

Pd-silicide의 이온혼합에 따른 미세구조 변화와 규소화합물 생성온도에 관한 Ar^+ 이온의 조사효과

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Ar^+ irradiation effect on the change of microstructure and
the silicide formation temperature of the ion beam mixed Pd-silicide

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Si(111) 기판 위에 Pd를 증착시킨 뒤 실온 하에 80 keV의 에너지를 가진 Ar^+ 이온을 Pd/Si 이중박막 위에 조사시켰다. Ar^+ 이온을 조사한 이중박막에 열을 가하면서 규소화합물의 생성온도와 표면상태의 개선 정도를 RBS, XRD, AES 등을 이용하여 연구하였다. Ar^+ 이온조사에 의하여 Pd_2Si 생성 온도는 현저하게 낮아지고 표면의 상태는 상당히 개선된 것으로 관측되었다. 이러한 보다 낮은 온도에서의 Pd-silicide 형성과 매끄러운 표면의 개질은 원자혼합 과정에 따라 박막사이의 구성성분의 분산에 의한 것으로 설명되어진다.

Key Words : Ar^+ irradiation, Pd-silicide formation temperature

소제목 : Ar^+ irradiation effect on the Pd-silicide formation temperature

1. Introduction

Recently, the ion beam mixing technique has been intensively investigated for application in the formation of silicide, because ion beam mixing induced silicides possess much smoother surfaces and interfaces, and better electrical properties in comparison with sintered silicides^{1) 6)}. However, most ion beam-mixing studies have been primarily conce-

rned about phase identification, phase transition, and parameters influencing spatial redistribution of the elemental species due to ion irradiation. Only a little attention was given to the investigation of the modification of surface microstructure such as grain growth^{4) 5)}, surface roughness¹¹⁾, and the change in silicide formation temperature¹²⁾ due to ion irradiation, which are very important factors in practical aspect.

Thus the present study is intended to investigate the effect of Ar^+ irradiation on the surface microstructure and the change in silicide formation temperature during post-annealing after Ar^+ irradiation in Pd/Si bilayered system.

2. Experimental procedure

A polished n-type Si(111) single crystal was cleaned by consecutive ultrasonic cleaning in trichloroethylene, acetone, methanol and 18 M Ω deionized water. After etching in 5% aqueous HF, a Pd film of 450Å in thickness was deposited on Si substrate. Mixing was carried out with a 150 keV accelerator at room temperature and under the base pressure of 2×10^{-10} Torr. To avoid further heating due to ion bombardment, the sample was glued onto a heat sink (copper block) with a thermally conductive heat compound. The Ar^+ ion energy was chosen to be 80keV so as to give the value of $R_p + \Delta R_p$ approximately equal to the Pd thickness, where R_p is the mean projected range of Ar^+ in Pd and ΔR_p is the standard deviation of R_p . Doses from 1×10^{15} Ar^+/cm^2 to 1.5×10^{16} Ar^+/cm^2 were used for mixing the Pd/Si bilayer at a beam current density of $1 \mu\text{A}/\text{cm}^2$.

The mixing profiles were analysed by means of 1.4 MeV He^+ backscattering(RBS) with target tilted to an angle of 78° to give and enhancement of the depth resolution. 1.4 MeV He^+ beam extracted from 2 MeV Van der Graaff was magnetically analysed and collimated to 1mm^2 spot on the sample. The energy of the backscattered He^+ ions was analysed with a surface barrier detector at a laboratory scattering angle of 160° . A

X-ray diffractometer (XRD, Cu- α radiation) was employed to identify the phase of the silicide induced by Ar^+ irradiation. Peak positions were determined using a computer attached to the X-ray diffractometer. Auger electron spectroscopy(AES) was used to study the change in Pd-silicide formation temperature during post-annealing after Ar^+ irradiation. The primary electron energy and the modulation voltage were maintained at 3 keV and 2.2 V peak-to peak, respectively. Sputtering was carried out with a 3 keV Ar^+ beam. To elucidate the mechanism for the reduction in silicide formation temperature, Pd or Si film was in-situ deposited and annealed under the base pressure of 5×10^{-10} Torr. The surface morphology of specimen was observed using scanning electron microscope(SEM).

3. Results and Discussion

Typical RBS spectra for Pd/Si bilayers irradiated with Ar^+ ions at the doses of 3×10^{15} Ar^+/cm^2 and 1×10^{16} Ar^+/cm^2 are shown in fig. 1. At the dose of 3×10^{15} Ar^+/cm^2 , the RBS spectra do not show any well developed steps on the high energy edge of Si and the trailing edge of Pd signal, suggesting that the formation of a stoichiometric compound has not occurred across the Pd/Si interface due to Ar^+ irradiation, that is, the trailing edge of Pd signal shifts to the lower energy, and the high energy edge of the Si-signal shifts to the higher energy. At the dose of 1×10^{16} Ar^+/cm^2 , the RBS spectrum shows clearly a well defined steps on the high energy edge of Si-signal and the whole range of Pd, representing the formation of a uniform mixed layer with atomic composition of Pd_2Si . In

general, the RBS observation is not sufficient for determining what compounds or equilibrium phases are present in the mixed layer. In this case, XRD technique is useful since this is possible to obtain diffraction patterns or peaks corresponding to the crystalline structures. Thus we performed the XRD observation.

The XRD patterns for the as-deposited sample and the samples mixed with 3×10^{15} Ar⁺/cm² and 1×10^{16} Ar⁺/cm² are shown in Fig 2. The values of 2θ and the (hkl) indices are shown in figure. Since deposited thickness of Pd layer is very thin, the substrate Si(111) peak appears. As compared with the $2\theta = 39.98^\circ$ for the as-deposited sample, the corresponding 2θ for Pd(111) peak is decreased to 39.26° , and the full width at half-maximum(FWHM) is increased from 0.45° to 0.89° after 3×10^{15} Ar⁺/cm² irradiation. The XRD pattern of the sample irradiated with 1×10^{16} Ar⁺/cm² exactly coincide with that of bulk Pd₂Si³⁾, which is the same as the RBS result shown in Fig 1.

The XRD peak shift might be arisen from the formation of the solid solution of Pd_{1-x}Si_x. Assuming that the ideal solid solution of Pd_{1-x}Si_x is induced by the Ar⁺ irradiation, and that the shift in 2θ is totally due to the formation of this solid solution, the value of x is found to be 0.5 from Fig. 2(a) and Fig. 2(b) using Vegard's law. But the broadening in FWHM for the Pd(111) peak cannot be explained by the formation of this solid solution.

Another possible explanation of the peak shift in Bragg's angle and the broadening in FWHM may be associated with the tensile strain and the defect generation due to Ar⁺ irradiation. If a uniform tensile strain is given to the material by the Ar⁺ irradiation, the

lattice spacing becomes larger than its equilibrium spacing, and the corresponding diffraction line shifts to lower angle. The lattice expansion calculated from the Pd(111) peak positions in Fig. 2(a) and Fig. 2(b) is found to be 1.8%. However, the Pd₂Si layer induced by Ar⁺ bombardment(Fig. 2(c)) does not reveal such a lattice expansion, even at the dose of 1.5×10^{16} Ar⁺/cm². Hung and Mayer²⁾ reported that Pd layer on Si formed Pd₂Si phase by Xe⁺ irradiation even at liquid nitrogen temperature, and this phase has the highest resistance against ion irradiation among the silicides. Thus we suggest that the phase of Pd₂Si induced by Ar⁺ bombardment does not reveal the lattice expansion because of its high stability against ion irradiation, and at lower dose below 1×10^{16} Ar⁺/cm² the tensile strain associated with Ar⁺ irradiation is thought to be the reason for the XRD peak shift for Pd(111) peak to a lower angle, and that the broadening of the FWHM of Pd(111) peak is caused by the dislocations and point defects induced by Ar⁺ irradiation.

It has been revealed¹⁰⁾ that, upon post-annealing, the silicide phase formed by ion beam mixing can transform into another phase somewhat lower those required to form that phase in direct heat treatment. For example, the PdSi phase has been obtained by annealing an ion implanted Pd/Si (or Pd₂Si/Si) sample at $350 \sim 400^\circ\text{C}$ ¹⁰⁾, while temperature as high as 750°C is needed to form that phase by direct annealing. Therefore, the following study was performed to elucidate the ion beam induced change in silicide formation temperature during post annealing at various ion doses.

The samples of as-deposited and irradiation

ted Pd/Si (3×10^{15} Ar⁺/cm² and 5×10^{15} Ar⁺/cm²) were heated in the AES system. The Auger spectrum for an unirradiated specimen prior to heating, but after sputtering to remove the contaminants, is shown in Fig. 3(a). As expected, only the Auger peaks corresponding to Pd(48, 80, and 330eV) appear. After annealing for 10 minutes at 208 °C, Si LVV single peak (92 eV) began to appear, while intensity of the Pd MNN AES peak (330eV) decreased slightly compared with that of the as-deposited sample (Fig. 3(b)). We could not obtain the split Si LVV spectrum that has been already identified as due to the Pd₂Si^{8, 9)}. After only 1 minute of sputtering, the Si peak was removed (Fig. 3(c)). The typical sputtering rate was estimated to be about 0.2 nm/min for Pd under the present experimental conditions. Thus it would appear that the Si LVV single peak evolved after annealing at 208 °C is due to a shallow enriched Si layer associated with Si surface segregation. The sample was then sputtered for 5 minutes to remove the whole segregated region and then reheated and the AES spectrum was checked at each temperature during the heating process. The pure Si LVV single peak appeared again at around 220 °C as shown in Fig. 3(d). After annealing at this temperature for 5 min., the pure Si LVV AES peak still remained. When the annealed specimen was sputtered for 10 min., the silicide (Pd₂Si) spectrum⁸⁾ consisting of 3 peaks (85, 90, and 94 eV) appeared as shown in Fig. 3(e), and the intensity of Pd MNN AES peak increased slightly compared with that of Fig. 3(d). Thus we conclude that the temperature required for the as-deposited sample to form metal-rich silicide (Pd₂Si) is at least 220 °C.

In order to determine the range of Si surface segregation, we performed AES depth profile with Ar⁺ sputter etching for 40 minutes. Fig. 4 shows the AES depth profile of Si and Pd for the sample annealed at 220 °C. The Si enriched layer in the sample annealed at 220 °C becomes thicker (~1nm) than that of the sample annealed at 208 °C (~0.2nm). After 10 minutes of sputter etching, the ratio of intensity of Si and Pd AES peak reveals a constant value representing that a uniformly mixed layer forms. From the quantitative AES analysis using the sensitivity factors of Si and Pd, the stoichiometric ratio of Pd_{1-x}Si_x in uniformly mixed layer is found to be $x \approx 0.36$, which is very close to the value of Pd₂Si phase.

We performed the AES observation for the samples irradiated with 3×10^{15} Ar⁺/cm² and 5×10^{15} Ar⁺/cm² during in-situ post annealing treatment. As can be seen in Fig. 3(f) and Fig. 3(g), a distinctive Si LVV Auger peak splitting representing the formation of Pd₂Si phase appears at 70 °C and 95 °C for the samples irradiated with the doses of 3×10^{15} Ar⁺/cm² and 5×10^{15} Ar⁺/cm², respectively. The Si Peak retained the same shape of Pd₂Si phase even after sputtering for 20 minutes at room temperature. We could not observe the Si surface segregation phenomena in the ion beam mixed sample. At the higher fluence of 1×10^{16} Ar⁺/cm² (Fig. 3(h)), it was found that the phase of Pd₂Si was formed at room temperature by Ar⁺ irradiation, which is consistent with the RBS and XRD results.

From these results, we found that the temperature required to convert a Pd/Si bilayer to the Pd₂Si phase is decreased appreciably from 220 °C for and unirradiated specimen

to 95°C, 75°C, and room temperature by Ar⁺ irradiation with the doses of 3×10^{15} Ar⁺/cm², 5×10^{15} Ar⁺/cm² and 1×10^{16} Ar⁺/cm², that is, the Ar⁺ irradiation reduces the Pd-silicide formation temperature appreciably.

Ion bombardment is known⁷⁾ to produce amorphous layer resulted from radiation damage due to ion irradiation or to desperse interfacial contaminations such as native oxides or impurities. In order to elucidate these effects on the reduction of Pd-silicide formation temperature and surface morphology of Pd-silicide layer, the following experiments have been carried out as shown schematically in Fig. 5.

To study the effect of radiation damage on the formation of a silicide phase, the Si substrates were predamaged with 5 keV Ar⁺ (1×10^{16} Ar⁺/cm²), and then exposed to air (Fig. 5(a)). Then the Pd film was deposited on the predamaged substrate in UHV chamber, and the deposited sample was subsequently annealed and analysed with AES. No difference in the silicide formation temperature was observed between the damaged and undamaged samples. This result suggests that the radiation damage in the substrate may not be primary factor responsible for the reduction of the silicide formation temperature.

Another factor of worth consideration is the Pd-Si interface. The Si substrate prepared by conventional chemical cleaning procedures contains at least one atomic layer of oxide and other impurities, which may act as a barrier for silicide formation. When Ar⁺ ions bombard the Pd/Si bilayer, this barrier may be dispersed as a result of atomic mixing process. Once the barrier is destroyed, nucleation and growth of the silicide phase can

be initiated even at low temperatures. This suggestion was confirmed by the following experimental results. Si layer of 10nm thick was deposited firstly on Si wafer and then Pd film was deposited on the top without breaking UHV condition, and then analysed with AES system (Fig. 5(b)). The metal-Si interface in this sample is believed to be relatively free of contamination compared to that of the sample prepared on chemically cleaned Si wafer. Direct annealing of this in-situ deposited Pd/Si sample results in the formation of silicide (Pd₂Si) at low temperature (150°C), which is similar to that observed in the ion beam mixed sample. However, when the deposited Si film is exposed to the air before the deposition of Pd film (Fig. 5(c)), the silicide formation requires a high temperature (220°C) similar to that of the as-deposited sample in Fig. 3. These results clearly indicate that the interfacial contamination (oxides or impurities) is an important factor in silicide formation. We suggest that a small amount of interfacial impurity (mainly native oxide layer in this case) can greatly affect the silicide formation in reaction Pd film with the Si substrate. The sharp native SiO₂ barrier prevents the silicide formation at the beginning of annealing. However, in the case of ion beam mixing, the sharp interface is smeared out and the oxide barrier is dispersed. Thus the silicide formation temperature is considerably decreased by ion beam mixing in comparison with direct annealing.

The dispersion of interfacial contamination or amorphization of Si substrate surface is known to have a very close relation with the smooth silicide formation. Fig. 6 shows SEM micrographs of the silicide film surfaces for

the unmixed sample and ion beam mixed samples. The as-deposited film was smooth, but after annealing at 220°C, the reacted film had microscopically rough surface as shown in Fig. 6(a). For the samples irradiated with Ar⁺ ion, the surface morphology of the silicide film was dramatically improved as shown in Fig. 6(b) and Fig. 6(c). The surface morphology of the ion beam mixed sample become smoother with increasing ion dose. These results also indicate that the dispersion of interfacial contamination (mainly Si native oxide) might play an important role for smooth silicide film formation. This oxide barrier removal due to the atomic mixing process might minimize spatial fluctuation in the silicidation reaction.

4. Conclusion

Evaporated Pd films on Si(111) substrates were irradiated by 80 keV Ar⁺ ion at room temperature. The RBS, XRD and AES results show that the Pd₂Si phase is formed at the

dose of 1×10^{16} Ar⁺/cm². At the doses below 1×10^{16} Ar⁺/cm², the XRD peak for Pd(111) shifts to a lower angle and FWHM becomes broad presumably due to the tensile strain and the dislocations or point defects induced by Ar⁺ irradiation. AES observations reveal that the temperature required to convert a Pd/Si bilayer to Pd₂Si phase is appreciably decreased from 220°C for and as-deposited sample to 95°C, 70°C, and 25°C by Ar⁺ ion irradiation with the doses of 3×10^{15} Ar⁺/cm², 5×10^{15} Ar⁺/cm², and 1×10^{16} Ar⁺/cm², respectively. And surface morphology of the silicide film is dramatically improved by Ar⁺ irradiation. From the AES results for a sample prepared on a predamaged Si substrate and direct annealing of in-situ deposited Pd/Si bilayered sample, Ar⁺ irradiation is believed to lead to the dispersion of interfacial contaminants owing to the atomic mixing process, and results in the reduction of Pd-silicide formation temperature and the smooth silicide film formation.

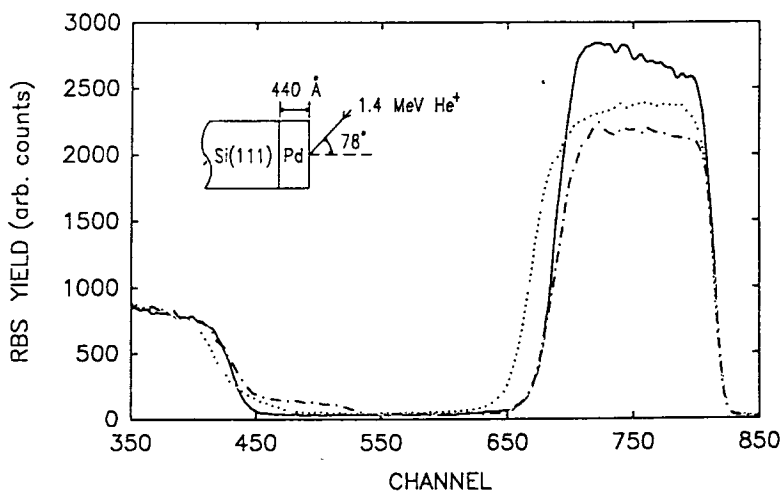


Fig. 1. RBS spectrum of (a) as-deposited sample (____) and samples irradiated by (b) 3×10^{15} Ar⁺/cm² (.....) and (c) 1×10^{16} Ar⁺/cm² (— · — · —).

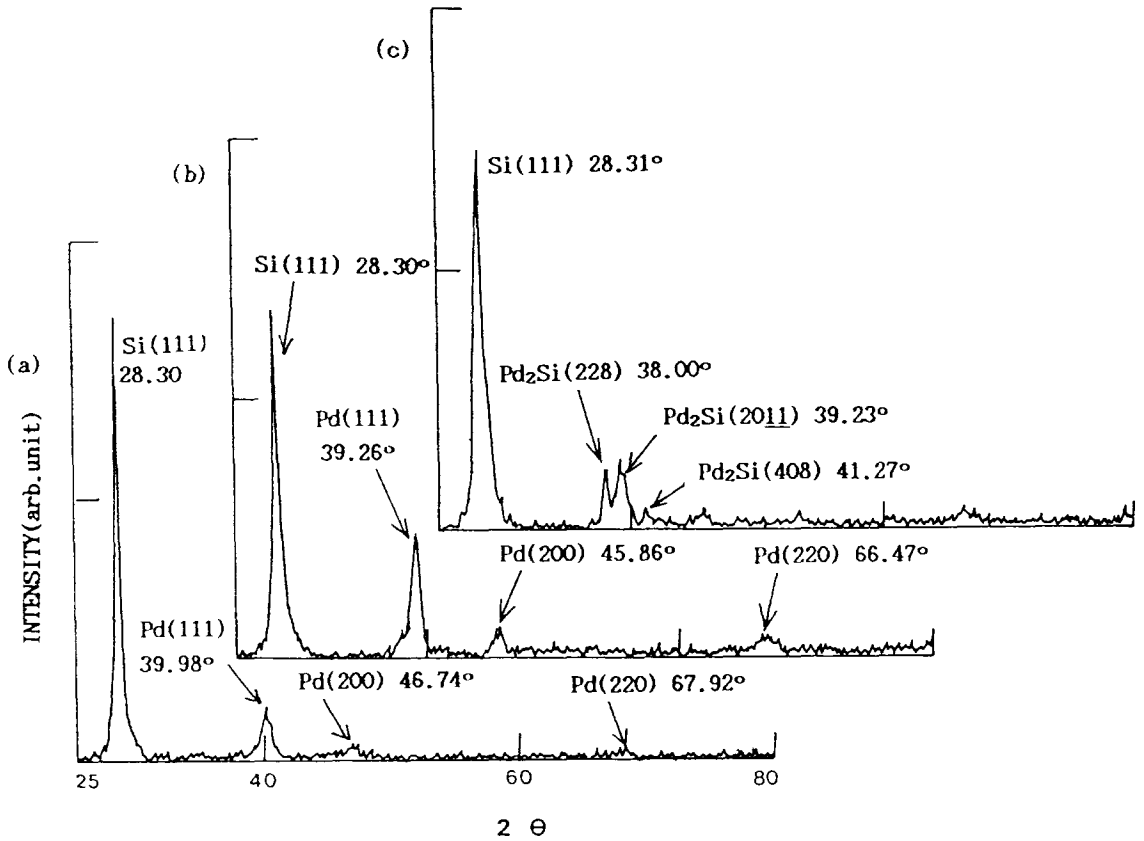


Fig. 2. X-ray diffraction patterns of Pd/Si(111) for (a) as-deposited sample and samples irradiated by (b) $3 \times 10^{15} \text{ Ar}^+/\text{cm}^2$ and (c) $1 \times 10^{16} \text{ Ar}^+/\text{cm}^2$.

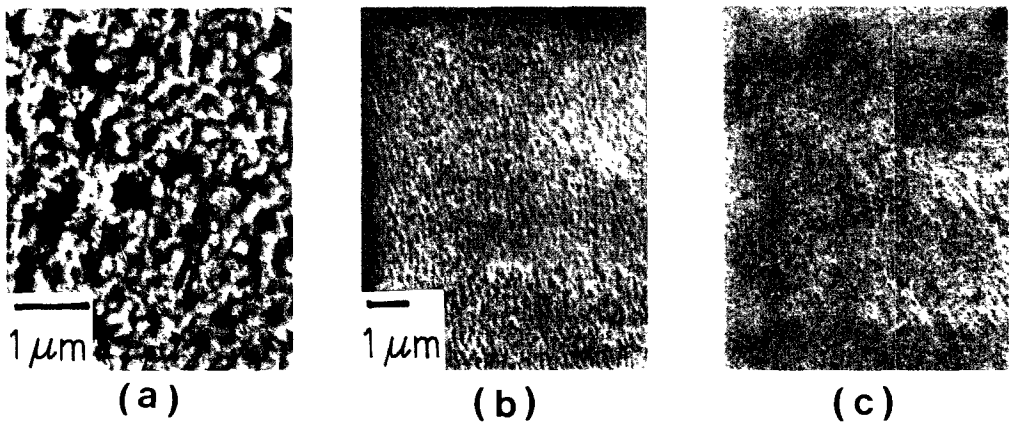


Fig. 6. SEM images of (a) as-deposited after annealing at 220°C and samples (b) irradiated by $3 \times 10^{15} \text{ Ar}^-/\text{cm}^2$ and annealing at 95°C and (c) irradiated by $1 \times 10^{16} \text{ Ar}^-/\text{cm}^2$ at room temperature

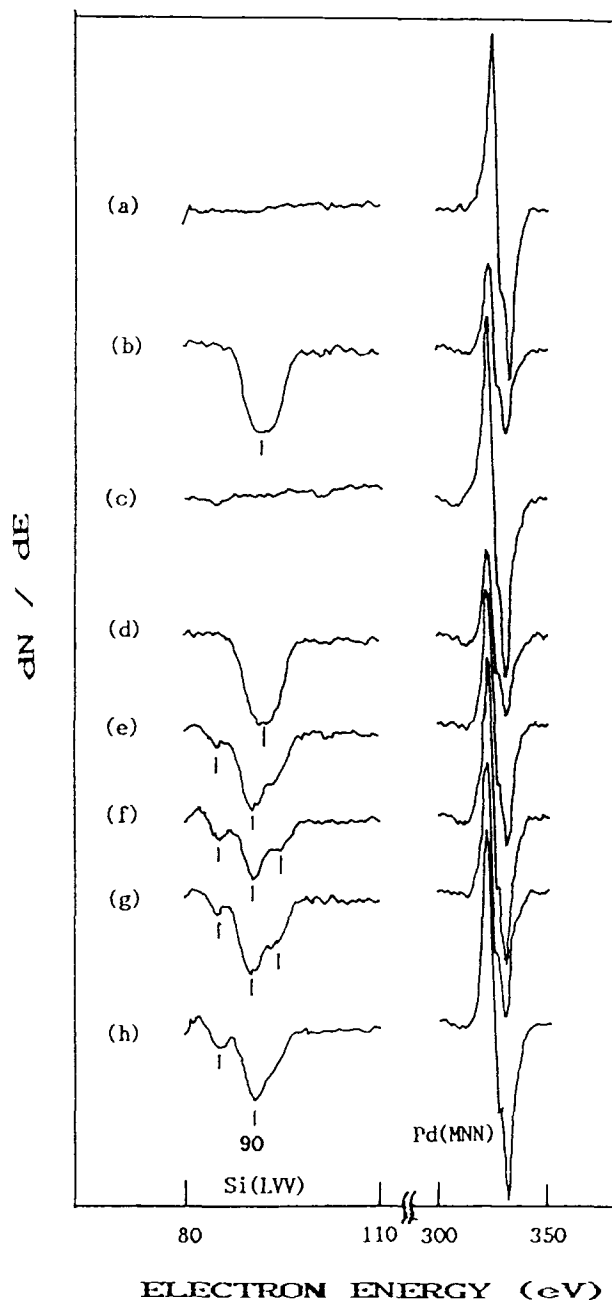


Fig. 3. AES spectrum of (a) as-deposited sample after sputtering, (b) annealing at 208°C, followed by (c) sputtering for 1 minute. (d) reheating at 220°C, followed by (e) sputtering for 10 minutes. For the samples irradiated by (f) $3 \times 10^{15} \text{ Ar}^+/\text{cm}^2$, (g) $5 \times 10^{15} \text{ Ar}^+/\text{cm}^2$, and (h) $1 \times 10^{16} \text{ Ar}^+/\text{cm}^2$, a distinctive Si LVV peak splitting appears at 96°C, 70°C, and 25°C, respectively.

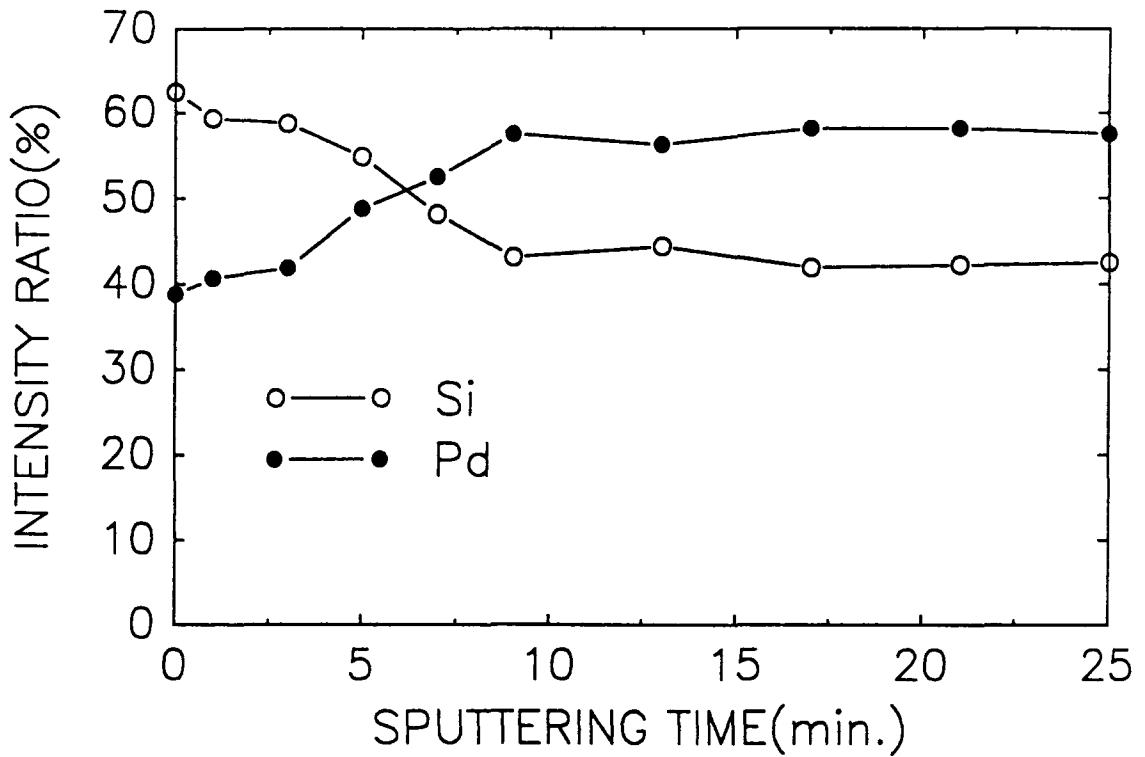
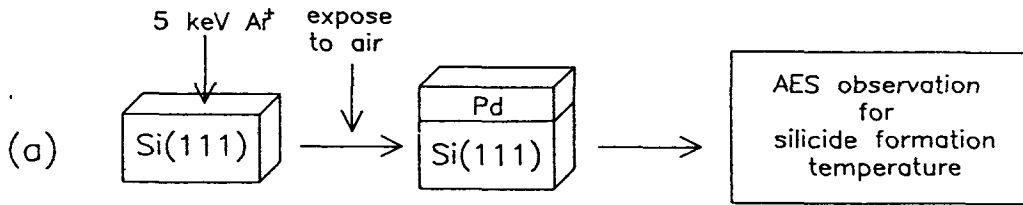


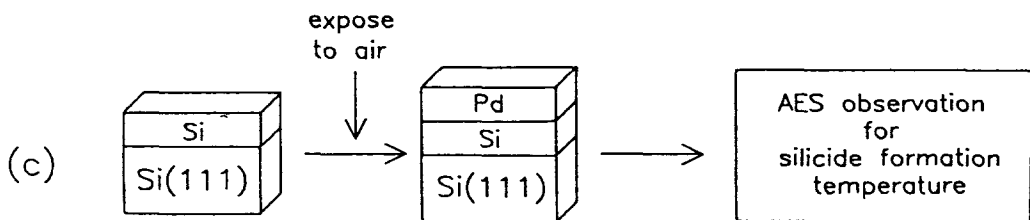
Fig. 4. AES depth profile of as-deposited Pd/Si(111) after annealing at 220°C.



Pre-damaged Si(111) substrate is exposed to air before deposition of Pd film.



In-situ deposition of Pd and Si films on Si(111) substrate.



Deposited Si film is exposed to air before Pd film is deposited.

Fig. 5. Schematic diagram of experiment performed to elucidate the mechanism of reduction in silicide formation temperature and the improvement of surface morphology due to ion bombardment.

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