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Built-in electric field enhancement/retardation on intermixing

C. D. Xu, T. Mei,^{a)} and M. K. Chin

School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

J. R. Dong and S. J. Chua

Institute of Materials Research and Engineering, Singapore 117602, Singapore

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The built-in electric field may impose a drift on charged point defects and may thus enhance or retard the intermixing during annealing. Electric field is built-in near the surface due to the pinning of surface Fermi level after argon plasma treatment on InP surfaces of InP/InGaAs quantum well samples. Subsequent annealing leads to different intermixing results due to the different field directions on InP cap layers in different doping types. Experiments also showed different influences of the built-in field on the two sublattices largely due to different charge numbers of point defects on the respective sublattices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2805018]

In developing various intermixing techniques¹⁻⁹ for photonic integrated circuit applications that tune the energy band gap in the postgrowth process, attention has often been paid on how point defects are introduced to enhance lattice interdiffusion, whereas the influence of defect migration has seldom been addressed. Seebauer and Kratzer have shown that the migration of charged defects is affected by the band bending at the defected interface in their work on charged point defects in semiconductors.¹⁰ The field-induced drift dominates the diffusion of charged defects due to the high electric field in the space charge region for highly doped samples.¹⁰ Apparently, the situation of defect migration may also influence the lattice interdiffusion such that the density of point defects is not the only factor that determines the result of intermixing. The built-in electric fields due to Fermi level (FL) lineup in materials with different types and levels of doping have different influences on migration of charged point defects, which lead to either enhancement or retardation of lattice interdiffusion. This phenomenon is demonstrated and investigated in this article using single quantum-well (QW) samples with *p*-type, undoped (*u*), and *n*-type InP top layers. Samples were processed using inductively coupled argon plasma (Ar-ICP) enhanced quantum well intermixing, whereas the intermixing results obtained in the three types of samples can be explained by the effect of the built-in electric field at the top cap layer due to the pinning of FL on InP surface.

The lattice-matched In_{0.53}Ga_{0.47}As/InP single QW sample structures used in this study were grown by metal organic vapor phase epitaxy on (100) oriented *n*⁺-type InP substrates. A 3.5 nm undoped In_{0.53}Ga_{0.47}As well layer is sandwiched between two 200 nm undoped InP layers, whereas the three types of samples were completed with an 800 nm InP cap layer undoped (weakly *p*-type due to unintentional background doping) or doped to $2 \times 10^{18} \text{ cm}^{-3}$ (Zn for *p* type and S for *n* type). The argon plasma process was done on samples for 1 min in Plasmalab System 100 with the rf power and the ICP power set at 400 and 500 W, respectively. After the plasma process, the rapid thermal annealing (RTA) processes were performed under flowing N₂ ambient

at 550 °C for durations ranging from 30 to 240 s. InP proximity caps were used to prevent the surfaces from P outdiffusion during annealing. No thermal shift was observed on all RTA-only samples under the given RTA conditions. The polarized photoluminescence (PPL) was measured from cleaved (110) edge facets of the samples at room temperature with a 1064 nm crystal laser for excitation.¹¹

Figure 1 shows the measured TE- and TM-PPL spectra for a series of annealing durations. The peak wavelengths for electron-heavy-hole (C-HH) and electron-light-hole (C-LH) ground-state transitions were obtained by fitting two-peak Gaussian curves to the TE- and TM- PPL spectra correlatively, and the diffusion lengths on the group V and III sublattices, L_V and L_{III} , were calculated from C-HH shift and C-LH shift.¹¹ The blueshifts of C-HH and C-LH transitions and the derived L_V and L_{III} are shown in Figs. 2(a) and 2(b).

FIG. 1. (Color online) Measured TE- and TM-PPL spectra for different annealing durations for samples with *p*-, *u*-, and *n*-InP cap layers experienced ICP exposure and RTA at 550 °C.

^{a)}FAX: +65-67933318. Electronic mail: etmei@ntu.edu.sg

FIG. 2. (Color online) Measured C-HH and C-LH blueshifts (a) and calculated diffusion lengths of group V and group III sublattices (b) vs annealing duration.

These figures show that intermixing in the three types of samples evolved in different ways during annealing. The largest blueshift is given by the sample with the *p*-type cap layer, while the smallest shift is given by that with the *n*-type cap.

In these samples, defects were created during the argon plasma process, in which P was preferentially sputtered^{12–15} to leave an In-rich region within a depth of the order of 150 Å or less.¹⁶ These defects were responsible for promoting intermixing in the RTA process. The effect of grown-in defects is negligible as no thermal shift was observed on RTA-only samples. The differences of the resulting diffusion lengths on the three samples imply different point defect fluxes from the surface toward the bulk. The flux of a certain type of defects J can be expressed as¹⁷

$$J = -D(\partial N/\partial x) + z\mu N\varepsilon(x), \quad (1)$$

where N is the defect concentration, D is the diffusion coefficient, z is the defect's charge number, μ is the mobility, and ε is the electric field. The defect flux contains a diffusion component due to the concentration gradient and a drift component induced by electric field. The effect of electric field ought to be investigated in order to explain different intermixing results obtained from samples with differently doped InP caps.

As reported by Deng *et al.*,¹⁸ both *n*- and *p*-doped InP encountered band bending due to the FL pinning at the surface after low energy argon bombardment. After high dosage bombardment, the FL is pinned at a similar level around 0.4 eV below the conduction band minimum (CBM).¹⁸ Other groups also reported the surface FL pinning at -0.4 to -0.6 eV from CBM.^{13,14,19} Newman *et al.* reported a smaller and finite range (within 0.2 eV) for the pinning level at *p*- and *n*-InP surfaces.²⁰ In our work, we verified the surface FL before and after ICP exposure on the undoped sample by x-ray photoemission spectroscopy (Fig. 3). In agreement with the published results,^{13,14,18–20} the FL changed from -0.9 to -0.5 eV after 1 min ICP exposure. Due to the pin-

FIG. 3. (Color online) Measured XPS spectra of an as-grown InP sample and a sample after argon-ICP exposure for 1 min. The inset shows that the binding energy of $\text{In}3d_{5/2}$ shifted after ICP exposure.

ning of surface FL, the band is bent 0.9 and 0.4 eV down, resulting in a positively charged surface on *p*- and *u*-InP caps, respectively, and 0.4 eV upward, resulting in a negatively charged surface for *n*-InP cap (Fig. 4). This band bending leads to a built-in electric field near the surface.

In the In-rich vicinity near the surface formed due to P preferential sputtering, major point defects include V_P vacancies, In_i interstitials, and In_P antisites. For the FL at -0.4 to -0.6 eV from CBM, the In_i and V_P in the space charge region are predicted to have $+2/+3$ and $+1$ charge states, respectively.^{21,22} The antisite defects are not considered in the discussion as they diffuse much more slowly than vacancies and interstitials. Obviously, as seen in Fig. 4, the motion of In_i and V_P was enhanced by the inward built-in electric field in *p*- and *u*-InP, but was suppressed by the outward field in *n*-InP. This explains the experimental results in Fig. 2 that samples with *p*- and *u*-InP caps achieved greater diffusion lengths than the sample with *n*-InP cap. The larger built-in electric field in *p*-InP also justifies its larger diffusion length than that for *u*-InP cap.

It was suggested that the decreased In/P ratio after annealing was due to the diffusion of excess In into the bulk,¹³ whereas it was also reported that much higher In/P ratio was

FIG. 4. Schematic band diagrams for (a) *p*-InP, (b) *u*-InP, and (c) *n*-InP showing enhancement [(a) and (b)] or suppression (c) of the diffusion of positively charged point defects from surface to bulk under the electric field within the space charge region.

obtained at the surface after annealing for n -InP than p -InP.²³ This is also explainable by the different direction of the built-in surface electric field, although no reason was stated therein.

It is also noted that intermixing did not take place on the two sublattices equally. Both cases of dominant group III and group V intermixing have been observed in Fig. 2. It is not simply a single factor to determine which sublattice of greater intermixing will occur. However, by comparing the diffusion length curves of p - and u -InP cap samples to those of the n -InP cap sample, we see that the difference of group III intermixing is larger, e.g., $\Delta L_{\text{III}}=10$ Å versus $\Delta L_{\text{V}}=7$ Å observed from p - and n -InP curves at 240 s. This shows that the influence of electric field on intermixing is more prominent for group III sublattice. Such influence is subjective to the charge number, the mobility, and the concentration of defects on the respective sublattice according to Eq. (1). The difference of the electric field influence is largely due to the substantial difference of the charge numbers, i.e., In_i 's charge number is double or triple of that of V_p . The difference of the influence is even more clearly illustrated by comparing u - and n -InP curves, e.g., $\Delta L_{\text{III}}=9.5$ Å versus $\Delta L_{\text{V}}=4$ Å at 240 s. In the p -InP cap sample, this was made less obvious due to the boosted group V intermixing. As reported in Refs. 24–26, the $[\text{V}_p\text{-Zn}]$ complexes can be easily formed in Zn-doped InP, whereas the migration energy of V_p in such a form decreases from 1.8 ± 0.2 eV to 1.3 eV.²⁶ Therefore, group V intermixing is boosted in the p -InP cap sample via such a mechanism, which enhances the diffusion component of the defect flux.

In summary, the effect of built-in electric field on intermixing is investigated in this study. The flux of charged defects is enhanced in samples with p - and u -doped caps and suppressed in that with n -doped cap because of opposite drift components under different field directions created at the surface due to Fermi level pinning, thus resulting in enhancement or retardation effect on intermixing. The field effect on intermixing is more prominent on group III sublattice than on group V sublattice, on which the difference of charge numbers of In_i and V_p has major contribution. This work may suggest a supplementary approach of control and optimization in an intermixing study.

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