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Suppressed intermixing in InAlGaAs/AlGaAs/GaAs and AlGaAs/GaAs quantum well heterostructures irradiated with a KrF excimer laser

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ABSTRACT The influence of gallium arsenide surface modification induced by irradiation with a KrF excimer laser on the magnitude of the quantum well (QW) intermixing effect has been investigated in InAlGaAs/AlGaAs/GaAs QW heterostructures. The irradiation in an air environment with laser pulses of fluences between 60 and 100 mJ/cm^2 has resulted in the formation of a gallium oxide-rich film at the surface. Following the annealing at 900 °C, up to 35 nm suppression of the band gap blue shift was observed in all the laser irradiated samples when compared to the non-irradiated samples. The origin of suppression has been discussed in terms of stress controlled diffusion.

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1 Introduction

Over the last twenty years, selected area post-growth modification of the quantum well (QW) bandgap structure through the interdiffusion process known as quantum well intermixing (QWI) has been the subject of numerous investigations [1, 2]. In AlGaAs/GaAs QW heterostructures, intermixing Al and Ga atoms at the well-barrier interface results in an increase of the effective band gap energy. This is accompanied by changes in the electronic confinement as well as the refractive index of the intermixed layer [3]. The thermally activated QWI process can be modified by the controlled introduction of impurities and defects to the QW material. For example, gallium vacancies (V_{Ga}) are known to enhance QWI in AlGaAs/GaAs [4]. Since this process could be induced in selected areas of a QW wafer, the QWI approach has been attractive for the fabrication of monolithically integrated optoelectronic devices [1].

The most frequently investigated methods of QWI include impurity induced intermixing [3], impurity-free vacancy diffusion [5] and QWI induced by ion implantation [6, 7]. QWI has also been achieved by selective area coating of QW wafers with different oxides, nitrides and fluorides fabricated by conventional thin film deposition techniques. Both enhanced [8] and reduced [9] intermixing has been observed depending on the physical and chemical properties of coating layers. Different lasers have also been investigated for intermixing of different III–V QW systems [10, 11]. Continuous wave (CW) and pulsed Nd:YAG lasers were found to induce significant interdiffusion in InGaAsP/InGaAs/InP quantum well heterostructures [10] and InAs/GaAs quantum dots [12]. Among the numerous QWI techniques, UV excimer laser controlled QWI (UV-QWI) has been proposed as a new approach potentially addressing limitations of other QWI techniques related to the control of the process, its reproducibility and spatial resolution [13]. In addition to the enhanced intermixing in InGaAs/InGaAsP QWs heterostructures [13] by UV-QWI, we have recently reported that the UV-QWI process can also lead to the suppression of intermixing [14]. We have shown that the short wavelength of the surface modifying radiation and the relatively shallow location of the QW allow suppression of QWI with a spatial resolution of as high as 1 μm [15]. In this paper we discuss the mechanism of excimer laser-induced suppression of the QWI process in InAlGaAs/AlGaAs/GaAs and AlGaAs/GaAs QW heterostructures.

2 Experimental details

Two laser diode heterostructures grown by molecular beam epitaxy were used for this study. The first one (Q1) consisted of two 7.5 nm thick GaAs quantum wells (QWs) separated by a 10.3 nm $Al_{0.43}Ga_{0.57}As$ barriers and buried 1 μm under the surface. The active region was grown on an n-type Se doped (100) GaAs substrate with a 100 nm GaAs and a 100 nm $Al_{0.43}Ga_{0.57}As$ buffer layers. Both layers were Se doped (1.7×10^{18} cm^{-3}). The structure was terminated with a C doped (1.8×10^{18} cm^{-3}) $Al_{0.43}Ga_{0.57}As$ optical confinement layer, which was 740 nm thick and a Zn-doped (7×10^{18} cm^{-3}) GaAs capping layer, which was 100 nm thick. This heterostructure was designed for lasing operation at 852 nm at room temperature.

The second heterostructure (Q2) was composed of a single 7 nm $In_{0.1}Al_{0.13}Ga_{0.77}As$ QW. The barriers were made of 400 nm thick AlGaAs graded index structure (GRIN) layers. The QW was positioned 2 μm below

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the wafer surface. This structure was grown on an n-type Si doped GaAs substrate with a C-doped (10^{18} cm^{-3}) buffer structure composed of a 200 nm GaAs layer and a 200 nm AlGaAs GRIN layer. Two 1500 nm $Al_{0.6}Ga_{0.4}As$ claddings, on each side of the well, assured optical confinement. This QW wafer was designed for lasing operation at 808 nm at room temperature.

Samples of 5 mm × 5 mm were cleaved from both wafers and solvent cleaned using a standard cleaning procedure. They were then irradiated with a KrF excimer laser operating at 248 nm at a pulse repetition rate of 3 Hz. The laser beam was shaped with a fly-eye array beam homogenizer to form a 7 mm × 7 mm top-hat profile. Samples were irradiated with 1000 pulses of fluences varying from 50 to 100 mJ/cm^2. The maximum surface temperature induced with a 100 mJ/cm^2 pulse has been estimated to be 250 °C. The air environment of the current experiment and multi-pulse irradiation are expected to lead to a significant deviation of the GaAs surface from stoichiometric conditions. Following the laser irradiation, all samples were annealed in a rapid thermal annealer (RTA) at 900 °C. The RTA treatment consists of a 15 s ramping from room temperature to the annealing temperature and a 30 s anneal at a set temperature. The annealing was carried out in a forming gas atmosphere (N_2 90% and H_2 10%) while cooling was done under nitrogen to prevent oxidation.

Low temperature (20 K) photoluminescence (PL) was used to characterize the samples. A frequency doubled Nd:YAG laser ($\lambda = 532$ nm) was used to excite the sample while the PL signal was dispersed by a monochromator and detected by a photomultiplier. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos HS system and a monochromatic Al K_α X-ray source. The atomic concentration of Ga, As and O were measured by analysing the Ga 3*d*, As 3*d* and O 1*s* photoelectron spectra. The thickness of the GaAs oxide layer (mostly composed of Ga_2O_3 and As_2O_3), d_{ox}, was estimated using the intensity ratio of the oxides and substrate. It was assumed that the oxide is a homogeneous mix of Ga_2O_3 and As_2O_3. For a given element, if the XPS spectrum shows both the oxide and the GaAs cap layer peaks, the oxide thickness can be obtained using the following equation [16]:

$$d_{ox} = \alpha_{ox} \sin\theta \ln\left(\frac{I_{ox}}{I_{sub}}\frac{D_{sub}}{D_{ox}}\frac{\alpha_{sub}}{\alpha_{ox}} + 1\right), \quad (1)$$

where the D_{sub}/D_{ox} is the density ratio between the substrate and the oxide while I_{ox}/I_{sub} is the photoelectron intensity ratio, α_{ox} and α_{sub} are the electron mean escape depths in the oxide and in the substrate, and θ is the photoelectrons exit angle relative to the surface. The electron mean escape depths in GaAs and in the oxide have been calculated using the Cumpson and Seah [17] model for the Ga 3*d* peak. These values are 2.6 and 2.0 nm in GaAs and in Ga_2O_3, respectively, while it is 2.5 nm for As 3*d* in both As_2O_3 and the substrate [16].

3 Results and discussion

Figure 1 shows the dependence of the blue shift amplitude as a function of the laser fluence for four samples from the Q1 wafer (square symbols) and five samples from the Q2 wafer (circle symbols) following laser irradiation and RTA. The results for RTA only (non-irradiated) samples indicate that the bandgap of the InAlGaAs/AlGaAs/GaAs and AlGaAs/GaAs quantum well structures was thermal shifted by 104 and 48 meV (43 and 27 nm), respectively. This compares with the shift reduction to only 15 and 9 meV (7 and 5 nm) for the same QW microstructures that were irradiated with 1000 pulses at 100 and 88 mJ/cm^2, respectively. These results confirm the role of the physical and chemical properties of the surface in controlling the amplitude of the intermixing mechanism that has been observed earlier [13, 18]. We argue that the oxide layer fabricated at the surface influences the interdiffusion through the locally induced thermal stress. For example, it has been demonstrated that deposition of Si_3N_4 on SiO_2 coated GaAs QW structure creates tensile stress which prevents SiO_2-enhanced V_{Ga} diffusion toward the quantum wells [19].

Figure 2 shows a dependence of the QW PL intensity for the processed samples following annealing. For Q1, an up to 260% PL intensity enhancement has been observed for the 88 mJ/cm^2 irradiated sample. For Q2, a 50% enhancement has been observed for the 84 mJ/cm^2 irradiated sample. This has been reduced to the initial level of the PL signal following the irradiation at 108 mJ/cm^2; processing with such laser fluence leads to microscopic surface damage that could explain this signal reduction. An enhancement of the PL signal has been reported previously for InGaAs/InGaAsP heterostructures pro-

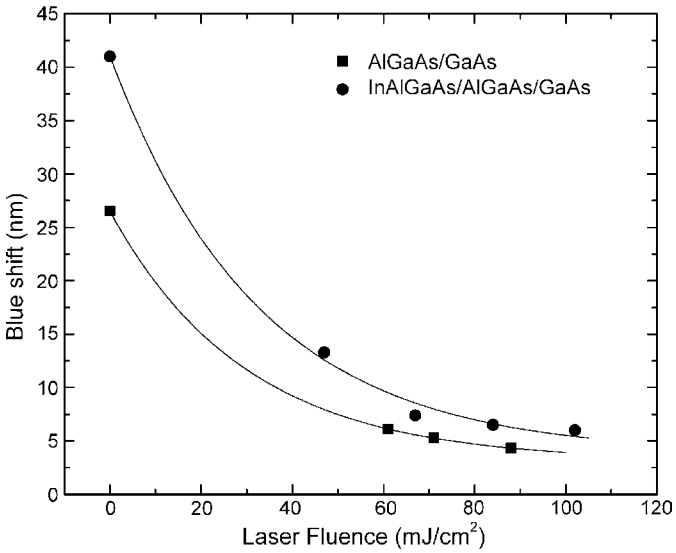

FIGURE 1 Dependence of the amplitude of blue shift in as-grown and 1000 pulse laser irradiated AlGaAs/GaAs (*squares*) and InAlGaAs/AlGaAs/GaAs (*circles*) samples following their RTA at 900 °C for 30 s

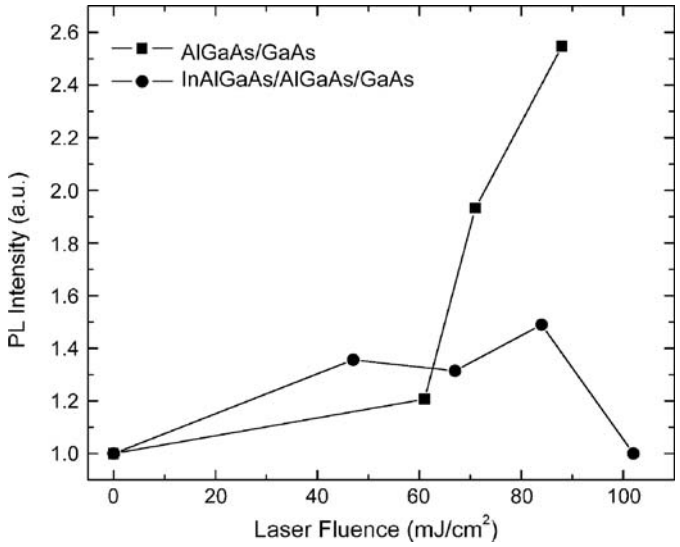

FIGURE 2 Intensity of the QW photoluminescence signal from AlGaAs/GaAs (*squares*) and InAlGaAs/AlGaAs/GaAs (*circles*) samples irradiated with pulses of different laser fluence and after RTA at 900 °C for 30 s

cessed with an XeCl ($\lambda = 308$ nm) excimer laser in air [20]. This result has been attributed to the formation of a thin Ga_xO_y layer on the surface of InGaAs.

The relative near-surface atomic concentration of Ga and As in as-grown and two laser irradiated samples (Q2) was estimated using XPS measurements as illustrated in Fig. 3. It shows a significant reduction of the GaAs-related Ga peak, which is accompanied by the growth of the Ga peak originating from Ga_2O_3. The non-stoichiometric ratio of arsenic oxides and gallium oxide and the presence of elemental arsenic in laser treated samples is due to transformation of As_2O_3 in Ga_2O_3 which can be described by the following formula:

$$2GaAs + As_2O_3 \rightarrow Ga_2O_3 + 4As\,. \quad (2)$$

The presence of native GaAs oxides is observed in the as-grown sample. All laser treated samples, however, showed a reduction in the overall arsenic concentration. This is due to the fact that As, As_2 and As_4 have a higher vapour pressure than Ga and, thus, the As atoms are relatively easily desorbed from the substrate. The laser treated samples also show an increase in the overall oxygen concentration which can be related to the enhanced GaAs oxidation induced by UV laser irradiation in air [16].

XPS results revealed that laser irradiation of GaAs induced the growth of gallium rich oxide on the sample surface. From XPS data, the calculated overall thickness of the oxide ($Ga_2O_3 + As_2O_3$) layer formed at the surface of the 1000 pulses irradiated Q2 sample was calculated using (1) and the results are plotted in Fig. 4 as a function of the laser fluence. It can be seen that a 5.5 nm thick oxide layer has been formed following the irradiation at 100 mJ/cm^2. Energy dispersive X-ray spectroscopy results on Q1 show a qualitatively similar increase of oxygen concentration after laser treatment.

We argue that the laser-induced formation of the oxide layer is responsible for the reduced amplitude of the QWI effect. This is in agreement with the results reported earlier showing that due to the greater thermal expansion coefficient of gallium oxide ($7.3 \times 10^{-6}\,K^{-1}$) than that of GaAs ($5.73 \times 10^{-6}\,K^{-1}$), the presence of gallium oxide will induce an interdiffusion-reducing stress in annealed GaAs [21]. Of particular interest is that the substrate/oxide interface fabricated by the irradiation with the excimer laser most likely contains fewer relaxation sites, as the investigated oxide has been naturally grown instead of being physically deposited. This could explain the high efficiency of a 5 nm thick film, predominantly composed of gallium oxide, in suppressing the intermixing that led to a reduction of the bandgap shift by 80.7 meV (35 nm) in comparison to the as-grown and annealed Q2 samples. Interestingly, for the same type of structure and similar annealing conditions, ~ 40 meV and ~ 29 meV suppressions have been reported using 150 nm thick TiO_2 coating [22] and 90 nm of Ga_xO_y on 200 nm of SiO_2 bilayer coating [21], respectively.

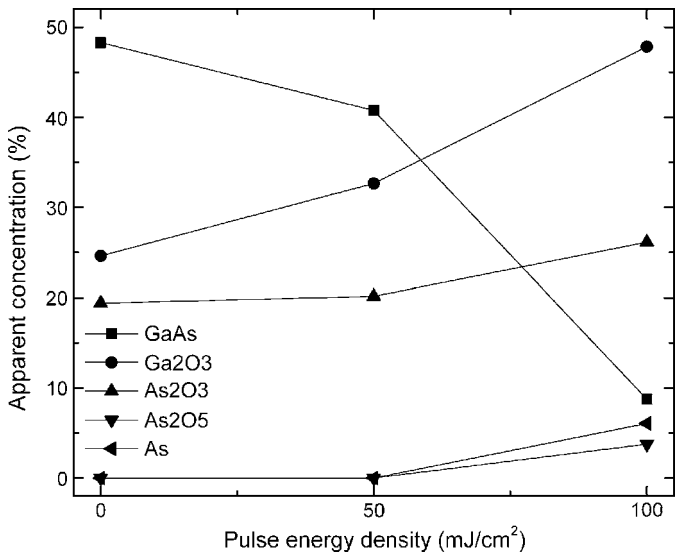

FIGURE 3 Atomic concentrations of Ga and As XPS peaks related to GaAs (■), Ga_2O_3 (●), As_2O_3 (▲), As_2O_5 (♦) and As (▼) in as-grown and laser-irradiated (no RTA) InAlGaAs/AlGaAs/GaAs samples

4 Conclusions

We have investigated the influence of a KrF excimer laser generated layer of an oxide material at the surface of GaAs on the quantum well intermixing process in AlGaAs/GaAs and in InAlGaAs/AlGaAs/GaAs QW

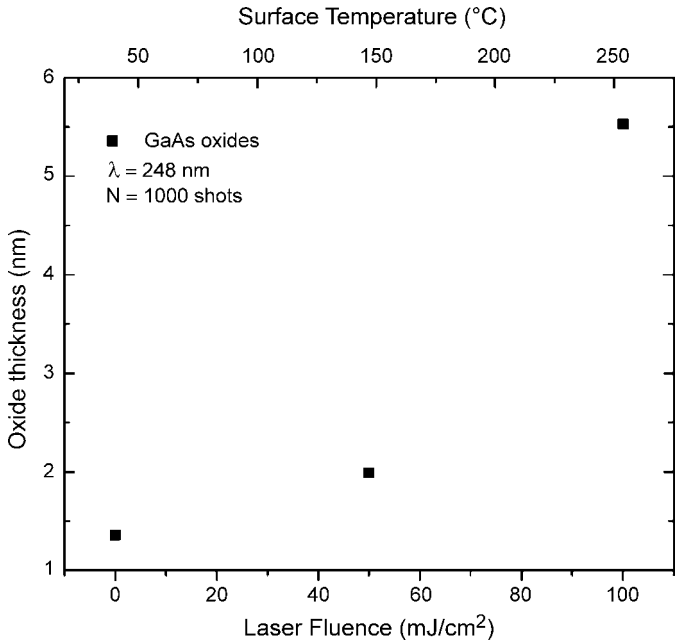

FIGURE 4 Overall calculated oxide thickness (Ga_2O_3 and As_2O_3) on the surface of GaAs irradiated with a KrF laser in an air environment. Calculated surface temperatures induced with the laser are indicated on the *top axis* of this figure

heterostructures. XPS measurements showed that the irradiation with a laser delivering pulses of 60 to 100 mJ/cm^2 in an air environment leads to the formation of a predominantly gallium oxide rich layer. Rapid thermal annealing of such samples has resulted in up to 35 nm retardation of the bandgap shifting amplitude in comparison to the non-irradiated samples. We argue that the mechanism responsible for this behaviour is the reduced intermixing due to the Ga_2O_3-induced tensile stress in the investigated QW microstructures. The ability to fabricate gallium oxide rich regions on a wafer irradiated with an excimer laser, e.g., by a laser projection lithography technique, has the potential application for the simplified fabrication of multi-bandgap QW wafers when compared to conventional QWI techniques involving selective area ion-implantation or oxide deposition. In addition, this new excimer-laser-based process for suppressed bandgap shifting can be used in conjunction with other QWI approaches to create high-contrast zones in multi-bandgap structures.

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REFERENCES

1 E.H. Li (Ed.), *Semiconductor Quantum Wells Intermixing* (Amsterdam, Netherlands, 2000)
2 J.H. Marsh, Semicond. Sci. Technol. **8**, 1136 (1993)
3 L.J. Guido, G.S. Jackson, W.E. Plano, K.C. Hsieh, N. Holonyak, R.D. Burnham, J.E. Epler, R.L. Thornton, T.L. Paoli, Appl. Phys. Lett. **50**, 609 (1987)
4 S. Mitra, J.P. Stark, J. Mater. Sci. **26**, 6650 (1991)
5 J.H. Teng, J.R. Dong, S.J. Chua, D.A. Thompson, B.J. Robinson, A.S.W. Lee, J. Hazell, I. Sproule, Mater. Sci. Semicond. Proc. **4**, 621 (2001)
6 S. Charbonneau, E.S. Koteles, P.J. Poole, J.J. He, G.C. Aers, J. Haysom, M. Buchanan, Y. Feng, A. Delage, F. Yang, M. Davies, R.D. Goldberg, P.G. Piva, I.V. Mitchell, IEEE J. Sel. Top. Quantum Electron. **4**, 772 (1998)
7 V. Aimez, J. Beauvais, J. Beerens, D. Morris, H.S. Lim, B.S. Ooi, IEEE J. Sel. Top. Quantum Electron. **8**, 870 (2002)
8 A.S. Helmy, N.P. Johnson, M.L. Ke, A.C. Bryce, J.S. Aitchison, J.H. Marsh, I. Gontijo, G.S. Buller, J. Davidson, P. Dawson, IEEE J. Sel. Top. Quantum Electron. **4**, 661 (1998)
9 J. Beauvais, J.H. Marsh, A.H. Kean, A.C. Bryce, C. Button, Electron. Lett. **28**, 1670 (1992)
10 J.J. Dubowski, Y. Feng, P.J. Poole, M. Buchanan, S. Poirier, J. Genest, V. Aimez, J. Vac. Sci. Technol. A **20**, 1426 (2002)
11 B.S. Ooi, T.K. Ong, O. Gunawan, IEEE J. Quantum Electron. **QE-40**, 481 (2004)
12 J.J. Dubowski, C.N. Allen, S. Fafard, Appl. Phys. Lett. **77**, 3583 (2000)
13 J.J. Dubowski, U.S. Patent No. 6.514.784 (4 February 2003)
14 J. Genest, J.J. Dubowski, V. Aimez, Proc. SPIE **550**, 5451 (2004)
15 J. Genest, J.J. Dubowski, V. Aimez, N. Pauc, D. Drouin, M. Post, J. Phys.: Conf. Ser. **59**, 605 (2007)
16 C.F. Yu, D.V. Podlesnik, M.T. Schmidt, H.H. Gilgen, R.M. Osgood, Chem. Phys. Lett. **130**, 301 (1986)
17 P.J. Cumpson, M.P. Seah, Surf. Interf. Anal. **25**, 430 (1997)
18 C.J. Hamilton, S.E. Hicks, B. Vogele, J.H. Marsh, J.S. Aitchison, Electron. Lett. **31**, 1393 (1995)
19 A. Pepin, C. Vieu, M. Schneider, H. Launois, Y. Nissim, J. Vac. Sci. Technol. B **15**, 142 (1997)
20 J.J. Dubowski, P.J. Poole, G.I. Sproule, G. Marshall, S. Moisa, C. Lacelle, M. Buchanan, Appl. Phys. A **69**, S299 (1999)
21 L. Fu, J. Wong-Leung, P.N.K. Deenapanray, H.H. Tan, C. Jagadish, G. Bin, R.N. Lamb, R.M. Cohen, W. Reichert, L.V. Dao, M. Gal, J. Appl. Phys. **92**, 3579 (2002)
22 P.L. Gareso, M. Buda, L. Fu, H.H. Tan, C. Jagadish, Appl. Phys. Lett. **85**, 5583 (2004)