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FINAL REPORT

**OPTICAL CHARACTERIZATION OF
DEFECTS IN SEMICONDUCTORS**

PSF PROJECT: PSF/RES/C-QU/PHYS(71)

**DR. M. ZAFAR IQBAL
(PRINCIPAL INVESTIGATOR)**

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FINAL RESEARCH REPORT

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SUMMARY

Characterization of deep-level defects in semiconductor materials is at the heart of modern semiconductor science and technology due to their influence in the electronic properties of these materials. Photoluminescence spectroscopy is a powerful technique for the characterization and detailed understanding of the nature of the shallow and deep-level defects in semiconductors.

In this project we have carried out experiments using the photoluminescence (PL) technique, providing valuable experience to the research students in the semiconductor physics laboratory and yielding interesting data. It may be added that this marked an exciting new development since it is for the first time in Pakistan that the photoluminescence spectroscopy technique has been introduced. The work carried out under the project consists of following main parts:

- (a) A detailed PL study was undertaken to characterize the silver defect system in silicon.
- (b) A detailed photoluminescence investigation of the effects of Al doping on GaAs grown by molecular beam epitaxy (MBE-GaAs) was carried out. Crystals with 0.1%, 1% and 3% Al doping have been studied. Our study on these materials presents results on the optical characteristics of the lowest Al composition GaAs reported to date.
- (c) Some preliminary investigations have been carried out on the effect of alpha-irradiation on the photoluminescence properties of both n- and p-type InP.

PSF Project No.PSF/C-QU/ PHYS(71)

FINAL RESEARCH REPORT

OPTICAL CHARACTERIZATION OF DEFECTS IN SEMICONDUCTORS

DETAILED REPORT

(a) INTRODUCTION

Photoluminescence spectroscopy has emerged as a powerful technique for the characterization of semiconductors. It can be used to provide information on both the fundamental optical characteristics of the material as well as the optically active defects in the material. A variety of electronic transitions possible via the shallow and deep levels associated with the defect states lead to optical emissions with characteristic energies and other features. These form the basis of the photoluminescence spectroscopy which can be skilfully used to provide fingerprints of the defects which play a fundamental role in controlling the properties of semiconductors.

FIRST PROJECT YEAR:

The equipment purchased through the PSF grant was intended to be combined with some additional equipment which was procured under an NSRDB project. During the short time available after the procurement of the equipment, the following technical tasks were performed:

1. Installation of electrical power and cooling water supply for the Argon-ion laser was carried out and the laser was tested for performance after its installation.
2. The monochromator, which already existed in our laboratory, was reinstalled in the photoluminescence laboratory and was again calibrated to ensure precision and accuracy for the photoluminescence experiments. A considerable amount of time and effort had gone to ensure proper geometry and alignment of the various components, crucial for reliable results.

3. The Germanium detector was installed and tested for quality of vacuum which is necessary for liquid nitrogen cooling. The relevant optics were also procured and set up for the photoluminescence experiment.

4. Preliminary tests and measurements on the working of the system were successfully completed in the first year of this project.

SECOND PROJECT YEAR:

In the second project year, the experimental work was divided into two categories:

- (1) Deep-level luminescence in silver-doped silicon
- (2) Luminescence in Al-doped GaAs.

THIRD PROJECT YEAR:

In the final year of this project,

- (i) The computerization of the photoluminescence (PL) set up was done. This facility will enable us to record and store the PL data directly in a computer for further analysis.
- (ii) The work on Al - doped GaAs was extended to samples with higher doping levels to investigate the effects of Al on the PL quality of the AlGaAs material.
- (iii) Photoluminescence study of alpha-irradiated InP was also initiated.

(b) RESULTS AND DISCUSSION

I. SILVER DEFECT IN SILICON

A. Motivation

Transition metal related defects in silicon form an important subject of research on defects in semiconductors¹. Transition metals are among the fastest diffusers in crystalline silicon, their presence gives rise to a number of luminescence bands in silicon in the energy range 0.7-1.1 eV. We had decided to work on silver as a first study owing to the inherent interest in this system and our electrical study on this system using the DLTS technique in the recent past². This defect system was also chosen to gain confidence in the working of

our set up since this problem would provide an example with some recently reported data to compare our own results with. This system comprised silver related defects in Si.

B. Results and Discussion

PL spectra of silver doped silicon

Silver is an important defect in Si because (a) it is one of the transition metals which forms an interesting and important class of defects in semiconductors and (b) it is known to introduce a near mid-gap deep acceptor level ($E_C - 0.54$ eV) in the band gap of Si - the importance of such deep levels in semiconductors is well established in the literature³. Most of the work on Ag-related defect centres in Si so far have primarily focussed on their electrical characteristics⁴. The investigations of their optical characteristics have only recently started to appear in the literature⁵. This provided an added impetus to our work on this system using PL. The preliminary results of our study were reported in a paper presented at the Second Baragali School on Electronics - copy attached (Annexure I).

Detailed measurements on the temperature dependence of the interesting silver-donor related luminescence spectra have also been obtained. The typical spectra obtained at different temperatures show that the dominant lines in the spectrum lie in the region of photon energies 761-786 meV. The lines which are of interest are labelled A, B and C. These lines are identified with the presence of silver. The temperature variation revealed some interesting results in the PL spectra. As the temperature is raised, (i) A and B lines decrease in intensity with the decrease in A being faster than for B. The energy position of these peaks do not change with temperature; (ii) The C peak increases in intensity strongly, while its energy position does not change with temperature. The C-line which increases in strength with temperature according to the data presented, represents transition from an excited state of the Ag-donor which starts to be populated at higher temperatures. The increase in the occupancy of this higher lying state with temperature leads to the increasing strength of the C line. The ratio of the integrated intensities of the C and the A lines is plotted on a semilog plot. The linear variation with inverse temperature on this plot clearly shows an Arrhenius behaviour, pointing to a thermally activated character of this transition, in accordance with the Boltzmann law determining the occupancy of states. From the slope of this line a thermal activation energy of 4.9 meV is obtained which corresponds very closely to the observed energy separation of the C and the A lines. This is the direct evidence linking the C and the A lines to the same centre.

The transition energy of the main A line matches very closely with the energy difference between the conduction band edge and the donor level. Our calculations for E_b (binding energy of the exciton to the localized defect state) yields a value of 0.37 eV which is in excellent agreement with the theoretically predicted value⁶. Thus A line is interpreted to result from an exciton bound to the ground state of the silver donor state $E_V+0.34$ eV in silicon.

C. Conclusions

A photoluminescence study has been carried out on Si doped with silver, yielding interesting results about the optical transitions from the silver-donor defect. The detailed characteristics of the PL signal from this defect have been investigated. In particular, the temperature dependence data on the luminescence intensity of silver-related band have been obtained. The analysis of the data clearly shows that the A line originates from the exciton bound to the silver donor state at $E_V+0.34$ eV in Si. Evidence is also provided, showing that the C line is a transition involving an excited state of the silver-donor defect.

II. NEAR-BAND-EDGE LUMINESCENCE IN MBE- GaAs

A. Motivation

Near-band-edge luminescence forms an interesting subject in the study of semiconductors. It is particularly important to assess the crystal quality of compound semiconductors which are generally prone to a lot of imperfections, often linked with their inherent growth problems. The sharpness (width) and the structure of the band-edge luminescence lines provides information on the crystalline perfection of the material as well as any shallow-level defects that may be present in the material. GaAs is a particularly good semiconductor for such investigations since, due to its direct band-gap, band edge luminescence has high efficiency in this material.

Photoluminescence (PL) spectroscopy has been commonly employed as an effective tool for the characterization of GaAs and AlGaAs, insofar as it provides particularly useful information on the relatively shallow defect levels in the band gap, which may provide strongly competing paths for carrier recombination against the desired radiative path for a particular optical application. PL spectroscopy thus provides complementary data to those provided by DLTS.

We have characterized Al-doped MBE-grown GaAs using photoluminescence spectroscopy. The single crystal samples were grown using the MBE facility at Chalmers Technical University in Sweden under our collaborative link. One of the problems with GaAs grown in ultra high vacuum, using MBE technique, is that, in spite of the clean conditions of growth, a number of deep level defects are found to be present in this material. These were first reported by Lang et al⁷ and are commonly referred to as M0, M1, M2,....., M8 defects. Obviously these defects are highly undesirable since they would adversely affect the quality of GaAs for fast integrated electronics and optoelectronics applications.

The main motive for our work on Al doping of GaAs was to investigate the influence of this isovalent dopant on the deep-level defect content of MBE GaAs, since two other isovalent dopants, In and Sb, have already been demonstrated to be very effective in reducing the concentration of the unwanted deep levels M0, M1.....M8 in MBE GaAs. Samples with three different levels of Al doping, 0.1%, 1% and 3% have been investigated in our study.

B. Main Results

PL spectra were measured over a wide temperature range in our work. Since our close-cycle cryostat does not permit temperature below 10K, measurements below 10K were performed using the low temperature facility at the Technical University of Berlin during a short visit by the principal investigator. The detailed results of our study on $Al_xGa_{1-x}As$ system have been reported in J. Appl. Phys., **80**, 5932 (1996) - copy attached (Annexure - II).

PL spectra and their temperature dependence

The spectrum consists of three prominent peaks of relatively high intensity labelled as A, B and C peaks, corresponding to transitions at 1.517 eV, 1.496 eV and 1.481 eV in the 0.1% Al-doped samples. In addition a minor peak at 1.509 eV is also observed. Temperature dependence of the PL spectra was also studied in detail. While an overall decrease in the luminescence intensity is observed with an increase in temperature, the side band consisting of the B, C, and D lines is seen to quench more rapidly than the A line. At about 50 K the side band is fully quenched. Detailed quantitative data have been obtained on the peak intensity variation with temperature.

The overall characters of the spectra in the 1% and 3% Al doped samples appear to be similar to the 0.1% case, although the relative intensities of the various features show a

significant variation with the Al doping. The centres of the various peaks are seen to shift systematically to higher energies with the increase in Al doping from 0.1% to 0.3%. From the comparison of the PL studies on these three types of samples, we have observed that the over all PL output goes down strongly as the Al doping increase above 0.1%. The total integrated intensity is found to go down about five times with increase in Al doping from 0.1% to 1%, while a further reduction of about 35 is observed as the Al content increases to 3%. Temperature dependence of the PL spectra for the 1% and the 3% Al doped GaAs samples was also investigated in detail. The overall luminescence intensity is seen to decrease as the sample temperature increases. This suggests that the competing non-radiative recombination phenomena increase as we go from 0.1% to 1% Al doping. Deep level defects introduced during growth and impurity doping could provide such non-radiative recombination paths in the material. Our study thus indicates that the deep level defects are strongly enhanced with the increase in Al concentration in GaAs at least in the range 0.1% - 1%.

Excitation power dependence of the spectra

The PL spectra of the three types of samples were measured at a number of different excitation intensities, spanning three order of magnitude, at 8k to study the excitation power dependence of the various transitions. The spectra show a pronounced increase in the intensity of peak A with increasing excitation power, relative to the rate of increase of the side band comprising the B and C lines. At the lowest excitation intensities the B and C lines dominate the spectra while at higher intensities, the A line becomes the dominant peak .

The integrated intensities for the various peaks (obtained from gaussian fits to the line shapes) have been plotted as a function of the excitation power for the 0.1%, 1% and 3% Al doped samples. From these plots, it is observed that the intensity of the X and the A line increases about 1000-fold as the excitation power is increased by the same factor. The corresponding increase in the B and C lines is by about a factor of 100. It is clear, therefore, that with the increase in excitation power, the B and the C lines tend to saturate, since the luminescence intensity for these lines increases at a rate lower than the excitation power. A power-law dependence ($I \sim P^n$) of luminescence intensity (I) on the excitation power (P) is observed for each composition. For the 1% and 3% Al doped samples the variation of the C-line intensity with excitation power is fitted by two different exponents (n) in the low and high power ranges.

C. Discussion

The main features of our near-band-edge photoluminescence spectra consist of a relatively sharp zero-phonon excitonic peak (A) and two broad defect-related features (B and C). From the peak position, spectral sharpness and excitation power dependence, the peak A is identified as an excitonic peak. Our gaussian line-shape deconvolution analysis reveals two components in this peak. The small high energy feature X is assigned to the free-exciton transition, from its supralinear excitation power dependence, with a possible contribution from the free electron-hole recombination. The lower energy major component of A is interpreted as the bound excitonic peak. In addition to a component with an activation energy of a few meV, the temperature dependence of the intensity reveals a bound exciton transition with an activation energy varying from ~ 34 meV to ~ 41 meV over the three types of samples. This relatively high activation energy suggests a significant contribution from some defect bound exciton. This energy, however, appears too high to be ascribed to the neutral carbon acceptor. The random alloy fluctuations could also be a possible source of bound excitons in our materials, since the local crystalline disorder is known to bind excitons in alloy semiconductors⁸. The width of the bound exciton component of the A peak is seen to increase with Al content. This is the result of alloy broadening associated with increasing randomness in the occupancy of the cation site by Ga or Al.

The peak B corresponds to a transition from the conduction band to a shallow acceptor (e, A^0) with an overlap from the donor-acceptor (D^0, A^0) pair transition. The temperature dependence of the intensity data reveals an activation energy close to that of the carbon acceptor (~ 26 meV), known to be a common impurity in GaAs. Our 2K spectrum for the 0.1% Al samples provides an indication of a structure within the carbon-related peak B presumably corresponding to the free-to-bound and donor-acceptor pair transitions at this centre, but this structure is lost in the corresponding peak for the 1% and 3% Al samples, probably as a result of alloy broadening of both transitions.

Peak B is followed, at lower energy, by a structure consisting of two peaks as revealed by the gaussian lineshape analysis. The higher energy component (peak D) is probably the free-to-bound emission at the Si acceptor centre also observed by Chand et al⁹ in their MBE GaAs samples. The lower energy transition (peak C) involves a deeper defect ascribed to some complex of carbon¹⁰ or carbon and silicon⁹. The differential thermal ionization of the shallower carbon acceptor causes a more rapid quenching of the B peak relative to the defect-complex peak C with increase in temperature, as observed in our spectra.

Reynolds et al¹¹ have carried out the only investigation which is closest to our Al composition. Their lowest Al composition being 0.8%. We have carried out a comparison of the X peak position with the extrapolated linear fits to the 2K data of Reynolds et al and also with that of the calculated variation obtained from the modified Varshni formula¹². It is clear from this comparison that neither the extrapolation of Reynolds et al's fit nor the Varshni equation appear to be valid in our composition regime. Both of these show a shift of energy positions with x which is much lower than our observed variation over the range $0.001 < x < 0.03$.

The interesting result that emerges from a combination of our earlier reported DLTS results and the present photoluminescence study of Al doped GaAs is a sharp reduction in the luminescence output accompanied by a pronounced increase in the deep level concentration with increase in Al content of the material. It is quite clear from this result that the deep levels observed in DLTS act as centres of strong nonradiative recombination. Although it is not clear as to which of the observed M levels are the most effective recombination centres, but the level M7 is observed to show the most pronounced increase as Al content goes from 0.1% to 1%. This suggests that probably this centre is the dominant nonradiative defect in MBE grown GaAs.

Another effect of the increase of Al doping is the change in relative intensity of the high energy peak (A) in photoluminescence, attributed to the overlap of free- and bound-excitonic transitions. This implies that the increase in nonradiative centre density accompanying the increased Al doping causes a stronger reduction in the intensity of these transitions as compared to the acceptor-related (peak B) and the defect-complex related (peak C) transitions. The relative intensity of the exciton-related A peak to that of the impurity-related sideband (B+C) is seen to decrease by about a factor of 3 as the Al doping increases from 0.1% to 1% while a further decrease by a factor of ~1.5 is observed in this ratio in the 3% Al doped material, at 2K.

These observations are to be contrasted with the case of In doping reported in a number of publications¹³. In is seen to lead to a decrease in M-level densities with an accompanying increase in photoluminescence emission for low doping. With a further increase in In concentration, the PL intensity is reported to either saturate or show a downward trend. Chang et al¹⁴ also found a maximum in the PL intensity at an In doping of 0.065% in their $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$ samples, beyond which a sharp reduction in the overall luminescence intensity as well as a reduction in the ratio of the bound-exciton to lower energy sideband intensity, similar to that clearly seen in our 2K spectra, is observed.

D. Conclusions

Data on the optical properties of MBE grown $\text{Al}_x\text{Ga}_{1-x}\text{As}$, with the lowest Al content reported to date, have been provided. Photoluminescence shows shallow-bound exciton features, carbon acceptor related free-to-bound peak and defect complex-related luminescence features, probably involving Si. A feature attributed to free-to-bound transition at the Si acceptor can also be resolved in the spectrum for the 0.1% Al doped material, which is not seen in the material with higher Al content. In addition, a deep defect-related emission band with well defined phonon replicas can be seen in the material with 0.1% and 1% Al doping close to 1.407 eV and 1.425 eV, respectively. This is tentatively assigned to complexes involving native defects. The bound exciton luminescence shows a marked decline relative to the other two features with the increase in Al doping. A pronounced decrease in the overall, integrated luminescence output is observed with increasing Al content, attributed to the strong non-radiative recombination competition from the increasing deep level content observed in our DLTS study. It is, therefore, to be concluded that Al doping does not serve the purpose of deep-level reduction in MBE GaAs as known for the other impurities isovalent to Ga, namely In and Sb, at least for the growth conditions used in our work. The analysis of our photoluminescence results provides new data on the free- and bound-exciton peak shift with the Al fraction x in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ in the low Al-content material which cannot be obtained from an extrapolation of the previously reported data with Al concentrations down to ~1%.

III. PHOTOLUMINESCENCE STUDY OF ALPHA-IRRADIATED InP

The study of the effects of alpha-irradiation on p- and n-type has recently been carried out in our laboratory using photoluminescence (PL) technique. In unirradiated p-InP three peaks have been observed at energies 1.415 eV, 1.379 eV and 1.335 eV. The temperature and power dependence of these peaks is measured and analysed. Comparing with the data available in literature, these peaks are identified as bound-exciton (BE) peak, conduction band to acceptor transition (e - A) peak and the LO phonon replica band of the e - A peak. Preliminary results are presented below.

In irradiated p-InP, overall PL intensity has decreased. This clearly shows that due to irradiation, some non-radiative centres have been created which result in non-radiative transitions and hence decrease in the PL signal is observed. The BE peak is not observed in the irradiated sample, even at the highest excitation power. This means that irradiation results in the formation of some complexes which suppress the near-band-edge excitonic transitions. The only major peak observed in the spectra of irradiated p-InP is a peak

with energy 1.374 eV i.e. shifted towards lower energy by 4.9 meV as compared to e - A peak of pre irradiation spectrum. This peak is found to be shifted towards higher energy with increase in excitation power. The final position of this peak at high excitation power is almost same as that of the e - A peak in unirradiated sample. It is concluded that irradiation has resulted in the formation of such centres which act as donors and these observed transitions may be acknowledged as donor - acceptor pair transitions involving these radiation-induced defects.

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PUBLICATIONS

1. Photoluminescence spectroscopy and its application to the study of silver doped silicon
Imran Asghar, Zia-ul-Hasnain and M. Zafar Iqbal
Baragali School of Electronics held on 18-23 June, 1994.

2. Influence of Al doping on deep levels in MBE GaAs
Umar S. Qurashi, M. Zafar Iqbal, N. Baber and T.G. Andersson
18th Int. Conf. Defects in Semiconductors, Sendai, Japan, July 23 - 28, 1995.
3. Photoluminescence study of Al doping in GaAs grown by molecular-beam epitaxy
Umar S. Qurashi, M. Zafar Iqbal and T.G. Andersson
J. Appl. Phys. 80, 5932 (1996).
4. Effects of γ -radiation on MOCVD grown p-type InP studied by Photoluminescence
Khalid M. Khalid, Umar S. Qurashi, M. Zafar Iqbal and Nasim Zafar
(submitted).

(e) GRADUATE STUDENTS

M.PHIL.

Three research students obtained their M.Phil. degrees working on the photoluminescence project.

1. Syed Zia-ul-Hasnain
2. Imran Asghar
3. Khalid M. Khalid (in progress)

Ph.D.

Umar Saeed Qurashi completed his Ph.D. degree. Part of his work consisted of photoluminescence studies on Al-doped GaAs carried out under this project.

(f) SCIENTISTS

1. Prof.Dr. M. Zafar Iqbal - Principal Investigator
2. Syed Zia-ul-Hasnain
3. Imran Asghar
4. Umar Saeed Qurashi
5. Khalid Mahmood Khalid

ANNEXURE I

Photoluminescence spectroscopy and its application to the study of silver doped silicon

Imran Asghar, Zia-ul-Hasnain and M. Zafar Iqbal

Semiconductor Physics Laboratory,
Department of Physics, Quaid-i-Azam University,
Islamabad.

Abstract

A brief introduction to photoluminescence (PL) technique and preliminary results from photoluminescence study of silver-related deep levels in silicon are presented. The electronic structure of the defects where the emission occurs, is discussed in the light of the investigation of the temperature dependence of the luminescence spectra.

Introduction

Impurities from III or V group of the periodic table in Si or Ge introduce shallow levels in the band-gap having the binding energy less than 0.1 eV, while the impurities not belonging to adjacent groups usually introduce deep levels having binding energy more than 0.1 eV¹. The fundamental role of deep levels in semiconductors is well established. An important consequence of the presence of deep impurities in semiconductors is the reduction of minority carrier lifetime. This reduction in minority carrier lifetime can result in diodes with reverse recovery times in the nanosecond range. Deep impurities also play very significant role in limiting the emission efficiency of light emitting diode (LEDs). For these reasons the characterization of defect states is a very important area of semiconductor research.

Photoluminescence is one of the powerful techniques to study the defect levels. In photoluminescence a photon is absorbed by a semiconductor creating an electron-hole pair which then recombine and emit another photon. Any impurity or lattice defect can serve as a recombination centre if it is capable of receiving a carrier of one type and subsequently capturing the opposite type of carrier, thereby annihilating the pair. The photoluminescence process consists of three stages: (1) creation of electron-hole pairs by absorption of exciting photons, (2) recombination of electron hole pairs, releasing the excess energy as photons and (3) escape of the recombination radiation from the sample. Since the exciting light is absorbed in creating electron-hole pairs, the strongest excitation of the sample takes place near the surface. As a result, most of the

photoluminescence experiments are arranged to examine the light emitted from the irradiated side of the sample. This is often called *front surface photoluminescence*. In thin samples with relatively low absorption of recombination light, the *back surface* or *transmission luminescence* can be exploited.

The close relationship of photoluminescence to many radiative devices such as semiconductor lasers, light emitting diodes, electroluminescence panels, cathodoluminescence of cathode ray tubes and many others, is evidence of its importance. Photoluminescence is also emerging as a major tool of basic research² on semiconductors for the following reasons.

- (a) high sensitivity; some features which are not prominent in absorption measurements become dominant in luminescence spectra.
- (b) sample handling is easy as compared to absorption measurements which require special preparation of samples with parallel and properly polished surfaces.
- (c) luminescence experiments can be done on bulk material or thin epitaxial layers with equal ease. This technique can also be used to study materials in which contact or junction technology is not adequately developed or in high resistivity materials where electroluminescence would be inefficient.

In the present study we are concerned with deep levels introduced by transition metals. The transition metals are among the fastest diffusers in crystalline silicon. Their presence gives rise to a number of luminescence bands in the energy range (0.7-1.1) eV. Silver is such a transition metal, which when introduced into silicon gives rise to two deep levels: one, an acceptor level near the middle of the band-gap (E_A at $E_C - 0.54$ eV) and the other a donor level, in the lower half of band-gap (E_D at $E_V + 0.35$ eV)³. The work described in this paper relates to the development of the photoluminescence technique in our laboratory and the study of silver-related defects in silicon as an example of the application of the technique.

Experimental Details

Our experimental arrangement is shown in block diagram in Fig.1. The excitation source is the 514.5 nm line of an Ar-ion laser. F1 is the filter which eliminates interference from non-lasing lines in the laser plasma which fall within the spectral region of interest. After filtering, the laser light is modulated for AC detection with the help of a chopper which also provides the reference frequency to the lock-in amplifier. After reflection from the mirror M the light falls on the sample, mounted on the cold finger of a

closed cycle helium cryostat which is designed for cool down to 10K. PL signal from the sample is collected by a combination of lenses L_1 and L_2 and focussed on the entrance slit of the spectrometer. Filter F2 prevents excitation light from entering the spectrometer. The light from the sample is composed of several spectral lines, which is analysed by the spectrometer and detected by a liquid nitrogen cooled Ge detector. The output of the detector is fed to a lock-in amplifier. The signal from this amplifier is displayed on an X-t chart recorder. By scanning the spectrometer, the complete PL spectrum in the desired wavelength range is obtained on the X-t recorder.

Our spectrometer is a 1-meter, single grating instrument. The grating used for the present work has 300 rulings/mm and works in the wavelength range $1.3 \mu\text{m}$ to $4.0 \mu\text{m}$. The North-Coast Ge detector used to detect the PL signal has a working wavelength range of $0.8 \mu\text{m}$ to $1.7 \mu\text{m}$. Thus with the present set-up we are limited to the wavelength range $1.3 \mu\text{m}$ to $1.7 \mu\text{m}$.

Our samples are prepared from high resistivity float zone silicon. Silver is evaporated on both sides of the sample and then diffused into it at a temperature of 1100°C for five hours.

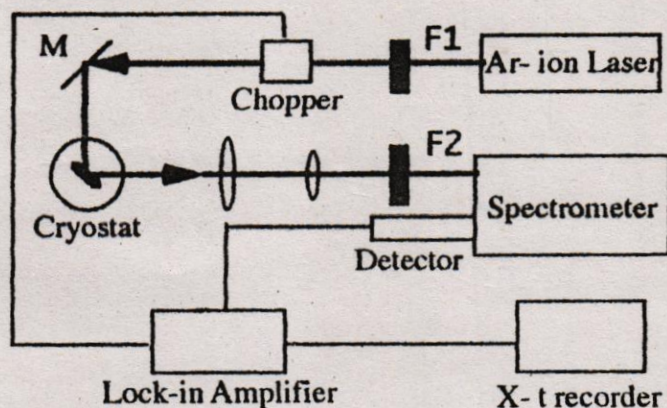


Fig.1 Block diagram of the experimental arrangement

Results and Discussion

Fig.2 shows the luminescence spectrum from our silver doped samples at 13K over the wavelength range ($1.3\mu\text{m}$ - $1.7\mu\text{m}$). The spectrum consists of a luminescence band in the region of photon energies 0.76-0.78 eV, approximately. The expanded spectrum in this region is shown in Fig.3. This reveals that the spectrum at 13K consists of primarily two prominent lines corresponding to photon energies 778.9 meV and 779.8 meV, labelled as A and B lines, respectively. In addition, two weak and broad features probably corresponding to the phonon replicas of the above mentioned zero-phonon lines appear at 773.5 meV and 763.5 meV.

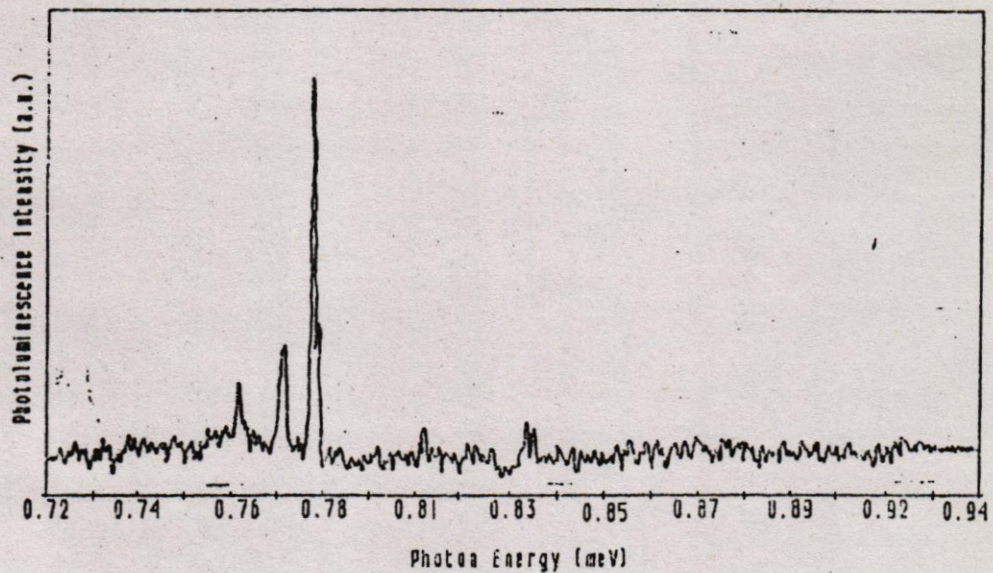


Fig.2. Photoluminescence spectrum at 13 K

As the temperature of the sample is raised to about 16K, however, an interesting new line emerges at photon energy ~ 784.5 meV. This line is labelled as the C-line in our spectra. Interesting changes in the PL spectrum are observed when we raise the sample temperature or the excitation intensity (which also causes an increase of temperature). These can be seen in Fig.3 where the silver related PL spectra are shown at three different temperatures. The interesting effects are seen to consist of

- a decrease in the height of the A- and the B-line with an accompanying increase in their widths, and
- a strong increase in the intensity of the C-line, with increase in temperature.

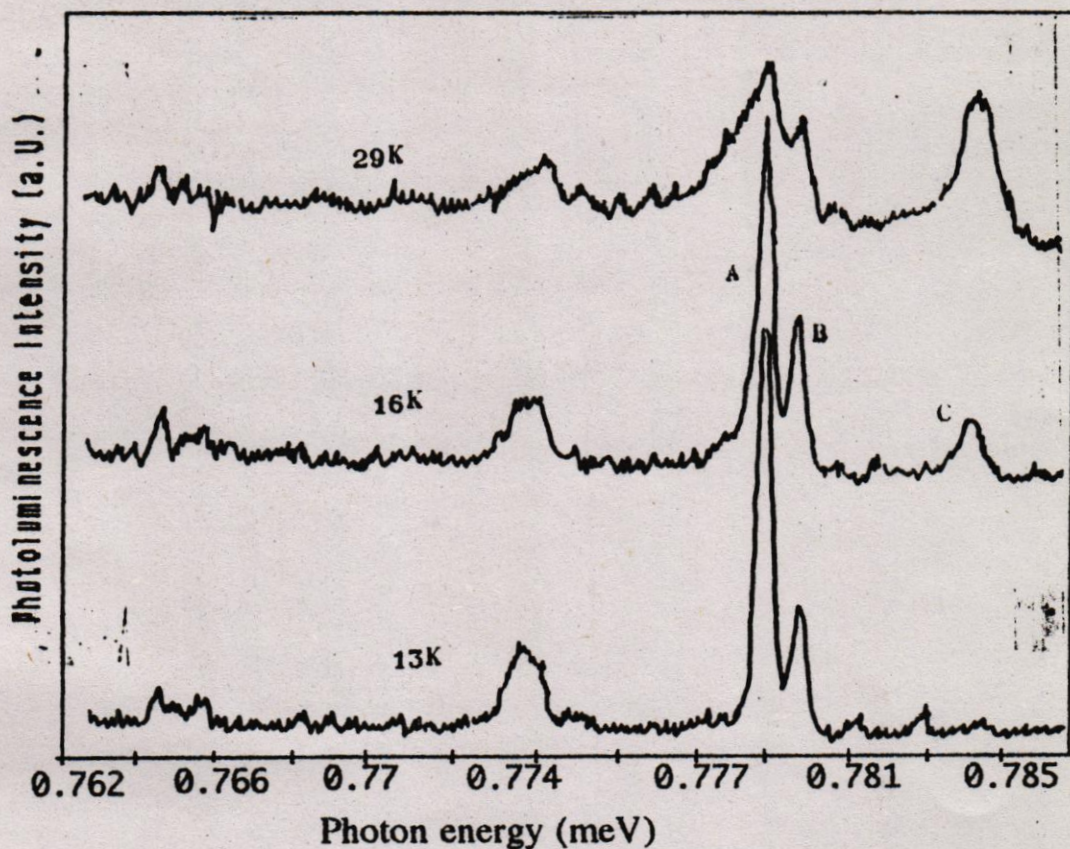


Fig.3 PL Spectra at different temperatures

The main line corresponds to a zero-phonon transition at 778.9 meV since no shift in its position is observed with the increase of temperature. Assuming this to correspond to the energy difference between the ground state and the excited state of a silver related defect, this line is interpreted to originate from Ag donor level located at $E_v + 0.35$ eV in the band-gap of silicon. The energy difference between the band-gap of Si at these temperatures (~ 1.16 eV) and the above mentioned energy position of the donor level (0.35 eV) very closely match with the transition energy (~ 0.78 eV) of the A-line. The fact that the intensities of the three lines vary simultaneously with temperature and, in particular, the strong increase in the intensity of the C-line as the A- and B-line decrease in intensity, clearly suggest some coupling between the transitions associated with these three lines. This variation leads to the interpretation that the B- and the C-line are probably the additional excited states of the same silver related defect from which the A-line originates. If this suggestion is correct, the intensities of the B- and the C-line relative to that of the A-line should vary according to the relative occupancies of these excited states. These, in turn are normally expected to vary approximately according to the Boltzmann law. The quantitative investigation of the variation of the relative intensities B/A and C/A is thus proposed to provide a means to test the above interpretation and to confirm whether the A, B and C excited states do indeed form a coupled system of states associated with the silver donor. Such investigations are in progress in our laboratory.

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ANNEXURE II

Photoluminescence study of Al doping in GaAs grown by molecular-beam epitaxy

Umar S. Qurashi and M. Zafar Iqbal^(a)

Semiconductor Physics Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan

T. G. Andersson

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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A detailed photoluminescence investigation of the effects of Al doping on GaAs grown by molecular-beam epitaxy is reported. Materials with 0.1%, 1%, and 3% Al doping have been studied. Viewed as an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy semiconductor, our study on these materials presents results on the optical characteristics of the lowest Al composition material reported to date. Photoluminescence spectra show three major peaks. Detailed measurements on the dependence of these spectra on temperature and excitation power have been carried out to characterize the various transitions responsible for the luminescence peaks. A near-band-edge exciton peak, a carbon acceptor-related free-to-bound transition, and a defect complex-related luminescence peak, probably involving silicon, are identified as the main features of our luminescence spectra. The integrated luminescence intensity shows a strong quenching with the increase in Al doping, thus supporting the increase of nonradiative deep-level centers with Al doping, concluded from our earlier reported deep level transient spectroscopy study. The relative intensity of the excitonic peak shows a stronger decrease than that of the other luminescence features. New data on the shift of the excitonic transition energy with Al content x in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, for the lowest x values yet reported, are provided by our photoluminescence study. © 1996 American Institute of Physics. [S0021-8979(96)05220-6]

I. INTRODUCTION

GaAs, as the primary material for fast electronic device technology, is marred by the presence of native defects such as EL2 produced in high concentrations in crystals grown by all conventional techniques. Molecular-beam epitaxy (MBE) was expected, and has proven, to be the source of GaAs free from this defect. This material, however, suffers from a series of as yet unidentified defects labeled M0, M1, ..., M8, first reported by Lang *et al.*¹ The relative concentrations of these defects are known to depend on the growth conditions, i.e., temperature and vapor pressure of As as compared to that of Ga during growth and to a certain extent on the contamination of the MBE growth system used.² Three of these defects, M1, M3, and M4 giving rise to levels in the upper half-gap at energy positions $E_c - 0.17$ eV, $E_c - 0.28$ eV, and $E_c - 0.45$ eV, are known to be dominant, in general, and have been observed in most of the studies.

A number of different methods have been tried to eliminate or at least reduce these deep level defects in MBE GaAs. One successful method seems to be the introduction of isoelectronic impurities during growth. Indium³ and antimony⁴ have, in particular, shown a significant promise in suppressing the M levels. Aluminum, an impurity isovalent to Ga, is another such candidate which has not been tried as a dopant for this purpose, even though AlGaAs alloy semiconductors have found numerous applications. We have recently carried out the first Al doping experiments, and deep level transient spectroscopy (DLTS) investigations of the Al doped material with Al content varying from 0.1% to 3% have been reported.⁵

In brief, the DLTS spectra for 0.1% Al samples show nine peaks in electron emission, labeled U1–U9, while at least seven distinct peaks labeled U1*–U7* are seen in 1% Al-doped samples. These levels have been identified as the counterparts of the levels M0–M8 typically observed in MBE GaAs. The emission rates are found to show a systematic shift to lower values with the increase in Al doping from 0.1% to 1%. The important result of the DLTS analysis is that the cumulative concentration of deep levels shows a significant increase as Al doping is increased, from 0.1% to 1%. This increase is as high as by a factor of 200 for the level M7. The relative concentrations of the various levels are also observed to change with this change in Al doping. From this trend and the fact that our Schottky barriers on the 3% Al doped material showed extremely poor electrical quality, preventing the direct observation of deep level spectra, we concluded that the deep level content of the 3% Al material must be still higher than that of the 1% Al doped material. This was further corroborated by our preliminary photoluminescence measurements which showed a strong quenching of the signal with increase in Al doping from 0.1% to 1% and a complete extinction in the 3% Al doped samples.⁶ These results and the obvious interest in GaAs as an optical material motivated us to carry out a detailed study of the optical characteristics of our Al-doped materials with a view to investigating the possible correlation between the effects of Al doping on the electrical and optical characteristics of MBE-grown GaAs.

Photoluminescence (PL) spectroscopy has been commonly employed as an effective tool for the characterization of GaAs and AlGaAs, insofar as it provides particularly useful information on the relatively shallow defect levels in the

^(a)Electronic mail: semcon@physics.sdnpk.undp.org

band gap, which may provide strongly competing paths for carrier recombination against the desired radiative path for a particular optical application. PL spectroscopy thus provides complementary data to those provided by DLTS. Kunzel and Ploog⁷ reported the first high-resolution PL study of high-quality undoped GaAs grown by MBE. Skromme *et al.*⁸ later carried out a detailed study of Si-doped MBE GaAs. A number of other studies⁹ provided a detailed picture of the various defect-related luminescence paths commonly observed in MBE-grown GaAs. These studies were further stimulated by a growing realization of AlGaAs as an important material, in its own right, for the band-gap engineered devices based on GaAs. A large number of investigations on the various compositions of MBE-grown Al_xGa_{1-x}As have since been carried out, providing a wider and deeper understanding of these important alloy semiconductors, summarized in a recent review article by Pavesi and Guzzi.¹⁰ Because of the wide range of applications of the GaAs/AlGaAs system, the improvement and study of the optical and electrical characteristics of these materials continue to attract considerable research activity.¹¹ While most of these studies have concentrated on relatively high (>10%) Al composition of this alloy in both the direct- and indirect-band-gap regimes, it would be worthwhile to investigate its properties in the very low-Al end of the alloy composition range to provide a comprehensive picture covering the complete range of compositions.

The results of our PL study are reported here, yielding a clearer and more detailed understanding of the effects of Al doping on MBE GaAs which was the prime motive of our work. At the same time the results of our study on low-Al content Al_xGa_{1-x}As (0.001 ≤ x ≤ 0.03) would serve to complement the available information on this alloy semiconductor in this important composition range. It may be pointed out that this is the lowest Al content AlGaAs ever studied by DLTS or PL and no data are previously available in this composition range—the lowest composition for which PL data have been reported so far being ~1% Al,¹² to the best of our knowledge.

II. EXPERIMENTAL DETAILS

A. Samples

A Varian Gen-II MBE system was used to grow 1.5-μm-thick layers of Si-doped Al_xGa_{1-x}As with the compositions x=0.001, 0.01, and 0.03 at 625 °C, in As-rich conditions, on n⁺-GaAs substrates with a thin buffer layer grown *in situ*. The typical free carrier concentrations were found to be ~2×10¹⁵ cm⁻³ from capacitance-voltage measurements on evaporated gold Schottky barriers. The details of the growth may be found in Ref. 13. The composition of our Al_xGa_{1-x}As alloys is normally determined from the reflection high-energy electron-diffraction (RHEED) oscillations data. The x values are plotted as a function of inverse temperature of the source and the low x values for our present samples are determined by extrapolation of this curve to the low x region using the vapor pressure of Al appropriate for our samples. Relative values of x were also checked using secondary-ion-mass spectroscopy (SIMS). The estimated er-

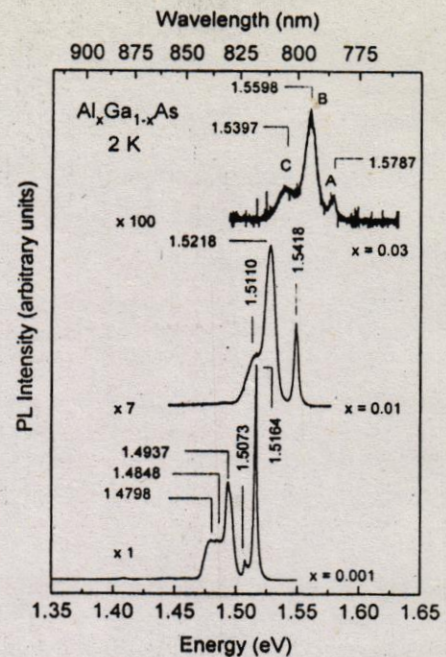


FIG. 1. PL spectra of Al-doped GaAs obtained at 2 K.

ror in x would range from ~10% in our x=0.03 samples to a worst figure of ~50% in the x=0.001 samples. For PL measurements the as-grown samples were used without any further treatment.

B. Photoluminescence measurements

Photoluminescence experiments were carried out using two different closed-cycle refrigerator systems capable of cooling the samples to minimum temperatures of 10 and 8 K. Spectra at 2 K were obtained using a bath-type pumped liquid-helium cryostat. Conventional reflection grating dispersive spectrometers (0.5 and 1 m) were used for the spectral analysis of luminescence from the samples. An argon-ion laser was used as the excitation source at 514.5 nm wavelength for all spectra. A liquid-nitrogen-cooled North Coast Ge detector was used for the detection of the photoluminescence signal via the usual lock-in amplifier based technique, except for the 2 K experiments where the detector was a GaAs-cathode photomultiplier tube.

III. RESULTS

A. Photoluminescence spectra

A detailed PL study with carefully optimized collection of the signal followed our DLTS work to thoroughly investigate the optical quality of our Al-doped GaAs layers. With this optimized collection optics it was possible to detect the weak PL signal spectra even from the 3% Al doped samples. The typical PL spectra for the three types of samples at 2 K, obtained at low excitation power (10 mW) are displayed in Fig. 1. The overall characters of the spectra appear to be similar for all three cases, although the relative intensities of the various features show a significant variation with the Al doping. The centroids of the spectra are seen to shift system-

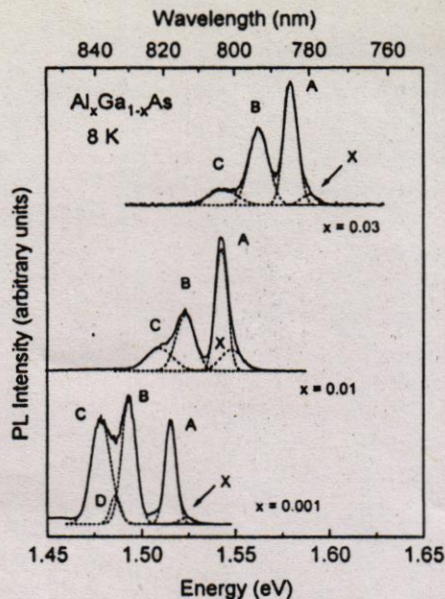


FIG. 2. PL spectra at 8 K (solid curves) showing the deconvoluted structure after Gaussian peak fits (dashed curves). X and D are additional peaks revealed by deconvolution. Peak D is seen only in the 0.1% Al samples.

atically to higher energies with increase in Al content from 0.1% to 3%. Three prominent peaks labeled A, B, and C are seen to be present in all three spectra. A small feature between the peak A and the side band consisting of peaks B and C is also observed in the low-temperature photoluminescence spectrum of the 0.1% Al sample. It is clear that line A dominates the emission spectrum of the sample with the lowest (0.1%) Al doping while the predominant emission in both the higher Al-doped (1% and 3%) samples is the B-line. The ratio of the A line to the side band (B+C) intensities is seen to decrease markedly with the increase in Al doping. A dramatic decrease in the overall luminescence intensity with increase in Al doping is clearly visible from these spectra. The total integrated intensity is found to go down about five times with increase in Al doping from 0.1% to 1%, while a further reduction by a factor of about 35 is observed as the Al content increases to 3%.

B. Deconvolution analysis

In view of the possibility of the overlapping spectral lines in our luminescence spectra, as is particularly evident in the case of the lower-energy sideband of B and C lines, we have carried out a deconvolution using a multi-Gaussian fit procedure based on ORIGIN 3.5 software. The procedure consists of fitting Gaussian line shapes to the most prominent peaks in the spectra and then demanding best fits to the remainder of the spectral output until no further peaks can be found by the program. This analysis shows the presence of a small additional peak X at the high-energy tail of the peak A. Similarly the best fit to the sideband in the spectra of 0.1% Al samples is obtained with the incorporation of an additional peak labeled D, overlapping the B and C peaks, as shown in Fig. 2. The existence of these additional peaks becomes even more evident from a similar analysis of the

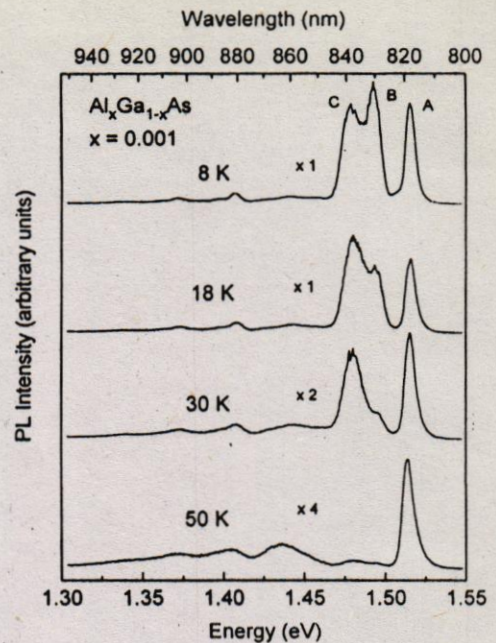


FIG. 3. Variation of the PL spectra for the 0.1% Al doped samples with temperature.

spectra for higher excitation powers encountered during the investigation of the excitation power dependence of the luminescence intensity, which is to be described later (Fig. 9). In case of the 1% and 3% Al doped material, deconvolution shows the small high-energy component X to be present in the A peak but the side band can be satisfactorily fitted to a sum of two Gaussian peaks only, as seen in Fig. 2. So, the peak D is absent in these higher Al content samples.

In order to obtain a better identification of the dominant luminescence lines we carried out a detailed study of the characteristics of the photoluminescence spectra. This included the investigation of the temperature and excitation power dependence of these spectra over a wide range. The results of these investigations are presented below.

C. Temperature dependence of the spectra

1. 0.1% Al doping

Figure 3 shows typical PL spectra measured in the range 8–80 K for the GaAs samples with 0.1% Al doping. While an overall decrease in the luminescence intensity is observed with an increase in temperature, the side band consisting of the B, C, and D lines is seen to quench more rapidly than the A line. Within this band, the B line quenches at a much faster rate than the C line. The contribution of the D line becomes negligibly small above about 30 K. At about 50 K, the side band is almost fully quenched. The relatively weak features at ~ 1.44 and ~ 1.41 eV in these spectra, assigned to the phonon-assisted and defect-related transitions, are discussed later.

The integrated intensities of the A (bound-exciton part), B, and C peaks for this material after deconvolution of the

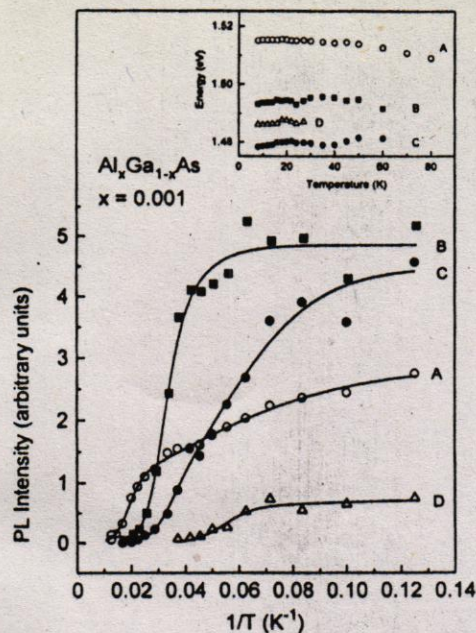


FIG. 4. PL intensity for the different spectral lines of the 0.1% Al doped samples as a function of inverse temperature (points). Solid curves represent theoretical fits to Eq. (1). The inset shows the peak positions as a function of temperature.

spectra are plotted as a function of the reciprocal temperature in Fig. 4. An analysis of these data has been carried out using the well-known relation¹⁴

$$I = \frac{I_0}{1 + \sum_i C_i \exp(-E_i/kT)} \quad (1)$$

where I_0 is the saturation intensity, E_i is the activation energy, and C_i a temperature-independent constant characteristic of each transition. The solid curves in Fig. 4 represent theoretical fits to this equation. The intensity versus temperature data are, in general, found to follow a double-exponential fit to Eq. (1). The activation energies E_i obtained from these fits are given in Table I. The errors in these values are significant, as expected, in view of the large scatter in the data, probably caused by uncertainties of our deconvolution of the overlapping peaks. Dotted entries in Table I indicate the unavailability of reliable numbers.

TABLE I. Activation energies are shown for the three major luminescence peaks obtained from the theoretical fits of the temperature dependence of intensity to Eq. (1) for the different compositions of $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

Peak \ x	Activation energy (meV)		
	0.001	0.01	0.03
A	34.3±4.2 2.6±0.3	33.9±5.1 7±3	41.2±3.3 ...
B	27.7±5.7 5.0±0.8	25.4±4.2 7.0±2.0	24.9±3.8 5.3±1.7
C	30.3±1.9 ...	23.6±8.0

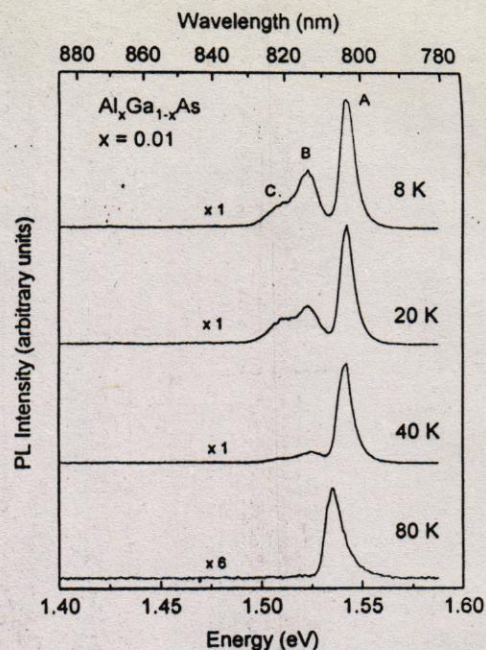


FIG. 5. PL spectra as a function of temperature for the 1% Al doped GaAs samples.

The positions of the different peaks in the spectra are plotted as a function of the temperature in the inset of Fig. 4. A significant monotonic shift to lower energies can be seen in the position of peak A with the increase in temperature.

2. 1% Al doping

Figure 5 shows typical variation in the PL spectra with temperature of the 1% Al doped GaAs samples. Here, the A line remains the dominant feature at all temperatures, with the expected decrease in the overall luminescence intensity as the temperature increases. Although the side band consisting of the B and C peaks shows a far more rapid quenching as compared to the A line; a markedly faster quenching of the B peak relative to the C peak with increasing temperature, similar to that seen in case of the 0.1% Al sample, is not observed here. The intensity of the B peak is seen to be higher than that of the C peak even at the highest temperatures.

The intensities of the peaks A, B, and C along with the respective theoretical fits to Eq. (1) are shown in Fig. 6. The thermal activation energies obtained from these fits are given in Table I.

3. 3% Al doping

The variation of PL spectra with temperature for this case is shown in Fig. 7. Here, the bands corresponding to the three types of emission are broader than in the case of the other two types of samples. The side band is again found to undergo a much stronger thermal quenching as compared to the dominant A line. However, the relative quenching rates of the B and the C components appear to follow the same order as for the 1% Al doped material.

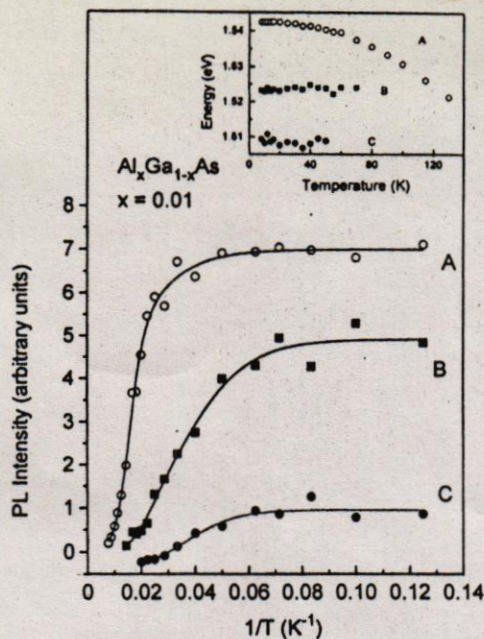


FIG. 6. Variation of the luminescence intensity of the various peaks with temperature for the 1% Al doped samples (points) fitted to the formula of Eq. (1) shown by solid curves. Variation of the peak energies with temperature is shown in the inset.

The intensities of the three bands as a function of temperature are plotted in Fig. 8. The theoretical fits to Eq. (1) are again shown by solid curves. The activation energies obtained from this theoretical analysis are also given in Table I. The low signal-to-noise ratio does not permit any reliable activation energy data on the C peak in this case.

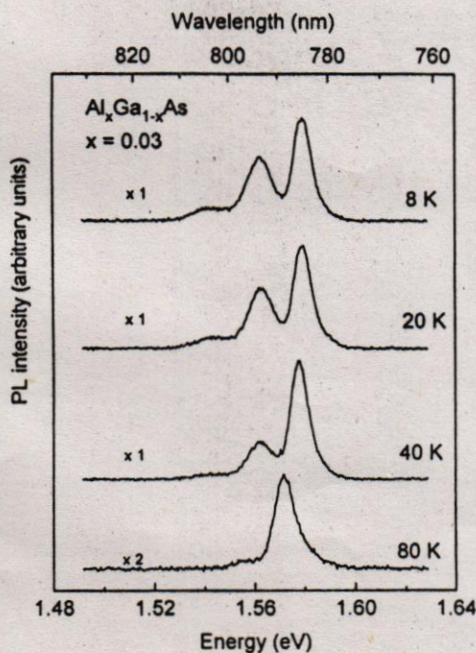


FIG. 7. PL spectra at different temperatures for the 3% Al doped GaAs.

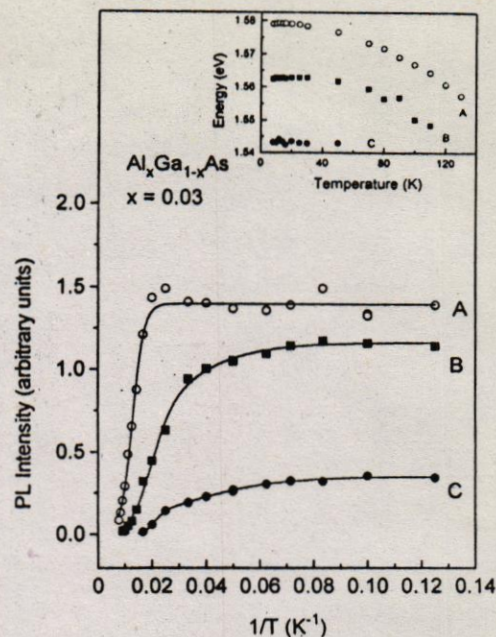


FIG. 8. Luminescence intensity for various peaks in the spectra of the 3% Al samples vs inverse temperature (points) with the theoretical fits to Eq. (1) plotted as solid curves. Peak positions as a function of temperature are shown in the inset.

D. Excitation power dependence of the spectra

The PL spectra of the three types of samples were measured at a number of different excitation intensities, spanning three orders of magnitude, at 8 K to study the excitation power dependence of the various transitions. Typical spectra at different excitation powers for the 0.1% Al doped samples are shown in Fig. 9(a). The spectra show a pronounced increase in the intensity of peak A with increasing excitation power, relative to the rate of increase of the side band comprising the B and C lines. At the lowest excitation intensities the B and C lines dominate the spectra but the A line takes over as the excitation intensity is increased, becoming the dominant peak at higher intensities.

The integrated intensities for the various peaks (obtained from Gaussian fits to the line shapes) are plotted as a function of the excitation power for the 0.1% Al doped samples in Fig. 9(b). As can be seen from this plot, the intensity of the X and the A line increases about 1000-fold as the excitation power is increased by the same factor. The corresponding increase in the B and C lines is by about a factor of 100. A similar behavior is seen for the corresponding lines in the spectra for samples with 1% and 3% Al doping, as shown in Figs. 10 and 11. It is clear, therefore, that with the increase in excitation power the B and the C lines tend to saturate, since the luminescence intensity for these lines increases at a rate lower than the excitation power. A power-law dependence ($I \propto P^n$) of luminescence intensity I on the excitation power P is observed for each composition as seen from the plots of Figs. 9(b)–11(b). The exponent n is given on the log–log plot for the respective lines in each case. For the 1% and 3% Al doped samples the variation of the C-line inten-

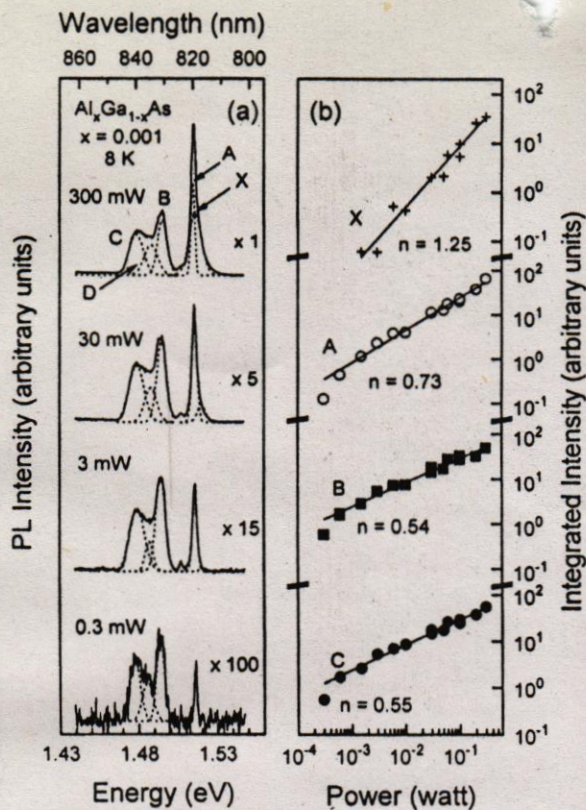


FIG. 9. (a) Variation of the PL spectra with excitation power for the 0.1% Al doped samples at 8 K. (b) Excitation power dependence of the PL intensity of the different spectral lines. Solid lines show fits to power-law variation with the exponent n given against each line.

sity with excitation power is fitted by two different exponents in the low- and high-power ranges.

E. Phonon replicas

PL peaks corresponding to some phonon-assisted transitions are also seen in our spectra (Fig. 12). One- and two-phonon replicas of the B and C lines with the participation of the ~ 36 meV LO phonon can be clearly observed in the low-temperature spectra of the 0.1% Al doped samples. The poor signal-to-noise ratio, however, allows the observation of only the one-phonon LO replicas of these lines in the 1% Al doped samples while hardly any phonon replicas can be observed in the spectra of the 3% Al doped samples. The one-phonon replica band close to ~ 1.44 eV in the case of 0.1% Al samples is seen to become more pronounced up to ~ 50 K, reflecting the increased phonon population at higher temperatures.

F. Deep defect peak

A significant peak Δ with a small side band is observed at 1.407 eV, about 108 meV below the dominant peak A in the spectra of our 0.1% Al doped samples, Fig. 12. This feature is followed by at least two clear phonon replicas corresponding to the 1- and 2-LO phonons. Similar features at correspondingly displaced positions are also observed in the spectra for 1% Al doped samples. This deep-level defect

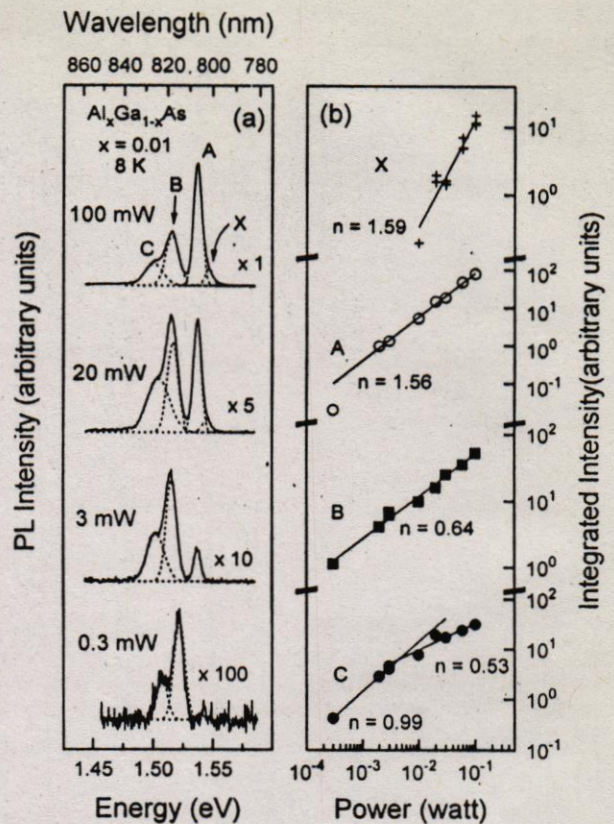


FIG. 10. (a) 8 K PL spectra of the 1% Al doped samples at different excitation powers. (b) PL intensity of the different spectral lines as a function of excitation power. Solid lines represent power-law fits to the data using the respective exponents.

peak shows very little change in intensity relative to the main luminescence band with the increase in temperature, as seen in Fig. 3.

IV. DISCUSSION

The main features of our near-band-edge PL spectra consist of a relatively sharp zero-phonon excitonic peak (A) and two broad defect-related features (B) and (C). From the peak position, spectral sharpness, and excitation power dependence, the peak A is identified as an excitonic peak. Our Gaussian line-shape deconvolution analysis reveals two components in this peak. The small high-energy feature X is assigned to the free-exciton transition, from the supralinear excitation power dependence shown in Figs. 9–11, with a possible contribution from the free-electron–hole recombination. The lower-energy major component of A is interpreted as the bound excitonic peak. The main contributions to the bound excitonic peak are known^{7,15} to come from a number of transitions including the shallow neutral-donor-bound-exciton (D^0, X), the ionized-donor-bound-exciton (D^+, X), and the neutral- and ionized-acceptor-bound-excitons (A^0, X) and (A^-, X). In addition to a component with an activation energy of a few meV, the temperature dependence of the intensity reveals a bound exciton transition with an activation energy varying from ~ 34 to ~ 41 meV over the three types of samples. This relatively high activation energy

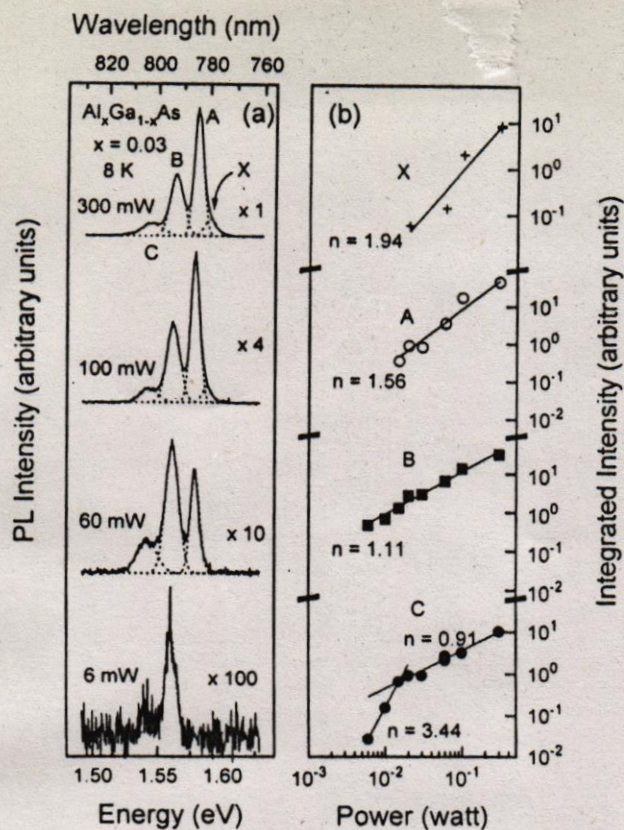


FIG. 11. (a) Variation of the PL spectra with excitation power for the 3% Al doped samples at 8 K. (b) Excitation power dependence of the luminescence intensity of the different lines. Power-law fits with the exponent n are shown by solid lines.

suggests a significant contribution from some defect bound exciton. This energy, however, appears too high to be ascribed to the neutral carbon acceptor. The random alloy fluctuations could also be a possible source of bound excitons in our materials, since the local crystalline disorder is known to

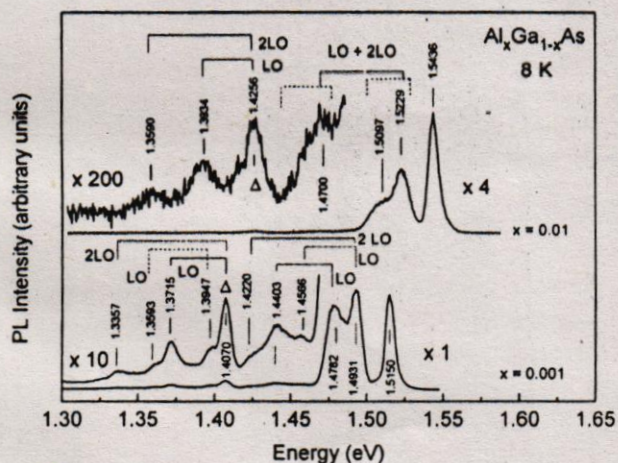


FIG. 12. 8 K PL spectra for the 0.1% and 1% Al doped samples with magnification of the low-energy part. The LO-phonon replicas of the B and the C lines and the deep defect line Δ can be seen on the expanded part. Phonon replicas could not be seen in the 3% Al samples due to poor PL output.

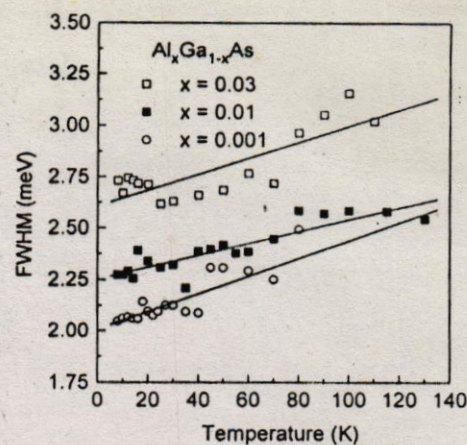


FIG. 13. Full width at half-maximum (FWHM) of the deconvoluted bound-exciton component of the A peak as a function of temperature for the three compositions $x=0.001$, 0.01 , and 0.03 of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples.

bind excitons in alloy semiconductors.¹⁶ The width of the bound exciton component of the A peak is plotted in Fig. 13 as a function of temperature for the three compositions. Although the data are subject to considerable scatter, partly due to errors of line-shape fitting procedure and partly due to poorer signal-to-noise ratio of the high-temperature spectra, especially for the higher Al content samples, yet a clear increase of the linewidth of the bound-exciton peak can be seen with Al content. This is the result of alloy broadening associated with increasing randomness in the occupancy of the cation site by Ga or Al.

The peak B corresponds to a transition from the conduction band to a shallow acceptor (e, A^0) with an overlap from the donor-acceptor (D^0, A^0) pair transition. The temperature dependence of the intensity data reveals an activation energy close to that of the carbon acceptor (~ 26 meV), known to be a common impurity in GaAs. Our 2 K spectrum for the 0.1% Al samples provides an indication of a structure within the carbon-related peak B presumably corresponding to the free-to-bound and donor-acceptor pair transitions at this center, but this structure is lost in the corresponding peak for the 1% and 3% Al samples, probably as a result of alloy broadening of both transitions.

Peak B is followed, at lower energy, by a structure consisting of two peaks as revealed by the Gaussian line-shape analysis. The higher-energy component (peak D) is probably the free-to-bound emission at the Si acceptor center also observed by Chand *et al.*¹⁷ in their MBE GaAs samples. The lower-energy transition (peak C) involves a deeper defect ascribed to some complex of carbon by Briones and Collins.¹⁸ The (e, A^0) and (D^0, A^0) structure of this luminescence feature was established by Skromme *et al.*⁸ Later, Chand *et al.*¹⁷ suggested the involvement of both C and Si in this complex, since they could only observe this luminescence line in their Si-doped MBE GaAs samples. The differential thermal ionization of the shallower carbon acceptor causes a more rapid quenching of the B peak relative to the defect-complex peak C with increase in temperature, as observed in our spectra (Fig. 3).

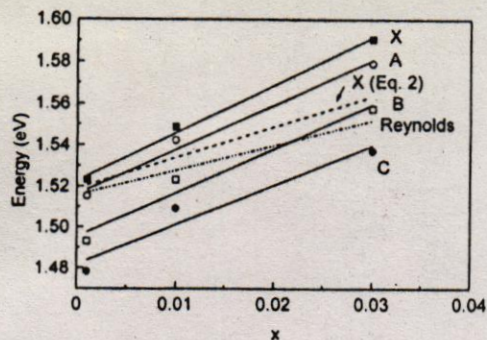


FIG. 14. Shift of the observed positions of the different spectral peaks at 8 K with Al content x shown along with linear fits. The extrapolated linear fits to the 2 K data of Reynolds *et al.* (Ref. 12) and the calculated variation from the modified Varshni Eq. (2) are also shown for the free-exciton peak X.

The small peak at 1.507 eV observed in our 2 K spectrum for 0.1% Al samples is the defect-related g peak observed by Kunzel and Ploog⁷ and others.^{17,19} It has generally been ascribed to a Ga-vacancy defect, although its identity is not fully established. The disappearance of the g line in the spectra for 1% and 3% Al doped samples may have been caused by plugging of the Ga vacancies by the Al atoms with increased Al doping. The origin of the deep transition at 1.407 eV with a shoulder at 1.395 eV in our 0.1% Al samples and the corresponding features in the higher Al-doped samples is not clear. A peak at a similar position in GaAs has been reported due to a free-to-bound transition at the Mn impurity;¹⁰ but, luminescence bands due to $\text{Si}_{\text{As}}-\text{V}_{\text{As}}$ and $\text{C}_{\text{As}}-\text{V}_{\text{As}}$ complexes at similar positions have also been observed in heat-treated Si-doped GaAs.²⁰ Similarly, bands at nearby positions have been reported for $\text{Si}_{\text{As}}-\text{V}_{\text{Ga}}$ and $\text{Si}_{\text{As}}-\text{As}_{\text{Ga}}$ complexes in GaAs.¹⁰ Some evidence has recently been reported by de Paula, Meleiros-Ribeiro, and de Oliveira²¹ for a $\text{Si}_{\text{As}}-\text{V}_{\text{As}}$ complex-related band about 160 meV below the band-to-band transition in their MBE-grown Si-doped $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ samples. Since some shift in the reported energy positions for GaAs would be expected due to the occupancy of some of the group-III atom sites by Al in our Al-doped materials, it is likely that the deep defect band, under discussion, in our spectra is caused by one or more of these complexes.

Reynolds *et al.*¹² have reported the only study which comes closest to our compositions—the lowest composition of their samples being 0.8% Al. Using high-resolution PL, they have resolved the various contributions to their bound-exciton peaks and provided data on the variation of the peak position with the composition x . We compare our results with the extrapolated straight line fits to their data in Fig. 14. The positions of the various peaks in our spectra are plotted as a function of the Al content x along with the linear fits. Also included in this figure is the calculated free exciton peak position based on the band-gap variation with x obtained from the modified Varshni equation,¹⁰ incorporating both T (temperature) and x dependence,

$$E_g^{\Gamma}(T, x) = \frac{A(T) + B(T)x + Cx^2}{D(T) + Ex} \text{ eV}, \quad (2)$$

where

$$A(T) = 341.87 + 1.5194T - 5.5 \times 10^{-4}T^2 \text{ eV K},$$

$$B(T) = 466.71 + 1.48T - 3.3 \times 10^{-4}T^2 \text{ eV K},$$

$$C = 130.24, \text{ eV K},$$

$$D = 225 + T \text{ K},$$

$$E = 88 \text{ K},$$

A free exciton binding energy of 4.2 meV corresponding to the observed value for GaAs, has been subtracted from the band-gap values obtained from the above equation to obtain the free exciton peak position—the estimated change in the binding energy of the exciton with Al fraction is known²² to be too small (~ 0.2 meV for the highest $x=0.03$ samples) to make any observable difference to these numbers. It is clear from this comparison that neither the extrapolation of Reynolds *et al.*'s fit nor the above equation appear to be valid in our composition regime. Both of these show a shift of energy positions with x which is much lower than our observed variation over the range $0.001 \leq x \leq 0.03$.

→ The interesting result that emerges from a combination of our earlier reported DLTS results and the present PL study of Al-doped GaAs is a sharp reduction in the luminescence output accompanied by a pronounced increase in the deep level concentration with increase in Al content of the material. It is quite clear from this result that the deep levels observed in DLTS act as centers of strong nonradiative recombination. Although it is not clear as to which of the observed M levels are the most effective recombination centers, the level M7 is observed to show the most pronounced increase as Al content goes from 0.1% to 1%. This suggests that probably this center is the dominant nonradiative defect in MBE-grown GaAs.

Another effect of the increase of Al doping is the change in relative intensity of the high-energy peak (A) in PL, attributed to the overlap of free- and bound-excitonic transitions (Fig. 1). This implies that the increase in nonradiative center density accompanying the increased Al doping causes a stronger reduction in the intensity of these transitions as compared to the acceptor-related (peak B) and the defect-complex-related (peak C) transitions. The relative intensity of the exciton-related A peak to that of the impurity-related side band (B+C) is seen to decrease by about a factor of 3 as the Al doping increases from 0.1% to 1% while a further decrease by a factor of ~ 1.5 is observed in this ratio in the 3% Al doped material, at 2 K.

These observations are to be contrasted with the case of In doping reported in a number of publications.²³ In is seen to lead to a decrease in M-level densities with an accompanying increase in PL emission for low doping. With a further increase in In concentration the PL intensity is reported to either saturate or show a downward trend. Chang *et al.*²⁴ also found a maximum in the PL intensity at an In doping of 0.065% in their $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$ samples, beyond which a sharp reduction in the overall luminescence intensity as well as a reduction in the ratio of the bound-exciton to lower-energy side band intensity, similar to that clearly seen in our 2 K spectra, is observed.

V. CONCLUSIONS

Data on the optical properties of MBE-grown $\text{Al}_x\text{Ga}_{1-x}\text{As}$, with the lowest Al content reported to date, have been provided. PL shows shallow-bound-exciton features, carbon-acceptor-related free-to-bound peak, and defect-complex-related luminescence features, probably involving Si. A feature attributed to the free-to-bound transition at the Si acceptor can also be resolved in the spectrum for the 0.1% Al doped material, which is not seen in the material with higher Al content. In addition, a deep defect-related emission band with well-defined phonon replicas can be seen in the material with 0.1% and 1% Al doping close to 1.407 and 1.425 eV, respectively. This is tentatively assigned to complexes involving native defects. The bound-exciton luminescence shows a marked decline relative to the other two features with the increase in Al doping. A pronounced decrease in the overall integrated luminescence output is observed with increasing Al content, attributed to the strong nonradiative recombination competition from the increasing deep level content observed in our DLTS study. It is, therefore, to be concluded that Al doping does not serve the purpose of deep-level reduction in MBE GaAs as known for the other impurities isovalent to Ga, namely In and Sb, at least for the growth conditions used in our work. The analysis of our PL results provides new data on the free- and bound-exciton peak shift with the Al fraction x in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ in the low-Al-content material which cannot be obtained from an extrapolation of the previously reported data with Al concentrations down to $\sim 1\%$.

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