The Study of a-Si Film Crystallization using an XeCl Laser Annealing on the Plastic Substrate

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Abstract

We reported the a-Si crystallization using a XeCl excimer laser annealing on the plastic substrate. The poly-Si film is able to grow in the low temperature and light substrate like a plastic. For the preparation of sample, substrate is cleaned by organic liquids. The film of CeO_2 layer as the buffer layer was grown by sputtering methods. After a-Si film deposition using ICPCVD, the film was crystallized by XeCl excimer laser. In this paper, we present the crystallization properties of a-Si on the plastic substrate

1. Introduction

Recently, the portable electronics have been in strong demand for applications in personal information display such as e-book, portable digital assistants (PDAs), mobile computers and cellular phones using a plastic substrate [1]. As plastic substrates such as polycarbonate (PC), polyethylene terephthalate (PET) have a limitation of low process temperature, it is impossible to use them at the substrate temperature over 100 °C. Low temperature crystallization process induces the problems like the abnormal grain growth and random nucleation. In order to solve above-mentioned problems, we used the substrate buffer layer having two roles. Firstly, to reduce the crystallization temperature even more, we deposited the CeO_2 layer. Because the CeO_2 film thickness is similar to lattice constant and crystal structure is same as crystal Si, CeO_2 film plays an important role of "seed layer" in the steps of post-crystallization process. Seed materials make it possible to grow the poly-Si films at a low substrate temperature by providing the surface like a single crystal Si. Plastic substrates are organic materials basically made up of the elements such as C, O and H. Those elements bring about the contamination of active layer during the crystallization. Also, CeO_2 film plays an important role of "passivation layer" that prevents the movement of impurity. In this paper, we report the influence of CeO_2 film as a function of deposition condition in the XeCl excimer laser crystallization of Si film.

2. Experimental

We have used the polycarbonate (PC) of 1 mm thickness as a plastic substrate. PC substrate has a property of good chemical endurance about acid or alkali solution and clear transmittance but it is very weak in the temperature over 100℃. Therefore, all processes using a PC substrate must be carried out at room temperature. The a-Si film is grown by ICPCVD

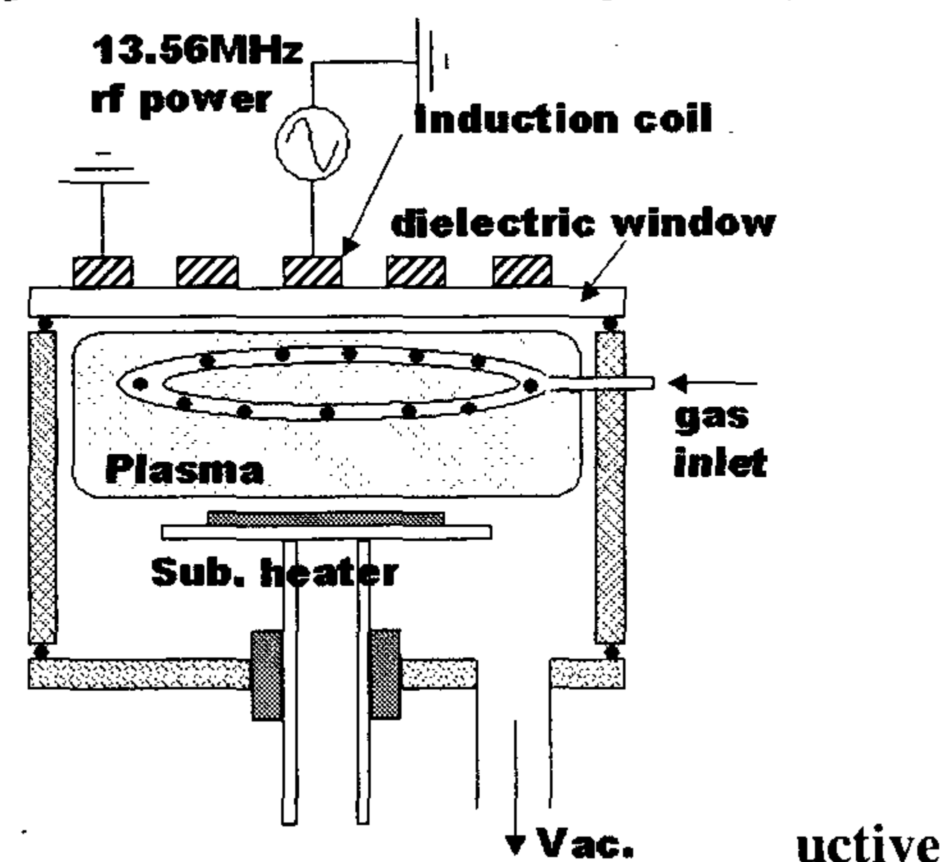

Figure uctive coupled plasma reactor

methods [2] at the room temperature as shown in the figure 1. The plasma source was generated by rf power. It generates the inductive coupled plasma from top induction coil through dielectric quartz window. The inductive coupled plasma is generated by an

inductively coupled azimuthal electric field produced by a flat dielectric coil. Applied voltage to the dielectric coil at 13.56 MHz generates an oscillating magnetic field around the coil, which penetrates into the plasma and produces an azimuthal electric field. In our reactor, the azimuthal electric field is zero on the axis and zero on the wall, thereby peaking in an annular region at roughly half the radius. The deposited a-Si was dried at 100℃ in the vacuum environment for preventing the moisture effects. Firstly, we irradiated it with the 308nm XeCl excimer laser without buffer layer for the crystallization of a-Si. The crystallization system consists of an excimer laser operating at 308nm with the beam size of 5 x 5 mm and pulse duration of 1 Hz. The laser beam intensity was varied between 180mJ/cm^2 and 350mJ/cm^2. Secondly, we deposited the CeO_2 film as seed layer using a sputtering method to study the effect of initial crystallization. Sputtering system was installed as the configuration of Ce metal target (4", 99.999%), the distance being 4 cm between target and substrate. The whole process was carried out at room temperature. We experienced many difficulties to grow the film of CeO_2 at room temperature. The continuous deposition of the film for 30 minutes leads to the bending of PC substrate due to the rise in temperature by the impact of heavy ions. In order to solve this problem, we tried by switching the plasma ON and OFF repeatedly using a shutter. In the ON Plasma condition the film was grown on the substrate, but at OFF Plasma condition, the substrate was cooled. This is how we could deposit the CeO_2 film at the room temperature.

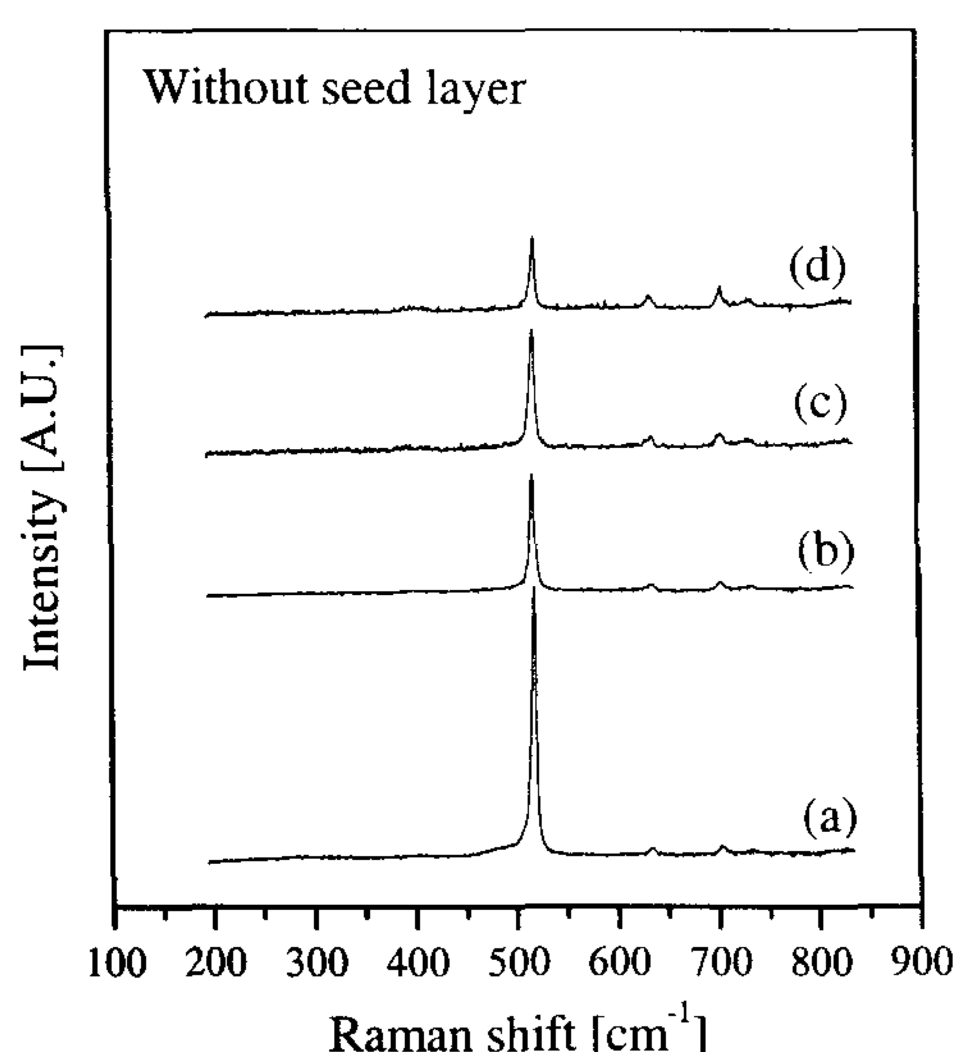

Figure 2. Raman spectroscopy as a function of XeCl excimer laser energy (a) 180mJ/cm^2, (b) 230mJ/cm^2, (c) 320mJ/cm^2, (d) 350mJ/cm^2.

3. Results and discussion

Figure 2 exhibits Raman spectroscopy as a function of laser energy from 180mJ/cm^2 to 420mJ/cm^2. As the laser energy increases, the Raman peak intensity decreases but we cannot observe amorphous phase shoulder in the 480cm^{-1}. This result means that the higher laser energy makes it thinner than low laser energy. It indicates that high energy density induced thin film ablation. The ratio of crystalline volume fraction (X_c) is represented by $X_c=I_{520}/(I_{520}+I_{500}+\sigma I_{480})$ [3], where I_{480}, I_{500} and I_{520} are integrated intensities of the peaks at 480, 500 and 520cm^{-1} respectively and σ is the ratio of the integrated Raman cross section for a-Si to c-Si. For a small grain size, we can take the correction factor as unity ($\sigma\approx1$). As the laser intensity increases, Xc value decreases from 87.22% to 77.76%. The Xc difference of 10% presents almost same values if we consider the film thickness. The figure 3 exhibits the surface morphologies as a function of laser intensity. As the laser intensity increases, the surface morphology gets rougher in the laser-crystallized poly-Si. Also, the grain shape was changed to irregular. The grain has a shape of the ball like feature in the low intensity of 180mJ/cm^2 but was changed to irregular as the laser intensity increases. This means that the high laser intensity has a bad influence on the surface roughness and uniformity of the grain size.

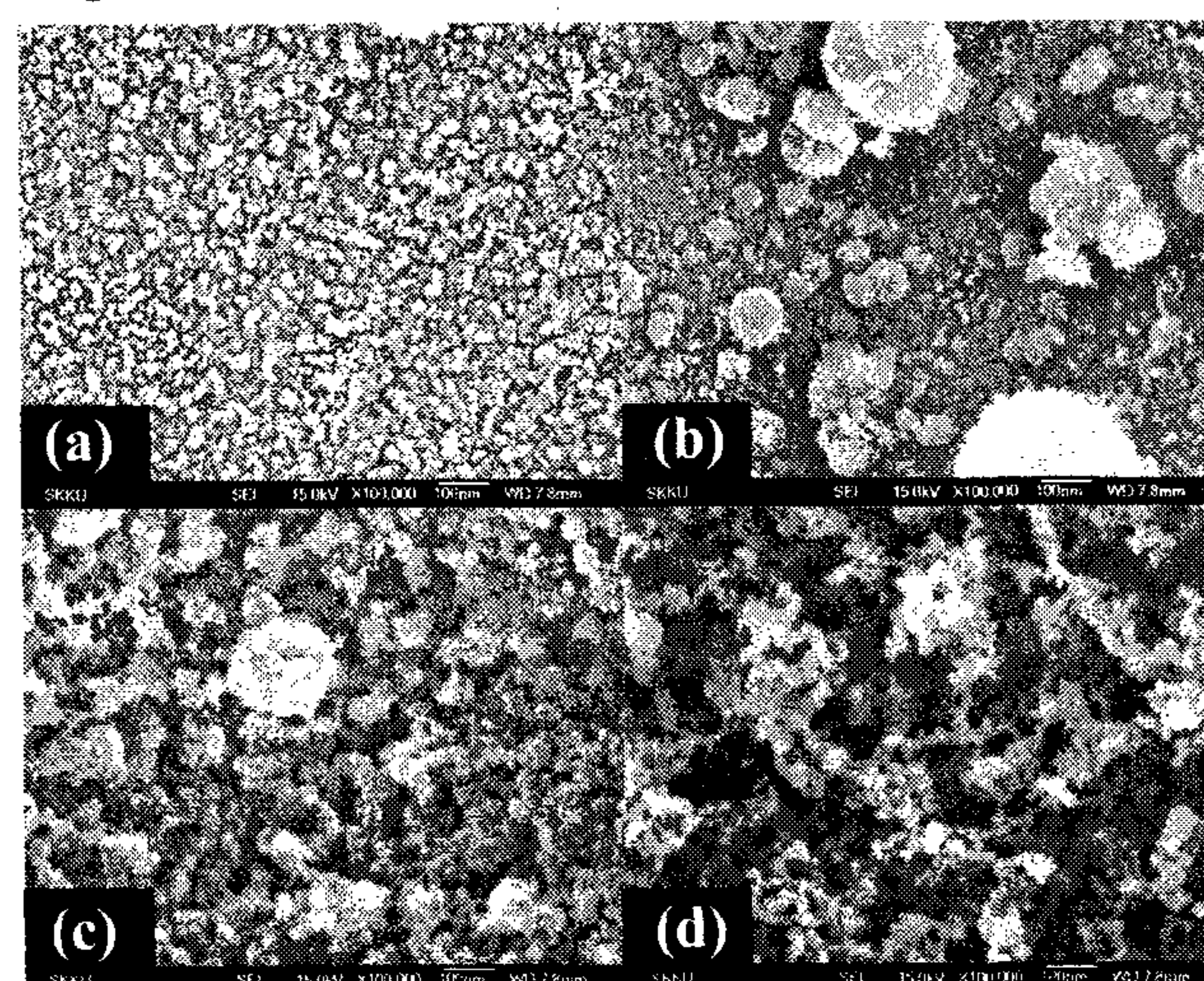

Figure 3. Laser crystallized poly-Si surface morphology as a function of laser intensity (a) 180mJ/cm^2, (b) 230mJ/cm^2, (c) 320mJ/cm^2, (d) 350mJ/cm^2(magnitude=x100,000).

The figure 4 shows the UV transmittance of the sample as a function of gas pressure of the deposited a-Si films before crystallization. The UV reflectance spectrum shows peaks corresponding to the electronic transitions of crystalline silicon in the Brillouin zone at E_1=365 nm and E_2=275 nm [4]. The lowest transmittance of a-Si films was measured around the wavelength of 365nm. But, we could not detect the peaks in the 275nm. These observations show that Si films grown were the very small-grained μc-Si. There is highest value of transmittance of over 70 % at the wavelength around 550 nm. The high transmittance indicates low absorbance of light beam. The different optical property causes different crystallization properties as shown the figure 5, which represents the results of Raman spectroscopy of the samples crystallized to the 320mJ/cm^2. These results are the proof of the fact that the crystallinity is possible to be improved in the as-deposited a-Si having a low transmittance.

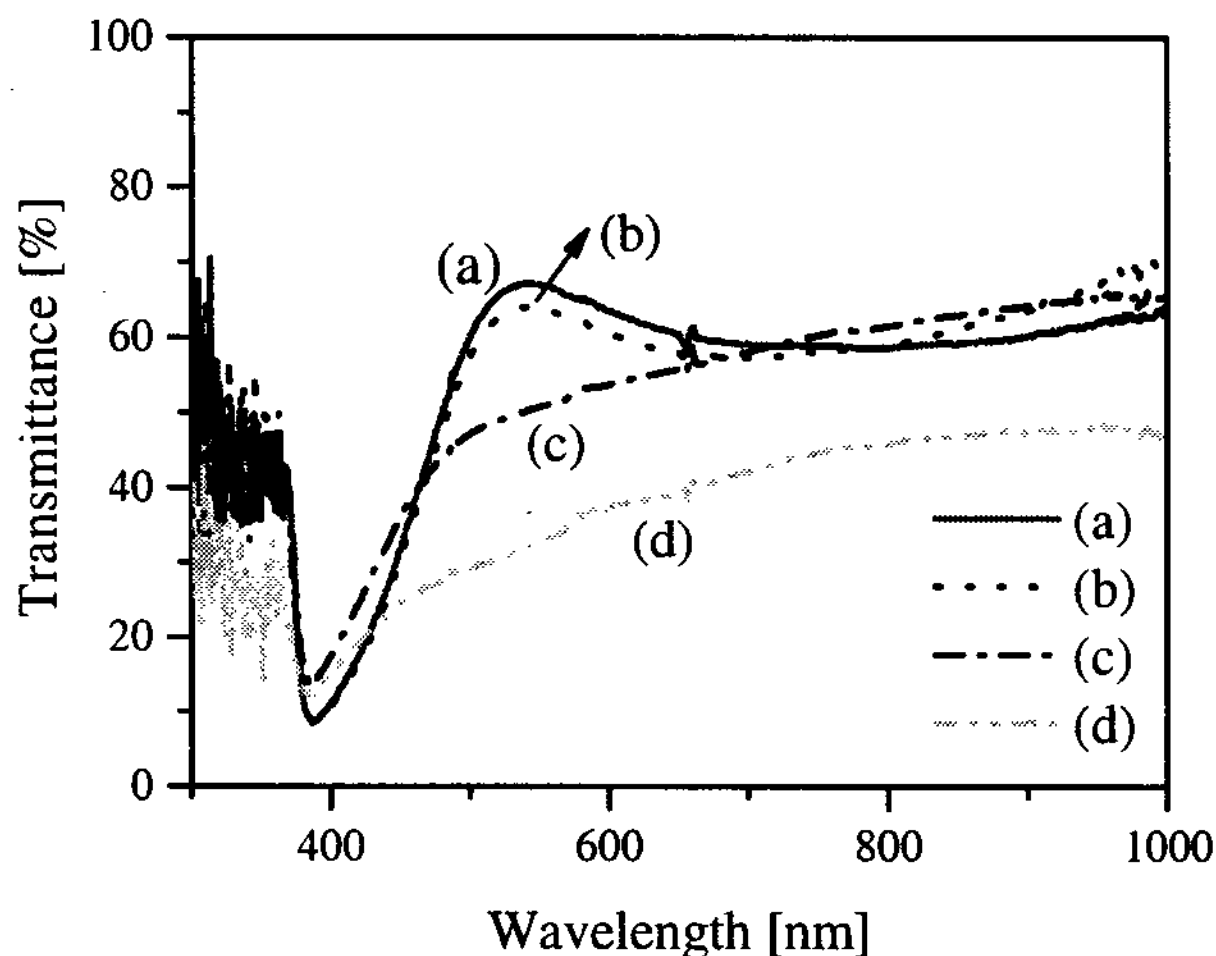

Figure 4. UV transmittance spectroscopy of a-Si film as a function of process pressure (a) 120mTorr, (b) 140mTorr, (c) 150mTorr, (d) 170mTorr.

Secondly, crystalline orientation of CeO_2 seed layer is shown in the figure 6. As the Ce metal seed layer deposition time increases, the intensity of (111) orientation was increased. Especially, the samples of (c) and (d) have the difference in plasma ON and OFF time. The sample of (c) was deposited for 15 times ON plasma for 2min with OFF plasma for 2 min, with the total time of 30 minutes. In the case of the sample (d), it was deposited for 6 times ON plasma for 5 minutes and with OFF plasma also for 5 min. The photographs inserted in figure 6 show that the intensity of the sample of (c) is higher than that of the sample of (d) and also the deposition is more uniform. These results demonstrate that the long deposition time of less than 2 minutes gives a good uniformity and good crystalline properties. Therefore, we selected the sample of (c) in the figure 6 as the optimized seed layer.

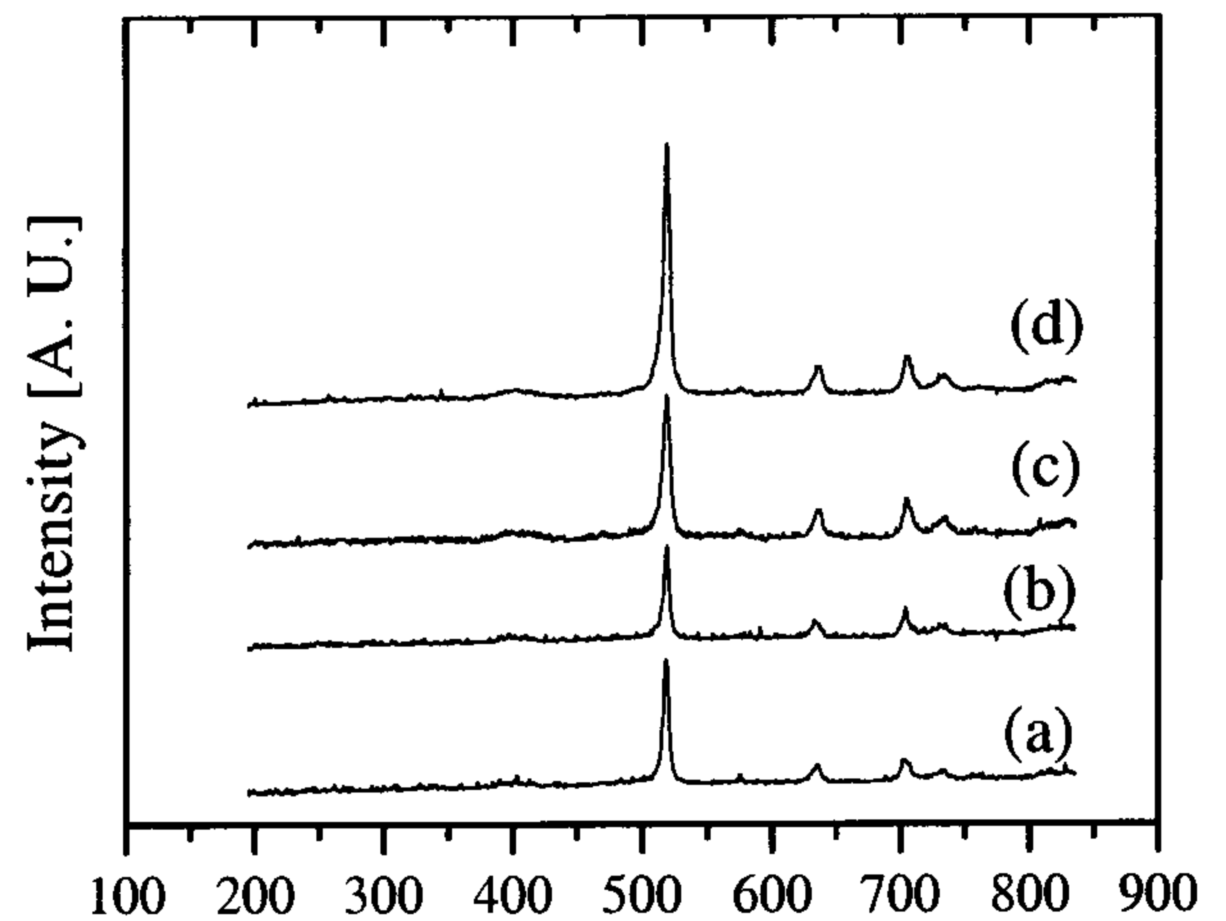

Figure 5. Raman spectroscopy as a function of process pressure (a) 120mTorr, (b) 140mTorr, (c) 150mTorr, (d) 170mTorr.

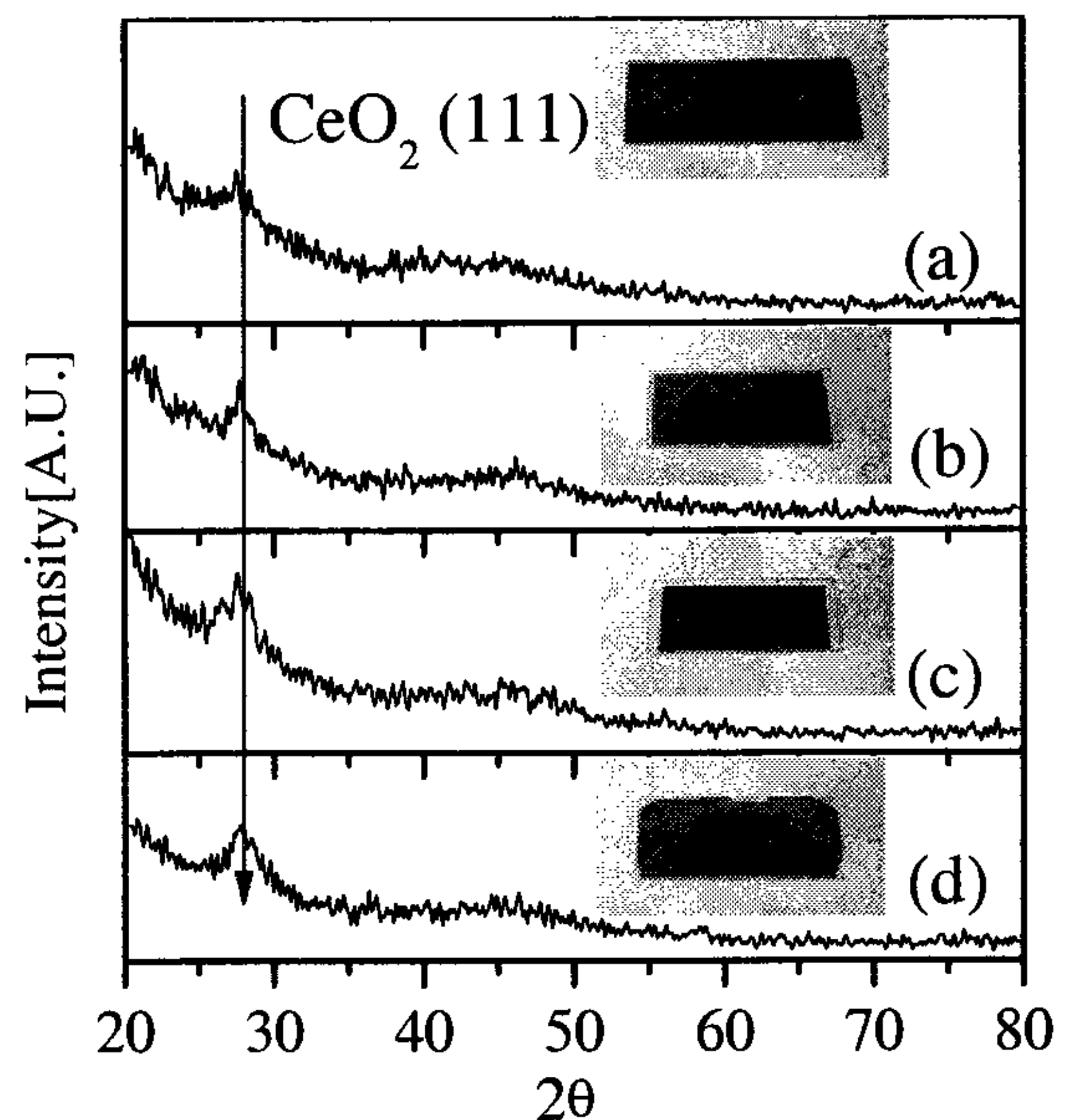

Figure 6. X-ray diffraction pattern of CeO_2 films deposited at the room temperature on the PC substrate. Ce seed layer deposition time is (a) 10min, (b) 20min, (c) 30min (15 times ON plasma for 2 min and with OFF plasma for 2min), (d) 30min (6 times ON plasma for 5 min and with OFF

plasma for 5 min). Inserted photographs represent surface image of the samples respectively.

Finally, we studied the laser crystallization a-Si films having a seed layer on the PC substrate. Figure 7 illustrates the Raman Spectroscopy as a function of laser energy. As the laser energy increases from 50mJ/cm^2 to 108mJ/cm^2, Raman intensity also increases. There is the same result with laser crystallization without seed layer. But, the amorphous phase around 480cm^{-1} was observed to all samples. It means that the crystallization did not perfectly progress in the lower energy than that in the case of no seed layer. But, we know that the crystallization is possible to the low energy of 70mJ/cm^2. In the minimum laser energy of 50mJ/cm^2, Raman spectrum of a-Si phase only shows a broad shoulder around 480cm^{-1}. Maybe, this energy indicates a minimum energy for laser crystallization with seed layer films. Although the samples of (c) and (d) were irradiated with different energy densities, it was calculated almost the same crystalline volume fraction of 78%. Also, many large holes appeared at the laser energy of 108mJ/cm^2 as shown the figure 8. It is considered to be the effect of thin film ablation by induced laser energy. After all, the surface holes are disappeared at minimum energy of 50mJ/cm^2. Because it does not crystallize at the energy of 50mJ/cm^2, it implies that the laser energy of 85mJ/cm^2 is optimized laser crystallization energy for a-Si with CeO_2 seed layer.

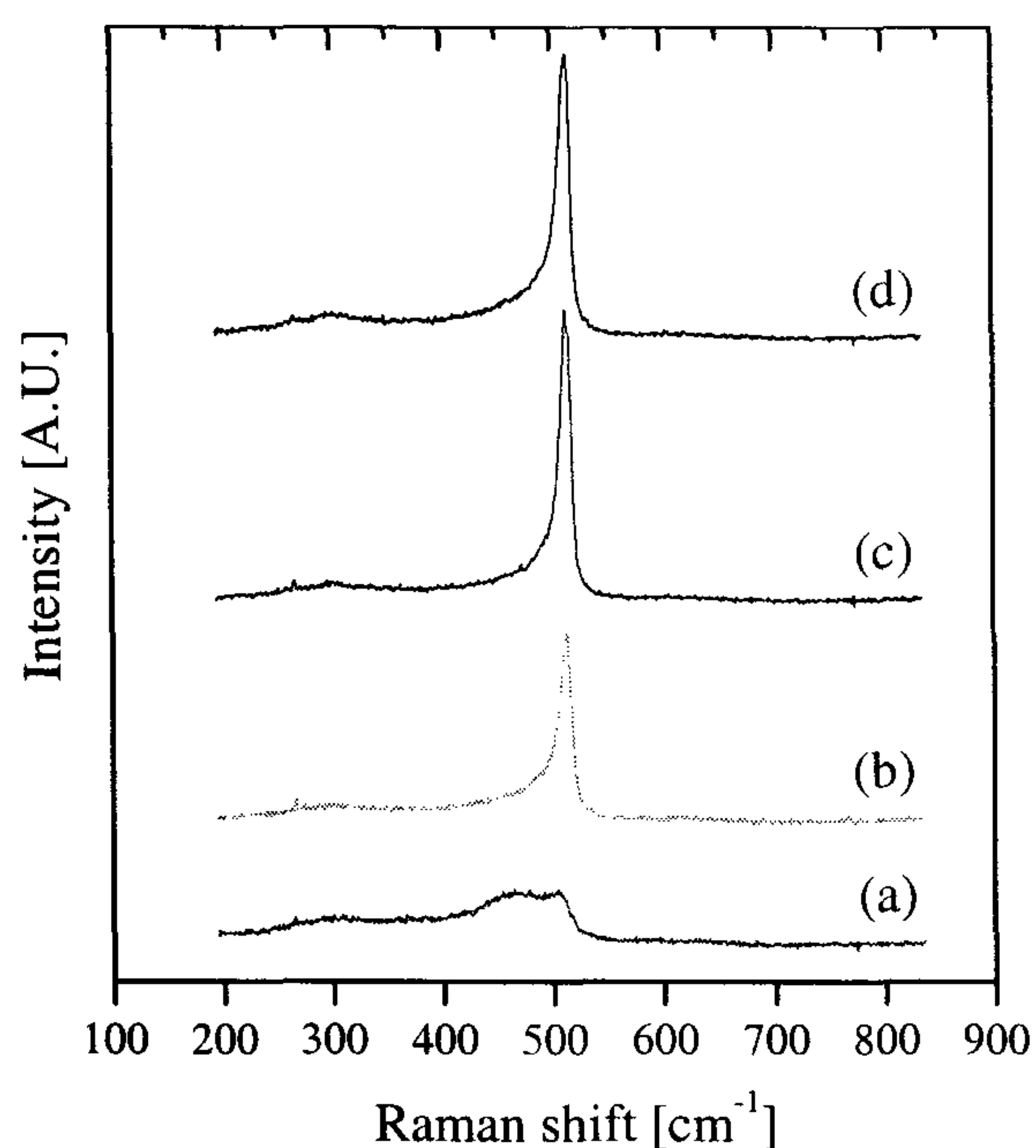

Figure 7. Raman spectroscopy as a function of laser energy (a) 50mJ/cm^2, (b) 70mJ/cm^2, (c) 85mJ/cm^2, (d) 108mJ/cm^2.

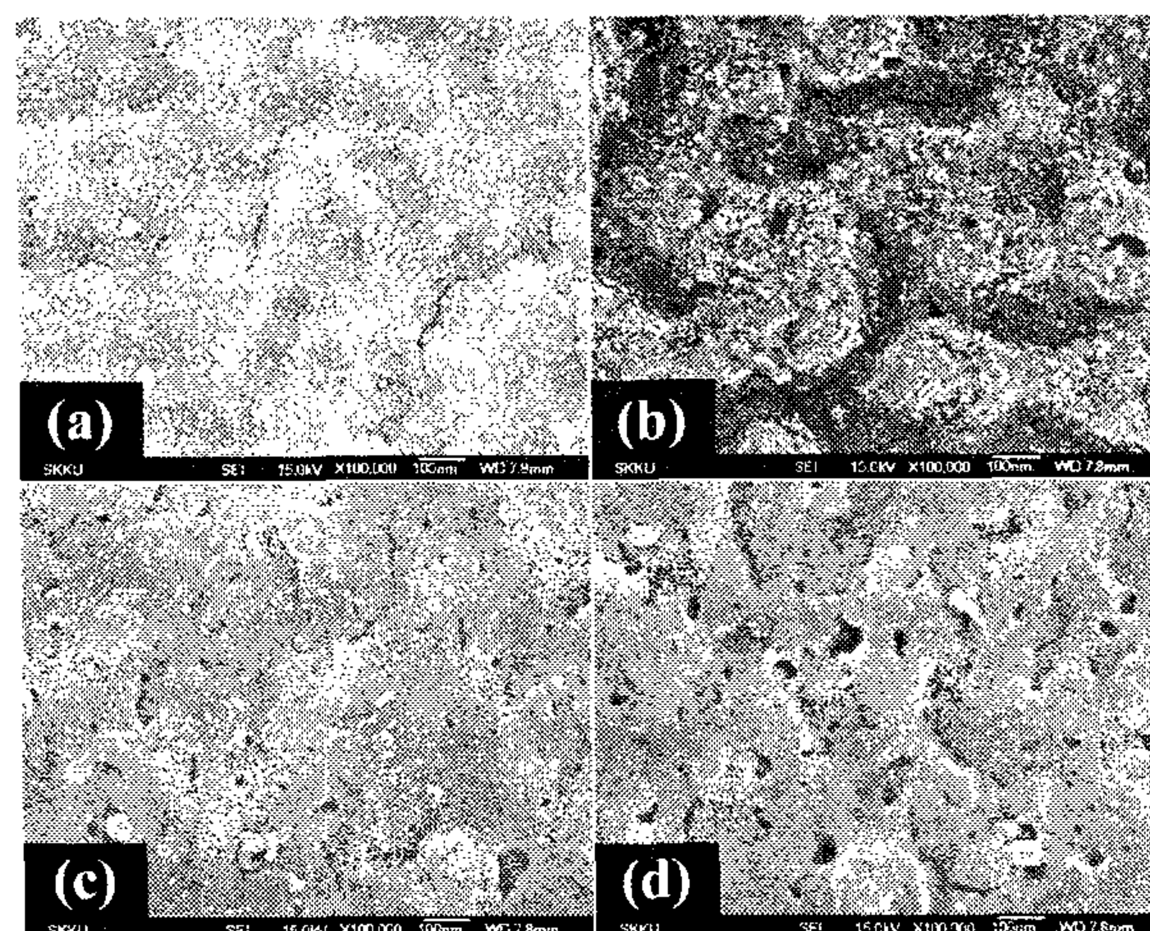

Figure 8. SEM surface images of laser crystallized film with CeO_2 seed layer as a function of (a) 50mJ/cm^2, (b) 70mJ/cm^2, (c) 85mJ/cm^2, (d) 108mJ/cm^2.

4. Conclusion

In this paper, the crystallization of a-Si films on the PC substrate using a XeCl excimer laser and CeO_2 seed layer has been reported. The a-Si was crystallized with the laser of high energy density of over 180mJ/cm^2 without seed layers. In order to deposit CeO_2 seed layer, we could grow the films as ON / OFF plasma repeatedly. The a-Si with seed layer could be crystallized at very low energy density of 85 mJ/cm^2 without large holes induced laser energy.

5. Acknowledgements

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6. References

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