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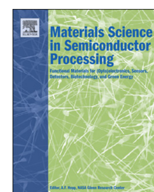

The influence of substrate temperature on the hydrogenated microcrystalline silicon growth through hollow cathode plasma

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ABSTRACT

we exhibited the micro-hollow cathode (MHC) discharge to perform plasma enhanced chemical vapor deposition of hydrogenated microcrystalline silicon (μc-Si:H) in this paper. The role of substrate temperature on the μc-Si:H crystalline was focused. After testifying three substrates, glass, indium tin oxide (ITO) coating glass, and ITO coating polyimide (PI), we obtained over 80% crystalline volume fraction of μc-Si:H formed on the glass substrate. It was found that even the substrate temperature was as low as 120 °C the microcrystal Si can still be grown on ITO coating PI. We believe the high ionization rate in MHC due to hollow cathode effect promotes the microcrystal Si formation.

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1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) consists of amorphous Si, large columnar crystals, small grains and grain boundary after preparation by chemical vapor deposition [1]. As one of the most interesting alternatives in photovoltaic cells due to the high stability against light induced degradation, high absorption coefficient and high cell efficiency [2–4] μc-Si:H based solar cell has attracted more attention from laboratory to industry. Thus, the high deposition rate and low deposition temperature were intensely explored for the low cost of μc-Si:H film deposition. In particular, if the growth temperature is below 150 °C the devices can be facilitated on high transparent plastics, like polyethylene (PE), polyethylene naphthalate (PEN), polyethylene terepthalate (PET) and other polymeric flexible substrates [5,6]. As known [7] the flexible solar cells are emergently demanded in special fields, like aerospace, flexible clothing, army and fieldworks where foldable, portable and wearable devices are required.

Besides, the high crystallinity μc-Si:H is always favorable to the giant microelectronics like thin-film transistors (TFTs) [8,9].

Therefore, In this work the influence of substrate temperature on the μc-Si:H film structure and properties was exploited when micro-hollow cathode (MHC) plasma was used for a plasma enhanced chemical vapor deposition (PECVD) process. For hollow cathode discharge, because of the superposition of negative glow zone the secondary electrons emitted from the hollow cathode walls contribute significantly to plasma density enhancement in the hole region and downstream [10,11]. The secondary electrons emitted from the wall of the hole surface by ion bombardment are accelerated to the opposite wall and are rebounded by the negative potential of the wall to increase the collision and generate the hollow cathode effect (HCE). Thus, in HCE the ionization is very high, the plasma density is high and the electron temperature is small, i.e. the plasma generated in HCE demonstrates as high as $10^{13}/cm^3$ in density, and as low as ~2 eV in electron temperature [12]. When the hole

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size is small to micrometer, moreover, the discharge in the hole is called micro-hollow cathode discharge (MHCD), which can realize the HCE at a high working pressure, even atmospheric pressure, based on Paschen law.

With MHC plasma source we then achieved μc-Si:H films growing at the temperature as low as 120 °C. We then carefully compared the growth rate, crystalline and morphology on different substrates related to the substrate temperature.

2. Experiments

A home-made MHC plasma setup was employed for μc-Si:H thin film deposition, where SiH_2Cl_2 and H_2 were used as precursor and reductive gas, respectively. The power source to ignite the plasma is radio frequency (RF) 27.12 MHz (AE, USA). This newly designed MHC has been adopted for μc-Si:H deposition, which demonstrated a drastic reduction in concentration of dangling bond in μc-Si:H films prepared at high deposition rates and at high purity [13,14]. During deposition the gap of cathode-to-substrate was fixed at 20 mm when the base pressure was 5×10^{-3} Pa and applied power (P_w), and working pressure (P_r) were constant at 100 W, 200 Pa, respectively.

In order to explore the role of substrate temperature (T_s) on the film growth, 120 °C, 150 °C, 250 °C and 300 °C were selected for this investigation where three substrates were employed to compare the characterizations of grown films.

The deposited-film structures were analyzed by X-ray diffraction (XRD) pattern and Raman spectroscopy. The crystalline volume fraction (X_c) was estimated from Raman spectra, where the exciting wavelength of Ar laser source is 532 nm. Surface profilometer was also used for the films thickness measurement. The surface morphology was obtained by atomic force microscopy (AFM, Veeco, USA).

3. Results and discussion

The validity of MHC was proved by the high crystallinity of as-deposited film. Fig. 1 shows the Raman spectrum and XRD pattern of films prepared by this plasma source. From the Raman spectrum shown in Fig. 1(a) we resulted that film consisted of amorphous, large columnar crystals, small grains and grain boundary Si after deconvoluted the Raman spectrum at 480 cm^{-1}, 510 cm^{-1} and 520 cm^{-1} following Gaussian mode. The small grains and grain boundary of Si were seemly the major components of film. The high crystalline at 300 °C is evident by XRD pattern in Fig. 1(b), the remarkable peaks at 28.32°, 47.28°, and 56° corresponding to (111), (220) and (311) facets of crystal Si indicate that the as-deposited films were high crystalline.

In order to quantify the films we then calculated their X_c, which is defined as: $X_c=(I_c+I_b)/(I_c+I_b+I_a)$, where I_a, I_b, and I_c, are the amorphous component at 480 cm^{-1}, intermediate tiny nanocrystalline component at 510 cm^{-1}, and integrated intensity of the regular crystalline component at 520 cm^{-1}, respectively [15–17]. Based on data on Fig. 1(a) then we obtained the component of film is about 13% of amorphous Si at 480 cm^{-1}, 27% of large columnar crystals at 510 cm^{-1}, and ca. 60% of small grains at 520 cm^{-1}.

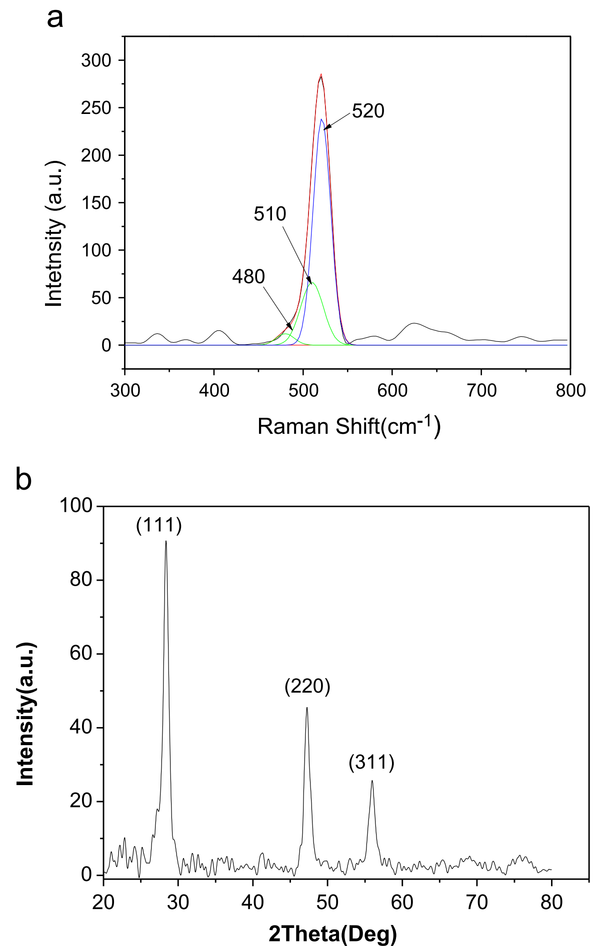

Fig. 1. The analysis of μc-Si:H films by (a) Raman spectroscopy; (b) XRD patterns ($P_w=100$ W, $P_r=200$ Pa, $T_s=300$ °C, and $R=0.015$).

We then focused on the influence of the substrate temperature T_s in the film structures. Fig. 2(a)–(c) shows the Raman spectra at various T_s on three substrates, respectively, and Fig. 2(d) summarizes the estimated X_c. We noticed that all samples appeared remarkable peaks around 510–520 cm^{-1}, which were increased with the temperature. We believe that the heated hydrogen atoms diffusing sufficiently on surface benefit to the high crystalline formation, i.e. the surface diffusion coefficient (length) on the hydrogen-covered surface is enhanced by elevating substrate temperature.

Moreover, based on the chemical annealing mode the hydrogen atoms can easily break the weaker Si–Si bonds and form network structure of a-Si:H, which bond with new precursor radicals to from strong Si–Si bonds (crystalline structure) at a high temperature [18]. The a-Si:H interchanging with hydrogen plasma once hydrogen atoms flowing through the film may also contribute to subsurface area crystal formation because of the lack of hydrogen plasma etching at high temperature.

In Fig. 2(d) we noticed that the similar trend of X_c increment with temperature on glass and ITO coating glass rather than on ITO coating PI. For glass and ITO coating glass substrate, X_c is always increasing with the

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