Novel impurity-free interdiffusion in GaAs/AlGaAs quantum wells by anodization and rapid thermal annealing

Shu Yuan,[a] Yong Kim,[b] and C. Jagadish[c]
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, The Australian National University, Canberra ACT 0200, Australia

P. T. Burke and M. Gal
School of Physics, University of New South Wales, Sydney, New South Wales, NSW 2052, Australia

J. Zou, D. Q. Cai, and D. J. H. Cockayne
Electron Microscope Unit and Australian Key Centre for Microscopy and Microanalysis, The University of Sydney, New South Wales, NSW 2006, Australia

R. M. Cohen
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

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A novel impurity-free interdiffusion technique utilizing pulsed anodization and subsequent rapid thermal annealing at temperatures near 900 °C was reported. Enhanced interdiffusion was observed in the presence of an anodized GaAs capping layer in GaAs/AlGaAs quantum well structures. Transmission electron microscopy studies show evidence of interdiffusion. Photoluminescence spectra from interdiffused samples show large blue shift and no significant linewidth broadening. Possible mechanism of interdiffusion was discussed. © *1997 American Institute of Physics.* [S0003-6951(97)00810-3]

Interdiffusion techniques have been used to modify materials and device properties in recent years. Interdiffusion between quantum well (QW) and adjacent barriers results in a change in quantum well shape which in turn modifies the subband energies in the conduction band and the valence band. As a result, the interband transition energy and refractive index are modified, and interdiffusion has been used to fabricate lasers with different wavelengths without etching or epitaxial regrowth.[1] Selective interdiffusion has also been used to define optically transparent waveguides[2] and lasers with saturable absorbers.[3] There are currently two kinds of interdiffusion techniques, one is the impurity-induced interdiffusion (IID),[4–6] another is the impurity-free interdiffusion (IFID).[7,8] IID usually introduces substantial undesired changes in the material resistivity and trap concentrations. IFID can create large bandgap energy shifts without such problems associated with IID. In the GaAs/AlGaAs system, SiO_2 and Si_3N_4 are commonly used to promote and prevent interdiffusion, respectively. SiO_2, however, reacts with Al when in direct contact with AlGaAs, and thus generates Si which behaves as an impurity source. Si_3N_3, on the other hand, causes considerable strain.[7]

In this letter, we report the use of pulsed anodized oxide as the point defect diffusion source for IFID. We have recently applied this technique to enhance the photoluminescence (PL) and cathodoluminescence (CL) signals from V-grooved quantum wires and obtained both spectrally and spatially well-resolved light emission from quantum wires.[9] The pulsed anodization technique has recently attracted attention as a new way of creating current blocking layers for ridge-waveguide quantum well laser fabrication, since it was simple, reliable, and cost-effective.[10] Pulsed anodized InGaAs single quantum well lasers grown by metalorganic chemical vapor deposition (MOCVD) were fabricated and found to have a threshold current of 5 mA.[11]

The samples for this study were grown by low pressure MOCVD on the same p^+-GaAs wafer and thus have the same structure. The wafer was Zn-doped at 1×10^{19} cm^{-3} concentration and 2° off ⟨100⟩ towards ⟨110⟩. A 500 nm GaAs buffer layer was first grown onto the substrate. Then four GaAs QWs separated by 50 nm $Al_{0.54}Ga_{0.46}As$ barriers were grown sequentially with thicknesses of 8.2, 3.6, 2.1, and 1.2 nm, respectively, as determined from 12 K PL measurements. A final 100 nm GaAs layer was grown over the QW structure. All the epilayers were nominally undoped. Samples of area of 8×8 mm were cleaved from this wafer. Half of each sample was then covered with thermal glue and anodized in ethylene glycol: de-ionized water: phosphoric acid electrolyte (40:20:1 by volume) at room temperature.[11] The pulse width was 1.0 ms, the period was 12.0 ms, the total pulsed anodization time was 4 min. The leading edge of the pulsed anodization current density was fixed at 40 mA/cm^2. The area covered with thermal glue was unanodized, while anodization took place in the uncovered area to form a native oxide layer. When the pulse was on, anodization took place, and when the pulse was off, the anodic oxide was etched slowly by the electrolyte. After anodization, samples were rinsed with deionized water, followed by acetone to remove the thermal glue, then by deionized water and N_2 blow dried. The final anodic oxide layer was about 60 nm thick. Each sample was then cleaved into two 4×8 mm pieces, so that each piece has half area anodized (4×4 mm) and half area unanodized (4×4 mm). This enables a reasonable transmission electron microscopy (TEM) and PL comparison between anodized and unanodized areas after interdiffusion process. The interdiffusion was carried out in a rapid thermal annealing (RTA) chamber with GaAs

[a]Electronic mail: shu.yuan@anu.edu.au
[b]Present address: Semiconductor Materials Research Center, Korea Institute of Sciences and Technology, P.O. Box 131, Cheongryang, Seoul, Korea.
[c]Electronic mail: cxj109@rsphysse.anu.edu.au

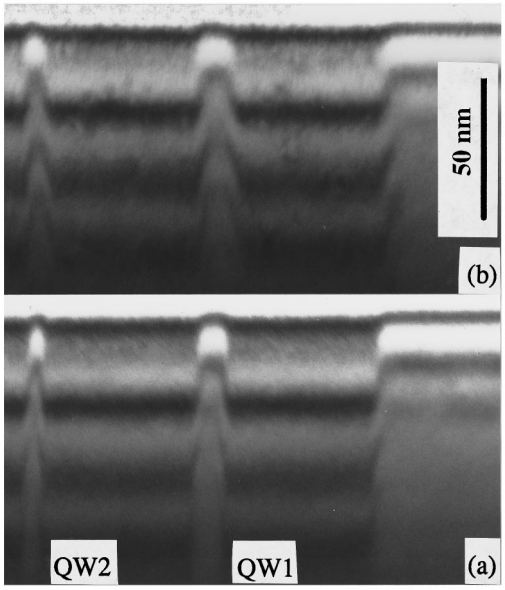

FIG. 1. TEM micrographs of unanodized (a) and anodized (b) GaAs/AlGaAs quantum well structures annealed together at 950 °C for 105 s.

proximity cap. Samples were annealed in Ar ambient at 900 and 950 °C for 30–120 s after a rise time of 25 s.

After the interdiffusion process, TEM was used to check the structural properties of these samples. 90° wedge TEM specimens were prepared by the cleavage method. These specimens, oriented along the [100] zone axis, were investigated in a Philips EM 430 operating at 300 keV. Figure 1 is a pair of bright-field images from a sample annealed at 950 °C for 105 s without [Fig. 1(a)] and with [Fig. 1(b)] anodization. A few dark lines (thickness fringes) parallel to the edge can be seen. Their distance from the edge is sensitive to the chemical composition. Therefore, four GaAs wells separated by AlGaAs barriers can be distinguished by the shift in the fringes. In the following we denote the 8.2 nm QW, 3.6 nm QW, the 2.1 nm QW, and the 1.2 nm QW as QW1, QW2, QW3, and QW4, respectively. In Fig. 1, QW1 and QW2 are shown. Comparing images of Fig. 1, the contrast at the interfaces is more gradual for the anodized area [Fig. 1(b)] than for the unanodized area [Fig. 1(a)], indicating a broadening of quantum wells in the anodized area after RTA. The interdiffusion was also confirmed by secondary ion mass spectroscopy (SIMS) studies.

12 K PL measurements were performed using an Ar ion laser beam (514.5 nm), a spectrometer, and a Si detector. For anodized samples without RTA treatment and unanodized samples with RTA treatment, the PL energies do not show significant shift. Figure 2 compares PL spectra of two typical anodized samples and an unanodized sample after RTA treatment at 900 °C for 30 and 120 s. Relative to the unanodized but annealed sample, the QW peaks for the anodized samples were all shifted considerably towards shorter wavelength (blueshift) after RTA. This indicates the anodized GaAs layer enhances the interdiffusion in the structures below it. For anodized samples, the full widths at half maximum (FWHM) of the PL peaks are more or less the same as the as-grown sample, no matter they are annealed or not.

The PL signal from QW4, which is the most narrow QW

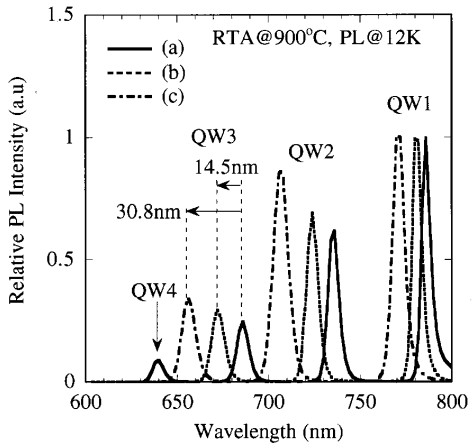

FIG. 2. Photoluminescence spectra of GaAs/AlGaAs quantum well samples annealed at 900 °C. The spectra were normalized to the peak from QW1 for each sample. Three samples were shown here: (a) unanodized sample annealed for 30 s, (b) anodized sample annealed for 30 s, and (c) anodized sample annealed for 120 s.

(1.4 nm) and is closest to the surface, disappears after RTA treatment. This narrow well has become indirect material after interdiffusion process, as the Al content in the barriers was 54% initially. In Fig. 3 we plot relative PL energy shift for anodized samples annealed at 900 °C as a function of RTA time. The relative PL shift is the PL energy difference between anodized area and unanodized area on the same piece of sample annealed together. PL peaks from QWs of the unanodized areas (the reference samples) show little blueshift after RTA, in agreement with thermal stability studies of GaAs/AlGaAs single quantum wells using photoreflectance.[12] Anodized samples, however, show significant blueshift of QW PL peak energies with increasing RTA time and temperature.

It is known[13] that, at elevated temperatures, oxides of Ga and of As are thermodynamically stable relative to GaAs oxide. It is clear from our results that the anodically formed oxides are associated with the enhancement of group III interdiffusion. The interdiffusion results imply that the concentration of a native point defect, i.e., a group III vacancy or

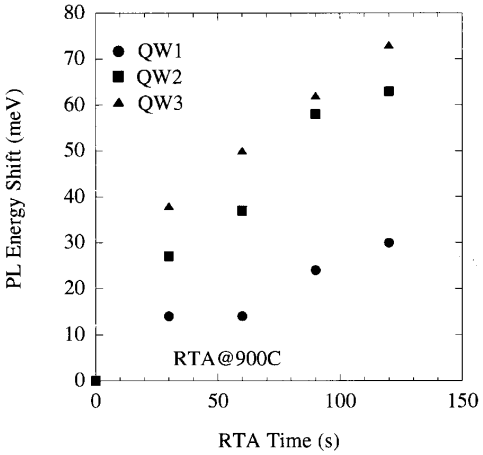

FIG. 3. 12 K PL energy shift of anodized GaAs/AlGaAs quantum well structures with respect to unanodized samples annealed at 900 °C as a function of RTA time.

interstitial, is increased at elevated temperatures when annealing under an anodic oxide. For the impurity-free enhanced interdiffusion induced in GaAs by a deposited SiO_2 layer,[7] it is often assumed that an increased Ga vacancy concentration enhances the interdiffusion. However, the chemical interactions between GaAs and a hydrated mixture of Ga and As oxides are presumably quite different than those between GaAs and SiO_2. Based upon previously reported measurements,[14] we expect that the residual water in an anodically oxidized layer induces further oxidation of the GaAs at elevated temperatures. We consider it is likely that this high temperature oxidation causes the injection of the native defects which enhance the interdiffusion. However, it remains to be determined whether or not wet oxidation causes the injection of Ga interstitial atoms, similar to the injection of Si interstitials during the oxidation of Si.[15] Work is in progress to understand the processes affecting the interdiffusion during and after oxidation.

In conclusion, we have reported a novel and simple way of impurity-free interdiffusion, namely, pulsed anodization and subsequent rapid thermal annealing. This was confirmed by TEM and PL studies. We have demonstrated large blueshift in the PL energies due to anodic oxide enhanced interdiffusion. The interdiffusion mechanism appears to be caused by point defect injection associated with the anodic oxide layer.

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