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X-Ray Emission Spectroscopic Analysis for Crystallized Amorphous Silicon Induced by Excimer Laser Annealing

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The results of investigating $SiL_{2,3}$ X-ray emission valence spectra of amorphous silicon films irradiated by excimer laser are presented. It is found that laser annealing leads to crystallization of amorphous silicon films and the crystallinity increases with the laser energy density from 250 to 400 mJ/cm^2. The vertical structure of the film is investigated by changing the accelerating voltage on the X-ray tube, and the chemical and structural state of Si_3N_4 buffer layer is found not to be changed by the excimer laser treatment.

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I. INTRODUCTION

The development of methods to crystallize amorphous silicon (a-Si) is of great interest in connection with the improvement of channel mobility of thin film transistors (TFT) [1]. Excimer laser annealing has been shown to be a convenient method to crystallize a-Si on a low-cost glass substrate [2]. Moreover, localized irradiation by the laser beam allows selective crystallization of a-Si, so that the driver circuits and the low mobility pixel TFT's can be fabricated on a single substrate [3]. It has been shown that 1-dimensional scanning of a line shape excimer laser beam can produce large area polycrystalline silicon films with good uniformity, and UV reflectance spectroscopy, Raman spectroscopy, transmission electron microscopy, X-ray diffraction, and atomic force microscopy have been used to characterize these films [4,5]. In the present paper the excimer laser irradiated a-Si films were analyzed by using ultrasoft X-ray emission spectroscopy with high spatial and energy resolution [6]. Recently this technique was successfully applied to study the dependence of the crystallization of diamond-like films on the temperature of the Si substrate [7] and to characterize the local crystalline silicon (c-Si) precipitation in excimer laser irradiated Si_3N_4 films [8].

II. EXPERIMENTAL

300-nm thick Si_3N_4 buffer layers were deposited onto Corning 7059 glass substrates followed by 50-nm thick hydrogenated amorphous silicon (a-Si:H) films by using plasma-enhanced chemical vapor deposition technique. Before laser annealing, the a-Si:H films were preannealed at 420°C for 3 hours in N_2 atmosphere to prevent explosive eruption of hydrogen. A KrF excimer laser (wavelength 248 nm, pulse width 20 ns) was used to crystallize the a-Si films. The laser beam was focussed in the vertical direction (Gaussian profile) and elongated in the horizontal direction (flat-top profile) by cylindrical lenses to form a line shape beam of 1 mm (full width at half maximum of Gaussian profile) $\times$ 70 mm. Laser peak energy densities of 250-400 mJ/cm^2 were used to prepare the samples for X-ray emission spectroscopic measurements [5].

Ultrasoft $SiL_{2,3}$ X-ray emission spectra (XES) of excimer laser irradiated a-Si films were measured by a small-spot X-ray spectrometer with a diffraction grating (600 lines/mm, radius of curvature = 2 m) and electron beam excitation [6]. The spatial and the energy resolutions were 3-5 μm and 0.4 eV, respectively. The accelerating voltage on the X-ray tube was varied from 2 to 6 kV, and the anode current was 130 nA.

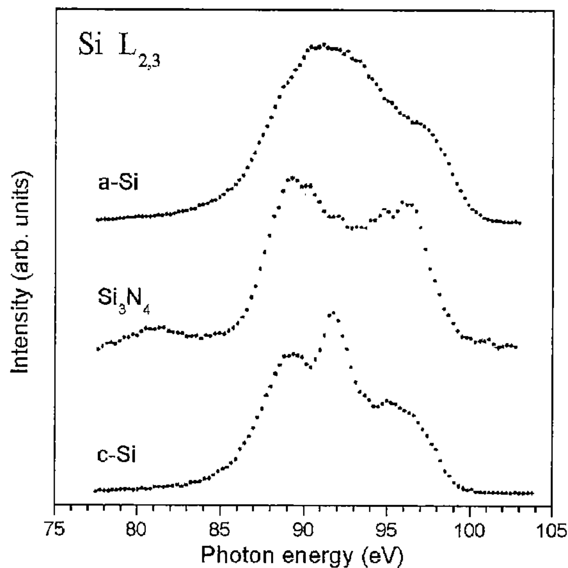


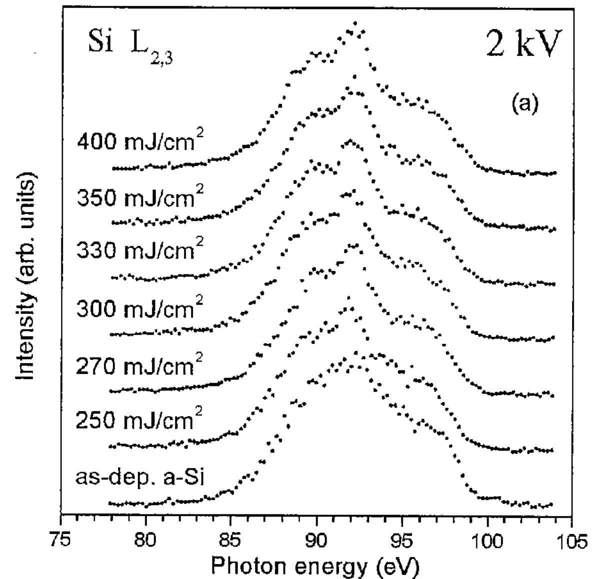
FIG. 1. $SiL_{2,3}$ XES of reference samples a-Si, Si_3N_4, and c-Si.

reference samples a-Si, c-Si and Si_3N_4 were measured in the same condition.

III. RESULTS AND DISCUSSION

$SiL_{2,3}$ The X-ray emission valence spectra correspond to 3s → 2p transition when the electron-beam-induced vacancy on the Si-2p core level is filled by valence Si-3s electrons. The intensity distribution of $SiL_{2,3}$ XES gives information on the Si-3s distribution in the valence band. It was shown in Ref. [6–9] that $SiL_{2,3}$ XES are very sensitive to chemical bonding and their fine structures are different in a-Si, c-Si [9] and Si_3N_4 [8] (see Fig. 1). This implies that by using $SiL_{2,3}$ XES it is possible to distinguish between amorphous and crystalline states of elemental Si under different treatments and also to discern them from Si_3N_4. We have shown that excimer laser irradiation of Si_3N_4 films leads to breaking of Si-N bonds and precipitation of c-Si, which was identified by X-ray emission spectroscopy [8].

The results of measuring $SiL_{2,3}$ XES of a-Si films irradiated by excimer laser are shown in Figs. 2 and 3 for various accelerating voltages V = 2-6 kV on the X-ray tube. For each excitation energy the spectra of samples are obtained for various laser energy densities. According to estimations given in Ref. [10] by measuring $SiL_{2,3}$ XES, at V = 2 kV we can detect the silicon at the probing depth of 400 Å and at V = 6 kV, 5000 Å. Thus by changing the accelerating voltages on the X-ray tube from 2 to 6 kV, we can measure the XES from an a-Si film (V = 2 kV) and from an a-Si film with an underlying Si_3N_4 buffer layer (V = 3-6 kV).



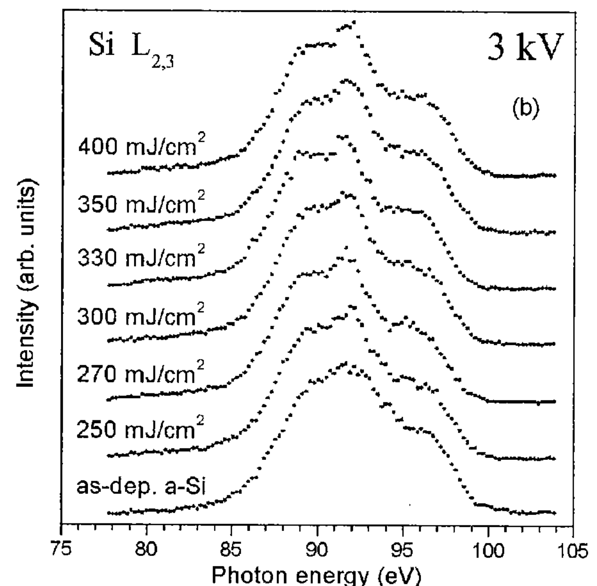
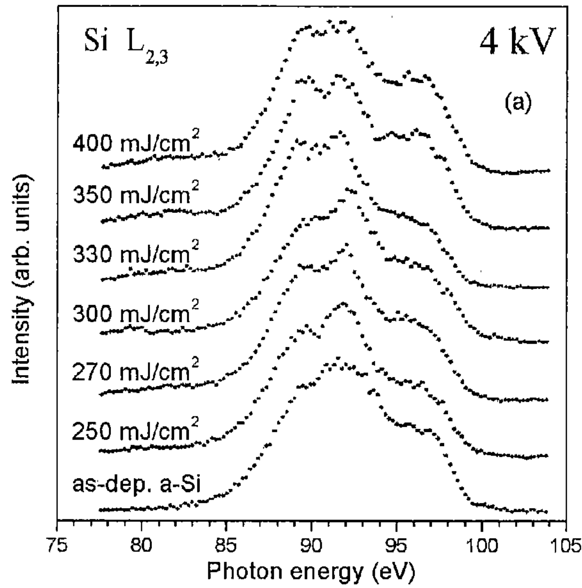
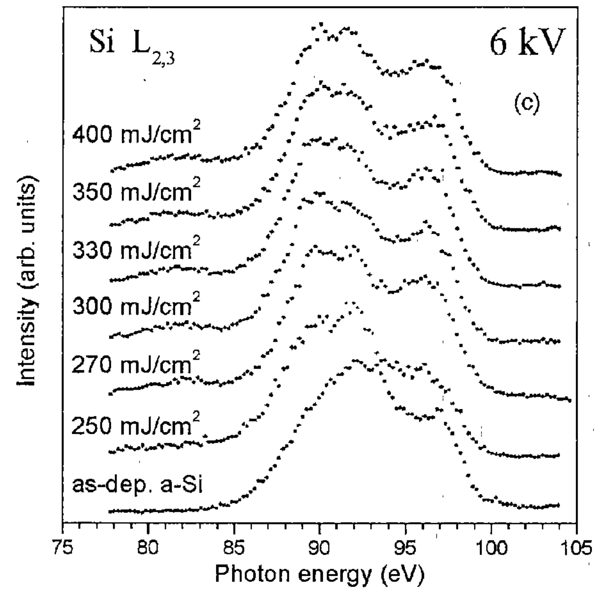


FIG. 2. $SiL_{2,3}$ XES of excimer laser annealed a-Si films measured at 2 kV (a) and 3 kV (b).

As is known from Fig. 2 (a) the fine structure of $SiL_{2,3}$ XES of the as-deposited Si film is very similar to that of the a-Si reference sample with a fine structure at E = 89 - 92 eV implying the smearing of the two peaks typical for the spectrum of c-Si (Fig. 1). The irradiation of this film by excimer laser at the energy density of 250 mJ/cm^2 (Fig. 2 (a)) leads to the recovery of the two-peak structure indicating the crystallization of a-Si film. According to our calculations, $SiL_{2,3}$ XES of a-Si film irradiated with a laser





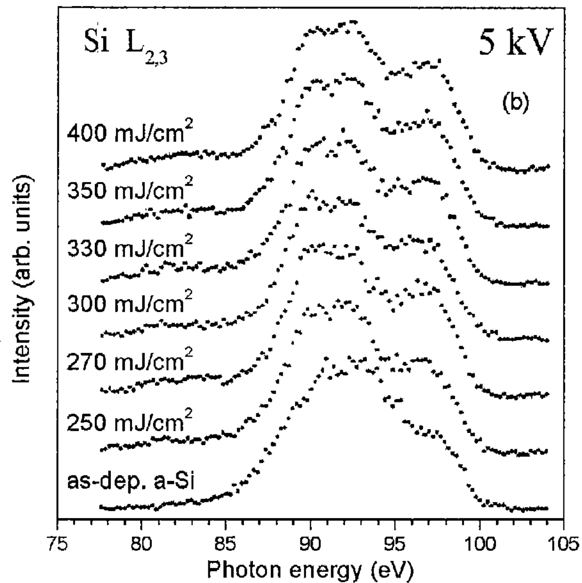


FIG. 3. $SiL_{2,3}$ XES of excimer laser annealed a-Si films measured at 4 kV (a), 5 kV (b), and 6 kV (c).

energy density of 300 mJ/cm^2 can be reproduced by the superposition of the spectra of the as -deposited Si-film and the c-Si given in the ratio of intensities 1:1 (see Fig. 4). Further increasing of the laser energy density up to 400 mJ/cm^2 does not yield much change of the common fine structure distribution of $SiL_{2,3}$ XES of the irradiated a-Si films (see Fig. 2(a)) but results in more distinct formation of the two peaks at E = 89 and 92 eV which shows the increasing crystallinity of the irradiated a-Si film. The formation of these two peaks is most clearly observed in samples for highest laser energy densities, 350 and 400 mJ/cm^2. This conclusion is in accordance with the results of Raman spectroscopy measurements obtained in our previous work given in Ref. [4]. Thus we conclude that the crystallinity of the excimer laser irradiated a-Si films increases with the laser energy density.

In $SiL_{2,3}$ XES of the irradiated a-Si films measured at V = 3-6 kV (Figs. 2 (b) and 3 (a, b, c)), we can see the contribution of the signal from the Si_3N_4 buffer layer. $SiL_{2,3}$ XES of Si_3N_4 has a two-peak structure (with peaks centered at E = 89 and 96 eV in the ratio

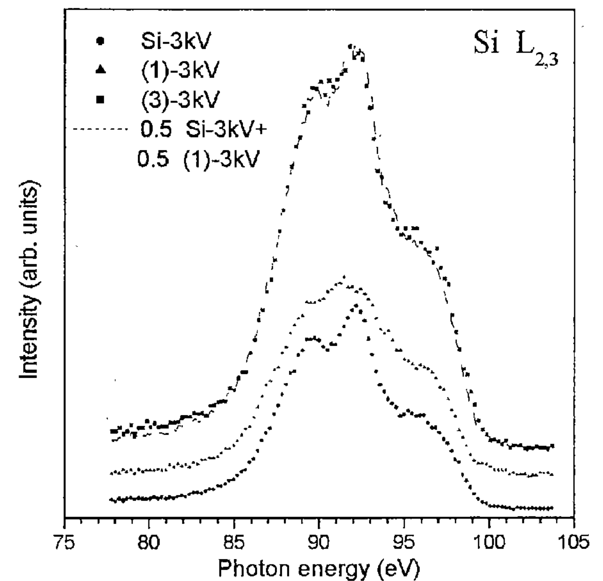


FIG. 4. Simulation of $SiL_{2,3}$ XES of a-Si film irradiated with laser energy density of 300 mJ/cm^2 (3) by the superposition of the spectra of as-deposited Si-film (1) and c-Si given in the ratio 1:1. (All spectra are measured at 3 kV.)

of intensities 1:1.17) which reflects the hybridization of Si-3s-N-2p states in the valence band and the low-energy satellite at E = 81 eV genetically connected with mixed Si-3s-N-2s states. Further increasing of accelerating voltage on the X-ray tube (up to 6 kV) is accompanied by the increasing of Si_3N_4 contribution, and the fine structure of $SiL_{2,3}$ XES shows the typical characteristics of Si_3N_4 with the appearance of a low-energy satellite at E= 81 eV.

As mentioned before, we have observed local c-Si precipitation in Si_3N_4 film induced by excimer laser irradiation by using the same XES technique [7]. However our experimental results show that Si_3N_4 buffer layers in the samples under investigation are not affected by excimer laser irradiation. Otherwise the contribution of c-Si signals to the spectra measured at higher accelerating voltages on the X-ray tube would consistently increases, which is not observed in our experimental spectra. From these results we conclude that the upper Si layer absorbs most of the excimer laser energy and thus the lower Si_3N_4 buffer layer is not affected by excimer laser irradiation.

IV. CONCLUSION

We have shown that XES is a novel technique for characterization of excimer laser irradiated a-Si films to investigate the influence of laser energy density on the crystallization of a-Si films and also to study the dependence of the chemical and structural state of the Si_3N_4 buffer layer on excimer laser beam treatment. From the measurements of $SiL_{2,3}$ X-ray emission valence spectra of a-Si films irradiated by excimer laser, we found that the changes of the spectra of irradiated films are attributed to the crystallization of the a-Si films, and that the crystallinity increases with the laser energy density from 250 to 400 mJ/cm^2. It has also been found that the structural and chemical state of the Si_3N_4 buffer layer is not affected by excimer laser irradiation.

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REFERENCES

[1] A. J. Snell, K. D. Mackenzie, W. E. Spear, and P. G. LeComber, Appl. Phys. **24**, 357 (1981).

[2] T. Sameshima, M. Hara, and S. Usui, Jpn. J. Appl. Phys. **28**, 1789 (1989).

[3] K. Shimizu, O. Sugiura, and M. Mastmura, Jpn. J. Appl. Phys. **29**, L1775 (1990).

[4] Y. M. Jhon, D. H. Kim, H. Chu, and S. S. Choi, Jpn. J. Appl. Phys. **33**, L1438 (1994).

[5] Y. M. Jhon, D. H. Kim, H. Chu. C. W. Lee, and S. S. Choi, Mat. Res. Soc. Symp. Proc. **354**, 647 (1995).

[6] E. Z. Kurmaev, V. V. Fedorenko, S. N. Shamin, A. V. Postnikov, G. Wiech, and Y. Kim, Physica Scripta **T41**, 288 (1992).

[7] E. Z. Kurmaev, S. N. Shamin, Y. Kim, Materials Letters **19**, 123 (1994).

[8] E. Z. Kurmaev, S. N. Shamin, V. E. Dolgih, K. Kurosawa, K. Nakamae, Y. Takigawa, A. Kameyama, A. Yokotani, and W. Sasaki, Jpn. J. Appl. Phys. **33**, L1549 (1994).

[9] E. Z. Kurmaev and G. Wiech, J. Non-Cryst. Solids **70**, 187 (1985).

[10] V. R. Galakhov, V. V. Fedorenko, S. N. Shamin, L. V. Elokhina, Yu. M. Yarmoshenko, and A. A. Bukharaev, Appl. Surf. Sci. **72**, 73 (1993).