

## Growth of crystalline grains in microcrystalline silicon films

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Growth of crystalline grains has been studied using atomic hydrogen plasma exposure on thick ( $\sim 190$  nm) microcrystalline silicon films ( $\mu\text{c-Si:H}$ ) with a low crystalline volume fraction ( $\sim 7\%$ ). Raman spectra reveal that the intensity near  $520\text{ cm}^{-1}$  increases after hydrogen exposure. Cross-sectional transmission electron micrographs of  $\mu\text{c-Si:H}$  films exposed to atomic hydrogen show the growth of crystalline grains extending from surface to bulk, approximately 100 nm. These results suggest that crystal formation in  $\mu\text{c-Si:H}$  films is likely to be caused by chemical annealing.

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Microcrystalline silicon ( $\mu\text{c-Si:H}$ ), as a good substitute for amorphous silicon ( $a\text{-Si:H}$ ), is very promising for large-area electronic applications such as solar cells and thin film transistors because of its stable electronic properties against light exposure, high doping efficiency, and high mobility. In particular,  $\mu\text{c-Si:H}$  films can be easily grown at substrate temperatures of  $200\text{ }^{\circ}\text{C}$ – $300\text{ }^{\circ}\text{C}$  by plasma-enhanced chemical vapor deposition (PECVD) using either high hydrogen-diluted silane<sup>1–3</sup> or a layer-by-layer (LBL) deposition technique,<sup>4,5</sup> which repeatedly alternates the deposition of  $a\text{-Si:H}$  film and then exposure of hydrogen plasma. The detailed formation mechanism of  $\mu\text{c-Si:H}$ , however, still remains unclear.

Two aspects regarding the formation of  $\mu\text{c-Si:H}$  have been considered: the growth precursor for grains and the growth mechanism for grains. The growth precursor is generally believed to be the  $\text{SiH}_3$  radical,<sup>6,7</sup> but there are various suggestions for the growth mechanism for grains: typically the surface diffusion model which involves the formation of crystalline grains due to the surface diffusion of the growth precursors enhanced by the hydrogen coverage,<sup>3</sup> the etching model, which involves the formation of crystalline grains due to the selective etching of the  $a\text{-Si:H}$  phase by hydrogen atoms,<sup>8</sup> and the chemical annealing model that suggests that atomic hydrogen penetrates into the  $a\text{-Si:H}$  subsurface region and breaks some fraction of the Si-Si bonds, allowing the structural relaxation of amorphous phase and a transition to the crystalline phase.<sup>5</sup> The former two models are based on a surface reaction of precursors during deposition. In these cases crystalline grains continue to grow as long as the precursors are supplied, resulting in an epitaxial-like growth of grains. On the other hand, the latter, in particular, useful for explaining the  $\mu\text{c-Si:H}$  formation by the LBL technique, is based on a restructuring of subsurface after deposition. These suggestions basically demonstrate the formation of crystallites in the region ranging from surface to subsurface, several angstroms in depth.

In this work we report the growth of crystalline grains in the bulk region when  $\mu\text{c-Si:H}$  films are exposed to atomic hydrogen plasma after deposition. The growth of crystalline grains was verified by Raman back-scattering spectroscopy and cross-sectional transmission electron microscopy. It was found that crystalline grains were formed in the region rang-

ing from surface to bulk of about 100 nm in depth, demonstrating that chemical annealing is more likely to be responsible for the formation of crystallites in the  $\mu\text{c-Si:H}$  films.

$\mu\text{c-Si:H}$  films of about 190 nm thick were deposited on Corning 7059 glasses at a substrate temperature of  $220\text{ }^{\circ}\text{C}$  by plasma-enhanced chemical vapor deposition (PECVD) using argon (Ar)-diluted silane ( $\text{SiH}_4$ ) gas, which was mixed using a fixed flow rate of  $\text{SiH}_4$  (5 sccm) and Ar (100 sccm). The plasma reactor consists of two capacitively coupled parallel disk electrodes. The plasma was produced using an excitation power of  $30\text{ mW/cm}^2$  and a frequency of 13.56 MHz. Pressure during deposition was 1 Torr. The as-grown  $\mu\text{c-Si:H}$  samples exhibit a dark conductivity of about  $10^{-8}\text{ S/cm}$  at 300 K, a dark conductivity activation energy of about 0.81 eV, and a crystalline volume fraction of about 7%. After deposition, the samples were subsequently exposed to atomic hydrogen plasma at the same temperature as the substrate one. Atomic hydrogen plasma was also generated by PECVD using pure hydrogen (99.999%) gas. A pressure of 500 mTorr and a flow rate of 180 sccm were employed for hydrogen plasma. The microstructures of samples were studied using Raman spectroscopy and transmission electron microscopy (TEM). Raman spectra, which were excited by the 514.5 nm Ar-ion laser line, were measured using a liquid nitrogen cooled CCD detector at room temperature. TEM micrographs were measured using a JEOL JEM 2010 instrument operating at 200 keV.

Figure 1 shows the Raman spectra taken on  $\mu\text{c-Si:H}$  films exposed to atomic hydrogen plasma for different time, together with as-grown sample (solid line). It is seen that the spectra exhibit two peaks: a broad peak near  $480\text{ cm}^{-1}$  and a sharp peak near  $520\text{ cm}^{-1}$ , which are usually attributed to amorphous and crystalline silicon phases, respectively. Figure 1 shows that the peak intensities are changed by variation in exposure time. The sharp peak near  $520\text{ cm}^{-1}$  grows up with increasing exposure time, demonstrating that crystallinity of  $\mu\text{c-Si:H}$  film can be enhanced by atomic hydrogen exposure after deposition. Furthermore, Fig. 1 shows that the broad peak near  $480\text{ cm}^{-1}$  increases with hydrogen exposure time, although its intensity is lower than that near  $520\text{ cm}^{-1}$ , indicating that an amorphous silicon phase can be also induced by hydrogen exposure.

The enhancement of crystallinity by atomic hydrogen ex-

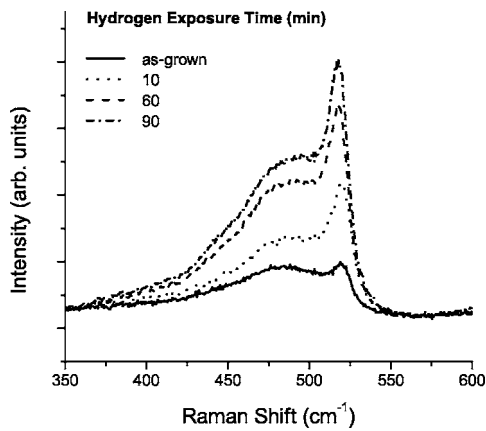


FIG. 1. Raman spectra of  $\mu c$ -Si:H films exposed to atomic hydrogen plasma for a different time. Note that intensity near  $520 \text{ cm}^{-1}$  dominates after exposure.

posure was studied in terms of the volume fraction of the crystalline phase using Raman spectrum. The Raman spectrum was decomposed into two components using a Gaussian function: the amorphous phase component peaked at  $480 \text{ cm}^{-1}$  and the crystalline phase component peaked at  $520 \text{ cm}^{-1}$ . Using the relation,<sup>9</sup>  $V_c = I_c / (I_a + I_c)$ , where  $V_c$  is the volume fraction of crystalline phase, and  $I_a$  and  $I_c$  are the integrated area intensities of decomposed spectra peaked at  $480$  and  $520 \text{ cm}^{-1}$ , respectively, we calculated the volume fraction. Figure 2 shows the integrated area intensities ( $I_c$ ) and volume fractions ( $V_c$ ) of the crystalline phase obtained from the samples exposed to hydrogen plasma for a different time. It is seen that both vary within an exposure time shorter than 10 min, increasing the crystalline phase with exposure time, but they are nearly independent of exposure time after 10 min. This indicates that the growth of crystalline grains does not continue to proceed under hydrogen exposure. This growth limitation may be due to a lack of sources being transformed into a crystalline phase.

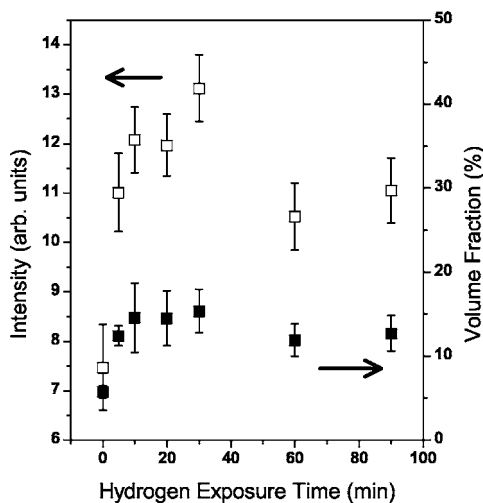


FIG. 2. Plots of integrated area intensity (open squares) and volume fraction (filled squares) obtained from a Raman signal due to the crystalline phase as a function of the hydrogen exposure time. Note that both are nearly independent of hydrogen exposure time after 10 min.

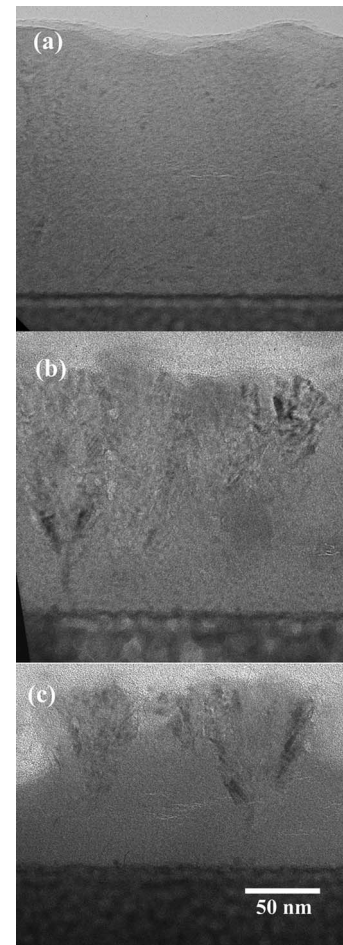


FIG. 3. Cross-sectional transmission electron microscope images of  $\mu c$ -Si:H films unexposed (a) and exposed (b) and (c) to atomic hydrogen plasma. The images in (b) and (c) were obtained after 10 and 90 min exposure, respectively. Note that crystalline grains were formed in the region ranging from surface to bulk. The resulting grains are also approximately conic in shape and their sizes are nearly independent of exposure time.

Besides the qualitative analysis of the grain growth by hydrogen exposure using Raman spectroscopy, the detailed growth of grains in  $\mu c$ -Si:H films was studied using cross-sectional transmission electron microscopy (XTEM). Figure 3 shows XTEM images of  $\mu c$ -Si:H films without (Fig. 3(a)) and with (Figs. 3(b) and 3(c)) atomic hydrogen exposure. The XTEM images shown in Figs. 3(b) and 3(c) were obtained from the samples exposed to atomic hydrogen plasma for 10 and 90 min, respectively. It is clearly seen that the unexposed sample reveals no definite grains, while the samples exposed to atomic hydrogen exhibit crystalline grains with an approximately conic shape. Figures 3(b) and 3(c) also show that there are no definite differences in the size and distribution of grains in two samples (10 and 90 min exposure), consistent with the results shown in Fig. 2. Figures 3(b) and 3(c) show clearly that the crystalline grains after hydrogen exposure were formed in the region ranging from the surface to the bulk, similar to those observed in  $\mu c$ -Si:H films grown by usual deposition methods such as standard hydrogen dilution and LBL.<sup>10</sup> In this case, however,

it should be noted that the grains were formed without the supply of film-growth precursors. This fact means that the surface reaction processes, such as surface diffusion and selective etching, may not be suitable for understanding the present results.

On the other hand, the chemical annealing process is more likely to be suitable for the present results. The chemical annealing process, which is achieved by hydrogen atoms permeated into film after deposition, gives rise to the structural relaxation for the formation of crystalline grains.<sup>5</sup> The formation of crystallites by atomic hydrogen exposure as shown in Figs. 3(b) and 3(c) means that hydrogen atoms should permeate through at least 100 nm. It is shown that atomic hydrogen inserts more easily into strained Si-Si bonds in *a*-Si:H,<sup>11,12</sup> and that atomic hydrogen can permeate through a depth of more than 130 nm.<sup>13</sup> In the present studies the unexposed samples were grown under deposition conditions near the onset of  $\mu$ c-Si:H, as shown in Fig. 1. Such deposition conditions produce an *a*-Si:H phase containing a great number of strained Si-Si bonds and a porous SiH<sub>*n*</sub> phase, which play a crucial role in the formation of crystallites.<sup>14,15</sup> The formation of crystalline grains by atomic hydrogen exposure seems to be achieved by a combination of these film properties and chemical annealing. From the presented results, as a result, it is suggested that the crystal formation in  $\mu$ c-Si:H films is likely to be occurred by chemical annealing rather than others.

It should be, in general, expected that the amount of strained and/or porous phases would be fixed for the samples

prepared using the same deposition conditions. This situation may limit the continuous growth of crystalline grains by hydrogen exposure, as shown in Fig. 2. Many of studies on  $\mu$ c-Si:H have reported the existence of incubation layer near the substrate, where no crystallites are formed, and the conical grains in shape as shown in Figs. 3(b) and 3(c).<sup>10,16</sup> In the present case, the amount of strained and/or porous phases may increase with increasing thickness, even though there are no definite crystalline grains. These would cause a limitation of grain growth up to about 100 nm in depth and conical grains in shape, as seen in Figs. 3(b) and 3(c). On the other hand, Fig. 1 shows that both of the Raman intensities due to amorphous and crystalline phases after hydrogen exposure are higher than those of as-grown sample. Figure 1 suggests that the strained and/or porous phases are transformed into amorphous and crystalline phases.

In conclusion, thick  $\mu$ c-Si:H film ( $\sim$ 190 nm) with a low crystalline volume fraction ( $\sim$ 7%) was exposed to atomic hydrogen plasma after the growth of the film. We have observed that crystalline grains are formed in the region ranging from surface to bulk, about 100 nm, and that the resulting grains are approximately conic in shape. From the results it is suggested that crystalline grains in  $\mu$ c-Si:H films may be formed by chemical annealing process.

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