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Formation of Nanocrystallites in the nc-Si Films by Co-sputtering Aluminium and Silicon

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Abstract. The nanostructural and optical features of Al-doped Si thin films, which were prepared by co-sputtering Al-chips and a Si main target, were investigated in terms of Al-doping and post-deposition heat-treatment conditions; the heat treatment was carried out at temperatures of 400 ~ 1100 °C. The structural and chemical features are related with the photoluminescence (PL) phenomena of the films. The PL intensity as well as the concentration of Si nanocrystallites were increased by doping particular amount of Al in the films.

Introduction

Si is an indirect band structured material with a band gap of ~ 1.1 eV. Therefore, it emits little visible light at R.T. and as a result has not been applied in optoelectronic devices [1]. However, photoluminescence (PL) phenomena have recently been observed from Si films with Si crystallites of less than 5 nm in size. The luminescence is extremely sensitive to the size and fraction of the Si nanocrystallites.

Recently, the aluminium-induced crystallization (AIC) technique has been utilized to produce of crystallites in amorphous Si films. It is known that the overall layer exchange of Si with Al films or vice versa occurs during the transformation from amorphous to crystalline phases [2]. The Al migrates from interface into Si layers, dissociating a large number of Si-Si bondings [3]. However, there has been little experimental observation about the formation Si nanocrystallite in the AIC processing; in particular the effect of thermal annealing and doping techniques needs to be investigaed in detail.

In this study, we investigated the effect of Al-doping on the formation of nanometer-scale crystallites in nanocrystalline Si (nc-Si) thin films. The nanostructural, chemical, and optical features of nc-Si thin films were systematically investigated as a function of the amount of doped-Al and heat-treatment conditions.

Experimental Procedure

RF magnetron sputter techniques were used to prepare Al-doped nc-Si thin films on silicon wafers. A cylindrical pure Si target and parallelepiped Al chips were utilized as a main as well as auxiliary sputter targets, respectively; Si target and Al chip were $\Phi 2'' \times 5$ mm and $1 \times 1 \times 0.5$ mm in size, respectively; Al chips were located on top of the Si main target for simultaneous sputtering of Al and Si, and the amount of Al in the films was varied with the number of Al chips. Post-deposition heat-treatments were carried out at temperatures of 400, 600, 800 and 1100°C, respectively, for 60 min in nitrogen atmosphere.

The presence of nanocrystallites in the Al-doped nc-Si thin films was identified by transmission electron microscopy (TEM, CM200, Philips) and X-ray diffraction (XRD, Philips, PW-3020); in particular, a high-voltage electron microscope (HVEM, operating at 1.25 MV) was used to record high resolution images of nanocrystallites in the films. The chemical state of Si and Al was examined by X-ray photoelectron spectroscopy (XPS, 2803-S, SSI). PL measurements were performed at room temperature using a spectrofluorophotometer (SPEX, 1403).

Results and Discussion

Structural Analysis. Fig. 1(a) shows the XRD patterns of the nc-Si films which were prepared with 4 Al-chips and then post-deposition heat-treated at tempertiures of 400 ~ 1100 °C. The films, which were post-deposition heat-treated at temperatures of 800 and 1100 °C, exhibit the presence of crystallites; the diffraction peaks at 2θ = 28.4° and 47.3° correspond to (111) and (220) of Si, respectively. The diffraction peaks of (111) and (220) Si in the films which were heat-treated at 800 °C are broad, while those of the films which were annealed at 1100°C appear to be sharp. This indicates that the Al-doped nc-Si films were further crystallized during the heat-treatments. Two different types of crystallites with ~ 3.5 and ~ 14.5 nm in size were observed, which correspond to the broad and the sharp fits, respectively, in Fig. 1(b) [4]. The crystallite size of the nc-Si films prepared at 1100 °C is ~ 50 nm. The crystallinity and crystal-size distribution of the films prepared at 1100 °C appear to be much different from that prepared at 800 °C.

Fig. 1(c) shows the XRD patterns of the films which were prepared with various sputter target conditions. These films were heat-treated at 800 °C. As the amount of Al chips is increased, the (111) and (220) diffraction peaks of Si become sharper. It seems that the Al doping contributes to the increase in the crystallization of nc-Si.

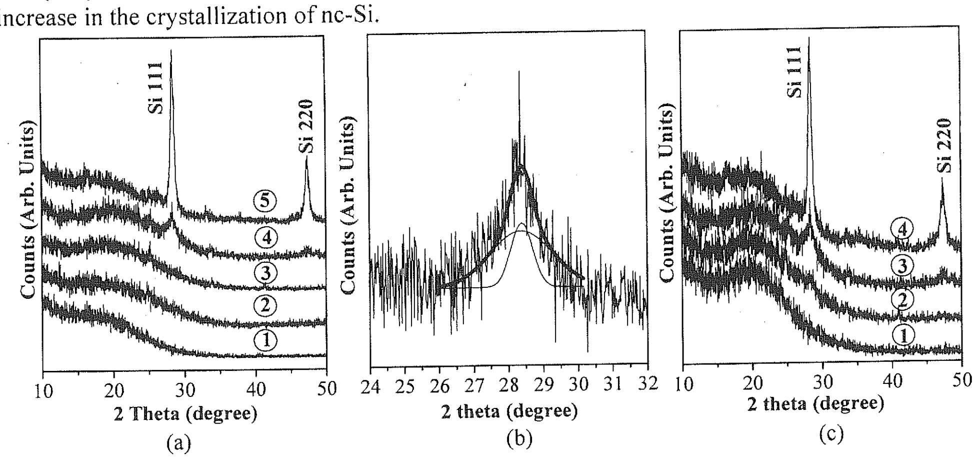

Fig. 1. (a) XRD patterns of the nc-Si films; XRD result ① was from as-prepared films; the films were post-deposition heat-treated at ② 400, ③ 600, ④ 800, and ⑤ 1100 °C for 15 min, respectively;. (b) Deconvolution of (111) XRD spectra ④ in Fig. 1(a). (c) XRD patterns of the films; these films were prepared with ① only the Si main target, ② 2 Al-chips and the Si main target, ③ 4 Al-chips and the Si main target, and ④ 8 Al-chips and the Si main target, and then heat-treated at 800 °C, respectively.

Fig. 2 shows high-resolution TEM images of the Al-doped nc-Si films. Fig. 2(a) illustrates the films which were post-deposition heat-treated at 800 °C for 60 min. This micrograph clearly illustrates the presence of ~ 3.5 nm-sized Si nanocrystallites in the films. Fig. 2 (b) and (c) show that Al-doped films which were heat-treated at 800 and 1100 °C for 60 min, respectively. The nc-Si films, which was prepared with 4 Al-chips and then heat-treated at 800 °C, are composed of an amorphous phase as well as nanocrystallites of around 3 and 5 nm in size. The HRTEM results are in good agreement with the XRD results. The films which were prepared with 8 Al-chips and then heat-treated at 1100 °C appear to contain more crystallites joining each other and/or overlapped; the size of the crystallites ranges from several to dozens nm.

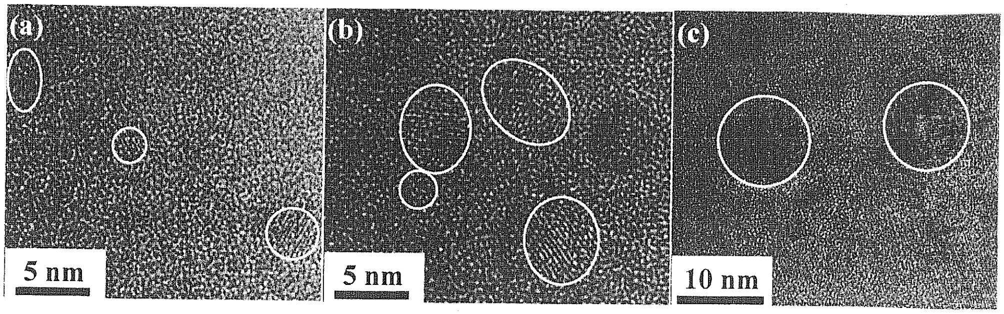

Fig. 2. High-resolution TEM images of the nc-Si films. (a) The films were post deposition heat-treated at 800 °C for 60 min. (b) The films were prepared with 4 Al-chips and then heat-treated at 800 °C for 60 min. (c) the films were prepared with 4 Al-chips and then heat-treated at 1100 °C for 60 min.

Chemical Analysis. Fig. 3 (a) and (b) show the XPS results of the films; film (a) was prepared with 4 Al-chips and then heat-treated at 800 °C, while film (b) were prepared without Al-chips and then heat-treated at 800 °C for 60 min, respectively. It has been reported that the peak at ~ 99.6 eV in the Si-related XPS spectrum stands for the Si2p binding energy of Si-Si bondings, while the peak at ~ 102.4 eV does for Si-O bondings [5]. The increase in the intensity of the peak at ~ 99.6 eV with raising Al concentration indicates an increase in the Si crystallization.

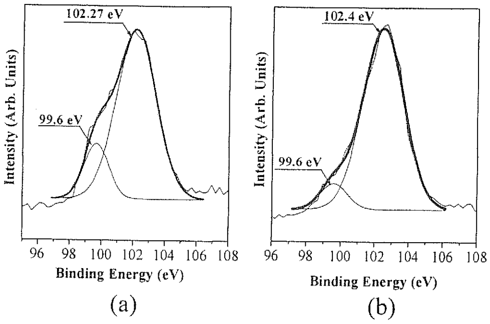

Fig. 3 XPS spectra of the films. Fits corresponding to Si-Si and Si-O bondings are seen at 99.6 and 102.4 eV, respectively. (a) Nc-Si films were prepared with 4 Al-chips and heat-treated at 800 °C for 60 min. (b) Nc-Si films were prepared without Al-chips and then heat-treated at 800 °C for 60 min.

Optical features. Fig. 4 (a) shows the PL spectra of the nc-Si films; the films were prepared with 4 Al-chips and then heat-treated at 800 °C for 60 min. Prominent PL peaks are observed at ~ 420, ~ 480, and ~ 580 nm, respectively. In contrast, Fig 4 (b) shows the PL spectra of the nc-Si films which were prepared without Al-chips and then heat-treated at 800 °C for 60 min.; broad PL spectra are seen in the range from 400 to 700 nm.

It is considered that the presence of PL peaks at ~ 420, ~ 480, and ~ 580 nm is related with the crystallization in the nc-Si films [6]. There is a significant difference in the intensity distribution of the PL spectra from 400 to 700 nm among the different type films. The presence of Al in the nc-Si films may create more nuclei, compared to the nc-Si films prepared without Al-chips, providing a condition at which crystallites with particular sizes like ~3 and ~5 nm are favorably produced in the films. More study is underway to understand the presence of particular sized nc-Si. According to the nanocrystallite size distribution obtained by the TEM images and XRD data, ~ 3-nm and ~ 5 nm-sized nanocrystallites are dominant in the films. Quantum confinement effect enlarges the band gap of nanocrystallites (≤ 10 nm), increasing the oscillator strength and giving rise to efficient and visible luminescence [7]. A distribution of the crystallite size may be responsible for the broad PL spectra of the nc-Si thin films. Fig. 4 (c) shows the PL spectra of the nc-Si films prepared with 8

Al-chips and then heat-treated at 800 °C for 60 min. The PL intensity of the film decreases while the PL shoulder remained weakly at ~ 450 and ~540 nm, respectively. As shown in the XRD results in Fig. 1(c), the size of Si nanocrystallites is expected to be above 10 nm, which is far from the size for the quantum confinement effect.

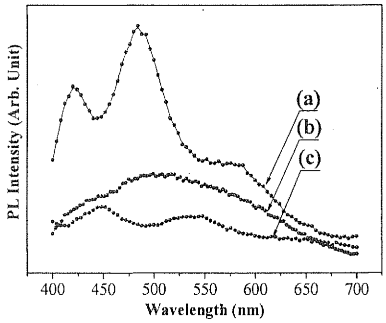

Fig. 4. PL spectra of the nc-Si films. (a) The films were prepared with 4 Al-chips and then heat-treated at 800 °C for 60 min. (b) The films were prepared without Al-chips and then heat-treated at 800 °C for 60 min. (c) The films were prepared with 8 Al-chips and then heat-treated at 800 °C for 60 min.

Conclusion. The nanostructural and optical features of Al-doped Si thin films were investigated in terms of Al-doping and post-deposition heat-treatment conditions. The structural and chemical features are related with the PL phenomena of the films. The films prepared without Al-chips contain ~ 3.0 nm-sized Si nanocrystallites. The PL intensity as well as the concentration of Si nanocrystallites were increased by doping particular amount of Al in the films. In particular, the intensity of the PL spectra of the films prepared with 4 Al-chips and then heat-treated at 800 °C increased significantly at wavelengths of ~ 420, ~480, and ~ 580 nm. It is highly likely that the observed increase of the PL intensity is caused by the increase in the total volume of the ~ 1.0, ~3.0 and ~ 5.0 nm-sized nanocrystallites in the films.

Acknowlegdment

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