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Quantum well intermixing in GaInNAs/GaAs structures

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We report on the characteristics of quantum well intermixing in GaInNAs/GaAs structures of differing N content. Rapid thermal annealing combined with SiO₂ caps deposited on the surface of the samples is used to disorder 1.3 μm GaInNAs/GaAs multiquantum wells which have been preannealed *in-situ* to the stage of blueshift saturation. The different effects of two capping layer deposition techniques on the interdiffusion of In–Ga have been compared, particular regarding the role of sputtering processes. The dependence of quantum well intermixing-induced photoluminescence blueshift on N concentration has provided extra information on the intrinsic properties of the GaInNAs/GaAs material system. We found that the blueshift decreases as the N concentration increases. This finding not only rules out the possible mechanism of N–As interdiffusion, but also demonstrates the alloy stability of GaInNAs due to the strong bond between In–N. © 2003 American Institute of Physics. [DOI: 10.1063/1.1627950]

I. INTRODUCTION

The quantum well intermixing (QWI) technique has proven to be one of the most advantageous approaches to modifying the properties of semiconductor quantum well structures in a controllable way.¹ The primary advantage of QWI is that it avoids complicated regrowth processes, and therefore is cost effective and reliable. Indeed, QWI has been employed in various material systems for advanced optoelectronic devices and photonic integrated circuits (PICs) or optoelectronic integrated circuits (OEICs).^{2–4} In recent years, dilute III–N–V alloys, especially GaInNAs, have been recognized as materials which promise high performance optical communication systems.⁵ Based on the favorable properties of GaInNAs/GaAs structures, various devices have been developed including ridge waveguide lasers,⁶ vertical cavity surface-emitting lasers,⁷ vertical cavity semiconductor optical amplifiers,⁸ and saturable Bragg reflectors for mode-locking applications.⁹ In order to extend the application of this material system, especially for PICs or OEICs, selective QWI has been demonstrated recently in GaInNAs/GaAs structures using different SiO₂ deposition methods and post-thermal annealing.¹⁰ Under thermal annealing at a temperature lower than 800 °C, a strong QWI process occurred in sputtered SiO₂-capped samples, while a negligible effect oc-

curred in plasma enhanced chemical vapor deposited (PECVD) SiO₂-capped samples. It was shown that the QWI is due to the interdiffusion of In–Ga composition, as opposed to N–As, between the quantum wells (QWs) and the barriers. In this article, we report more detailed studies of the dependence of interdiffusion on annealing temperatures and capping conditions. We have clarified that the point defects generated by atomic bombardment during the sputtered SiO₂ deposition play a contributory role in two ways. First, the point defects at the interface enhance the outdiffusion of Ga atoms into the SiO₂ layer and lead to lowering of the threshold temperature for QWI. Second, the point defects diffuse into the quantum wells and directly promote the interdiffusion of In–Ga between the QWs and the barriers. We compare the carrier lifetime in disordered and nondisordered samples, and show that the defects diffused into the active QWs act as nonradiative centers and decrease the photoluminescence (PL) decay time. In addition, we studied the N-concentration dependence of QWI in GaInNAs/GaAs structures. We found that the blueshift decreases as the N concentration increases. This finding not only rules out the possible mechanism of N–As interdiffusion, but also demonstrates the alloy stability of GaInNAs due to the strong In–N bond.

II. EXPERIMENT

The GaInNAs/GaAs multiquantum well (MQW) heterostructures were grown by molecular-beam epitaxy on semi-

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insulating GaAs (100) substrates. The structures consisted of five GaInNAs QWs embedded in GaAs barriers and capped by a 40 nm layer of GaAs. The nominal thicknesses for the well and barrier layers are 8 and 30 nm, respectively. Ultrahigh-purity N₂ was injected through a radio-frequency (rf) plasma source operating at a frequency of 13.56 MHz to generate active N species. The growth temperature was 450 °C. The indium content in the quantum wells is 27.2% as measured from a GaInAs reference sample, while the N content varied from 0.5% to 1.14% for specific samples as determined by high resolution x-ray diffraction analysis. The as-grown structures have previously been the subject of detailed PL excitation (PLE) spectroscopic studies.¹¹ The completed structures were annealed *in situ* at 700 °C under nitrogen flow for 30 min. This annealing process increased the PL intensity and assured blueshift saturation as demonstrated by the negligible additional blueshift under further annealing below 800 °C. The material was cleaved into samples ~3 mm×~3 mm which were then left either uncapped (for reference) or coated with ~50-nm-thick SiO₂-capping layers deposited by either PECVD or rf sputtering. Then, rapid thermal annealing (RTA) was performed in a rapid thermal processing system. During thermal processing, the samples were kept in a flowing nitrogen ambient, and a silicon or GaAs wafer covered the surface to protect the samples. The PL measurements were performed under excitation by a high-power diode laser (670 nm). The PL signal was dispersed by a 0.46-m-grating monochromator and detected by a thermoelectrically cooled Si/InGaAs detector using standard lock-in techniques. For time-resolved PL (TRPL) measurement, the sample was optically pumped with 290-nm-laser pulses of 10 ps width and 9.5 MHz repetition rate. In this case, the PL signal was collected and analyzed with a 1.3-m-grating monochromator equipped with a microchannel plate multiplier tube used in a single-photon counting mode. The decay lifetimes were measured at the spectral peak positions of each sample at 10 K.

A secondary ion mass spectroscopy (SIMS) technique was used to measure the composition depth profile of selected samples. This measurement was performed using a Cs⁺ primary ion source as a sputtering gun and positive secondary ion as an analysis source.

III. RESULTS AND DISCUSSION

Figure 1 shows typical room-temperature PL spectra of PECVD SiO₂-capped and sputtered SiO₂-capped Ga_{0.728}In_{0.272}N_{0.0114}As_{0.9886}/GaAs MQW samples annealed at various temperatures for 180 s. For sputtered SiO₂-capped samples, RTA gives rise to a clear blueshift of PL, while the PL peaks in PECVD SiO₂-capped samples have barely shifted. The PL energy shifts of the samples with N content of 1.14% as a function of annealing temperature are shown graphically in Fig. 2 for three different capping conditions. Noncapped samples show no energy shift after annealing up to 800 °C, which confirms that the *in situ* annealing had indeed led to a saturated PL blueshift. The small shift at 850 °C represents the native thermal diffusion of composition between the QWs and the barriers. The negligible interdiffusion

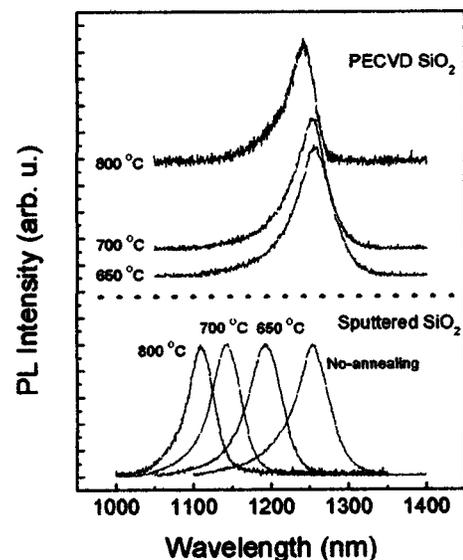


FIG. 1. Normalized PL spectra of Ga_{0.728}In_{0.272}N_{0.0114}As_{0.9886}/GaAs structures annealed at different temperatures for 180 s. The upper and lower groups of curves represent the samples capped with PECVD and sputtered SiO₂, respectively. Some of the spectra have been shifted vertically for clarity.

in the temperature range of interest confirms the unambiguous assignment of the QWI process. Our investigations by using PLE and SIMS analyses have shown that the large PL energy shift in sputtered SiO₂-capped samples corresponds to the increase of the band gap in the QW structure due to the enhanced interdiffusion of In–Ga between the GaInNAs QWs and the GaAs barriers.¹⁰ Meanwhile, PECVD SiO₂-capped samples exhibit very little blueshift even when the annealing temperature is as high as 800 °C. By 850 °C, however, such samples show a large blueshift compared with the noncapped sample, which clearly demonstrates some involvement of the SiO₂ layer at a high temperature. This re-

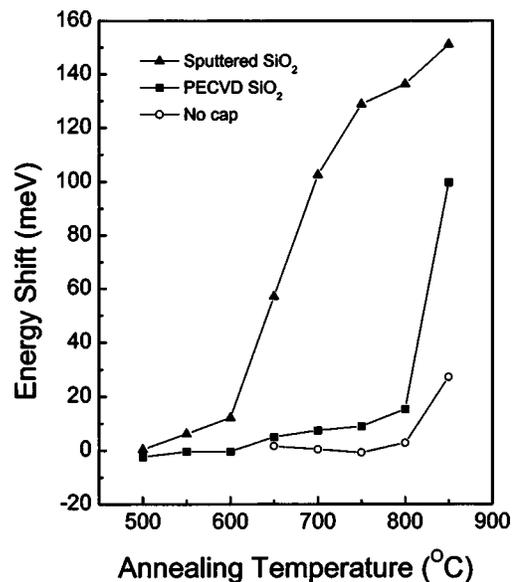


FIG. 2. Dependence of PL energy shifts of Ga_{0.728}In_{0.272}N_{0.0114}As_{0.9886}/GaAs structures with different capping conditions on annealing temperatures. The annealing duration is fixed to be 180 s.

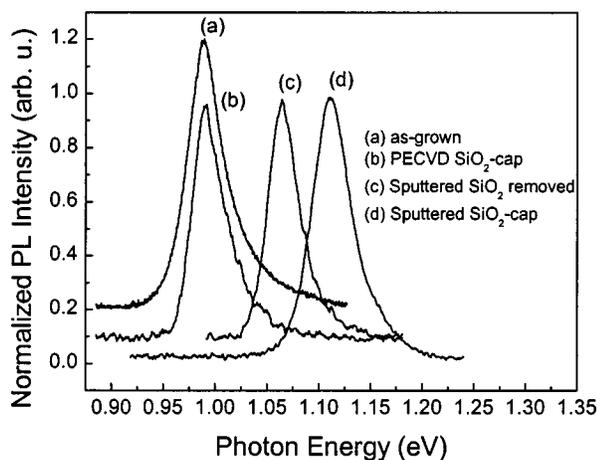


FIG. 3. Normalized PL spectra of $\text{Ga}_{0.728}\text{In}_{0.272}\text{N}_{0.0114}\text{As}_{0.9886}/\text{GaAs}$ structures with different capping conditions annealed at $750\text{ }^\circ\text{C}$ for 180 s. Curve (a) represents the spectrum of as-grown sample for reference.

result is similar to the well-known impurity-free vacancy disordering (IFVD) process.^{12–14} The IFVD process has been ascribed to the outdiffusion of Ga into the SiO_2 cap during the annealing process. This results in the generation of Ga vacancies close to the semiconductor surface which then thermally diffuse into the active region during the annealing process and promote the interdiffusion of atoms in the wells and barriers.¹² Our SIMS composition analysis has confirmed both the outdiffusion of Ga atoms into the PECVD SiO_2 layer and the interdiffusion of In–Ga between the QWs and the barriers in $850\text{ }^\circ\text{C}$ annealed sample (not shown here).

In order to elucidate the role which the sputtering process played in QWI, we removed the sputtered SiO_2 layer and then annealed the sample. We found that in this case, the postannealing gives rise to a PL blueshift of about 76 meV, as shown in Fig. 3, which illustrates the PL spectra with different capping processes after the same annealing conditions ($750\text{ }^\circ\text{C}$ for 180 s). As there is no involvement of the SiO_2 -capping layer in the cap-removed case, this result implies that point defects have diffused into the QW zone and have promoted the interdiffusion directly. It is also noted that the sputtered- SiO_2 -capped sample demonstrated an extra blueshift of about 47 meV, which suggests the involvement of SiO_2 layer in the interdiffusion when present. This additional interdiffusion can be attributed to Ga outdiffusion induced disordering process (IFVD). This is confirmed in the composition analysis by means of SIMS.

Figure 4 shows the complete SIMS composition profile of a $\text{GaInNAs}/\text{GaAs}$ sample with 1.14% N content which was capped with sputtered SiO_2 and then annealed at $750\text{ }^\circ\text{C}$ for 180 s. As the sputtering rate for each layer has not been calibrated, we use the operating time on the horizontal axis to represent the depth. The position of the five QW structures is clearly indicated by the peaks of In and N composition. The extra N peak at the silica–sample interface is ascribed to the adsorption of N from the air. In this intermixed sample, the N concentration is about the same as the as-grown one, but the In concentration in the QW is substantially reduced due to the interdiffusion. This result is entirely consistent with our previous observation that the interdiffusion takes

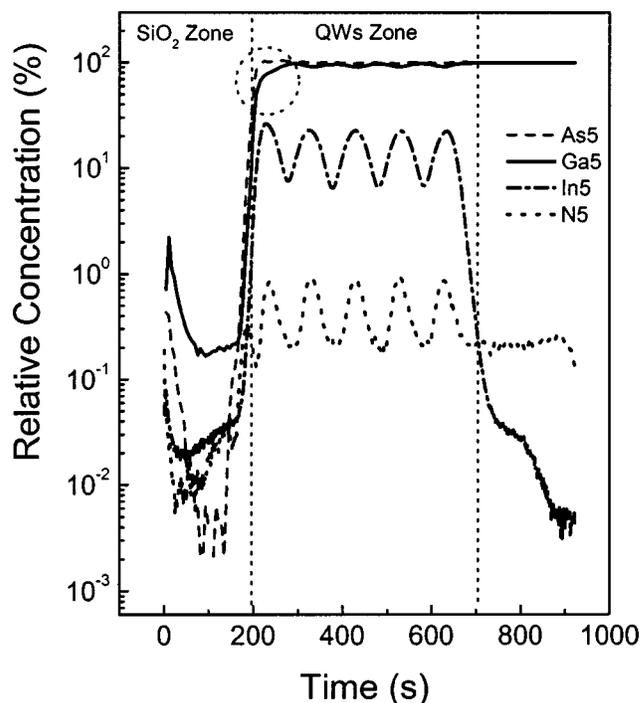


FIG. 4. Complete composition profiles by SIMS of a $\text{Ga}_{0.728}\text{In}_{0.272}\text{N}_{0.0114}\text{As}_{0.9886}/\text{GaAs}$ MQW sample which was capped with sputtered SiO_2 and has been annealed at $750\text{ }^\circ\text{C}$ for 180 s.

place between the group-III atoms.¹⁰ Moreover, it is noted that near the dielectric–sample interface, the Ga composition decreases substantially while the As composition does not (see the Ga and As composition distribution highlighted by the circle in Fig. 4). When looking at the composition distribution in the silica layer close to the sample interface, it is found that the Ga content is much higher than other elements. This result provides direct evidence of Ga outdiffusion from the sample into the SiO_2 layer. It has been noted earlier that in PECVD SiO_2 -capped samples, IFVD-induced QWI does not take place at $750\text{ }^\circ\text{C}$ but does at temperatures higher than $850\text{ }^\circ\text{C}$. The lowering of the temperature for IFVD is apparently related to the point defects generated during the sputtering process. By comparison, it is concluded that sputtered- SiO_2 -capped samples promote the QWI in two ways. First, the point defects generated by the sputtering process diffuse into the active zone and directly lead to the enhancement of interdiffusion of In–Ga. Second, the point defects promote the outdiffusion of Ga atoms into the capping layer, and which leads to extra diffusion and lowering of the temperature threshold for QWI. The former mechanism is very similar to the well-known ion implantation-induced QWI,¹⁵ and the latter one to the IFVD process. The simultaneous presence of these two mechanisms provides advantages for practical application. First, the lowering of threshold temperature for QWI is favorable to device processing because unwanted high-temperature processes are avoided. Second, the strong QWI allows the band gap modification limitation set by the saturation effect due to the damage of the crystalline surface in the implantation-induced QWI process to be surpassed,¹⁵ and makes possible the real-

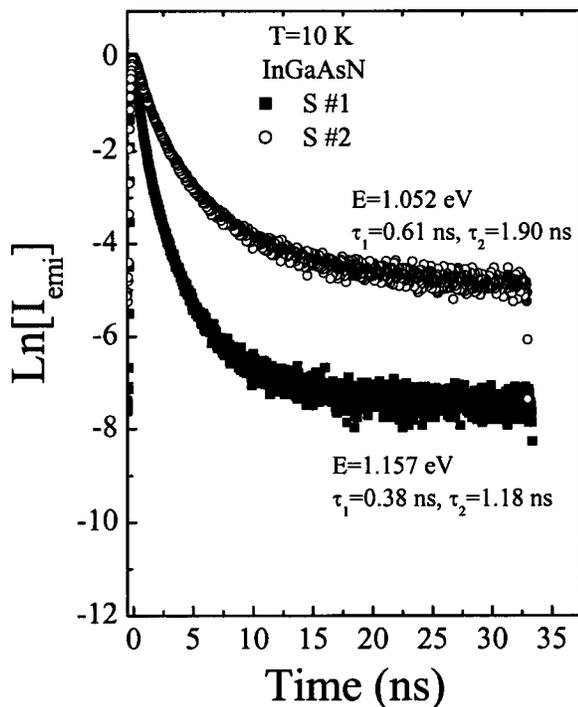


FIG. 5. TRPL decay for $\text{Ga}_{0.728}\text{In}_{0.272}\text{N}_{0.0114}\text{As}_{0.9886}/\text{GaAs}$ structures annealed at 750°C for 180 s. S1 and S2 represent samples with PECVD and sputtered SiO_2 caps, respectively.

ization of spatially selected multibandgaps in a single annealing process.

Figure 5 shows the temporal profiles of the PL intensity at a temperature of 10 K detected at the PL peak energy for two different samples. One of the samples is capped with PECVD SiO_2 and annealed at 700°C for 180 s, and has not been disordered as shown in Figs. 1 and 2. The other is capped with sputtered SiO_2 , annealed under the same conditions, and has been apparently disordered. In both cases, the PL decay cannot be fitted with a single-exponential function, but can be well fitted by double-exponential function. This feature is typical of PL from localized states; the early stage with fast decay time is associated with the transfer of carriers from shallow localized states to deeply localized states and the subsequent slow decay is related to the radiative lifetime of carriers at the corresponding energy levels.¹⁶ Compared with the nonintermixed sample, the two decay components in the intermixed sample decrease from 0.61 and 1.9 ns to 0.38 and 1.18 ns, respectively. This reduction in the lifetimes can be ascribed to point defects introduced in the QWs which act as nonradiative recombination centers.¹⁷ Of course, these nonradiative recombination centers include both the point defects generated by sputtering which have diffused into the QW zone and the Ga vacancies due to the outdiffusion of Ga into the SiO_2 -capping layer.

Figure 6 shows the PL energy shift as a function of temperature for samples of various N concentrations. All of the samples demonstrate a similar tendency: Below 600°C , there is very little QWI, between 600 – 750°C the PL energy increases rapidly, and after that point the rate of increase slows down and gradually saturates. It is interesting to note that in the N concentration range from 0.5% to 1.14%, the PL en-

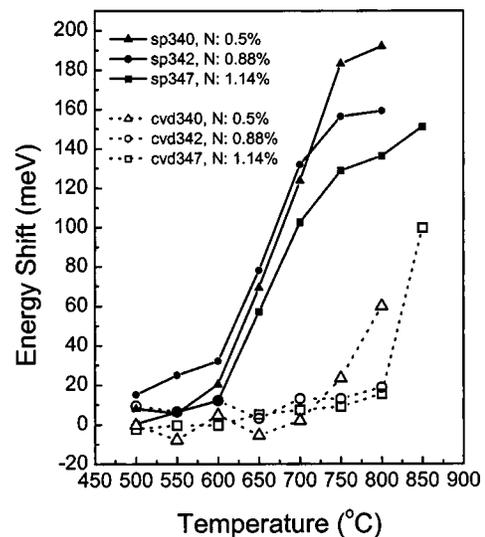


FIG. 6. Dependence of PL energy shifts of GaInNAs/GaAs structures with different N content on annealing temperatures. The annealing duration is fixed to be 180 s. The solid and empty symbols denote sputtered and PECVD SiO_2 -capped samples, respectively.

ergy shift increases with the decrease of N content. This tendency provides further support for our contention that the QWI originates from the interdiffusion of In–Ga rather than N–As, because otherwise the PL blueshift would increase with the increase of N content in the QWs. In fact, as shown by the SIMS data of Fig. 7, the contrast of indium content between the QWs and the barriers (inverse indication of the degree of interdiffusion) increases with the N concentration. Therefore, the N-concentration dependent PL blueshift is indeed correlated with the dependence of the interdiffusion of In–Ga on N concentration in the QWs. On the other hand,

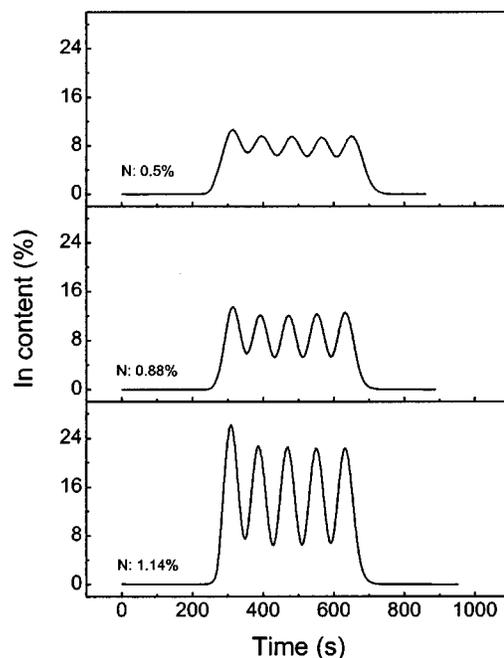


FIG. 7. Comparison of In composition profiles of GaInNAs/GaAs structures with different N contents which have been capped with sputtered SiO_2 and annealed at 750°C for 180 s.

the observed features also suggest that the introduction of N into InGaAs increases the stability of the material, which is apparently consistent with the fact that the bond strength of N–In is larger than that of As–In. Since the N atoms demonstrate the effect of inhibiting the In atoms in GaInNAs QWs diffusing out of the QWs, it is also suggested that after *in situ* annealing, the N atoms are mainly bonded to In atoms. Given the fact that in as-grown (non-*in situ* annealing) samples, the N environment is dominated by Ga–N bonds (due to the 73% composition of Ga), the N content dependence of QWI seems to provide supportive evidence that the *in situ* annealing may change the bond configuration of N from Ga-rich in as-grown sample to In-rich after *in situ* annealing.^{18–21}

IV. CONCLUSIONS

We have systematically studied the properties of SiO₂-cap-layer-induced QWI in GaInNAs/GaAs structures of differing N content. RTA, combined with SiO₂ caps deposited on the surface of samples by different techniques, has been used to disorder 1.3 μm GaInNAs/GaAs MQWs which have been preannealed *in situ* to the stage of blueshift saturation. The different effects of these two deposition techniques on the interdiffusion have been compared, and the role of the sputtering process has been manifested. We clarified that the interdiffusion mechanism in PECVD SiO₂-capped samples is due to Ga vacancies generated by the outdiffusion of Ga into the SiO₂ layer and this process takes place only at rather high temperatures. The contributory role of the sputtering process is that point defects generated by atomic bombardment during the sputtered SiO₂ deposition enhance the outdiffusion of Ga atoms and lead to the lowering of threshold temperature for QWI. The point defects may also directly promote the interdiffusion between the QWs and the barriers. We presented the carrier lifetime in disordered and nondisordered samples, and showed that the defects diffused into the active QWs act as nonradiative centers and decrease the PL decay time. In addition, we have studied the N-concentration dependence of QWI in GaInNAs/GaAs structures. We found that the blueshift decreases as the N-concentration increases. This finding not only rules out the possible mechanism of N–As interdiffusion, but also demonstrates the alloy stability of GaInNAs due to the strong bond of In–N.

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