The effect of original crystalline phase on solid phase crystallization of hydrogenated silicon thin films

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A B S T R A C T

Hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) films fabricated on glass substrate are crystallized through solid phase crystallization process. In this study, the crystalline phase in μc-Si:H films could decrease process temperature, but prevent the film from crystallized completely. In counterpart, the a-Si:H films need higher annealing temperature to achieve crystallization, but could reach a better crystallinity. The fact that μc-Si:H films do not crystallize completely is attributed to the initial microcrystals in the μc-Si:H films, which avoid the relaxation of the film structure and inhibit the crystallization process. In addition, the effusion of hydrogen could promote the relaxation of a-Si but not induce direct crystallization.

1. Introduction

Polycrystalline silicon (poly-Si) thin films have gained much attention in recent years because they present higher carrier mobility than amorphous silicon (a-Si) films and potential for cost reduction in solar cells [1]. The deposition of a-Si films followed by a crystallization process has been approved as an effective method to fabricate poly-Si film. The most conventional crystallization method is solid phase crystallization (SPC) [2,3]. Other available methods, such as excimer laser annealing (ELA) [4,5] and metal induced crystallization (MIC) [6,7], are also currently investigated. ELA requires high production costs while grain size is not uniform [8]. MIC allows obtaining large grains at low process temperature but its major disadvantage has to do with metallic impurities that remain in the films after crystallization, which generally prevents its wide use [9]. Among these processes SPC is the easiest and the simplest method, which could be yielded by conventional furnace annealing [2]. Plasma enhanced chemical vapor deposition (PECVD) and evaporation are considered to be inexpensive and practical ways to obtain hydrogenated amorphous silicon (a-Si:H) and non-hydrogenated amorphous silicon (a-Si) films, respectively, for the development of large area poly-Si film. By using SPC of PECVD deposited a-Si:H, Matsuyama et al. [10] obtained columnar grains

with lengths up to 5 μm. In turn, Song et al. [11] fabricated a-Si films by evaporation and obtained poly-Si films by SPC with grain sizes around 0.8–1.5 μm.

The PECVD process incorporates hydrogen into the films during deposition. The structure of a-Si:H films plays an important role in the subsequent annealing process. Some researchers [12–15] pointed out that the hydrogen concentration in a-Si:H film could remarkably affect the nucleation rate and the grain growth. Kim et al. proposed that hydrogen could not influence crystallization directly, but H_2 dilution and deposition rate of a-Si:H films could impact on grain nucleation during the SPC process [16]. Moreover, Nakazawa [17] and Lee [18] reported that the grain size of annealed a-Si:H films deposited by PECVD decreased with increasing substrate temperature. Although much attention has been put on how the structure of silicon films influences the SPC process, there are still few reports about the effect of crystalline phase on SPC of silicon films.

In this work, a-Si:H, μc-Si:H and a-Si films with different crystalline fractions were prepared by PECVD and electron beam evaporation to investigate the crystalline phase effect on the SPC process. Some characterization methods, such as Raman scattering, X-ray diffraction (XRD), infrared transmittance and ultraviolet–visible spectrum transmittance and reflectance (UV–VIS transmittance and reflectance), were used to get an insight of the structural evolution of the silicon films during annealing. How the original crystalline phase and the hydrogen concentration impact on the SPC process was also discussed.

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2. Experiments

Soda-lime glass was used as substrate for film deposition. Prior to deposition, the glass substrates were cleaned with deionized water and detergent (TDA7, Franklab). After ultrasonic treatment with deionized water for 10 min, the substrates were dried by a high pressure N_2 purge. 350 nm-thick a-Si:H and hydrogenated microcrystalline silicon (μc-Si:H) films were deposited by PECVD (multi-chamber cluster, MVSystem). The substrate temperature was controlled at 180 °C, while chamber base pressure was around 10^{-8} Torr. An in situ thickness measurement system (SQC-310, INFICON) was used to control and monitor film thickness during deposition. The a-Si:H films were prepared with pure SiH_4 (silane) gas under 0.36 Torr and RF (13.56 MHz) power of 2.5 W. The growth rate was controlled at around 0.08 nm/s. The μc-Si:H films were deposited with SiH_4 gas highly diluted with H_2, resulting in a low deposition rate. Thus, a very high frequency power source (VHF, 20 W@60 MHz) was introduced to control the deposition rate at around 0.09 nm/s. The working pressure was 0.75 Torr while the fluxes of SiH_4 and H_2 were 4 and 96 sccm, respectively. The a-Si:H and μc-Si:H films were controlled mainly at same deposition rate in this study. Different deposition conditions of these two type of samples might result in a small difference on deposition rate, however this difference was sufficiently small and could be accepted in the experiments. In turn, the a-Si samples were obtained by using electron beam evaporation. The substrate temperature was also 180 °C and the growth rate was about 0.3–0.5 nm/s. The different samples of a-Si:H, μc-Si:H and a-Si were treated in a conventional tube furnace of dry nitrogen ambient and then cooled in situ to room temperature. During annealing, the different samples of a set of each type were annealed at each temperature of 500, 550 and 600 °C for a period of 4–24 h, respectively.

In this study, characterization of the annealed samples involved Raman, X-ray diffraction (XRD), Fourier transform infrared (FTIR) and UV–VIS measurements. All Raman scattering measurements (HORIBA, T64000) were performed with a focused green laser beam (λ = 514.5 nm, 10 mW, integral time = 50 s) through a 10% attenuation slice to prevent the laser induced crystallization. A 50× long distance objective lens was used to form a spot size of 2 μm on the samples. XRD was carried out by using a Bruker D8 Advance diffractometer operating with the Cu $K_α$ line (at 40 kV and 30 mA). FTIR and UV–VIS transmittance and reflectance were measured in a Perkin-Elmer Spectrum 400 and SHIMADZU UV-3101PC System, respectively. The optical gap was calculated from UV–VIS transmittance and reflectance data. The absorption coefficient (α) can be estimated as

$$\alpha = -\frac{\ln\ (T/(1-R))}{d} \qquad (1)$$

where T and R are the transmittance and reflectance of samples, respectively, and d is the film thickness. Some previous researchers [19] reported that the optical gap corresponds to the energy for which the optical absorption coefficient changes from one range of magnitude to the other. The energy of photon, where absorption coefficient is 10^4 cm^{-1} denotes the optical gap (E_{04}), as is widely accepted for silicon films [20].

3. Results and discussion

3.1. Raman analysis

Raman spectra are generally used to analyze the Si–Si bonding configurations. Figs. 1–3 show the Raman spectra of (a) a-Si:H, (b) μc-Si:H and (c) a-Si samples annealed at 500, 550, 600 °C for 4–24 h, respectively. As known from previous reports [21–23], there are mainly two Raman characteristic peaks in the range
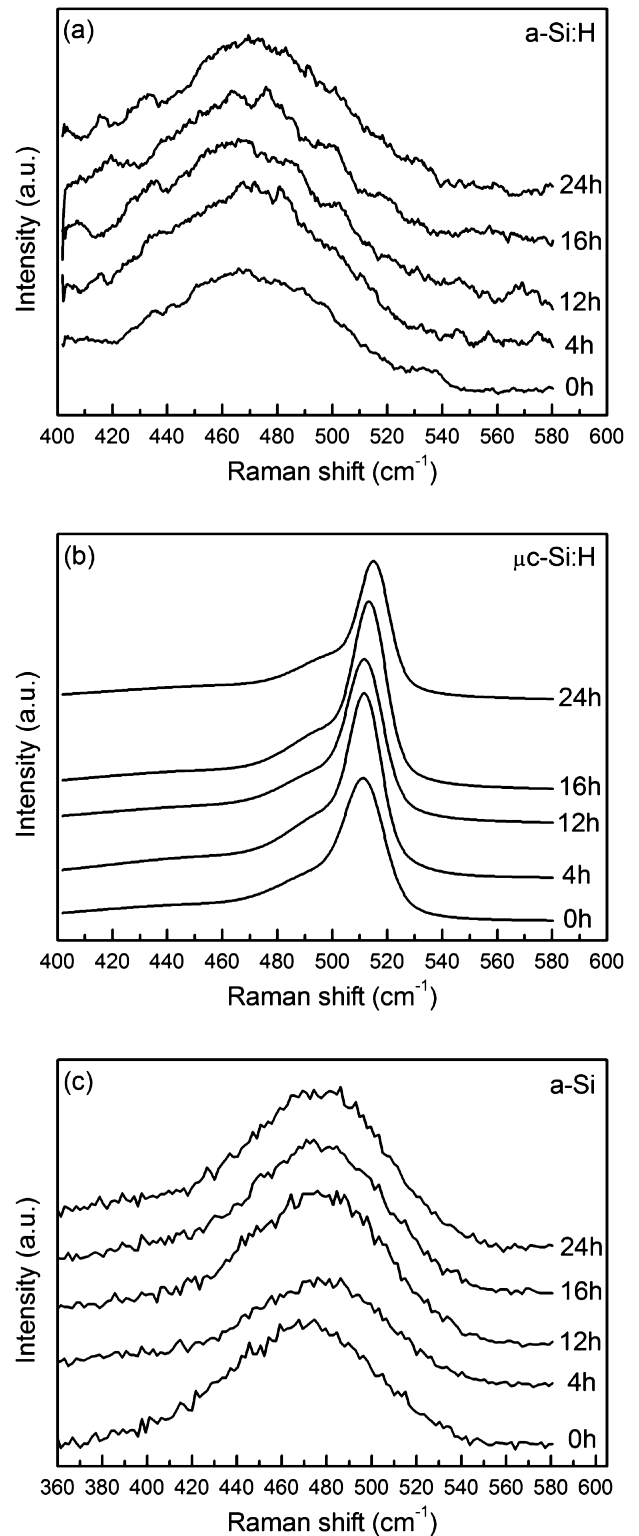

Fig. 1. Raman spectra of different silicon films annealed at 500 °C: (a) a-Si:H, (b) μc-Si:H and (c) a-Si.

of 400–600 cm^{-1}. The broad peak at around 465–480 cm^{-1} is attributed to a-Si, while the sharper peak appearing at around 500–521 cm^{-1} corresponds to the crystalline silicon (c-Si).

As shown in Fig. 1, a shift to higher wavenumbers is observed in the Raman spectra of a-Si:H, μc-Si:H and a-Si samples annealed at 500 °C. The Raman spectra of a-Si:H and a-Si samples present only one peak at about 465 cm^{-1}, belonging to a-Si, which indicates that