APPLIED PHYSICS LETTERS VOLUME 76, NUMBER 12 20 MARCH 2000

Control of the band-gap shift in quantum-well intermixing using a germanium interlayer

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(Received 20 September 1999; accepted for publication 25 January 2000)

A simple technique for controlling the shift in band gap in AlGaAs/GaAs and InGaAs/GaAs quantum-well (QW) structures is reported. It involves the evaporation of a thin Ge layer and then covering it with spin-on silica followed by rapid thermal annealing. The quantum-well intermixing was suppressed in the presence of this Ge layer between the sample surface and the spin-on silica. The interdiffusion rate was reduced by more than one order of magnitude compared to that without the Ge interlayer. The blueshift of the band gap can be controlled by varying the thickness of the Ge interlayer. A differential band-gap shift of more than 100 meV can be achieved with a 500 Å Ge interlayer for both the AlGaAs/GaAs and InGaAs/GaAs QW structures. The optical quality of the material was not deteriorated by the Ge cover compared to the SiO_2 cover as seen from the photoluminescence intensity and spectral linewidth. Using an appropriate mask, this technique has the potential to tune the band gap in selected areas across a single wafer. © *2000 American Institute of Physics.* [S0003-6951(00)02812-6]

The ability to induce band-gap variation at selected areas across a wafer is an essential requirement for the fabrication of monolithic integrated photonic circuits. This can be achieved by selective epitaxial growth,[1] or postgrowth quantum-well (QW) intermixing. The localized QW intermixing is capable of blueshifting the QW emission energy by several tenths of meV in predefined regions on the wafer. This technique has been successfully applied to the fabrication of low-loss waveguides and integrated photonic devices.[2,3] There are several methods to induce quantum-well intermixing.[4–7] Among them, the impurity-free vacancy disordering (IFVD) is considered promising for its simplicity, resulting in low damage to the crystal quality and low optical losses. IFVD is usually implemented by capping the semiconductor wafer with the dielectric layer, either to enhance or to suppress the intermixing, followed by thermal annealing. Various dielectric cap layers have been studied in different material systems to achieve selective quantum-well intermixing.[8,9] SiO_2 is most commonly used to enhance the quantum-well intermixing due to the large solubility of Ga in the SiO_2 film, while Si_3N_4, SrF_2 are used to suppress the intermixing. The interdiffusion on group-III atoms is carried out by the native defects, i.e., group-III vacancies V_{III}, and interstitials I_{III}. The group-III sublattice interdiffusion coefficient in IFVD depends not only on the diffusion coefficient of the group-III vacancies, but also on their concentrations, $[V_{III}]$. The degree of QW intermixing can be spatially controlled across a wafer if one is capable of spatially controlling the number of generated vacancies, which subsequently diffuse through a heterostructure. This can be achieved by controlling the silica cap properties to control the solubility of Ga in SiO_2 film or by controlling the number of the Ga vacancies generated on the semiconductor surface by metallurgical reactions.[6,10] In this letter, we report the use of a thin Ge layer and spin-on silica film to control the degree of quantum-well intermixing in AlGaAs/GaAs and InGaAs/GaAs quantum-well structures.

Doped and undoped $Al_{0.3}Ga_{0.7}As$/GaAs QW structures and $In_{0.2}Ga_{0.8}As$/GaAs QW structures were used here. They are all grown by low-pressure metal–organic vapor-phase epitaxy. For the doped $Al_{0.3}Ga_{0.7}As$/GaAs samples, first a layer of 200-nm-thick GaAs was grown on a GaAs substrate followed by a 150-nm-thick $Al_{0.3}Ga_{0.7}As$ lower cladding layer doped with Si to $2\times10^{18}\,cm^{-3}$ and a 50-nm-undoped $Al_{0.3}Ga_{0.7}As$ confinement layer. The active region consists of three 7 nm GaAs quantum wells separated by 25 nm $Al_{0.3}Ga_{0.7}As$ barriers. The upper cladding layer was a 250 nm $Al_{0.3}Ga_{0.7}As$ doped with C to $2\times10^{19}\,cm^{-3}$. The structure was capped with a further 30 nm of GaAs. The undoped $Al_{0.3}Ga_{0.7}As$/GaAs QW structure has exactly the same structure as the doped one except that there is no doping in the cladding layer. The InGaAs/GaAs QW structure had a 1 μm GaAs buffer layer grown on the GaAs substrate followed by an 8 nm $In_{0.2}Ga_{0.8}As$ single-quantum well. The structure was capped with a 300 nm GaAs layer on the top. The Ge layer was deposited on the sample surface by e-beam evaporation with different thicknesses varying from 0 to 50 nm for different samples. After the evaporation of the Ge layer all the samples were then coated with a spin-on silica layer with a

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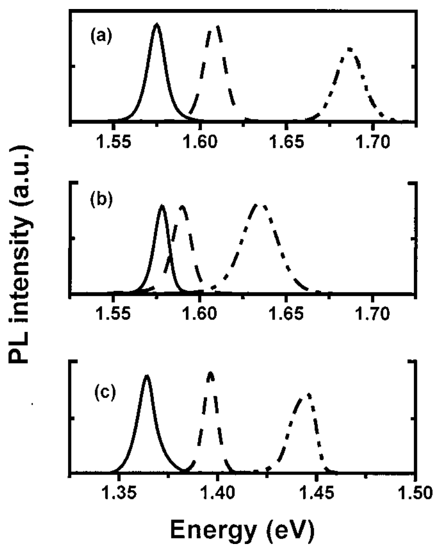

FIG. 1. Low-temperature (7 K) photoluminescence spectra of quantum-well samples with and without a Ge interlayer after rapid thermal annealing for 30 s. (a) Undoped $Al_{0.3}Ga_{0.7}As/GaAs$ QW annealed at 850 °C; (b) doped $Al_{0.3}Ga_{0.7}As/GaAs$ QW annealed at 850 °C; and (c) undoped $In_{0.2}Ga_{0.8}As/GaAs$ QW annealed at 825 °C. The solid line is the PL spectrum for the as-grown sample; the dashed line is for the sample covered with a 200-Å-thick Ge layer and then a SiO_2 layer, the dash-dot-dot line is for sample covered with the SiO_2 layer only.

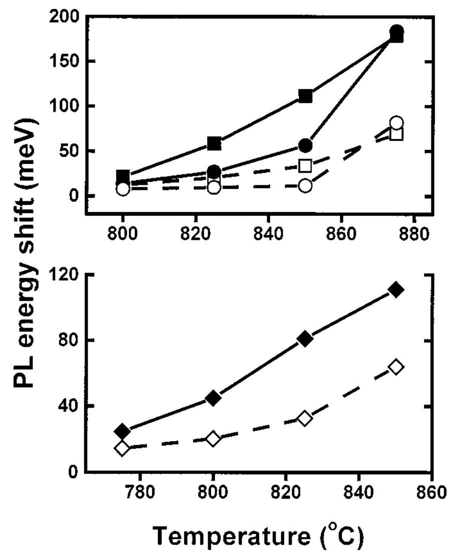

FIG. 2. PL peak energy shift as a function of the annealing temperature for a duration of 30 s. The solid symbols ■, ●, and ◆ are for undoped $Al_{0.3}Ga_{0.7}As/GaAs$, doped $Al_{0.3}Ga_{0.7}As/GaAs$, and undoped $In_{0.2}Ga_{0.8}As/GaAs$ quantum wells with the SiO_2 covering, respectively, while the open symbols □, ○, and ◇ are for the samples with a 200 Å Ge interlayer, respectively.

thickness of 150 nm. Previous studies have shown that spin-on silica is an effective dielectric encapsulant layer to enhance quantum-well intermixing.[11] The wafer was then baked at 120 °C for 1 h in air. The samples were proximity capped and put side by side in a rapid thermal processor (RTP) in N_2 ambient during thermal annealing. Photoluminescence (PL) measurements were conducted at 7 K realized by a close-cycle helium cryostat. The excitation source was a 488 nm Ar^+ laser and the luminescence signal was dispersed by a 0.75 m monochromator.

Figure 1 shows the low-temperature (7 K) PL spectra after thermal annealing of (a) undoped $Al_{0.3}Ga_{0.7}As/GaAs$, (b) doped $Al_{0.3}Ga_{0.7}As/GaAs$, and (c) undoped $In_{0.2}Ga_{0.8}As/GaAs$ QW samples with 200-Å-thick Ge interlayer (dashed line) and with a 1500-Å-thick spin-on SiO_2 layer only (dash-dot-dot line). The PL spectra of the as-grown samples were also shown as the solid line. The RTP were conducted at 850 °C for 30 s for the $Al_{0.3}Ga_{0.7}As/GaAs$ samples and 825 °C for 30 s for the $In_{0.2}Ga_{0.8}As/GaAs$ sample. For the undoped $Al_{0.3}Ga_{0.7}As/GaAs$ QW structures, the samples with spin-on silica capping exhibit a blueshift of 111.5 meV at the annealing condition, while the samples deposited with the 200 Å Ge interlayer and then spin-on silica exhibit a blueshift of only 33.7 meV. The intermixing was greatly suppressed by 77.8 meV with the existence of the Ge interlayer. The 200 Å Ge interlayer suppressed the blueshift from 56 to 12 meV for the doped $Al_{0.3}Ga_{0.7}As/GaAs$ structure and from 81 to 32 meV for the $In_{0.2}Ga_{0.8}As/GaAs$ structure as compared to the samples capped with SiO_2 in the same thermal annealing process. In view of the PL peak intensity and width, the signals from the samples with the Ge interlayer are better than that from the samples with the SiO_2 covering only for all the three QW structures. This confirms that the Ge layer does not significantly degrade the optical properties of the materials in QW intermixing, at least giving a material quality comparable to that with the SiO_2 capping. The doped $Al_{0.3}Ga_{0.7}As/GaAs$ structure shows a much smaller PL peak blueshift than that of the undoped one. This is consistent with the previous reports which attribute this to suppression of the negatively charged group-III vacancies in the *p*-type material, and hence, show a smaller band-gap shift.[12,13] The amount of PL blueshift versus the annealing temperature is plotted in Fig. 2. At 800 °C for $Al_{0.3}Ga_{0.7}As/GaAs$ QWs and 775 °C for the $In_{0.2}Ga_{0.8}As/GaAs$ QW, the difference in the energy shifts between the samples with and without the 200 Å Ge interlayer are not so obvious. As the annealing temperature increases, the energy blueshift rapidly increases for the samples capped with SiO_2 only (solid line), while there is a much less increase for samples with the 200 Å Ge interlayer (dashed line). A differential blueshift of more than 100 meV can be achieved between doped and undoped $Al_{0.3}Ga_{0.7}As/GaAs$ QW structures, with and without the 200 Å Ge interlayer when annealed at 875 °C for 30 s. For the $In_{0.2}Ga_{0.8}As/GaAs$ QW, the difference is about 47 meV when annealed at 850 °C for 30 s. A thicker Ge layer evaporated onto the GaAs surface can suppress the intermixing more efficiently, as shown in Fig. 3. Using a 500-Å-thick Ge layer, the QW intermixing is almost totally suppressed with blueshifts less than 10 meV. The interdiffusion coefficient calculated for the undoped $Al_{0.3}Ga_{0.7}As/GaAs$ quantum wells was reduced to $4\times10^{-17}\,cm^2/s$, compared to that of $5\times10^{-16}\,cm^2/s$ for the SiO_2 capped samples. Over one order of magnitude change of the group-III interdiffusion coefficient can be achieved by varying the Ge layer thickness from 0 to 500 Å. This provides a method to realize control of the band-gap change across a wafer by the evaporation of Ge layers with varying thicknesses on different regions of the GaAs surface. Actually, multiwavelength laser devices have been successfully fabricated by applying this technology. It will be reported elsewhere.

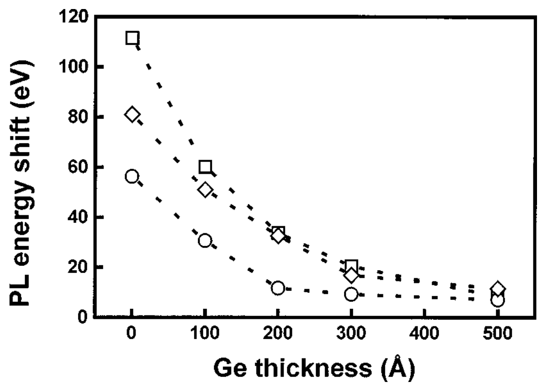

FIG. 3. PL peak energy shifts as a function of the thickness of Ge interlayer. Thermal annealing were conducted at 850 °C for 30 s for both undoped (open square □) and doped (open circle ○) $Al_{0.3}Ga_{0.7}As/GaAs$ QWs, and 825 °C for 30 s for the undoped $In_{0.2}Ga_{0.8}As/GaAs$ QW (open diamond ◇). Dotted lines are to guide the eye.

For the impurity-free vacancy-enhanced interdiffusion in GaAs systems by a deposited SiO_2 layer, it is well believed that an increased Ga vacancy concentration is responsible for the enhancing of interdiffusion. In addition to the high diffusion coefficient of Ga in SiO_2, the thermal stress at the interface of GaAs and SiO_2 also plays a very important role in enhancing the out-diffusion of Ga atoms into the SiO_2 film.[13] The SiO_2 deposited by different methods may have a different degree in enhancing QW intermixing due to their different properties. A recent study shows that by exposing the silica film used in the process of IFVD to oxygen plasma, the QW intermixing can be greatly suppressed. The inhibition of intermixing is ascribed to the changing of the properties and porosity of the SiO_2, which indicates that H_2O and air in the film pores play a key role in assisting and preventing the Ga out-diffusion.[11] The spin-on silica film can reduce the threshold temperature at which significant QW intermixing takes place by about 90 °C, which may be because it is more porous and contains more H_2O than the conventional plasma-enhanced chemical-vapor desposition SiO_2. The combination of the Ge layer evaporated on the GaAs surface followed by spin-on silica may have several functions in suppressing QW intermixing. The Ge has a similar expansion coefficient to that of GaAs, while the thermal expansion coefficient of SiO_2 is ten times less than that of GaAs. The thermal stress induced at the Ge–GaAs interface during the RTP is, therefore, much lower than that for a SiO_2–GaAs interface. The thin Ge layer acts as a ''soft'' interlayer that will result in less Ga out-diffusion. The Ge interlayer also acts as a barrier for the Ga diffusion into SiO_2. The low diffusion coefficient of atomic Ga through this barrier layer would limit the mass-transport flux of atomic Ga from the GaAs into the spin-on silica layer. Furthermore, this Ge interlayer can react with SiO_2 and the residual H_2O in the silica layer during high-temperature thermal annealing to produce GeO_2 and Si. This will change the properties of the silica layer, and hence, reduce the diffusivity of Ga in such film. All these will contribute to the inhibition of the Ga out-diffusion into the silica layer, and hence, limit the number of Ga vacancies available for the interdiffusion in the heterostructure. Increasing the Ge layer thickness will increase the barrier thickness, further reducing the thermal stress caused by SiO_2 and changing the properties of the silica film, to further suppress the QW intermixing. The diffusion of atomic Ge and Si into the QW structure would lead to impurity-induced QW intermixing. However, neither the Ge itself nor the Si produced in the reaction of Ge with SiO_2 appears to act as an impurity source here since the QW intermixing was suppressed with increasing Ge layer thickness and the doped $Al_{0.3}Ga_{0.7}As/GaAs$ structure showed a reduced extent of intermixing, which cannot be explained by the impurity-induced QW intermixing.

In conclusion, we have reported the control of the extent of QW intermixing by using an evaporated Ge layer and followed by a spin-on silica layer in both doped and undoped $Al_{0.3}Ga_{0.7}As/GaAs$ QW structures and an undoped $In_{0.2}Ga_{0.8}As/GaAs$ QW structure. The band-gap blueshifts can be controlled by varying the thickness of the Ge layer. A differential band-gap shift of more than 100 meV can be achieved in the areas with and without the Ge interlayer in a single wafer. The inhibition of the QW intermixing is ascribed to the reduced interface stress, barrier effect of the Ge interlayer, and the change of the properties of the SiO_2 layer. This process has the potential to be an effective method to realize spatially selective QW intermixing.

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