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Description	

Low-temperature crystallization of amorphous silicon using atomic hydrogen generated by catalytic reaction on heated tungsten

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A method for crystallizing amorphous silicon (*a*-Si) films at low temperatures is proposed. In the method, *a*-Si films are crystallized at temperatures lower than 400 °C by annealing in the presence of atomic hydrogen. The hydrogen atoms are generated by catalytic cracking reaction of H₂ gas on a heated tungsten catalyzer in the catalytic chemical vapor deposition apparatus. It is found that the crystalline fraction of such an *a*-Si film is increased from 0% to several tens %, and at the same time the *a*-Si film itself is etched with the rate of several tens nm/min by annealing in atomic hydrogen. This increment of crystalline fraction appears dependent on the quality of initial *a*-Si films. It is implied that there are several types of *a*-Si even if the difference among *a*-Si films cannot be detected by Raman scattering spectroscopy and other means for measurements. © 1999 American Institute of Physics. [S0003-6951(99)01415-1]

Polycrystalline silicon (poly-Si) films have been widely applied to various electronic devices such as solar cells and thin film transistors. However, amorphous silicon (*a*-Si) incubation layer of several tens nm thickness is often formed at the initial step of poly-Si growth on a glass substrate¹ and the performance of devices using such poly-Si deteriorates. Therefore the development of the crystallization method of such an incubation layer at temperatures lower than the distortion temperature of low-cost glass substrates, usually lower than 400 °C, is required.

The authors have developed a novel low-temperature deposition method, named the catalytic chemical vapor deposition (Cat-CVD) method,²⁻⁴ often called the hot-wire CVD method. In the method, deposition gases are decomposed by catalytic cracking reactions on a heated catalyzer placed near the substrates. Poly-Si films are obtained at temperatures lower than 400 °C using a SiH₄ and H₂ gas mixture.⁵ Additionally, atomic hydrogen is effectively generated by cracking H₂ on a heated catalyzer.

In the present work, we propose a new crystallization method of *a*-Si films at temperatures lower than 400 °C, named the atomic hydrogen anneal (AHA) method. In the method, *a*-Si films are exposed to atomic hydrogen generated by the catalytic cracking reaction in a Cat-CVD system. Structural properties of *a*-Si films subjected to AHA are investigated.

Details of the Cat-CVD apparatus have already been mentioned elsewhere.⁶ Here, a tungsten wire with a diameter of 0.75 mm and a length of 190 cm was used as the catalyzer. The distance from the catalyzer to the substrate was about 5 cm. Substrate temperature and catalyzer temperature were measured by a thermocouple attached to the substrate and an infrared thermometer through a quartz window, respectively. Thus, the measured substrate temperature in-

cludes the effect of both thermal radiation and irradiation of heated gas.

The initial Si films before AHA were prepared by the Cat-CVD method. We expect that the effect of AHA depends on structural properties of initial Si films. So far, it is known that the crystalline fraction of poly-Si films prepared by the Cat-CVD method was controlled by changing the flow-rate ratio of SiH₄ and H₂.⁷ Therefore it is expected that *a*-Si films with various structural properties are obtained by changing the flow-rate ratio. In this case, the flow rate (FR) of H₂, FR(H₂), was fixed to 30 sccm and that of SiH₄, FR(SiH₄), varied from 1 to 8 sccm. The initial Si films of 800 nm thickness were deposited on fused quartz substrates. In both the deposition and AHA, catalyzer temperature and substrate temperature were 1600 and 350 °C, respectively. The gas pressures of deposition and AHA were from 0.9 to 2.0 mTorr and 300 mTorr, respectively. The initial Si films were exposed to air and film thickness and Raman spectra were measured. Then Si films were subjected to AHA. In order to measure the change of film thickness, half of the initial Si film was masked with a stainless steel plate during AHA.

It is known that the chemical transport takes place during hydrogen plasma treatment.⁸ In this phenomenon, Si film deposited inside of the chamber is etched by a H atom. Then, the Si species arrive at the substrate. In this case, Si film is deposited with a high H dilution ratio and has a high crystalline fraction. In order to determine the existence of such phenomena, fused quartz and a single-crystalline Si substrate were also set together with the initial Si film. However, no deposition of film was detected on those substrates. Thus, it was confirmed that the chemical transport was negligible at least under the experimental conditions used.

The etching rate by AHA was measured using a stylus profile meter. The structural properties of Si films were studied by the Raman scattering spectroscopy using the excited light of 514.5 nm wavelength of an argon ion laser at room temperature. The crystalline fraction was determined from

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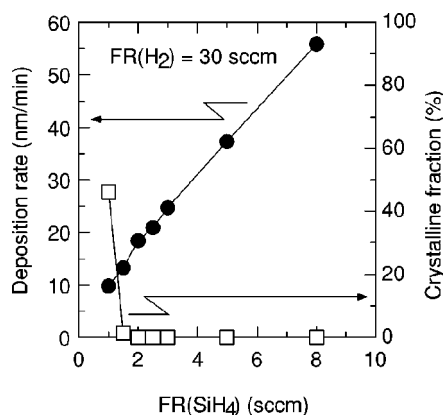


FIG. 1. Deposition rate and crystalline fraction for Si films prepared with various $\text{FR}(\text{SiH}_4)$. $\text{FR}(\text{H}_2)$ was fixed to 30 sccm. The crystalline fraction of those films was estimated from Raman spectra.

the areal ratio of the signal due to the crystalline phase at 520 cm^{-1} to the sum of the signals due to both the crystalline phase and the amorphous phase at 480 cm^{-1} .

The deposition rate and the crystalline fraction of initial Si films for various $\text{FR}(\text{SiH}_4)$ are shown in Fig. 1. As $\text{FR}(\text{SiH}_4)$ increases, the deposition rate linearly increases and the crystalline fraction suddenly decreases from 50% to 0%. Initial Si films deposited with $\text{FR}(\text{SiH}_4)$ larger than 2 sccm were amorphous. It is known that the amorphous phase was selectively etched compared with the crystalline phase by atomic hydrogen.⁹ Therefore, as the H_2 dilution ratio increases, the crystallinity is improved.

The relationship between $\text{FR}(\text{SiH}_4)$ at the initial Si deposition and etching rate by AHA is shown in Fig. 2. AHA was carried out at 300 mTorr for 10 min. The thickness of poly-Si films deposited with $\text{FR}(\text{SiH}_4) = 1\text{ sccm}$ is not changed. As $\text{FR}(\text{SiH}_4)$ increases from 1 to 2 sccm, the etching rate increases because of the increment of the ratio of the amorphous phase. The structural properties of each *a*-Si film deposited with $\text{FR}(\text{SiH}_4)$ larger than 2 sccm are indistinguishable by Raman measurements. However, the etching rates of those films are apparently different. This implies that there are various *a*-Si structures whose difference cannot be detected by Raman measurements as we expected above.

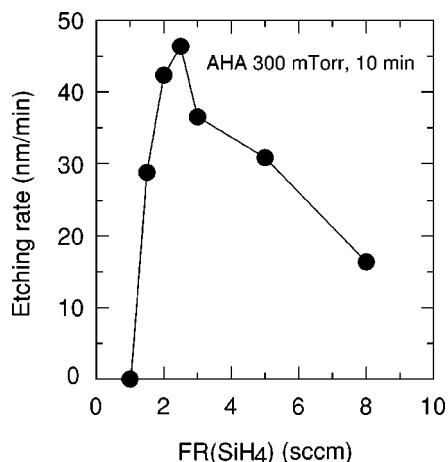


FIG. 2. Relationship between $\text{FR}(\text{SiH}_4)$ at initial Si deposition and etching rate by AHA.

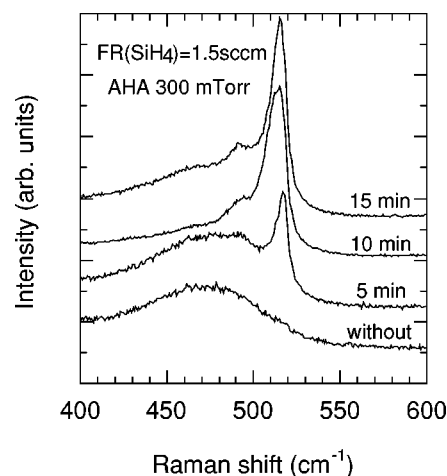


FIG. 3. Raman spectra of the film deposited with $\text{FR}(\text{SiH}_4) = 1.5\text{ sccm}$ and of the film subjected to AHA for 5, 10 and 15 min.

Raman spectra of the initial Si film deposited with $\text{FR}(\text{SiH}_4) = 1.5\text{ sccm}$ and of the film subjected to AHA for various times are shown in Fig. 3. AHA was carried out at 300 mTorr. The phonon bands due to the crystalline phase are observed at Raman spectra of films subjected to AHA. It is clear that the crystallization of *a*-Si occurs by AHA. The role of atomic hydrogen was investigated by the same experiment using He instead of H_2 at 300 mTorr for 20 min. Raman spectra of initial Si films deposited with $\text{FR}(\text{SiH}_4) = 1.5\text{ sccm}$ and of the film exposed to He with the same catalyzer and substrate temperatures are shown in Fig. 4. In this case, crystallization of *a*-Si films does not occur. Therefore, it is confirmed that the crystallization by AHA is related to the chemical reaction of atomic hydrogen. The change in the crystalline fraction by AHA at 300 mTorr for 10 min is shown in Fig. 5. The data shown by open squares are same as those in Fig. 1. Crystalline fractions of Si films deposited with low $\text{FR}(\text{SiH}_4)$ such as 1.5 and 2.0 sccm are increased by 30%–60% with AHA. However, the crystallization does not occur for initial Si films deposited with $\text{FR}(\text{SiH}_4)$ larger than 5 sccm. It implies that a particular *a*-Si structure which is likely to be crystallized really exists.

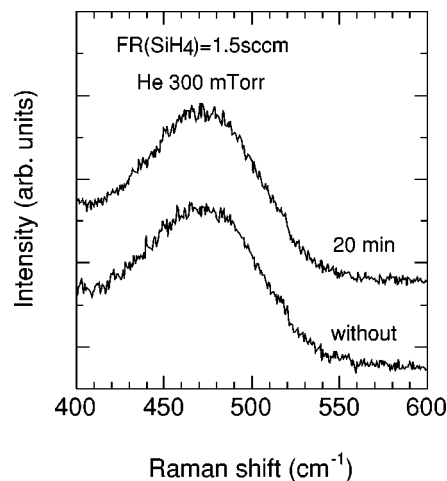


FIG. 4. Raman spectra of the film deposited with $\text{FR}(\text{SiH}_4) = 1.5\text{ sccm}$ and of the film exposed to He with the catalyzer temperature of $1600\text{ }^\circ\text{C}$ and the substrate temperature of $350\text{ }^\circ\text{C}$.

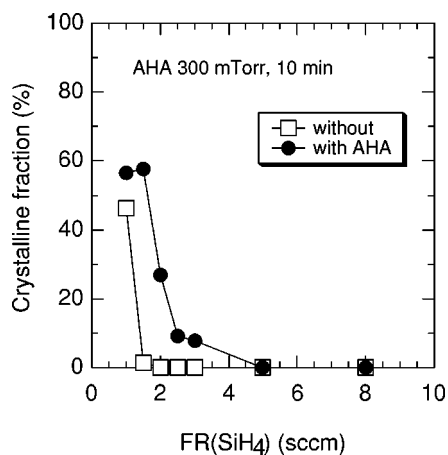


FIG. 5. Change of crystalline fraction by AHA for Si films prepared with various FR(SiH₄). Open and closed symbols show the crystalline fraction without AHA and with AHA, respectively.

The following conclusions are obtained: (1) some *a*-Si films were crystallized by AHA; (2) crystallization and etching by AHA depend on structural properties of initial *a*-Si films; and (3) there are various structures of *a*-Si whose dif-

ference cannot be detected by the conventional Raman measurements.

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