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The effects of substrate temperature on the properties of diphasic nanocrystalline silicon thin films

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A series of diphasic nanocrystalline silicon thin films was prepared by PECVD technique. The effects of substrate temperature on the properties of the films were investigated. The results show that crystalline volume fraction and grain size in the films increase with increasing T_s. The improved structures lead to higher mobility lifetime product and better stability. While the photosensitivity decreases due to the formation of a conductive percolation channel or the shift of Femi-level in the diphasic films. In our case, the diphasic nanocrystalline silicon thin film deposited at 200 ^{0}C can gain both the fine photoelectrical properties and high stability.

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1. Introduction

The hydrogenated amorphous silicon (a-Si:H) thin films have been intensely studied during the last two decades due to their promising application in photovoltaics, thin film transistors, and optoelectronics[1-3]. Light-induced defect generation in the material is a major impediment in the development of amorphous silicon thin film technology [4]. The metastability of a-Si:H films upon light soaking is thought to be closely related to the amorphous network structure, whereas the structural improvement may finally lead to the formation of hydrogenated nanocrystalline silicon (nc-Si:H), which consists of Si nanocrystallites embedded in the amorphous network [5],[6]. It has been confirmed that in order to gain both the fine photoelectrical properties and high stability, one of the key points is to control the crystalline volume fraction [7].

The diphasic nc-Si:H thin films are generally prepared by plasma enhanced chemical vapor deposition (PECVD) system using a gas mixture of silane(SiH_4) and hydrogen(H_2). Hydrogen is an etchant and etches away the disordered regions effectively leaving behind the ordered structure [8]. The effects of hydrogen dilution on structural and photoelectrical properties of the diphasic nc-Si:H thin films have been extensively studied, but a few reports are available about the role of substrate temperature on the properties of the films[9]. In this paper, we present experimental results on the impacts of substrate temperature on the structural parameters, photoelectrical properties and stability of the films. We also discuss the dependence of photoelectrical properties and stability on the structure of the films.

2. Experimental

Transition films from amorphous to nanocrystalline silicon, approximately 1 μm thick, were deposited by VHF(60 MHz)-PECVD technique, using a varying substrate temperature(T_s) from 140 ^{0}C to 350 ^{0}C, while the hydrogen dilution, gas pressure and VHF power density were kept unchanged at 16, 800 mw/cm^2 and 133Pa, respectively. Microstructure of the films was characterized by Micro-Raman scattering spectra. The Raman scattering measurements were performed with a multi-channel modular triple Raman system (JY-T64000) with a confocal microscopy. A 100x microscope objective lens was used for focusing the laser beam and the collection of the scattered light. The spot diameter of the focused laser beam on the sample is about 1 μm. The solid state diode laser (532 nm) with the power of 0.5 mw from Coherent company-Verdi-2 was used as the excited source. Photo- and dark conductivity (σ_{ph}, σ_d) and activation energy of the films were measured using coplanar aluminum electrodes. Light-induced changes of σ_{ph} were measured on the samples exposed to a heat-filtered white light of 100 mW/cm^2. Mobility life-time ($\mu\tau$) product can be estimated from the steady state photoconductivity of the film.

3. Results and discussion

3.1 Raman spectra

Fig. 1 shows Raman spectra of the silicon films deposited at different substrate temperature of 140 ^{0}C, 170 ^{0}C, 200 ^{0}C, 250 ^{0}C, 300 ^{0}C and 350 ^{0}C. The

arrangement of the spectra in this figure is in the sequence from top to bottom with T_s decreasing. It can be seen that for the sample of T_s = 140 ^{0}C the spectrum shows typical features of a-Si vibration mode, while for the samples of $T_s \geq$ 170 ^{0}C, besides the a-Si vibration mode there are features related to the crystalline phase. As one example, the Gaussian deconvolution of the Raman spectrum of the T_s = 250 ^{0}C sample is demonstrated in Fig. 2. In this spectrum there are four peaks located at around 476 cm^{-1}, 429 cm^{-1}, 326 cm^{-1} and 145 cm^{-1}, corresponding to TO, LO, LA and TA modes in a-Si, respectively [10], and two peaks at 516 cm^{-1} and 505 cm^{-1}, attributed to the TO mode of Si nanocrystals and the vibration mode related to the interfaces of Si nanocrystals with a-Si matrix [11], respectively. The crystalline volume fraction f in the samples could be evaluated using the following equation [12]:

$$f=I_c/(I_c+kI_a) \quad (1)$$

where I_c and I_a denote the integrated intensity of crystalline and amorphous phase related peaks, and k (~0.9) is the ratio of the cross section for the amorphous to crystalline phase [13]. As can be seen in Fig. 3, with increasing substrate temperature from 140 ^{0}C to 350 ^{0}C, the crystalline volume fraction in the films gradually increases from 0 to 50.3%.

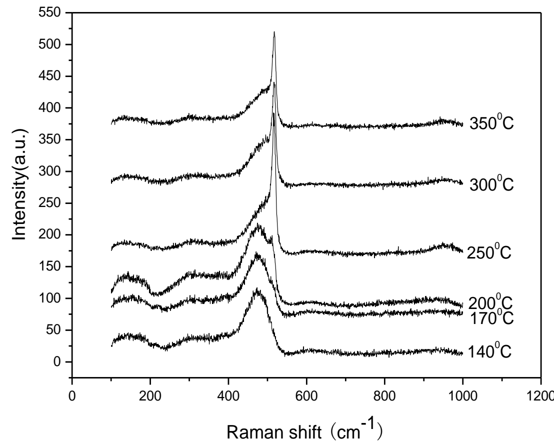

Fig. 1. Raman spectra of the silicon films deposited at different substrate temperature.

Mean grain size D could be calculated from Raman spectra using the bond polarizability model [14]:

$$\Delta\omega(D)=-A(a/D)^{\gamma} \quad (2),$$

Where $\Delta\omega(D)$ is the red shift of TO peak of Si nanocrystals from 520 cm^{-1} induced by phonon confinement effect, a is the lattice constant of Si (a=0.543 nm), and A=97.462 cm^{-1} and γ =1.39 are two constants that describe the phonon confinement in nanocrystalline spheres. The results show that with increasing substrate temperature from 140 ^{0}C to 350 ^{0}C, the grain size in the films gradually increases from 0 to 7.2 nm.

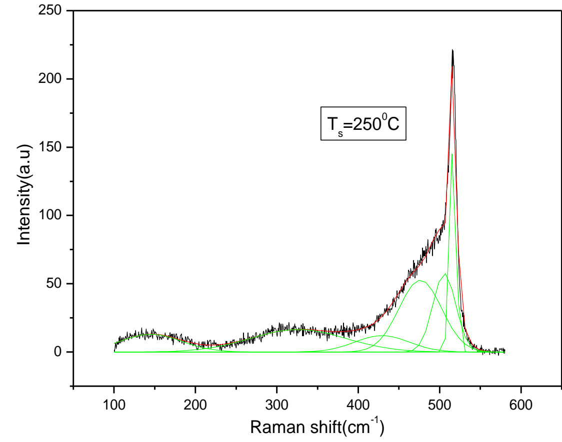

Fig. 2. The Gaussian deconvolution of the Raman spectrum of the T_s = 250^{0}C sample.

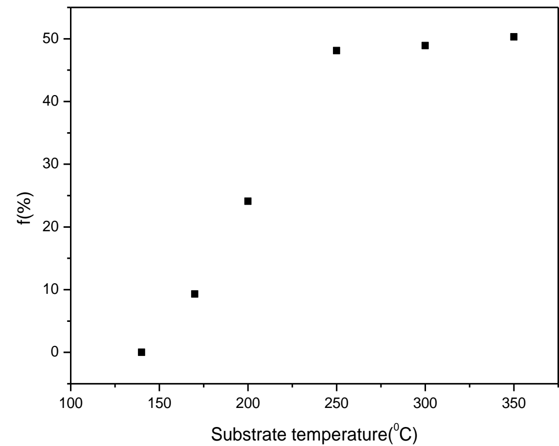

Fig. 3. The crystalline volume fraction in the films versus substrate temperature.

In general, energy relaxation of adatoms on the growing surface of the films is very important for improving the network structure. The ordered structure can be obtained if the precursors have a large diffusion coefficient. The higher the substrate temperature is, the higher thermal energy can be provided to the precursors. As a result, the more ordered structure forms due to the larger diffusion coefficient. This may explain why the crystalline volume fraction and grain size increase with increasing T_s.

3.2 photoelectrical properties

To examine the photoelectrical properties of the silicon films the mobility life-time product (μτ) have been estimated from the steady state photoconductivity according to the following equation:

$$\sigma_{ph}= q\eta\mu\tau F(1\text{-}R)(1\text{-}e^{-\alpha d})/d \qquad (3)$$

where q denotes magnitude of the electron charge, η-quantum yield; F-flux of photons; R-reflection coefficient; α-absorption coefficient, d-thickness of the films. The deduced $\mu\tau$ product is shown in Fig. 4. It can be seen that the $\mu\tau$ product increases from ~1×10^{-7} cm^2/V to 2×10^{-5} cm^2/V with Ts increasing from 140 ^{0}C to 300 ^{0}C. This indicates that the transport properties become better in the diphasic nanocrystalline silicon than that in a pure amorphous state due to the improved structure. However, the $\mu\tau$ product decrease with T_s further increasing to 350 ^{0}C. A.L.B. Neto [15] et al proposed that highly crystalline silicon films present high defect densities because of the interaction of impurities with the column boundaries. It is obvious that high defect densities will lead to the worse transport properties.

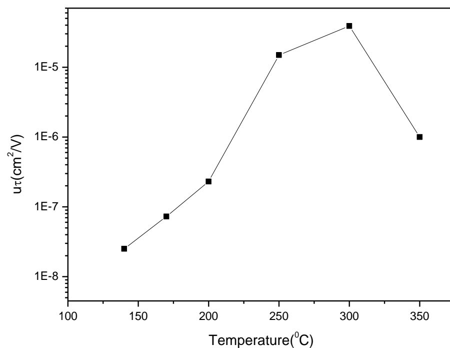

Fig. 4. Mobility lifetime product versus the substrate temperature.

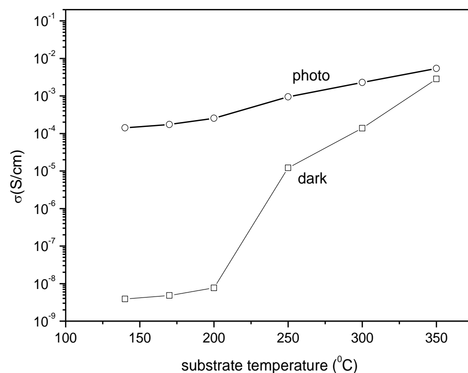

Fig. 5. The photo- and dark- conductivity of the films prepared at different substrate temperature crystalline volume fraction in the films Versus substrate temperature.

Fig. 5 shows the photo- and dark- conductivity of the films versus T_s. Both σ_d and σ_{ph} increase with increasing T_s. However, the photosensitivity defined as σ_{ph}/σ_d decreases from 10^4 to 10^0 because σ_d increases more quickly than σ_{ph}. On one hand, the increase of σ_d can be attributed to the formation of a conductive percolation channel in the diphasic films [16]. On the other hand, the shift of Fermi-level due to n-type doping by oxygen impurities or presence of native defects may be the responsible mechanism affecting σ_d. In general, photosensitivity should be more than 10^2 for device quality material. Fig. 6 shows the activation energy (E_a) of the films. It can be seen that E_a increases with increasing T_s which is in agreement with the photosensitivity results.

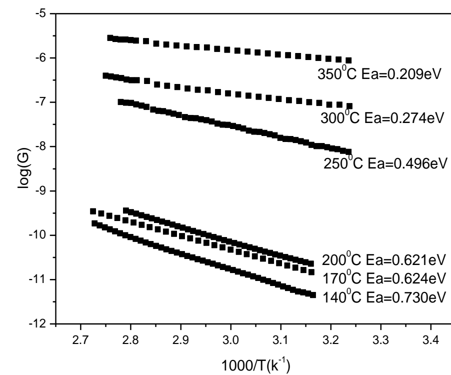

Fig. 6. The activation energy of the films prepared at different substrate temperature.

3.3 Stability upon light soaking

Light induced degradation in the diphasic silicon film is much smaller than that in a typical amorphous silicon film as shown in Fig. 7, where the light-induced changes in photoconductivity were measured under 100 mw/cm^2 light. It can be seen that the photoconductivity of the typical a-Si:H deposited at 140 ^{0}C decreases monotonously with light soaking. The stability of diphasic nanocrystalline silicon films upon light soaking improves significantly due to the structural improvement.

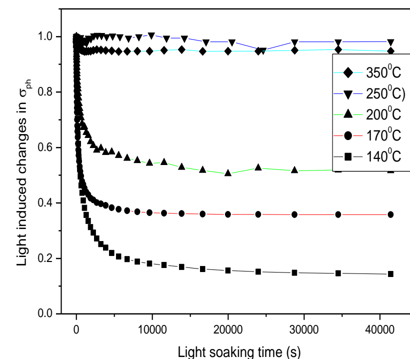

Fig. 7. Light induced changes in σ_{ph} of the films prepared at different substrate temperature.

4. Conclusions

Transition films from amorphous to nanocrystalline silicon were prepared by VHF-PECVD technique. The effects of substrate temperature on the properties of the films were investigated. The results show that crystalline volume fraction and grain size in the films increase with increasing T_s. The improved structures lead to higher $\mu\tau$ product and better stability. While the photosensitivity decrease due to the formation of a conductive percolation channel or the shift of Femi-level in the diphasic films. In our case, the diphasic nanocrystalline silicon thin film deposited at 200 ^{0}C can gain both the fine photoelectrical properties and high stability.

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