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Suppression of thermal atomic interdiffusion in C-doped InGaAs/AlGaAs quantum well laser structures using TiO₂ dielectric layers

P. L. Gareso,^{a)} M. Buda, L. Fu, H. H. Tan, and C. Jagadish

Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

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The effects of thermal annealing on C-doped InGaAs/AlGaAs quantum well laser structures capped with titanium dioxide (TiO₂) layers were investigated. The atomic interdiffusion was greatly suppressed by the presence of a TiO₂ capping layer during annealing, inhibiting even the thermal intermixing observed in the uncapped sample. An increase in the amount of lattice contraction associated with the presence of substitutional carbon C_{As} after annealing without a capping layer was observed, but not after annealing with a TiO₂ capping layer. Capacitance–voltage measurements confirmed the electrical activation of carbon after annealing without a dielectric layer and show a negligible change after annealing using a TiO₂ capping layer. The possible mechanisms involving both the atomic intermixing on the group III sublattice and carbon activation on the group V sublattice and the implications for optoelectronic device integration using impurity-free intermixing are discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1833563]

Quantum well intermixing is a postgrowth method that enables the monolithic integration of different optoelectronic devices. This technique is used to modify the band gap in selected areas of quantum well structures (QWs) through the intermixing of atoms in the quantum well and barrier interfaces.^{1,2} Intermixing in the active region can be achieved by several techniques including ion implantation,^{3,4} impurity induced disordering,⁵ and impurity free vacancy disordering (IFVD).⁶ Among the various techniques used to generate the intermixing, IFVD has shown to be very effective for device applications since it is simple and the amount of residual defects that are created by the intermixing process is much lower than by ion implantation and impurity diffusion. The deposition of SiO₂ layers and subsequent rapid thermal annealing (RTA) enhances the intermixing, while a recent study has demonstrated that TiO₂ cap layers effectively inhibited the intermixing.⁶ In that study, the suppression of the intermixing in InGaAs/GaAs quantum dots was achieved and attributed to the thermal stress introduced by the large thermal expansion coefficient of TiO₂ compared with GaAs. However, that study only refers to undoped material, while the vast majority of applications in optoelectronic integration use devices based on a p-i-n junction, such as laser diodes and modulators for example.

The purpose of the present letter is to study the effects of annealing p-i-n laser diode structures with TiO₂ dielectric layers for applications related to optoelectronic integration on the same chip using quantum well active regions. For such applications, that involve a high temperature annealing step at about 900 °C, carbon is the dopant of choice due to its lower diffusivity. A large energy shift was observed when the samples were annealed without any capping layer. In contrast, the samples that were deposited with TiO₂ demonstrated a very small energy shift in comparison with the as-grown samples. At the same time, the additional electrical activation of the carbon dopant is observed after annealing without a capping layer, but not after annealing with TiO₂

cap layers, indicating that when the intermixing process takes place, it affects not only the group III In and Ga (Al) atoms but also carbon atoms that are electrically active when occupying a group V lattice site.

The QW laser structure used in this experiment was grown on a (100) *n*⁺ GaAs substrate using low pressure metalorganic chemical vapor deposition (MOCVD). We used a thin *p*-Al_{0.60}Ga_{0.40}As cladding layer structure which uses the asymmetric design of the optical field distribution that most of it lies in the *n*-type layers and only a small part of the distribution is found near the top surface.⁷ In addition, the structure is well suited for intermixing in the GaAs based system, where the diffusion length of Ga vacancies is of the order of 0.1 μm. The thin *p*-cladding layers have a nominal thickness of 0.3 μm and 5 × 10¹⁷ cm⁻³ doping level. The top *p*⁺⁺ GaAs contact layer was highly doped (>5 × 10¹⁹ cm⁻³). Both the *p*-cladding layer and the GaAs contact layer were doped with carbon using CCl₄. The active region consists of two In_{0.20}Ga_{0.80}As undoped QWs which were separated by Al_{0.20}Ga_{0.80}As barrier layers, while the bottom *n*-type cladding layers were doped with Si. TiO₂ dielectric capping layers with nominal thickness of 150 nm were deposited on the top GaAs contact layer by electron beam evaporation. The samples were annealed under Ar flow in a rapid thermal annealer in the temperature range of 875–925 °C for 60 s. During annealing, the samples were sandwiched between two GaAs substrates to minimize arsenic loss. Reactive ion etching (RIE) using Ar/CHF₃ chemistry with rf power of 200 W was used to remove TiO₂ after annealing. Low temperature photoluminescence (PL) at 77 K was performed to characterize the energy shift of the emission from the active region, using a diode-pumped solid-state frequency doubled green laser at 532 nm for excitation and a cooled InGaAs photodetector at the output slit of a 0.5 m monochromator. Electrochemical capacitance voltage (*EC*–*V*) profiling measurements were carried out using a Bio-Rad *EC*–*V* profiler model PN-4300PC using front contacts. Double-crystal x-ray diffraction (DCXRD) measurements were performed using a Bede QC2a system.

^{a)}Electronic mail: plg109@rpsphysse.anu.edu.au

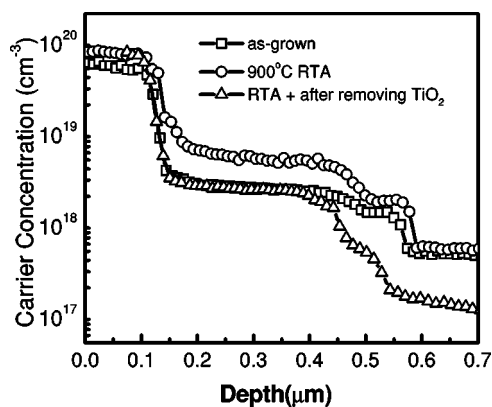


FIG. 1. $EC-V$ depth profile of carrier concentration in the InGaAs/AlGaAs laser diode structures doped with carbon.

Figure 1 shows the carrier concentration profile of the C-doped InGaAs/AlGaAs laser structures before and after annealing. It can be seen that after RTA, the concentration of electrically active carbon dopants increases by 29% in the top GaAs layer and by 58% in the AlGaAs confinement layer for the uncapped sample, compared with the as-grown wafer. The increase of the hole density after annealing at this high temperature is surprising, since all previous studies made on carbon doped layers grown by a variety of methods such as molecular beam epitaxy (MBE), gas source MBE, and MOCVD reported carbon activation after annealing at about a 500 °C, but dopant passivation after annealing at temperatures in the range 700–900 °C.^{8–11} For the sample annealed with a TiO₂ layer, the TiO₂ layer was removed using RIE before $C-V$ measurement. The carrier profile for first 0.07 μm of the surface is not shown, since part of the top GaAs layer was also removed during the RIE of the TiO₂ layer. In addition to that, part of the remaining top GaAs contact layer was damaged by the etching process, so we mostly rely on the data concerning the AlGaAs p -type cladding layer inside the structure. In this layer, the doping profile was comparable to the carrier profile in the as-grown samples.

In order to further investigate the intriguing $EC-V$ results, DCXRD was performed on these samples. The x-ray rocking curves taken before and after annealing for both uncapped and TiO₂ capped samples are depicted in Fig. 2. Carbon has a smaller covalent radius (0.77 Å) compared to As (1.20 Å) or Ga (1.26 Å).¹² As a result, when present

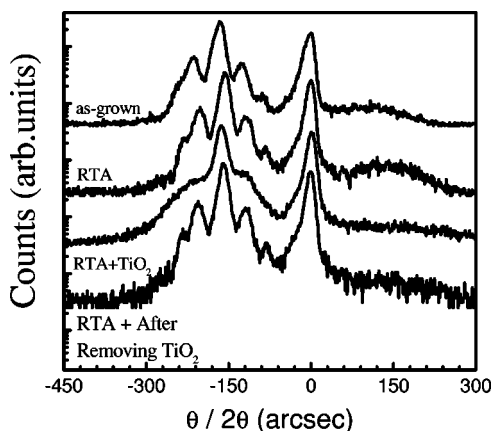


FIG. 2. DCXRD spectrum of C-doped InGaAs/AlGaAs laser structures.

in excess of about 10^{19} cm^{-3} , it causes lattice contraction that can be easily monitored using DCXRD in InGaAs/AlGaAs/GaAs structures because all other layers are under compressive stress. Thus, the peak on the right (tensile) side of the substrate peak in x-ray rocking curves is directly related to the presence of carbon in the highly doped p^{++} top GaAs contact layer. The doping level in the AlGaAs cladding layer is too small to give a sizeable effect in these curves. Modeling of the x-ray rocking curve indicates a layer of slight strain for the as-grown sample, with an average contraction $\Delta a/a = 412 \times 10^{-6}$. For the annealed sample the lattice contraction is $\Delta a/a = 520 \times 10^{-6}$, corresponding to a 26% increase in lattice contraction. This value should be compared with 29% electrical activation obtained from the $EC-V$ measurements. Due to the thickness of the top contact layer, the C-related peak of the DCXRD spectrum is small and broad, resulting in an error bar of 5%–10%. However, we refer to the relative differences between two x-ray spectra and the error for the difference is smaller than the added error for each spectrum because all layers have the same thickness and only the amount of strain differs after annealing.

For the sample annealed with TiO₂ layer, if this layer is not removed after annealing, the curvature that it imposes on the laser structure is large enough to destroy most of the interference fringes on compressive side and partly on the tensile side of the x-ray rocking curve. On the other hand, when the TiO₂ is removed by etching, a considerable part of the top p^{++} GaAs is removed too, and the corresponding amplitude in the x-ray rocking curve becomes too small to be picked up in the dynamical range of the detector (Fig. 2, bottom curve). If the $\Delta a/a = (520 \pm 25) \times 10^{-6}$ lattice mismatch is only attributed to the presence of substitutional carbon C_{As}^- , the corresponding carrier concentration in the p^{++} GaAs carbon doped layer would amount to $6.5 \times 10^{19} \text{ cm}^{-3}$, in good qualitative agreement with the $EC-V$ measurements that show a corresponding value of $7.4 \times 10^{19} \text{ cm}^{-3}$. The estimation of the lattice mismatch caused the presence of carbon was made using the following relationship:¹³ $\Delta a/a = -7.95 N_{C,As} \times 10^{-18} - 1.50 N_{C-C} \times 10^{-18} - 6.94 N_{C-H} \times 10^{-18}$ where $N_{C,As}$, N_{C-C} , N_{C-H} are the densities (in cm^{-3}) of substitutional carbon, C–C interstitial pairs (that become the major cause of acceptor compensation at high doping levels) and passivation centers due to incorporation of hydrogen in an interstitial site, respectively. If we assume that the passivation is due to only C–C pairs (i.e., $N_{C-H} = 0$), then the change in lattice contraction after annealing is 22% for a 29% change in electrical activation. On the other hand, if we assume the passivation is due to only C–H pairs (i.e., $N_{C-C} = 0$), then the change in lattice contraction after annealing is only 3% for a 29% change in electrical activation. Clearly from the earlier estimation, the 22% change in lattice contraction is closer to 26% as determined by DCXRD measurements. It can thus be concluded that the carbon activation after annealing at 900 °C is mostly likely due to the removal of C–C interstitial pairs, contrary to previous work that reported the introduction of these compensation centers.^{8–10,13}

Figure 3(a) displays the low temperature (77 K) photoluminescence spectra of C-doped InGaAs/AlGaAs QW samples before and after annealing. The emission peak was observed at 903 nm for the as-grown sample, due to recombination in the InGaAs quantum well active region. It is interesting to note that the linewidth and the intensity of the PL

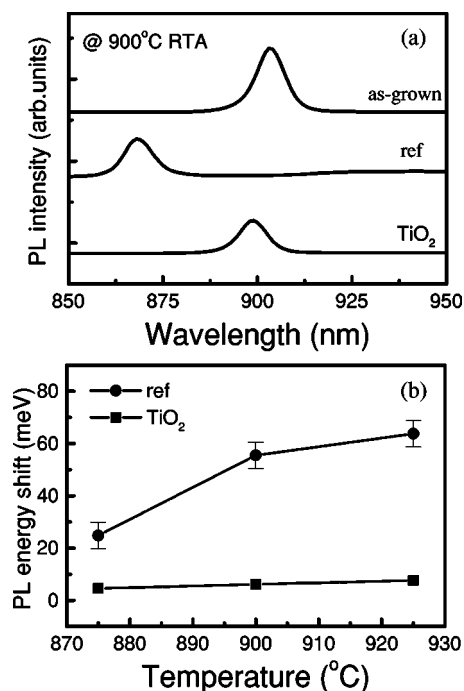


FIG. 3. (a) Low temperature photoluminescence spectra of C-doped InGaAs/AlGaAs laser structures annealed at 900 °C, 60 s. (b) PL energy shift of C-doped InGaAs/AlGaAs laser structures as a function of annealing temperature (60 s) for TiO₂ capping layers in comparison with the reference region.

emission do not change significantly after annealing at 900 °C, which indicates that the good quality of quantum well is maintained. Figure 3(b) displays the energy shift of the PL peak from the InGaAs/AlGaAs laser structures as a function of annealing temperature. At 900 °C, the thermal effect contributed to about 50 meV. In contrast, very little shift (<10 meV) was observed after annealing for the samples that capped with TiO₂, which indicated that the thermal intermixing was greatly suppressed by TiO₂ layer. The reason for suppression of interdiffusion by TiO₂ has previously been reported⁶ and is related to the difference in lattice expansion coefficient between semiconductor and TiO₂ layer. Tensile stress imposed by the TiO₂ on the semiconductor suppresses the diffusion of point defects (group III vacancies) which causes the interdiffusion. The layer of TiO₂ also suppresses the additional electrical activation of the carbon atoms in comparison to a sample without the capping layer, as seen from the *EC-V* results. For the C-C interstitial pairs

to be electrically activated, not only the bonds need to be broken and also the C atoms have to sit in the lattice sites of group V atoms (*p* type). It is unlikely that suppression of the group III vacancy diffusion is the cause for the suppression of electrical activation. Most likely with the TiO₂ cap, As outdiffusion from the semiconductor surface is inhibited or minimized. The creation of As vacancies for the sample capped with TiO₂ is much reduced compared to an uncapped sample and, hence, the additional dopant activation was not observed in this case.

In summary, we have studied the suppression of atomic interdiffusion in C-doped InGaAs/AlGaAs QW p-i-n laser structures using TiO₂ cap layers. The *EC-V* profiles and x-ray rocking curves clearly show that some of the carbon dopant is activated after annealing at 900 °C without any capping layer, and not passivated as previously reported. The electrical activation of carbon does not occur if the annealing is made using a TiO₂ dielectric layer due to suppression of As outdiffusion. For the sample coated with TiO₂, a negligible PL shift was observed after annealing at 900 °C, indicating that the thermal intermixing is greatly inhibited by TiO₂ capping layers. This shows that the use of TiO₂ is a very attractive option for optoelectronic integration.

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- ¹E. H. Li, *Semiconductor Quantum Wells Intermixing* (Gordon and Breach, Amsterdam, 2000).
- ²J. H. Marsh, *Semicond. Sci. Technol.* **8**, 1136 (1993).
- ³H. H. Tan, J. S. Williams, C. Jagadish, P. T. Burke, and M. Gal, *Appl. Phys. Lett.* **68**, 2401 (1996).
- ⁴H. H. Tan and C. Jagadish, *Appl. Phys. Lett.* **71**, 2401 (1997).
- ⁵D. G. Deppe and N. Holonyak, Jr., *J. Appl. Phys.* **64**, R93 (1988).
- ⁶L. Fu, P. Lever, H. H. Tan, C. Jagadish, P. Reece, and M. Gal, *Appl. Phys. Lett.* **82**, 2613 (2003).
- ⁷M. Buda, J. Hay, H. H. Tan, J. Wong-Leung, and C. Jagadish, *IEEE J. Quantum Electron.* **39**, 625 (2003).
- ⁸M. C. Hanna, A. Majerfeld, and D. M. Szmyd, *Appl. Phys. Lett.* **59**, 2001 (1991).
- ⁹W. E. Hoke, P. J. Lemonias, D. G. Weir, H. T. Hendriks, and G. S. Jackson, *J. Appl. Phys.* **69**, 511 (1991).
- ¹⁰C. Abernathy, S. Pearton, M. Manasreh, D. Fisher, and D. Talwar, *Appl. Phys. Lett.* **57**, 294 (1997).
- ¹¹G. Li and C. Jagadish, *Appl. Phys. Lett.* **69**, 2551 (1996).
- ¹²C. Giannini, A. Fischer, C. Lang, K. Ploog, and L. Tapfer, *Appl. Phys. Lett.* **61**, 183 (1992).
- ¹³W. Li and M. Pessa, *Phys. Rev. B* **57**, 14627 (1998).