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Effect of plasma source power on the nanocrystallization of silicon thin films by reactive particle beam assisted chemical vapor deposition

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Abstract

The effect of radio frequency antenna power on the physical and chemical properties of nanocrystalline silicon deposited by reactive particle beam assisted chemical vapor deposition were systematically studied using various powers. Nanocrystalline Si embedded in an amorphous matrix was analyzed by X-ray diffraction and Raman spectroscopy. Films that were deposited under high power formed large grains due to high accelerated particle energy and high density in plasma. Using X-ray photoelectron spectroscopy, the chemical state of nanocrystalline silicon films was revealed to have Si–Si bonds. Further, an increase in antenna powers induced a roughened surface morphology, as well as changes in the dark conductivity and optical bandgap in Si films.

Keywords: A. Films; B. Spectroscopy; C. Electrical properties; E. Functional applications

1. Introduction

Nanocrystalline silicon (nc-Si) is a polymorphous material composed of nanocrystalline silicon embedded in an amorphous silicon matrix. Nanocrystalline silicon related devices are more stable under light soaking conditions than hydrogenated amorphous silicon (a-Si:H). Further, nc-Si thin film transistors (TFTs) exhibit higher stability than a-Si:H TFTs under prolonged periods of gate bias stress. However, lack of precise control over nano-sized grains, low deposition rate, high substrate temperature, lack of uniform distribution, surface damage and defect formation by ionized particle bombardment have hampered the use of deposition methods for nanocrystalline silicon [1]. Further, the conventional chemical vapor deposition (CVD) process that supplies the required energy for reaction by substrate heating can cause substrate deformation problems and surface damage because of high substrate temperatures and charged particles, respectively.

CVD deposition by reactive particle beam (RPB) assisted inductively coupled plasma (ICP) can control the energy of the deposited particles within a range of 1–100 eV [2]. The RPB generation system consists of an internal antenna for plasma generation and a silicon reflector. Working gases are then ionized after insertion into the plasma generated previously by the internal antenna. The ions in the plasma sheath between the plasma and reflector are then accelerated to a metal reflector, where they are reflected. After reflection, these ions are neutralized mainly through Auger neutralization. Finally, the ionized particles in the plasma and neutralized particles come together to form the reactive particle beam source. This energy-controllable RPB source is then deposited on the substrate where it forms a thin film thorough an ICP type CVD process. RPB, with a proper level of kinetic energy, can supply sufficient heating energy to the thin film for reaction without additional substrate heating and reduce charged particle damage at the surface of films.

In this research, to understand the effects of rf antenna power on an RPB assisted CVD system, the structural, chemical, optical and electrical properties of silicon thin films containing nanocrystallites were investigated by varying the rf source power from 700 to 1100 W.

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2. Experimental

Nanocrystalline silicon films were deposited using a RPB assisted CVD system at room temperature. The working gases were a mixture of SiH_4, He and H_2. Working pressure was 2 mTorr during deposition, and the power of the rf antenna was 700, 900, and 1100 W while the SiO_2 shield was used. The 0 bias was loaded for RPB generation on the silicon reflector. Film thickness was controlled to be 130 nm and deposition rate was 1.2 Å/s. The crystal structure of the films was analyzed by X-ray diffraction using beam line 10B at Pohang Light Source (PLS) in Korea with $\lambda = 1.5409$ Å, $E = 8.04621$ KeV. The chemical states of the films were analyzed using high-resolution photoemission spectroscopy beam line 8A2 at PLS with 630 eV. Raman measurements were conducted with a LabRam HR (Jobin-Yvon, France) using a 0.5 mW Ar laser (514.532 nm). Electrical conductivity was measured using an HMS 3000 Hall Effect measurement system (Ecopia, Korea). Surface morphology was studied by atomic-force microscopy (AFM) using a XE-100 (Park systems) in non-contact mode. Optical band gap was measured with a UV visible spectrometer (V-570, Jasco).

3. Results and discussion

Fig. 1 shows the XRD patterns of the nc-Si films with rf powers of 700–1100 W. The three diffraction peaks at 28.2°, 47.2°, and 55.7° correspond to the (1 1 1), (2 2 0) and (3 1 1) crystal planes of silicon, respectively. In the case of RPB assisted ICP type CVD, the accelerating energy was determined as the sum of the plasma potential and reflector bias voltage. Yoo et al. observed that the particle energy loss during reflection and the measured RPB energy were about 40% of the reflector bias voltage when using a particle energy analyzer. As such, the RPB energies are approximately half that of the impinging ion energies [3]. In this experiment, the reflector bias voltage was fixed at 0 V to confirm the effect of plasma condition change which resulted from rf antenna power variation. An increase in rf antenna power means that RPB plasma density and bombardment energy of particles increased.

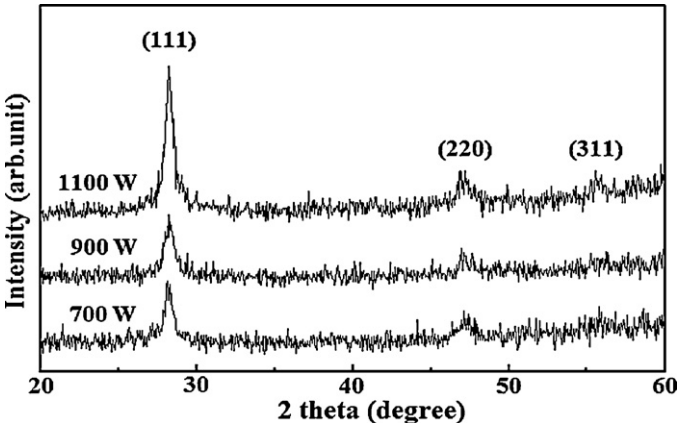

Fig. 1. XRD patterns of nanocrystalline silicon films deposited on silicon substrates at different rf antenna powers of 700 W, 900 W, and 1100 W.

In our study, the intensity of diffraction peaks increased with an increase in rf antenna power from 700 to 1100 W. Likewise, the full with half maximum (FWHM) of (1 1 1), (2 2 0), and (3 1 1) peaks also decreased. The intensity and FWHM changes reveal that the films achieved higher crystallinity with increasing power [4,5]. In particular, the (1 1 1) peak became sharper and showed higher intensity at an rf power of 1100 W, revealing that high rf power promoted (1 1 1) preferred orientation growth of nc-Si. Also, the (3 1 1) peak intensity also increased with increasing rf power, and these results confirmed that high index plane growth requires a high energy for crystallization.

To further analyze the crystalline state of the silicon films, Raman spectroscopy measurements were performed. Fig. 2 shows the Raman spectra of the silicon films deposited at different rf powers ranging from 700 to 1100 W. The silicon film deposited at 700 W shows high intensity of amorphous peaks and low intensity of crystalline peaks together. The amorphous phase peak intensity decreased gradually with increasing rf power, and the crystalline phase peak shows opposite tendency. Silicon films which were deposited at 900 and 1100 W are dominated by the nanocrystalline phase state. Amorphous silicon shows a broad peak centered around 475 cm^{-1}, originating from displacement of the bridging silicon atom along a line bisecting two tetrahedral units; whereas, for crystalline Si, the very narrow line at 520 cm^{-1} is attributed to transverse optical (TO) phonons [1]. The sharp peak centered around 510 cm^{-1} in this measurement was representative of an intermediate state of silicon between the amorphous and crystalline phases. This peak was attributed to a defective part of the nano sized small crystalline phase originating from either crystallites with diameters less than 10 nm, a silicon wurzite phase resulting from twins, or bond dilation at grain boundaries [6]. The nanocrystalline size (D) in the amorphous silicon matrix could be estimated according to [1]:

$$D = 2\pi\left(\frac{B}{\Delta\omega}\right)^{1/2} \quad (1)$$

In Eq. (1), $\Delta\omega$ is the shift of the nanocrystalline Si peak at 522 cm^{-1}, and B is a constant equaling 2.24 $cm^{-1}nm^2$. Nano-

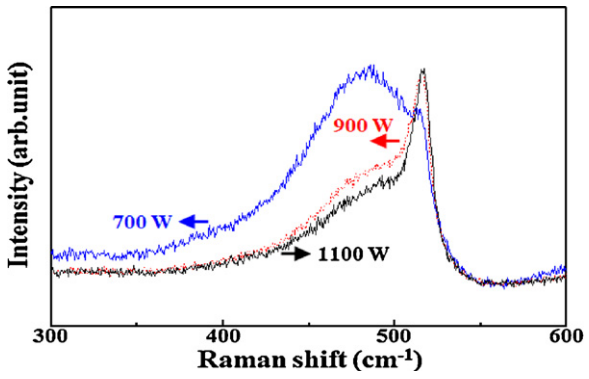

Fig. 2. Raman spectra of nanocrystalline silicon films deposited at different rf antenna powers of 700 W, 900 W, and 1100 W.

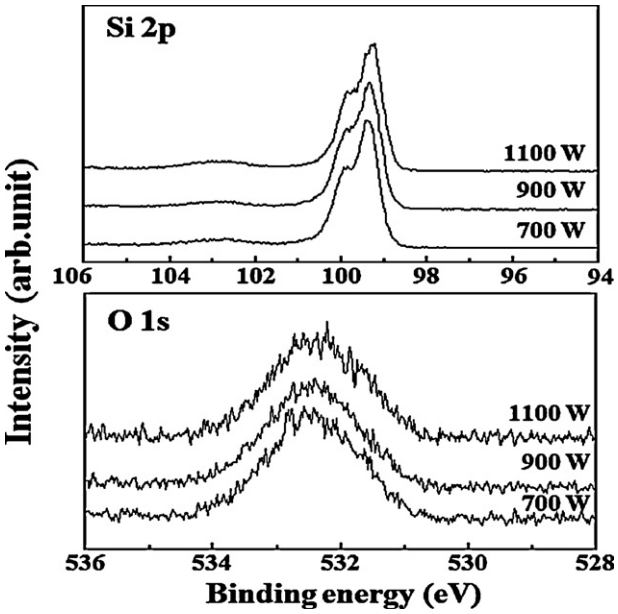

Fig. 3. Photoemission spectra of Si 2p and O 1s of nanocrystalline silicon films deposited at different rf antenna powers of 700 W, 900 W, and 1100 W.

crystalline Raman peaks that were shifted from 513.3 cm^{-1} via 515.2 cm^{-1} to 515.9 cm^{-1} with increasing rf power corresponded to higher crystalline states. Specifically, the sizes of crystallites in silicon films deposited at 700, 900 and 1100 W were calculated as 3.19, 3.61, and 3.81 nm, respectively. Also, the crystalline volume ratio (X_c) of the nanocrystalline silicon thin film was calculated from the deconvolution of Raman spectra measured around 350–550 cm^{-1} [7]. The calculated crystalline volume ratio increased from 12.2 to 36.5 to 40.8% with increasing rf power from 700 to 900 to 1100 W, respectively. Increased nanocrystallite size with rf power is due to the increased plasma density, thus allowing for more efficient SiH_4 dissociation, resulting in an increase in the reactive particle beam flux to the substrate surface. The ion bombardment energy of particles deposited under high rf power had higher internal energies and show better crystallinity than silicon films deposited at lower rf powers [8].

Fig. 3 shows the photoemission spectra of Si 2p and O 1s of silicon nanocrystallites embedded in amorphous silicon films deposited under different rf antenna powers. In the Si 2p spectra, the main peak was a strong photoelectron peak of Si $2p_{3/2}$ at 99.3 eV originating from Si–Si bonds. In the O 1s spectra, the main binding energy was found to be 532.4 eV, which is different from the O 1s binding energy in SiO_2 (532.9 eV) but the same as the binding energy of oxygen, which either forms hydroxides or is physically absorbed on silicon surfaces. In this work, the SiO_2 antenna shield tube was used for plasma generation; however, there was no contamination effect on the silicon films because normally when silicon binds with oxygen and forms the Si–O bonds of SiO_2, the binding energy of Si 2p is 103.6 eV [9]. Furthermore, the chemical bonding state did not appear to change with rf power, whereas only the internal energy states of the films were changed.

The influence of rf power on the surface morphology of films was studied using AFM and the results are given in Fig. 4. The root mean square (RMS) roughnesses of nc-Si films deposited with 700, 900 and 1100 W were 0.741, 0.874, and 0.878 nm, respectively. This increase in RMS roughness came from a size increase in crystallites corresponding to increased energy due to rf power. The observed enlarged silicon nanocrystallites in the amorphous matrix with increasing rf power agreed well with the results of XRD measurements in Fig. 1.

The optical bandgaps of the silicon films were deduced from the optical transmission and the reflectance spectra (Fig. 5). The calculated optical bandgap values were 1.94, 2.25, and 2.21 eV for rf powers of 700, 900, and 1100 W, respectively. Normally, in the case of 1100 W of rf power, a decrease in the optical

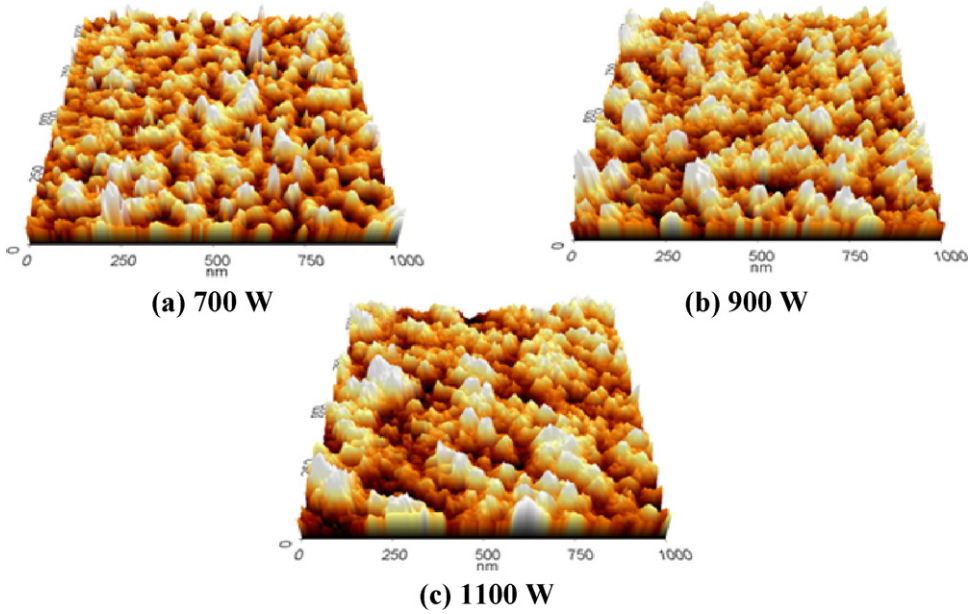

Fig. 4. AFM surface images of nanocrystalline silicon films deposited at different rf antenna powers of (a) 700 W, (b) 900 W, and (c) 1100 W.

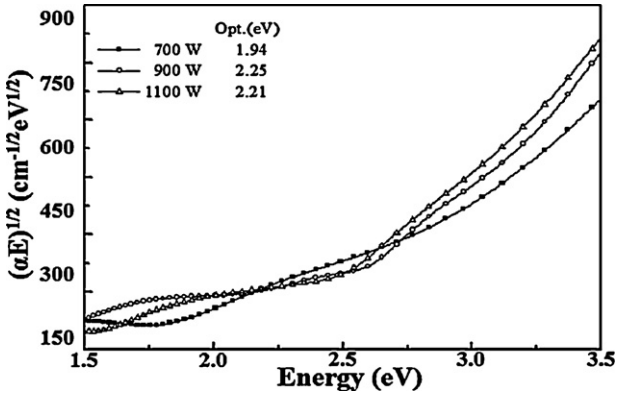

Fig. 5. Optical spectra of nanocrystalline silicon films deposited at different rf antenna powers of 700 W, 900 W, and 1100 W.

bandgap should have been observed when considering the enlargement in silicon nanocrystallite size as observed in the XRD results of Fig. 1. However, with increasing rf power, the enhancement in crystallinity observed is due mainly to two factors: (1) an increase in nanocrystallite size (crystalline quality) and, (2) an increase in the volume ratio of nanocrystalline phase to amorphous silicon matrix. Generally, the optical bandgap of nanocrystallite embedded amorphous Si increases when the amount of nanocrystallites is increased in an amorphous matrix [10]. Therefore, it could be said that the increase in the optical bandgap with increasing rf power was due to an increased crystallite to amorphous volume ratio [11]. Hence, the optical bandgap decreased slightly with increasing rf power from 900 to 1100 W because the enlargement in nanocrystallite size becomes more important than the nanocrystalline volume ratio increase. The dark conductivity of nc-Si films was measured for various rf antenna powers and were found to be 1.57×10^{-6}, 3.71×10^{-7}, and 1.08×10^{-6} S/cm, for 700, 900 and 1100 W, respectively. An increased volume ratio of nc-Si with increasing rf power from 700 to 900 W would interrupt the conduction of electrons. But, in the case of an rf power increase from 900 to 1100 W, the increase in nc-Si size would reduce the grain boundary area and contribute to electron conduction. Based on the above results, deposition by an RPB assisted ICP type CVD system was found to be effective for the deposition of amorphous silicon films containing embedded nanocrystallites whose size is controllable by varying the rf antenna power, which results in an internal energy change.

4. Conclusions

We formed silicon films embedded with nanocrystallite silicon at room temperature with RPB assisted CVD by varying the rf antenna powers. The nanocrystallite size in the films increased with increasing rf antenna power. Further, it was revealed that the high internal energy state of the film that was deposited under high rf antenna power could be crystallized easier than that with low rf power. The chemical bonding state of nc-Si films was not changed; however, the surface roughness was increased with increasing rf power. Based on changes in optical bandgap and dark conductivity with increasing rf power, we confirmed that RPB assisted deposition reduced the activation energy needed for nc-Si formation and control of the size of nanocrystallites by varying the rf antenna power was possible.

Acknowledgements

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