Surface morphology of SiO₂ coated InP/InGaAs/InGaAsP microstructures following the irradiation with ArF and KrF excimer lasers

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ABSTRACT

Successful fabrication of devices from quantum well-internixed material requires efficient control of its surface morphology. To address this problem, we have employed atomic force microscopy to study surface morphology of InP/InGaAs/InGaAsP QW microstructure coated with d_{SiO₂} = 50, 150, 190, 243 and 263 nm thick SiO₂ films. Both ArF (193 nm) and KrF (248 nm) excimer lasers have been used to irradiate series of samples with up to 400 pulses of fluence 76 to 156 mJ/cm². The roughness (σ_{RMS}) of SiO₂ layer after both lasers irradiation and RTA decreases as the pulse number increases. Following RTA, a smoother surface morphology was observed for all irradiated samples. The cap InP layer was found to have a relatively smaller roughness (~ 0.4 nm) due to the protection provided by the SiO₂ layer during excimer laser irradiation and high temperature RTA. For samples coated with 50- or 150-nm-thick SiO₂ and irradiated by the ArF laser, the blueshift is only obtained when the SiO₂ layer was ablated. However, the sample coated with 243-nm-thick SiO₂ (d_{SiO₂} ≈ λ_{KrF}), following the 75-pulse-irradiation with the KrF laser at 124mJ/cm² and RTA, showed a smooth surface (σ_{RMS} = 1.8 nm) and maximum blueshift of 74 nm achieved without removal of the SiO₂ layer.

Keywords: Surface morphology, Quantum Well Intermixing, InP/InGaAs/InGaAsP microstructure, ArF excimer laser, KrF excimer laser, blueshift, SiO₂ layer, photonic devices

1. INTRODUCTION

Post growth quantum well intermixing (QWI) is an attractive method to engineer the bandgap of quantum well (QW) semiconductors. It allows active and passive components to be integrated monolithically at relatively reduced costs. Various QWI techniques have been developed, including impurity free vacancy intermixing, impurity induced intermixing, plasma assisted intermixing and laser induced intermixing. Excimer laser irradiation on III-V semiconductors surfaces has been investigated for this purpose due to its simplicity in achieving selected area bandgap engineering of GaAs and InP based QW microstructure.

Impurity free vacancy disordering technique has been investigated, where a SiO₂ layer deposited on top of InP based multiple quantum well (MQW) and quantum dot (QD) microstructures was used to facilitate intermixing through In and Ga atom outdiffusion, or efficient creation of group V interstitials that promote intermixing during rapid thermal annealing (RTA). However, in continuous wavelength (CW) Nd:YAG laser RTA, group V atoms outdiffuse reaching SiO₂ layer through microcracks created during laser processing which enhance the As/P intermixing in InAs/InP QD microstructure.

Due to the relatively low thermal and chemical stability of III-V compound semiconductors, laser irradiation can alter the structural, optical and electronic properties of these materials. For instance, it was reported that the Atomic Force
Microscopy (AFM) measured surface roughness of InP irradiated by a nanosecond UV laser ($\lambda=337$ nm) increases systematically with the laser pulse number.$^{12}$ However, the InP surface crystalline structure and chemical composition remain unchanged for up to 6000 pulses of the below-ablation threshold fluence. At higher pulse fluences, nanosecond lasers are reported to decompose thermally InP and lead to a preferential removal of phosphorous.$^{13}$

It is well known that SiO$_2$ layer is relatively transparent to ArF and KrF excimer laser wavelengths,$^{14}$ and it has been shown that KrF laser irradiation of a SiO$_2$ coated Si wafer can melt Si and create a periodic surface structure, without removal of the SiO$_2$ layer.$^{15}$ However, the cross sectional SEM micrographs show that some Si protrudes the SiO$_2$ layer and, thus, a modified interface profile is observed.$^{16}$ Simulation of laser interaction with SiO$_2$ coated materials indicates that the SiO$_2$ layer can be melted or ablated if the laser fluence is large or the substrate adjacent to the SiO$_2$ layer has a large absorption at this wavelength.$^{17}$

In this study, we used both ArF and KrF lasers to irradiate InGaAs/InGaAsP microstructures coated with InP and different thickness SiO$_2$ layers. The surface morphology of SiO$_2$ and InP layers was examined with AFM after both laser irradiation and RTA.

2. EXPERIMENT

A schematic cross-section of the investigated QW structure is shown in Figure 1. It consists of 5 6-nm-thick In$_{0.47}$Ga$_{0.53}$As wells separated by 4 10-nm-thick In$_{0.33}$Ga$_{0.67}$As$_{0.52}$P$_{0.48}$ barriers. The QW structure is grown on n-doped InP substrate and is designed to emit at 1.540 $\mu$m at room temperature. Samples, typically 8 mm x 8 mm, were first cleaved from a wafer and cleaned with standard solvents. Layers of SiO$_2$, $d_{\text{SiO}_2}=50, 150, 190, 243$, and 263 nm thick were deposited on top of the QW structure by a plasma enhanced chemical vapour deposition (PECVD) method. The SiO$_2$ films had their extinction ratio of $10^{-7}$ at the incident wavelength of 632.8 nm.

![Figure 1. Schematic cross-section of the investigated QW structure.](image)

We used an ArF laser ($\lambda=193\text{nm}$) delivering 16 ns pulses of fluence in the range of 67-150 mJ/cm$^2$, and a KrF ($\lambda=248$ nm) laser delivering 23 ns pulses of fluence in the range of 100-190 mJ/cm$^2$. Double microlens fly-eye-array homogenized laser beams were used to project a circular mask on the sample surface. With computer controlled X-Y-Z-Theta sample stages, the two setups allowed for the processing of samples at different sites of approximately 0.9 and 1.4 mm in diameter for ArF and KrF laser, respectively. The irradiation was carried out in an ambient air environment.

Following the irradiation, the sample was annealed with a commercial RTA processor (Jetfirst) in an atmosphere of mixed hydrogen and nitrogen (0.1: 0.9) at 700 °C for 2 minutes. Thus, the annealing conditions for different sites on the same sample were nominally the same. After RTA, the SiO$_2$ layer was removed by immersing the whole sample in a 10% solution of HF in deionized H$_2$O.$^{18}$

Room temperature photoluminescence (PL) measurements were carried out with a commercial mapper (Philips PLM-150). A Nd:YAG laser was used to excite the sample while the luminescence was dispersed by a monochromator and detected by an InGaAs photodiode array. The PL maps were obtained based on the QW electron-hole recombination peak, which for the as-grown material was located at 1540 nm.

Sample surface morphology was imagined with an Atomic Force Microscope (AFM) (Digital Instrument, Nanoscope III) operating in a tapping mode. An etched single-crystal silicon tip with a rectangular, single beam cantilever TESP (Digital Instruments) was used for collecting AFM images. The TESP tip radius is around 5-20 nm, the cantilever spring constant
is 20-100 N/m and the resonance frequency is around 200-400 kHz. The tapping mode images were collected at scan rate of 1.97 Hz for 5 μm x 5 μm region and at 1.45 Hz for 2.5 μm x 2.5 μm, or smaller region, (512 points line), which is reported to have higher accuracy in roughness measurements. The root mean square surface roughness, $\sigma_{RMS}$, of the investigated samples was determined as the standard deviation of $Z$ in the given region:

$$\sigma_{RMS} = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{av})^2}{N}}$$

where $Z_{av}$ is the average $Z$ value in this region, $Z_i$ is the i-th $Z$ value, $N$ is the point within this region.

A commercial profilometer (Tencore alphastep 200) has been used to measure the ablation depth of the laser irradiated sites.

3. RESULTS AND DISCUSSIONS

3.1 ArF laser induced QWI on samples coated with SiO$_2$ layer

The bandgap energy of SiO$_2$ (9 eV) is greater than photon energy of both ArF (~6.4 eV) and KrF (~5.0 eV) lasers. Hence, the SiO$_2$ layer should absorb only weakly the radiation of these lasers. Figure 2 shows PL maps of samples coated with 50 and 150 nm thick SiO$_2$ layers that were irradiated with the ArF laser at pulse fluence of 76 mJ/cm$^2$. PL maps and microscope images are shown in top and bottom rows of each series. It can be seen that SiO$_2$ layers were not ablated completely, even with 400 pulses. Also, the results indicate that an obvious blueshift takes place only in the regions where the SiO$_2$ layer is ablated. This suggests that for the investigated 50 and 150 nm thick SiO$_2$ layers, the ArF radiation is not efficient to generate defects in the InP layer that would promote the intermixing process.

![Figure 2](image)

Figure 2. Room temperature PL maps and microscopic pictures of a series of spots on SiO$_2$ (50 and 150 nm thick) coated QW microstructures irradiated with ArF laser at 76 mJ/cm$^2$.

Figure 3 shows 2.5 μm x 2.5 μm 2D AFM images of the as-grown, 150 nm thick, SiO$_2$ layer (Fig. 3a), and after it was irradiated with 20 (Fig. 3b) and 100 pulses (Fig. 3c) of the ArF laser. In each case, the as-grown and laser irradiated samples were RTA for 2 min at 700° C. One notices that the laser-irradiated sites have, qualitatively, similar grain structure as that of the as-grown material. The grain structure is formed during PECVD, with the grain size depending on the SiO$_2$ layer thickness. The corresponding cross-section profiles, shown in Fig. 3 below each AFM image, indicate that the grain size of the investigated SiO$_2$ layer is around 60 nm. For a quantitative analysis of the surface roughness, the $\sigma_{RMS}$ amplitude is plotted in Figure 4 as a function of the number of the irradiating pulse. We can see that the surface roughness amplitude decreases from 1.31 nm for the as-grown material to 1.07 nm for the 150-pulse-irradiated material. It is likely that laser-induced densification of SiO$_2$ and/or partial melting are the mechanisms responsible for this surface smoothing effect.
Figure 3. 2D AFM micrographs illustrating surface morphology of a 150 nm thick as-grown layer of SiO\(_2\) (a), and following the irradiation with 20 (b) and 100 pulses (c) of the ArF laser at 76 mJ/cm\(^2\). In each case, the as-grown and laser irradiated samples were RTA for 2 min at 700\(^\circ\) C.

![AFM micrographs of SiO\(_2\) surface](image1)

Figure 4. Roughness amplitude (\(\sigma_{\text{RMS}}\)) of the SiO\(_2\) surface after ArF laser irradiation at 76 mJ/cm\(^2\) with different pulse number and RTA for 2 min at 700\(^\circ\) C.

![Graph of RMS roughness vs pulse number](image2)

Figure 5 illustrates surface morphology of InP after the SiO\(_2\) layer was etched with the HF:H\(_2\)O solution. The site irradiated with 100 pulses seems smoother than that of the as-grown material. Also, fewer nanoparticles have been observed on the laser-irradiated sites than on the as-grown material. The average roughness (\(\sigma_{\text{RMS}}\)) of the laser-irradiated sites, shown in Figure 6, fluctuates around 0.4 nm. This figure also shows that the roughness uncertainty decreases with the number of pulses and gets closer to the one of a non-irradiated site. This demonstrates that SiO\(_2\) layer protected InP surface from direct ArF laser irradiation, which is consistent with the absence of the laser-induced intermixing process observed in this case.

![Graph of RMS roughness vs pulse number and InP surface](image3)
Figure 5. AFM micrographs of the InP surface after ArF laser irradiation with 76 mJ/cm² and RTA and after removing SiO₂ layer

Figure 6. The RMS roughness of InP layer after ArF laser irradiation, RTA and after removing SiO₂ layer vs. pulse number for 76 mJ/cm²

Figure 7 shows the 5 µm x 5 µm 2D and 3D AFM images of the InP surface revealed after the 150-nm-thick SiO₂ layer was ablated with 100 pulses of the ArF laser. The formation of a grating-like laser induced periodic surface structure (LIPSS)²⁴ is clearly observed in this region. The grating LIPSS period and height are around 1 µm and 10 nm, respectively. Figure 7 (a) also shows the presence of numerous 12 nm deep nano-holes on the processed surface. The roughness of this region is 2.11 nm, which compares to ~ 0.5 nm of the as-grown InP surface. We note that following the RTA step, the surface defects created during the ArF laser interaction with the InP layer induced, in this case, a 38 nm blueshift.
3.2 KrF laser induced QWI on samples coated with SiO$_2$ layer

Figure 8 (a) shows PL maps and microscopic pictures of SiO$_2$ coated samples that were irradiated with the KrF laser at 156 mJ/cm$^2$ (Fig. 8a) and 128 mJ/cm$^2$ (Fig. 8b). It is evident that the 50 nm thick SiO$_2$ layer is ablated with 50 pulses at 156 mJ/cm$^2$. A partial removal of the 150 and 190 nm thick SiO$_2$ layers is observed following their irradiation with up to 200 pulses. A profilometric scan of the 150-pulse irradiated sample, initially coated with a 150 nm thick SiO$_2$ layer, revealed the formation of a 10 nm deep crater. This could be related to a partial ablation and/or densification of the laser-irradiated SiO$_2$ layer. In addition, numerous laser-induced microcracks have been observed for these samples. The microscopic pictures and PL maps of sites from samples coated 263 nm thick SiO$_2$, after KrF laser irradiation at 128 mJ/cm$^2$ and RTA, show no obvious laser ablation and blueshift for 50 and 100 pulses irradiated sites. At 200 pulses, the color of the SiO$_2$ layer changes significantly, which suggests that some structural changes take place in the laser-irradiated SiO$_2$.

Figure 8. Room temperature PL maps and microscopic pictures of a series of spots on SiO$_2$ (50, 150, 190 and 263 nm thick) coated QW microstructures irradiated with the KrF laser at 156 mJ/cm$^2$ (a) and 128 mJ/cm$^2$ (b) and the indicated number of pulses.
The results for samples coated with the 243-nm-thick SiO₂ layer, i.e., \(d_{\text{SiO₂}} \approx 2 \lambda_{\text{KrF}}\), are summarized in Figure 9. It can be seen that the KrF laser irradiation with 124 mJ/cm² and RTA leads to blueshifts that, with the exception of the 200-pulse irradiated site, take place without the removal of the SiO₂ layer. The upper and lower numbers shown for each site in this figure indicate the laser pulse number and the average amplitude of blueshift, respectively. For example, it can be seen that the 8-pulse irradiated site has been blueshifted by 70 nm, and that the maximum blueshift of 74 nm is achieved after irradiation with 75 pulses. We note that a uniform blueshift of 59 nm has been achieved following the irradiation with only 5 laser pulses. Figure 10 summarizes the net blueshift vs. pulse number of both as-grown (uncoated) material and samples coated with a 243 nm thick SiO₂ layer following their irradiation with the KrF laser and the RTA step. The maximum blueshift for sample coated with 243 nm SiO₂ layer is less than that for the uncoated samples irradiated in an air environment. This may be due to the lower number of defects created on the surface of SiO₂ coated InP. It can be seen that for both samples, the blueshift increases with increasing the pulse number, then it has a tendency to saturate. At N>50 pulses, the blueshift for the uncoated sample decreases due to the obvious ablation effect which reduces the ‘reservoir’ of laser created defects. However, for the sample coated with the 243 nm SiO₂ layer, the blueshift does not decrease, likely due to the protection against ablation that is provided by the SiO₂ layer.

![Figure 9. Room temperature PL map of an InP/InGaAs/InGaAsP QW microstructure after KrF laser irradiation and RTA. The pulse number and the blueshift amplitude are shown by the top and bottom numbers, respectively.](image)

![Figure 10. Net blueshift amplitude dependence on the pulse number of the KrF laser delivering 124 mJ/cm² and irradiating the surface of uncoated InP (square symbols) and SiO₂ (243 nm thick) coated InP cap (circle symbols). The results obtained after 2 min RTA at 700°C.](image)

Table 1 shows the measured blueshift amplitude for a non-irradiated uncoated QW microstructure and for non-irradiated microstructures coated with \(d_{\text{SiO₂}} = 50, 150, 190, 243 \) and 263 nm thick SiO₂ films. A 13 nm blueshift is observed for the microstructure coated with a 243 nm thick SiO₂, which is similar to the blueshift for the uncoated \((d_{\text{SiO₂}} = 0 \text{ nm})\) sample. These results demonstrate that the RTA-induced outdiffusion of In or P atoms from the InP/InGaAs/InGaAsP QW microstructure is negligible and, therefore, no efficient atomic intermixing can occur at the applied RTA temperature.

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Table 1

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Bluemplitude (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>13</td>
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<tr>
<td>Coated with 50 nm SiO₂</td>
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<tr>
<td>Coated with 150 nm SiO₂</td>
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<tr>
<td>Coated with 243 nm SiO₂</td>
<td>13</td>
</tr>
<tr>
<td>Coated with 263 nm SiO₂</td>
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Table 1. Blueshift amplitude vs. thickness of the SiO₂ layer for non-irradiated QW microstructures.

<table>
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<tr>
<th>SiO₂ layer thickness (d_{\text{SiO₂}}) (nm)</th>
<th>0</th>
<th>50</th>
<th>150</th>
<th>190</th>
<th>243</th>
<th>263</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blueshift (nm)</td>
<td>13</td>
<td>11</td>
<td>10</td>
<td>11</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

The microscopic images of sites irradiated with 2, 25, 75 and 100 pulses of the KrF laser at 124 mJ/cm² are shown in Figure 11. The color change of the SiO₂ layer is likely related to the laser-induced densification and, consequently, change of the refractive index of this material.²⁵ The profilometry measurements have indicated that the overall thickness reduction of the irradiated SiO₂ layer does not exceed 10 nm.

![Microscopic images of KrF irradiated samples coated with a 243 nm SiO₂ layer and irradiated with the KrF laser at 124 mJ/cm² (after RTA).](image)

Figure 11. Microscopic images of KrF irradiated samples coated with a 243 nm SiO₂ layer and irradiated with the KrF laser at 124 mJ/cm² (after RTA).

![AFM micrographs of as-grown SiO₂ (a) and the SiO₂ layer irradiated with 2 pulses (b) and 25 pulses (c) of the KrF laser at 124 mJ/cm² (before RTA).](image)

Figure 12. AFM micrographs of as-grown SiO₂ (a) and the SiO₂ layer irradiated with 2 pulses (b) and 25 pulses (c) of the KrF laser at 124 mJ/cm² (before RTA).

Figure 12 shows AFM micrographs of as-grown, 243 nm thick SiO₂ layer and the same thickness SiO₂ layer irradiated with 2 and 25 pulses of the KrF laser at 124 mJ/cm², before it was RTA. The grain structure of the material is well seen for both irradiated and non irradiated sites. The average grain size of this SiO₂ layer is around 50 nm, which is smaller than that of the 190 nm thick SiO₂ layer. The average grain height, measured by AFM, decreases from 5.22 nm (Fig. 12b) to 4.02 nm (Fig. 12c) as the pulse number increases up to 25 pulses.

The AFM images of the 243 nm thick SiO₂ layer, after it was RTA, are shown in Figure 13. The average grain height of the irradiated structures is reduced likely due to laser-induced melting.²⁰ This causes the roughness decreases by around
0.1 nm after RTA as demonstrated in Figure 14. The initial roughness decrease when N=20 is due to laser heating and melting grain structure. Then it increases because of the nano-features creation at larger pulse number. Finally, it decreases again due to obvious laser material melting and partial removing of SiO₂ layer. The minimum achieved roughness is demonstrated on site irradiated with 20 pulses which gives 66 nm of blueshift.

![AFM micrographs of as-grown SiO₂ and the SiO₂ layer irradiated with 2 pulses and 25 pulses of the KrF laser at 124 mJ/cm² (after RTA).](image)

Figure 13. AFM micrographs of as-grown SiO₂ (a) and the SiO₂ layer irradiated with 2 pulses (b) and 25 pulses (c) of the KrF laser at 124 mJ/cm² (after RTA).

![RMS roughness of the SiO₂ layer after KrF laser irradiation at 124 mJ/cm² vs. pulse number before and after RTA.](image)

Figure 14. The RMS roughness of the SiO₂ layer after KrF laser irradiation at 124 mJ/cm² vs. pulse number before and after RTA.

The InP surface morphology of a non-irradiated InP and after the 2 and 25 pulse KrF laser irradiation (124 mJ/cm²) of InP coated with the SiO₂ layer is shown in Figure 15. The results are shown after RTA and the removal of the SiO₂ layer. Numerous nano-holes created in InP can be seen for the 2 and, especially, for the 25-pulse irradiated surface. None of these nano-holes have been found on non-irradiated sites, hence, the role of the KrF laser is evident in the formation of these nano-holes. It can be seen that the nano-hole depth increases from 2.5 nm to 3.3 nm and the width increases from 39 nm to 73 nm as the pulse number increases from 2 to 25 pulses. The density of nano-holes is also greatly increased for the 25 pulse irradiated site. We observed 8 nm deep, 83 nm wide nano-holes on sites irradiated with 100 pulses of the KrF laser (these results are not shown here). The formation of nano-holes leads to the increased average roughness of the irradiated surface, while the density of nano-holes saturation is observed at a large pulse number. The amplitude of
blueshift dependence with pulse number follows the same behavior, as it can be seen in Figure 10. Therefore, it seems that the presence of nano-holes is somehow responsible for the intermixing process. The nano-holes may enhance P atom outdiffusion and create P vacancies, similarly to microcracks reported in QW irradiated with CW laser RTA.\textsuperscript{10}

![Figure 15. AFM surface morphology of a non-irradiated InP (a) and after the 2 pulse (b) and 25 pulse (c) KrF laser irradiation (124 mJ/cm\textsuperscript{2}) of InP coated with the SiO\textsubscript{2} layer. The results are shown after RTA and the removal of the SiO\textsubscript{2} layer.](image)

![Figure 16. The RMS roughness of the InP layer irradiated with different pulses of the KrF at 124 mJ/cm\textsuperscript{2}, followed by the RTA step. The results are shown after the SiO\textsubscript{2} layer has been removed.](image)

### 4. CONCLUSION

We have investigated morphology of SiO\textsubscript{2} and InP layers used for capping the InP/InGaAs/InGaAsP QW microstructure that were irradiated with the ArF and KrF excimer lasers. The SiO\textsubscript{2} roughness was found to decrease by increasing the pulse number of both lasers. We found out that the InP layer has a relatively smooth surface ($\sigma_{\text{RMS}} \approx 0.4 \text{ nm}$) due to the protection provided by the SiO\textsubscript{2} layer during the excimer laser irradiation and high temperature RTA. For sample coated with 50 or 150 nm SiO\textsubscript{2} layer irradiated by the ArF laser, the blueshift is observed only in the region where the SiO\textsubscript{2} layer is ablated. The InP surface is altered by the ArF and KrF laser irradiation and results in the increased roughness. On the other hand, the maximum blueshift of 74 nm was achieved on sample coated with a 243 nm thick SiO\textsubscript{2} layer ($d_{\text{SiO2}} \approx \lambda_{\text{ArF}}$) showing a smooth surface ($\sigma_{\text{RMS}} = 1.8 \text{ nm}$) after 75-pulse-radiation with the KrF laser at 124 mJ/cm\textsuperscript{2}. A
relatively large number of nano-holes have been observed in the InP layer irradiated with the KrF laser. The presence of these nano-holes coincides with the enhancement of the QWI process.

5. ACKNOWLEDGEMENT

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