Characterization of microcrystalline silicon thin films prepared by a layer-by-layer technique with a PECVD system

C. O. Kim, T. U. Nahm and J. P. Hong

Department of Physics, Hanyang University, Seoul 133-791, Korea

(Received October 13, 1999)

Abstract — Possible role of hydrogen atoms on the formation of microcrystalline silicon films was schematically investigated using a plasma enhanced chemical vapor deposition system. A layer-by-layer technique that can alternate deposition of α-Si thin film and then exposure of H_2 plasma was used for this end. The experimental process was extensively carried out under different hydrogen plasma times (t_2) at a fixed number of 20 cycles in the deposition. Structural properties, such as crystalline volume fractions and grain shapes were analyzed by using a Raman spectroscopy and a scanning electron microscopy. Electrical transports were characterized by the temperature dependence of the dark conductivity that gives rise to the calculation of activation energy (E_a). Optical absorption was measured using an ultra violet spectrophotometer, resulting in the optical energy gap (E_{opt}). Our experimental results indicate that both of the hydrogen etching and the structural relaxation effects on the film surface seem to be responsible for the growth mechanism of the crystallites in the μc-Si thin films.

I. Introduction

Since microcrystalline (μc-Si) and ploycrystalline (poly-Si) silicon thin films appear to have extremely superior doping efficiency, higher mobility and lower dark conductivity, they have been dramatically developed for the next generation of micro electronic devices in near future. Up to now, there has been a lot of effort focused on the fabrication of these films using post annealing methods, such as a solid phase crystallization (SPC) technique, rapid thermal annealing (RTA), and excimer laser annealing (ELA) treatment, etc. Particularly, the ELA method is rapidly used to efficiently deposit the μc-Si and the poly-Si thin film in the industrial area, even though it stringently requires expensive process and precise uniformity control [1-3]. However, the direct deposition of the μc-Si and the poly-Si thin films at the deposition temperature of less than 300°C is increasingly required for simple fabrication and low cost process. Therefore, a layer-by-layer (LBL) technique has been investigated as one of useful and visible techniques of the direct deposition [4-7]. This technique is typically a repetition of amorphous silicon film deposition at a time of t_1 and then hydrogen plasma treatment under a time of t_2. It have been proved to provide μc-Si thin film with reasonable volume fraction.

However, insight for the growth mechanism and the role of hydrogen atoms in this technique was not fully given. Furthermore, there is still a lot of controversial due to extremely complexity of the μc-Si deposition, despite the large number of experiments [8-10]. Three basic growth mechanisms have presently been proposed to understand crucial role of atomic hydrogen on the formation of the μc-Si thin film. One is a "growth zone" model that stresses structural relaxation due to the penetration of atomic hydrogen [11-12]. The other is a "surface reaction" that pays significant attention to the surface coverage of atomic hydrogen and then promotes the film precursors to react easily [13]. Another is an "etching process" that postulates partial equilibrium between the deposition of film precursors and the etching of atomic hydrogen [14]. Recently, it has been reported about the "chemical transport" that addresses film radicals transferred to the anode from the cathode [15].

In this letter, we deposit the μc-Si thin film using a layer-by-layer technique to further understand probable role of hydrogen atom on the formation of the μc-Si film. The process was extensively done at various hydrogen exposure times (t_2) at a fixed number of 20 cycles. A conventional plasma

enhanced chemical vapor deposition (PECVD) system was used for the LBL deposition. A Raman spectroscopy (Model: Jasco NR 1100) and a SEM (scanning electron microscopy) analysis were taken to study structural properties, including crystalline volume fractions (X_c) and grain shapes. For the electrical characteristics of the μc-Si thin film, the dark conductivity was determined as a function of temperature in order to calculate an activation energy (E_a). In addition, an UV spectrophotometer (Cary 17-D Varian inc.) was used to investigate the optical energy gaps of the film.

II. Experiments

A layer-by-layer technique is typically based on the sequence of α-Si:H deposition and exposure of hydrogen atom in a single chamber. During the LBL deposition, the amorphous phase film was prepared on corning glasses using 100% pure silane gas for regularly timed interval of t_1. And then the hydrogen plasma treats the surface of the amorphous phase film for hydrogen exposure time of t_2. Before the deposition, all the substrates were cleaned for 30 min in the Acetone and Methanol solution and then pre-cleaned with a gaseous mixture of H_2 and He for 15min inside the chamber. In our experiment, the pretreatment process of the substrate inside the chamber seems to have a little effect on the crystallinity of the μc-Si thin film.

At first, the LBL deposition was systematically performed as a function of hydrogen treatment time from 30 s to 180 s in order to get detailed information of the growth mechanism and the possible role of hydrogen atoms in the formation of the μc-Si thin film. In this case, the time intervals of each gas were set at 60 s and 120 s, respectively. The predetermined thickness of α-Si:H thin film was about 85 Å for the first deposition time of 60 s, and the hydrogen atoms expose the growth surface for the time of 120 s. Each thickness per cycle was carefully measured by using a Sloan Dektak3 profilometer. The deposition rate was analyzed by dividing the total film thickness by the total time per cycle. Table 1(a) shows a schematic diagram of our LBL technique that is slightly different from other group's schemes [8-10].

All of the experiments were carried out in the

Table 1. (a) Schematic diagram of the deposition of μc-Si thin films and (b) typical deposition parameters for higher crystal volume fractions in the growth of μc-Si thin films.

RF power on	➤
H₂	➤
SiH₄	➤
60s **120s**	

(a)

Parameters	Conditions
SiH₄	3 sccm
H₂	50 sccm
Power	0.85 W/cm₂
Pressure	250 mTorr
t_1	60 sec
t_2	120 sec
Temperature	250°C

(b)

PECVD reactor that was operated with a rf glow discharge of 13.56 MHz. Corning glasses were used as substrates. During the deposition, a SiH_4 flow rate of 3sccm and a H_2 rate of 50 sccm were chosen at the pressure of 250 mtorr. The rf-power density was about 0.85 W/cm^2 and the substrate temperature was 250°C. The details of typical deposition conditions were shown in the Table 1(b).

After the deposition, the μc-Si thin film was characterized by using structural and electro-optical methods. The structural information, such as crystalline volume fractions (X_c) was deduced by a Raman scattering spectroscopy. The surface morphology and the cross-sectional structure were investigated by the SEM figures. The absorption coefficient (α) was investigated by means of the UV spectrophotometer in the visible range of the spectrum, which led to the estimation of optical energy gap (E_{opt}). The I-V characteristic as a function of temperature was made for the dark conductivity and then the calculation of the activation energies (E_a). For the conductivity, all the measurements were done in high vacuum condition. The film deposited on the corning glass was heated to up to 180°C at a rate of 5 K/min and subsequently cooled down again to room temperature. Before the measurement, all the samples were prepared with planar

metal electrodes made by Al.

III. Results and Discussion

To get meaningful role of hydrogen atoms on the formation of the µc-Si thin film, the hydrogen exposure times in the LBL deposition were varied from 30 to 180 sec, where the number of cycle was fixed at 20 cycles. Figure 1 shows the deposition rate as a function of hydrogen treatment time. The deposition rate was deduced from the film thickness divided by the deposition time per cycle. As shown in this figure, the deposition rate decreases as the hydrogen exposure time is raised. The drop in deposition might, in part, be due to the surface etching effect by the hydrogen atom; that is, there might be more etching process pronounced at larger hydrogen exposure times [8].

Figure 2 exhibits Raman scattering spectra depending on the hydrogen exposure time. As shown in this figure, the shift of the amorphous peak to the crystalline position was observed with the increasing time of the hydrogen exposure plasma. The significant peak of crystallization at 520 cm^{-1} clearly started to be observed at 60 sec exposure time, compared with the peaks at less than 60 sec. The crystallization then was saturated at more than 90 sec. These experimental results would imply that initial hydrogen exposure on thin amorphous phase priminarily determine most of the crystallite in the film
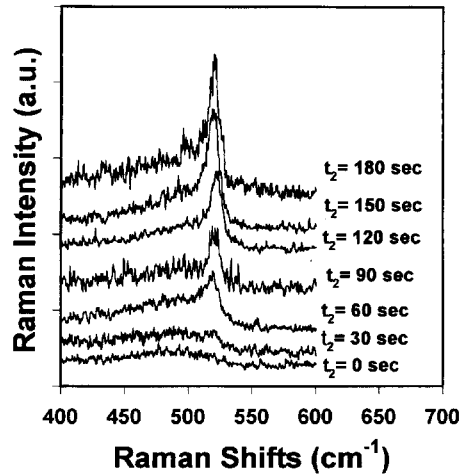

Fig. 2. Raman scattering spectra of µc-Si thin films as a function of hydrogen exposure time. The crystallization peak was clearly observed at 520 cm^{-1}.

[4]. Higher exposure times seem to be independent to the crystallization. However, in general, the structural enhancement with the increasing hydrogen time is well-known to have strong relation with the role of atomic hydrogen plasma on the surface of the film. Therefore, the increase in the Raman intensities up to 90 sec might be due to the impinging of hydrogen atom on the film surface; that is, the impingement of the hydrogen atom would enhance some structural relaxation in the Si-network, resulting in the increasing crystallinity [12]. However, the
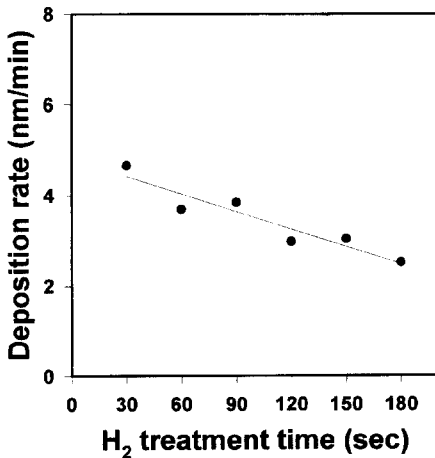

Fig. 1. Deposition rate of the µc-Si thin films as a function of hydrogen treatment time. In this case, the number of cycle was fixed at 20 cycles.
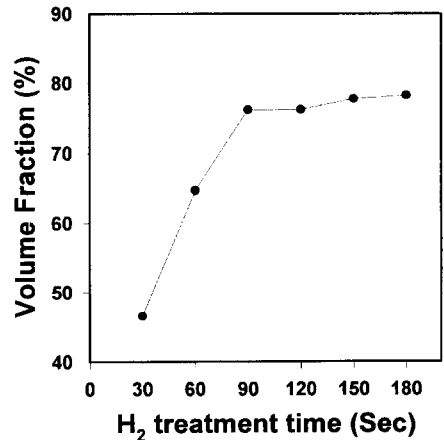

Fig. 3. Volume fraction (X$_c$) verse hydrogen exposure times. The X$_c$ was calculated from the Raman spectra at each different hydrogen time.

saturation at much larger hydrogen treatment times would be due to comparable surface etching effects by a large amount of hydrogen atoms. Therefore, there may be a balance between the stuctural relaxation and the surface etching process [8].

Figure 3 displays the volume fraction (X_c) verse hydrogen exposure times, where the X_c means the ratio of TO phonon intensities of the amorphous and the crystalline phases at 480 cm^{-1} and 520 cm^{-1}, respectively. As shown in this figure, the X_c increases dramatically up to the 90s and then saturates after that time. At less than 60 sec, the grains were small and there were some vacancies. A mixture of some crystallites embedded in an amorphous phase was still observed over the whole range of exposure times. Further work is under way to obtain the film with complete crystallite without any remaining amorphous phase.

Figure 4 shows a typical cross-sectional SEM figure of the μc-Si thin film deposited at hydrogen exposure time of 60 sec. As shown in this figure, the interface layer between the crystalline phase and the glass substrate was clearly observed as an amorphous phase. The thickness of this amorphous phase was about a few hundred Å. The crystal grains surrounded by the grain boundary exhibit the columnar shapes that extend vertically through the whole film thickness in the growth structure. The SEM figures (not shown in this letter) also indicate that with increasing exposure time, the samples became
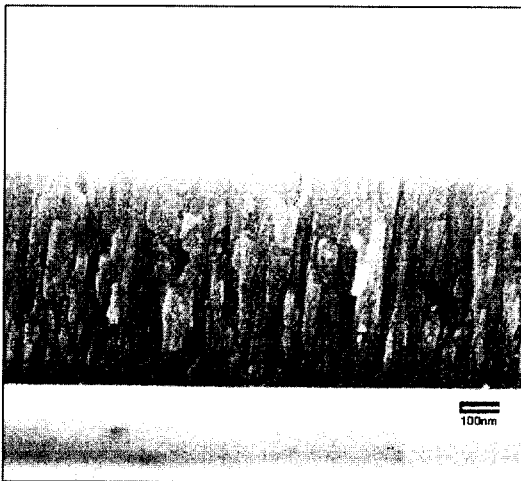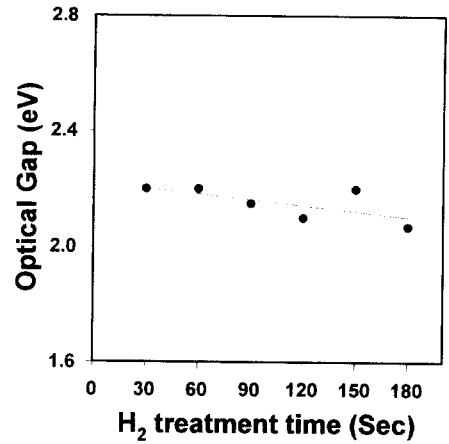

Fig. 5. Optical gap as a function of hydrogen time. The optical gaps were deduced from measurement of an absorption coefficient (α) using a UV spectrophotometer.

dense. However, there was not any significant change observed in the crystalline phase at larger hydrogen exposure time, as expected in the Fig. 3.

In order to examine electro-optical properties of the films, the optical gap as a function of hydrogen time is displayed in Fig. 5. The gaps were deduced from an absorption coefficient (α) measured by the UV spectrophotometer and then they were estimated from the Tauc formula. As shown in this figure, the optical gap slightly decrease as the hydrogen exposure time is raised. It would mean that the hydrogen atom was diffused into the Si network, but it might not substitute for the Si atom during the LBL process [11]. It was also thought that
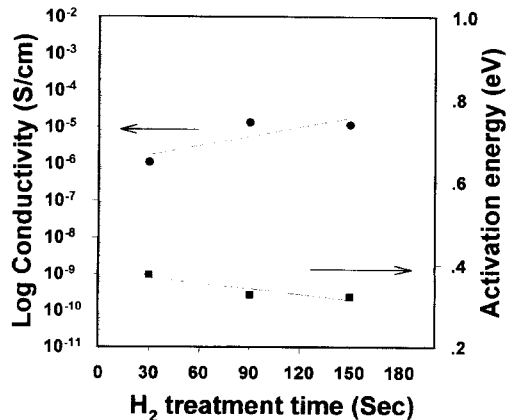

Fig. 4. Typical cross-sectional SEM figure of the μc-Si thin films at hydrogen exposure time of 60 sec.

Fig. 6. Log conductivity and Activation energy (E_a) plotted as a function of hydrogen exposure time (t_2).

the lower optical gap might be attributed to the lower trap levels, contributing the lower optical gap as the exposure time increases.

Figure 6 displays the log conductivity and the activation energy plotted as a function of hydrogen time. The slopes in the Arrhenius plot over the whole temperature range result in the deduction of the activation energy at various hydrogen exposure time. As shown in this figure, the conductivity increases with the increasing hydrogen exposure time. The behavior of the conductivity seems to be related to the higher volume fraction with increasing exposure time. On the other hand, the reduction in the activation energy might be due to the structural change of Si- network on the film growth zone, resulting in the structural relaxation for micro-crystallization [11]. In our experiment, all of the sample exhibits lower activation energy than below half of the optical gap. It suggests that the Fermi level position through the gap moves towards the conduction band. This trend was found to be reproducible during all the experiment.

Currently, further work is under the way in order to identify clear role of the hydrogen atom for comparable presence between the structural variation and the etching process.

IV. Conclusions

Microcrystalline thin films were prepared using a LBL technique with a conventional PECVD system in order to investigate possible role of hydrogen atom on the formation of the μc-Si film. The experiment focuses on the hydrogen treatment time. High crystallization of about $X_c > 80\%$ was obtained at more than hydrogen exposure time of the 90 sec without any post annealing treatment on the film. The electrical properties were characterized by temperature-dependent dark conductivity that leads to an estimation of activation energy (E_a). The optical properties, such as optical gaps were treated using an UV spectrophotometer. The experimental results suggest that both of the selective etching and the

structural relaxation effect on the film surface seem to be responsible for the growth mechanism of the crystallites.

Acknowledgements

References

[1] G. K. Giust and T. W. Sigmon, *Appl. Phys. Lett.* **70**, 767 (1997).
[2] C. H. Oh, Ozawa and M. Matsumura, *Jpn. J. Appl. Phys.* **37**, L 492 (1998).
[3] D. K. Fork, J. B. Boyce and R. I. Johnson, *Appl. Phys. Lett.* **68**, 2138 (1996).
[4] S. Hamma and P. Roca I Cabarrocas, *Thin Solid Films* **296**, 11 (1997).
[5] K. Saitoh, M. Kondo, M. Fukawa, T. Nishimiya and A. Matsuda, *Appl. Phys. Lett.* **71**, 3403 (1997).
[6] P. Roca I Cabarrocas, S. Hamma and A. Hadjadi, *Appl. Phys. Lett.* **69**, 529 (1996).
[7] T. Arai, T. Nakamura and H. Shirai, *Jpn. J. Appl. Phys* **35**, L 1161 (1996).
[8] L. Layadi, P. Rocai Cabarrocas and B. Drevillon, *Physical Review* B, **52**, 5136 (1995).
[9] K. Nomoto, Y. yrano, J. L. Guizot, G. Ganugly and A. Matsuda, *Jpn. J. Appl. Phys.* **29**, L 1372 (1990).
[10] H. Shirai and T. Arai, *J. Non-Cryst. Solid* **198**, 931 (1996).
[11] K. Nakamura, K. Yoshino, S. Takeoka and I. Shimizu, *Jpn. J. Appl. Phys.* **34**, 442 (1995).
[12] Y. H. Yang, M. Kaityar, G. F. Feng, N. Maley and J.R. Abelson, *Appl. Phys. Lett.* **68**, 1769 (1994).
[13] R. Robertson and A. Gallagher, *J. Chem. Phys.* **85**, 3623 (1986).
[14] I. Solomon, B. Drevillon, H. Shirai and N. Layadi, *Non-Crystal. Solids* **164**, 989 (1993).
[15] K. Saitoh, M. Kondo, M. Fukawa, T. Nishimiya, A. Matsuda, W. Fukako and I. Himizu, *Appl. Phys. Lett.* **71**, 3403 (1997).