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Crystallographic study of semi-insulating polycrystalline silicon (SIPOS) doped with oxygen atoms

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Thermally deposited silicon films doped with oxygen atoms and used as passivation films on silicon devices have been studied with transmission electron microscopy, x-ray diffraction, and ESCA. The films contain at least two phases, silicon microcrystals and silicon oxide. The size of the microcrystals in as-deposited films was dependent both on the deposition temperature and on the oxygen concentration. Heat treatment caused crystal growth which depended mainly on the annealing temperature and weakly on the annealing time. The lattice constant of the microcrystals was directly related to their size. The silicon oxide phase in as-deposited films was found to be $\text{SiO}_{1.4}$. The results suggest "mosaic" model of the films which are amorphous when the diameter of the silicon microcrystals was less than 10 Å.

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I. INTRODUCTION

The reliability of silicon devices is considerably dominated by surface effects. In planar technology, a thermally grown silicon dioxide layer is used as a passivation film on the surface. A silicon dioxide film, however, has some disadvantages, e.g., it cannot protect the underlying silicon surface from the influence of electronic charges accumulated on the oxide film.

An oxygen-doped polycrystalline silicon film, which is named SIPOS (semi-insulating polycrystalline silicon), used as a substitute for a silicon dioxide film of planar devices is discussed in the literature¹⁻³ and exhibits a number of excellent properties.

As reported before,⁴ SIPOS has a high density of localized states in the energy gap, which pin the Fermi level near midgap. This feature of SIPOS is very similar to that of amorphous silicon.⁵ SIPOS, however, has been considered so far as "polycrystalline" silicon doped with oxygen atoms as expressed by its name because the deposition temperature is relatively high, e.g., 650 °C.

In this paper, we report on the size and the lattice constant of silicon microcrystals in SIPOS measured with transmission electron microscopy and x-ray diffraction and also on some evidences of the existence of the silicon oxide phase proved by ESCA (electron spectroscopy for chemical analysis).

II. EXPERIMENTS

SIPOS film, 2000 Å thick, for transmission electron microscopy was deposited in the same manner as described in our previous paper.⁴ The silicon wafer, of which the surface had been thermally oxidized to a thickness of 5000 Å, was used as a substrate. After deposition, the substrate (silicon wafer and oxide layer) was etched off first with a solution of $\text{HF} + \text{HNO}_3 + \text{HAc}$ and then with a dilute solution of HF . SIPOS film, 1 μm thick, for x-ray diffraction and ESCA measurements was directly deposited onto a silicon wafer.

Most of the specimens were deposited at 650 °C, and some of them were deposited at 600 or 700 °C. Heat

treatment was performed in a dry-nitrogen-gas atmosphere typically for 5 min. The oxygen concentration of SIPOS was measured with an electron probe micro-analyzer. The flatness of the oxygen depth profile in the bulk of SIPOS film was proved by Auger analysis with an *in situ* argon sputtering technique, while the native oxide layer with a thickness of several Å was found on the surface. A reference polycrystalline silicon without oxygen atoms was also prepared by the same method mentioned above.

Three kinds of observations were performed with the transmission electron microscope: (1) selected-area ($1 \mu\text{m}^2$) electron diffraction, (2) a bright-field image, and (3) a dark-field image formed by Si (111) reflection. The electron energy was 200 keV, and the resolution of the image was about 10 Å. $\text{CuK}\alpha$ was used for x-ray diffraction, and powder from the crystalline silicon was used as a reference of the Bragg angle. For an ESCA study, a Dupont 650B with a $\text{MgK}\alpha$ (1254 eV) x-ray source was used. The energy resolution of the equipment was about 1.1 eV, and the pressure in the system was $(0.5-1.0) \times 10^{-7}$ Torr. To avoid the influence of the native oxide layer, chemical etching with a dilute (5%) HF solution was performed just before the measurements. The validity of the surface treatment by this method will be discussed in Sec. IV. The gold film, 5-10 Å thick, was evaporated onto the specimen in the ESCA equipment in order to use Au 4f peaks (82.7 and 86.4 eV) as a binding-energy reference.

III. RESULTS

A. Size of silicon microcrystals in SIPOS

The size of silicon microcrystals (R) was evaluated by two different methods.

Bright spots corresponding to the silicon microcrystals were observed in the dark-field images as shown in Fig. 1. The crystal size directly measured from the photographs are illustrated in Fig. 2, where dotted circles indicate the specimens exhibiting no clear spots in the dark-field images, i.e., the crystal size in these specimens is less than 10 Å even if there exist "crystals". In pure polycrystalline silicon, the crystal size is relatively large and fluctuates widely as

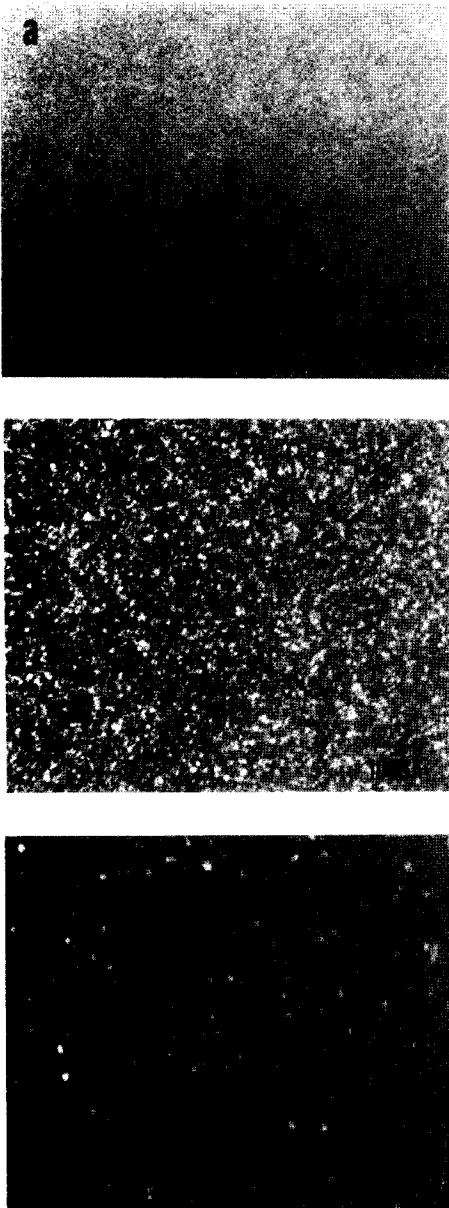


FIG. 1. Dark-field images of SIPOS with 15 at.% oxygen and deposited at 650°C. Specimens are (a) as-deposited (b) annealed at 900°C, and (c) annealed at 1100°C.

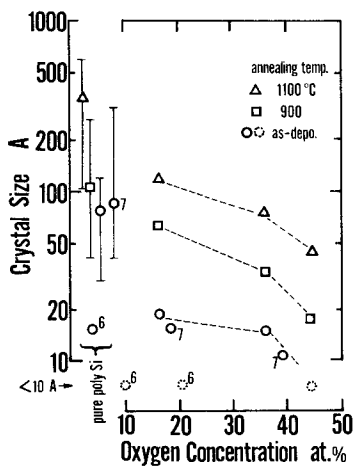


FIG. 2. Size of silicon microcrystals in SIPOS evaluated from bright spots in dark-field images. Small numerals 6 and 7 indicate the deposition temperatures to be 600 and 700°C, respectively. Others were deposited at 650°C.

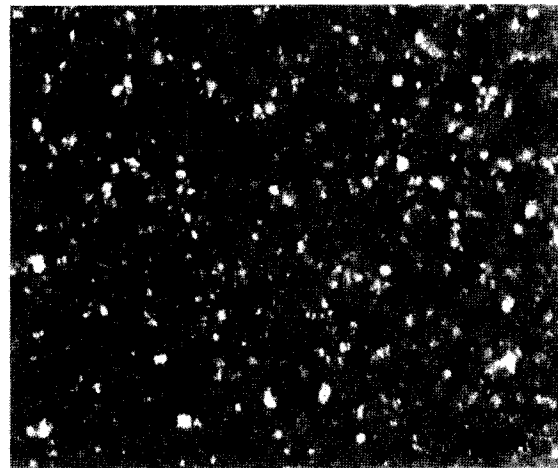


FIG. 3. Dark-field image of pure polycrystalline silicon as-deposited at 650°C.

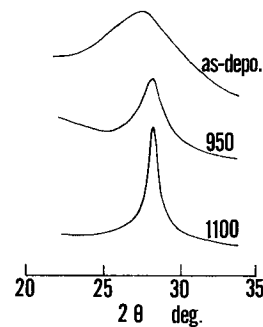


FIG. 4. Changes of the Si (111) x-ray reflection peak induced by heat treatment. The specimen is 650°C deposited SIPOS with 15 at.% oxygen.

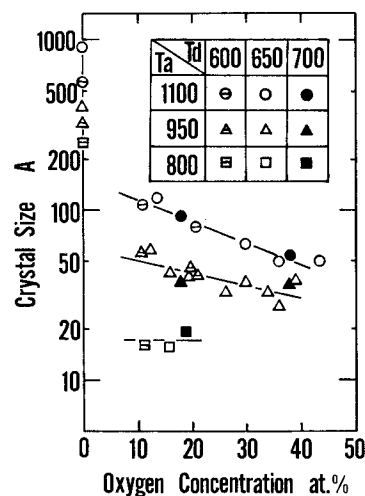


FIG. 5. Size of silicon microcrystals in SIPOS evaluated from the peak widths of Si (111) x-ray reflection. T_d and T_a indicate the deposition and annealing temperatures, respectively.

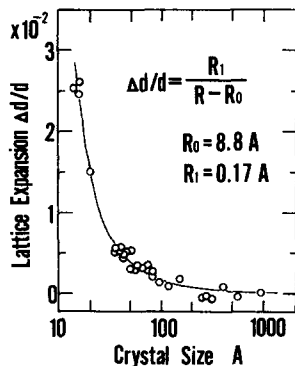


FIG. 6. Relations between the crystal size and the lattice expansion. The solid curve indicates the empirical equation inserted in the figure.

shown in Fig. 3. The range of the fluctuation is indicated by the scale in Fig. 2. On the other hand, the crystal size is relatively uniform in SIPOS.

The peak width of x-ray diffraction (W) is related to the diameter of crystals (R) by the following equation:

$$R = K\lambda / (\beta \cos \theta), \quad (1)$$

where λ is the wavelength of the x-ray, θ is the Bragg angle, K is the Scherrer constant, and β is the corrected peak width and given by⁶

$$K/\beta = (1/0.9) \left(\frac{1}{2} W^2 \left[1 + \left[1 - \frac{4}{3} (\delta/W)^2 \right]^{1/2} \right] - b \right), \quad (2)$$

where δ is the resolution of the spectrometer ($=0.072^\circ$ in our case) and b is the splitting of $K\alpha_1$ and $K\alpha_2$ [$=0.124^\circ$ in the case of Si (111) reflection]. Figure 4 shows the typical peaks corresponding to Si (111) reflection, and Fig. 5 shows the relation between the crystal size obtained from the peak width of Si (111) reflection and the oxygen concentration. The peaks of as-deposited specimens were too wide to estimate R well. The results shown in Fig. 5 have an error of about 30% induced by the lattice strain distribution.⁷ Within this error, Figs. 2 and 5 reveal relatively good agreement. Both Figs. 2 and 5 indicate that the crystal size in heat-treated SIPOS does not depend on the deposition temperature, but depends mainly on the annealing temperature and slightly on the oxygen concentration.

B. Lattice constant of silicon microcrystals

The lattice constant d was determined by x-ray diffraction. In all specimens, d 's were larger than that of crystalline silicon. The lattice expansion $\Delta d/d$ had direct relations to the crystal size rather than to the respective parameters such as oxygen concentration,

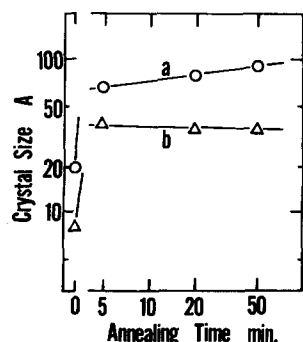


FIG. 7. Isothermal annealing effects on the crystal growth. Specimens are (a) SIPOS with 12 at.% oxygen and (b) SIPOS with 39 at.% oxygen. Both of them were deposited at 650°C and annealed at 950°C .

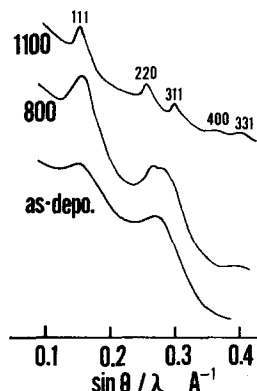


FIG. 8. Changes of the electron diffraction pattern of SIPOS with 15 at.% oxygen induced by heat treatment. Electron energy is 200 keV.

annealing temperature, or deposition temperature. Figure 6 shows this relationship, and it can be described by a simple empirical equation

$$\Delta d/d = R_1 / (R - R_0), \quad (3)$$

where $R_1 = 0.17 \text{ \AA}$ and $R_0 = 8.8 \text{ \AA}$.

Equation (3) indicates that the microcrystals smaller than R_0 do not exist any more in a "crystalline" state. This state can be called an "amorphous" state.

C. Isothermal annealing effects

Figure 7 illustrates the isothermal annealing effects on the crystal growth of silicon microcrystals measured with x-ray diffraction. The crystal growth in both specimens proceeded very rapidly within 5 min, and then only gradual crystal growth was observed in the specimen with 12 at.% oxygen. SIPOS with 39 at.% oxygen revealed no growth. From this fact, it is reasonably stated that the crystal size of heat-treated specimens mainly depends on the annealing temperature and weakly depends on the annealing time.

D. Selected-area electron diffraction

Figure 8 shows photodensitometer traces of electron diffraction patterns of SIPOS with 15 at.% oxygen. The specimen annealed at 1100°C showed almost the same pattern as polycrystalline silicon, while in the as-deposited specimen, Si (220) and Si (311) peaks were overlapped to form one broad peak. In the specimen annealed at 800°C , two peaks were partially overlapped.

In the electron diffraction, the relation between the crystal size and the peak width is also roughly given by Eq. (1), substituting the electron wavelength for λ and setting $K=1$ and $\beta=W$. Using Eq. (1), the crystal size which gives the overlapping of the Si (220) and Si (311) peaks is estimated to be $R \leq 20 \text{ \AA}$. This case corresponds to the specimen annealed at 800°C in Fig. 8, and the value of R ($=20 \text{ \AA}$) agrees well with the size of bright spots observed in the dark-field image.

E. Bright-field image

The contrast of the bright-field image of the SIPOS film can be classified into three categories:

(1) Dark spots corresponding to the bright spots in the dark-field image are shown in Fig. 9(a). This kind

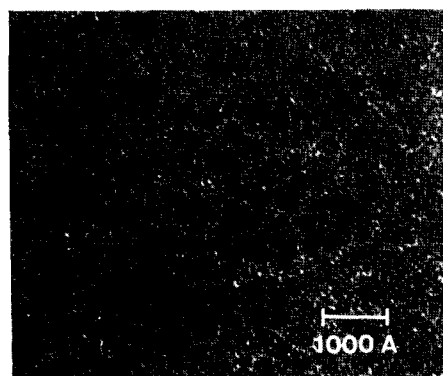
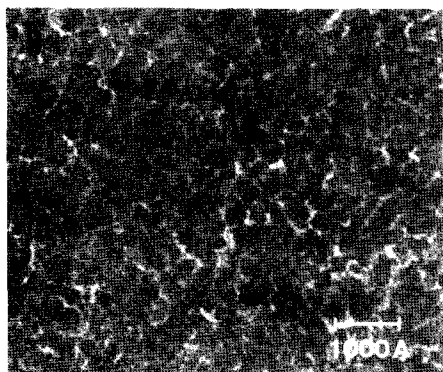
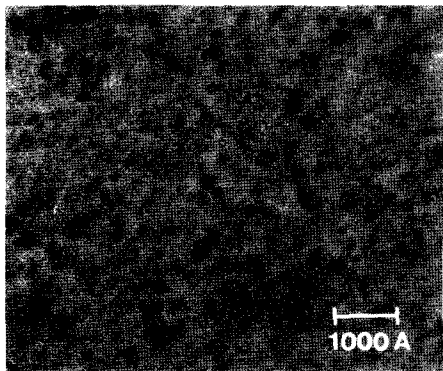


FIG. 9. Bright-field images. Specimens are (a) 1100°C annealed SIPOS with 15 at.% oxygen, (b) as-deposited SIPOS with 43 at.% oxygen, and (c) 1100°C annealed SIPOS with 43 at.% oxygen. All were deposited at 650°C.

of contrast was observed in specimens with low oxygen concentration or in specimens annealed at a relatively high temperature.

(2) Cobweblike contrast, e.g., observed in as-deposited SIPOS with 43 at.% oxygen, is shown in Fig. 9(b). This kind of contrast is very similar to that of amorphous germanium which is attributed to a void network.⁸

(3) Mosaiclike contrast observed in 1100°C-annealed SIPOS with 43 at.% oxygen is shown in Fig. 9(c). Since this specimen contains a large number of oxygen atoms, this contrast is possibly due to the local fluctuation of components in the SIPOS film.

Classification of SIPOS according to the contrast of the bright-field image is illustrated in Fig. 10.

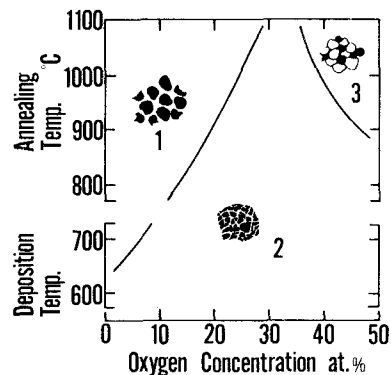


FIG. 10. Classification of SIPOS according to the contrast of bright-field images. Numerals indicate the categories mentioned in the text.

F. Silicon oxide in SIPOS

ESCA was used to investigate the chemical states of silicon atoms in SIPOS.

The Si 2*p* spectra of as-deposited SIPOS consist of two peaks as shown in Fig. 11. The binding energy of the lower-energy peak (98.3 eV) is very close to that of a *p*-type silicon single crystal (97.9 eV). The difference in binding energy is only 0.4 eV, and it possibly corresponds to the difference in the Fermi level. The lower-energy peak is therefore due to silicon atoms in silicon microcrystals. The higher-energy peak (101.3 eV) is due to silicon atoms in a quite different phase which is possibly silicon oxide.

IV. DISCUSSION

The size of silicon microcrystals in as-deposited SIPOS depends both on the deposition temperature and on the oxygen concentration, while the size of microcrystals in heat-treated SIPOS is mainly related to the annealing temperature.

The crystal growth induced by heat treatment can be divided into two stages. In the first stage, as soon as the temperature is elevated, very rapid crystal growth proceeds within a considerably short period. In the second stage, gradual crystal growth follows. As seen in

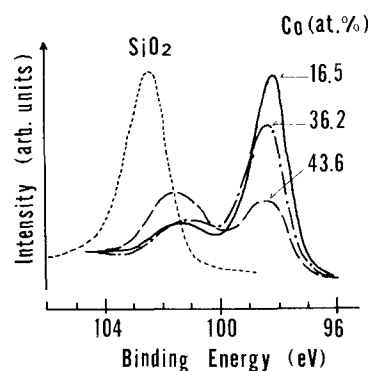


FIG. 11. Si 2*p* ESCA spectra of SIPOS as-deposited at 650°C and thermally grown silicon dioxide. Numerals in the figure indicate the oxygen concentrations of the specimens.

Fig. 7, the rate of growth in the second stage depends on the oxygen concentration. In Figs. 2 and 5, the crystal size of heat-treated specimens depends slightly on the oxygen concentration. This dependence, therefore, can be considered to be due to the second-stage growth mentioned above. If so, it is concluded that the first-stage growth has only annealing temperature dependence and the second-stage has oxygen concentration dependence. Furthermore, we speculate as follows: In the first stage, microcrystals "melt" because such small particles, as found in SIPOS, have high surface (interface) energy which can lower the melting point to a temperature determined by their size.⁹ In the second stage, gradual crystal growth follows due to the diffusion of silicon atoms, which depends on the oxygen concentration.

The lattice constant of microcrystals is, as expressed by Eq. (3), determined by their size only. The size is so small that the surface energy takes a large ratio in the total energy of the microcrystal. The lattice constant of such a small particle is therefore governed mainly by the surface energy. The application of this idea to the microcrystals in SIPOS leads us to the following statements. Even though two microcrystals, which have the same crystal size, exist in different SIPOS with different oxygen concentrations or annealed at different temperatures, these microcrystals should have the same material surrounding them. If the material is silicon oxide or free surface, oxygen concentration or the density of localized states would exceed the measured value,⁴ respectively. Therefore, we believe the material to be the disordered silicon.

ESCA spectra of the Si 2*p* level indicate that there are two kinds of silicon atoms in SIPOS, one of which is silicon atoms in silicon microcrystals and the other is possibly silicon atoms in silicon oxide. The higher-energy peak shows a binding-energy shift of 3.0 eV. Raider and Flitsch¹⁰ reported that silicon atoms in silicon dioxide experience a 4.4-eV chemical shift and silicon atoms in silicon monoxide experience a 2.2-eV chemical shift. They also reported that a linear, or nearly linear, empirical relationship exists between changes in binding energy and changes in oxygen content of silicon oxide. Using their results, the chemical

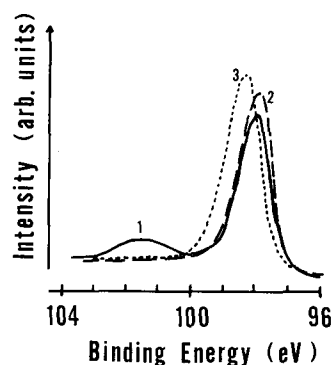


FIG. 12. Si 2*p* ESCA spectra of *p*-type silicon single crystals and pure polycrystalline silicon. Specimens are (1) a silicon single crystal before the chemical etching treatment, (2) a silicon single crystal just after etching, and (3) pure polycrystalline silicon just after etching.

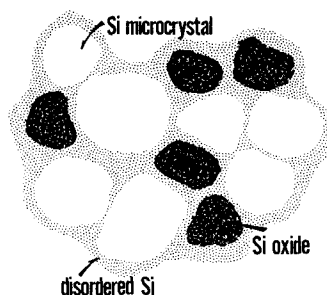


FIG. 13. "Mosaic" model of SIPOS. Heat-treated SIPOS with about 15 at.% oxygen is assumed for the figure.

composition of silicon oxide in as-deposited SIPOS is expressed as SiO_{1.4}. There is left some doubt, however, whether the higher-energy peak was due to the native oxide layer which might remain on the surface even after the chemical etching treatment. Figure 12 shows three ESCA spectra of a silicon single crystal before and after etching and of pure polycrystalline silicon after etching. Figure 12 indicates that the native oxide layer which might remain on the surface even after the etching was not detectable in our measuring conditions. Comparing Figs. 11 and 12, we believe that the higher-energy peaks shown in Fig. 11 come from the bulk of the SIPOS film and that SIPOS contains silicon oxide.

Following the discussions mentioned above, we propose the "mosaic" model of SIPOS as shown in Fig. 13.

The lattice expansion possibly causes the increase of the energy gap. In the previous paper,⁴ we reported that the energy gap of SIPOS was considerably larger than that of crystalline silicon. The difference is, however, too large to be attributed to the lattice expansion only. For example, the increase of the energy gap of 940 °C annealed SIPOS with 36 at. % oxygen is about 0.4 eV.⁴ On the other hand, the increase of the energy gap due to the lattice expansion can be calculated by the following equation:

$$\frac{\Delta d}{d} = \frac{1}{3} \frac{\Delta v}{v} = \frac{1}{3} \frac{1}{v} \frac{\Delta v}{\Delta p} \frac{\Delta p}{\Delta E_g} \Delta E_g, \quad (4)$$

where *v* is the volume, *p* is the pressure, *E_g* is the energy gap, $\Delta E_g/\Delta p = -1.97 \times 10^{-12}$ eV cm²/dyn, and $(1/v)(\Delta v/\Delta p) = -0.98 \times 10^{-12}$ cm²/dyn in the case of crystalline silicon.¹¹ Calculation of Eq. (4) using $\Delta d/d = 8 \times 10^{-3}$, which is obtained from Figs. 2 and 6, results in a value of $\Delta E_g = 0.05$ eV. Therefore, the increase of the energy gap of SIPOS should be mainly due to the localization of the band tail.

V. CONCLUSIONS

The crystallographic structure of SIPOS was investigated with transmission electron microscopy, x-ray diffraction, and ESCA. We conclude:

- (1) SIPOS contains silicon microcrystals and silicon oxide.
- (2) Crystal size in as-deposited SIPOS is determined by the deposition temperature and the oxygen concentra-

tion. In some cases, silicon microcrystals are less than 10 Å, and SIPOS film is considered to be in an "amorphous" state.

(3) SIPOS annealed at temperatures higher than 900 °C contains silicon microcrystals, the size of which depends mainly on the annealing temperature and weakly on the oxygen concentration.

(4) The lattice constant of microcrystals is larger than that of crystalline silicon and is a function of their size only.

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¹T. Aoki, T. Matsushita, H. Yamoto, H. Hayashi, and Y. Kawana, *Electrochemical Society Spring Meeting*, Extended

Abstracts 74-1 (Electrochemical Society, Princeton, N.J., 1974), A 64.

²T. Matsushita, T. Aoki, T. Otsu, H. Yamoto, H. Hayashi, M. Okayama, and Y. Kawana, *Jpn. J. Appl. Phys. Suppl.* **15**, 35 (1975).

³H. Mochizuki, T. Aoki, H. Yamoto, M. Okayama, M. Abe, and T. Ando, *Jpn. J. Appl. Phys. Suppl.* **15**, 41 (1975).

⁴M. Hamasaki, T. Adachi, S. Wakayama, and M. Kikuchi, *Solid State Commun.* **21**, 591 (1977).

⁵See, for instance, N. F. Mott and E. A. Davis, *Electronic Processes in Non-crystalline Materials* (Clarendon, Oxford, 1971), Chap. 2.

⁶R. Brill, *Z. Kristallogr. Kristallgeom. Krystallphys.* **68**, 387 (1928).

⁷Exactly speaking, the broadening of the peak of x-ray diffraction is induced both by the crystal size and the lattice strain distribution η . Since the contribution of the lattice strain is given by $2\eta \sin\theta/\lambda$, the true crystal size must be obtained by plotting the peak widths of various reflections against $\sin\theta/\lambda$, and the value of R in the case $\sin\theta/\lambda \rightarrow 0$ gives the true R according to Eq. (1). In our case, however, the intensity of the reflected x-ray was so weak that the plotting was not performed. The error by neglecting the contribution of η is assumed to be within 30%.

⁸T. M. Donovan and K. Heineman, *Phys. Rev. Lett.* **27**, 1794 (1971).

⁹M. Takagi, *J. Phys. Soc. Jpn.* **9**, 359 (1954).

¹⁰S. I. Raider and R. Flitsch, *J. Electrochem. Soc.* **123**, 1754 (1976).

¹¹H. F. Wolf, *Silicon Semiconductor* (Pergamon, New York, 1969), Chap. 1.