PHYSICAL REVIEW B VOLUME 34, NUMBER 7 1 OCTOBER 1986

Kinetics of phase transformation from PdSi to Pd_2Si

Toyohiro Chikyow and Iwao Ohdomari
School of Science and Engineering, Waseda University, Shijuku-ku, Tokyo 160, Japan

Setsu Suzuki
Advanced Material Laboratory Inc., Sohka-shi, Saitama Prefecture 240, Japan

(Received 22 January 1986)

We have investigated a phase transformation from PdSi to Pd_2Si using x-ray diffraction and scanning electron microscopy combined with Auger-electron-spectroscopy analysis. PdSi initially formed by annealing an epitaxial Pd_2Si layer on Si at 850 °C transformed to Pd_2Si by a postannealing below 750 °C. After the phase transformation, small grains of Pd_2Si and Si have been observed. Ninety percent of the surface area of the sample postannealed at 650 °C was covered with Pd_2Si grains, while only 75% of the surface area was covered with Pd_2Si grains for the sample postannealed at 750 °C. The period for the transformation was measured as a function of the postannealing temperature and had a concave temperature dependence with a minimum at 650 °C. The difference in the surface morphologies and the temperature dependence of the transformation period can be explained on the basis of nucleation and mass transport. The rate of the nucleation is a function of the supercooling which is faster at lower annealing temperatures. Mass transport for growth of Pd_2Si nuclei is controlled by diffusion of atoms, the coefficient of which is higher at higher annealing temperatures.

I. INTRODUCTION

Phase transformation from PdSi to Pd_2Si was first reported by Tsauer *et al.* by annealing PdSi below 750 °C.[1] This result is obviously contradictory to the existing binary-phase diagrams given by Hansen[2] and Elliott.[3] They attributed the phase transformation to the excess interfacial free energy of the PdSi/crystalline-Si interface because the transformation occurred only when the PdSi layer was in contact with the crystalline-Si substrate.[1] Tu also examined the phase transformation by means of x-ray diffraction and discussed the phenomenon from a viewpoint of volume free-energy change, ΔG.[4]

These works shed light on the reversible phase transformation between Pd_2Si and PdSi. However much has not been discussed on the inconsistency with the existing phase diagrams and reaction kinetics.

A new phase diagram proposed by Langer and Wachtel based on new experimental data predicts that PdSi is stable only above 824 °C and below this temperature Pd_2Si is stable.[5] Thus one of the major problems associated with the reversible phase transformation has been solved. The remaining problem is a reaction kinetics.

In the present work, we have measured the time necessary for phase transformation from PdSi to Pd_2Si (designated as the phase-transformation period hereafter) as a function of annealing temperature and found that both the degree of supercooling and mass transport control the phase-transformation period. We also discuss the surface morphology of Pd_2Si after the phase transformation in terms of nucleation and growth which also are dependent on the degree of supercooling and the mass transport.

II. EXPERIMENTAL PROCEDURE

Si(111) wafers with resistivity of $4 \sim 7$ Ω cm were used throughout the whole experiment. After the usual cleaning processes, a thin oxide layer was grown on a Si substrate in a boiling mixture of $NH_4OH:H_2O_2:H_2O = 1:2:7$ and etched in a diluted HF solution just before loading into a vacuum chamber.

Pd films of 100 nm were deposited onto the Si substrates with an electron gun in vacuum lower than 3×10^{-6} Pa. Samples were heated at 250 °C for an hour in dry N_2 to form Pd_2Si and subsequently at 850 °C for an hour to form PdSi. The uniformity of the PdSi layers formed by the two-step heat treatment was much better than the ones formed by a single heat treatment at 850 °C. The PdSi layers were further heat treated at a temperature lower than 824 °C for several hours to transform PdSi to Pd_2Si (designated as postannealing hereafter). Phases of the films at each annealing stage were identified by x-ray diffraction and morphology by scanning electron microscopy (SEM) and Auger-electron spectroscopy (AES).

III. RESULTS

Figure 1 shows a series of x-ray spectra of a sample after successive annealing at 250 °C, 850 °C, and 750 °C. After the heat treatment of 250 °C for an hour, peaks of Pd_2Si and Pd were observed as shown in Fig. 1(a), indicating the coexistence of epitaxial Pd_2Si with (0016) orientation parallel to Si(111) and the unreacted Pd layer. A subsequent annealing at 850 °C for an hour converted both the Pd_2Si and the unreacted Pd into PdSi with polycrystalline structure as shown in Fig. 1(b). This is the expected result from the temperature of phase transformation from Pd_2Si to PdSi; 824 °C on a Si(111) substrate.[5] A fur-

©1986 The American Physical Society

ther annealing at 750 °C for 24 h transformed PdSi back to Pd_2Si as shown in Fig. 1(c). Annealing of PdSi at 650 °C for 24 h also transformed the PdSi back to Pd_2Si. The Pd_2Si films thus formed were not epitaxial to the Si substrates but polycrystalline. The results were very similar to the ones reported previously.[1,4]

Figures 2(a) and 2(b) show surface morphology of the samples after the postannealing at 750 °C and 650 °C for 24 h, which were observed by SEM. Dark and bright regions in the figures are identified with Si and Pd_2Si from the AES signal shape analysis. For the sample postannealed at 750 °C [Fig. 2(a)], the Pd_2Si region covers 75% of the surface area and the Si region 25%. For the sample postannealed at 650 °C [Fig. 2(b)], surface morphology was similar to the one postannealed at 750 °C, but the ratio of coverage with Pd_2Si is different. Pd_2Si covers 90% of the surface and Si only 10%.

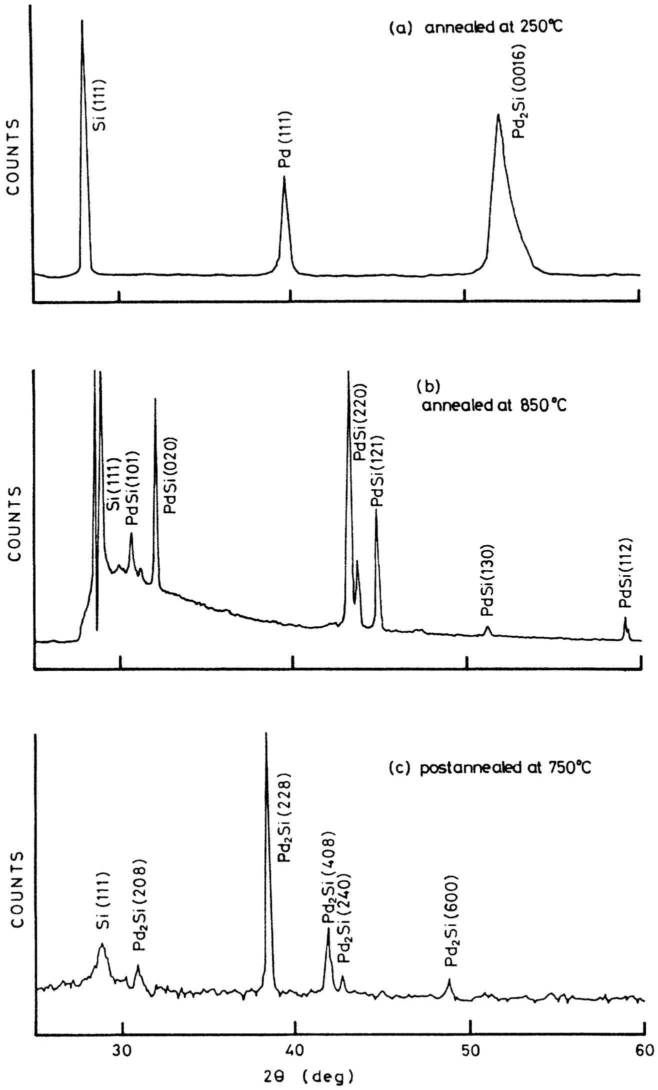

FIG. 1 X-ray diffraction patterns for the samples after the successive annealing at (a) 250 °C, (b) 850 °C, and (c) 750 °C. (a) Shows that the epitaxial Pd_2Si exists and the unreacted Pd films remain after the annealing at 250 °C for an hour. (b) The spectra of the polycrystalline PdSi after the successive annealing at 850 °C for an hour following the first annealing at 250 °C. (c) The spectra of the polycrystalline Pd_2Si, indicating that the reversible phase transformation from PdSi to Pd_2Si occurred by the postannealing at 750 °C for 24 h following the second annealing at 850 °C.

Cross-sectional SEM micrograph of the sample postannealed at 750 °C for 24 h is shown in Fig. 2(c). It is clearly seen that the Pd_2Si region is wider at the surface and narrower at the interface like a trapezoid. In this connection, in the sample postannealed at 800 °C for 24 h, semispherelike small Pd_2Si grains about 20 nm in diameter were observed at the PdSi surface. This obviously indicated that Pd_2Si nucleates at the PdSi surface and then grows isotropically until the growth front reaches the PdSi-Si interface. Figure 2(d) also shows the cross-sectional micrograph of the sample postannealed at 650 °C for 24 h. There can be seen a clear difference from the one postannealed at 750 °C. The silicide region is almost entirely Pd_2Si. In addition, the thickness of the silicide layer is rather thinner than that of initial PdSi and this thickness value is very close to that of Pd_2Si formed by the first annealing at 250 °C.

In order to examine the reaction kinetics for the Pd_2Si formation, the period for phase transformation was measured as a function of annealing temperature. The period was defined as that for disappearance of PdSi peaks in x-ray diffraction spectra by postannealing below 824 °C. Si samples with PdSi overlayers were annealed at 750 °C, 650 °C, 600 °C, and 550 °C for several hours. The result is shown in Fig. 3. 200-nm-thick PdSi is transformed to Pd_2Si by the postannealing at 750 °C, 650 °C, and 600 °C, for 9 h, 6 h, and 14 h, respectively. At 550 °C, the annealing for 24 h was not long enough to convert the PdSi completely to Pd_2Si. The result is shown by the triangle in Fig. 3. Clearly much longer annealing time is necessary. A dashed vertical line indicates the temperature for the phase transformation from Pd_2Si to PdSi; 824 °C. From Fig. 3 the phase transformation period has a minimum around 650 °C.

IV. DISCUSSION

Detailed atomic motion during the phase transformation is not known yet, but we can explain the temperature dependence qualitatively by taking the nucleation rate and mass transport into consideration. Suppose the initial stage of the reversible phase transformation is controlled by the nucleation of Pd_2Si at the PdSi surface. In general, the nucleation rate N can be expressed as follows:

$$N \propto \exp\left[-\frac{\Delta G^*}{kT}\right]. \tag{1}$$

Here, ΔG^* is an activation energy for nucleation and kT has the usual meaning. ΔG^* has a dependence on the degree of supercooling ΔT from the phase-transformation

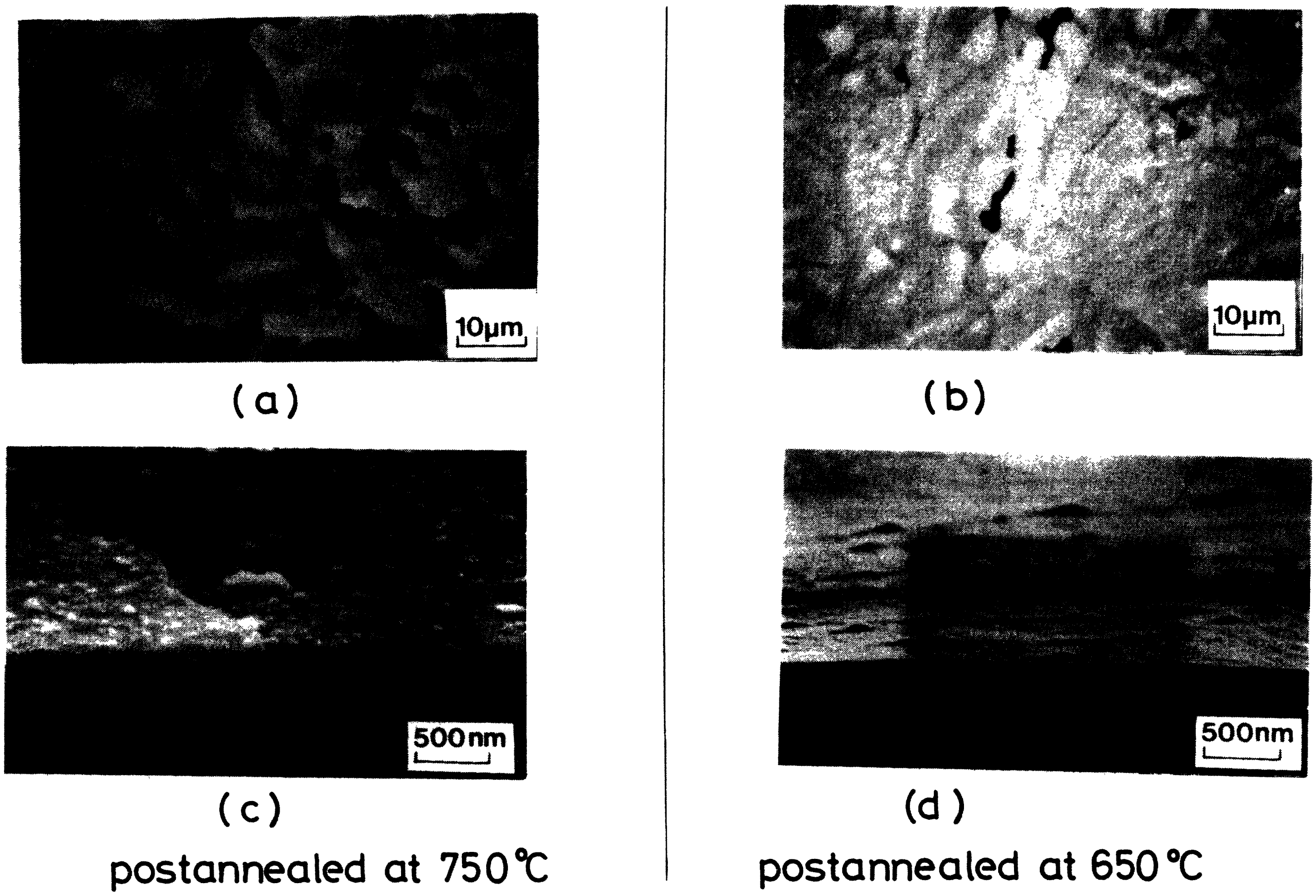

FIG. 2. Surface morphologies and cross-sectional SEM micrographs. (a) and (c) show the surface morphology and cross-sectional view of the sample postannealed at 750 °C for 24 h. Surface was divided into bright Pd_2Si regions and dark Si regions. From the micrograph of (c) it was found that the Pd_2Si region has a reversed trapezoid structure. (b) and (d) are the surface and cross-sectional micrographs of the one postannealed at 650 °C for 24 h. The surface was almost covered with Pd_2Si layer. The cross-sectional view also indicates the same structure.

temperature. A relation between ΔG^* and ΔT is given by the classical nucleation theory[6] as follows:

$$\Delta G^* = \frac{16\pi\sigma^3 V}{3(\Delta S)^2(\Delta T)^2} . \tag{2}$$

Here σ is the specific surface energy, V the volume of the nuclei, and ΔS the entropy change from PdSi to Pd_2Si. From Eqs. (1) and (2), greater ΔT will reduce ΔG^* which, in turn, will increase the nucleation rate considerably. Since, when the kinetics are nucleation limited, the phase transformation period is inversely proportional to the nucleation rate, the shorter period results. This situation is denoted by an ascending curve to the right in Fig. 4.

On the other hand, the phase transformation period depends also on grain growth which is controlled by mass transport. The diffusion coefficient D has a temperature dependence as follows:

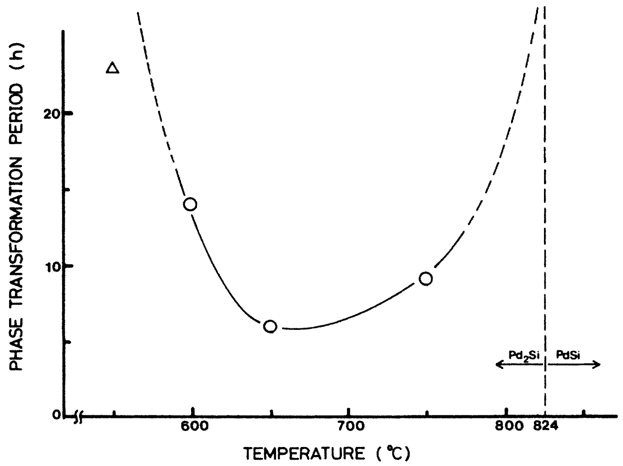

FIG. 3. Phase transformation period from PdSi to Pd_2Si as a function of the annealing temperature. Dashed vertical line at 824 °C denotes the phase transformation temperature in the PdSi-Pd_2Si system. Circles are the period for complete transformation and the triangle is the one for incomplete transition.

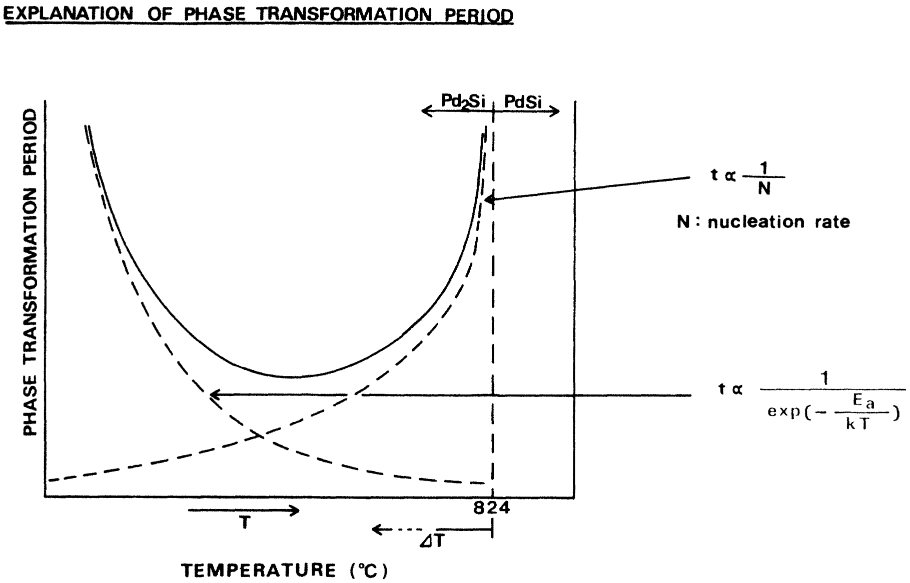

FIG. 4. Explanation for the concave curve of the phase transformation period. There are two contributions: One is the nucleation rate of Pd_2Si (descending curve to the right) and the other is mass transport (ascending curve to the right).

$$D = D_0 \exp\left[-\frac{E_a}{kT}\right]. \tag{3}$$

Here D_0 is a prefactor and E_a is an activation energy for diffusion. At higher temperature, the diffusion coefficient becomes larger and this leads to a decrease in the phase transformation period. This tendency is also shown in Fig. 4 with a descending curve to the right. Linear combination of these curves gives the temperature dependence of the total period for the phase transformation (solid curve), which is qualitatively close to the relation obtained by the experiment.

The difference in surface morphology shown in Fig. 2 can also be explained in terms of the nucleation rate of Pd_2Si and mass transport. At 750 °C, the amount of supercooling is not so great and nucleation occurs at the well-separated portion of the PdSi surface. The reaction for Pd_2Si formation is expressed as

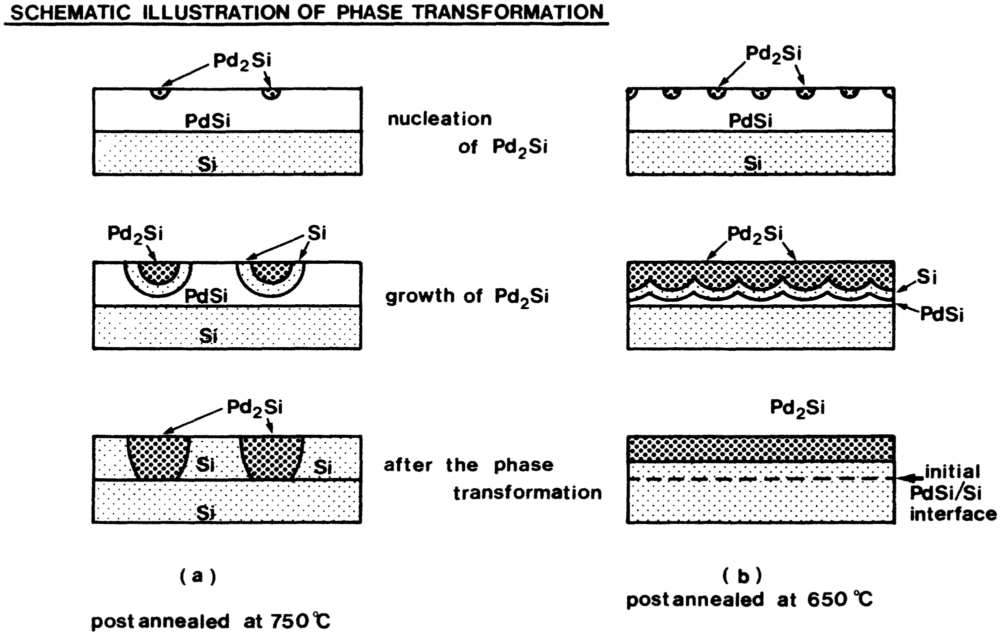

FIG. 5. Schematic illustrations of the phase transformation from PdSi to Pd_2Si. (a) The case of the sample postannealed at 750 °C. Surface consists of the Pd_2Si region and the Si region. The thickness of the transformed layer is close to the initial PdSi thickness. (b) The case of the one postannealed at 650 °C. Surface is almost covered with the Pd_2Si layer. The thickness of the transformation region is a little thinner than the initial PdSi layer.

$$2\mathrm{PdSi} \rightarrow \mathrm{Pd_2Si} + \mathrm{Si} \, . \quad (4)$$

The subsequent grain growth occurs rather quickly due to high diffusivity of atoms at high temperature. Although the diffusing species during the phase transformation are not identified yet, for the grain growth of Pd_2Si of 1 cm^3 to take place, Si atoms numbering 1.0×10^{22} atoms/cm^3 have to go out and Pd atoms numbering 1.44×10^{22} atoms/cm^3 have to come in. This would indicate that both Si and Pd atoms move, and the grown Pd_2Si grains are surrounded by Si skins with thickness much thinner than the diameter of the grains. After the growth front of the grains reaches the original PdSi/Si interface, further grain growth is allowed only in the direction parallel to the surface. Consequently, as schematically shown in Fig. 5(a), large grains of Pd_2Si become separated by Si regions. In other words, Si atoms used for the normal transformation from Pd_2Si to PdSi are predominantly emitted laterally without changing the consumed Si thickness very much.

At 650 °C, contribution of the nucleation is relatively greater than the mass transport. In the early stage a number of Pd_2Si nuclei appear on the PdSi surface which coalesce during subsequent grain growth to form an almost continuous Pd_2Si film. Then the mass transport predominantly occurs vertically, which results in a considerable decrease in the consumed Si thickness. This situation is schematically drawn in Fig. 5(b). The reduction was actually observed as shown in Fig. 2(d).

V. CONCLUSIONS

We have investigated the phase transformation from PdSi to Pd_2Si in terms of surface morphology and the phase transformation period using x-ray diffraction, SEM, and AES. Throughout the experiments the following has been concluded.

(1) PdSi transforms back to Pd_2Si by heat treatment below the phase transformation temperature, 824 °C.

(2) After the phase transformation, the surface region of the samples was divided into Pd_2Si and Si. For the sample postannealed at 750 °C for 24 h, 75% of the surface area was Pd_2Si and 25% was Si. For the one postannealed at 650 °C for 24 h, Pd_2Si and Si were 90% and 10%, respectively.

(3) The phase transformation period has a temperature dependence with a minimum around 650 °C. This is a result of two competing factors, the nucleation rate of Pd_2Si at PdSi surface due to supercooling and the mass transport for the grain growth of Pd_2Si.

(4) The difference in the surface morphology can be explained by two contributions of the nucleation rate and the mass transport.

ACKNOWLEDGMENTS

The authors are grateful to K. Konuma and H. Aochi of Waseda University for their cooperation.

---

[1] B. Y. Tsaur and M-A Nicolet, Appl. Phys. Lett. **37**, 708 (1980).
[2] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[3] R. P. Elliott, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill, New York, 1965).
[4] K. N. Tu, J. Appl. Phys. **53**, 428 (1982).
[5] H. Langer and E. Wachtel, Z. Metallkd. **72**, 767 (1981).
[6] D. Turnbull, J. Chem. Phys. **20**, 411 (1952).

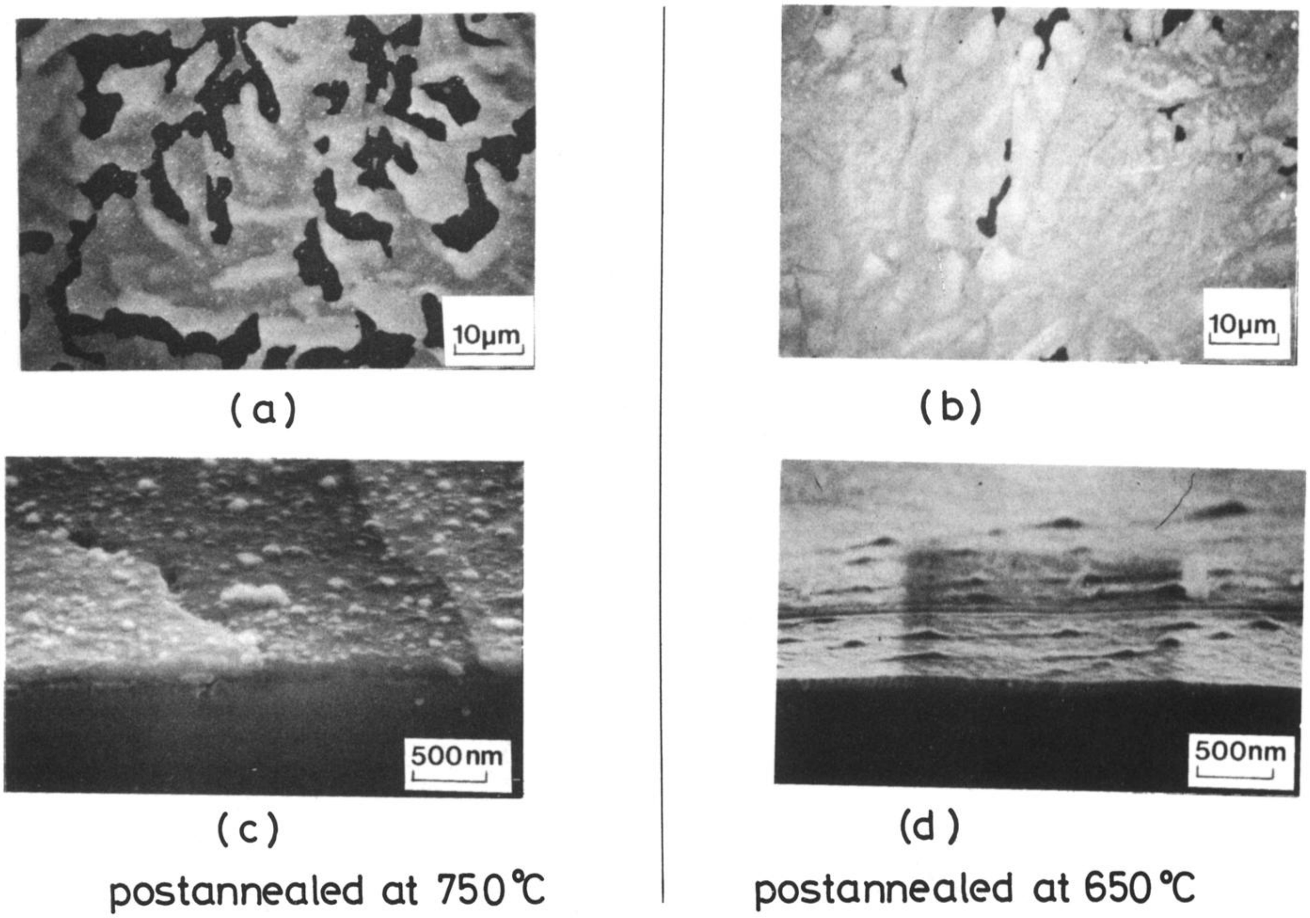

FIG. 2. Surface morphologies and cross-sectional SEM micrographs. (a) and (c) show the surface morphology and cross-sectional view of the sample postannealed at 750 °C for 24 h. Surface was divided into bright Pd_2Si regions and dark Si regions. From the micrograph of (c) it was found that the Pd_2Si region has a reversed trapezoid structure. (b) and (d) are the surface and cross-sectional micrographs of the one postannealed at 650 °C for 24 h. The surface was almost covered with Pd_2Si layer. The cross-sectional view also indicates the same structure.