Thermally Deposited Amorphous Silicon

F. Mieno, T. S. Sukegawa, J. Iizuka, H. Miyata, H. Nomura, A. Tsukune, and Y. Furumura

Advanced Development Division, Electronic Devices Group, Fujitsu Limited, Kamikodanaka, Nakahara-ku, Kawasaki 211, Japan

ABSTRACT

We investigated a thermally deposited amorphous silicon (TAS) film before and after annealing. We used monosilane (SiH_4) or disilane (Si_2H_6) as the Si source gas at a deposition pressure of 0.1 to 0.5 Torr. The activation energy of SiH_4 deposition was 1.7 eV (560 to 600°C) and that of Si_2H_6 was 0.6 eV (510 to 570°C). From TEM observation, the TAS film from 450°C Si_2H_6 deposition was completely amorphous without crystals and had a smooth surface. Film deposited at 560°C had a few crystals at the Si/SiO_2 interface and had a few bumps on the Si surface. After annealing, the mean grain size of 450°C-Si_2H_6 film was about 2 μm and that of 560°C-SiH_4 film was about 0.3 μm. We also evaluated the crystallinity by XRD and Raman spectroscopy. Films deposited at lower temperatures after annealing showed strong <111>-orientations and high crystal qualities.

In ultra large scale integrated (ULSI) device fabrication, vertical size reduction has become as important as reduced overall geometries. Higher quality, thinner films (less than 50 nm) and clean interfaces are needed to fabricate shallower structures. High-quality thin polysilicon films are used as gate electrodes in MOS devices, TFT bodies in SRAMs, emitter electrodes in bipolar devices, capacitor electrodes in DRAMs, and resistors. Also, hemispherical grains (HSG) for capacitor electrodes in 64-MBDRAMs,[1,2] and selective polysilicon deposition for filling contacts[3] have been reported. We reported low-temperature Si film deposition from Si_2H_6 for TFT bodies and electrodes.[4-9]

Little research has been done on Si films deposited at temperatures below 550°C, because low-temperature deposition is thought to be too slow to be practical. Deposition from higher silanes, however, is expected to produce higher deposition rates at lower temperatures. Before and after annealing, we studied the quality of films deposited from Si_2H_6 at temperatures ranging from 450 to 620°C. We call this film TAS to distinguish it from plasma-enhanced CVD (PECVD) amorphous silicon.

Experiment

We deposited Si films on thermally grown oxide in a low pressure CVD (LPCVD) reactor. We used SiH_4 and Si_2H_6 as Si source gases with the deposition temperatures ranging from 550 to 620°C for SiH_4 and 450 to 620°C for Si_2H_6, and the deposition pressure from 0.2 to 0.5 Torr. For crystallization, we used N_2 annealing temperatures ranging from 600-1100°C.

We measured film thicknesses by measuring step heights after Si etching a masked substrate. We evaluated the crystallinity by transmission electron microscopy (TEM), transmission electron diffraction (TED), x-ray diffraction (XRD), and Raman spectroscopy. For TED measurements, we used selected area diffraction. For XRD, we used a special apparatus that allowed measurements of films as thin as 200 nm. We observed surface features with a TEM replica method and scanning electron microscopy (SEM). In the TEM replica method, samples were treated as indicated in Fig. 1. We studied crystallization of samples on a heated stage by micro-Raman spectroscopy.

Results and Discussion

Deposition rate.—We measured the Arrhenius plots for SiH_4 and Si_2H_6 at a deposition pressure of 0.2 Torr (Fig. 2). Flow rates of SiH_4 and Si_2H_6 were 50 sccm and 15 sccm. The activation energy of SiH_4 was 1.7 eV (560-600°C) and that of Si_2H_6 was 0.6 eV (510-570°C). Below 580°C, Si_2H_6 deposited Si faster than SiH_4, even though its flow rate was lower. This suggests that the reaction efficiency of Si_2H_6 is better than that of SiH_4, and for deposition temperatures below 580°C, SiH_4 produces unwanted by-products. Therefore, Si_2H_6 is a good Si source gas for low-temperature deposition.

Surface features.—We studied the surface features with a TEM replica method and cross-sectional TEM. Figure 3 shows the surface features of a 450°C-Si_2H_6 film replica

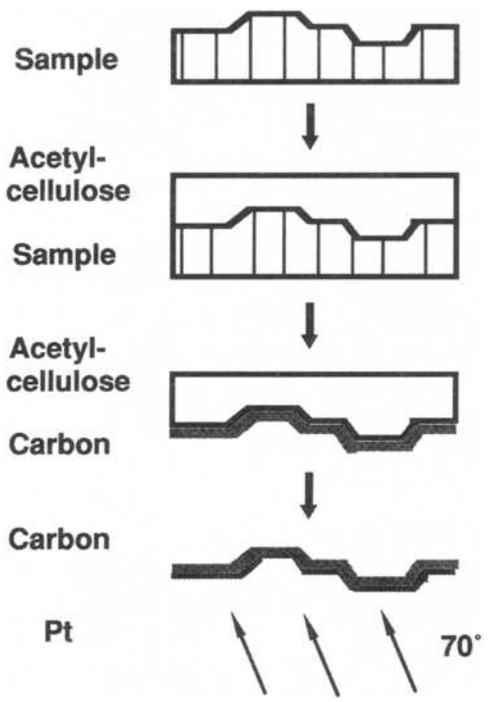

Fig. 1. Preparation of a replica TEM sample.

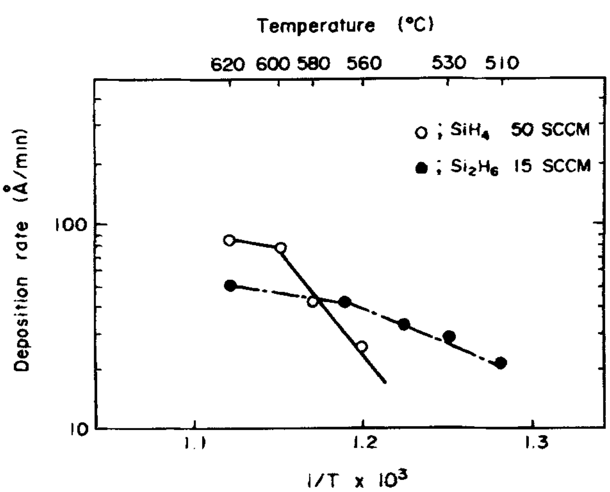

Fig. 2. Arrhenius plots of SiH_4 and Si_2H_6 deposition.

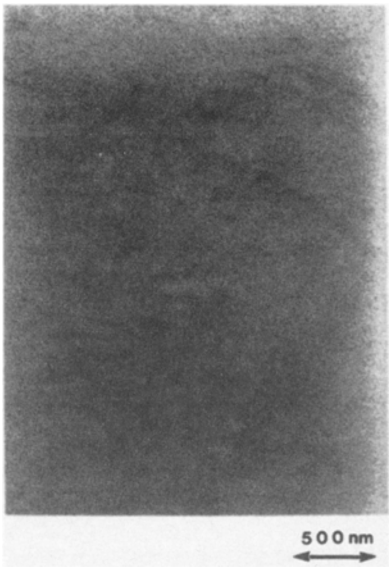

Fig. 3. Surface replica TEM image of Si_2H_6 film deposited at 450°C.

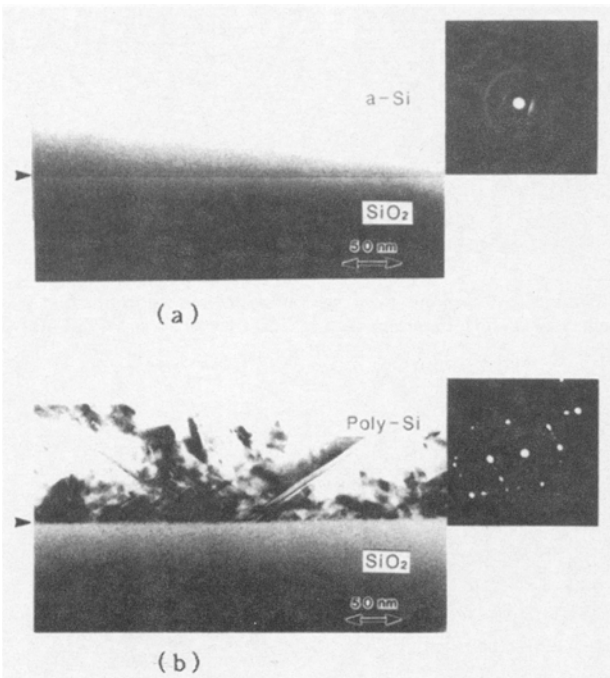

Fig. 4. Cross-sectional transmission electron micrographs and TED patterns of Si_2H_6 films deposited at 450°C (a) as deposited, and (b) after N_2 annealing at 600°C for 2 h.

observed by TEM. In a cross-sectional-view transmission electron micrograph (Fig. 4a), we observed a 10-μm length of the sample using 50,000 to 300,000 magnified micrographs. The transmission electron micrograph of the replica shows a very smooth surface, and the cross-sectional TEM observation shows a flat surface. Figure 5 shows the transmission electron micrograph of a 560°C-SiH_4 film surface replica. Observing a 390-μm^2 area of this sample using 25,000 magnified micrographs, we found 50-nm diam bumps on the flat surface. Figure 6 shows the cross-sectional transmission electron micrograph of this sample. Observing a 70-μm length of this sample using 50,000 to 100,000 magnified micrographs, we found a smooth surface with a few bumps 30 nm high. The bumps look like the hemispherical grains (HSG) reported by Watanabe *et al.*[1] They noted that a surface migration of Si atoms during annealing under reduced pressure after deposition forms 0.1-μm HSGs.

The transmission electron micrograph of a 620°C-SiH_4 film surface replica (Fig. 7), and the cross-sectional transmission electron micrograph of a 620°C-SiH_4 film show a surface roughness of about 20-30 nm, which is same as that indicated in other reports.[10]

We annealed samples at 600°C in N_2 for 2 h, then we observed the surface features.

Figure 8 shows the transmission electron micrograph of a 450°C-Si_2H_6 film surface replica, and Fig. 4b shows the cross-sectional transmission electron micrograph. We observed a 20-μm length of the sample using 100,000 magnified micrographs. Even after the film was crystallized completely by annealing, the surface remained smooth. This may be due to a native oxide cover or less thermal energy for surface migration. We observed the surface features of a 560°C-SiH_4 film after annealing using a TEM

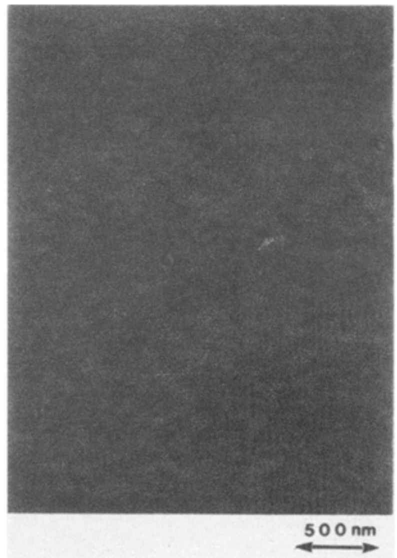

Fig. 5. Surface replica TEM image of SiH_4 film deposited at 560°C.

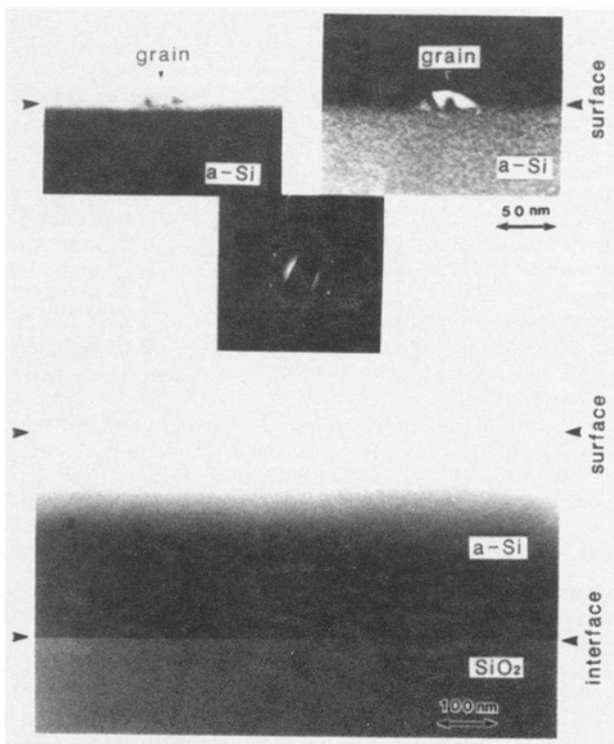

Fig. 6. Cross-sectional transmission electron micrographs and TED pattern of an SiH_4 film deposited at 560°C.

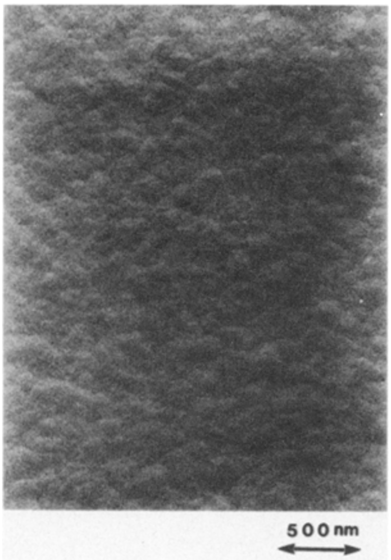

Fig. 7. Surface replica TEM image of SiH_4 film deposited at 620°C.

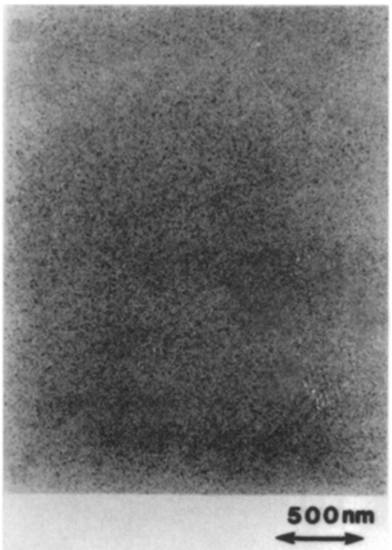

Fig. 8. Surface replica TEM image of Si_2H_6 film deposited at 450°C after N_2 annealing at 600°C for 2 h.

image of the surface replica and a cross-sectional-view TEM image along a 36-μm length of the sample using 50,000 to 100,000 magnified transmission electron micrographs (Fig. 9). The surface features were not changed by annealing.

We also observed the surface features of a 620°C-SiH_4 film after annealing using a TEM image of the surface replica and a cross-sectional-view TEM image. The surface features changed little.

From these results, lower deposition temperature films deposited from Si_2H_6 have smooth surfaces even after crystallization. Polysilicon with a smooth surface is advantageous in fabrication of TFT bodies, and gate and capacitor electrodes, because rough surfaces cause dielectric breakdowns.

Crystal quality.—TEM observation.—Using TEM, we evaluated the films' crystallinity before and after annealing at 600°C for 2 h.

Figure 4a shows the cross-sectional transmission electron micrograph and the TED pattern of a 450°C-Si_2H_6 film before annealing. We observed a 10-μm length of the sample using 50,000-300,000 magnified micrographs. The film was not crystalline, with the TED pattern exhibiting broad, diffuse rings characteristic of an amorphous film. The transition temperature, above which a polycrystalline structure forms, is about 580°C at a pressure of 0.2 Torr.[11] Because the deposition temperature of 450°C was much lower than the transition temperature, we obtained completely amorphous silicon. Also, the deposition rate is a key

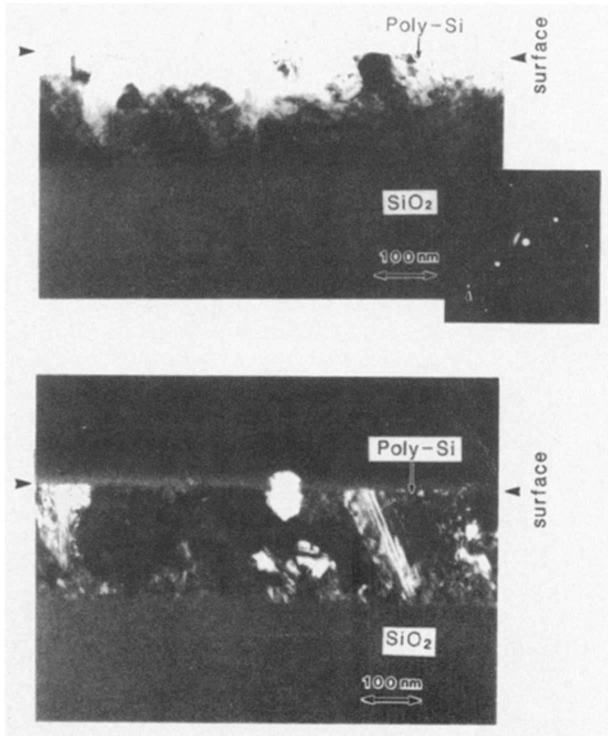

Fig. 9. Cross-sectional transmission electron micrographs and TED pattern of an SiH_4 film deposited at 560°C after annealing at 600°C for 2 h.

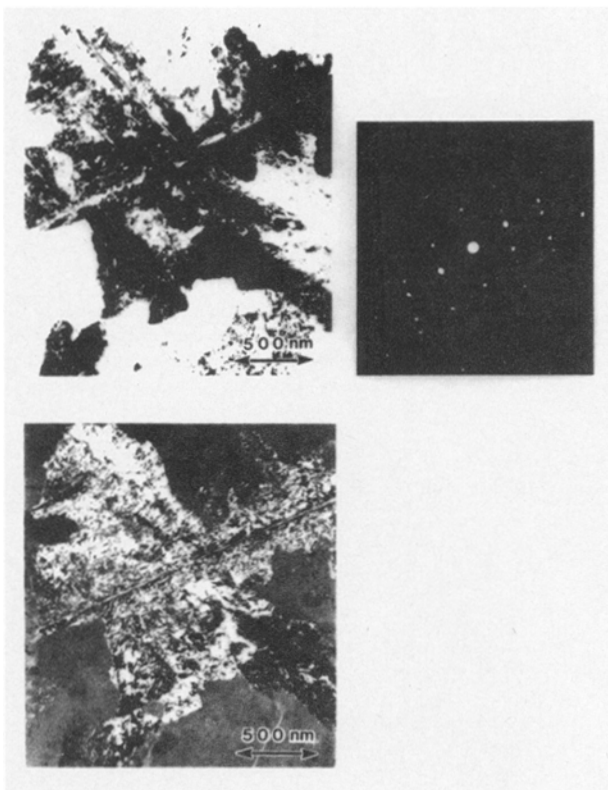

Fig. 10. Plane-view transmission electron micrographs and TED pattern of an Si_2H_6 film deposited at 450°C after N_2 annealing at 600°C for 2 h.

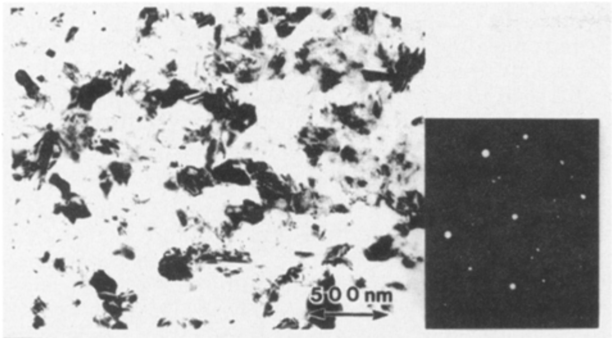

Fig. 11. Plane-view transmission electron micrograph and TED pattern of an SiH_4 film deposited at 560°C.

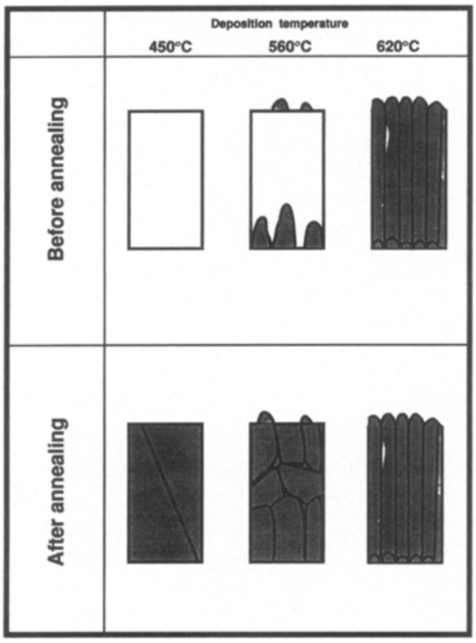

Fig. 12. TEM observation summary.

to producing a completely amorphous structure, since higher deposition rates reduce the surface mobility of adatoms at lower deposition temperatures and prevent formation of crystalline structures. The opposite case is epitaxial films, which form at higher temperatures and lower deposition rates.

Figure 4b shows the cross-sectional transmission electron micrograph and the TED pattern of an annealed sample. Observing a 20-μm length using 100,000 magnified micrographs revealed a large monocrystalline grain with twin boundaries and the TED pattern had twin spots. Polysilicon deposited at 620°C using LPCVD shows a ring-and-dot pattern. The crystal quality of 450°C-Si_2H_6 film after annealing was better than that of conventional LPCVD polysilicon.

Figure 10 shows the plane-view transmission electron micrograph and the TED pattern of a 450°C-Si_2H_6 film after annealing. Upper and lower micrographs correspond to bright and dark field images. We observed a very large grain of about 3 μm with twin boundaries and small defects, and the TED showed a spot pattern. The mean grain diameter was about 2 μm, calculated[12]

$$d = 1.5\ l/mn$$

where d is the mean grain diameter, l is the line length on the micrograph, m is the micrograph magnification, and n is the number of grain boundaries crossed by the line. We used 26 transmission electron micrographs and 12 cross-sectional-view transmission electron micrographs to calculate the mean grain diameter.

The reason for the larger grain formation is considered to be less nuclei in the amorphous film. One cause of nucleation is thought to be stress at the Si/SiO_2 interface,[13] where crystal growth begins.[14]

We observed a 560°C-SiH_4 film before annealing by cross-sectional TEM (Fig. 6). These micrographs indicate crystals at the Si/SiO_2 interface. Because the deposition temperature of 560°C was close to the transition temperature, crystallization occurred during deposition due to interface stress,[13] microcrystallites, and/or particles.

The upper micrographs in Fig. 6 show bumps on the Si surface, and the left and right micrographs correspond to bright and dark field images. We performed TED at the bump, and the spot pattern indicated that the bump was crystalline.

At the transition temperature, local epitaxial growth may occur. For example, Ohmi *et al.* reported epitaxial growth at 550°C using Si_2H_6.[15] It is possible that, during deposition, nuclei crystallized in a gas phase deposited on the surface and/or nuclei were caused by the surface migration of adatoms. Crystalline bumps were then grown selectively. Shimizu *et al.* observed large bumps on the polysilicon film and they thought the formation mechanism was a local selective growth.[16]

Figure 9 shows the cross-sectional transmission electron micrographs and the TED pattern of a 560°C-SiH_4 film after annealing. Upper and lower micrographs correspond to bright and dark field images. A few grains were vertically stacked and the polysilicon had a random structure with the bumps on the surface acting as crystallization nuclei. The TED pattern showed spots indicating that the crystal quality of the film was better than that of conventional polysilicon but worse than a 450°C-Si_2H_6 film after annealing.

Figure 11 shows the plane-view transmission electron micrograph and the TED pattern of the film. From Ref. 12

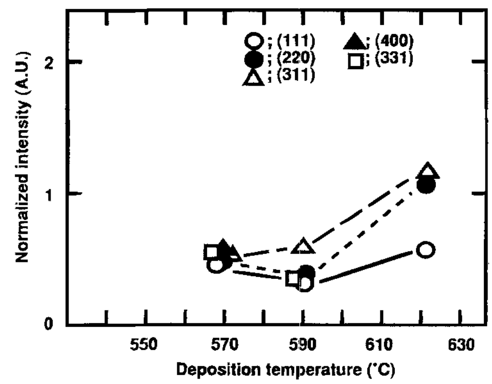

Fig. 13. Normalized intensity of diffraction reflections *vs.* deposition temperatures.

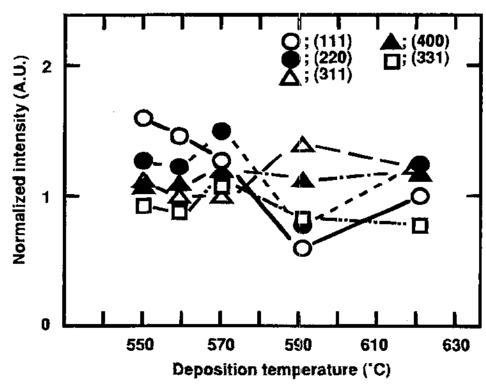

Fig. 14. Normalized intensity of diffraction reflections *vs.* deposition temperatures.

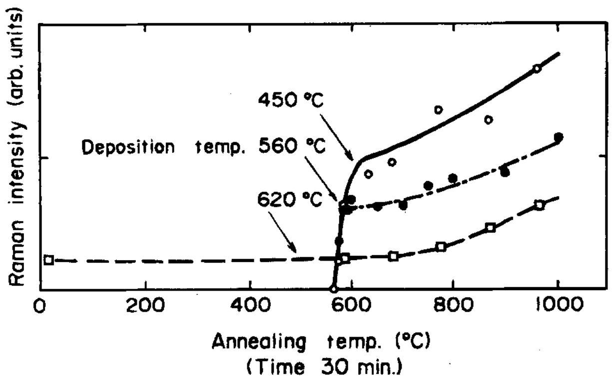

Fig. 15. Raman intensity at 520 cm^{-1} *vs.* annealing temperatures.

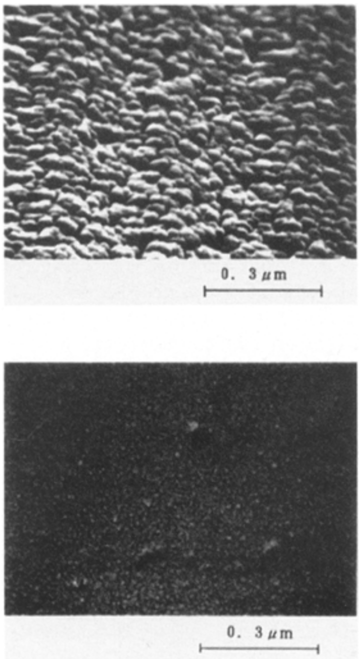

Fig. 16. SEM images of films thinner than 5 nm deposited at (a) 625°C from SiH_4, and (b) 450°C from Si_2H_6.

the average grain size was about 0.3 μm. The TED showed strong and weak spots, indicating that the crystal quality of the film was better than conventional polysilicon.

Figure 12 summarizes the TEM observations. The columnar structure of the 620°C-SiH_4 film was unchanged during N_2 annealing at 600°C for 2 h.

We can conclude that crystals in the amorphous phase must be eliminated to obtain large grains after annealing, and for this, low-temperature deposition and a high deposition rate are promising.

X-ray diffraction.—We studied the relationship between deposition temperature and x-ray diffraction patterns before and after annealing for a film 0.2 μm thick. The normalized peak intensity for the samples before annealing (Fig. 13) shows that below 560°C, the films have no peaks. A 560°C-SiH_4 film is basically amorphous with crystals at the Si/SiO_2 interface, as we saw by TEM. Above 570°C, we saw peaks, and at 590°C, <311>-orientations dominate. Above 590°C, <220>-, and <311>-orientations increase rapidly, and polycrystalline structures form.

The normalized intensity for samples annealed at 1100°C for 30 min in N_2 (Fig. 14) shows that at lower deposition temperatures, peaks are observed and <111>-orientations dominate. The peak intensity of lower temperature deposition is larger. At 590°C, <311>-orientations dominate and <111>-orientations are minor. At 620°C, <111>-orientations increase, but <220>-orientations still dominate. Changes during annealing are the least in at 620°C-deposited films.

It is considered that in the completely amorphous phase, grains tend to be <111>-oriented, and at the transition region, crystallites act as the nuclei of crystallization. So, above the transition region, the dominant texture remains unchanged during annealing.

Raman spectroscopy.—We evaluated the relationship between annealing temperature and crystallinity using Raman spectroscopy at 520 cm^{-1}.[17,18] We annealed samples for 30 min in N_2 (Fig. 15). An SiH_4 film deposited at 620°C shows a peak gradually increasing with annealing temperatures above 620°C. In contrast, an SiH_4 film deposited at 560°C drastically changes when annealed at 570°C. Below 570°C, there was no peak around 520 cm^{-1}, but above 570°C, we observed a large peak whose intensity increased with the annealing temperature. An Si_2H_6 film deposited at 450°C had this same feature with a higher intensity when annealed above 570°C. This change at 570-600°C occurs at the poly/amorphous transition region during LPCVD. We studied the activation energy of crystallization (Fig. 15) and found that at 570-600°C, it is about 7 eV, and above 600°C, it is about 0.2 to 0.4 eV. The silicon self-diffusion process has an activation energy of about 5 eV, which is the same as the Si realignment process.[11] Therefore, during the change, the Si realigns and dehydrates. The 450°C-Si_2H_6 film had 7 atoms percent (a/o) hydrogen.[19]

The Raman intensity at 520 cm^{-1} indicates the Si crystallinity,[17,18] with the crystal quality above the transition temperature given as follows:

Good
450°C-Si_2H_6 film > 560°C-SiH_4 film > 620°C-SiH_4 film
Poor

Results indicate a lower deposition temperature produces better crystal quality.

Initial stages of deposition.—To examine the difference of deposition mechanisms between conventional polysilicon and TAS, we observed films thinner than 5 nm. Since the deposition rate of 625°C-SiH_4 was 9 nm/min, we deposited for 33 s obtaining a film thinner than 5 nm on a substrate with thermally grown oxide (Fig. 16a). Since the deposition rate of 450°C-Si_2H_6 was 2 nm/min, we deposited for 150 s. We observed crystallite nuclei with nucleus densities of about 7×10^{10} cm^{-2}. This indicates that nuclei have formed and were coalescing. Films thinner than 5 nm cannot be deposited under conventional polysilicon deposition conditions.

It has been reported that increasing deposition temperatures decrease the nucleus density and increase the nucleus size.[20] When sites are distributed on an SiO_2 surface, Si adatoms will migrate towards the sites to make Si nuclei, which tend to grow larger at higher temperatures.

The opposite case is thought to be TAS film deposition. When the deposition temperature is low, the migration length is short and the nuclei will be small. If the deposition rate is high at a low temperature, the adatoms may cluster during the deposition and form a film of small clusters. Figure 16b shows an SEM image of a 450°C-Si_2H_6 sample of a film with a smooth surface. Because we only considered the deposition rate, we assumed the deposited film to be 5 nm thick. In general, however, an incubation time exists before deposition, therefore, the deposited film is actually thinner than the calculated thickness, especially in the early stages of deposition.

Conclusions

The activation energies of SiH_4 and Si_2H_6 deposition were 1.7 and 0.6 eV. Below 580°C, Si_2H_6 deposited Si faster than SiH_4, despite the lower flow rate of Si_2H_6. This suggests that Si_2H_6 is a good Si source gas for low-temperature deposition.

The surface of 450°C-Si_2H_6 film was very smooth, with the smooth surface retained during crystallization. The unchanged surface features may be due to a native oxide cover or less thermal energy for surface migration.

The 450°C-Si_2H_6 film was completely amorphous before annealing and had mainly <111>-oriented large grains about 2 μm in diameter after annealing. The completely amorphous structure causes large grain formation after crystallization.

The 560°C-SiH_4 film had crystalline bumps on a smooth amorphous surface, which acted as nuclei during crystallization. As a result, after annealing, a few grains with diameters of about 0.3 μm were stacked vertically.

The activation energy at the transition was about 7 eV, which suggests that the Si realigns and dehydrates at the transition.

The 625°C-SiH_4 sample with depositions less than 5 nm showed nuclei, but the 450°C-Si_2H_6 sample with depositions less than 5 nm showed a film with a plane surface. In the initial stages of deposition, crystallites act as nuclei in conventional polysilicon, but small clusters act as nuclei and form a thin film in TAS.

Acknowledgments

We thank H. Tsutikawa, T. Ono, J. Nakano, M. Yoshida, Y. Namiki, K. Yanagida, and S. Asuma for their encouragement.

Manuscript submitted May 13, 1993; revised manuscript received Dec. 20, 1993.

Fujitsu Ltd. assisted in meeting the publication costs of this article.

REFERENCES

1. H. Watanabe, N. Aoto, S. Adachi, T. Ishijima, E. Ikawa, and K. Terada, in *Extended Abstracts of the 22nd Conference on Solid State Devices and Materials,* p. 873, Japanese Society of Applied Physics (1990).
2. Y. Hayashide, H. Miyata, J. Mitsuhashi, M. Hirayama, T. Higaki, and H. Abe, *ibid.,* p. 869.
3. T. Aoyama, C. Ogawa, M. Sugiyama, H. Takemura, F. Toyokawa, M. Sakamoto, and T. Tashiro, *ibid.,* p. 665.
4. T. Nakazawa, T. Eshita, F. Mieno, Y. Furumura, M. Maeda, and K. Yanagida, in *Extended Abstracts of the Fall Meeting of the Japanese Society of Applied Physics,* p. 579 (1987).
5. F. Mieno, T. Nakazawa, A. Shimizu, T. Hara, Y. Katagiri, Y. Furumura, K. Wada, and K. Yanagida, in *Extended Abstracts of the Spring Meeting of the Japanese Society of Applied Physics and Related Societies,* p. 635 (1989).
6. F. Mieno, T. Sasaki, H. Miyata, H. Nomura, A. Tukune, J. Iizuka, and Y. Furumura, in *Extended Abstracts of the Spring Meeting of the Japanese Society of Applied Physics and Related Societies,* p. 644 (1990).
7. J. Iizuka, F. Mieno, T. Sasaki, H. Miyata, H. Nomura, A. Tukune, and Y. Furumura, *ibid.,* p. 645.
8. F. Mieno, T. Sasaki, H. Miyata, H. Nomura, A. Tukune, J. Iizuka, and Y. Furumura, *ibid.,* p. 645.
9. K. Itabashi, K. Mizutani, T. Koga, M. Matumiya, S. Kawashima, M. Sakata, T. Ema, T. Yabu, K. Toyoda, N. Suzuki, and H. Shimada, *IEDM Tech. Dig.,* 477 (1991).
10. T. I. Kamins, *This Journal,* **121,** 681 (1974).
11. T. I. Kamins, *Polycrystalline Silicon for Integrated Circuit Applications,* p. 49, Kluwer Academic Publishers (1988).
12. F. C. Hall and W. J. Howk, *J. Metals,* **5,** 565 (1953).
13. M. Reiche, Institute of Physics Conference Series No. 117, Sec. 4, p. 201 (1991).
14. M. Horiuchi, T. Kobayashi, and S. Aoki, in *Extended Abstracts of the Spring Meeting of the Japanese Society of Applied Physics and Related Societies,* p. 635 (1989).
15. K. Yamada, T. Ohmi, M. Morita, H. Suzuki, and C. M. Soh, Abstract 555, p. 829, *The Electrochemical Society Extended Abstracts,* Vol. 91-2, Phoenix, AZ, Oct. 13-17, 1991.
16. A. Simizu, K. Kurita, F. Mieno, T. Takada, T. Ono, and K. Inayoshi, Abstract 451, p. 656, *The Electrochemical Society Extended Abstracts,* Vol. 90-2, Seattle, WA, Oct. 14-19, 1990.
17. F. Sato, Y. Hirano, K. Goto, and J. Chikawa, in *Extended Abstracts of the 25th Conference on Solid State Devices and Materials,* p. 579, Japanese Society of Applied Physics (1990).
18. M. Matsuo, S. Inoue, and T. Hashizume, *ibid.,* p. 437.
19. Y. Mishima, M. Hirose, Y. Osaka, K. Nagamine, Y. Ashida, N. Kitagawa, and K. Isogaya, *Jpn. J. Appl. Phys.,* **22,** 46 (1983).
20. T. I. Kamins, *IEEE Trans. Parts, Hybrids, and Packaging,* PHP-10, p. 221, IEEE (1974).