

Diffusion length measurements of microcrystalline silicon thin films prepared by hot-wire/catalytic chemical vapor deposition (HWCVD)

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Abstract

Hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) films prepared by using the hot-wire/catalytic chemical vapor deposition (HWCVD) technique at low substrate temperatures between 185 °C and 220 °C with different silane concentrations (SC) were investigated using steady-state photocarrier grating (SSPG) and the steady-state photoconductivity methods (SSPC). Crystalline volume fractions (I_C^{RS}) obtained from Raman spectroscopy change from 0.22 to 0.77. The diffusion length (L_D) is measured at generation rates between $G=10^{19}$ and 10^{21} cm^{-3} s^{-1} . L_D changes from 27 nm to 270 nm, with maximum values around SC=5%. The dependence of L_D on SC is similar to that observed for similar quality microcrystalline silicon films prepared using the VHF-PECVD technique. The grating quality factor, γ_0 , drops from about 0.9 to 0.5 after transition to the microcrystalline regime as indication of scattering from surface patterns.

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1. Introduction

Hot-wire chemical vapor deposition (HWCVD) processes have become one of the powerful techniques in producing microcrystalline silicon ($\mu\text{-Si:H}$) material with a precise control on the crystalline volume fraction of solar cell films in the past few years [1–3]. Recent experimental results on $\mu\text{-Si:H}$ materials produced by this technique show that the best solar cell performance is obtained in a microcrystalline growth regime close to the transition to amorphous growth conditions [3,4]. Crystalline volume fraction on these types of films is usually inferred from Raman spectroscopy for structural analysis [5]. Steady-state photocarrier grating method (SSPG) and steady-state photoconductivity (SSPC) methods have been used for the characterization of both minority and majority carrier transport properties of a-Si:H and $\mu\text{-Si:H}$ films or materials between these two regimes [6–8]. A correlation between electronic properties and

structural properties related with deposition conditions around the transition region from $\mu\text{-Si:H}$ to a-Si:H growth is an important issue to improve solar cell efficiency.

In this work, we investigate the relationship between diffusion length measured with SSPG experiments and crystalline volume fractions obtained from Raman Spectroscopy on the $\mu\text{-Si:H}$ films, which were selected from various silane concentrations, ranging from highly crystalline to nearly amorphous, prepared by the HWCVD technique.

2. Experimental details

Undoped hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) films were fabricated by using the hot-wire/catalytic chemical vapor deposition (HWCVD) technique with tantalum filaments at temperatures between 1650 °C and 1800 °C, substrate temperatures between 185 °C and 220 °C, and with different silane concentrations, SC ($=[\text{SiH}_4]/[\text{SiH}_4+\text{H}_2]$), by varying the flow ratio of silane and hydrogen gas between 2% and 10%. The films were deposited on glass substrates (Corning 7059 and/or Corning

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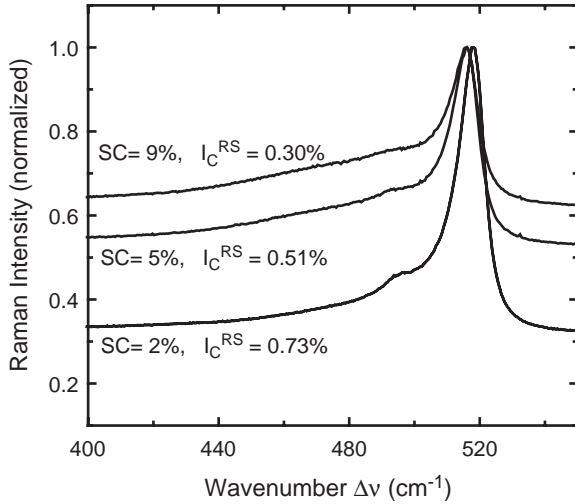


Fig. 1. Raman intensity versus wave number between 400 and 540 cm^{-1} from samples prepared in the transition region from microcrystalline to amorphous growth using the SCs from 2% to 9%.

1737) with a film thickness between 520 nm and 965 nm on a substrate area of $10 \times 10 \text{ cm}^2$. The total gas pressure was changed between 3 Pa and 20 Pa to create different crystalline volume fractions changing from amorphous to crystalline regime. The substrates were partly covered with 100 nm electron beam evaporated chromium films before each deposition to cutoff contribution from the glass for the Raman measurements.

The experimental configuration for the SSPG technique is given in previous reports [6,7]. In the SSPG experiment, one measures the ratio β of the ac photocurrents with and without the grating created by two coherent laser beams due to interference fringes (inhomogeneous photocarrier distribution regions) between electrodes of a sample by changing the grating period, A , defined as $A = \lambda / [2\sin(\theta/2)]$, where λ is the laser wavelength and θ is the angle between the two incoming laser beams. The diffusion length L_D and grating quality fitting parameter ϕ are obtained from β versus A plots by using nonlinear least square fit to the following SSPG equation:

$$\beta = 1 - \frac{2\phi}{\left[1 + \left(\frac{2\pi L_D}{A}\right)^2\right]^2}. \quad (1)$$

The SSPG grating quality factor γ_o is calculated from $\gamma_o = (\phi/\gamma_d\gamma)^{1/2}$, where ϕ is the SSPG fitting parameter obtained from the fit to experimental β versus A curve, γ is the exponent of the photoconductivity σ_{ph} vs. generation rate G , and γ_d is the dark conductivity reducing factor defined as $\gamma_d = \sigma_{ph} / (\sigma_{ph} + \sigma_{dark})$ [7,8]. The quality factor γ_o is a measure of light scattering from rough surface and other imperfections of the experimental setup or the samples themselves.

A He–Ne Laser with a wavelength of 633 nm was used to measure small-signal photocurrents at 10 V dc bias

voltage between the coplanar contacts with a gap of 0.5 mm of $\mu\text{-Si:H}$ samples using a Stanford Research lock-in amplifier SR 830. All the steady-state grating conditions given in the Ref. [7] have been satisfied in the present work.

3. Results and discussion

The Raman scattering experiment was performed using 488 nm laser light. In Fig 1, Raman intensity as a function of wave number between 400 and 540 cm^{-1} is shown for $\mu\text{-Si:H}$ samples prepared in the transition region between SC from 2% to 9%. The crystalline volume fraction (I_C^{RS}) was calculated from integrated intensity ratio,

$$I_C^{RS} = (I_{520} + I_{500}) / (I_{520} + I_{500} + I_{480}), \quad (2)$$

by de-convolution of the spectral data into three characteristic Gaussian peaks representing amorphous phase at 480 cm^{-1} , grain boundary phase at 500 cm^{-1} and crystalline contribution at 520 cm^{-1} . I_C^{RS} is used as a semiquantitative measure of the crystalline volume fraction.

In Fig. 2, the photocurrents ratio β is plotted versus the grating period A . The diffusion length L_D and the grating quality factor ϕ are obtained from a nonlinear least square fit to the function defined in Eq. (1). The L_D values obtained for the intrinsic $\mu\text{-Si:H}$ films are shown in Fig. 3a as a function of SC, where L_D shows a maximum around SC of 5%. It is important to note that the set of intrinsic $\mu\text{-Si:H}$ films studied here originates from slightly different deposition parameters such as substrate temperature and pressure. Therefore, SC is not the only parameter to determine the microstructure of these films. For this reason, crystalline volume fraction, I_C^{RS} , is used to compare the effects of microstructure on the L_D values. In Fig. 3b, the diffusion length is shown as a function of I_C^{RS} evaluated from the Raman data obtained around the transition growth region

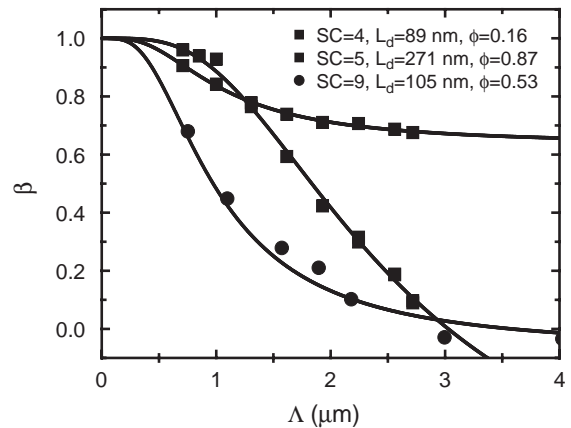


Fig. 2. Photocurrent ratio β versus grating period (A) for SC from 4% to 9%. The lines are nonlinear least square fits to the function defined in Eq. (1). L_D (diffusion length) and ϕ (grating quality parameter) are the fitting parameters.

from amorphous to microcrystalline. The diffusion length appears to have a maximum around I_C^{RS} of 0.5 and then decreases with higher crystalline volume fraction. The highest L_D of 271 nm and the highest grating quality factor γ_0 of 0.96 is obtained for the sample prepared with the lowest substrate temperature of 185 °C, with SC of 5% and I_C^{RS} of 0.51, with the total gas pressure of 3.5 Pa. A possible reason for low values of diffusion length at highly crystalline region might be due to increasing defect density created by hydrogen dilution on the walls of individual columnar microcrystalline grains inside the structure [9]. However, low diffusion length for the amorphous films is attributed to defect states related with unsaturated silicon dangling bonds (DB).

In addition, the effect of microstructure due to changing SC and other deposition parameters is also obtained from the grating quality factor ϕ . Most of the high quality microcrystalline silicon films do not exhibit a perfect

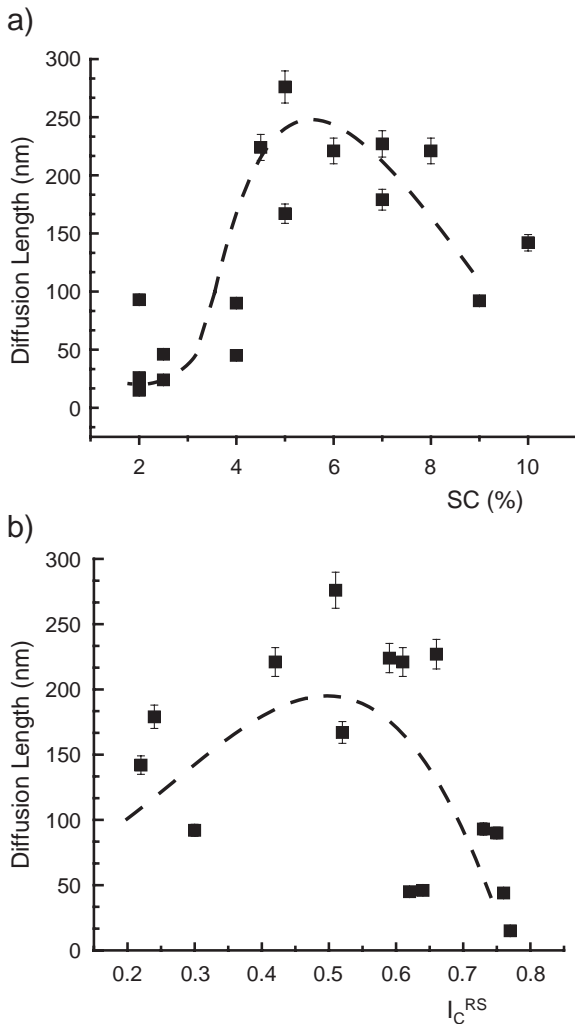


Fig. 3. (a) Diffusion length versus SC. The dashed lines are guides to the eye only. (b) Diffusion length versus I_C^{RS} obtained from Raman data for the films prepared in the transition growth regime with SC between 2% and 8%. The dashed line is a guide to the eye.

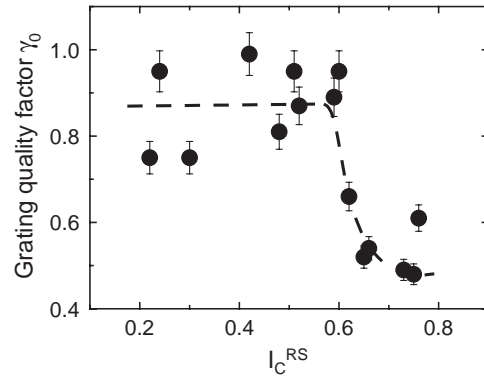


Fig. 4. Grating quality factor γ_0 versus crystalline volume fraction, I_C^{RS} .

mirror-like surface. Surface scattering has been shown to decrease the grating quality fit parameter ϕ in SSPG experiments [10]. The effect of the crystalline volume fraction I_C^{RS} on the grating quality factor γ_0 is shown in Fig. 4. In the amorphous and low crystalline region, γ_0 values are around 0.9 and decrease to 0.5 after the transition to the microcrystalline growth regime. The smaller values of the grating quality factor γ_0 most probably result from light scattering from nano-crystalline patterns on the surface of $\mu\text{-Si:H}$ films at the highly crystalline region prepared by HWCVD technique.

4. Summary

Intrinsic microcrystalline silicon thin films were prepared by the HWCVD technique with various silane concentrations. Crystalline volume fractions I_C^{RS} change from 0.22 to 0.77 for SC between 10% and 2%, respectively, obtained from Raman scattering. The diffusion length L_D shows a maximum value of 271 nm around SC=5% and corresponding I_C^{RS} of 0.51 for the sample with lowest substrate temperature of 185 °C and then decreases with increasing I_C^{RS} probably as a result of the increasing defect density originating from the unsaturated dangling bonds in the amorphous region and defects on the wall of grains due to the etching effect of hydrogen dilution in highly crystalline region. The grating quality factor γ_0 decreases substantially from 0.9 to 0.5 after transition to the microcrystalline regime indicating the effects of light scattering from surface patterns of high crystalline intrinsic films.

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