

Effect of Annealing on the Vertical Structural Distribution of Solution-Processed a-Si:H Films

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Abstract

We investigate structure distribution of solution-processed (Sol. P) hydrogenated amorphous silicon (a-Si:H) films along a thickness direction by Raman spectroscopy. Sol. P a-Si:H films have a stress distribution along the thickness direction, and the degree of distribution depends on annealing temperature and time. These results give us a suggestion about the formation mechanism of Sol. P a-Si:H films through out-gassing and network reconstruction.

1. Introduction

One of the serious problems for solar cells is high fabrication cost due to the utilization of large-sized and costly apparatuses. Use of a solution process would solve this problem [1, 2]. We have previously reported that a-Si:H films can be formed by spin-coating and annealing of "Si ink" [3]. We have already fabricated p-i-n structure solar cells by the solution process, and confirmed cell operation [4]. In Ref. 3, we have reported the result of Raman measurement in entire a-Si:H films. Those indicate that higher annealing temperature gives the a-Si:H films higher short range order (SRO). Large amount of gases are released from the surfaces of a-Si:H films during annealing [5], which may lead to different structure between the surfaces and bottoms of the a-Si films. In this study, we report a structure distribution in Sol. P a-Si:H films along a thickness direction evaluated by Raman Spectroscopy.

2. Experimental

Si ink as a precursor for a-Si:H consists of polydihydrosilane ($-(\text{SiH}_2)_n-$) and cyclooctane as a solvent. Polydihydrosilane was synthesized by photo-induced ring-opening polymerization of cyclopentasilane (CPS: Si_5H_{10}), and dissolved in cyclooctane at a concentration of 20-25 wt.%. We produced a-Si:H films by spin-coating Si ink onto quartz substrates and annealing them in a globe box, in which O_2 concentration and dew point were kept at less than 0.5 ppm and -75°C , respectively. After annealing, thickness of the a-Si:H films were 160-200 nm.

We first investigated the effect of annealing temperature (T_p) on the structure of a-Si:H films. The samples were annealed at $T_p = 360, 390, 420^\circ\text{C}$, for a fixed annealing

time of $t_p = 15$ min. In order to determine the effect of high T_p , we carried out an additional annealing at 500°C for 15 min on the sample annealed at $T_p = 420^\circ\text{C}$. We also investigated the influence of annealing time on the Sol. P a-Si:H film structure. Annealing time was varied from 20 sec to 30 min at a fixed $T_p = 390^\circ\text{C}$.

In Raman measurement, we employed three lasers: He-Cd laser ($\lambda = 442$ nm), Ar^+ laser ($\lambda = 488$ nm), and He-Ne laser ($\lambda = 633$ nm). He-Ne laser has a long penetration depth (≈ 300 nm), and the results obtained by using this laser are related to entire films. The other two lasers have a much shorter penetration depth (≈ 20 nm), and surface-sensitive Raman spectra can be obtained. In order to use lasers with short penetration depth for measuring the internal structure of films, we repeated Ar reactive ion etching (RIE).

In Raman spectra of the a-Si:H films, a transverse optical (TO) peak, whose position $\omega = 470\text{-}480\text{ cm}^{-1}$, is an important parameter to evaluate SRO and film stress. The full width at half maximum (FWHM) of TO (Γ_{TO}) is related with SRO [6]. TO peak position (ω_{TO}) is associated with both SRO and stress [7, 8].

3. Results and Discussion

Fig. 1 shows the Ar^+ laser Raman spectra of Sol. P a-Si:H films prepared at $T_p = 390^\circ\text{C}$ for $t_p = 15$ min. Apparently, the TO peak shifts to lower wavenumber in the region near the surface. Figs. 2(a) and (b) show the ω_{TO} and Γ_{TO} in various T_p as a function of remaining thickness, respectively. All the samples in this figure were annealed for 15 min and measured with Ar^+ laser. ω_{TO} is lower near the surface and higher close to the substrate. At higher T_p , not only the value of ω_{TO} but also the gradient of ω_{TO} from surface to bottom (substrate) region become smaller, and ω_{TO} seems to reach a constant value ($\approx 471\text{ cm}^{-1}$) at high T_p . On the other hand, we find no clear tendency of Γ_{TO} against remaining film thickness shown in Fig. 2 (b). These facts mean that there is no significant difference in SRO between the surface and bottom region, while the difference in tensile stress exists. This is probably because of gas release from the surface of a-Si:H films during annealing. At low T_p , gas release occurs more severely near the surface region, resulting in larger gradient of tensile stress along the thick-

ness direction. At high T_p , large amount of gases are released also from the interior of film, and large tensile stress are thus generated through the entire films.

Fig. 3 shows the He-Ne laser Raman spectra of the Sol. P a-Si:H films prepared at $T_p = 390$ °C for $t_p = 20$ sec to 30 min. At $t_p = 20$ sec and 1 min, the spectra are far different from the others, indicating that the films are not fully converted to a-Si:H. ω_{TO} and Γ_{TO} dramatically change for longer t_p , which means that SRO is significantly improved and the a-Si:H films have larger tensile stress at longer t_p . Figs. 4(a) and (b) show the ω_{TO} and Γ_{TO} for various t_p as a function of remaining thickness, respectively. ω_{TO} tends to be lower near the surface and higher near the substrate. For longer t_p , the value of ω_{TO} becomes small, and reaches a constant value (≈ 473 cm^{-1}). The gradient of ω_{TO} between the surface and bottom region becomes largest at $t_p = 4$ min. As in the case of Fig. 2(b), no clear tendency is seen in Γ_{TO} depending on thickness. The tendency in ω_{TO} can be considered as increase in tensile stress due to the enhanced gas release, similar to the effect of T_p . For $t_p < 1$ min, a-Si:H network is not formed sufficiently, and no significant tensile stress exists. At $t_p \approx 4$ min, a-Si:H is formed along with gas release, and gradient of tensile stress becomes large. For long t_p , large amount of gases are released also from interior of films, resulting in larger tensile stress and smaller stress distribution along thickness direction.

4. Conclusions

We have confirmed the existence of stress distribution in Sol. P a-Si:H films along the thickness direction. The stress distribution can be considered to be due to a gas release from the film surface. The idea of stress dependence on T_p and t_p give us a suggestion of the formation mechanism of a Sol. P a-Si:H film: outgassing and Si network reconstruction are critical for the film formation.

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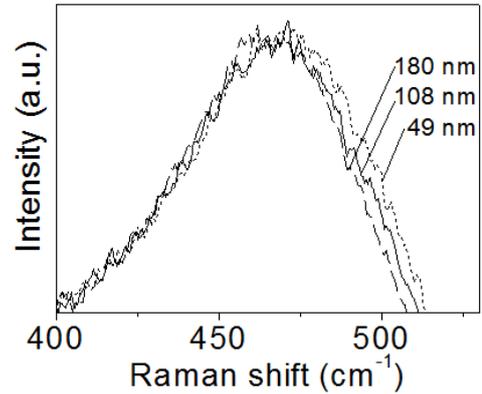


Fig. 1 Raman spectra of the Sol. P a-Si:H films prepared at $T_p = 390$ °C for $t_p = 15$ min. The spectra were measured with Ar^+ laser. The values shown on right side in the figure are remaining a-Si:H thickness after (or without) RIE.

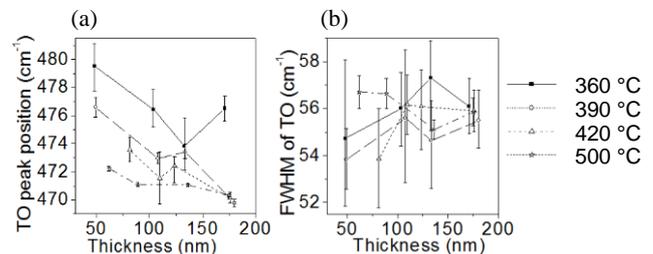


Fig. 2 (a) ω_{TO} and (b) Γ_{TO} of TO peaks in the Raman spectra of a-Si:H films formed at various T_p as a function of remaining thickness.

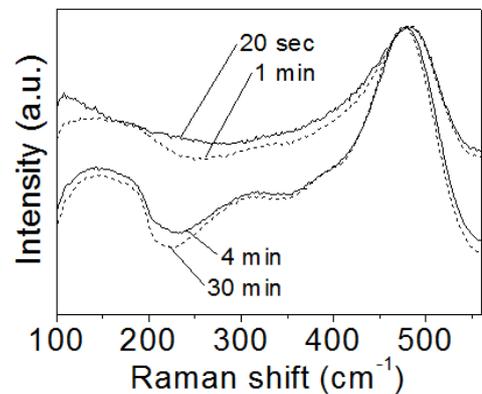


Fig. 3 Raman spectra of Sol. P a-Si:H films prepared at $T_p = 390$ °C for $t_p = 20$ sec to 30 min. The spectra were measured with He-Ne laser.

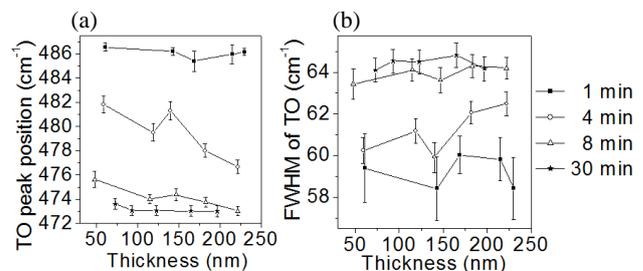


Fig. 4 (a) ω_{TO} and (b) Γ_{TO} of TO peaks in the Raman spectra of a-Si:H films formed in various t_p as a function of remaining thickness.