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Low Temperature Nucleation of Silicon Crystal in Amorphous Phase with Synchrotron Radiation

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Amorphous silicon films with a thickness of 300nm were made by electron cycrotron resonance plasma enhanced chemical vapor deposition at high temperatures. Raman spectroscopy revealed that micro-crystals can be formed in these films with X-ray irradiation from synchrotron radiation at much lower temperatures (around $50^{o}C$) than are used in thermal annealing. Electron spin resonance measurements showed that defects are also introduced into amorphous phase with X-ray irradiation. Low temperature nucleation is discussed in consideration of these defects.

1. INTRODUCTION

A Low temparature method of preparing large-grain polycrystalline silicon film has been sought for TFTs and other SOI structures. Solid-phase crystallization of amorphous silicon (a-Si) shows promise and several control techniques have already been reported, including impurity doping,[1-2] ion implantation,[3] and selective nucleation at surface steps of the substrate.[2,4-5]

We reported previously that X-ray irradiation using synchrotron radiation is an effective way to enhance solid-phase homogeneous nucleation during post-annealing for hydrogenated a-Si.[6] It was also found that the epitaxial growth of a-Si proceeds at lower temperatures than in thermal annealing, and that hiqh quality thin film crystals can be obtained with X-ray irradiation. These effects are thought to be due to the enhancement of atomic diffusion caused by inner-shell electron excitations.[6]

In this work, we investigate the in-situ formation of silicon micro-crystals in amorphous films at low temperatures with X-ray irradiation of synchrotron radiation.

2. EXPERIMENTAL

A-Si films were deposited onto (100) silicon single crystal substrates by electron cycrotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD). The temperature of the substrate was kept at $500^{o}C$ in order to suppress the introduction of hydrogen and to obtain an a-Si network structure of high short range order. The a-Si films were about 300nm thick. The deoposition rate was fixed at about 70nm/min for all specimens.

X-ray irradiation was performed using synchrotron radiation at the Photon Factory in National Laboratory for High Energy Physics (KEK), operated with an acceleration voltage of 2.5GeV and a storage ring current of about 300mA through beryllium windows. The X-rays had photon energies larger than 4keV (beam line, BL-15b). The temperature of the substrates during irradiation was found to be around $50^{o}C$ by thermocouples for the above irradiation conditions. Rough calculations estimated that the number of photons absorbed by 300nm-thick a-Si should be 1×10^{14} photons/cm^2s, assuming an average absorption rate of 10^{-3}, which is equivalent to 3×10^{18} photons/cm^3.

The crystallinity of the specimen was investigated by laser Raman spectroscopy with an Ar ion laser (wavelength:488.0nm). The electron spin density was measured by electron spin resonance (ESR) at room temperature. Post-annealing of the specimen by furnace was performed in an N_2 atmosphere.

3. RESULTS AND DISCUSSIONS

Figure 1 shows Raman spectra for as-deposited and as-irradiated specimens. Irradiation was conducted for 140 minutes. The as-deposited specimen shows the typical Raman spectra for the a-Si state. The broad peak centered at around 480 cm^{-1} is attributed to transverse optical (TO) phonon modes. With the as-irradiated specimen, a sharp peak due to crystallization (c-Si peak) can be seen at 521cm^{-1} in addition to the broad TO peak.

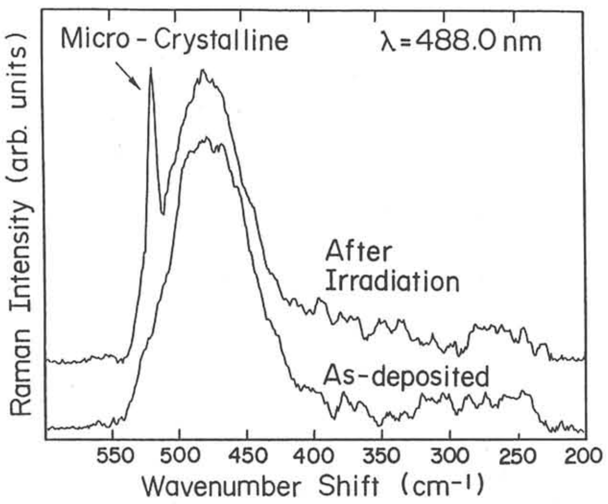

Fig.1 Raman spectra for as-dposited and as-irradiated a-Si. The peak at $521cm^{-1}$ is due to crystallization.

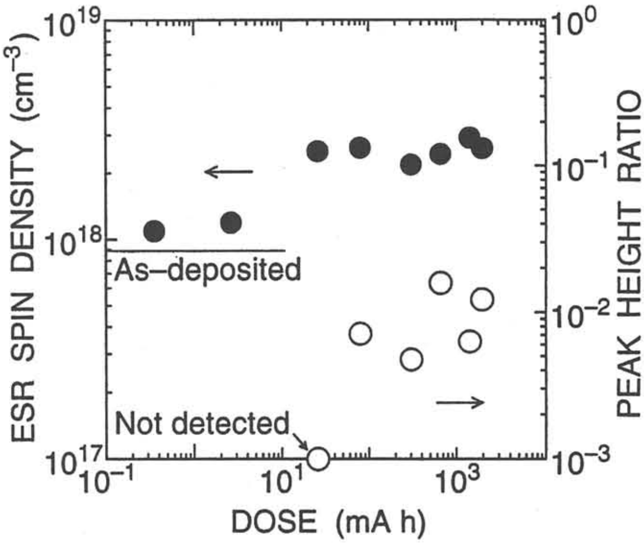

Fig.2 X-ray dose dependence of c-Si Raman peak intensity (○) and ESR spin density (●). Raman peak height ratios (I/I_0) are plotted, where I and I_0 are peak height for the irradiated specimen and single crystal

In our previous experiments on hydrogenated a-Si deposited at low temperature by conventional plasma CVD, such in-situ nucleation of micro-crystals, as shown in Fig.1, was not observed under similar X-ray irradiation conditions.[6] It was confirmed that the full width at half maximum of the TO peak for ECR-PECVD a-Si used in this work is much smaller than those of previous work. Since the small value of this parameter indicates the small average bond angle distortion,[7] ECR-PECVD a-Si is essentially suitable for crystallization. The in-situ nucleation of micro-crystals at much lower temperatures than in thermal annealing, as shown in Fig.1, is thought to be due to this atomic structure of ECR-PECVD a-Si.

The change in intensity of the c-Si peak is shown in Fig.2 as a function of X-ray dose, which is defined here as the product (mAh) of irradiation time (hours) by storage ring current (mA). No c-Si peak was observed for smaller irradiation doses of less than 20 mAh. For larger doses, the c-Si peak is clearly seen in the spectra and the intensity of the peak increases gradually with the dose. This incubation time for nucleation of the crystals indicates that nucleation does not occur by local heating in the places, where high energy X-ray photons are absorbed.

An increase in the intensity of ESR signals was observed for the irradiated specimens. The g-value of these signals coincides with that for the as-deposited state, which is close to 2.006. These spins can thus be attributed to a dangling bond (D^0 center).[8] The density of ESR spins is also plotted against the X-ray dosage in Fig.2. It increases rapidly with the dose in the range lower than 20 mAh and tends to saturate at a value of $2.7x10^{18}$ spins/cm^3 before crystallization occurs. These ESR spins seem to be due to vacancy-interstitial pair formation caused by inner-shell electron excitations.[6] It is probable that excess point defects over the saturation of ESR spins enhance the crystallization.

In order to establish the existence or otherwise of an effective energy range of X-ray photons to form ESR spins in the wide spectra of synchrotron radiation, depth dependence of ESR spin density was compared with the attenuation characteristics of X-ray photons, as shown in Fig.3. Four a-Si films with 0.4mm-thick substrates were superimposed and simultaneously irradiated with X-rays, as shown in the inset of Fig.3. The irradiation dose was 700 mAh. The attenuation curve alone cannot explain the obtained depth profile of ESR spin density for X-rays having photon energies smaller than about 9keV or larger than about 19keV. Observing Fig.2, it seems to correspond with the profile of the total number of photons absorbed by a-Si films.

Figure 4 shows the crystallization characteristics with post-thermal annealing. The intensities of the c-Si Raman peak for the irradiated and nonirradiated a-Si films normalized by the value for single crystal substrate are plotted as a function of the annealing temperature. The X-ray dosage was approximately 2000 mAh. Annealing was conducted for 30 minutes for all specimens. The peak intensity was large for the irradiated specimens in the low temperature range below 650°C. For higher temperatures above 650°C, differences between them are negligible. It

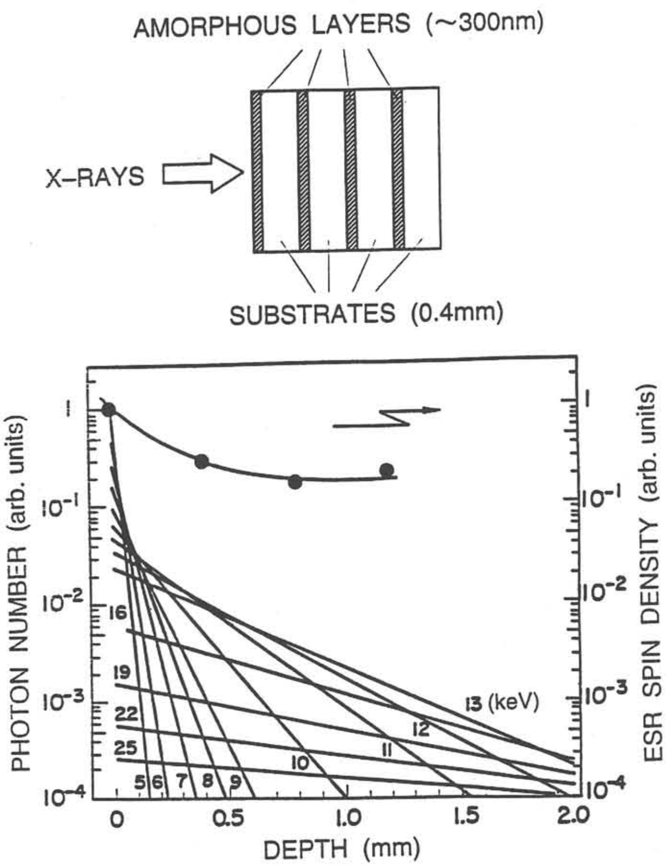

Fig.3 Depth dependence of ESR spin density (●) and the calculated attenuation of photon numbers for respective photon energies (solid curves). Those are normalized by the values for the top a-Si film. Experimental configuration is shown in the inset.

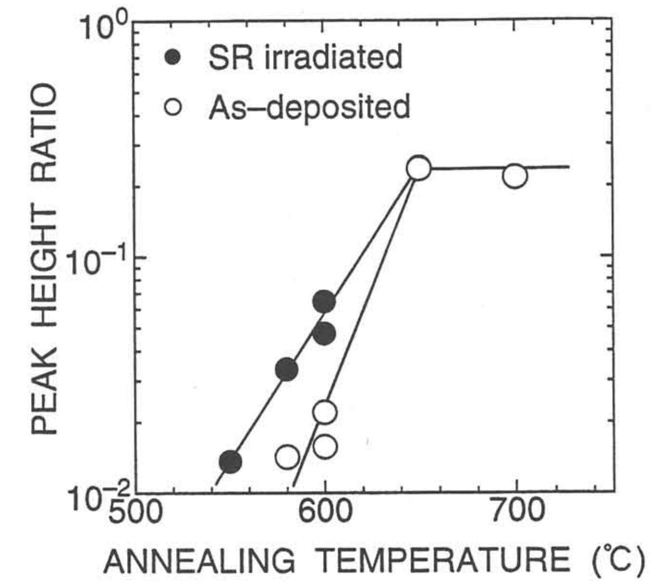

Fig.4 Comparison of crystallization by post thermal annealing after irradiation between irradiated (●) and nonirradiated (○) a-Si. Irradiation dose was 2000 mAh and annealing time was 30 minutes. The peak height ratios

is clear from the peak height for the nonirradiated specimen that crystallization with X-ray irradiation, as shown in Fig.2, is equivalent to thermal annealing at about 580°C. Since the peak height ratio due to micro-crystals in X-ray irradiation is at most 1.6×10^{-2} (Fig.2), the enhanced crystallization of the irradiated specimen annealed at 580°C or 600°C must be due to the growth of these micro-crystals. This method of introducing micro-crystals into amorphous phase with X-ray irradiation thus has strong potential as a low temperature preparation technique for polycrystalline silicon films.

4. CONCLUSION

In-situ nucleation of micro-crystals in ECR-PECVD a-Si has been demonstrated at near room temperatures with X-ray irradiation from synchrotron radiation. Nucleation occurs in the amorphous state with ESR spins of saturated density. Remarkable photon energy dependence of ESR spin formation was not observed. Crystallization of the irradiated ECR-PECVD a-Si can be enhanced by post-thermal annealing.

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