Molecular beam epitaxial growth of high-purity AlGaAs

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We report molecular beam epitaxial (MBE) growth of AlGaAs in the previously unexplored temperature range exceeding 800 °C for which excellent material can be achieved. Photoluminescence reveals bound excitonic linewidth as sharp as 3.6 meV, which is among the narrowest ever reported for material of equivalent Al mole fraction. In this temperature range carbon impurity concentrations are found to be dramatically reduced while temperature-dependent data provide information from which an understanding of carbon incorporation during MBE growth emerges.

It has long been recognized that growth purity is essential for achievement of high electron mobilities and improved optical performance in Al-based III-V heterostructures. Of particular importance to these efforts is carbon impurities known to incorporate in III-V lattices with detrimental electronic consequences. Although there exists much evidence of carbon incorporation in semiconducting materials, its origin and behavior are made uncertain by overwhelming complexities in either the growth processes or specific growth conditions.[1-3] At present, no reliable understanding has emerged which can predict its behavior. Following the earlier works of Tsang *et al.*,[4] the present effort investigates molecular beam epitaxial (MBE) growth of AlGaAs in the previously unexplored temperature range exceeding 800 °C where excellent material was realized. Carbon incorporation is detected with certainty and the observed kinetics provide an understanding of the hydrocarbon III-V surface impurity problem for the first time. The thermodynamic consequences of carbon incorporation are subsequently considered from which other reported carbon impurity behavior can be described.

Growth of AlGaAs alloys was performed in a Vacuum Generator 80 horizontal chamber equipped with elemental sources while As_4 was used for the group V flux. Growth was performed on undoped (100) GaAs substrates by methods described elsewhere.[5] Substrate temperatures were measured by means of a calibrated pyrometer. One factor limiting growth temperature was substrate detachment from the molybdenum block which occurred reproducibly above 900 °C due to rapid loss of indium solder. The only variation in the results to be presented was the growth temperature; other growth conditions remained identical. The order of growth was permuted so that systematic variations in the growth environment were not a factor. The samples were grown $\sim 1\ \mu m$ thick. The Hall effect could not be measured probably due to surface and interface depletion of mobile carriers.

Photoluminescence (PL) measurements were performed on samples thermally anchored to a superfluid helium bath while the excitation source was the focused 5145-Å line of an argon laser. Excitation intensity variations were accomplished by means of neutral density filters inserted into the optical path. Luminescence spectra for samples grown at high temperatures are presented in Fig. 1. Each individual spectrum consists of high- and low-energy components; no other peaks were observed. The splitting of approximately 25 meV between the two prominent peaks is observed to vary with growth temperature. The overall blue shift in spectral energies for increasing substrate temperature arises from significant Ga desorption which becomes more severe in this high-temperature growth range. The smooth continuation of Fisher's reported dependence of layer composition on growth temperature[6] implies no unusual difference in growth chemistry or kinetics has occurred. Comparing the samples grown at 870 °C and 800 °C, a 3000× increase in bound exciton photoluminescence intensity was obtained.

The gradual increase in splitting of two prominent emission peaks for increasing substrate temperature or composition (21→22→26 MeV) unambiguously identifies the low-energy component to be a band to carbon acceptor (BA) transition. More complete confirmation is provided as follows. The transition energetics of the carbon acceptor deduced by Stringfellow and Linnebach[7] are precisely mimicked by the present splitting while the deepening of the carbon acceptor for increasing Al mole fraction found here is in excellent agreement with the reported data of Ballingall and Collins.[8] Furthermore, excitation intensity measurements

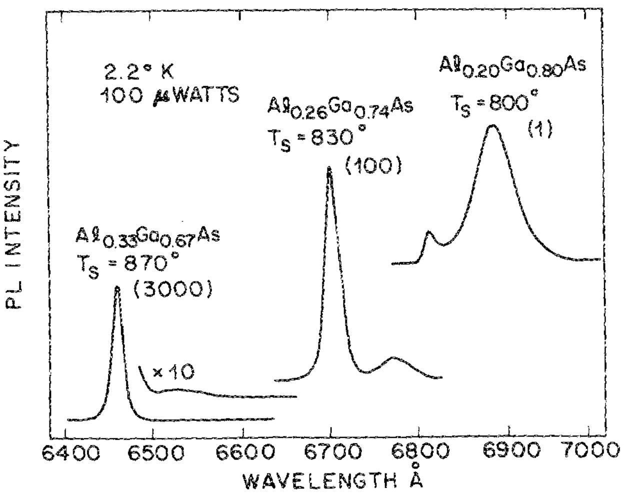

FIG. 1. Photoluminescence spectra for AlGaAs grown at various temperatures. The numbers enclosed in parentheses correspond to the relative luminescence intensity received for each sample. The AlAs mole fraction x is 0.20, 0.26, and 0.33 for the three samples shown.

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performed on the high-temperature-grown sample show no energy-shift dependence for the low-energy component which is characteristic of a BA transition rather than donor acceptor pair transition. Evidence indicating the sharp high-energy component to be an impurity assisted bound exciton (BE) is discussed later.

The composite data of Fig. 1, in addition to confirming temperature-related improvements in the PL spectra, reveal that carbon incorporation in the lattice is greatly diminished by high-temperature growth as evidenced by the intensity behavior of the BA component alone. Qualitatively, this behavior is entirely different from that found for metalorganic chemical vapor deposition growth where increased carbon incorporation in AlGaAs occurs for higher substrate temperatures.[2] Metalorganic growth involves breaking direct aluminum–carbon bonds of the metalalkyl with a temperature dependence that influences carbon incorporation. This situation is not present for MBE growth. The data found here thus present an opportunity to unravel carbon incorporation during MBE growth, a long sought after result. Nevertheless, accurate kinetics are required to distinguish among various incorporation mechanisms. We next show such kinetics can be deduced from our photoluminescence results.

It is possible to quantify the spectra of Fig. 1 with precision in order to establish a relationship between carbon incorporation and growth temperature. By implementation of simple chemical reaction equations governing the recombination process[9] in ratio form, unknown factors such as absolute quantum efficiencies, Auger process, and deep level traps which otherwise complicate spectral intensities are minimized. The recombination probability for the BA transition is proportional to the product nN_a, where N_a is the concentration of carbon acceptors. The BE corresponding rate is given by the product np with n and p the concentration of electrons and holes. The ratio BA/BE at fixed excitation power is then proportional to the carbon acceptor concentration. Complexity in the above analysis develops when impurity concentrations become so low that they are the rate limiting factor for the BE recombination probability instead of quasiparticle generation. However, pumping density dependence performed on the sample grown at high temperatures and shown in Fig. 2 reveals the BE intensity increase linearly without saturation, thus this particular concern is not applicable to the present analysis.

The dependence of the ratio BA/BE, or carbon acceptor concentration on substrate temperature is shown in Fig. 3. A clear Arrhenius dependence is inferred by the data. It is not possible that the observed dependence is explained by carbon outdiffusion from the substrate. Changes in the surface stoichiometry, induced in accordance with MBE growth kinetics by the different growth temperatures employed here, cannot solely explain our data. The latter tends to produce autocompensation,[1,10] an effect not supported by our photoluminescence data. Instead, we consider the role of a fundamentally different mechanism: hydrocarbon desorption. We next show our results as well as others are consistent with carbon incorporation from the growth surface where principally CO and CH_4 impinge and desorb.

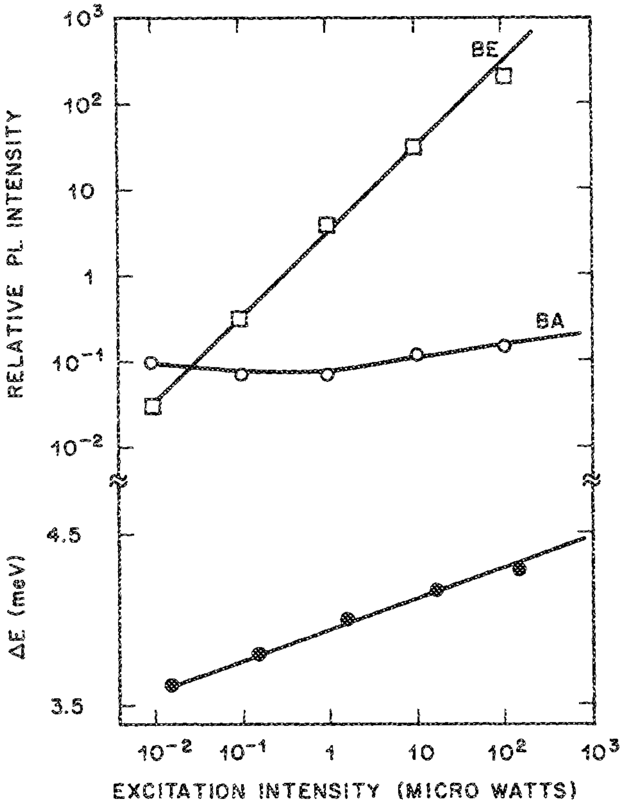

FIG. 2. Excitation intensity dependence of the linewidth (closed circles) along with the relative luminescences intensity behavior of the BA transition (open circles) and BE transition (squares) obtained for the sample grown at 870 °C.

Impurity desorption kinetics when applied to the Arrhenius datum of Fig. 3 produce an energy of 190 meV for molecular carbon species bound to the AlGaAs surface. Closed shell molecular structures such as CO and CH_4 assume outer electronic valence configurations which chemically resemble inert rare gas atoms and therefore should bind to semipolar III-V surfaces through weak van der Waal forces. The heat of adsorption inferred from the present data is in excellent agreement with values reported for other closed shell species bound to surfaces.[11] Owing to the induced dipolar character of the van der Waal's bond, it can be expected that the heat of adsorption for closed shell impurities should scale in proportion to the III-V surface dipole moment exposed. More exact treatments of induced bonding suggest that a squared dependence on surface polarity should be expected.[12] Thus an AlAs surface should bind hydrocarbons stronger than InSb material.

Other MBE carbon impurity behavior can also be explained. The particular situation of interest occurs for smaller heats of adsorption where the surface desorption rate can exceed the partial pressure of carbon related impurity species. There exists no practical configuration of thermodynamic coordinates (i.e., pressure and temperature) for which equilibrium is achievable; the surface population and incorporation rate are theoretically predicted to be zero. For higher heat of adsorption and under equilibrium conditions carbon incorporation should vary with power law dependences on temperature and impurity pressure. Phenomena

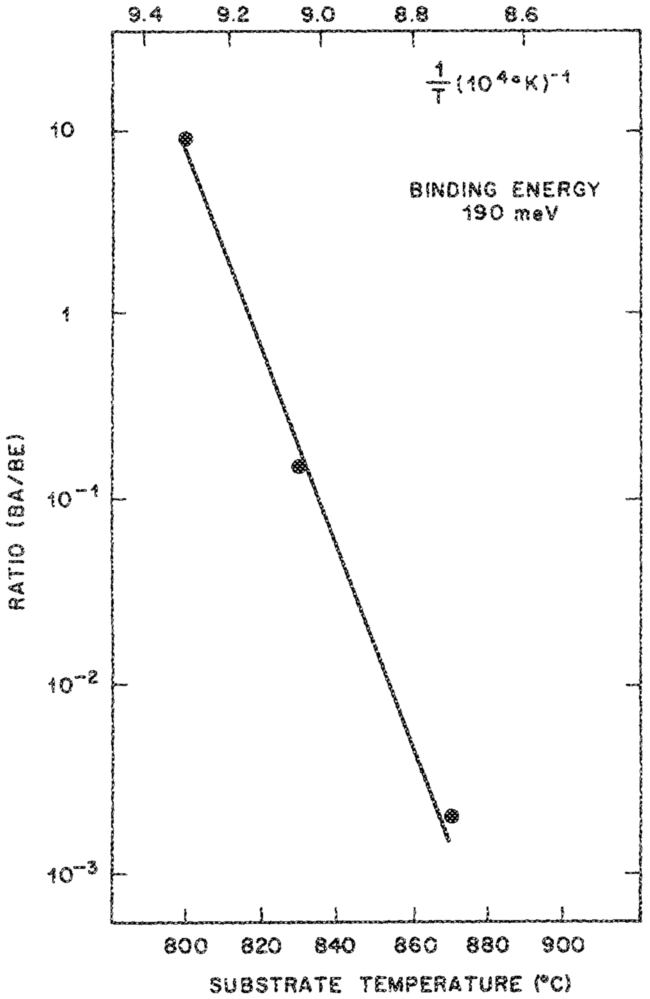

FIG. 3. Ratio of integrated intensity for the BE and BA transitions corresponding to different growth temperatures for AlGaAs. The four decade change in this parameter is fit well by an Arrhenius dependence with an activation energy corresponding to 190 meV.

indicative of this type of behavior can be found in the literature. Ilegems and Dingle[3] have found no detectable carbon incorporation for growth on (100) GaAs in CO and CH_4 environments which suggests thermodynamic factors are in proximity to a switch-off condition. For increasing surface polarity offered by alternative GaAs growth orientations, proportionately larger binding can be expected, leading to increased carbon incorporation. This is consistent with the results of Wang *et al.*[1] where nearly six times larger carbon incorporation occurs on the more polar (311) GaAs growth orientation in comparison to the (100) surface.

The spectra of Fig. 1 reveal that high quality AlGaAs is achievable for growth temperatures of 870 °C as evidenced by a minimization of impurity assisted photoluminescence transitions. The 3.6-meV linewidth observed for this sample is among the narrowest reported for AlGaAs. Excitation intensity dependence of BE linewidth shown in Fig. 2 implies an impurity assisted excitonic process as expected for the mild broadening along with the absence of profile shifts and asymmetry (not shown here) under five decade increase in excitation intensity. Such behavior is expected when quasiparticle migration to preferred low-energy recombination sites in the crystal is kinetic and energetically blocked by trapping at impurity sites. Such behavior is qualitatively explained by Schubert's and Tsang's[13] analysis of spectral photoluminescence line shapes in semiconductor alloys. The free exciton is not resolved in the present work nor in other work reported in the literature except for Ref. 14 for Al mole fraction greater than 0.30. Nor is our observed linewidth for the BE (3.6 meV) in accordance with Singh's and Bajaj's quantum mechanical alloy broadening calculations[15] (1.3 meV) but instead suggests that larger disorder effects should be expected as reported by Schubert *et al.*[16] (5.0 meV).

In summary, excellent optical quality AlGaAs has been prepared by growth at very high temperatures. Carbon incorporation has been found to greatly diminish owing to hydrocarbon desorption on the growth surface front. We have presented a way to use photoluminescence measurements to study the kinetics of hydrocarbon adsorption on III-V surfaces. Our results imply that hydrocarbons are bound to the surface of AlGaAs with an energy of 190 meV. Binding to other III-V surfaces should scale in proportion to the square of the surface dipole moment.

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