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

Yoo Sakuma¹, Keisuke Ohdaira¹,², Takashi Masuda¹,³, Hideyuki Takagishi¹,², Zhongrong Shen¹,², and Tatsuya Shimoda¹,²,³

¹JAIST
1-1 Asahidai, Nomi-city, Ishikawa 923-1292, Japan
Phone: +81-761-51-1553 E-mail: s1230022@jaist.ac.jp
²JST-ALCA
³JST-ERATO

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 outgassing 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 films 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 bottom 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 polydi-hydrosilane (-(SiH₂)ₙ-) and cyclooctane as a solvent. Polydi-hydrosilane was synthesized by photo-induced ring-opening polymerization of cyclopentasilane (CPS: Si₅H₁₀), 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 glove box, in which O₂ 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 (T₆) on the structure of a-Si:H films. The samples were annealed at T₆= 360, 390, 420 °C, for a fixed annealing time of t₆=15 min. In order to determine the effect of high T₆, we carried out an additional annealing at 500 °C for 15 min on the sample annealed at T₆= 420 °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 T₆= 390 °C.

In Raman measurement, we employed three lasers: He-CD laser (λ = 442 nm), Ar⁺ laser (λ = 488 nm), and He-Ne laser (λ = 633nm). 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 ω = 470-480 cm⁻¹, is an important parameter to evaluate SRO and film stress. The full width at half maximum (FWHM) of TO (Γ₁0) is related with SRO [6]. TO peak position (ω₁0) 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 T₆= 390 °C for t₆=15 min. Apparently, the TO peak shifts to lower wavenumber in the region near the surface. Figs. 2(a) and (b) show the ω₁0 and Γ₁0 in various T₆ as a function of remaining thickness, respectively. All the samples in this figure were annealed for 15 min and measured with Ar⁺ laser. ω₁0 is lower near the surface and higher close to the substrate. At higher T₆, not only the value of ω₁0 but also the gradient of ω₁0 from surface to bottom (substrate) region become smaller, and ω₁0 seems to reach a constant value (≈ 471 cm⁻¹) at high T₆. On the other hand, we find no clear tendency of Γ₁0 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 T₆, 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 $T_p = 390^\circ C$ 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. $\omega_{TO}$ and $\Gamma_{TO}$ 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 $\omega_{TO}$ and $\Gamma_{TO}$ for various $t_p$ as a function of remaining thickness, respectively. $\omega_{TO}$ tends to be lower near the surface and higher near the substrate. For longer $t_p$, the value of $\omega_{TO}$ becomes small, and reaches a constant value ($\approx 473$ cm$^{-1}$). The gradient of $\omega_{TO}$ 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 $\Gamma_{TO}$ depending on thickness. The tendency in $\omega_{TO}$ 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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References