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Impurity free vacancy disordering of InGaAs quantum dots

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The effect of thermal interdiffusion on In(Ga)As/GaAs quantum dot structures is very significant, due to the large strain and high concentration of indium within the dots. The traditional high temperature annealing conditions used in impurity free vacancy disordering of quantum wells cannot be used for quantum dots, as the dots can be destroyed at these temperatures. However, additional shifts due to capping layers can be achieved at low annealing temperatures. Spin-on-glass, plasma enhanced chemical vapor deposited SiO_2, Si_3N_4, and electron-beam evaporated TiO_2 layers are used to both enhance and suppress the interdiffusion in single and stacked quantum dot structures. After annealing at only 750 °C the different cappings enable a shift in band gap energy of 100 meV to be obtained across the sample. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1803948]

I. INTRODUCTION

In order to achieve integration of optoelectronic devices, such as lasers and modulators, it is necessary to have a method to tune the band gap of the active region. Postgrowth techniques have an advantage over other methods due to their simplicity. Impurity-free vacancy disordering (IFVD) is a well-known technique for modifying the emission wavelength of a semiconductor quantum well.[1,2] It is the simplest method to create different amounts of interdiffusion in different regions of a sample. The method involves depositing a layer of dielectric film (normally silicon dioxide) on top of the sample before heat treatment. Ga vacancies are created near the capping layer/GaAs interface by out-diffusion of Ga atoms into the capping layer. The resulting vacancies diffuse down through the sample, enhancing atomic interdiffusion between the different layers. In the case of a quantum well, the atomic interdiffusion causes a blue shift in the luminescence. The amount of vacancies created (therefore the degree of interdiffusion) depends on the properties of the dielectric layer[2–4] and the annealing conditions (i.e., temperature and time). The solubility of Ga in the capping layer is the most important parameter, along with the thickness of the layer which determines the number of Ga atoms that can be absorbed into the layer. The mismatch between the thermal expansion coefficients of the layers and the semiconductor also plays an important role.

The different thermal expansion coefficients of the layers and semiconductor will cause the capping layer/GaAs interface to be stressed during annealing, with the GaAs in either tensile or compressive strain depending on the thermal expansion coefficient of the cap layer. A compressively strained interface enhances the movement of the Ga vacancies created at the capping layer/GaAs interface during annealing, whereas tensile strain will trap these vacancies at the interface creating large defect clusters.[5] If the strain created is large enough it will also penetrate into the underlying layers. In this way different capping layers can be used to suppress interdiffusion in some regions while other regions are enhanced. Multiple layers of dielectrics can be used to create different energy shifts again, by one layer enhancing interdiffusion while the other suppresses it. By varying the thicknesses of the layers used the amount of shift can be controlled.[6]

The effect of thermal interdiffusion on quantum dots is very large, due to their high In content, large interfacial area, and large strain. The additional interdiffusion created by IFVD can be small relative to the thermal interdiffusion, which is enhanced by the presence of defects due to low temperature growth. It has been though that annealing at high temperatures is required to activate the out-diffusion of Ga. These high temperatures have been shown to degrade the quantum dots.[7] Some preliminary work has been done on quantum dots using different capping layers.[8–10] This has shown that additional shifts can be seen at relatively low annealing temperatures. Large additional shifts from sputtered thermal interdiffusion of the quantum dot structures is very significant, due to the high concentration of indium within the dots. The traditional annealing conditions used in impurity free vacancy disordering of quantum wells cannot be used for quantum dots. However, additional shifts due to capping layers can be achieved at low annealing temperatures. Spin-on-glass, PECVD SiO_2, Si_3N_4, and TiO_2 layers are used to both enhance and suppress the interdiffusion in single and stacked quantum dot structures. Differential shifts of up to 100 meV can be achieved with annealing at only 750 °C. SiO_2 and smaller additional shifts from plasma enhanced chemical vapor deposition (PECVD) SiO_2 are seen at annealing temperatures from 700 °C.[9,10] As the amount of thermal interdiffusion in quantum dots is large, methods to suppress interdiffusion are also required if devices with a large range of wavelengths are to be fabricated. In this work we study the thermal stability of InGaAs (QDs) and how different dielectric layers affect the interdiffusion of the QDs.

II. EXPERIMENTAL DETAILS

The samples used in this study consist of either a single layer or a three-layer stack of InGaAs quantum dots. The

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samples were grown by low-pressure metal-organic chemical vapor deposition. The $In_{0.5}Ga_{0.5}As$ quantum dots were grown at 550 °C before the temperature was ramped up to 650 °C for the growth of a 2000 Å cap of GaAs above the dot layer(s). In the stacked dot structures the dot layers were separated by 300 Å of GaAs. Two types of stacked dot structures were investigated, one set included a thin GaP layer between each dot layer to provide strain compensation.[11]

After growth the samples were capped with different dielectric films and annealed. The annealing was carried out by rapid thermal annealing under argon ambient and proximity capping. Silicon oxide, silicon nitride, and titanium oxide layers were used to create different amounts of enhancement or suppression of interdiffusion in the samples. The silicon oxide layers were deposited by either PECVD or a spin-on-glass (SOG) film. The spin-on-glass layers were spun at 3000 rpm for 30 s and cured for 15 min at 300 °C. This curing temperature has been found to be the minimum necessary to create a large amount of IFVD.[4] The thickness of the films was approximately 2000 Å. The SOG layers were either undoped or doped with Ga to change the properties of the layer. Around 2000 Å of PECVD silicon oxide was deposited at RT. At low deposition temperatures (room temperature) the layer is oxygen rich and more porous than films deposited at higher temperatures.[12] It has been found with quantum well samples that these films created more interdiffusion.[3] The porosity affects the solubility of the Ga atoms in the layer. Silicon nitride was deposited by PECVD at 300 °C to create the best quality layer, with the least amount of interdiffusion. Titanium oxide was deposited by *e*-beam evaporation. Photoluminescence spectra were measured at both room temperature and 10 K. The samples are excited with an argon-ion laser at 514.5 nm and the luminescence was detected using a cooled Ge detector.

III. THERMAL ANNEALING EFFECTS ON THE LUMINESCENCE

The photoluminescence spectra from a single QD layer annealed without dielectric capping for 30 s from 750–900 °C are shown in Fig. 1(a) 10 K and (b) RT. After annealing at 750 °C and above the dot luminescence is blue shifted and narrowed. This shows that the interdiffusion process is initiated at a much lower temperature than in quantum wells, where no significant shift is seen till high tempertures (850–900 °C).[1] The as-grown dot luminescence peaks at 1052 nm, with a linewidth of 81 meV at low temperature. At room temperature the peak shifts to 1158 nm with a slightly increased linewidth of 89 meV. The wetting layer (WL) luminescence can be seen as a high energy shoulder (960 nm at 10 K) to the dot luminescence in the as-grown spectrum. No change is seen in the relative intensities between this high energy shoulder and the dot peak at various excitation powers. Also it is found that the high energy shoulder significantly decreases in intensity with increasing temperature while the dot peak stays bright at higher temperatures. This indicates that the shoulder is not an excited state of the dot and is acting similar to a quantum well, i.e., the wetting layer in the Stranski-Kranstanow growth mode.

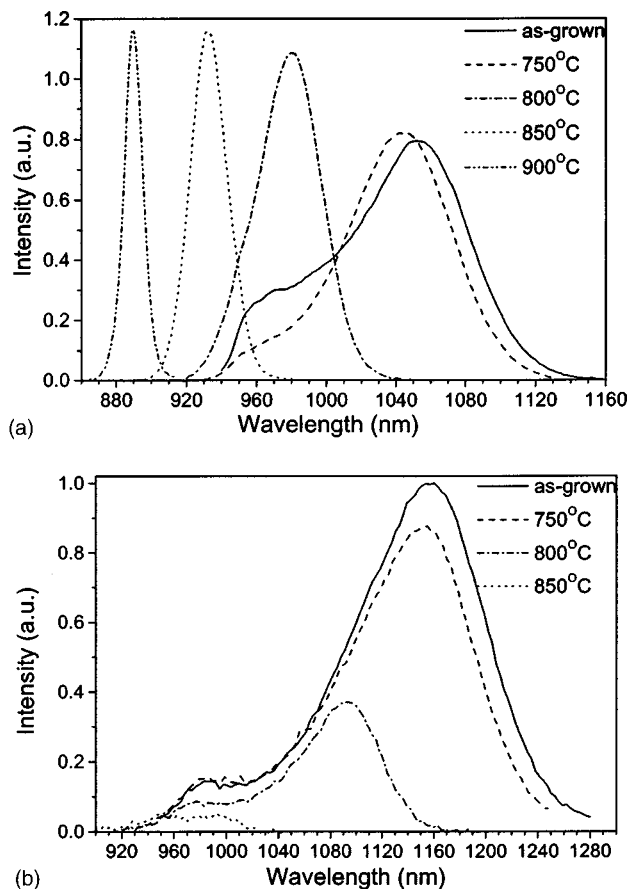

FIG. 1. Photoluminescence spectra of a single layer of quantum dots annealed from 750–900 °C for 30 s (a) 10 K (b) 300 K.

The dot luminescence is blue shifted by 220 meV when annealed at 900 °C for 30 s. The linewidth is reduced to 19 meV or 23% of the original linewidth. This linewidth reduction could come from several processes. Some report that as the dots increase in size (and decrease in In composition) there is a greater homogeneity in the size distribution (hence narrowing of emission spectra).[8,9] This would require a nonuniform interdiffusion of the ensemble to take place during annealing. Others believe that the interdiffusion is creating a two-dimensional-like system and at high annealing temperatures the dots become a quantum well.[7]

After annealing the quantum dot luminescence is enhanced at low temperatures, this is attributed partly due to the spectral narrowing and also to the annealing out of grown-in defects due to the low-temperature growth required for QDs. At room temperature the luminescence intensity is similar to the as-grown intensity for the 750 °C anneal but above 800 °C the dot luminescence intensity is greatly reduced [Fig. 1(b)], in contrast to the low-temperature luminescence. This could be due to carrier leakage from the shallower interdiffused QD potential. After annealing at 850 °C the room temperature PL is very low and has a broad double peak structure which is not seen in the low temperature luminescence spectrum. Also note in the low-temperature luminescence that at 800 °C the WD peak is still visible as a shoulder but it is no longer visible at 850 °C. At this high annealing temperature significant interdiffusion takes places leading to a very shallow confining potential for the dots. At

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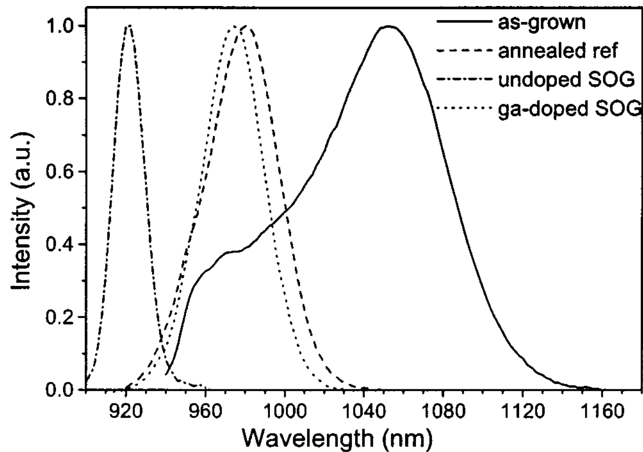

FIG. 2. Low-temperature (10 K) photoluminescence spectra of quantum dots annealed at 800 °C for 30 s with and without spin-on glass capping layers.

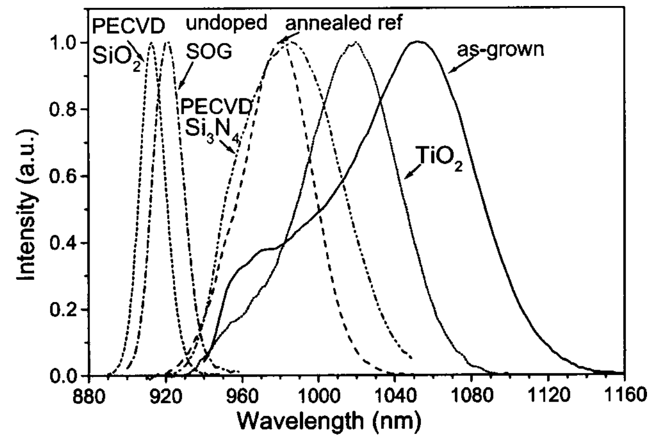

FIG. 3. Low-temperature (10 K) photoluminescence spectra of quantum dots with SiO_2, TiO_2, and Si_3N_4 capping layers annealed at 800 °C for 30 s.

low temperatures carrier transfer from the WL to the dots leads to a narrow luminescence peak from the QDs. However, at room temperature carriers have enough thermal energy to transfer from QDs to the WL, so a broad emission is seen.

IV. CONTROLLED INTERDIFFUSION

In order to fabricate photonic integrated circuits it is important to be able to have different amounts of shift created in different regions. This can be achieved by capping regions with different capping layers. Two types of spin-on-glass (SOG) were deposited on the samples, undoped or doped with Ga. The low-temperature luminescence is shown in Fig. 2. The undoped spin-on-glass film creates a large amount of additional interdiffusion, above that caused by thermal energy. The Ga-doped film shows very little additional shift from the annealed sample without any capping layer. By doping the film with Ga the diffusion of Ga out of the sample into the capping layer will be reduced. As this is the mechanism for vacancy creation the IFVD will be reduced, which has been demonstrated for quantum wells.[13]

One problem with using spin-on-glass films for IFVD is that there is very little control over the thickness of the film. The thickness of the layer as well as chemical composition can change the amount of interdiffusion created by the layer. The PECVD process allows us to change the thickness by changing the deposition time. The quality (or porosity) of the layer can be controlled by changing the deposition parameters, such as the deposition temperature. By changing the thickness of the film, the amount of interdiffusion can be controlled as the thicker film can accommodate more Ga atoms that out-diffuse. The amount of additional interdiffusin saturates when the layer is about 800 Å thick.[13] In this study 2000 Å thick films are deposited.

Another way of controlling the porosity is to control the chemical composition of the layer. Mixtures of SiO_xN_y have been used to create different amounts of shifts.[2] Ga atoms are insoluble in Si_3N_4, so the amount of shift created by PECVD Si_xN_y is controlled by the amount of oxygen incorporation from the source gas. In this study a 2000 Å layer of Si_3N_4 was deposited at 300 °C to create the best quality Si_3N_4 layer that creates no additional interdiffusion. In Fig. 3 it can be seen that the sample capped with PECVD silicon nitride has no additional shift from that of the thermal interdiffusion (no capping) whereas the PECVD silicon oxide shows the largest additional shift, larger than for the spin-on-glass.

Various capping layers have been found to enhance interdiffusion, but as the thermal shift is so large for quantum dots, the additional shifts have been found to be small in comparison to those achieved by using the same layers on quantum well samples. Work has been carried out to try to suppress the thermal interdiffusion.[6] This has been achieved by changing the stress at the dielectric/semiconductor interface. SiO_2 has a much smaller thermal expansion coefficient[14] (0.52×10^{-6} °C^{-1}) than GaAs (6.03×10^{-6} °C^{-1});[15] this creates a stress on the SiO_2/GaAs interface region during annealing. This translates into a compressive stress in the GaAs and helps to drive the Ga vacancies into the sample, thereby enhancing interdiffusion.[13,16] Other materials which have a larger thermal expansion coefficient than GaAs create tensile stress at the surface of the sample. Titanium oxide (thermal expansion coefficient[12] of 8.2×10^{-6} °C^{-1}) is an example where tensile stress is created at the interface. When tensile stress is created at the surface it has been found that agglomerations of vacancies are formed, rather than free movement of vacancies.[13,16] In Fig. 3 it can be seen that the titanium oxide layer is able to partially suppress thermal interdiffusion. There is also a large concentration of vacancies from the low-temperature growth very close to the dot region, the titanium oxide cannot completely inhibit their movement at higher temperature anneals. The differential shift from the TiO_2 to the SiO_2 peak is approximately 140 meV.

V. INTERDIFFUSION OF SINGLE LAYER VERSUS STACKED DOT STRUCTURES

In this section the interdiffusion created by capping layers was compared in a single layer and a three-layer stacked dot structure. Two different stacked structures were studied, one with GaP strain compensation layers and the other with a reference structure. The growth of the GaP strain compen-

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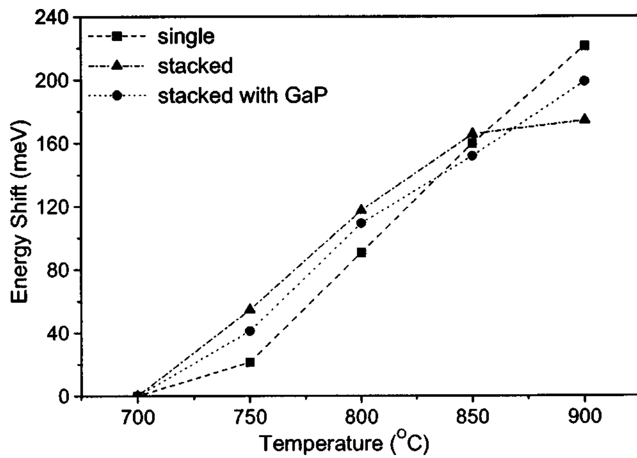

FIG. 4. Thermal shifts for single and stacked layers with and without GaP strain compensation layers.

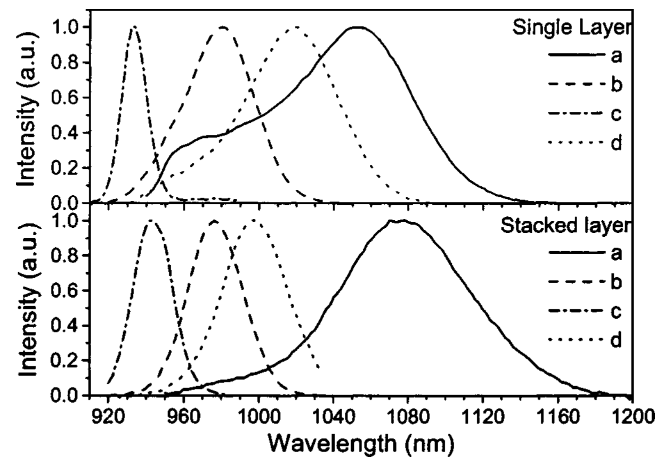

FIG. 5. Low-temperature (10 K) photoluminescence spectra of single and stacked quantum dots with various capping layers (a) as-grown, annealed at 800 °C for 30 s with (b) no capping layer, (c) SiO_2 and (a) TiO_2.

sation layers is described elsewhere.[11] The 300 Å GaAs barriers between each dot layer were grown at the same temperature as the dot growth (550 °C), which is much lower than normal GaAs growth temperature, therefore may introduce additional defects. The capping layers are deposited as described previously for the single layer.

Similar to the single layers, large energy shifts, narrowing, and increased intensity are seen in the photoluminescence of the stacked-layer structures after annealing. The energy shifts created by thermal interdiffusion of the two stacked layer structures together with the single layer for comparison are shown in Fig. 4. The stacked structures have increased energy shifts at low annealing temperatures. This could be due to the larger concentration of defects in the GaAs grown at low temperatures surrounding the dots in the stacked structure. These defects enhance the interdiffusion process during annealing. At higher annealing temperatures (>850 °C) the stacked dot structures have less energy shift than the single layer structure. This could be due to the large strain associated with the stacked QD structure, where strain relaxation might have partly taken place, having an opposite effect on the PL energy shift from interdiffusion.

The stacked structures were capped with PECVD silicon dioxide and e-beam evaporated titanium oxide. The energy shifts created by these two capping layers were compared with uncapped regions and the energy shifts created in single layer structures. The photoluminescence spectra of the reference stacked structures compared to a single layer with the different cappings are shown in Fig. 5. The effect of the capping layer is reduced for the stacked sample, because the thermal interdiffusion is greater. There are more grown-in defects close to the quantum dots in the stacked structure which compete with the vacancies introduced by the capping layers. Therefore, the vacancies created by the capping layer are not as significant an effect as in the case of single layers. Similarly, the strain caused by the titanium dioxide is not able to completely suppress the movement of grown-in defects that are close to the active region. The energy shifts seen in uncapped and capped samples from all three types of samples are shown in Fig. 6. With the GaP strain compensation layers the titanium oxide cap has a much larger suppression effect. This is due to the tensile strain created by the strain compensation layers that helps to suppress movement of the vacancies around the dot region. The GaP strain compensation layers slightly reduce the effect of the silicon oxide layer but as it was such a large effect to begin with, the differential between the SiO_2 and TiO_2 regions is actually larger with the strain compensation layers. The differential shifts between SiO_2 and TiO_2 are around 100 meV for the stacked structure with GaP but only 80 meV for the stacked structure with no GaP layers.

It seems that at high annealing temperatures, saturation in the interdiffusion occurs. This is most noticeable in the additional interdiffusion created by silicon oxide capping. In the single layer case the additional interdiffusion created is constant above an annealing temperature of 800 °C. The saturation of IFVD using PECVD SiO_2 or SOG capping has only been observed in high-temperature anneals when the capping layer is thin and becomes saturated with Ga atoms.[2] This does not occur in this case, as no saturation is seen using the same layers on QW samples.[13] Also note that although the single layer QD structure is saturated, the stacked layer continues to have increased additional interdiffusion.

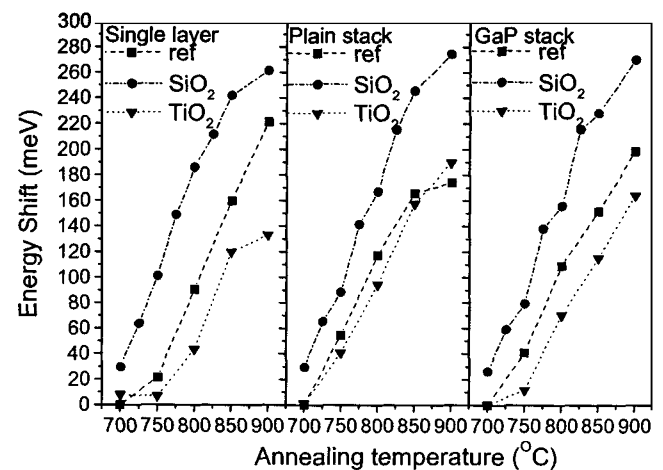

FIG. 6. Total shifts for single and stacked layers with and without capping layers of SiO_2 and TiO_2, after annealing at various temperatures for 30 s.

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However, the additional interdiffusion created in the stacked layer structures is less than in the single layer case, due to the increased thermal interdiffusion. Similar amounts of enhancement are only reached for the highest annealing temperatures. The saturation may occur due to a competition between interdiffusion and strain relaxation. The room temperature luminescence intensity is much reduced after annealing at the higher temperatures, indicating a strain relaxation process. The difference in the stacked dot case may be due to the increased grown-in defects from the low growth temperature of the barriers. Considering the fact that Ga vacancies caused by the capping layer only diffuse from the one direction (opposite the growth direction) towards the QDs, it is difficult for them to compete with the grown-in defects distributed all over the sample to make additional contribution to interdiffusion. Hence, an increase in the IFVD is seen at higher temperatures for the stacked structures while the single layer IFVD saturates. Strain effects in stacked-layer structure may also be playing a more significant role in determining IFVD, and further studies are required to elucidate this issue.

VI. CONCLUSION

The interdiffusion of single and stacked layer quantum dot structures have been studied. The thermal interdiffusion is found to be a large effect and requires impurity free vacancy disordering to be carried out at lower temperatures than previously used for quantum well samples. Spin-on-glass and PECVD silicon oxide capping layers have been used to enhance the interdiffusion while silicon nitride can be used to protect the surface without any additional interdiffusion. Titanium oxide can be used to suppress the thermal interdiffusion, providing a large range of wavelength tuning. Differential shifts between silicon oxide and titanium oxide are around 140 meV for a single layer of dots but are reduced to 80 meV stacked structures without GaP strain compensation layers. using GaP strain compensation layers increases the differential shift to 100 meV.

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