

# Growth of high quality $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$ layers on Si substrates by metalorganic chemical vapor deposition

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High quality epitaxial layers of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  have been grown on Si substrates by adopting thermal cycle annealing. The quality of the  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  has been assessed by photoluminescence, deep-level transient spectroscopy, and double-crystal x-ray diffraction studies. The emergence of a new luminescence emission (1.718 eV), high concentrations of shallow levels, passivation of a deep level (0.43 eV), and dislocation reduction in the high-temperature thermal cycle annealed samples have been explained by a silicon diffusion mechanism and the formation of complex point defects. Deep-level emission at 0.64 eV has been attributed to disordering in the epitaxial layers. © 1996 American Institute of Physics. [S0021-8979(96)05818-5]

## I. INTRODUCTION

Epitaxial growth of III–V compounds and their alloys on Si substrates have received considerable interest for optoelectronic integrated circuits (OEICs) and minority-carrier devices such as solar cells, laser, etc. Integration of III–V devices on Si will provide low cost, light weight, good thermal conductivity, and excellent mechanical strength. However, the crystal quality of a heterostructure on Si is inferior due to large lattice mismatch and difference in thermal expansion coefficients. These two major problems result in the generation of high dislocation density and residual stress in the epitaxial layers. To improve the quality of the layers several attempts such as growth of low-temperature nucleation layers and strained layer superlattice as buffer layers, *in situ* or post-growth annealing, thermal cycle growth have been made.<sup>1–4</sup> Though these efforts improved the crystallinity of the heterostructure, there is still a long way to achieve the dislocation density to the order of  $10^4 \text{ cm}^{-2}$  for practical applications.<sup>5</sup> The mechanism of dislocation reduction is not yet understood thoroughly due to the limited knowledge of physics of defects in semiconductors.<sup>6</sup>

This article describes the growth of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  on Si substrates and characterization of crystal quality by photoluminescence (PL), deep-level transient spectroscopy (DLTS) and double-crystal x-ray diffraction (XRD). Improvements of crystal quality of the  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  layers on Si by optimizing the thermal cycle annealing temperature (TCA) will also be described. We report PL, double-crystal XRD, and DLTS results of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  on Si for the first time. We propose a mechanism of annihilation of dislocations at the

expense of point defects and point defect complexes in addition to coalescence of dislocations by dislocation bending due to high-temperature thermal cycle annealing.

## II. EXPERIMENT

Heteroepitaxial layers of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  were grown on (100)  $n^+$ -Si substrates oriented  $2^\circ$  off towards [011] by atmospheric pressure metalorganic chemical vapor deposition (MOCVD). The source materials were trimethyl gallium (TMG), trimethyl aluminum (TMA), and arsine ( $\text{AsH}_3$ ). No intentional doping was performed. Heteroepitaxial growth sequences of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  on a Si substrate is shown in Fig. 1. Two-step growth method and *in situ* TCA were adopted. Prior to the two-step growth of a GaAs buffer layer the Si substrates were preheated to  $1020^\circ\text{C}$  for about 5 min in a hydrogen ambient to remove the surface native oxide on the substrate. TCA was performed during the growth of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  buffer layers in two steps. At the intermediate stage of the  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  buffer layer growth of  $0.7 \mu\text{m}$  from the GaAs surface two thermal cycles and three thermal cycles at the end of remaining  $0.7 \mu\text{m}$  buffer layer growth were performed. Finally,  $1.6\text{-}\mu\text{m}$ -thick layer has been grown for the present investigation. Three specimens, TCA<sub>1</sub>, TCA<sub>2</sub>, and TCA<sub>3</sub>, were grown by changing the maxima of the thermal cycle at 1000, 950, and  $900^\circ\text{C}$  and keeping the minima at  $300^\circ\text{C}$ , respectively. The growth temperature of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  was  $800^\circ\text{C}$  for all three samples. More details about the growth, TCA and solar cell conversion efficiency over 20% are available elsewhere.<sup>7</sup>

Photoluminescence spectra were recorded at 77 K using a 514.5 nm Ar-ion laser as an excitation source. GaAs PMT was used as a detector. The power of the excitation laser

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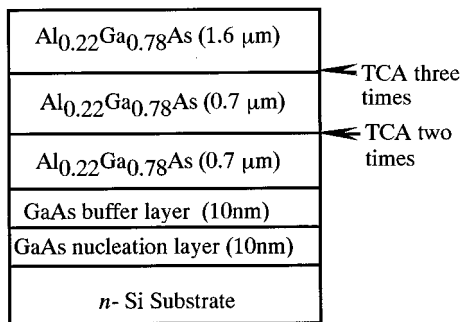


FIG. 1. Schematic cross-sectional view of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$ . Two thermal cycles and three thermal cycles are performed during the growth of the  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  buffer layer at 0.7 and 1.4  $\mu\text{m}$  respectively.

source was 100 mW and it was also increased to study the dependence of PL intensity and peak energy with excitation intensity.

Gold Schottky contacts of various diameters were made on  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  with AuSb/Au ohmic contacts on the rear side of the Si substrate. Deep-level transient spectra have been measured using an automated (HORIBA DA1500) system. Shallow-level and deep-level concentrations, capture cross sections, and activation energies have been estimated.

The x-ray rocking curve was recorded for the [400] reflection using  $\text{Cu } K\alpha$  radiation by Rigaku double-crystal x-ray diffractometer. The samples were mounted on a rotatable holder and two measurements were made for each sample. After each measurement, the sample was rotated  $180^\circ$  on the sample stage for the second spectrum. The two spectra were averaged to eliminate the error due to tilt in the epitaxial layer.

### III. RESULTS

Three samples with three different TCA temperatures were studied. Photoluminescence spectra of all the three samples are shown in Fig. 2. At 1.738 and 1.718 eV two luminescence emissions are observed which correspond to

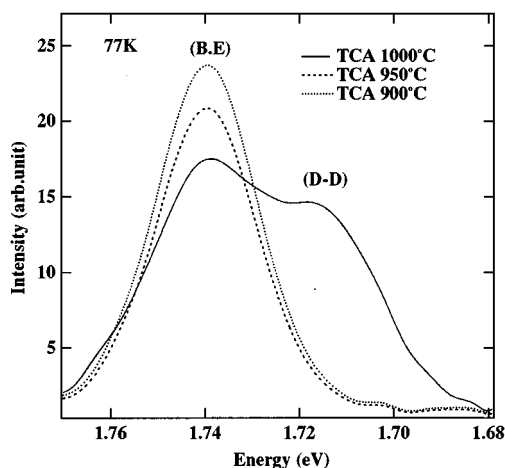


FIG. 2. PL spectra of thermal cycle annealed  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$  at 77 K. The thermal cycle annealing maximum temperature is kept as 900, 950, and 1000  $^\circ\text{C}$ , respectively.

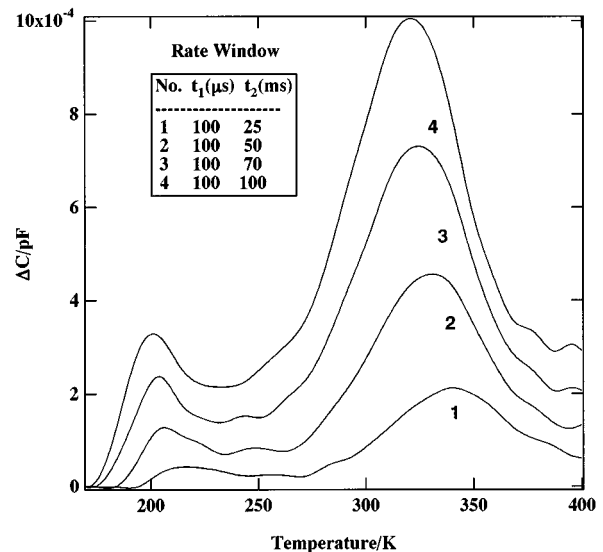


FIG. 3. DLTS spectra for 900  $^\circ\text{C}$  thermal cycle annealed  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$  showing two deep levels.

$\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  band emission (BE) and a deep emission, respectively. The emergence of the 1.718 eV peak is not observed in  $\text{TCA}_2$  and  $\text{TCA}_3$  samples. The new emission is named as donor-donor (D-D) peak, and it is attributed to vacancy arsenic-silicon group III ( $\text{V}_{\text{As}}\text{-Si}_{\text{III}}$ ) complex defects, which will be discussed in detail.

Typical DLTS spectra of the 900  $^\circ\text{C}$  TCA sample ( $\text{TCA}_3$ ) are shown in Fig. 3. The activation energies of the deep levels have been calculated from the Arrhenius plots. Capture cross section and the concentration of the deep levels have been estimated by isothermal capacitance transient spectroscopy (ICTS). No appreciable difference in the results of  $\text{TCA}_2$  and  $\text{TCA}_3$  samples is obtained and only the data for  $\text{TCA}_1$  and  $\text{TCA}_3$  are listed in Table I. As shown in the table,  $\text{TCA}_3$  sample exhibits two deep levels E1 and E2, whereas  $\text{TCA}_1$  has a single-level E1. Shallow-level concentrations of these samples,  $\text{TCA}_1$ ,  $\text{TCA}_2$ , and  $\text{TCA}_3$ , are  $3.89 \times 10^{17}$ ,  $8.0 \times 10^{16}$ ,  $7.76 \times 10^{16} \text{ cm}^{-3}$ , respectively. Normally in AlGaAs the oxygen contaminated deep traps were observed at 0.7 and 0.53 eV. However, no such levels exist in all the three samples.

The results of double-crystal x-ray diffraction studies of AlGaAs grown on Si are shown in Fig. 4. Double-crystal XRD data for AlGaAs/Si are not available in the literature, however, the present report is the best value of full width at half maximum (FWHM) for any III-V semiconductors grown on silicon substrates.<sup>8,9</sup> A very low value of FWHM (92 arcsec) is obtained for the first time.

### IV. DISCUSSION

In undoped AlGaAs the main point defects are vacancies of group III or arsenic (As), interstitials of group III or As and antisites of group III or As depending on the growth environment. When growth is performed in an arsenic-rich ambient, as in the case of MOCVD growth, the epilayer contains predominantly group III vacancies, As antisites, As interstitials, and complex defects formed by the combination of

TABLE I. Emission activation energy ( $\Delta E$ ), capture cross section ( $\sigma_g$ ), and deep-level concentration ( $N_t$ ) measured in  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$ .

Sample	$\Delta E$ (eV)	$\sigma_g$ ( $\text{cm}^2$ )	$N_t$ ( $\text{cm}^{-3}$ )
TCA900 °C			
Level E2	0.43	$9.33 \times 10^{-15}$	$9.58 \times 10^{13}$
Level E1	0.64	$1.45 \times 10^{-13}$	$2.20 \times 10^{14}$
TCA1000 °C			
Level E1	0.64	$1.04 \times 10^{-9}$	$2.56 \times 10^{15}$

these point defects. When AlGaAs is grown on a Si substrate, Si can be incorporated in the epilayer by two ways.<sup>9,10</sup> The first one is through the gas phase reaction, this means that the hydrogen carrier gas may interact with available Si in the growth ambient by out-diffusion of silicon from the silicon substrate and/or the hydrogen may react chemically with the silicon substrate and possibly form silicon-hydrogen complex gas molecules such as  $\text{SiH}_4$ , etc. Secondly, the Si from the substrate diffuses through the interface defects and dislocations and is incorporated in the epilayers. Therefore undoped GaAs or AlGaAs grown on Si substrates by MOCVD always results in *n*-type material unless otherwise the epilayers are heavily doped with *p*-type impurities. As in the case of GaAs, in AlGaAs also the formation of Frenkel defects may be predominantly due to gallium interstitials and vacancies rather than aluminum. Because of the higher bond strength of Al-As than that of Ga-As, the generation of Frenkel defects by aluminum is less probable. This reduces the density of interstitials that reach the surface region and fill the element III vacancy generated by the thermal cycle heat treatment. Doping with Si impurities also enhances the creation of Ga vacancies in GaAs which has been confirmed by slow positron beam technique.<sup>11</sup> Therefore the density of gallium vacancies in the surface region will be very large in thermally treated and Si-doped AlGaAs layer. Even the small lattice mismatch between GaAs and AlAs makes the AlGaAs material itself less stable than GaAs, the growth of AlGaAs on Si leaves more room for the formation of point defects and complexes due to large lattice mismatch and difference in thermal expansion coefficient.

In the case of Si-doped *n*-type GaAs there are about 25 possible pair complexes of two point defects out of  $\text{Si}_{\text{Ga}}$ ,  $\text{Si}_{\text{As}}$ ,  $\text{V}_{\text{Ga}}$ ,  $\text{V}_{\text{As}}$ ,  $\text{Ga}_i$ ,  $\text{Ga}_{\text{As}}$ ,  $\text{As}_{\text{Ga}}$ , and  $\text{As}_i$ .<sup>12</sup> There are in a whole 12 donor-acceptor pairs, 6 donor-donor pairs, 3 neutral/donor-acceptor pairs, and 4 neutral/donor-donor pairs. Tang *et al.*<sup>12</sup> have observed two photoluminescence peaks just below the band emission for Si-doped AlGaAs and attributed to  $\text{V}_{\text{As}}\text{-As}_{\text{Ga}}$  (donor-donor) for the lower-energy peak between 1.71 and 1.80 eV and  $\text{V}_{\text{As}}\text{-Si}_{\text{As}}$  (donor-acceptor) or  $\text{V}_{\text{As}}\text{-Si}_{\text{Ga}}$  (donor-donor) for the other slightly higher-energy peak between 1.80 and 1.86 eV depending on the composition of AlGaAs and V/III ratio. As shown in Fig. 2, for  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$  at about 20 meV below the band emission energy of 1.738 eV, a deep emission has been observed only for the TCA<sub>1</sub> samples (1000 °C TCA). PL intensity of both band emission and deep emission peaks showed almost linear dependence on the excitation intensity without shift in the peak position. The possible emission due to

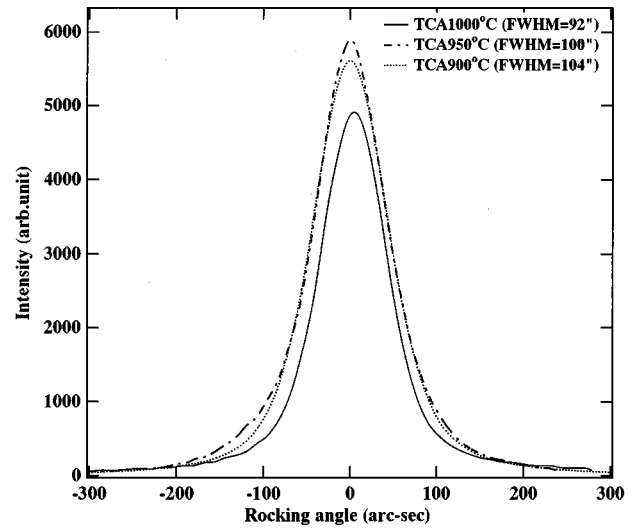


FIG. 4. The x-ray rocking curves of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$ . (Parameter: thermal cycle annealing temperature.)

donor-acceptor pair is ruled out, because the recombination rates are very slow for donor-acceptor pairs which are easily saturated as the excitation intensity increases. In other words a donor-acceptor emission band shifts towards higher energy. Considering the effect of high-temperature thermal cycle annealing on the enhancement of carrier concentration in the epitaxial layers, the probable pair complex defects which contribute for higher carrier concentration are 6 donor-donor pair complexes ( $\text{Si}_{\text{Ga}}\text{-V}_{\text{As}}$ ,  $\text{Si}_{\text{Ga}}\text{-Ga}_i$ ,  $\text{Si}_{\text{Ga}}\text{-As}_{\text{Ga}}$ ,  $\text{V}_{\text{As}}\text{-Ga}_i$ ,  $\text{V}_{\text{As}}\text{-As}_{\text{Ga}}$ ,  $\text{Ga}_i\text{-As}_{\text{Ga}}$ ). High silicon doping and the arsenic-rich growth ambient may favor the formation of  $\text{V}_{\text{As}}\text{-As}_{\text{III}}$  or  $\text{V}_{\text{As}}\text{-Si}_{\text{III}}$  complex defects in AlGaAs/Si. Therefore the emission at 1.718 eV could plausibly due to  $\text{V}_{\text{As}}\text{-As}_{\text{III}}$  or  $\text{V}_{\text{As}}\text{-Si}_{\text{III}}$  complexes.

The concentration of Si impurities at the interfaces is higher than that of heteroepitaxial layers at the top, moreover, the concentration of Si at the interfaces is very high close to the Si substrate. This is due to the increase of the high defect density at the AlGaAs/Si interfaces compared to AlGaAs/AlGaAs interfaces. Depth profile electrochemical etching measurements confirmed that at high-temperature thermal cycle annealed interfaces (sample TCA<sub>1</sub>) the concentration of Si impurities is higher than that of TCA<sub>2</sub>, TCA<sub>3</sub> samples. The generation of Si related complex defects in the epitaxial layer grown after the high-temperature thermal cycle treatment is more probable. This assumption is based on the existence of deep emission and high concentration of silicon for the TCA<sub>1</sub> samples. Since the growth ambient was arsine rich, Si may form  $\text{Si}_{\text{Ga}}^+$  mobile species.<sup>13</sup> This mobile species may in turn form  $\text{Si}_{\text{III}}\text{-V}_{\text{As}}$  complexes and contribute to enhanced carrier concentration in TCA<sub>1</sub> samples. This complex defects also aid the annihilation of dislocations and result in the low dislocation to the order of  $2 \times 10^7 \text{ cm}^{-2}$  measured by electron-beam-induced currents (EBIC).<sup>14</sup> Motion of the mobile species occurs on the group III sublattice by hopping into vacancies under high thermal stress and annihilates the dislocations. The thermal cycle annealing reduces the dislocations by two processes. The number one is

predominantly by motion and interaction of dislocations at the interface during TCA. The number two process is by annihilation of dislocations in the epitaxial layers grown after TCA by consuming generated point defects. From the results of double-crystal x-ray diffraction, it is evident that the full width half maximum (FWHM) decreases from 104 to 92 arcsec on increasing the thermal cycle temperature from 900 to 1000 °C. Though the crystallinity increases in terms of dislocations, quenching of intensity of rocking curves and photoluminescence emission is observed on increasing the thermal cycle annealing temperature due to high density of point defects and point defect complexes in the epitaxial layers.

DLTS spectra of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$  reveal that the  $(d, X)$  center related to the Si impurity (0.43 eV) almost disappears in the  $\text{TCA}_1$  samples and only one emission occurs at 0.64 eV. The deep emission (0.43 eV) in  $\text{AlGaAs}/\text{GaAs}$  has been attributed to Si impurity which is similar to 0.33 eV emission in Si-doped GaAs. The large change in emission energy due to deep donor level related to Si impurity between GaAs and  $\text{AlGaAs}$  has been shown to arise from the local alloy disorder which was absent in GaAs.<sup>15</sup> This defect level is normally called as  $\text{EL}_6$  in Si-doped GaAs and also disappears at higher doping concentration of silicon.

Increasing the TCA temperature, the concentration of Si impurities increases which in turn enhances the formation of  $\text{Si}_{\text{III}}\text{-V}_{\text{As}}$  complexes. For charge neutrality, at a higher concentration of Si where further doping of with Si is not possible, the  $\text{V}_{\text{As}}\text{-As}_{\text{III}}$  complexes may also coexist along with  $\text{Si}_{\text{III}}\text{-V}_{\text{As}}$  complexes and As antisite defects. This means that at a higher TCA temperature the concentration of point defects will be large. The origin of the 0.64 eV energy thermal emission is not very clearly known but the concentration of this level increases on increasing the thermal cycle annealing temperature. The thermal cycle annealing beyond 1000 °C resulted in a high density of visible cracks in the epitaxial layers and the experiments were restricted to the maximum TCA temperature of 1000 °C. Thermal emission close to 0.64 eV was also observed in  $\text{GaAs}/\text{Si}$  and  $\text{AlGaAs}/\text{GaAs}$ . The thermal emission at 0.66 eV observed in  $\text{GaAs}/\text{Si}$  has been related to dislocations without detailed explanation.<sup>16</sup> Epitaxial layers of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  have been grown on GaAs by MOCVD at different doping concentration of selenium.<sup>17</sup> Deep-level free layers were obtained at low doping concentration of Se, whereas higher Se doping (above  $2 \times 10^{17} \text{ cm}^{-3}$ ) resulted a single-hole trap at 0.65 eV. The origin of this trap was not discussed. In the present study the high-temperature thermal cycle annealing passivates the deep trap (E2) and increases the concentration of (E1) level in  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$ . Time-resolved photoluminescence data of these samples also exhibit longer lifetimes (0.9 ns) for higher TCA samples and the details will be reported separately. From the photoluminescence spectra of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}/\text{Si}$ , it

is very clear that the 0.43 eV emission disappears only in the sample in which the (D-D) emission appears. The silicon impurity in the deep energy state has been passivated due to the high concentration of single point defects and two point defect complexes formed by silicon. This passivation also increases the concentration of deep level (E1). Therefore impurity-induced disordering in the heteroepitaxial layers by the generation of  $\text{V}_{\text{As}}\text{-As}_{\text{III}}$  or  $\text{V}_{\text{As}}\text{-Si}_{\text{III}}$  complex defects may be responsible for the 0.64 eV emission.

## V. CONCLUSION

High-temperature thermal cycle annealing increases the crystal quality of  $\text{Al}_{0.22}\text{Ga}_{0.78}\text{As}$  layers on Si substrates. Very narrow FWHM-XRD values and passivation of deep levels have been reported for the first time. The PL emission observed at 1.718 eV has been attributed to donor-donor complex defects. High carrier concentration, quenching of x-ray rocking curve intensity, and photoluminescence intensity in high-temperature thermal cycle annealed  $\text{AlGaAs}$  samples have been addressed. The feasibility of dislocation reduction at the expense of generated point defects has been discussed.

## ACKNOWLEDGMENT

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