

Effect of reflector bias voltage on the nanocrystallization of silicon thin films by reactive particle beam assisted chemical vapor deposition

Sun Gyu CHOI, Jin-Nyoung JANG,* MunPyo HONG,* Kwang-Ho KWON** and Hyung-Ho PARK†

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

*Department of Display and Semiconductor Physics, Korea University, Chungnam 339-700, Korea

**Department of Control and Instrumentation Engineering, Korea University, Chungnam 339-700, Korea

In the present study, the effects of reflector bias voltage on the physical and chemical properties of nanocrystalline silicon deposited by reactive particle beam assisted chemical vapor deposition were systematically studied using various reflector bias voltages. During deposition, the substrate temperature was kept at room temperature. Nanocrystalline Si embedded in an amorphous matrix structure was analyzed by X-ray diffraction and Raman spectroscopy. Films that were deposited under high reflector voltage formed large grains due to largely accumulated internal energy. Using X-ray photoelectron spectroscopy, the chemical state of nanocrystalline silicon was revealed to have only metallic Si bonds. Further, an increase in reflector voltage induced a roughened surface morphology, an increased dark conductivity, and a decreased optical band gap in Si films.

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1. Introduction

Nanocrystalline silicon (nc-Si) is a polymorphous material composed of nanocrystalline silicon embedded in an amorphous silicon matrix.¹⁾ Nanocrystalline silicon is a promising material for electronic and optoelectronic devices by reason of its wide and near-direct bandgap characteristics. 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, precise control over nano-sized grain, as well as their uniform distribution, have been main problems of formation research for nanocrystalline silicon films.²⁾ To overcome these troubles, several kinds of deposition methods including capacitively coupled radio-frequency (rf) plasma enhanced chemical vapor deposition (PECVD), hot wire chemical vapor deposition, very high-frequency PECVD, and electron cyclotron resonance CVD have been used to generate nanocrystalline silicon films.³⁾ However, all of these deposition methods are associated with problems such as low deposition rate, high substrate temperature, surface damage, and defect formation by ionized particle bombardment. Further, the conventional CVD process that supplies the required energy for reaction by substrate heating causes substrate deformation problems and surface damage because of high substrate temperatures and charged particles, respectively.

Deposition technology by the reactive particle beam (RPB) assisted inductively coupled plasma (ICP) type chemical vapor deposition (CVD) system can control the energy of the deposited particles within a range of 1–100 eV.^{4),5)} The schematic diagram of RPB generation system which consists of an internal antenna

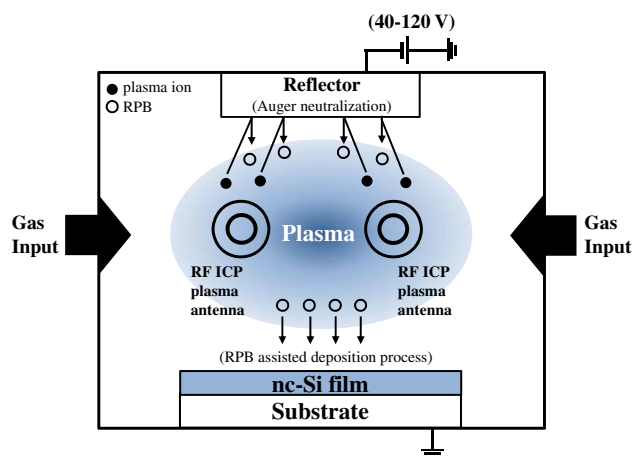


Fig. 1. (Color online) Schematic diagram of RPB assisted ICP CVD system.

for plasma generation and a silicon reflector was shown in Fig. 1. 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.⁶⁾ The neutralized particle energy as well as neutralization and recoil efficiency vary as functions of the reflector materials, surface roughness, and impinging angle, etc.⁷⁾ Finally, the ionized particles in the plasma and neutralized particles come together to form the reactive particle beam source. This energy-controllable reactive particle beam source is then deposited on the substrate where it forms a thin film through an ICP type CVD process. RPB, with a proper level of kinetic energy, can supply sufficient heating energy to the thin film for

† Corresponding author: H.-H. Park; E-mail: hhpark@yonsei.ac.kr

reaction without additional substrate heating and reduce charged particle damage at the surface of films.

In this research, to understand the effects of reflector bias voltage on an RPB assisted CVD system, the structural, chemical, optical and electrical properties of silicon thin films containing nanocrystallites were investigated by varying the bias voltage of reflector from 40 to 120 V.

2. Experimental procedure

Nanocrystalline silicon films were deposited using a reactive particle beam assisted CVD system. The process chamber was evacuated to a base pressure of 4×10^{-6} Torr using a turbo-molecular pump. The working gases were a mixture of silane (SiH_4), helium (He), and hydrogen (H_2), and the working pressure was 2 mTorr during deposition. The RF bias for the ICP antenna was 1100 Watts while the SiO_2 antenna shield tube was used. Bias voltages of 40, 80, and 120 were loaded for reactive particle beam generation on n-type silicon reflectors. During the deposition of thin films, the substrate temperature was maintained at room temperature. Thicknesses of deposited Si thin films were measured by an alpha step. Film thickness was 80 nm and deposition rate was 0.6 \AA/s . The crystal structure of the films was analyzed by X-ray diffraction (XRD) beam line 10B at Pohang Light Source (PLS) with $\lambda = 1.5409 \text{ \AA}$, $E = 8.04621 \text{ keV}$. The chemical state of films were analyzed by high-resolution photo-emission spectroscopy (HR-PES) beam line 8A2 at PLS. Raman measurements were conducted with a LabRam HR using the 514.532 nm line of an Ar laser for excitation. Electrical conductivity of Si films was measured using a Hall effect measurement system. Surface morphology was studied by atomic-force microscopy (AFM) using an XE-100 (Park systems) in non-contact mode. Optical band gap was measured with a UV visible spectrometer (V-570, Jasco). Lastly, nanocrystalline silicon films were deposited on two different types of substrates: Si(100) substrate for XRD, PES, AFM, electrical conductivity measurement and corning 1737 glass substrate for Raman spectroscopy and optical transmittance analysis.

3. Results and discussion

The crystal structures of the RPB assisted nanocrystalline silicon films generated at various bias voltages were examined by X-ray diffraction. **Figure 2** shows the XRD patterns of the deposited nanocrystalline silicon films with a reflector bias of

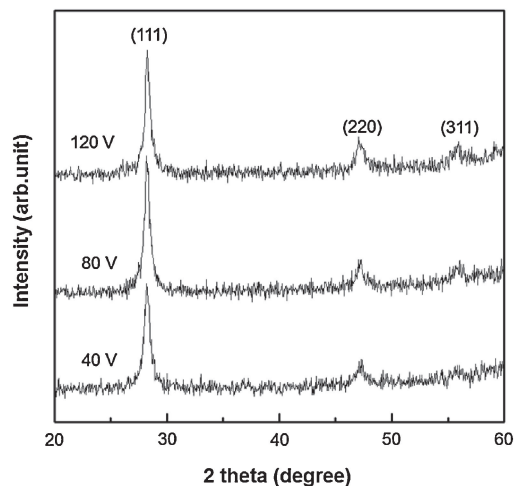


Fig. 2. XRD patterns of nanocrystalline silicon films deposited on silicon substrates as a function of reflector bias voltages.

40 to 120 V. The three diffraction peaks at 28.2° , 47.1° , and 55.8° correspond to (111), (220) and (311) crystal planes of silicon, respectively. These peaks revealed nanocrystalline Si formation of the deposited films.³⁾ In the case of reactive particle beam assisted ICP type CVD system, the accelerating energy was determined as the sum of the plasma potential and reflector biased voltage. Yoo et al. observed that the particle energy loss during reflection and the measured reactive particle beam energy were about 40% of the reflector bias voltage when using a particle energy analyzer.⁸⁾ As, the reactive particle beam energies are approximately half that of the impinging ion energies.⁹⁾ Thus when the bias voltage was 30 V with a plasma potential of 10 eV, the impinging ions were accelerated up to 40 eV, and the energy of the reflected particles subsequently decreased to about 20 eV. Further, an increase in reflector bias voltage means that reactive particles could have higher energy.

In this study, the intensity of diffraction peaks increased with an increase of bias voltage from 40 to 120 V. Likewise, the full width half maximum (FWHM) of (111), (220), (311) also decreased. The intensity and FWHM changes revealed that the film with high crystallinity. Especially, the (311) peak became sharper at a bias voltage of 120 V. Taken together, these results confirm that a high index plane growth requires a high energy for crystallization.

To further analyze the crystalline state of RPB assisted CVD deposited nanocrystalline silicon films, Raman spectroscopy measurement were performed. **Figure 3** shows the Raman spectra of the silicon films deposited at different reflector bias voltages ranging from 40 to 120 V. An Ar laser at 0.5 mW of power was used to check the phase state (crystalline or amorphous). The amorphous phase peak intensity decreased gradually with increasing reflector bias voltage. The amorphous silicon showing a broad Raman spectrum peak centered around 475 cm^{-1} originates 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} was attributed to transverse optical (TO) phonons.²⁾ The sharp peak centered around 510 cm^{-1} in these measurements 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 bound-

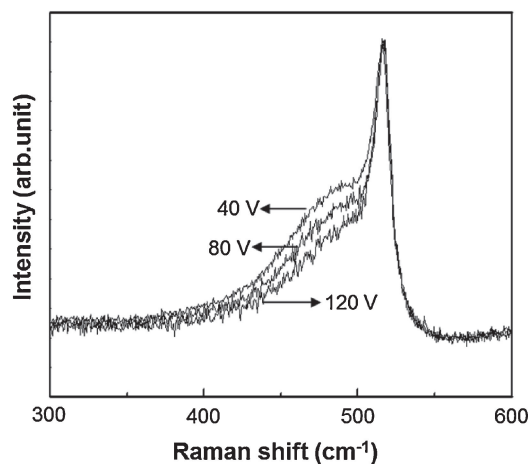


Fig. 3. Raman spectra of nanocrystalline silicon films deposited at different reflector bias voltages of 40, 80 and 120 V.

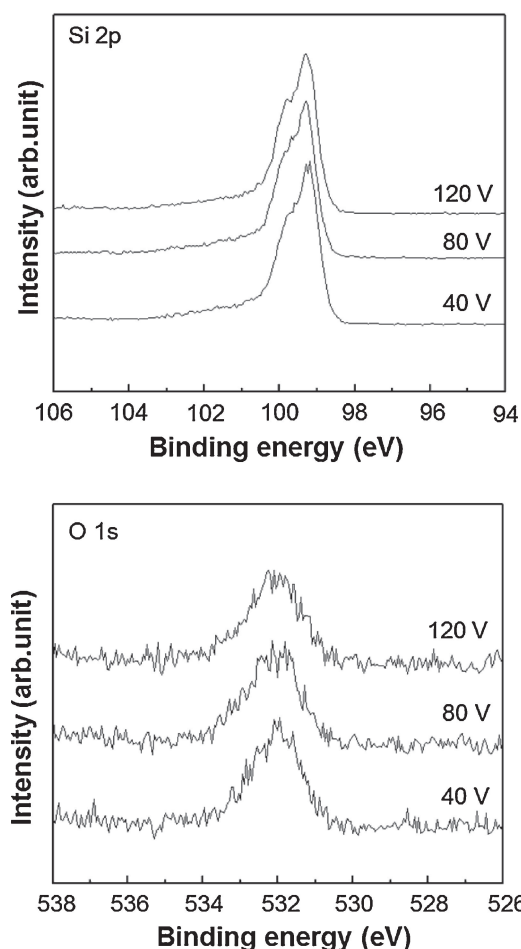


Fig. 4. Photoemission spectra of Si 2p and O 1s of nanocrystalline silicon films deposited at different reflector bias voltages.

aries.^{10)–12)} The nanocrystalline size in the amorphous silicon matrix could be estimated using the following formula:²⁾

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

where $\Delta\omega$ is the shift in the nanocrystalline peak from the crystalline Si at 522 cm^{-1} and B is a constant equal to $2.24\text{ cm}^{-1}\text{ nm}^2$. Nanocrystalline Raman peaks that were shifted from 515.8 cm^{-1} via 516.5 cm^{-1} to 517.0 cm^{-1} with increasing reflector bias voltages corresponded to higher crystalline states. Specifically, the crystalline size of the silicon films deposited with 40, 80 and 120 V were calculated as 3.78, 4.01, and 4.21 nm, respectively. From the above results, it appeared that the crystalline nature of RPB assist-deposited silicon films could be changed with reflector bias voltage. The films deposited under high reflector bias voltage (high energy of deposited particles) had higher internal energies and better crystallization than silicon films deposited at lower reflector bias voltages.

The chemical state of amorphous silicon films were resolved by photoemission spectroscopy analysis at PLS with 630 eV. **Figure 4** shows the photoemission spectra of Si 2p and O 1s of silicon nanocrystallites embedded amorphous silicon films deposited under different reflector bias voltages. In Si 2p spectra, a strong photoelectron peak of Si $2p_{3/2}$ at 99.3 eV originated from metallic silicon was mainly found. In the O 1s spectra, the main binding energy was found to be 532.0 eV, which was 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 hydroxide or is

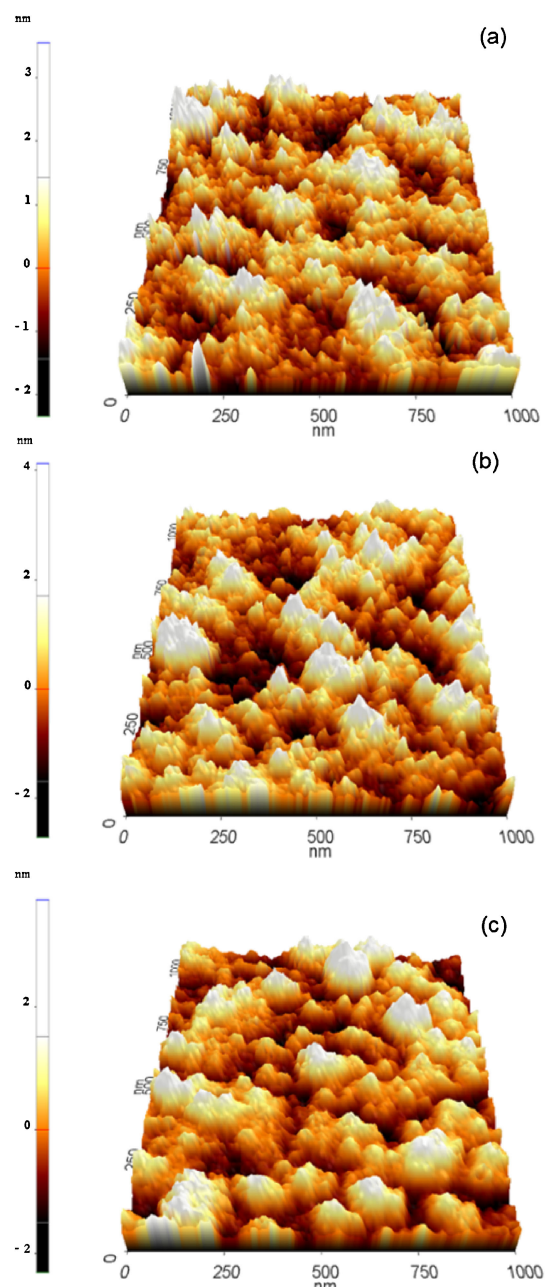


Fig. 5. (Color online) AFM surface images of nanocrystalline silicon films deposited at different reflector bias voltages (a) 40 V, (b) 80 V and (c) 120 V.

physically absorbed on silicon surfaces.¹³⁾ 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 Si–O bonds of SiO_2 , the binding energy of Si 2p is 103.6 eV.^{14),15)} Furthermore, the chemical bonding state did not appear to be changed with reflector bias voltage, whereas the internal energy states of the films were changed.

The influence of reflector bias voltage on the surface morphology of the films was studied using AFM (**Fig. 5**). Surface morphology was measuring in non-contact mode.¹⁶⁾ The root mean square (RMS) roughness of nanocrystalline silicon films deposited with 40, 80 and 120 V were 0.726, 0.867, and 1.000 nm, respectively. The increase in RMS roughness came

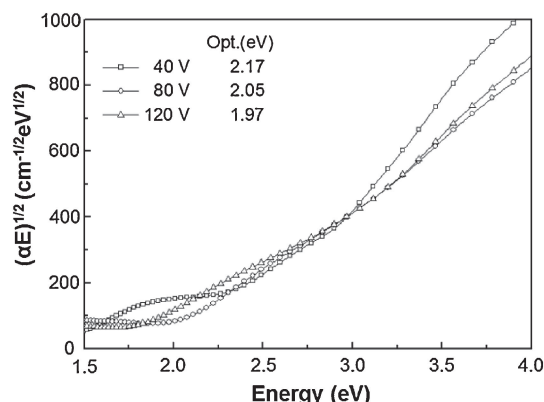


Fig. 6. Optical spectra of nanocrystalline silicon films deposited as a function of reflector bias voltages.

from the size increase of crystallites corresponding to increased internal energy due to increasing reflector bias voltage. As observed in the XRD results given in the Fig. 2, an increase in the reflector bias voltage induced an enlargement of silicon nanocrystallites in the amorphous silicon substrate.

The optical bandgap of the silicon films were deduced from the optical transmission and the reflectance spectra (Fig. 6). Optical bandgap, E_0 , is commonly estimated by extrapolation of a linear plot of $(\alpha E)^{1/2}$ versus $E - E_0$, where E is photon energy, to the $\alpha = 0$ value. The calculated optical bandgap values were 2.17, 2.05, and 1.97 eV with 40, 80 and 120 volts of reflector bias voltage, respectively, which agreed well with the results of XRD and AFM. The decrease in the optical bandgap could be associated with the size increase in the silicon nanoparticles.^{17)–19)}

The dark conductivities of the silicon films with reflector bias voltage change were measured. The dark conductivity values with reflector voltages of 40, 80, and 120 V were 3.80×10^{-3} , 1.53×10^{-2} , and 3.02×10^{-2} S/cm, respectively. This increase was thought to be due to the enlarged nanocrystalline silicon in the Si film with increasing bias voltage. The nanocrystallite size increase would have interrupted generation of the grain boundary and contributed to a conduction of electrons. Based on the above results, the new deposition technology of RPB assisted ICP type CVD was found to be effective for the deposition of amorphous silicon films containing embedded nanocrystallites whose size is controllable by varying reflector bias voltage, which results in a proportional internal energy change.

4. Conclusions

We formed silicon films embedded with nanocrystallite silicon at room temperature with RPB assisted CVD by varying the reflector bias voltage. The nanocrystallites size in the films increased with increasing reflector bias voltage. Further, it was revealed that the high internal energy state of the film that was deposited under high reflector voltage could be crystallized easier than with low reflector bias voltage. The chemical bonding state

of the nanocrystalline silicon films was not changed; however, the surface roughness increased with increasing reflector voltage. Based on the decrease in optical bandgap and the increase in dark conductivity with increasing reflector voltage, we confirmed that RPB assisted deposition reduced the activation energy needed for nanocrystallite silicon formation and controlled the size of nanocrystallites by varying the reflector bias voltage.

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