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13. ABSTRACT (Maximum 200 words)

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The goal of this project was to study the effects of GaAs doping with dimethylaluminum methoxide during OMVPE growth. Incorporation of both aluminum and oxygen was analyzed as a function of growth conditions (growth temperature, V/III ratio, reactor pressure, growth rate, and DMAlMO mole fraction) by Secondary Ion Mass Spectroscopy. The aluminum content changed only slightly with deposition parameters but oxygen incorporation exhibited thermally activated behavior with the activation energy of 2.0 eV. At temperatures below 500°C oxygen content approached that of aluminum indicating that Al-O is incorporated as a pair into GaAs. The oxygen concentrations were as high as $5\times10^{19}cm^{-3}$ without degrading surface morphology. Layers with high oxygen content exhibited short carrier lifetime (very weak near-band-edge photoluminescence) and high resistivity as determined by C-V profiles and Hall effect measurements. Localized Vibrational Mode spectroscopy proved that aluminum and oxygen atoms remain bonded as pairs in the volume of the epilayer. This is the first successful attempt at controlled introduction of impurity complexes into semiconductors.

14. SUBJECT TERMS
GaAs, Oxygen, MDCVP, Growth, Buffer Layer

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FINAL TECHNICAL REPORT

PROJECT TITLE:	High Resistivity Buffer Layers by Oxygen Doping
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PRINCIPAL INVESTIGATOR:	Marek Skowronski
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AMOUNT AWARDED:	$ 34,267

This Final Technical Report summarizes the research effort sponsored by AFOSR/NE for the period of September 1, 1991 to August 31, 1993. The original STATEMENT OF WORK is included as a Section 1. This is followed by detailed description of technical accomplishments (Sections 2.1 through 2.4) and list of publications.

1. STATEMENT OF WORK

The goal of this project is to establish feasibility of growing high resistivity buffer layers of GaAs by oxygen doping. We intend to grow GaAs epilayers on n-type and semi-insulating GaAs substrates and dope them with aluminum and oxygen. The dopant source to be used is a novel compound: dimethylaluminum methoxide. Secondary Ion Mass Spectrometry will be used to determine the total oxygen and aluminum content and relate this to growth conditions. In particular, the effect of growth temperature on efficiency of oxygen and aluminum incorporation into GaAs will be investigated. The deposition temperature will be changed between 500 °C and 800 °C. The flow rate of DMAlMO will be correlated with concentration and type of point defects incorporated into GaAs layer. The primary characterization technique for defect assessment will be the localized vibrational mode absorption. Using ^{18}O isotope enriched DMAlMO will allow to determine the number of oxygen atoms involved in each defect and isotope shift due to naturally occurring ^{69}Ga and ^{71}Ga will be used to identify local symmetry of each center.

Two more technology related issues are the quality of overgrowth and thermal stability of electrical properties of buffer layers. Both the morphology of overgrowth and its electrical properties will be assessed. We plan to use Hall effect (electron concentration and mobility) to determine degree of compensation possibly caused by memory effect and photoluminescence to evaluate concentration of recombination centers. Thermal stability of electrical properties will be determined by Hall effect measurements before and after short (30 s) and long (2 hr) term annealing at typical processing temperatures.

2. RESEARCH RESULTS

2.1 Organometallic Vapor Phase Epitaxy System

During the initial part of the research period the effort has been focused on finishing the installation and testing of the Organometallic Vapor Phase Epitaxy system. The system itself has been purchased from Thomas Swan Ltd. but several critical components had to be either added or retrofitted. These included:

1) Activated charcoal exhaust scrubber has been designed, components have been purchased, assembled, and tested. The exhaust part of the OMVPE system is shown schematically in Fig. 1. The scrubber and all tubing is made of stainless steel and its vacuum integrity is better than 10^{-9} Torr. In order to prolong the life of the charcoal charge and reduce toxic waste, the scrubber has been fitted with oxygen line for controlled oxidation of reaction products.

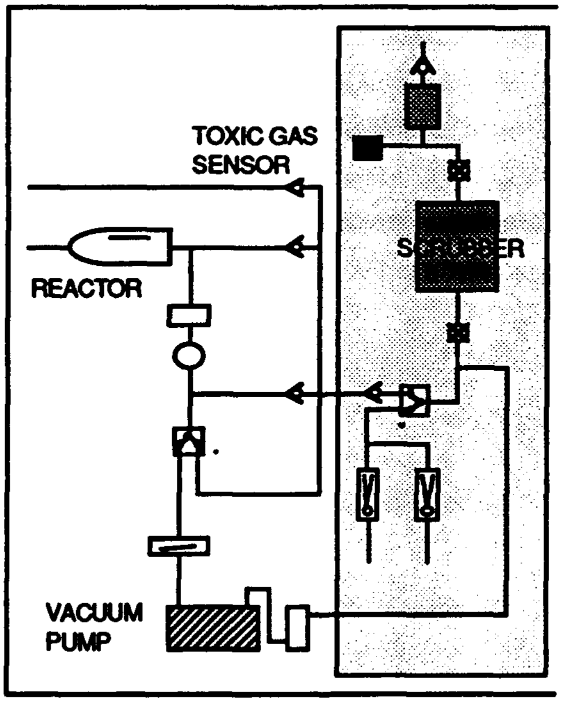

Fig. 1 Exhaust of OMVPE system (dotted area) designed and constructed at MSE.

2) Gas delivery systems for hydrogen and nitrogen process gases have designed, assembled and vacuum leak tested. Both nitrogen and hydrogen lines are equipped with purge panels (donated by Bell Communication Research, Red Bank, NJ) and catalytic pre-purifiers.

3) Toxic gas detection system has been purchased using funds from ONR grant, installed and tested.

4) Metalorganic sources have been purchased from American Cyanamid Co. and Advanced Technology Materials, installed, and tested.

5) Additional double dilution line for n-type dopant (tellurium) has been retrofitted and tested.

2.2 Growth and characterization of undoped and tellurium doped GaAs.

In order to determine the effects of doping, the properties of undoped layers had to be thoroughly characterized. We have investigated GaAs growth in the temperature range of 500 °C to 750 °C. The morphology of resulting layers have been determined by Nomarski contrast optical microscopy and specular surfaces have been obtained in the whole temperature range by adjusting the V/III ratio. The growth rate varied between 0.7 µm/hr to 2.0 µm/hr for optimized growth conditions and was controlled by the flow and decomposition of trimethylgallium. The decrease of growth rate was observed at low growth temperatures. The as-deposited undoped layers have been p-type with carrier concentrations in the 1-10 x 10^{15} cm^{-3} range and hole mobility up to 4,000 cm^2/Vs. This result indicates that layers are of very high quality. The p-type conduction is most likely due to incorporation of residual carbon from trimethylgallium. The near band gap photoluminescence spectra are dominated by excitonic emissions showing well defined free exciton and excitons bound to neutral acceptors (Fig. 2).

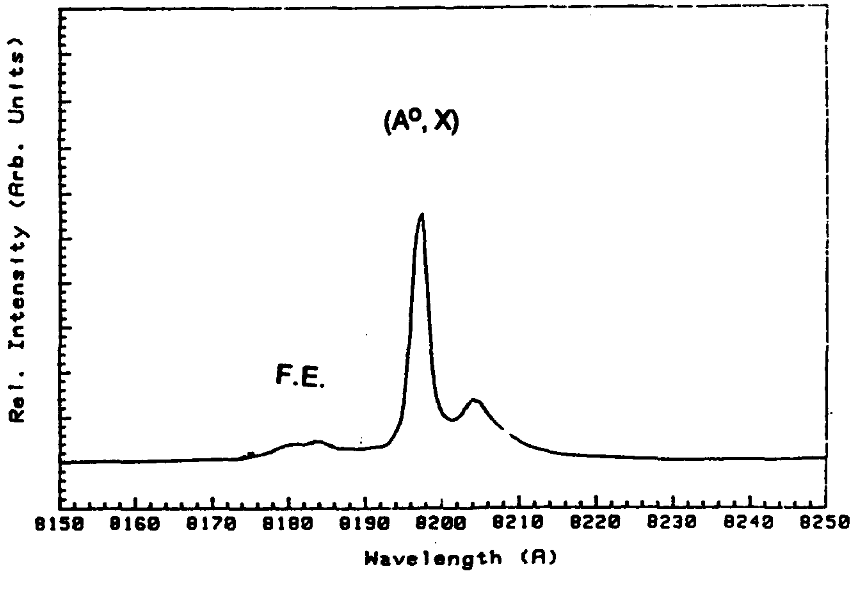

Fig. 2 High resolution photoluminescence spectrum of undoped GaAs epilayer grown at CMU.

Controlled tellurium doping experiments have been performed in the 500 - 700 °C temperature range. We have used liquid dopant source namely diethyl telluride (DETe). Carrier concentrations as high as 5×10^{19} cm^{-3} have been obtained with the lowest controlled electron concentration on the order of 1×10^{16} cm^{-3} (Fig. 3). This doping range covers the concentrations required for low resistivity Ohmic contacts as well as Deep Level Transient Spectroscopy. Tellurium was shown to exhibit slight memory effect probably due to adsorption of DETe on the walls of stainless steel tubing.

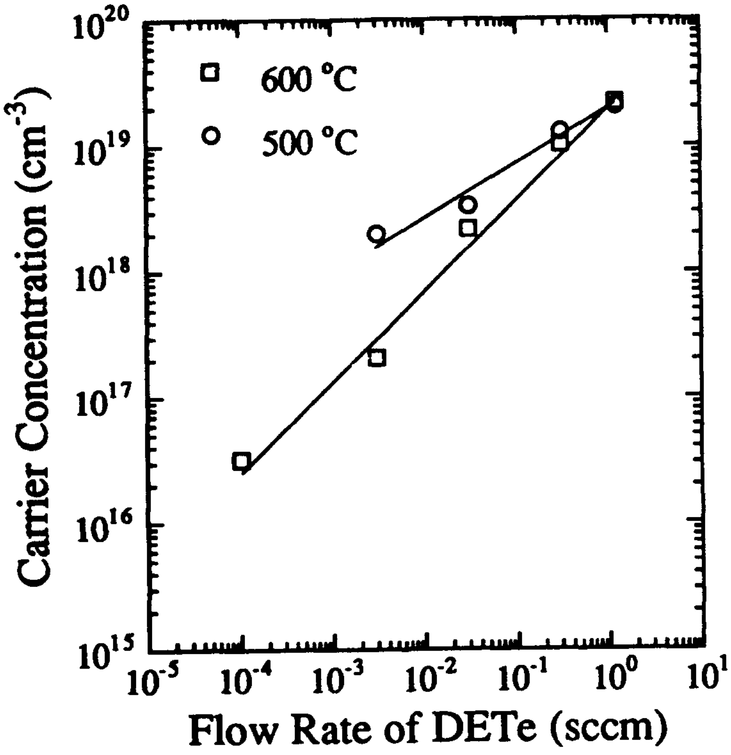

Fig. 3 Carrier concentration versus DETe flow rate and growth temperature.

2.3 Doping with dimethylaluminum methoxide

Doping of GaAs epilayers with dimethylaluminum methoxide was investigated in the 500 °C to 700 °C temperature range and 0.1 sccm up to 10 sccm DMAlMO flow rate. For most of deposition conditions we have been able to obtain specular surface morphology. At the high temperature / high doping level occasionally the surface was covered with small uniformly distributed features resulting in the hazy appearance of the layer. We have not observed any indications of gas phase reactions or change in dopant source over year and a half time period. Dimethylaluminum methoxide appears to be a stable "well behaved" metalorganic compound suitable for use in standard OMVPE growth.

The incorporation efficiency of aluminum and oxygen has been determined by Secondary Ion Mass Spectroscopy measurements performed by Thomas M. Rosseel of Oak Ridge National Laboratory. Several reference samples were also analyzed by Charles Evans and Associates of Redwood City, CA. The highest oxygen concentration achieved to date (with good surface morphology) is 5×10^{19} cm^{-3}. The interfaces are sharp with width smaller than 0.05 µm (this is a resolution limit of SIMS technique). There is no indication of oxygen memory effects in the form of prolonged transients. Also, SIMS results prove that no significant oxygen interdiffusion occurs at growth temperatures up to 700 °C.

The aluminum content in epilayers does not depend on deposition temperature and is proportional to the DMAlMO flow rate. Oxygen incorporation, on the other hand, depends strongly on deposition conditions and decreases rapidly with increasing growth temperature. The results of oxygen incorporation versus growth temperature are shown in Fig. 4.

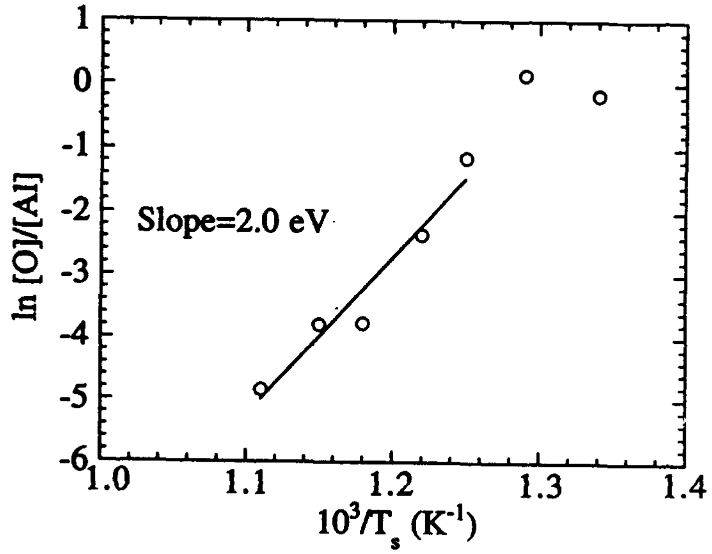

Fig. 4 Oxygen/aluminum ratio as a function of growth temperature.

In addition to growth temperature, we have investigated incorporation of aluminum and oxygen as a function of DMAlMO mole fraction, reactor pressure, V / III ratio, and the growth rate. These measurements allowed to propose a realistic model of DMAlMO decomposition and incorporation into GaAs. The results are described in detail and discussed in paper entitled " Incorporation of oxygen and aluminum in dimethylaluminum methoxide doped GaAs during Organo-Metallic Vapor Phase Epitaxy" accepted for publication in Journal of Crystal Growth. All the accumulated evidence indicates that oxygen is incorporated only if bonded to aluminum, or, in other words, in a form of a pair. The lower oxygen content at high growth temperatures is a direct result of breaking the Al-O bond on the growth surface and oxygen being swept away with the flow of carrier gas. This process is most likely mediated by atomic hydrogen or other reactive species produced during TMG and TBA decomposition. Optical characterization method indicate that Al-O pairs exist not only on the growth surface but in the volume of the layer as well.

2.4 Characterization of doped GaAs:Al-O layers

Several complementary characterization techniques have been used to assess effects of DMAIMO doping on properties of GaAs epilayers.

In photoluminescence experiments two important effects have been observed. In layers doped with DMAIMO the overall intensity of near band gap luminescence decreased by many orders of magnitude (Fig. 5). In particular layers grown at low temperatures (600 °C and below) exhibited no detectable near-band-gap photoluminescence. This effect is apparently caused by deep levels associated with oxygen doping. Since the sensitivity of our system allows for detection of signals four orders of magnitude lower than luminescence from undoped epilayers and the carrier lifetime in good quality GaAs is no more than 10^{-8} seconds we can estimate that the carrier lifetime in our samples is no more than 10^{-12} s. Materials with such an extremely short carrier lifetime can be employed in ultrafast photodetectors.

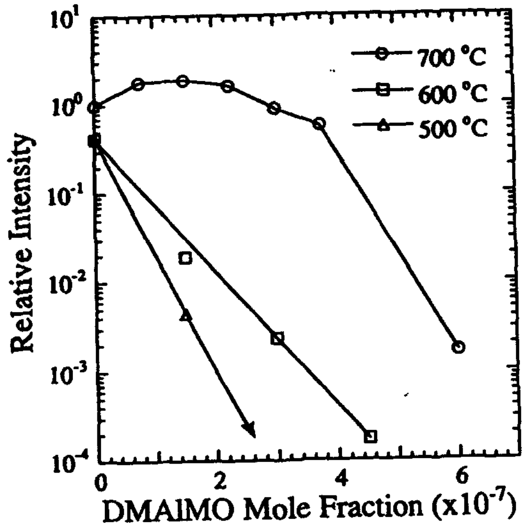

Fig. 5 Near-band-gap photoluminescence intensity versus DMAIMO mole fraction and growth temperature.

In DMAlMO doped epilayers grown at higher temperatures the luminescence intensity is also lower as compared to undoped specimen but the difference is not as pronounced due to lower oxygen content. In these samples new luminescence bands appear in the 840 - 1400 nm range (Fig. 6). Their intensities are correlated with DMAlMO flow rate and position indicates that they are due to deep levels within the band gap. In samples heavily doped with oxygen the dominant PL band is located in the infrared with the maximum at 1.5 μm. The origin of the centers responsible for this deep luminescence band is currently investigated by infrared photoluminescence in cooperation with Dr. Phil Yu of Wright State University.

The effects of doping on electrical properties of GaAs epilayers have been assessed by Hall effect measurements at room and liquid nitrogen temperatures. The layers were intentionally doped with tellurium resulting in electron concentration of $2x10^{18}$ cm^{-3} and then compensated by DMAlMO flow doping (growth temperature 500 °C). The heavily oxygen doped layers were fully depleted which proves the feasibility of depositing semi-insulating layers by OMVPE. We are currently completing a study of compensation mechanism in GaAs doped with DMAlMO by Hall effect and C-V profiling. The results will be presented during Fall MRS meeting in Boston (December 1993).

An important aspect of this research project is investigation of the atomic structure of oxygen-related centers. One of the major goals was to demonstrate the feasibility of controlled introduction of impurity complexes into semiconductor matrices. In order to clear this point we have performed Localized Vibrational Mode spectroscopy measurements in the 200 - 4000 cm^{-1} energy range. No LVM lines were detected in the range characteristic of isolated oxygen vibrations (700 - 900 cm^{-1}) although oxygen content was about an order of magnitude above the detection limit. This experiment conclusively proves that less than 10% of oxygen is present in the form of isolated centers and over 90% has to be present in the form of complexes, presumably with aluminum. The second indication that oxygen is present in the crystal in the form of pairs with aluminum is the observation of aluminum LVM intensity versus growth temperature. As the T_G decreases the oxygen content increases and below 500 °C approaches that of aluminum. At this point, most of aluminum should be present in the form of Al-O complexes and the Localized Vibration Mode absorption line due to isolated aluminum should disappear or at least decrease in intensity. This prediction has been fully verified experimentally by infrared absorption measurements performed in cooperation with Dr. M.O. Manasreh of Wright Patterson Air Force Base (Fig. 6). To our knowledge this is the first evidence of successful "molecular doping" - controlled introduction of impurity pairs into semiconductors. The value of this discovery goes beyond this particular material system (i.e. gallium arsenide doped with aluminum-oxygen complexes). Molecular doping concept is a generic doping scheme which could be applied to many other material problems and could allow the formation of "tailor" made defect centers.

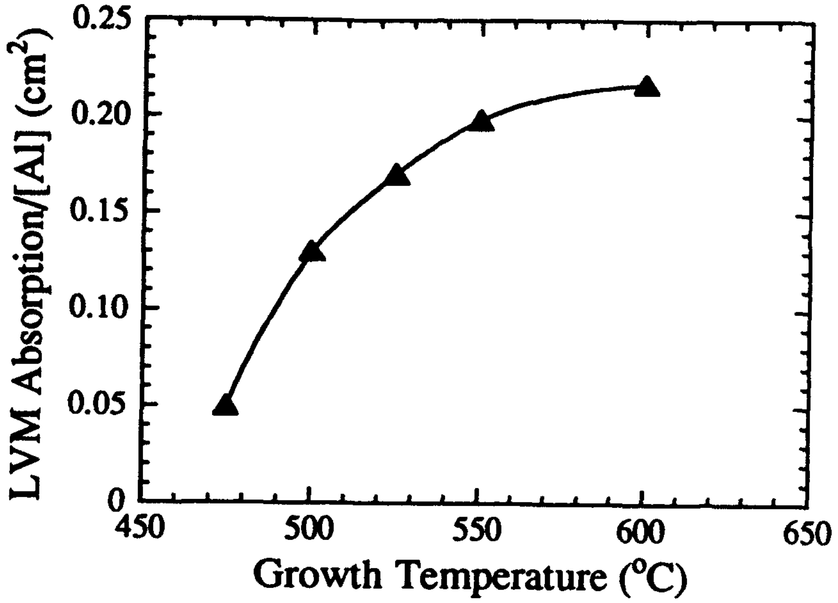

Fig. 6 Ratio of the isolated Al_{Ga} Localized Vibrational Mode absorption line intensity to aluminum concentration measured by SIMS versus growth temperature.

PUBLICATIONS AND CONFERENCES

Peer Reviewed Papers:

1. "Complexes of oxygen and native defects in GaAs", M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, Phys. Rev. B46, 9476 (1992).

2. "Oxygen and aluminum incorporation into GaAs epilayer by dimethylaluminum methoxide doping during metalorganic chemical vapor deposition" Y. Park and M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, and T. Rosseel, Oak Ridge National Laboratory, accepted for publication in Journal of Crystal Growth.

3. "Photoluminescence of GaAs doped with dimethylaluminum methoxide during Organo-Metallic Vapor Phase Epitaxy", Y. Park and M. Skowronski, Department of Materials Science and Engineering,

Carnegie Mellon University, Pittsburgh PA 15213, accepted for publication in Journal of Applied Physics.

4. " Compensation of shallow donors in GaAs doped with dimethylaluminum methoxide during Organo-Metallic Vapor Phase Epitaxy", Y. Park, M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh PA 15213, and R. Messham, Westinghouse Science and Technology Center, Pittsburgh, PA 15235, to be submitted in Journal of Applied Physics.

Conference and Presentations:

1. "Alkoxide doping of GaAs during Organo-Metallic Vapor Phase Epitaxy", Y. Park, M. Skowronski, and T.M. Rosseel, Department of Materials Science and Engineering, Carnegie Mellon University, Proc. Mat. Res. Soc. Symp. vol. 282, 75 (1993).

2. "Alkoxide doping of GaAs during MOCVD" M. Skowronski, seminar presented at Wright-Patterson Air Force Base, March 1993.

3. "Incorporation of oxygen and aluminum in dimethylaluminum methoxide doped GaAs", Y. Park, M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, and T.M. Rosseel, Oak Ridge National Laboratory, American Association of Crystal Growth Conference, Baltimore, August 1993.

4. "Effects of oxygen doping of GaAs epilayers grown by OMVPE" Y. Park, M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, and M.O. Manasreh, WL/ELRA, Wright-Patterson Air Force Base, accepted for presentation as an invited paper during Fall MRS Meeting in Boston (December 1993).

5. "Growth of high resistivity GaAs buffer layers by controlled oxygen doping" Y. Park and M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, to be submitted to Semi-Insulating III-V Materials Conference, Warsaw, June 1994.

PATENTS AND INVENTIONS

The goal of this project was to prove that controlled doping of GaAs with Al-O pairs will result in material suitable for applications in electronic devices. The low level of funding and limited time of the project ($34,000 over two years) did not allow us to deposit and test device structures. However, the results obtained so far are a clear in evidence that doping with DMAlMO is a viable way of producing high-resistivity buffer layers for device isolation and short lifetime material suitable for ultrafast photo switches. With the help of funding provided by National Science Foundation we intend continue this project with the special emphasis on device processing and testing. We also plan to cooperate with Westinghouse Science and Technology Center on using DMAlMO doping in deposition of GaAs on silicon.

ACCEPTED TO JOURNAL OF APPLIED PHYSICS

PHOTOLUMINESCENCE OF GaAs DOPED WITH DIMETHYLALUMINUM METHOXIDE DURING ORGANOMETALLIC VAPOR PHASE EPITAXY

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Photoluminescence (PL) measurements of GaAs doped with dimethylaluminum methoxide during Organometallic Vapor Phase Epitaxy are reported. Near band edge luminescence intensity decreases by at least a factor of 10^4 at low growth temperatures, which correlates well with incorporation of oxygen. Concomitantly, several new PL peaks appeared at 72 meV, 97 meV, 150 meV, 410 meV, and 510 meV below the band edge. Based on the dependence of PL peak position on excitation power density, these bands have been interpreted as due to donor-acceptor type transitions involving deep oxygen-related levels. Intensity of near band edge emission was not affected by annealing of doped layers at 800 °C in arsenic overpressure indicating that doping-induced deep centers are thermally stable.

1. Introduction

Oxygen impurity is known to form deep level traps in most semiconductors including GaAs[1,2] and $Al_xGa_{1-x}As$.[3] Its incorporation in both materials results in compensation of shallow donors[4-6] and decrease of carrier lifetime or luminescence efficiency.[7-9] $Al_xGa_{1-x}As$ epilayers heavily contaminated with oxygen are frequently semi-insulating[5] and sometimes do not exhibit any near band edge luminescence.[10] Because of these properties oxygen could be used as an intentional dopant producing highly compensated buffer layers for reduction of side- and back-gating in VLSI Integrated Circuits[11,12] or material with very low carrier lifetime suitable for ultrafast photoconductive switches.[13] However, intentional oxygen doping of GaAs during growth proved to be difficult. The typical oxygen content in melt grown crystals appears to be in the 10^{15} cm^{-3} range[14] and in intentionally doped epilayers it is below detection limit of all characterization methods.[15,16] For either of the two above applications the desired deep level concentration is between 10^{18} cm^{-3} (buffers) and 10^{20} cm^{-3} (photoconductors). Recently, it has been shown that high oxygen doping levels could be attained during Organometallic Vapor Phase Epitaxy (OMVPE) by using dimethylaluminum methoxide (DMAlMO).[17,18] Oxygen was observed to incorporate into the GaAs layer in concentrations up to 10^{20} cm^{-3} without degradation of surface morphology and to compensate up to 10^{18} cm^{-3} of shallow silicon donors. At this point, however, little is known about atomic structure of oxygen-induced centers in GaAs:DMAlMO and their properties such as ionization energies, capture cross sections, and thermal stability. In this paper we will discuss the effects of DMAlMO doping on photoluminescence (PL) spectra of GaAs.

2. Experimental procedures

All epilayers were grown by atmospheric pressure OMVPE in a horizontal reactor heated by infrared radiation. Substrates were Cr-doped semi-insulating GaAs wafers either exactly (001) or misoriented 2°

toward [110]. Wafers were used as received without cleaning or etching except for the 10 minute annealing at 750 °C in arsenic overpressure prior to growth. As starting compounds we have used trimethylgallium (TMG) maintained at -15 °C and tertiarybutylarsine (TBA, at temperature 2 °C) with palladium-purified H_2 as a carrier gas. The hydrogen flow was set at 4000 sccm and TMG and TBA mole fraction were 5×10^{-5} and 5.6×10^{-4}, respectively. These growth conditions correspond to approximately 1.5 µm/hr growth rate at 600 °C and 700 °C and 0.9 µm/hr at 500 °C. Samples were doped with DMAlMO maintained at 38 °C. All lines were heated to prevent DMAlMO condensation. Epilayers exhibited specular surface morphology with the exception of samples grown at 700 °C and high DMAlMO flow rates (mole fraction > 4.5×10^{-7}) which were uniformly hazy. Both doped and undoped layers grown at 500 °C had occasional hillocks which were most likely due to surface preparation. Since apparently they were not related to DMAlMO doping and their density was low (it could not affect measurement results) we have not attempted to optimize wafer cleaning. Photoluminescence measurements were performed with samples immersed in liquid helium (4.2 K). Excitation was provided by the 488 nm line of an Ar^+ laser and photoluminescence was analyzed by SPEX 1404 0.85 m double spectrometer and detected by either S20 photomultiplier (PMT) or North Coast liquid N_2-cooled Ge. The spectra have not been calibrated for spectral response of the system. For near band edge emission the changes are minimal but for the wavelengths longer than 870 nm for PMT and 1300 nm for Ge-detector sensitivity rapidly decreases and spectra could be significantly affected.

3. Results and discussion

The effects of DMAlMO doping on near band edge photoluminescence are shown in Fig. 1. All three layers were grown at 700 °C with DMAlMO mole fraction (a) X(DMAlMO) = 0, (b) X(DMAlMO) = 2.25×10^{-7}, and (c) X(DMAlMO) = 3.75×10^{-7}. The spectrum of undoped layer (a) exhibits an exciton peak at high energies (dominated by exciton bound to neutral acceptors) , free to acceptor transition at 1.494 eV, and donor to acceptor transition at 1.490 eV. The line position indicates that main acceptor is carbon most likely originating from methyl radicals produced during TMG decomposition. With increasing DMAlMO flow rate all PL peaks broaden (because of alloy broadening) and shift to higher energies while their integrated intensity is not affected significantly. Exciton peak shifts by as much as 8 meV for DMAlMO mole fraction of 3.75 x 10^{-7}. This is in agreement with Secondary Ion Mass Spectroscopy (SIMS) studies of DMAlMO doped GaAs.[19] At high temperatures oxygen concentration exhibits exponential decrease with growth temperature. At 700 °C the oxygen content is well below SIMS detection limit and could be expected not to affect the luminescence intensity. Aluminum concentration is proportional to DMAlMO flow rate and its incorporation results in the increase of the band gap and shift of the PL peaks. Distance between exciton and free to acceptor peaks does not change appreciably indicating that carbon most likely remains as the predominant impurity. However, peak at 1.492 eV shown in Fig. 1 (c) is an indication that there is an additional shallow acceptor present in doped layers.

More pronounced effects of oxygen doping on PL spectra were observed in epilayer deposited at lower growth temperature and higher DMAlMO flow rates. The change in integrated near band edge luminescence intensity (exciton and acceptor peaks) is shown in Fig. 2 as a function of DMAlMO mole fraction and growth temperature. All data points were normalized to the intensity of undoped sample grown at 700 °C. The near band edge luminescence intensity of layers grown at 700 °C does not change significantly with DMAlMO doping up to mole fraction of 3.75 x 10^{-7}, which is in agreement with discussion of Fig. 1. For higher flow rates, however, it decreases abruptly. This behavior correlates well with oxygen incorporation. It has been shown by SIMS that oxygen concentration increases super-linearly with DMAlMO mole fraction.[19] However, it should be noted that the surface morphology of samples grown at 700 °C and high DMAlMO flow rates degrades rapidly, which could lead to different incorporation mechanism of defects and/or oxygen. Layers grown at 500 °C and 600 °C show rapid decrease of intensity with increased doping, decrease being faster in layers grown at 500 °C. In fact, we were not able to detect luminescence from layers grown at 500 °C and mole fraction of 3×10^{-7} or above. Our best estimate is that the relative intensity from this layer in respect to undoped sample is below 10^{-4} which is visualized by the arrow in Fig. 2. A similar effect has been observed in $Al_xGa_{1-x}As$ epilayers grown by Metal-organic Molecular-Beam Epitaxy and heavily contaminated with oxygen. These layers were described as "optically dead".[10] Dramatic decrease of luminescence intensity is a direct indication that oxygen-related centers behave as deep level traps and serve as efficient nonradiative recombination centers. This result, together with very high achievable doping concentrations, suggests that doping with alkoxides can produce material with optimized $(\text{carrier lifetime})^{-1} \times (\text{carrier mobility})$ product which is required for ultrafast photoconductive switches. [20]

Besides decrease of near band edge luminescence intensity, doping of GaAs with DMAIMO results in appearance of several new luminescence peaks due to deep centers. Fig. 3 shows near infrared spectra of three layers grown at 700 °C with increasing DMAIMO mole fraction. The spectrum (a) ($X(\text{DMAIMO}) = 3.75 \times 10^{-7}$) was obtained on the same sample as presented in Fig. 1(c). In addition to exciton and (e, C^{o}_{As}) peaks discussed before there are four more peaks located at 1.470 eV, 1.450 eV, 1.425 eV, and 1.363 eV. In spectrum (b) corresponding to higher DMAIMO flow rate ($X(\text{DMAIMO}) = 4.5 \times 10^{-7}$) the three deep peaks are dominant and a new even deeper PL band appeared at 1.12 eV. Layer grown with DMAIMO mole fraction of 6.0×10^{-7} (Fig. 3 (c)) shows only very weak line close to the band gap and wide featureless PL band centered at 1.02 eV. All of the above bands most likely involve transitions between relatively deep levels and either band states or other impurities (i.e. donor - acceptor transitions). If this is the case, the distances between band edge and peak position should correspond to deep level ionization energy. These energies are 72 meV, 97 meV, 150 meV, 410 meV, 510 meV in order of increasing depth of a level and agree very well with values found by Bhatttacharya *et al.*[21] in $Al_xGa_{1-x}As$ epilayers grown by OMVPE and intentionally contaminated with oxygen. They reported observation of deep level PL peaks shifted by 78 meV, 100 meV, 160 meV, and 400 meV from the band edge. The shape of our spectra is very similar to ones reported by Goorsky *et al.*.[22] The number of observed PL bands indicates that doping with DMAIMO induces several different deep centers of, as of yet, unknown nature. Such behavior is to be expected since oxygen is known to easily form complexes with impurities and native defects in GaAs. It is also worth noting that one of well known oxygen-related defects in GaAs, the off-site substitutional oxygen on arsenic site, has a level 150 meV below conduction band[23,24] and could be responsible for one of the above PL bands.

Fig. 4 shows near infrared spectra of layers grown at lower temperatures. Samples (a), (b), and (d) were grown at 600 °C and DMAlMO mole fraction of 3.0×10^{-7}, 4.5×10^{-7}, 6.0×10^{-7}, respectively. As stated above, at constant DMAlMO flow rate oxygen is incorporated in much higher concentrations at 600 °C than at 700 °C. As a result, the spectra resemble the one obtained at 700 °C and high DMAlMO flow rates. There is only weak line close to the band gap and wide deep PL band centered at 1.02 eV. Similarly affected is the spectrum (e) obtained on layer grown at 500 °C and DMAlMO mole fraction of 1.5×10^{-7}. A separate question is the thermal stability of doping-induced centers. If this doping scheme is to be used for production of electronic devices the material should withstand typical processing temperatures without changing properties. In order to test thermal stability of oxygen-related centers we have annealed part of the epilayer used to obtain spectrum Fig. 4 (b) at 800 °C for 30 minutes in arsenic overpressure. Resulting spectrum is shown in Fig. 4 (c). There is virtually no change of PL intensity and the only effect observed was a slight shift of the deep PL band toward higher energies. This experiment asserts that deep non-radiative recombination centers can survive a thermal treatment above and the carrier lifetime remains extremely short.

Some insight into the nature of transitions observed in doped samples can be obtained from results presented in Fig. 5. All three spectra have been measured with changing excitation density on sample grown at 700 °C and X(DMAlMO) = 4.5×10^{-7}. Since the spectra were measured using photomultiplier in order to get wider range of excitation densities, the intensity decreases at long wavelengths. The most interesting feature of above spectra is the shift of two main peaks toward higher energies. This type of behavior is characteristic of donor-acceptor type transitions.

4. Summary

In conclusion, we have studied the effects of dimethylaluminum methoxide doping on photoluminescence of GaAs epilayers grown by OMVPE. The near band edge luminescence intensity decreases by many orders of magnitude upon doping, which correlates well with the incorporation of oxygen as determined by SIMS. The quenching of near band edge PL is believed to be caused by deep non-radiative recombination centers related to oxygen. Appearance of several deep PL peaks indicative of many different defects being formed. The preliminary annealing experiment proved that doping-induced centers are thermally stable at least up to 800 °C. All experiments suggest that DMAlMO doping could be an effective way to produce material suitable for ultrafast photoconductive switches based on GaAs.

Acknowledgements: This work was supported by NSF Grant No. DMR-9202683 and AFOSR Grant No. AFOSR-91-0373.

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Figure Captions

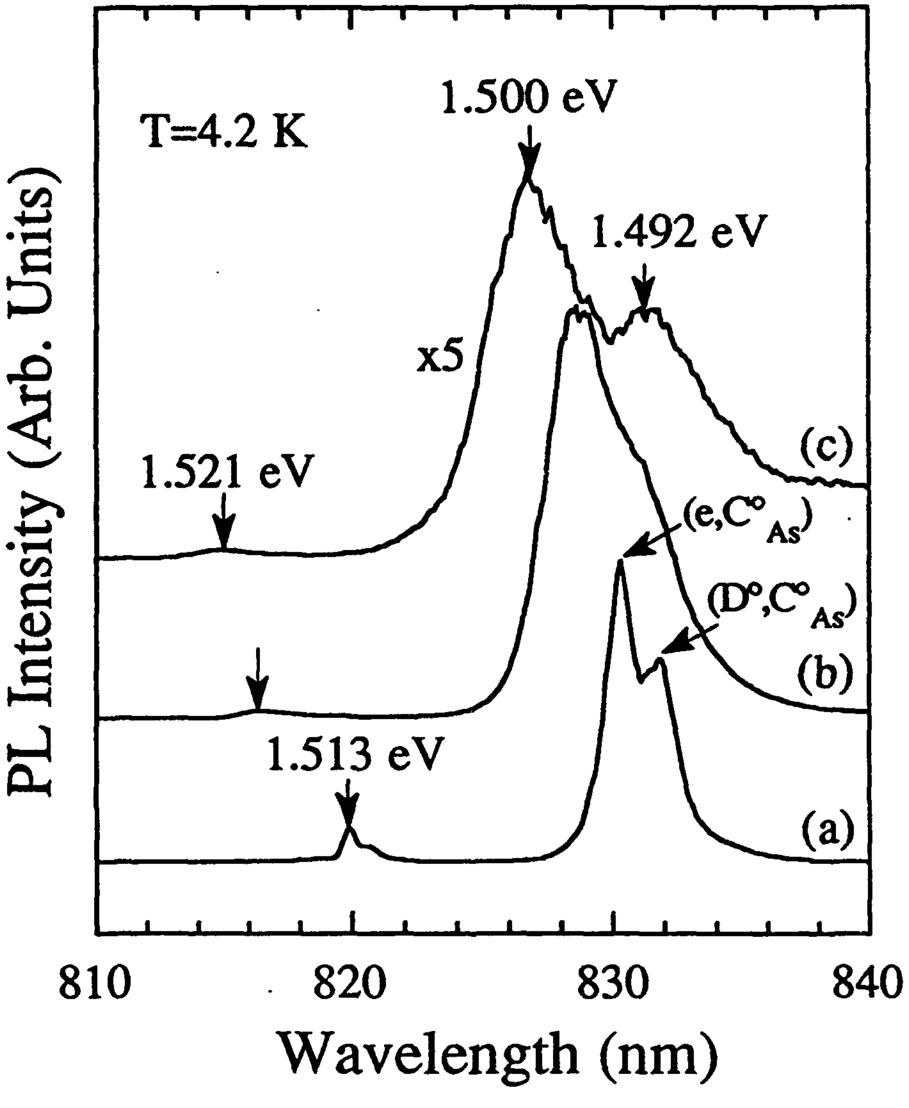
Fig. 1 Near band-edge photoluminescence spectra of GaAs doped with dimethylaluminum methoxide. Layers were grown at 700 °C and DMAlMO mole fraction of (a) X(DMAlMO) = 0, (b) X(DMAlMO) = 2.25×10^{-7}, and (c) X(DMAlMO) = 3.75×10^{-7}.

Fig. 2 Integrated intensity of near band edge emission (exciton and band to acceptor transitions) as a function of DMAlMO mole fraction and growth temperature.

Fig. 3 Deep level luminescence bands in GaAs induced by DMAlMO doping. Growth temperature T_G = 700 °C and DMAlMO mole fraction of (a) X(DMAlMO) = 3.75×10^{-7}, (b) X(DMAlMO) = 4.5×10^{-7} and (c) X(DMAlMO) = 6.0×10^{-7}.

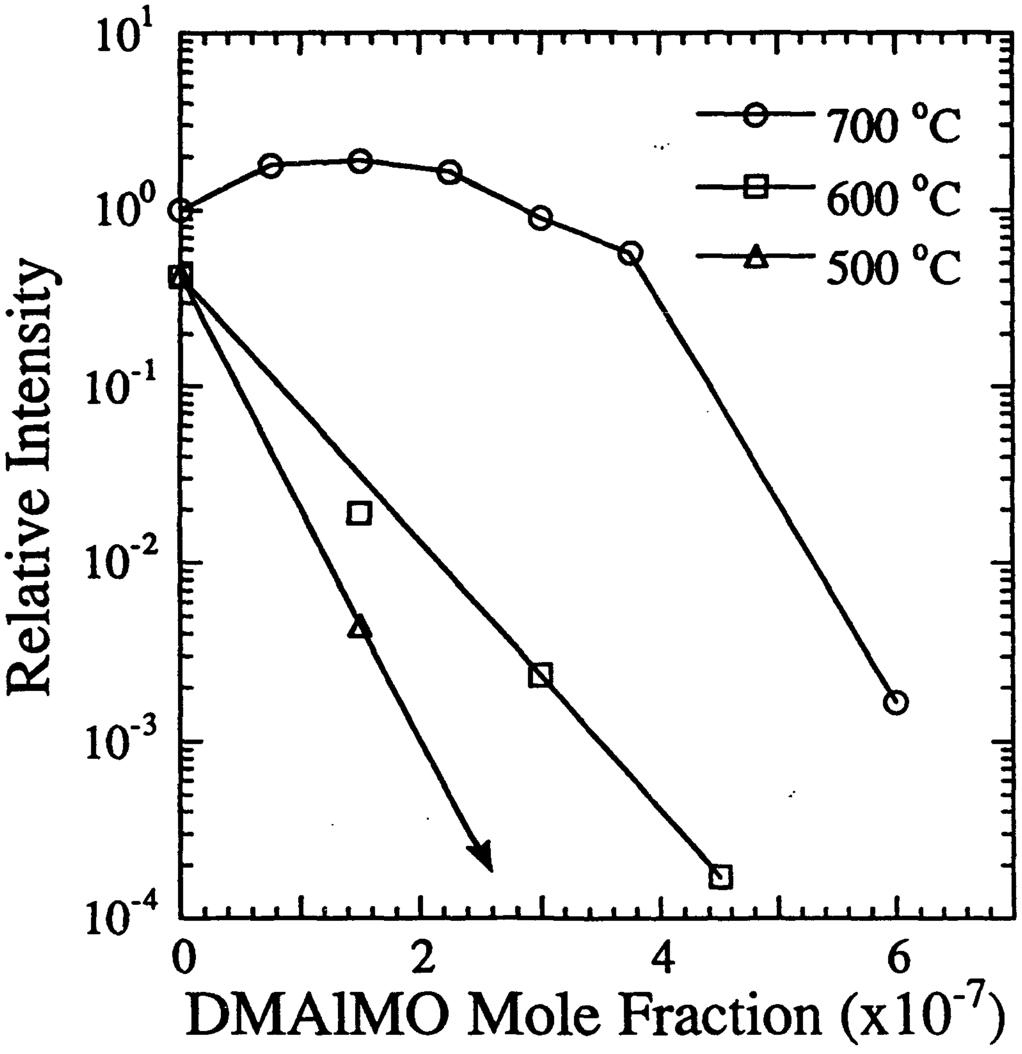
Fig. 4 Deep level luminescence bands in layers grown at (a) T_G=600 °C and X(DMAlMO) = 3.0×10^{-7}, (b) T_G=600 °C and X(DMAlMO) = 4.5×10^{-7}, (c) same as (b) but annealed at T_A = 800 °C for 30 minutes in arsenic overpressure (d) T_G=600 °C and X(DMAlMO) = 6.0×10^{-7} (e) T_G=500 °C and X(DMAlMO) = 1.5×10^{-7}.

Fig. 5 Spectra of layer grown at T_G = 700 °C and X(DMAlMO) = 4.5×10^{-7} obtained with laser power (a) 20 mW, (b) 100 mW, (c) 300 mW.



T=4.2 K
1.500 eV
1.492 eV
x5
1.521 eV
(c)
(e,C°$_{As}$)
(D°,C°$_{As}$)
(b)
1.513 eV
(a)
PL Intensity (Arb. Units)
810
820
830
840
Wavelength (nm)

Fig. 1



10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
Relative Intensity
0
2
4
6
DMAlMO Mole Fraction ($\times 10^{-7}$)
700 °C
600 °C
500 °C

Fig. 2

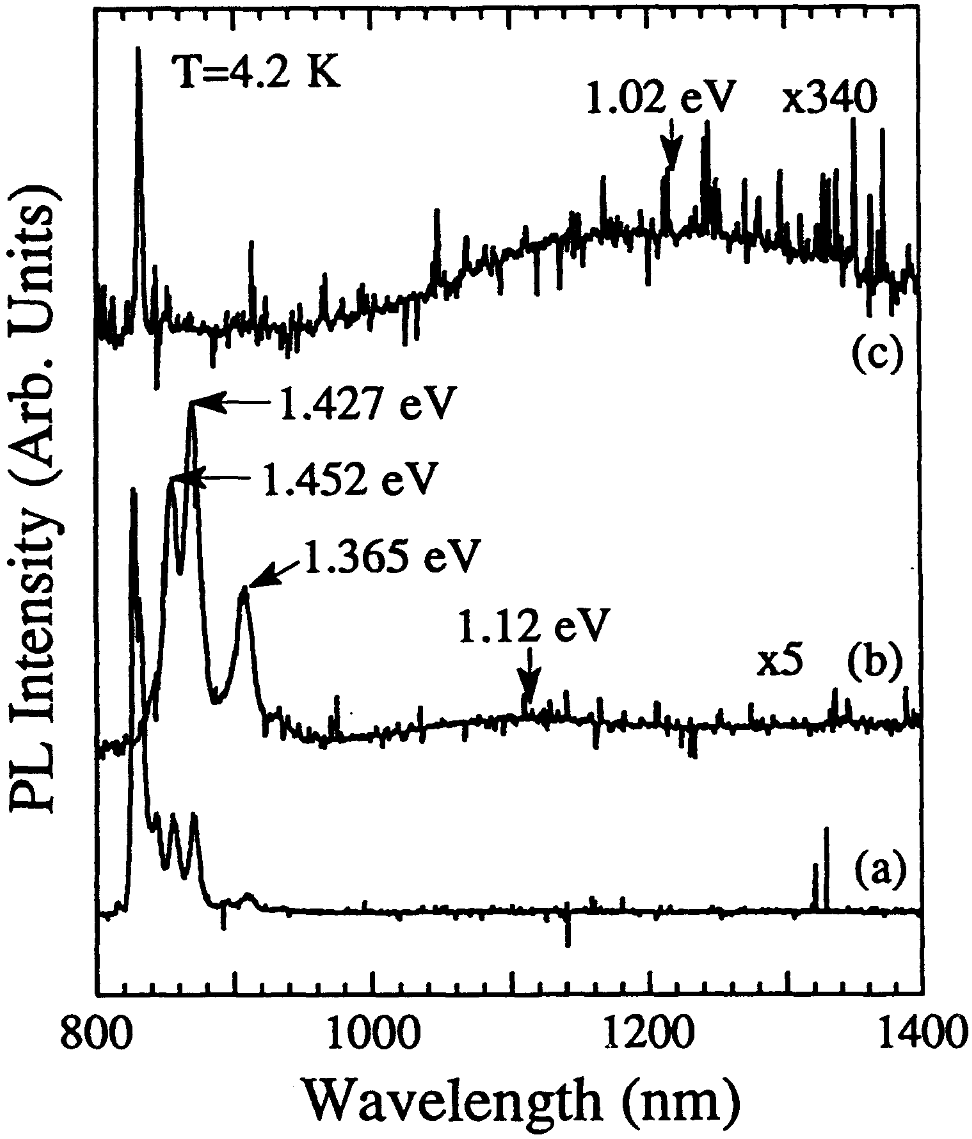

T=4.2 K
1.02 eV
x340
(c)
1.427 eV
1.452 eV
1.365 eV
1.12 eV
x5
(b)
(a)
PL Intensity (Arb. Units)
800
1000
1200
1400
Wavelength (nm)

Fig. 3

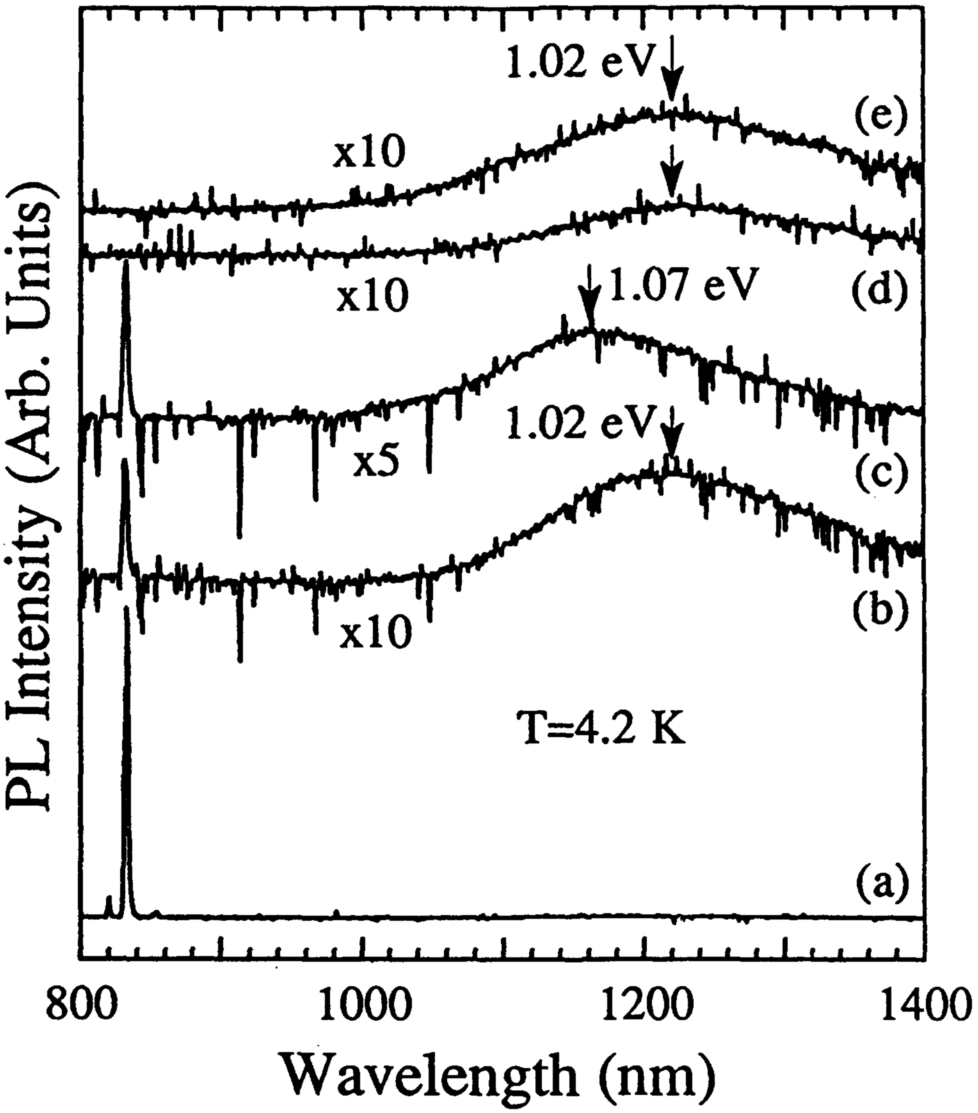

1.02 eV
(e)
x10
(d)
x10
1.07 eV
x5
(c)
1.02 eV
(b)
x10
T=4.2 K
(a)
PL Intensity (Arb. Units)
800
1000
1200
1400
Wavelength (nm)

Fig. 4

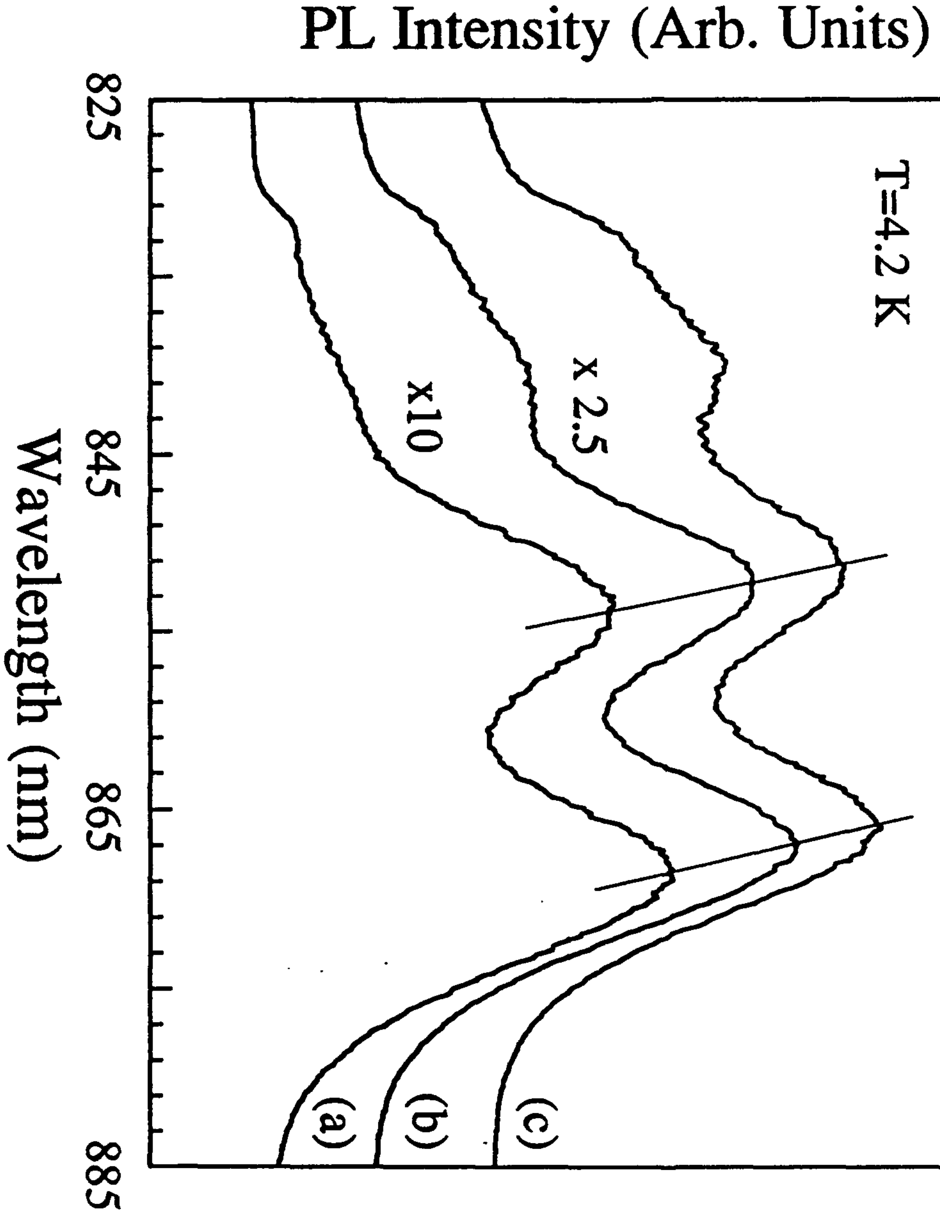

PL Intensity (Arb. Units)
T=4.2 K
x 2.5
x10
(a)
(b)
(c)
825
845
865
885
Wavelength (nm)

Fig. 5

ACCEPTED TO JOURNAL OF CRYSTAL GROWTH

INCORPORATION OF ALUMINUM AND OXYGEN IN DIMETHYLALUMINUM METHOXIDE DOPED GaAs DURING ORGANOMETALLIC VAPOR PHASE EPITAXY

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ABSTRACT

Dimethylaluminum methoxide (DMAlMO) was used as a deep level dopant source in GaAs epilayers grown by Organometallic Vapor Phase Epitaxy (OMVPE). The compound is stable, does not exhibit gas phase reactions in all investigated deposition conditions, and does not degrade surface morphology even at doping levels in excess of 10^{19} cm^{-3}. Incorporation of aluminum and oxygen into the epilayer was studied by Secondary Ion Mass Spectroscopy (SIMS) on multi-layered samples as a function of growth conditions: growth temperature, reactor pressure, dopant mole fraction in the gas phase, and growth rate. Both oxygen and aluminum are incorporated during deposition with oxygen concentration always lower but approaching that of aluminum at temperatures below 500 ^{o}C. At higher growth temperatures [O] / [Al] ratio decreases exponentially with activation energy of 2.0 eV. Incorporation of oxygen exhibits super-linear behavior at higher DMAlMO mole fractions.

1. INTRODUCTION

The isolation of GaAs electronic devices in integrated circuits is frequently accomplished by virtue of a high resistivity substrate and/or high resistivity buffer layer. However, the relatively low density of main deep compensating centers in semi-insulating undoped GaAs (EL2 concentration is usually in the 5×10^{15} - 2×10^{16} cm^{-3} range) results in low trap-filled-limit voltage and considerable side-gating in VLSI circuits [1]. It would be advantageous for GaAs technology to develop highly-compensated, high resistivity, epitaxial buffer layers. Several possible methods for deposition of buffer layers have been suggested, including undoped AlGaAs [2,3], chromium doped GaAs [4], and more recently, Low Temperature GaAs grown by Molecular Beam Epitaxy (MBE) [5,6]. However, such buffers have had limited success because of the lack of control over residual deep centers (undoped AlGaAs), the low solubility of transition metals in GaAs at typical epitaxial growth temperatures and the inability to grow LT GaAs by any other deposition technique except MBE.

In order to obtain high resistivity epitaxial GaAs suitable for buffer layers it is essential to controllably introduce a high concentration (5×10^{17} - 5×10^{18} cm^{-3}) of deep acceptors during deposition [1]. One of the candidates for this task is oxygen, which is known to form deep level centers in most semiconductors [7]. However, the highest reported oxygen concentration in intentionally doped GaAs is relatively low - it does not exceed 10^{16} cm^{-3} in crystals grown from the melt [8] and is below detection limits of all characterization techniques in epitaxial layers [9,10]. The concentration limit appears to be a consequence of the relatively weak bond formed between oxygen and the GaAs surface. At typical growth temperatures, such a bond is unstable and oxygen is swept away with the flow of a carrier gas. This situation changes dramatically for $Al_xGa_{1-x}As$ growth because of the high affinity of aluminum for oxygen [11,12]. The typical oxygen concentration in $Al_{0.3}Ga_{0.7}As$ is in the 10^{17} cm^{-3} range and can be as high as 10^{20} cm^{-3} at low growth temperatures [13-15]. It has been observed that oxygen in $Al_xGa_{1-x}As$ is electrically active and forms deep acceptors leading to the compensation of shallow donors

[2,12,16,17] and decreasing electron mobility [18]. The estimated ionization energy of the oxygen-related center in $Al_{0.3}Ga_{0.7}As$ is 0.6 eV and this center has been successfully used for growing semi-insulating epilayers [2].

Taking into account the fact that oxygen forms a deep-level center in the GaAs band gap [19,20], controlled oxygen doping may have applications in the growth of high resistivity GaAs buffer layers for reduction of side-gating or back-gating effects in GaAs IC technology. A number of attempts have been made at simulating oxygen contamination by controlled leaks of oxygen [2,16,21] and recently by intentional doping with dimethylaluminum methoxide (DMAlMO) [22,23], partially oxidized trimethylaluminum [24], or diethylaluminum ethoxide [25]. Specifically, the presence of the Al-O bond in DMAlMO suggests that the oxygen may be efficiently incorporated into GaAs along with a low level of aluminum. In DMAlMO-doped GaAs [22], oxygen was observed to incorporate into the layer in concentrations up to 10^{18} cm^{-3} without degradation of surface morphology. It resulted in compensation of the equivalent concentration of shallow silicon donors in GaAs, thereby depleting a co-doped layer.

Despite the potential advantages of DMAlMO doping, little has been published about such issues as the decomposition of DMAlMO, incorporation of oxygen and aluminum into GaAs, and the atomic structure and properties of doping-induced defects. In this paper we present a detailed study of the dependence of aluminum and oxygen concentration on the growth parameters such as growth temperature, DMAlMO mole fraction, growth rate and reactor pressure.

2. EXPERIMENTAL PROCEDURE

The layers were grown by Organometallic Vapor Phase Epitaxy (OMVPE) method in a horizontal reactor heated by infrared radiation. Substrates were (100) Cr-doped semi-insulating GaAs wafers misoriented 2° toward [110]. Substrates were used as-received without cleaning or etching prior to growth. The oxide layer was removed by thermal desorption at 750 °C for 10 minutes in the arsenic overpressure.

Trimethylgallium (TMG) and tertiarybutylarsine (TBA) were employed as starting compounds in the flow of palladium-purified H_2 carrier gas. The carrier gas flow was set at 4000 sccm and the TBA and TMG mole fractions were 5.6×10^{-4} and 5×10^{-5}, respectively, unless stated otherwise. Oxygen and aluminum were introduced in a form of dimethylaluminum methoxide ($(CH_3)_2AlOCH_3$) purchased from Advanced Technology Materials Inc (Danbury, CT). In both liquid and gas phase (at low temperatures) DMAlMO forms a trimer with the ring structure [26,27] and has a melting temperature of 36 °C. DMAlMO reacts with water and air in much the same way as trimethylaluminum (TMA) but otherwise is stable, i.e. it does not decompose at room temperature, polymerize, or disproportionate into alkoxides and TMA. We have used DMAlMO dopant for over a year and have not observed any changes in the vapor pressure which would be indicative of any instability. TMG, TBA, and DMAlMO bubblers were maintained at -15 °C, 2 °C and 38 °, respectively.

The oxygen and aluminum concentrations have been measured by Secondary Ion Mass Spectroscopy (SIMS) with the ORNL Cameca (Stamford, CT) ims 4f microprobe using Charles Evans and Associates (Redwood City, CA) ims xf control software, version 3.1. Because the samples charged to varying degrees depending upon concentration of dopants, data were collected using the auto-voltage mode. Offset voltages exhibited variations between epilayers and among different samples and ranged from 5 to 35 volts. For all measurements, the primary ion beam was rastered over a 200x200 micron area and pressure in the sample analysis chamber was less than 3×10^{-8} Torr. The mass resolution was approximately 600 and the energy slit was typically set to 50 volts. Depth profiles of aluminum were collected using an 8 keV O_2^+ primary ion beam and a current ranging from 80 to 120 nA. This corresponds to a sputter rate of approximately 0.3 to 0.5 nm/s. Oxygen depth profiles were collected using a 14.5 keV Cs^+ primary ion beam and currents ranging from 30 to 50 nA. This corresponds to sputter rates of 0.5 to 1 nm/s. Samples were heated in the evacuated (5×10^{-7} Torr) dual-sample inlet system for approximately one hour prior to oxygen analysis to reduce surface moisture. The depth profiles were converted to concentration using tabulated sensitivity factors (RFS), referenced to either As or Ga. Accuracy is estimated to within a factor of two. The crater depths were measured with a Tencor

Instruments (Mountain View, CA) alpha step, stylus profilometer. The layers closest to the substrate exhibited evidence of ion-beam induced roughness which was confirmed by optical microscopy.

The typical layer structure for SIMS measurements consisted of six layers each approximately 0.25 μm thick. The top and bottom layers (the last and first to be deposited, respectively) were undoped and the four intermediate layers were intentionally doped with DMAlMO. Since the oxygen and aluminum content in undoped epilayers and bulk GaAs wafers are below SIMS detection limits, the concentration of oxygen in undoped layers was assumed to be due to the instrumental oxygen background. All results quoted below have been corrected for this effect. In addition, the multilayer structure reduced the effects of surface/interface contamination and provided independent information on growth rate and interface sharpness. At the substrate temperature of 600 ^{o}C with typical mole fractions of TMG, TBA and DMAlMO at 5×10^{-5}, 5.6×10^{-4} and 3×10^{-7} respectively, the growth rate was 1.65 μm per hour.

3. RESULTS

The effects of DMAlMO doping on surface morphology was investigated in the temperature range of 500 - 700 ^{o}C and dopant mole fraction of 0 - 15×10^{-7}. The thickness of all layers deposited for morphology studies was approximately 1μm with the differences in the growth rate compensated by change in the deposition time. Surface morphologies were inspected using Nomarski interference contrast optical microscopy and the representative microphotographs are shown in Fig.1. Mirror-smooth surfaces were obtained on the undoped layers grown at 600 ^{o}C and 700 ^{o}C, while a few oval features were observed on the layer grown at 500 ^{o}C (Fig.1(a)). At this time no special attempt was made to eliminate these features (in terms of surface cleaning and optimization of deposition conditions) as their density was low and they did not interfere with the investigation of the effects of doping. Specular morphologies were also obtained for doped material grown at all three temperatures although the maximum DMAlMO mole fraction resulting in mirror surfaces decreases at higher growth temperatures (Fig. 2). Mirror-smooth surfaces indicate that there are no gas phase reactions between DMAlMO and TBA as these usually lead to the formation of particulates upstream from the susceptor and poor layer morphologies. Also none of the other experiments reported below indicate existence of such reactions. It is, however, possible that at high growth temperatures and high DMAlMO flow rates formation of the second phase (presumably aluminum oxide) occurs on the growth surface.

As expected, doping with DMAlMO allows for incorporation of both aluminum and oxygen into the layer. However, the concentrations of aluminum and oxygen in GaAs are markedly different which implies that different incorporation mechanisms are active. Fig. 3 shows the dependence of the growth rate and the aluminum and oxygen concentrations on the growth temperature. These layers have been grown at atmospheric pressure with constant DMAlMO mole fraction of 3×10^{-7} in the gas phase, and at temperatures between 475 °C and 650 °C. From Fig. 3(a), it is evident that the aluminum concentration is independent of growth temperature above 575 °C but below 575 °C it decreases with decreasing growth temperature. This could indicate incomplete pyrolysis of DMAlMO. In the same temperature range, the growth rates measured by SIMS depth profiles show a similar temperature dependence, decreasing by a factor of 5 in the range between 550 °C and 475 °C. This decrease is probably caused by lowering of the TMG decomposition rate. Since the aluminum concentration in the layer is a measure of relative DMAlMO/TMG decomposition and/or incorporation, the absolute decomposition rate of DMAlMO decreases even more rapidly than shown in Fig. 3(a). This behavior is consistent with the stronger aluminum-carbon and aluminum-oxygen bonds as compared with Ga-C in TMG.

The incorporation of oxygen is distinctly different. Fig. 3(b) presents the ratio of oxygen and aluminum concentrations as a function of growth temperature. At temperatures above 500 °C, the [O] / [Al] ratio decreases exponentially with a characteristic energy of 2.0 eV as determined from the Arrhenius plot. It is worth noting that similar behavior in the high temperature range, with the same characteristic energy, was observed by Goorsky *et al.* [22] in low pressure (76 Torr) OMVPE growth performed using arsine rather than TBA. At this point, based on the kinetic data available in literature, it is impossible to ascertain the pathways of DMAlMO decomposition. However, several features of this decomposition process are quite apparent. At temperatures below 500 °C the oxygen content saturates and approaches that of aluminum. The ratio of [O] / [Al] is 1.2 and 0.9 at growth temperatures of 500 °C and 475 °C, respectively. This indicates that the oxygen content at low temperatures is limited by the flux of DMAlMO toward the substrate and its decomposition rather than by the reactions leading to removal of oxygen. Thus, at temperatures below 500 °C, we have possibly reached the limit of one oxygen atom incorporated per each aluminum, which strongly suggests that oxygen is incorporated as a complex with aluminum. As stated above, the absolute concentrations determined by SIMS could be as much as a factor of two different from real values and, therefore, the complex in question could be AlO, Al_2O, or Al_2O_3.

In order to investigate incorporation of aluminum and oxygen at low pressures a series of layers have been deposited as a function of reactor pressure at a constant growth temperature (550 °C) and a DMAlMO mole fraction of $3x10^{-7}$. Both aluminum and oxygen concentrations decreased by about a factor of two between 760 Torr and 95 Torr. This could be interpreted as a result of increased linear gas velocity and, therefore, a decrease in the residence time. Since DMAlMO decomposition is not complete at 550 ° (as shown Fig.3(a)), shorter residence times could be responsible for the reduction of the aluminum and oxygen concentration at the lower reactor pressures. The [O] / [Al] ratio remained approximately constant throughout investigated pressure range [28].

The dependence of aluminum and oxygen concentrations on DMAlMO mole fraction is shown in Fig.4. The structure was grown at 600 °C at atmospheric pressure and DMAlMO mole fraction ranging from $3.8x10^{-8}$ to $1.2x10^{-6}$. The doping range was limited on the low flow side by the detection limit of our SIMS apparatus and on the high flow side by the degradation of surface morphology. Non-specular surfaces correspond to change of surface step density and in principle can result in different incorporation mechanism. Therefore, we had investigated only layers with mirror-like surfaces. As seen in Fig.4(a), the aluminum concentration is proportional to DMAlMO flow rate in the investigated flow range. On the other hand, Fig.4(b) shows that the oxygen concentration is proportional to DMAlMO flow rate up to the mole fraction of $3x10^{-7}$. For higher flows the oxygen concentration increases super-linearly. At the DMAlMO mole fraction of 1.2×10^{-6}, the oxygen concentration increases up to 3×10^{19} cm^{-3} or around 10% of aluminum concentration. At all flow rates the [O] / [Al] ratio is much smaller than 1 and as a consequence there are many more aluminum atoms on surface than Al-O molecules. For high flow rates, there is an increasing probability of an Al-O molecule interacting with an aluminum adatom and oxygen bonding with two aluminum atoms rather than only one. It is expected that the higher binding energy in this case would result in a higher oxygen incorporation probability. A reaction involving two DMAlMO molecules (or their decomposition products) produce a quadratic dependence of oxygen content on DMAlMO mole fraction, which would be in agreement with data in Fig. 4(b). The observed behavior is also consistent with the fact that oxygen incorporates into AlGaAs far more efficiently than into GaAs [12,14,22] The oxygen concentration in AlGaAs was described to be proportional to the product of concentration of oxygen species in group III sources and the sticking coefficient of oxygen to the growth site which is proportional to the aluminum concentration on the surface given by Al / (Al+Ga). Under our growth condition, since aluminum concentration is proportional to DMAlMO mole fraction, the oxygen concentration would be proportional to the square of the DMAlMO mole fraction.

Oxygen concentration is shown in Fig.5 as a function of growth rate. Layers were grown at 600 °C and a TMG mole fraction ranging from 1.25×10^{-5} to 1×10^{-4}, which corresponds to growth rates from 0.41 µm/hr to 3.3 µm/hr. The DMAlMO and TBA mole fractions in the gas phase were adjusted to maintain V/III ratio and DMAlMO/TMG ratio constant at 11 and 1.2×10^{-2}, respectively. As shown in Fig.5, the oxygen concentration increases by a factor of 2.5 with increasing growth rate while the aluminum profile did not show any change throughout the multilayer structure ($[Al] = 1.3 \times 10^{20}$ cm^{-3} for used growth conditions). This result is characteristic of dopants with high vapor pressures such as zinc [29] or tellurium [30]. However, in this case the mechanism is almost certainly different and is limited by kinetics rather than thermodynamics. In the case of the above dopants each atom interacts with the growth surface many times before it is finally either incorporated or swept with the carrier gas. This leads to establishment of local equilibrium. In case of the DMAlMO doping, once the oxygen-aluminum bond is broken it is unlikely that oxygen can re-attach itself to the layer surface because of the small number of aluminum adatoms on the growth surface. Irrespective of the exact nature of the process responsible for the loss of oxygen, it is clear that the probability of reactions leading to oxygen loss increases with the time the Al-O molecule remains on the surface. The slow growth rates are expected to result in lower oxygen content.

4. DISCUSSION

The data presented in this paper do not allow for identification of the exact pathways of DMAlMO decomposition and incorporation of oxygen and aluminum into GaAs. However, there is abundance of experimental data on the related system of oxygen incorporation into $Al_xGa_{1-x}As$. It has been suggested by several authors that the most likely oxygen source of oxygen contamination in OMVPE growth is the presence of alkoxides in the aluminum alkyl sources. Our results, therefore, could be considered as extension of these studies into the low aluminum content range and also have an advantage of controlled alkoxide flow rate. Several characteristic features of oxygen incorporation have been observed in all of these experiments [14,15,24]. These include increase of oxygen concentration with: (i) decreasing growth temperatures, (ii) decreasing V/III ratio, and (iii) increasing aluminum content.

Three different models have been proposed in order to explain these features. Akimoto *et al.* [31] suggested that the mechanism responsible for loss of oxygen at high growth temperatures is the re-evaporation of Al_2O suboxide from the growth surface. This mechanism would result in a decrease of aluminum concentration together with oxygen. Since these experiments have been performed on $Al_{0.3}Ga_{0.7}As$ a small change in Al content could not be detected. This model does not agree with our results (Fig. 3(a)) which show that there is no concomitant loss of Al at elevated temperatures.

Second model suggested that preferential loss of oxygen can be caused by uni-molecular Al-O bond fission [28]. There are two arguments against this interpretation. The first is a very high Al-O bond energy (122 kcal/mole) which makes such a process unlikely to occur at typical OMVPE growth temperatures. Therefore, the bond dissociation has to occur through intermediate steps involving other active species at the growth surface. These could include intrinsic species (Ga, Al, and As) or some of the other reaction products. If the dominant process involves only intrinsic species or if it is a uni-molecular bond fission, one could expect that a similar temperature dependence of oxygen content should be observed in Molecular Beam Epitaxy. This appears to be in contradiction to results of Achtnich *et al.* [32] who reported no change in oxygen content versus temperature and group V flux in MBE grown AlAs. This behavior is distinctly different from oxygen incorporation in OMVPE. However, it should be mentioned that Deep Level Transient Spectroscopy studies [33] suggest that in case of low aluminum content $Al_xGa_{1-x}As$ there is a increase in deep level concentration (thought as due to oxygen) at low growth temperatures.

The most likely pathway for oxygen removal at high temperatures is the reaction between oxygen and some of the reactive species produced during decomposition of alkyls and/or hydrides, and in particular atomic hydrogen as suggested by several authors [14,15]. Such a process would be an analog of a well known carbon contamination which is reduced by reaction with atomic hydrogen [34-36]. An added complication of DMAlMO decomposition process is a relatively strong oxygen bridge bond in associated alkoxides. As a result it is possible that at high temperatures DMAlMO trimers disproportionate into alkyls and alkoxides containing many alkoxy groups [37]. If this happens trimethylaluminum should result in incorporation of aluminum while more stable $Al(OCH_3)_3$ could be swept with the flow of the carrier gas. At this time we cannot comment on the relative importance of this process.

An important issue is the site occupied by impurities introduced during doping with DMAlMO. Aluminum undoubtedly occupies gallium site; there is no indication in the literature of aluminum in any other possible location. The site occupied by oxygen is less clear. In $Al_xGa_{1-x}As$, several authors suggested that oxygen forms a complex with aluminum occupying either interstitial or arsenic substitutional site [14,31]. This is to be expected because of the high Al-O bond strength and high statistical chance for oxygen to have an aluminum neighbor even for relatively low aluminum content. The probability of oxygen having aluminum nearest neighbor is higher than 0.5 in $Al_xGa_{1-x}As$ containing more than 16 % aluminum (this is assuming oxygen on arsenic substitutional site and no correlation between Al and O atoms). In our case, however, aluminum content is below one percent and the chances of forming Al-O complex are much smaller. Results presented above suggest that oxygen is incorporated into GaAs while bonded to aluminum but growth kinetics alone cannot determine if such pair will stay bonded in the bulk of the layer.

Two experimental results indicate that most of oxygen-aluminum complexes remain stable. Our preliminary infrared absorption measurements did not detect any absorption peaks due to Localized Vibrational Modes of isolated oxygen centers which are well known in GaAs [38]. Since the sensitivity of these experiments was estimated to be at least ten times higher than the oxygen content, as determined by SIMS, it appears that most of oxygen in DMAlMO doped GaAs is present in form of complexes with aluminum. One can interpret experimental results of Goorsky *et al.* [22] in a similar manner. Their Deep Level Transient Spectroscopy spectra show a number of deep level centers in GaAs:DMAlMO. None of them, however, corresponds to isolated oxygen A-center reported in bulk GaAs:O [19]. Further spectroscopic investigations are necessary to clarify the atomic structure of oxygen-aluminum complexes.

5. SUMMARY

Doping of GaAs epilayers with dimethylaluminum methoxide during OMVPE results in the incorporation of both oxygen and aluminum with the oxygen concentration always lower than that of aluminum. Good layer morphology can be achieved even for very high doping concentrations of 10^{20} cm^{-3} and wide range of deposition parameters. DMAlMO also exhibits other properties required of starting compounds for OMVPE i.e. it does not decompose or disproportionate into alkyls and alkoxides in the bubbler over an extended period of time and it does not prematurely react with TBA upstream from the susceptor. Incorporation of aluminum into GaAs epilayers is similar to that produced by trimethylaluminum while incorporation of oxygen exponentially decreases at temperatures above 525 ^{o}C with characteristic energy of 2.0 eV. At temperatures below 500 ^{o}C , the oxygen concentration saturates and approaches that of aluminum, which suggests that Al-O molecule is incorporated as a unit and possibly forms a complex in the epilayer.

Acknowledgments

Authors are indebted to Dr. T.F. Kuech and Dr. K.B. Starowieyski for their comments on the manuscript. This work was in part supported by NSF Grants No. DMR-9024401 and DMR-9202683, AFOSR Grant No. AFOSR-91-0373 and by US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract DE-AC05-84OR21400 with Martin Marietta Inc.

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FIGURE CAPTIONS

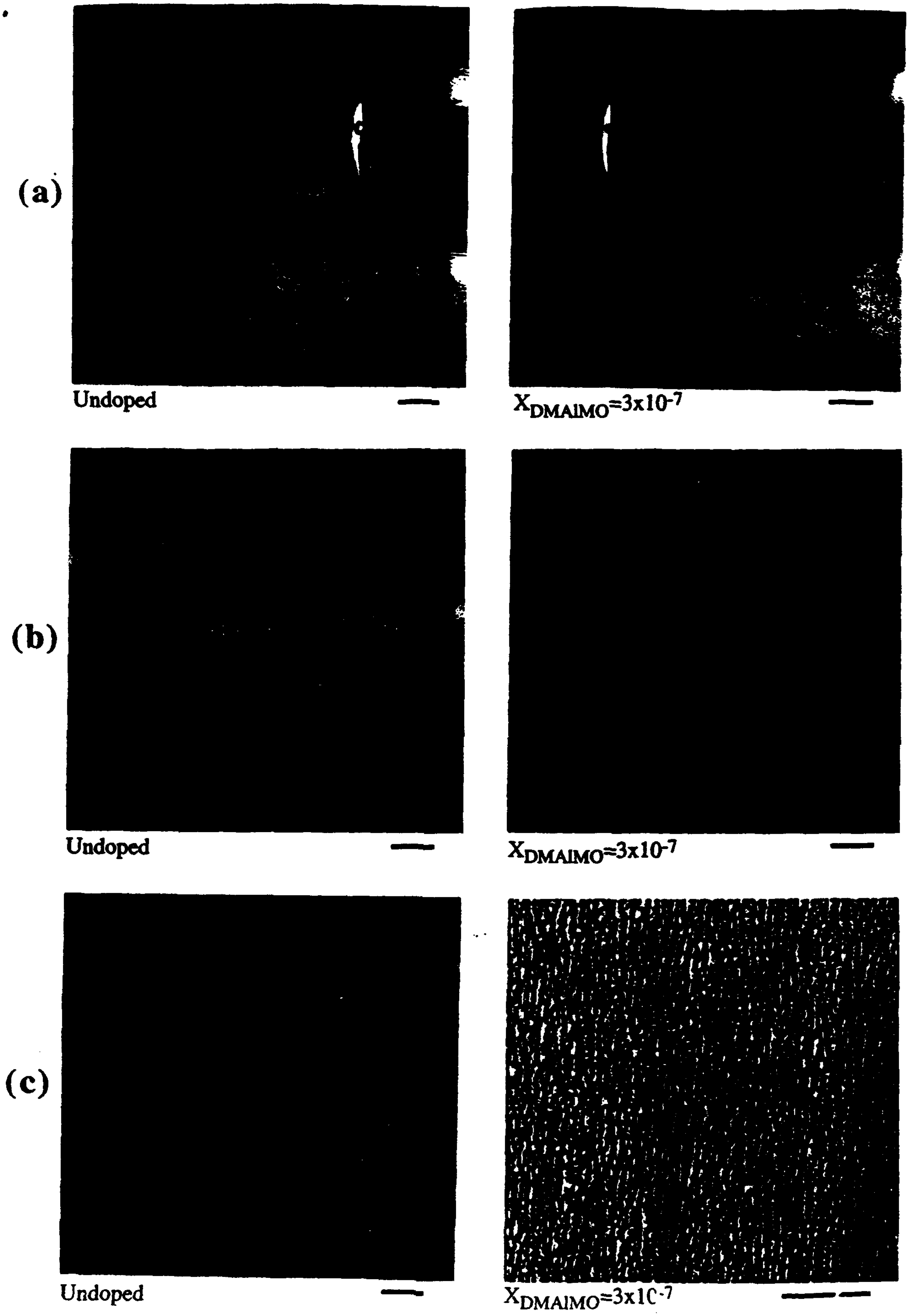
Fig. 1 Nomarski contrast optical microphotographs of surface morphologies on 1 μm thick GaAs epilayers doped with dimethylaluminum methoxide. Morphologies of undoped layers are shown on the left side while layers grown with 3×10^{-7} DMAlMO mole fraction are shown on the right. Deposition temperatures were (a) 500 °C (b) 600 °C and (c) 700 °C, respectively. Marker corresponds to 10 μm.

Fig. 2 Range of growth temperatures and DMAlMO mole fractions resulting in the specular surface morphologies (circles) and degraded surfaces (squares).

Fig. 3 (a) Growth rate and aluminum concentration in GaAs doped with dimethyaluminum methoxide versus growth temperature (layers grown at 760 Torr with mole fractions of TMG (X(TMG)) equal to 5×10^{-5}, X(TBA) = 5.6×10^{-4}, and X(DMAlMO) = 3×10^{-7}). (b) Ratio of oxygen and aluminum concentrations in the same samples.

Fig. 4 Aluminum (a) and oxygen (b) concentration in DMAlMO doped GaAs versus dopant mole fraction (T_G = 600 °C, reactor pressure p = 760 Torr, X(TMG) = 5×10^{-5}, X(TBA) = 5.6×10^{-4})

Fig. 5 Oxygen concentration as a function of growth rate (T_G = 600 °C, p = 760 Torr, ratios X(DMAlMO) / X(TMG) and X(TBA) / X(TMG) have been kept constant throughout the growth).



Undoped

$X_{DMAlMO}=3\times10^{-7}$

Undoped

$X_{DMAlMO}=3\times10^{-7}$

Undoped

$X_{DMAlMO}=3\times10^{-7}$

FIG 1

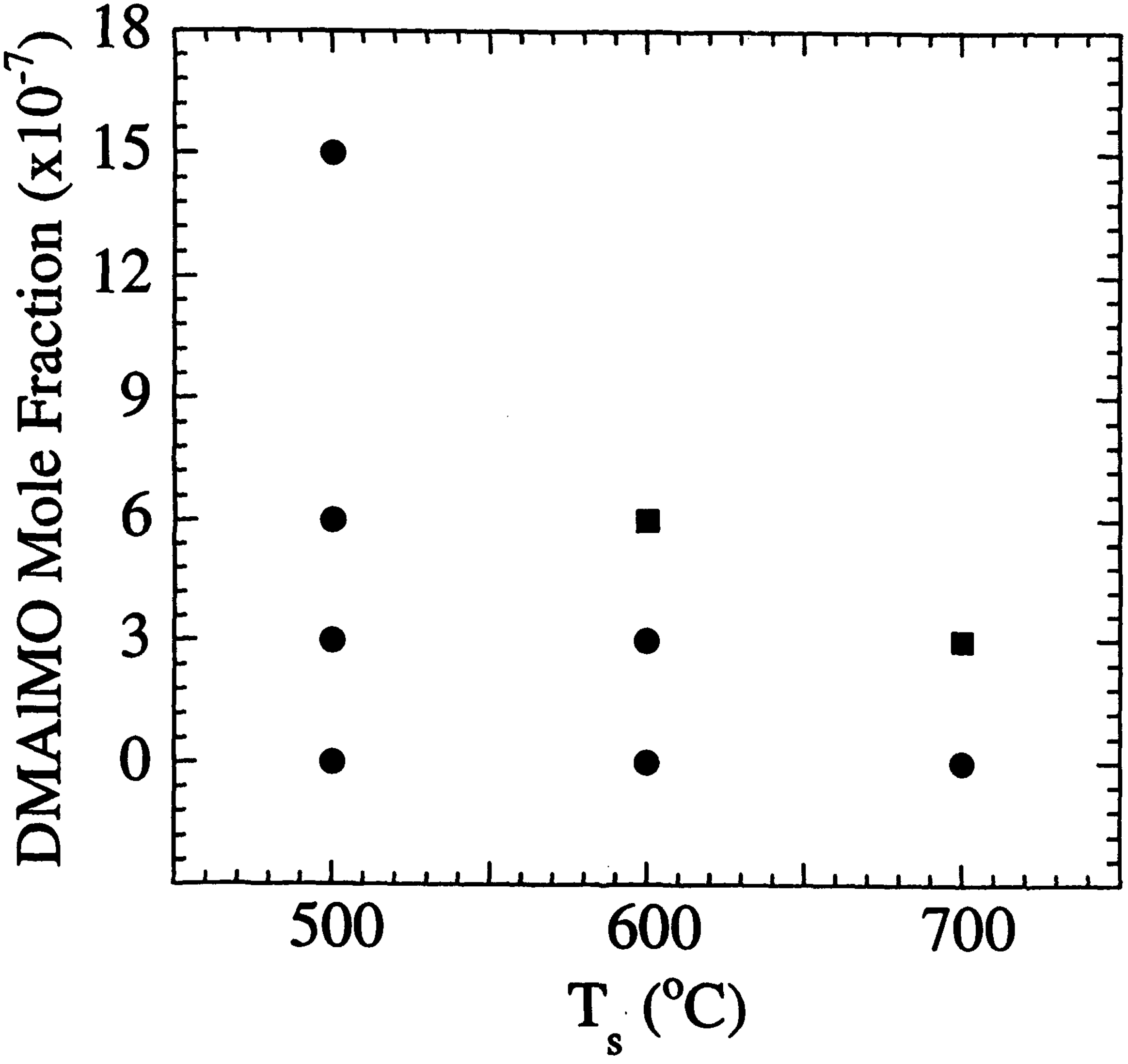
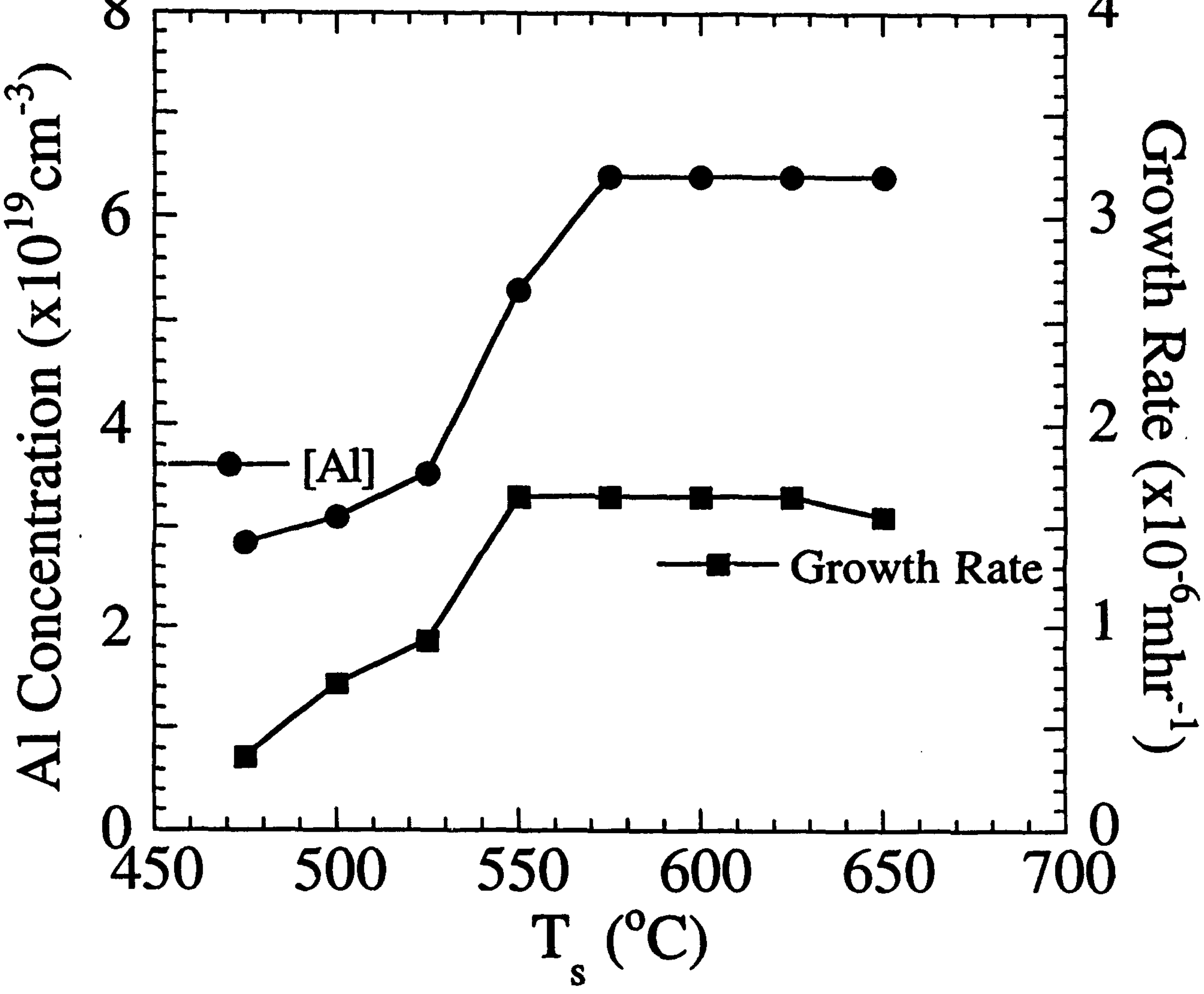
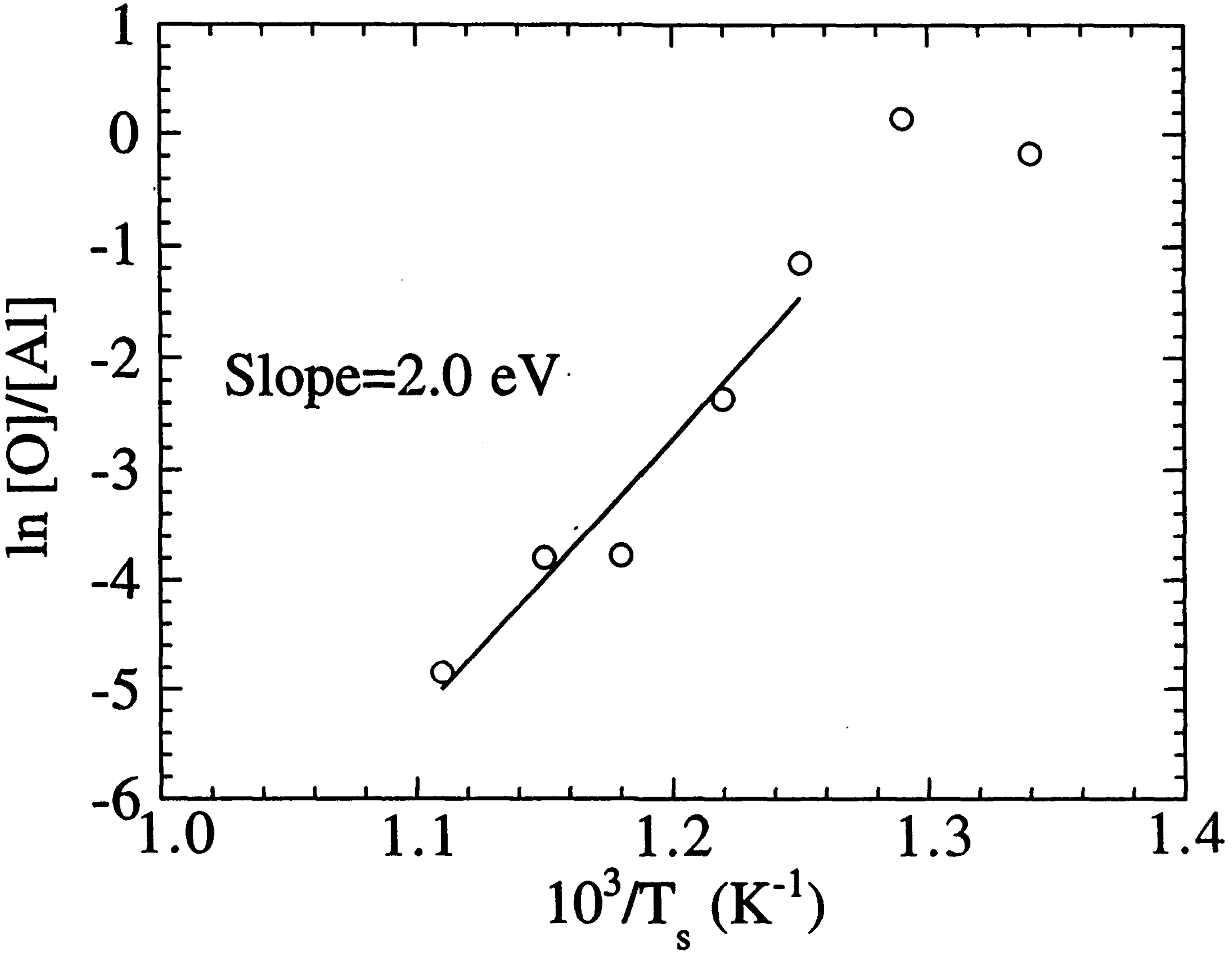


FIG 2

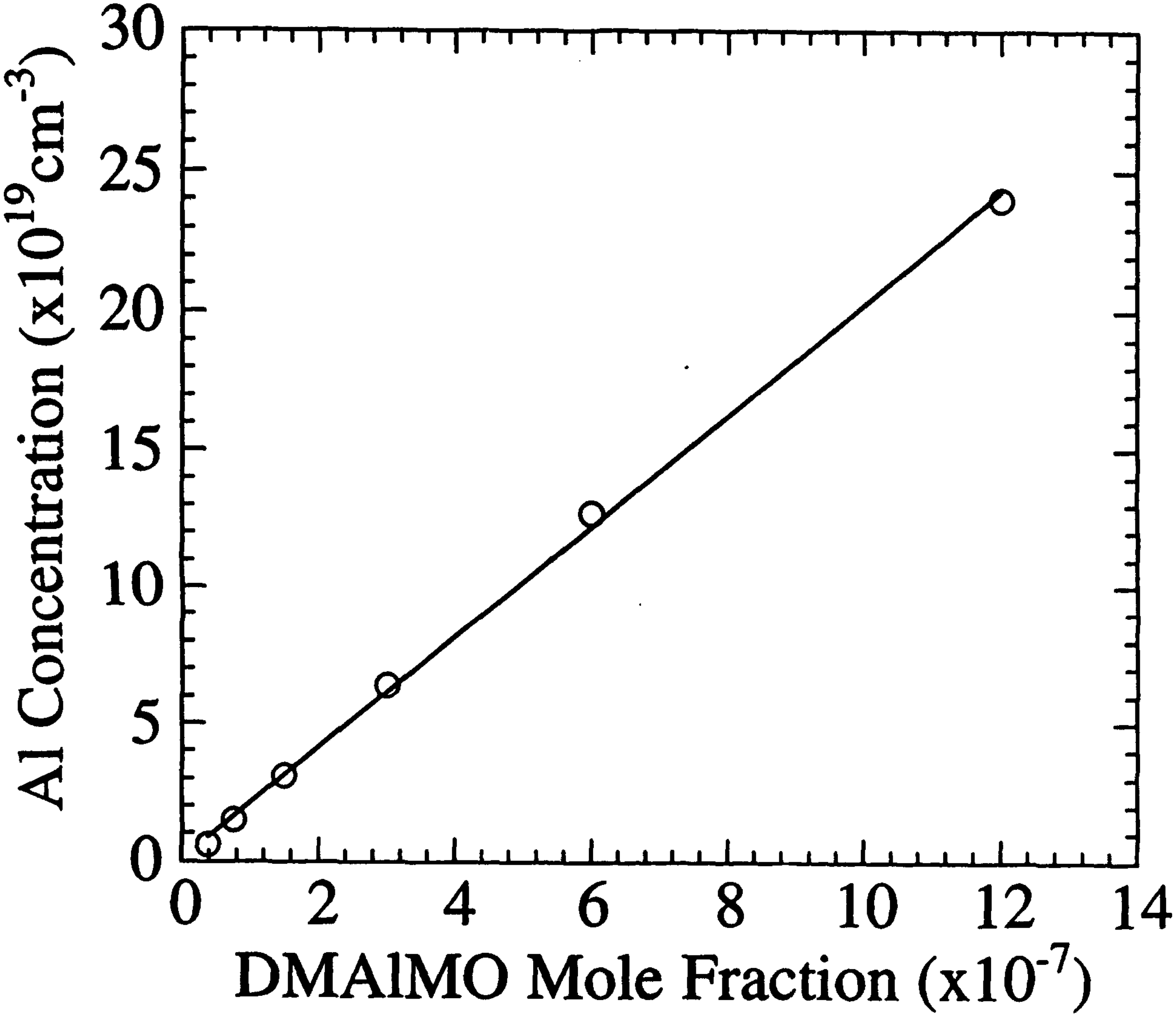

8
6
4
2
0
Al Concentration (x10^{19}cm^{-3})
4
3
2
1
0
Growth Rate (x10^{-6}mhr^{-1})
450
500
550
600
650
700
T$_s$ (°C)
[Al]
Growth Rate

(a)

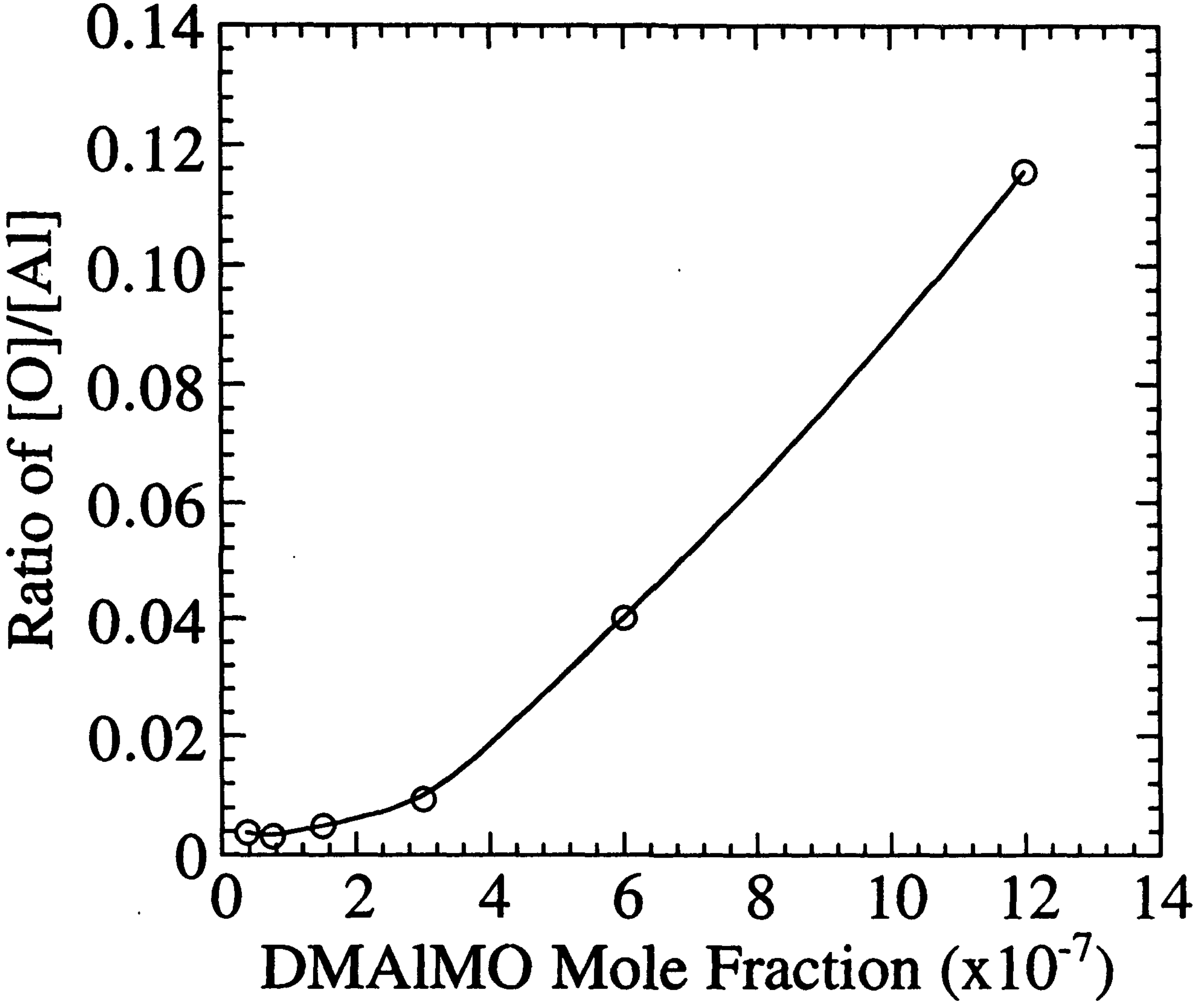
Fig 2



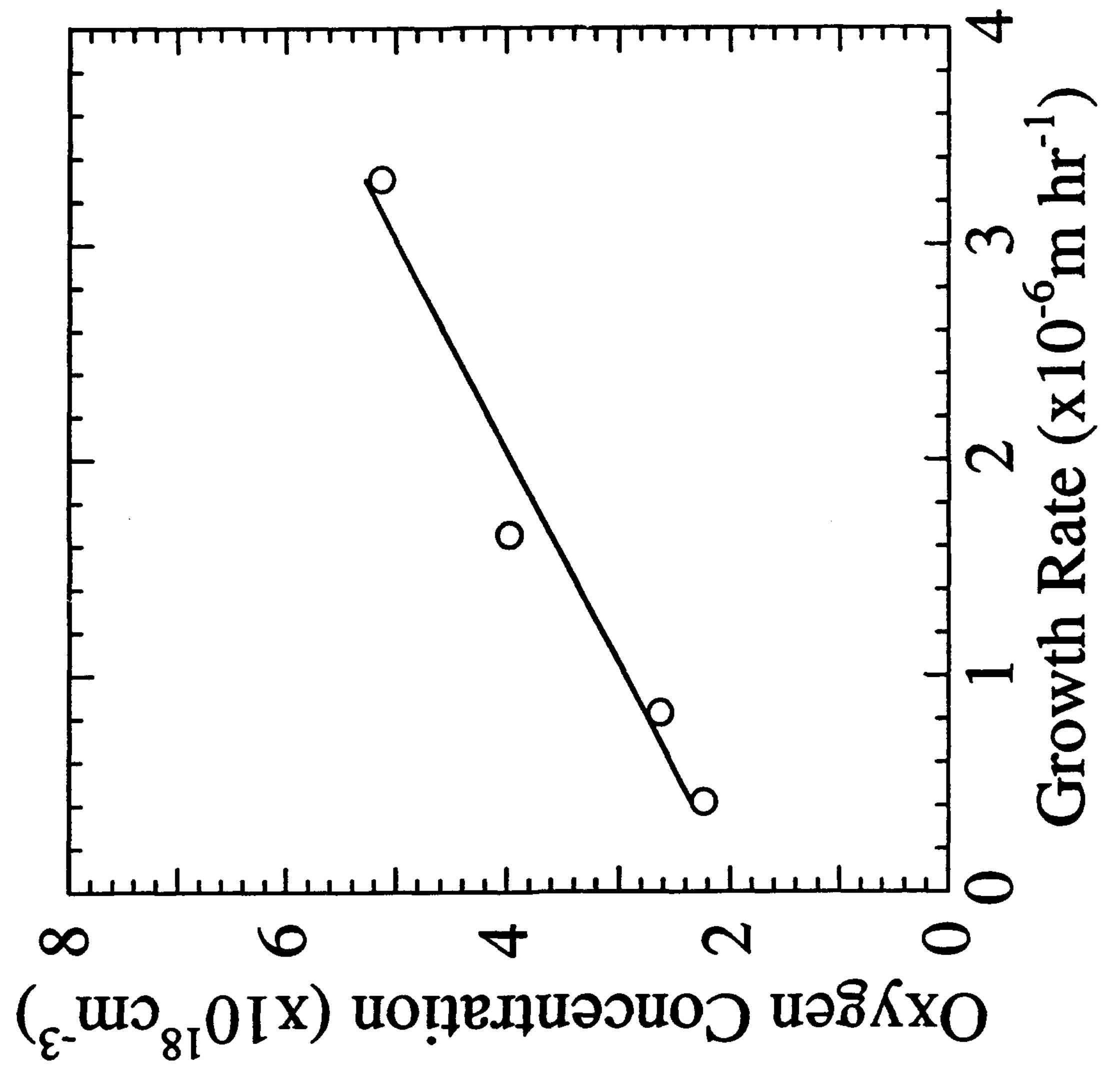
(b)


30
25
20
15
10
5
0
Al Concentration (x10^{19}cm^{-3})
0
2
4
6
8
10
12
14
DMAlMO Mole Fraction (x10^{-7})

(a)


Ratio of [O]/[Al]
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0
2
4
6
8
10
12
14
DMAlMO Mole Fraction (x10^{-7})

(b)


Growth Rate (x10^{-6}m hr^{-1})
0
1
2
3
4
Oxygen Concentration (x10^{18}cm^{-3})
0
2
4
6
8

ALKOXIDE DOPING OF GaAs DURING ORGANOMETALLIC VAPOR PHASE EPITAXY

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ABSTRACT

Doping of GaAs with dimethylaluminum methoxide and its effects have been studied during metalorganic vapor phase epitaxy. Oxygen concentration decreases exponentially with increasing growth temperature and the activation energy equal to 1.8 eV. Increase of oxygen content with decrease of V/III ratio indicates that oxygen most likely occupies arsenic site. Photoluminescence intensity was observed to decrease with increasing oxygen content and three new deep level luminescence peaks appeared at 75, 96, and 160 meV below the band gap. This, together with the fact that as-grown layers are fully depleted, indicates that oxygen is electrically active in OMVPE GaAs and forms deep non-radiative recombination centers.

INTRODUCTION

Oxygen is one of the most persistent contaminants in virtually all semiconductors and in particular in compounds containing aluminum. For many years the performance of OMVPE and MBE deposited AlGaAs lasers and Light Emitting Diodes has been consistently inferior to that of devices grown by LPE probably because of oxygen incorporation. There are numerous sources of possible *contamination:* traces of water and oxygen in arsine cylinders, leaks in the OMVPE system, oxygen adsorbed at walls of MBE apparatus, traces of oxides in gallium source in MBE, but the most important one appears to be the presence of alkoxides in the most commonly used metalorganic aluminum sources: $(CH_3)_3Al$ and $(C_2H_5)_3Al$.[1] Number of attempts have been made at simulating oxygen contamination by controlled leaks of oxygen[2-4] and recently by intentional doping with dimethylaluminum methoxide.[5,6]

The results of oxygen incorporation are usually detrimental to the layer quality. The presence of even traces of oxygen in material leads to the decrease of luminescence intensity[7-11] and lowering of solar cell efficiency.[12] This effect has been interpreted as due to formation of oxygen-related deep nonradiative recombination centers. It has also been observed that oxygen incorporation leads to compensation of shallow donors making AlGaAs layers semi-insulating[1-3,13] and decreasing electron mobility.[14] This observation led to application of oxygen compensated layers for gate isolation in GaAs FET structures.[15,16] Other potential applications of oxygen doped semiconductor layers are buffer layers for device isolation, surface passivation, and active layers in ultrafast photoconductive switches.

EXPERIMENTAL PROCEDURE

GaAs epilayers were grown on semi-insulating (100) GaAs substrates using trimethylgallium (TMG) and tertiarybutyl arsine (TBA). TBA was at 2 °C with typical H_2 flow of 50 sccm while TMG bubbler was maintained at -15 °C with hydrogen flow of 10

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sccm. This flow rate corresponds to approximately 1.5 μm/hr growth rate in most conditions. Total carrier gas flow was at 4,000 sccm. As a dopant we used dimethylaluminium methoxide (DMAlMO, $(CH_3)_2AlOCH_3$) maintained at 38 °C with H_2 flow between 1 and 10 sccm. The samples were characterized by Secondary Ion Mass Spectroscopy using a Cameca IMS-4f microanalyzer with some of the spectra obtained by Charles Evans and Associates of Redwood City, CA. Typical SIMS structure consisted of six layers each approximately 0.2 μm thick. The top and bottom layers (last and first to be deposited, respectively) were undoped and four intermediate layers were intentionally doped with DMAlMO. Such structure allowed for precise measurement of oxygen and aluminum content and additionally provided independent information on growth rate and interface sharpness. For all doping experiments DMAlMO flow and resulting aluminum content in the layer was lower than 1%. PL experiments were conducted on epilayers typically 1.5 μm thick with Ar^+ ion laser as an excitation source. The spectra were measured with either S20 photomultiplier or North Coast LN_2 Ge detector.

RESULTS AND DISCUSSION

Doping of GaAs with DMAlMO results in incorporation of both aluminum and oxygen. The aluminum content of epilayers is not a strong function of growth conditions and behaves in the same way as one could expect for doping with trimethylaluminum i.e. Al concentration is proportional to the DMAlMO mole fraction in the gas phase, does not change appreciably with growth temperature between 550 °C and 700 °C, does not depend on V/III ratio in 2-20 range, and increases by a factor of 1.6 with lowering of reactor pressure from 760 to 100 Torr. The incorporation of oxygen is distinctly different.

Oxygen concentration in DMAlMO doped GaAs epilayer as a function of growth temperature is shown in Fig. 1. Growth has been performed at atmospheric pressure and a constant DMAlMO flow rate of 2 sccm. At temperatures above 500 °C oxygen concentration

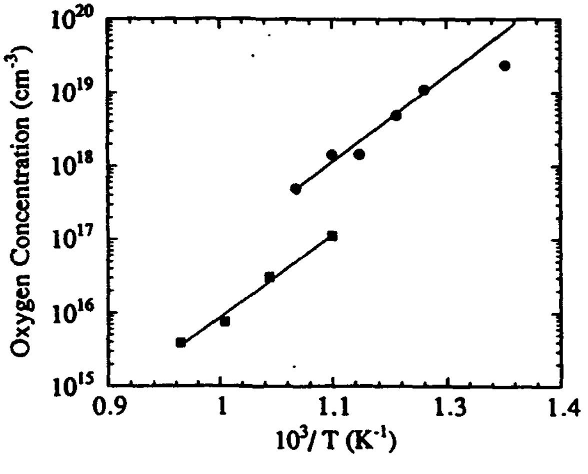

Fig. 1 Oxygen concentration in DMAlMO doped GaAs versus growth temperature. Present data are marked by circles, squares represent data of Goorsky *et al.*[5]

decreases exponentially with increasing growth temperature. The activation energy determined from the Arrhenius plot is 1.8 eV. It is worth noting that the same behavior and activation energy was reported by Goorsky et al. in the growth performed at low pressure (76 Torr) and using arsine rather than TBA.[5,6] Their results are included in Fig. 1 for comparison. The most likely decomposition route for the DMAlMO is through the bond cleavage:

$$(CH_3)_2AlOCH_3 \rightarrow CH_3AlOCH_3 + CH_3 \tag{1}$$

$$CH_3AlOCH_3 \rightarrow AlOCH_3 + CH_3 \tag{2}$$

$$AlOCH_3 \rightarrow AlO + CH_3 \tag{3}$$

with the last step occurring on the GaAs surface. At high temperatures this could be followed by breaking of the Al-O bond and oxygen evaporation which is responsible for the lowering of oxygen content. On the low temperature end of investigated growth range the measured oxygen concentration levels off. It is to be expected as at low temperatures Al-O bond cleaving is inefficient and oxygen content becomes limited by the DMAlMO mole fraction. The highest ratio of oxygen to aluminum observed at 475 °C was about 0.5. Given the error in absolute concentrations of SIMS technique we could be approaching the limit of incorporation of Al-O as a molecule i.e. each aluminum atom would be accompanied by oxygen. In principle, the dissociation of Al-O could be mediated by interaction with atomic hydrogen and organic radicals produced during decomposition of metalorganic compounds. In order to investigate this possibility a series of layers has been deposited as a function of reactor pressure at constant temperature (550 °C) and DMAlMO flow rate of 4 sccm. The results are presented in Fig. 2. The concentration of aluminum and oxygen slightly decreased with lowering of reactor pressure but their ratio stayed approximately constant. This result together with the same activation energy obtained at low pressure and atmospheric growth is a direct indication that the Al-O decomposition is a uni-molecular process and is not affected by growth chemistry.

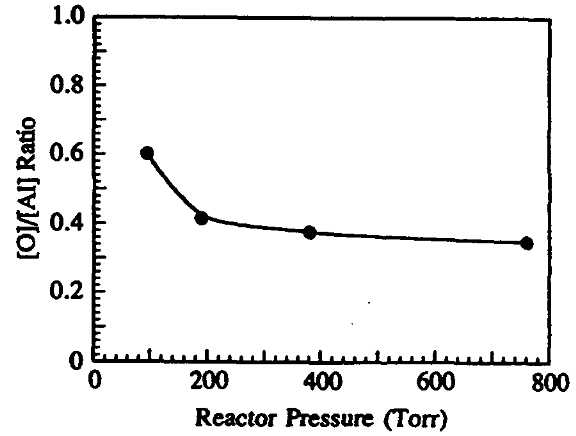

Fig. 2 Ratio of oxygen and aluminum concentration versus reactor pressure.

The natural bond length between aluminum and oxygen is about 0.18 nm and is much smaller than the bond length in AlGaAs lattice. Based on this argument it could be expected that oxygen occupies an interstitial position and as a consequence should not be electrically active. This is in contrary to the effects of AlGaAs doping with oxygen. Analysis of Fig.3 gives another insight into atomic structure of oxygen-related center. A series of layers have been deposited at 600 °C with pressure and DMAlMO and TMG flows kept constant and different TBA flows. This corresponds to V/III ratio in the 2 - 20 range. The oxygen concentration was observed to decrease with increasing V/III ratio by about a factor of three and this effect could be interpreted as due to the competition for sites between arsenic and oxygen. This would suggest that oxygen is bonded to aluminum and occupies the arsenic site.

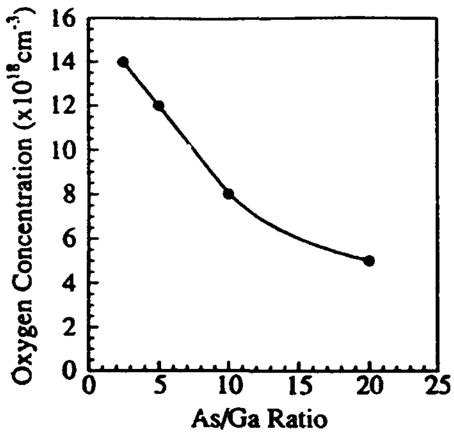

Fig. 3 Oxygen concentration versus V/III ratio (T_G=600 °C, f_{TMG}=10 sccm, f_{DMAlMO}=4 sccm).

The effects of oxygen incorporation have been investigated by photoluminescence. Fig. 4 shows the change near band-gap photoluminescence intensity versus growth temperature. All samples were grown at fixed TMG (10 sccm), TBA (50 sccm), and DMALMO (1 sccm) flow

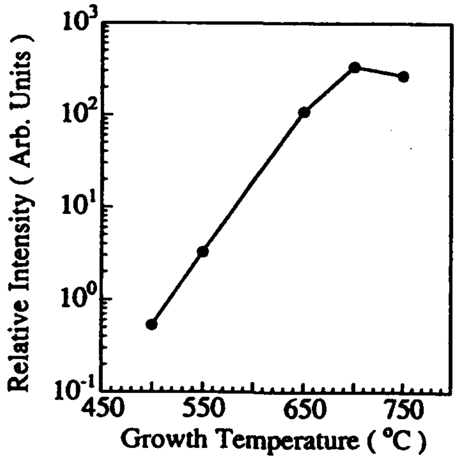

Fig. 4 Near band edge photoluminescence intensity versus growth temperature.

rates. The intensity decreased by more than three orders of magnitude between 650 °C and 500 °C. This change parallels the increase of the oxygen content in the layer and is interpreted as due to the presence of oxygen-related nonradiative recombination centers. Since the PL spectra for the undoped layers grown in the same temperature range show that the intensity change by the factor of two, the variation should be attributed to oxygen incorporation. In the high temperature range this trend is reversed and we observed increase of PL intensity between 700 °C and 750 °C. In particular the (e,A^{o}) peak due to neutral carbon increased indicating possible carbon contamination in high temperature range. Such behavior is in agreement with growth using trimethylaluminum. This effect will be further investigated by SIMS.

The effect of DMAlMO doping on spectra of GaAs epilayers deposited at 700 °C is shown in Fig.5. Besides intensity change discussed above several new features are visible. Peak labeled A due to conduction band-acceptor transition shifts to higher energies with increasing DMALMO flow. This is to be expected as the aluminum content of the epilayer increases. Thus increase in bandgap energy due to Al incorporation make the peak A shift towards higher energies. At higher DMAlMO flow rates a new peak appears on the low energy side of (e,C^{o}_{As}) transition (labeled C in Fig. 5). This may be attributed to incorporation of another acceptor originating from the DMAlMO source. The energy position of peak C suggests it could be due to either Si or Cd. Three additional peaks appear in layers deposited with high DMALMO flow rate. Two of them, labeled D and E, are shown in Fig. 5. Third peak has a maximum at 1.367 eV. Their large shift from the band gap indicates involvement of deep centers. Defect ionization energies estimated from the peak positions are 75 meV, 96 meV and 160 meV, respectively. Peaks with similar energies have been reported in OMVPE AlGaAs

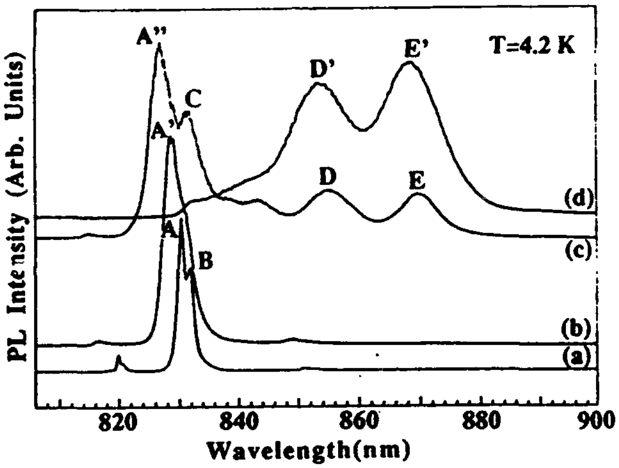

Fig. 5 Photoluminescence spectra on GaAs epilayers doped with DMAlMO (T_G=700 °C, f_{TMG}=10sccm, f_{TBA}=50 sccm; spectrum (a) f_{DMAlMO}=0, (b) f_{DMAlMO}=1.5 sccm, (c) f_{DMAlMO}=2.5 sccm, (d) f_{DMAlMO}=3.0 sccm)

layers contaminated with oxygen[9] and in GaAs intentionally doped with DMAlMO.[6] Peaks D and E shift toward higher energies upon increase of excitation density indicating that both are due to recombination in donor-acceptor pairs involving deep center. As of now the nature of these centers is not known and although clearly induced by oxygen doping these defects do not have to contain oxygen ion. For example it has been reported that oxygen contamination in GaP and AlGaAs is frequently associated with appearance of gallium interstitials.[17]

SUMMARY

Doping of GaAs epilayers with dimethylaluminum methoxide during OMVPE growth resulted in incorporation of both aluminum and oxygen. Oxygen concentration was shown to rapidly decrease with increasing growth temperature and V/III ratio but does not depend on reactor pressure. At low deposition temperatures concentration of oxygen approached that of aluminum indicating incorporation both atoms as a molecule. Oxygen-aluminum complexes are electrically active in GaAs. The photoluminescence intensity decreases with increasing oxygen content and new PL peaks due to deep defects were observed.

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