. High temperatures can enhance gas-surface reaction rates, surface diffusion, or product volatility, thereby accelerating the etch rate. Donnelly *et al.*⁵⁶ studied the effects of temperature on etching GaAs and InP in a chlorine plasma by observing the emissions from the plasma and the composition of the etched surface. The most intense emission arose from Ga (4172 Å) and In (4512 Å), generated by electron impact fragmentation of the chloride etch products from GaAs and InP. When the gas phase concentration of these chlorides was low, intensity of the emissions was proportional to the etch rate. Etching was shown to follow an Arrhenius dependence on substrate temperature. GaAs surfaces were Ga-rich following etching at all temperatures (As-to-Ga intensity ratio was about 1/2 of that for clean GaAs) and there was about one-half to one monolayer of chlorine coverage. Auger spectra recorded during Ar-ion sputtering of the etched InP surfaces showed an approximately 30 Å thick layer of InCl_3 for low temperatures (210°C), but relatively little chlorine for high temperatures (>250°C).

In order to elucidate some of the basic details of the etching process, the thermal and ion-assisted reactions of GaAs or InP with molecular chlorine have been investigated in a simple, well-characterized system.⁵⁷⁻⁵⁹ The conventional method of studying the reaction is by modulated molecular beam mass spectrometry. Modulation of the incident Cl_2 reactant coupled with phase-sensitive detection of the output signals improves the signal-to-noise ratio and provides information on the time delays due to surface reactions. Because scattered

chlorine spends no time on the surface, it appears in the output in the square-wave shape imparted to it by the mechanical chopping. The reaction products, however, usually are emitted with a time delay due to the finite speed of the surface reaction. This nonzero residence time results in a waveform which is distorted from the original square wave. This shape difference produces a phase lag with respect to the first Fourier component of the scattered chlorine signal. This phase lag contains information directly related to the kinetics of the chemical reaction on the crystal surface, provided that the time scale of the reaction is comparable to the period of the modulation of the incident beam.

Balooch *et al.*⁵⁷, by the use of this modulated ion beam technique, found that at 300 K 3.5 keV Ar^+ (20 $\mu\text{A}/\text{cm}^2$) ion bombardment in the presence of steady-state Cl_2 flux accelerated the etching rate of GaAs by a factor of 6. This acceleration was ascribed to rapid removal of a scale of relatively non-volatile gallium chloride from the reacting surface. Ameen and Mayer⁵⁹ used modulated beams of 1 keV Ne^+ to etch the surface of GaAs and measured kinetic energies of the products by time-of-flight wave form analysis. Ga and As atoms sputtered from clean surfaces had high kinetic energy, typical of sputtering processes. The chlorides and atomic species emitted in the presence of Cl_2 had substantially lower kinetic energies, on the order of 0.2–1 eV.

The characterization of ion-sputtered InP surfaces has been the focus of considerable activity. Various techniques have been employed such as low-energy electron diffraction (LEED)⁶⁰, AES⁶¹, X-ray photoelectron spectroscopy (XPS)⁶⁰, RBS⁶², photoluminescence (PL)⁶³ and Raman scattering.⁶³ It is well known that preferential sputtering of phosphorus generates an indium-rich surface upon ion bombardment. However, the detailed surface structure is still not well understood. Lau *et al.*⁶⁴ studied the effects of sputter etching and subsequent thermal annealing on n-type InP surfaces by measuring the photoemission spectra using both Al K_α and synchrotron radiation. Nondestructive depth profiling of the chemical structure of the sputtered surface was done by carrying out the spectral measurements at different azimuthal angles between the surface and the electron analyzer. It was found that the first and second monolayers had an In/P ratio of 2 after sputtering with 3 keV of Ar^+ at a low dose of $1 \times 10^{12}/\text{cm}^2$. Fifty percent of these two monolayers were assigned to metallic indium. Only 20% were assigned to bulk InP. The rest of the 30% had an average composition of InP_2 . The In 4d spectrum taken for a surface sputtered with a very high current density (120 $\mu\text{A}/\text{cm}^2$) of 2 keV Ar^+ with a photon energy of 80 eV and an emission angle of 45° is shown in Fig. 13.⁶⁴ The spectrum represents the different In components in the top two monolayers. The presence of In clusters is clearly shown by the sharp peak at the low binding energy side. The long tailing at the high binding energy side also demonstrates the presence of

Fig. 13 In 4d spectrum of a sputtered (100) InP surface using 80 eV photons. The binding energy scale has been fixed by assuming the In-In metal feature to have a binding energy of 16.84 eV.⁶⁴

defects with enrichment in P.

Recently, methane⁶⁵ or ethane⁶⁶ gas has successfully been employed as an etchant of InP and GaAs instead of chlorine. Hydrocarbon gases are neither toxic nor corrosive, and the reaction products of a hydrocarbon gas are more volatile than those of chlorine.

6 Disordering of Superlattices

6.1 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs system

The heterointerfaces of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs system are stable up to quite high temperatures. For example, Chang and Koma⁶⁷ have shown that appreciable Al-Ga interdiffusion at an AlAs-GaAs interface requires a high temperature. The activation energy for Al and Ga interdiffusion is high (>3.6 eV) and the diffusion constants are small (10^{-18} cm²/s at 850°C).⁶⁷ In 1981, Laidig *et al.*⁶⁸ demonstrated that a relatively low temperature (500–600°C) diffusion of Zn into AlAs-GaAs superlattices (SL's) and quantum-well heterostructures promotes the intermixing of Al and Ga and results in compositionally disordered $\text{Al}_x\text{Ga}_{1-x}\text{As}$. They also demonstrated that the crystal composition x is determined by the ratio between the AlAs single layer thickness and the GaAs single layer thickness. Material constants such as a bandgap energy and a refractive index of the compositionally disordered alloys have been shown to be different from those of SL's.⁶⁹ After this demonstration, there has been steady progress in understanding the fundamental mechanism responsible for impurity-induced layer disordering (IILD) and in making good use of IILD for the construction of a simple form of buried heterostructure lasers.

Lee and Laidig⁷⁰ measured the Zn diffusion coef-

ficients and the Al-Ga interdiffusion coefficients by SIMS and AES depth profiling. SL's were grown by MBE; each SL consisted of a series of alternating undoped AlAs and GaAs layers. The total SL thickness was 1.8 μm and the ratio of the AlAs layer thickness (L_B) to the GaAs layer thickness (L_Z) was constant ($L_Z/L_B \approx 1$). The SL's with the periods of 320 Å, 630 Å and 1100 Å, as determined by X-ray diffraction, were employed. The diffusion temperatures were 550–600°C. The Zn diffusion coefficients were around 10^{-12} cm²/s. The activation energy for the Zn diffusion process ranged from 3.1 eV for a 1100 Å/period SL to 2.1 eV for a 320 Å/period SL. The Al-Ga interdiffusion coefficient and the activation energy associated with the interdiffusion process were approximately 10^{-16} cm²/s and 1 eV, respectively, independent of the SL layer thickness. It has been shown⁷¹ by TEM and PL data that a single GaAs quantum well ($L_Z=70$ Å) confined by $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x \approx 0.3$) layers can, via low temperature (600°C) Zn diffusion, be interdiffused ("absorbed") into the confining layers without damaging the crystal or ruining its capability to operate as a continuous 300 K low threshold photopumped laser.

Soon after the discovery of the disordering by Zn diffusion, it has been demonstrated^{72,74} that AlAs-GaAs SL's can be disordered by the thermal diffusion or by the implantation of silicon which is a shallow donor in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$. For an implant dose of 10^{14} cm⁻² at 350 keV, compositional disordering has not occurred and considerable crystal damage was present before anneal. After annealing at temperatures less than the original growth temperature (750°C), the damage in the implanted region is removed and compositional disordering was extensive, though not complete. In comparison with a theoretical estimate⁷³ of the projected range and standard deviation of Si implanted into AlAs and GaAs, the center of the disordered region was approximately twice as deep as that expected and the width was *ca.* 1.5 x greater. In the thermal diffusion experiments⁷⁴, 100 Å of Si was electron beam evaporated onto the SL sample, which was then sealed in a quartz ampoule. The disordering depth was 2.4 μm for thermal annealing at 850°C for 10 h.

It has also been reported⁷⁵ that Zn diffusion into a GaP-GaAs_{1-x}P_x ($x \approx 0.6$) SL, at times and temperatures that will not cause ordinary thermal disordering, resulted in the intermixing of the group V elements, As and P, and layer disordering.

Nowadays, several processes are known to induce disordering; these include laser irradiation⁷⁶ and impurity-free vacancy diffusion⁷⁷, in addition to the diffusion or implantation of various impurities such as Zn, Si, S and Ge. Ralston *et al.*⁷⁶ have demonstrated that pulsed laser irradiation can be used to intermix GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ SL's. A series of pulsed excimer laser (KrF) irradiations with energy densities varying from 220 to 900 mJ/cm² was performed on a SL sample consisting of 40 periods of 100 Å GaAs layers alternat-

Fig. 14 Raman spectra of the GaAs- $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ superlattice sample. (a) as-grown region; (b) excimer laser irradiated region.⁷⁶

ing with 100 Å $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layers. Raman measurements were performed on both the annealed and unannealed regions of the samples to obtain a nondestructive indication of whether intermixing has occurred. Raman spectra of the GaAs-like phonon band are shown in Fig. 14.⁷⁶ The spectrum from the as-grown region (Fig. 14(a)) shows a longitudinal optical (LO) phonon peak at a frequency of 292 cm^{-1} , corresponding to the pure GaAs layers, as well as a GaAs-like LO phonon peak at 281 cm^{-1} , corresponding to the $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layers. After irradiating with an excimer laser pulse at an energy density of 220 mJ/cm^2 , the Raman spectrum (Fig. 14(b)) shows only a single broad GaAs-like LO peak at 286 cm^{-1} , corresponding to an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy with the expected median composition of $x \approx 0.15$. This indicates that, at least within the interaction depth of the Ar^+ laser beam employed for Raman measurements (550–600 Å), extensive intermixing of the original superlattice layers has occurred. The extent of the intermixing was studied using AES depth profiling. Figure 15(a)⁷⁶ shows both of the Ga and Al depth profiles through the first 20 periods (4000 Å) of the as-grown region of the sample. The effect of laser irradiation is demonstrated in Fig. 15(b), where complete intermixing of the first 11 periods (2100 Å) has occurred. The Al mole fraction of the intermixed alloy

Fig. 15 Sputter Auger profiles of the GaAs- $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ superlattice sample. (a) as-grown region; (b) excimer laser irradiated region.⁷⁶

is $x \approx 0.15$, as expected. The transition from the intermixed phase to the unperturbed SL structure is very abrupt.

6.2 InGaAs-InP system

The $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ -InP SL is an interesting material system because this system has two group III atoms and two group V atoms. Another interesting point is the effect of the lattice mismatch, which will be induced during intermixing, on the disordering process. Nakashima *et al.*⁷⁸ have studied the intermixing process of the InGaAs-InP SL's by Zn diffusion. X-Ray and SIMS analysis revealed that Zn diffusion induces the intermixing of group III atoms and has little effect on the group V atom profile, and this results in the lattice-mismatched SL layers. Even after Zn diffusion, however, the SL structure survives with some deformation. This is in contrast with the result for the GaAs-AlAs SL's, where the SL structure is completely disordered to become a uniform layer. These results suggest that the layer lattice mismatch has an effect on the intermixing mechanism. In the case of the GaAs-AlAs SL, the lattice-matching condition is almost satisfied and little additional strain energy is therefore induced by disordering. On the other hand, lattice mismatch or some strain does exist in the case of

InGaAs-InP. Thus the intermixing of group III atoms provides the additional strain energy, which would suppress the complete intermixing.⁷⁸

7 Conclusion

It is quite obvious from the preceding discussion and the list of references that surface sensitive analytical techniques are now indispensable to the development of the electronic industry. These techniques are useful both for the research into basic materials phenomena and for the development of new technologies for producing III-V semiconductor devices. Attempts at improving the ability to characterize the structure and composition of small areas and thin layers will be increasingly important as the III-V semiconductors continue to receive considerable interest in forming smaller size devices with carriers confined to one or zero degrees of freedom.

References

1. S. M. Sze, "Physics of Semiconductor Devices", 2nd ed., John Wiley & Sons, New York, 1981.
2. H. C. Casey, Jr. and M. B. Panish, "Heterostructure Lasers", Academic Press, New York, 1978.
3. J. J. Harris, B. A. Joyce and P. J. Dobson, *Surf. Sci.*, **103**, L90 (1981).
4. C. E. C. Wood, *Surf. Sci.*, **108**, L441 (1981).
5. Y. Morishita, S. Maruno, M. Gotoda, Y. Nomura and H. Ogata, *Appl. Phys. Lett.*, **53**, 42 (1988).
6. J. M. Van Hove, C. S. Lent, P. R. Pukite and P. L. Cohen, *J. Vac. Sci. Technol.*, **B1**, 741 (1983).
7. B. F. Lewis, T. C. Lee, F. J. Grunthaner, A. Madhukar, R. Fernandez and J. Maserjian, *J. Vac. Sci. Technol.*, **B2**, 419 (1984).
8. T. Sakamoto, N. J. Kawai, T. Nakagawa, K. Ohta and T. Kojima, *Appl. Phys. Lett.*, **47**, 617 (1985).
9. K. Sakamoto, T. Sakamoto, S. Nagao, G. Hashiguchi, K. Kuniyoshi and Y. Bando, *Jpn. J. Appl. Phys.*, **26**, 666 (1987).
10. W. T. Tsang, T. H. Chiu, J. E. Cunningham and A. Robertson, *Appl. Phys. Lett.*, **50**, 1376 (1987).
11. B. A. Joyce, P. J. Dobson, J. H. Neave, K. Woodbridge, J. Zhang, P. K. Larsen and B. Bölger, *Surf. Sci.*, **168**, 423 (1986).
12. B. A. Joyce, P. J. Dobson, J. H. Neave and J. Zhang, *Surf. Sci.*, **174**, 1 (1986).
13. L. P. Erickson, M. D. Longerborne, R. C. Youngman and B. E. Dies, *J. Cryst. Growth*, **81**, 55 (1987).
14. J. N. Eckstein, C. Webb, S. L. Weng and K. A. Bertness, *Appl. Phys. Lett.*, **51**, 1833 (1987).
15. J. P. Harbison, D. E. Aspnes, A. A. Studna, L. T. Florez and M. K. Kelly, *Appl. Phys. Lett.*, **52**, 2046 (1988).
16. V. D. Mattered, Jr., F. Capasso, J. Allam, A. L. Hutchinson, J. Dick, J. M. Brown and A. Westphal, *J. Appl. Phys.*, **60**, 2609 (1986).
17. R. Bisaro, G. Laurencin, A. Friederich and M. Razeghi, *Appl. Phys. Lett.*, **40**, 978 (1982).
18. J. F. Bresse, *J. Appl. Phys.*, **59**, 2026 (1986).
19. J. Cazaux, P. Etienne and M. Razeghi, *J. Appl. Phys.*, **59**, 3598 (1986).
20. Y. Suzuki and H. Okamoto, *J. Appl. Phys.*, **58**, 3456 (1985).
21. A. Ourmazd, J. R. Rentschler and D. W. Taylor, *Phys. Rev. Lett.*, **57**, 3073 (1986).
22. A. Ourmazd, W. T. Tsang, J. A. Rentschler and D. W. Taylor, *Appl. Phys. Lett.*, **50**, 1417 (1987).
23. L. Esaki and R. Tsu, *IBM J. Res. Dev.*, **14**, 61 (1970).
24. G. C. Osbourn, *Phys. Rev.*, **B27**, 5126 (1983).
25. F. W. Saris, W. K. Chu, C. A. Chang, R. Ludeke and L. Esaki, *Appl. Phys. Lett.*, **37**, 931 (1980).
26. W. K. Chu, F. W. Saris, C. A. Chang, R. Ludeke and L. Esaki, *Phys. Rev.*, **B26**, 1999 (1983).
27. J. M. Cole, L. G. Earwaker, A. G. Cullis, N. G. Chew and S. J. Bass, *J. Appl. Phys.*, **60**, 2639 (1986).
28. S. T. Picraux, L. R. Dawson, G. C. Osbourn and W. K. Chu, *Appl. Phys. Lett.*, **43**, 930 (1983).
29. J.-L. Lievin and C. G. Fonstad, *Appl. Phys. Lett.*, **51**, 1173 (1987).
30. B. Tuck and A. Hooper, *J. Phys.*, **D8**, 1806 (1975).
31. K. Ohtsuka, T. Matsui and H. Ogata, *Jpn. J. Appl. Phys.*, **27**, 253 (1988).
32. S. Reynolds, D. W. Vook and J. F. Gibbons, *J. Appl. Phys.*, **63**, 1052 (1988).
33. A. K. Chin, B. V. Dutt, H. Temkin, W. A. Bonner and D. D. Roccasecca, *Appl. Phys. Lett.*, **36**, 924 (1980).
34. H. Ando, N. Susa and H. Kanbe, *IEEE Trans. Electron Devices*, **ED-29**, 1408 (1982).
35. K. Kazmierski, A. M. Huber, G. Morillot and B. de Cremoux, *Jpn. J. Appl. Phys.*, **23**, 628 (1984).
36. O. Wada, *J. Appl. Phys.*, **57**, 1901 (1985).
37. S. Mahajan, A. K. Chin, C. L. Zipfel, D. Brasen, B. H. Chin, R. T. Tung and S. Nakahara, *Mater. Lett.*, **2**, 184 (1984).
38. E. Kuphal, *Solid State Electron.*, **24**, 69 (1980).
39. V. Parguel, P. N. Favennec, M. Gauneau, Y. Rihet, R. Chaplain, H. L'Haridon and C. Vaudry, *J. Appl. Phys.*, **62**, 824 (1987).
40. A. K. Chin, C. L. Zipfel, M. Geva, I. Camlibel, P. Skeath and B. H. Chin, *Appl. Phys. Lett.*, **45**, 37 (1984).
41. S. I. Rembeza, *Sov. Phys. Semicond.*, **3**, 519 (1969).
42. K. W. Wang, S. M. Parker, C. L. Cheng and J. Long, *J. Appl. Phys.*, **63**, 2104 (1988).
43. W. Rothmund and C. R. Fritzsche, *J. Vac. Sci. Technol.*, **16**, 968 (1979).
44. K. Gamo, T. Inada, J. W. Mayer, F. H. Eisen and C. G. Rhodes, *Radiat. Effects*, **33**, 85 (1977).
45. L. A. Christel and J. F. Gibbons, *J. Appl. Phys.*, **52**, 5050 (1981).
46. E. F. Kennedy, *Appl. Phys. Lett.*, **38**, 375 (1981).
47. D. E. Davies, J. J. Comer, J. P. Lorenzo and T. G. Ryan, *Appl. Phys. Lett.*, **35**, 192 (1979).
48. B. Tell, K. F. Brown-Goebeler and C. L. Cheng, *Appl. Phys. Lett.*, **52**, 299 (1988).
49. K. W. Wang, *Appl. Phys. Lett.*, **51**, 2127 (1987).
50. R. Carles, N. Saint-Cricq, A. Zwick, M. A. Renucci and J. B. Renucci, *J. Phys. Soc. Jpn.*, **49**, Suppl. A, 665 (1980).
51. A. S. Barker Jr. and A. J. Sievers, *Rev. Mod. Phys.*, **47**, Suppl. 2 (1975).
52. N. Saint-Cricq, R. Carles, J. B. Renucci, A. Zwick and M. A. Renucci, *Solid State Commun.*, **39**, 1137 (1981).
53. D. R. Myers, P. L. Gourley and P. S. Pearcy, *J. Appl. Phys.*, **54**, 5032 (1983).

54. E. Bedel, G. Landa, R. Carles, J. B. Renucci, J. M. Roquais and P. N. Favennec, *J. Appl. Phys.*, **60**, 1980 (1986).
55. A. C. Papadopoulos, F. Alexandre and J. F. Bresse, *Appl. Phys. Lett.*, **52**, 224 (1988).
56. V. M. Donnelly, D. L. Flamm, C. W. Tu and D. E. Ibbotson, *J. Electrochem. Soc.*, **129**, 2533 (1982).
57. M. Balooch, D. R. Olander and W. J. Siekhaus, *J. Vac. Sci. Technol.*, **B4**, 794 (1986).
58. S. C. McNevin, *J. Vac. Sci. Technol.*, **B4**, 1203 (1986).
59. M. S. Ameen and T. M. Mayer, *J. Appl. Phys.*, **63**, 1152 (1988).
60. C. R. Bayliss and D. L. Kirk, *J. Phys.*, **D9**, 233 (1979).
61. B. Gruzza, B. Achard and C. Pariset, *Surf. Sci.*, **162**, 202 (1985).
62. R. S. Williams, *Solid State Commun.*, **41**, 153 (1982).
63. D. J. Olego, R. Schachter, M. Viscogliosi and L. A. Bunz, *Appl. Phys. Lett.*, **49**, 719 (1986).
64. W. M. Lau, R. N. S. Sodhi, B. J. Flinn, K. H. Tan and G. M. Bancroft, *Appl. Phys. Lett.*, **51**, 177 (1987).
65. U. Niggebrugge, M. Klug and G. Garus, *Inst. Phys. Conf. Ser.*, **79**, 367 (1985).
66. T. Matsui, H. Sugimoto, T. Ohishi and H. Ogata, *Electron. Lett.*, **24**, 798 (1988).
67. L. L. Chang and A. Koma, *Appl. Phys. Lett.*, **29**, 138 (1976).
68. W. D. Laidig, N. Holonyak, Jr., M. D. Camras, K. Hess, J. J. Coleman, P. D. Dapkus and J. Bardeen, *Appl. Phys. Lett.*, **38**, 776 (1981).
69. N. Holonyak, Jr., W. D. Laidig, M. D. Camras, J. J. Coleman and P. D. Dapkus, *Appl. Phys. Lett.*, **39**, 102 (1981).
70. J. W. Lee and W. D. Laidig, *J. Electron. Mater.*, **13**, 147 (1984).
71. K. Meehan, J. M. Brown, M. D. Camras, N. Holonyak, Jr., R. D. Burnham, T. L. Paoli and W. Streifer, *Appl. Phys. Lett.*, **44**, 428 (1984).
72. J. J. Coleman, P. D. Dapkus, C. G. Kirkpatrick, M. D. Camras and N. Holonyak, Jr., *Appl. Phys. Lett.*, **40**, 904 (1982).
73. J. F. Gibbons, W. S. Johnson and S. W. Mylroie, "Projected Range Statistics", p. 5, Dowden, Hutchinson and Ross, Stroudsburg, 1975.
74. K. Meehan, N. Holonyak, Jr., J. M. Brown, M. A. Nixon, P. Gavrilovic and R. D. Burnham, *Appl. Phys. Lett.*, **45**, 549 (1984).
75. M. D. Camras, N. Holonyak, Jr., K. Hess, M. J. Loduwise, W. T. Dietze and C. R. Lewis, *Appl. Phys. Lett.*, **42**, 185 (1983).
76. J. Ralston, A. L. Moretti, R. K. Jain and F. A. Chambers, *Appl. Phys. Lett.*, **50**, 1817 (1987).
77. D. G. Deppe, L. J. Guido, N. Holonyak, Jr., K. C. Hsieh, R. D. Burnham, R. L. Thornton and T. L. Paoli, *Appl. Phys. Lett.*, **49**, 510 (1986).
78. K. Nakashima, Y. Kawaguchi, Y. Kawamura, Y. Imamura and H. Asahi, *Appl. Phys. Lett.*, **52**, 1383 (1988).

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