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Irradiation effects of 65 MeV Kr-ions on structure and optical band-gap of nc-Si:H films

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ABSTRACT

In this paper, hydrogenated nano-crystalline silicon (nc-Si:H) films with thickness of 1.0 μm were irradiated with 65 MeV Kr-ions, and the irradiation induced modification on structural and optical properties of the films are investigated. Characterization of the samples with X-ray diffraction shows that the average crystallite size decreases slightly from 10.9 to 9.4 nm, and the integrated intensity ratios of (220) to (111) peak and (311) to (111) peak remain nearly constant after irradiation. The Raman spectra results reveal that the crystalline fraction of the films decreases considerably from 65.6% to 10.3% and at same time the bond angle deviation of amorphous phase increases obviously from 7.7° to 11.5° with increasing the ion fluence. Moreover, the UV–Vis transmittance spectra results show that the optical band-gap decreases from 2.14 to 1.55 eV after irradiation. The irradiation induced atomic displacements leads to the amorphization of crystalline phase and the reduction in structural order of amorphous phase in the nc-Si:H films. The improvement of light absorption and the broadening of valence and conduction band-tails, which related to the decrease of crystalline fraction and short range order, respectively, are responsible for the reduction of optical band-gap.

1. Introduction

Hydrogenated nano-crystalline silicon (nc-Si:H) film consists of nano-scale silicon crystallites embedded in amorphous matrix, which makes it exhibits better optoelectronic properties than the hydrogenated amorphous silicon (a-Si:H) film [1]. Over the last two decades, nc-Si:H film has gained considerable attention on the basis of its potential applications to large area electronic devices, such as active-matrix liquid crystal displays, thin film transistors and solar cells. Numerous studies have been carried out to improve the structural and optoelectronic properties of nc-Si:H film in order to make it competitive for the device applications [2–4]. Nowadays, optimize the optoelectronic properties of nc-Si:H film by varying the deposition parameters under various deposition systems has been studied relatively extensively [5,6]. Some post-deposition techniques, such as plasma treatment [7] and laser annealing [8], have also been used to modify the structure and optoelectronic properties of the nc-Si:H film.

As a unique materials modification technique, energetic ion beam bombardment of thin films offers interesting possibilities to reduce the surface roughness, to synthesize new materials using ion mixing and to improve adhesion of thin films on solid substrates. In the case of silicon films, energetic ion implantation/irradiation has already been used in the modification on structural and optoelectronic properties. Experimental results show that the implantation of keV Si-ions on amorphous silicon (a-Si) film can effectively reduce the roughness of film surface without destroy the mechanical properties inside the film [9], ion tracks have been observed in a-Si film irradiated with 207 MeV Au-ions [10], 2.8 MeV Si-ions irradiation leads to the decrease of dark conductivity and photoconductivity of a-Si:H film [11] and 1 MeV Si-ions irradiation results in the decrease of optical band-gap of a-Si and a-Si:H films [12]. But so far, studies about irradiation effects on silicon films are mainly focus on the a-Si and a-Si:H films, irradiation induced modification of nc-Si:H film has not yet been well studied.

The aim of this work is to get insight into the irradiation effects of high energy heavy ions on the structural and optical properties of the nc-Si:H film. For this purpose, a set of samples fabricated on glass substrates were irradiated with 65 MeV Kr-ions at different fluences. X-ray diffraction, Raman scattering and UV–Vis transmittance spectroscopy were used to study the modification on structural and optical properties of the samples induced by the ion irradiation. The relationship between the microstructure and the optical properties is discussed.

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2. Experimental details

The nc-Si:H films with thickness of 1.0 μm were deposited on glass substrates by a hot-wire chemical vapor deposition system. Four parallel tungsten filaments were used as hot wires, and set above the substrates at a distance of 70 mm. Before the deposition process, the chamber was pumped down to a base pressure of 5.0×10^{-4} Pa. The silane (SiH_4) and hydrogen (H_2) were used as the reactant gases, and their flow were controlled by mass flow controllers in the deposition system. The detailed deposition parameters of the samples are summarized in Table 1. The size of the samples is 1.5 cm × 1.5 cm.

After deposition, the nc-Si:H films were irradiated at room temperature with 65 MeV Kr-ions in fluences of 1.0×10^{12}, 1.0×10^{13} and 1.0×10^{14} Kr-ions/cm^2, respectively. The irradiation experiment was carried out at Heavy Ion Research Facility in Lanzhou (HIRFL). The ion-beam sweeping was employed to ensure the uniform fluence distribution over 9 cm^2 area (3 cm × 3 cm). During the irradiation, the beam current was maintained at about 3 pnA (particle nano-ampere), which gives the mean flux was about 2.1×10^9 ions/(cm^2 s). The energy losses and projected range (R_p) were simulated with the Stopping and Range of Ions in Matter (SRIM) code [13]. The electronic (S_e) and nuclear energy losses (S_n) are 8.0 and 0.04 keV/nm, respectively. The projected range of incident ions is 13 μm, which is much larger than the thickness of the films.

The post-irradiated films were characterized using X-ray diffraction, Raman scattering and UV–Vis transmittance measurements. X-ray diffraction was carried out on a Philips X'Pert SW X-ray diffractometer operating using Cu K_α line (at 40 kV and 40 mA) in a θ–2θ drive configuration. The patterns were taken at a grazing angle of 1° and in the range of 2θ from 20° to 70°. Raman scattering spectra were recorded at room temperature on a JY-HR800 spectrometer in the region of 300–800 cm^{-1}. The excitation wavelength of laser is 532 nm, and the laser power was kept low enough to avoid any beam-induced crystallization during the measurement. The UV–Vis transmission spectra were recorded by using a Lambda 900 spectrophotometer. The analytical wave number is in the range of 200–1000 nm with a resolution of 1 nm.

3. Results

3.1. XRD analysis

Fig. 1 shows the XRD patterns of nc-Si:H films irradiated with different fluences. Three diffraction peaks at $2\theta = 28.4°$, 47.3° and 56.1°, which are corresponding to (1 1 1), (2 2 0) and (3 1 1) crystallographic orientations of nc-Si:H films respectively, are clearly observed in all patterns. From Fig. 1, it can be seen that the intensities of all diffraction peaks decrease as the ion fluence increases. This implies that the crystallinity of the nc-Si:H films decreases after irradiation. With the ion fluence increases from 0 to 1.0×10^{13} ions/cm^2, the XRD peak positions show no obvious changes. When the ion fluence achieves to 1.0×10^{14} ions/cm^2, the XRD peak positions increase by about 0.1°. This indicates that the lattice constant decreases slightly after irradiation with 1.0×10^{14} ions/cm^2. With the Scherrer's equation, the average crystallite size (d_{XRD}) in the films is estimated from the relation of $d_{XRD} = 0.9\lambda/\beta\cos\theta$, where λ, β and θ are the wavelength of X-ray, the full width at half maximum (FWHM) and Bragg angle of the diffraction peaks, respectively [4]. Moreover, the integrated intensity ratios of (2 2 0) to (1 1 1) peak and (3 1 1) to (1 1 1) peak are defined as $I_{(220)}/I_{(111)}$ and $I_{(311)}/I_{(111)}$, respectively. Table 2 gives the calculated values of I_{220}/I_{111} and I_{311}/I_{111} as well as d_{XRD} for samples irradiated with different fluences. From Table 2, one can see that the value of $I_{(220)}/I_{(111)}$ varies slightly between 0.38 and 0.43 and the value of $I_{(311)}/I_{(111)}$ is in the range of 0.25 and 0.29. According to literature [14], it is found that the value of $I_{(220)}/I_{(111)}$ can vary in a wide range from 1 to about 5 by increasing the deposition temperature. In this work, such a slight deviation in the values of $I_{(220)}/I_{(111)}$ and $I_{(311)}/I_{(111)}$ can be neglected. Therefore, it is been considered that the values of $I_{(220)}/I_{(111)}$ and $I_{(311)}/I_{(111)}$ remain nearly constant with increasing the ion fluence. Table 2 also shows that the crystallite size decreases slightly from 10.9 to 9.4 nm with the ion fluence increases from 0 to 1.0×10^{14} ions/cm^2.

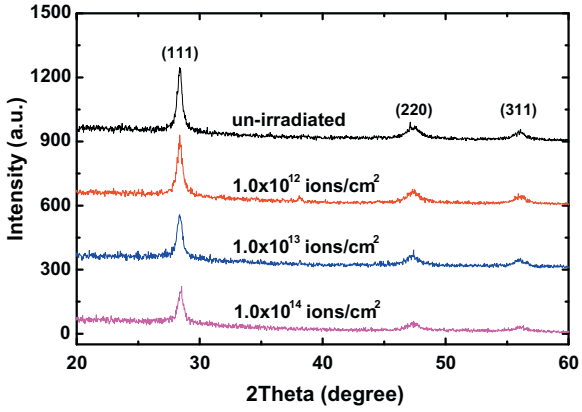

Fig. 1. XRD patterns of nc-Si:H films irradiated with different ion fluences.

3.2. Raman analysis

Raman scattering spectra of the samples irradiated with different fluences are shown in Fig. 2. For each spectrum, a deconvolution procedure was performed in order to determine the volume fraction of crystalline phase and the structural order of amorphous phase. The fitting results involved the following three parts: a crystalline peak located at about 520 cm^{-1}, an intermediate peak located at about 510 cm^{-1} and an amorphous peak located at about 480 cm^{-1}. Fig. 3 represents a typical deconvoluted Raman spectrum for the un-irradiated nc-Si:H film. The fitting results imply that with the ion fluence increases, the ratio of integrated intensity of peaks centered at 520 and 510 cm^{-1} over the total integrated intensity of all peaks decreases while the ratio of integrated intensity of peak centered at 480 cm^{-1} over the total inte-

Table 1
Deposition parameters of nc-Si:H films.

Deposition parameters	Value
Background pressure	5×10^{-4} Pa
Filament temperature	1600 °C
Process pressure	16 Pa
Substrate temperature	70 °C
SiH_4 flow	9 sccm
H_2 flow	63 sccm
Filament to substrate distance	7 cm
Deposition time	50 min

Table 2
The values of $I_{(220)}/I_{(111)}$ and $I_{(311)}/I_{(111)}$ as well as crystallite size (d_{XRD}) calculated from XRD patterns.

Ion fluence (ions/cm^2)	$I_{(220)}/I_{(111)}$	$I_{(311)}/I_{(111)}$	d_{XRD} (nm)
0	0.39	0.26	10.9
1.0×10^{12}	0.38	0.25	10.1
1.0×10^{13}	0.41	0.27	9.6
1.0×10^{14}	0.43	0.29	9.4