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Effects of hydrogen atmosphere on pulsed-DC sputtered nanocrystalline Si:H films

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ABSTRACT

Hydrogenated nanocrystalline silicon (nc-Si:H) films were prepared by a pulsed-DC magnetron sputtering method under an atmosphere of hydrogen/argon mixture. The effects of hydrogen concentration on the structural and electrical properties of the films were systematically investigated using grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy, and conductivity measurement. A threshold hydrogen concentration of about 70% was found necessary before any crystallinity was detectable. The deposition rate decreased monotonically with increasing hydrogen concentration, while the conductivity varied with crystallite size. The abnormally low conductivity level of these nc-Si:H films was due to the extraordinarily high defect density, which was attributed both to the enhanced ion bombardment from the pulsed-DC plasma and to the oxygen contamination from the target.

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1. Introduction

Hydrogenated nanocrystalline silicon (nc-Si:H) is a promising material for thin film solar cells with high efficiency and low cost because of its high mobility, electrical conductivity, energy conversion efficiency, and stability against prolonged light exposure compared with hydrogenated amorphous silicon (a-Si:H) [1–3], as well as the joint application for making multi-junction tandem cells. There are a variety of techniques to grow nc-Si:H thin films. Among them, direct growth by plasma-enhanced chemical vapor deposition (PECVD) and post-deposition growth by solid phase crystallization (SPC) and excimer laser annealing (ELA) of PECVD-made a-Si:H films have been the most frequently used. However, the SPC method has a too high crystallization temperature, while the ELA method has such problems as non-uniformity of grain growth and is expensive.

In comparison, magnetron sputtering can be an attractive alternative to prepare nc-silicon thin films because it has the advantage of not using toxic gases such as SiH_4, PH_3 and B_2H_6 and consequently, low equipment cost. Nevertheless, there have been few articles addressing this issue so far [4–10]. We are thus investigating the control of crystallinity including both the crystalline volume fraction and crystallite size of nc-Si:H thin films prepared by an pulsed-DC magnetron sputtering method, which possesses such intrinsic advantages as higher plasma density/activity and deposition rate in comparison to its DC and RF counterparts respectively.

2. Experimental

nc-Si:H films were deposited on Corning 1737 glass substrates by pulsed-DC magnetron sputtering. The sputtering system consisted of a 3″ balanced magnetron powered by a 1.5 kW pulsed-DC power supply, run at 50 kHz and 50% duty cycle. The target-to-substrate distance was 7 cm. The 99.999% pure (5 N) silicon target had a resistivity of about 0.01 Ω-cm (phosphorus-doped). The sputtering system was pumped down to a base pressure of 5×10^{-7} Torr before each deposition. The target was pre-sputtered in pure Ar for 10 min and then in working atmosphere for 5 min prior to each run. The films were made at a discharge power of 200 W, a substrate temperature of 200 °C, a working pressure of 14.1 mTorr, and a mixed atmosphere of H_2/Ar with H_2 concentration varying from 40 to 90%.

The films were characterized by grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy (632.8 nm, 8.5 mW, integration for 62.5 s) and transmission electron microscopy for structural analyses. The conductivity of films was measured using a four-point-probe method. Typical α-step was employed to measure the film thickness (~200 nm for all the samples), which leads to the calculation of the deposition rate. The chemical compositions of the films and the target were analyzed by secondary ion mass spectroscopy, and the defect density by the constant photocurrent method.

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3. Results and discussion

Similar to what is commonly found when using the PECVD process to make Si:H films, pulsed-DC sputtering of nc-Si:H films also requires an atmosphere exceeding a threshold hydrogen concentration. When sputtered at 14.1 mTorr, 200 W, and 200 °C, e.g., a concentration of about 70% H_2 is necessary before detectable diffraction peaks can be found in GIXRD, as shown in Fig. 1(a), where three sharp diffraction peaks at 28.5°, 47.5°, and 56.4°, corresponding to (1 1 1), (2 2 0), and (3 1 1) reflections respectively, are clearly observed. Unlike previous reports [4,6], there is no evidence of preferred orientation or texture in our films. The crystallite size estimated using the full width at half maximum (FWHM) of (1 1 1) and the Scherrer equation is about 10 nm at 80% H_2. It is also found that the peak heights increase with hydrogen concentration up to 80% H_2, then decrease upon further increase of hydrogen concentration to 90% H_2, as shown in Fig. 1(b). Seo et al. [6] found similar results when they used inductive coupled plasma to enhance the concentration of reactive hydrogen species during RF magnetron sputtering of Si:H films. They discovered that although the Si–H bonds in plasma might facilitate the crystallization of the Si films by increasing the diffusion length of Si precursors on the substrate surface, excessive hydrogen would interrupt the formation of Si–Si bonds and degrade the crystallinity of the Si films. Also shown in Fig. 1(b) is the effect of hydrogen concentration on grain size. Similar to the abovementioned peak height variation, the grain size exhibits a maximum at 80% H_2.

The hydrogen dependence of crystallinity can be further demonstrated by Raman scattering spectroscopy as shown in Fig. 2. At 40% H_2, the Si:H film is characterized by the a-Si related broadband centered at about 474 cm^{-1}. When the hydrogen concentration is increased, a transition from a-Si:H to nc-Si:H occurs as indicated by the emergence of the narrow band at about 520 cm^{-1}. To make a quantitative analysis, the spectrum can be decomposed into three components (as demonstrated by the inset of Fig. 3): the crystalline component peaked at about 520 cm^{-1}, the amorphous component peaked at about 480 cm^{-1}, and an intermediate component peaked at 494–507 cm^{-1} which is associated with bond dilation at grain boundaries [11]. The crystalline volume fraction, X_c, is estimated from $X_c = (I_c + I_{gb})/[I_c + I_{gb} + y(L)I_a]$, where I_c, I_a, and I_{gb} are integrated intensities of the crystalline, amorphous, and intermediate peaks, respectively, and y is the ratio of the cross-section for the amorphous to crystalline phase, which varies with the grain size L (nm), $y(L) = 0.1 + \exp[-(L/250)]$ [12]. Using the L values given by GIXRD in Fig. 1(b), we obtain the crystalline volume fraction X_c data shown in Fig. 3. One can see that X_c increases with hydrogen concentration up to 80%, then decreases with further increase of hydrogen. This is in good agreement with the results of GIXRD, except that Raman spectroscopy is more sensitive than GIXRD when the former reveals an X_c of about 30% while the latter shows no clear evidence of crystalline peaks at 60% H_2. The maximum X_c is about 50%. In addition, it is expected that the enhancement of the grain size and the crystallinity of the nc-Si:H films should correspond to a small shift of the wave number of the crystalline component peak towards the transverse optical (TO) phonon mode of c-Si at about

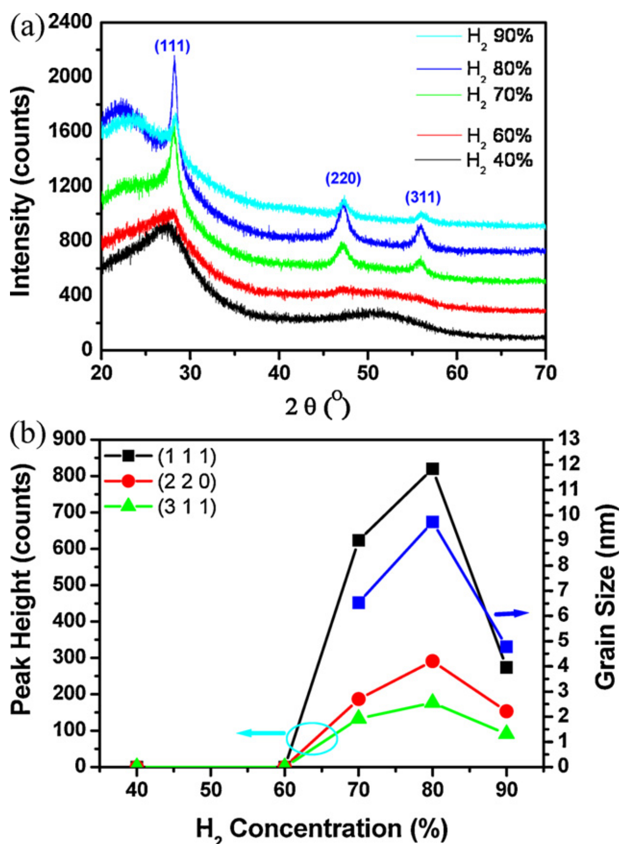

Fig. 1. Effects of hydrogen concentration on the (a) GIXRD pattern and (b) diffraction peak heights and grain size using (1 1 1) FWHM, of nc-Si:H films sputtered at 14.1 mTorr, 200 W, and 200 °C.

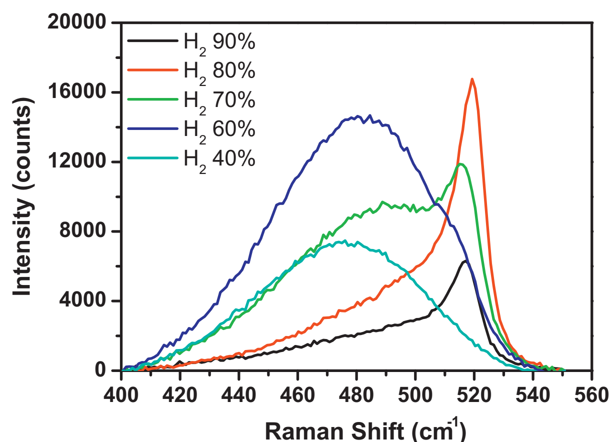

Fig. 2. Effect of hydrogen concentration on the Raman spectrum of nc-Si:H films sputtered at 14.1 mTorr, 200 W, and 200 °C.

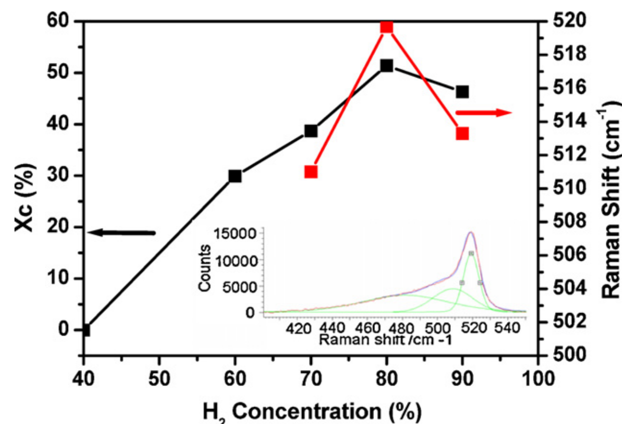

Fig. 3. The crystalline volume fraction, X_c, and the Raman shift of the crystalline component as functions of hydrogen concentration. Samples were sputtered at 14.1 mTorr, 200 W, and 200 °C. The inset demonstrates a typical deconvolution of Raman spectrum for calculation of X_c.

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