Control of silica cap properties by oxygen plasma treatment for single-cap selective impurity free vacancy disordering

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By exposing the SiO_2 films used as annealing caps in the process of impurity free vacancy disordering (IFVD) to an oxygen plasma, which is produced in a reactive ion etching machine, the effect of the exposed caps on quantum well intermixing can be substantially controlled. The effect of the oxygen treatment is manifested in inhibiting the Ga outdiffusion from GaAs/AlGaAs heterostructures. A selective IFVD process using identical silica caps has been obtained by selective exposure of the caps to oxygen plasma. Differential band gap shifts in excess of 100 meV were achieved with control samples exhibiting band gap shifts less than 10 meV. © *1999 American Institute of Physics.* [S0003-6951(99)02805-3]

Post growth control of the band gap of quantum wells using disordering techniques has recently become an alternative[1] to the customarily used etch and regrowth techniques[2] to realize photonic and optoelectronic integrated circuits. Etch and regrowth is often associated with low efficiencies and poor yields due to the nonradiative centers and oxides generated at the regrown interfaces. Impurity free vacancy disordering (IFVD) is widely used in quantum well intermixing (QWI) due to its simplicity, low optical losses, and low damage performance.[1,3] IFVD makes use of the diffusion of point defects, namely group three vacancies and interstitials, created by thermal treatment in a rapid thermal annealer (RTA). Samples are usually capped with dielectric layers, which either promote, or inhibit, the diffusion of Ga, and hence enhance or suppress QWI. Various dielectric cap ensembles have been studied to achieve a selective intermixing process.[4–6] SiO_2 is the most widely used cap due to the early work using such films for GaAs integrated circuit processing.[7,8] In this letter we report the use of a single type of SiO_2 cap to produce a spatially selective IFVD process, which does not depend on either the type or the doping of the GaAs/AlGaAs heterostructure it is used on, or the technique used to deposit the SiO_2.

In GaAs/AlGaAs heterostructures, QWI is based on the diffusion of Ga atoms out of and Al atoms into the QWs. The Ga/Al interdiffusion process has to be carried out through GaAs native defects, namely group III vacancies and interstitials, V_{III} and I_{III}. The self group III sublattice diffusion coefficient is dependent, not only on the diffusion coefficient of the group three vacancies $D_{V_{III}}$, but also on their concentration, $[V_{III}]$.[9,10] IFVD uses chiefly V_{III}, which results from the Ga outdiffusion in the dielectric cap at elevated temperatures to enhance interdiffusion.[11] The concentration of vacancies is, therefore, directly related to the number of Ga atoms which diffuse into the dielectric cap. Accordingly, if the solubility and/or diffusivity of Ga in a single cap can be controlled, then the amount of intermixing can also be controlled.[12] Although attempts have been made to obtain such a process, no success has been reported to date in having sufficient control of the dielectric film properties to produce a differential shift adequate for device applications.[13] It should be noted also that recently another alternative for obtaining differential shifts was achieved by controlling the status of the semiconductor surface before annealing.[12] Such an approach, although successful, might affect the quality of the surface after processing, jeopardizing the electrical contact quality of these surfaces.

Increasing the resistance of dielectric caps, especially SiO_2 and Si_3N_4, to erosion during reactive ion etching (RIE) is a topic of current interest.[14,15] One approach to film densification, which was demonstrated for SiO_2 films, is based on annealing silica at temperatures above 875 °C. Such high annealing temperatures make the processes only suitable for Si wafers and not for the III–V semiconductors because of their low thermal stability.[14] Another technique based on ion bombardment was demonstrated on Si_3N_4 films. In this technique Si_3N_4 films are exposed to oxygen plasma, which was found to increase their resistance to erosion during etching.[15] Such exposure was also reported to cause an increase in the refractive index of the films after exposure, which reached a maximum of 3.7% after 30 min treatment for a 140 nm Si_3N_4 film. The operating conditions for the oxygen plasma used in the treatment were: a radio frequency (RF) power of 50 W, an O_2 flow rate of 25 sccm, and a gas pressure of 100 mTorr, which result in a direct current (dc) self bias of 110 V. A set of experiments has been conducted to investigate the effect of exposing the silica caps used in IFVD to the same treatment that increases the resistance of Si_3N_4 masks to erosion.

The material used in the experiment was a metalorganic vapor phase epitaxy (MOVPE) grown waveguide structure with a 4 μm lower and 0.8 μm upper cladding layer of $Al_{0.41}Ga_{0.59}As$. The guiding region was a 78 period multiple quantum well (MQW) with 10 nm $Al_{0.38}Ga_{0.62}As$ barriers and 2.8 nm GaAs wells. Samples from the MQW wafer were capped with 200 nm of electron beam evaporated SiO_2 and exposed to the oxygen plasma for 30 min. They were then

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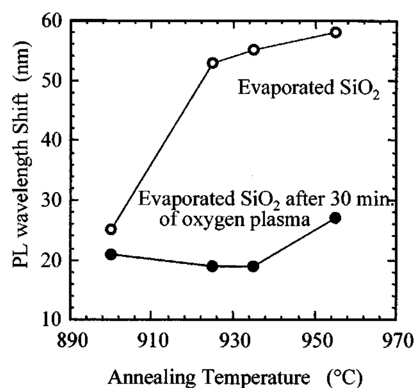

FIG. 1. Change in PL emission wavelength as a function of temperature for undoped MQW samples annealed for 60 s with 200 nm of evaporated SiO_2 cap (○). Change in PL emission wavelength is also shown for samples annealed after exposure to 30 min of oxygen plasma with parameters as reported in Ref. 15 (●).

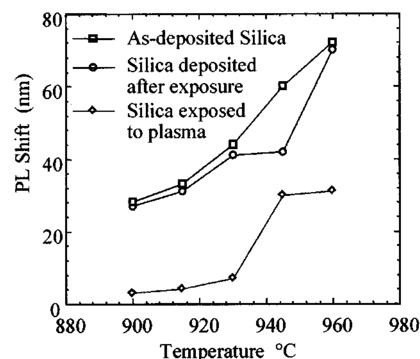

FIG. 2. Change in band gap emission wavelength as a function of temperature for p-i-n doped DQW samples annealed for 60 s with 350 nm of evaporated SiO_2 cap. Results shown are for samples annealed after exposure to 70 min of oxygen plasma with a flow rate of 5 sccm, at a pressure of 10 mTorr, and a power of 275 W (◇), annealed without exposure (□), and annealed with evaporated SiO_2 cap deposited after exposure to the same plasma process (○).

annealed along with control unexposed samples at different temperatures. The amount of the photoluminescence (PL) shift versus the annealing temperature is plotted in Fig. 1. The unexposed samples show amounts of intermixing three times larger than for the exposed samples. Differential band gap shifts in excess of 70 meV were achieved between the exposed and unexposed samples when annealed at 925 °C. Although the samples exposed to oxygen plasma intermix considerably less than the unexposed ones, they do show PL shifts as high as 20 nm. This is drawback when looking for a cap to completely inhibit intermixing. However this effect can be overcome by optimizing the plasma parameters for minimal intermixing, as will be explained below.

The material used in the optimization experiment was a 10 nm GaAs double quantum well in a positive-intrinsic-negative p-i-n doped heterostructure, which is a profile used for laser diodes.[1] Samples were covered with various thicknesses of electron beam evaporated SiO_2 and were then exposed to the oxygen plasma under different conditions. The optimum performance was obtained after exposing the samples for 70 min to an oxygen plasma with the following parameters: a film thickness of 350 nm, with a 5 sccm O_2 flow rate, a pressure of 10 mTorr and a power of 275 W. This set of conditions results in a self dc bias of 800 V. A set of samples with 350 nm of electron beam evaporated SiO_2 was then processed with these parameters. Another set of samples without SiO_2 caps was exposed to the plasma, and had an identical 350 nm of electron beam evaporated SiO_2 deposited after plasma exposure. A third set of samples was used as a reference, also coated with 350 nm of electron beam evaporated SiO_2. The PL shift versus the annealing temperature for the three sets of samples is plotted in Fig. 2. The samples with unexposed SiO_2 films exhibit intermixing within the expected range for the thickness of the cap, and the annealing temperatures used.[4] However, the samples exposed to the plasma exhibit minimal intermixing, less than 10 meV, for temperatures below 945 °C, above which intermixing extends to a few tens of mega-electron-volts. The samples exposed to the oxygen plasma prior to the deposition of silica caps show intermixing behavior very similar to that of the unexposed silica caps. This suggests that the plasma exposure does not affect the GaAs at surface, and the observed effects are due to changes in the cap properties. As can be seen in Table I, the refractive index of the silica films, at 633 nm, changed from 1.532 before to 1.474 after the exposure of plasma. The thickness of the film decreases by 10% after the exposure. This can be explained by the high bias, ≈800 V of the plasma, which can assist in sputtering off the film, by ion bombardment. Also, the etch rate of the exposed film is 5% less than that of the unexposed one.

The refractive index of the as-deposited films, being above that of the thermal oxide, indicates a Si rich film agreeing with previous reports for the same type of SiO_2.[16] The observed reduction in the refractive index, after plasma exposure, can be explained in one of two ways.

The first proposes that oxygen is incorporated in the films during plasma exposure so reducing the refractive of the layer but only within the ion penetration range. This would mean that the refractive index we measured after exposure is an average of two layers one identical to that of the original film, and the other oxygen rich. However, the ion energy is sufficient to allow penetration no further than ~5 nm in such an amorphous material, and so the observed reduction in refractive index is larger than would be expected from such a hypothesis.

Recent experiments showed that electron-beam deposited SiO_2 can have a pore fill factor of 0.23. Also 4.1% increase in the visible refractive index of the as-grown films after their exposure to air was observed. According to the effective medium approximation, this increase in the refractive index was ascribed to the incorporation of H_2O in the

TABLE I. Properties of the silica caps before and after exposure to 70 min of oxygen plasma with a flow rate of 5 sccm, at a pressure of 10 mTorr, and a power of 275 W.

Film property	Before exposure	After exposure	Relative change
Thickness (nm)	355	320	−9.8%
Refractive index	1.532	1.474	−3.9%
Etch rate ($nm\ min^{-1}$)	30	27	−10%

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film pores.[17] Another explanation proposes that during the oxygen treatment, the H_2O in the film pores will be desorbed and the pores, now free from H_2O, may be sealed by the ion exposure. This makes the effective refractive index of the pores 1 (the refractive index of air), instead of 1.33 (the refractive of H_2O). The measured reduction in the refractive index for our process, 3.9%, therefore agrees well with what has been previously reported due to the incorporation of H_2O.[17] Clearly this hypothesis of sealed pores needs verification by electron microscopy and this will be attempted. However, this assumption would indicate that H_2O and air in the film pores play a key role in assisting and preventing Ga outdiffusion and hence QWI, respectively.[18]

We have demonstrated control of the extent of QWI in various GaAs/AlGaAs heterostructures by exposing the SiO_2 films used in the process of impurity free vacancy disordering to an oxygen plasma, produced by a reactive ion etching machine. Control was observed for doped and undoped GaAs/AlGaAs samples. The control was also obtained for different types of SiO_2. According to the understanding of the process, the inhibition of intermixing can be ascribed to plasma exposure reducing the diffusivity of Ga in the cap. It seems that the reduced diffusivity of Ga in such films is due to changing the properties and porosity of the SiO_2 film. Further investigations of the plasma effect on the films are in progress. Such studies should unfold some of the mechanisms involved in IFVD. Selective exposure to oxygen plasma has been used to realize a selective IFVD process using identical silica caps, with band gap shifts in excess of 100 meV achieved with less than 10 meV shift underneath the unintermixed regions. The process has the potential to offer single step, low damage, spatially controllable IFVD.

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