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Silicide formation by Ar^+ ion bombardment of Pd/Si

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Palladium films, 45 nm thick, evaporated on to Si(1 1 1) were irradiated to various doses with 78 keV Ar^+ ions to promote silicide formation. Rutherford backscattering spectroscopy (RBS) shows that intermixing has occurred across the Pd/Si interface at room temperature. The mixing behaviour is increased with dose which coincides well with the theoretical model of cascade mixing. The absence of deep RBS tails for palladium and the small area of this for silicon spectra indicate that short-range mixing occurs. From the calculated damage profiles computed with TRIM code, the dominant diffusion species is found to be silicon atoms in the Pd/Si system. It is also found that the initial compound formed by Ar^+ irradiation is Pd_2Si which increases with dose. At a dose of 1×10^{16} Ar^+ cm^{-2}, a 48 nm thickness of Pd_2Si was formed by ion-beam mixing at room temperature.

1. Introduction

There has been a great interest in the utilization of metal silicides in silicon integrated circuit technology for ohmic or rectifying contact [1] and Schottky barriers [2] to achieve reliable and stable characteristics. It is well known [3, 4] that the near noble metal (platinum, palladium and nickel) forms a metal-rich phase (predominantly M_2Si) at the early stage of furnace annealing and then this phase transforms to MSi phase consuming all the available metal during further annealing.

The use of ion beams to induce metal–silicon reaction has received increasing attention in recent years. Compared to the conventional annealing method, the ion-beam mixing (IBM) process has many advantages [5] such as uniformity and reproducibility of silicide growth associated with the interface cleaning action, and a relatively low formation temperature due to the nucleated silicide.

The formation of metal-rich silicides such as Pd_2Si, Pt_2Si and Ni_2Si is particularly interesting from the viewpoints of thermodynamics and practical uses, because the reacted silicide films are known to be laterally uniform without any heat treatment after ion bombardment. Moreover, there are other interesting properties in Pd_2Si films formed on single crystal Si(1 1 1); because of the approximate matching of lattice parameters, the films grow epitaxially on to the Si(1 1 1) substrate by furnace annealing [6] or ion-beam mixing [7] and the epitaxial Pd_2Si films do not become amorphous on ion bombardment [8].

Lee *et al.* [9] found some intermixing of palladium films on silicon after bombarding with phosphorus ions, and van der Weg *et al.* [10] observed Pd/Si mixing using Ar^+ ions. Tsaur *et al.* [11] found that the Pd_2Si phase was formed near the Pd/Si interface at low dose Xe^+ ion bombardment and PdSi phase was formed near the Pd_2Si/Si interface at a high dose of Xe^+ ion bombardment or during subsequent thermal annealing at 300 to 400° C; Ishiwara [7] observed epitaxial growth of Pd_2Si film on Si(1 1 1) substrate by Ar^+ ion bombardment. However, these authors investigated only the Pd_2Si and PdSi phase formation or phase transition instead of investigating mixing mechanism or dose dependency.

The present investigation was intended to elucidate the basic mechanism involved in the ion-beam mixing process. The characteristics of ion-beam mixed layers were investigated by Rutherford backscattering spectroscopy (RBS) with varying Ar^+ ion dose. Then the experimental results are compared with the theoretical models of isotropic cascade mixing.

2. Experimental procedure

A polished n-type Si(1 1 1) single crystal (resistivity 20 Ωcm) was cleaned by consecutive ultrasonic cleaning in trichloroethylene, acetone, methanol, and 18 MΩ deionized water. After 10 sec etching in 5% aqueous HF, a palladium film, 54 nm thick, was vapour deposited on silicon at a rate of 0.1 nm sec^{-1} in a specially designed mixing chamber [12] to evaporate a uniform metal film and fabricate a laterally uniform mixed layer. The thickness of the palladium film was measured by a vibrating quartz crystal deposition monitor.

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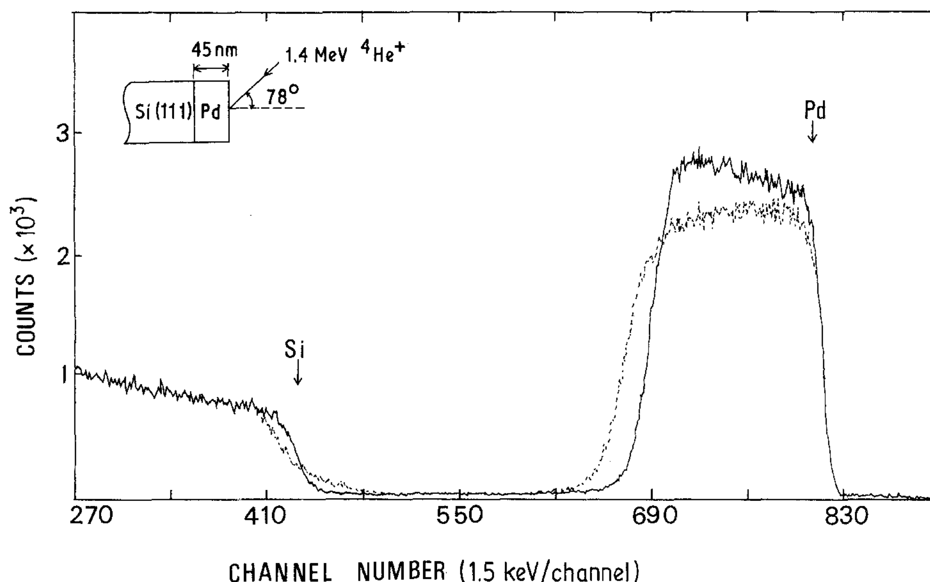

Figure 1 RBS spectra normalized to random silicon spectra for (——) a virgin sample and (- - -) a sample irradiated with 3×10^{15} Ar^+ cm^{-2} at 78 keV.

Mixing was carried out at a pressure of $\leqslant 2 \times 10^{-7}$ torr at room temperature. To avoid further heating due to ion bombardment, the sample was glued to the heat sink (sample holder) with a thermally conductive heat sink compound (Dow Corning 342 heat transfer compound). The Ar^+ ion energy (78 keV) was chosen so as to give projected ranges of approximately 45 nm ($R_p + \Delta R_p$). Doses from 1×10^{15} to 1.5×10^{16} cm^{-2} were used for mixing the bilayers of Pd/Si at an average beam current density of $1\,\mu A\,cm^{-2}$. The schematic diagram of 400 keV implanter which was employed for irradiation in this research could be found from our previously published paper [13].

The mixing profiles were analysed by means of 1.4 MeV He^+ backscattering (RBS) with the target tilted to an angle of 78° to give an enhancement of the depth resolution of a factor of 4.8. 1.4 MeV He^+ beam extracted from 2 MeV van der Graaff accelerator was magnetically analysed and collimated to a $1\ mm^2$ spot on the sample. The energy of backscattered He^+ ions was analysed with a surface barrier detector mounted 10 cm from the target at a laboratory scattering angle of 160°. The energy resolution of the analysing system is about 16 keV.

3. Results and discussion

Ion-beam mixing at the Pd/Si interface was determined using RBS for several doses. Fig. 1 shows typical RBS spectra normalized to random silicon spectra obtained from a virgin sample and the sample irradiated with 3×10^{15} Ar^+ ions cm^{-2}. The leading edge of the signals for the palladium and silicon elements are indicated by arrows in Fig. 1.

It can be seen from Fig. 1 that Ar^+ bombardment has caused broadening of the RBS spectra for palladium and silicon. The signal height in the region of palladium after irradiation is slightly reduced (and presumably the silicon signal yield, too) due to the transport of palladium into silicon (and vice versa). In addition, the signal position of the rear edge for palladium shifted to the lower energy after irradiation, while the front edge of silicon is shifted to the higher energy. Both of these facts clearly indicate that intermixing has occurred across the Pd/Si interface by Ar^+ ion bombardment at room temperature.

The area of the RBS spectra for the unirradiated and irradiated sample should remain the same if the sputtering during Ar^+ implantation does not occur. Thus the total intermixed atoms can be represented as the area difference between virgin and irradiated spectra at the rear and front edges for palladium and silicon, respectively. A close examination of Fig. 1 reveals that a weak signal corresponding to a deep silicon tail appears. But there is no such tail for palladium. According to Besenbacher *et al.* [14], the deep tails arise from the long-range mixing associated with recoil relocation of silicon. The absence of deep tails for palladium and the small area of the deep tail for silicon in this study indicate that the short-range mixing is the dominating process.

RBS spectra at a higher dose of 1×10^{16} Ar^+ cm^{-2} are plotted in Fig. 2. The spectra for as-deposited Pd/Si system and for after irradiation at 1×10^{16} Ar^+-cm^{-2} are shown in the same figure for comparison. The total palladium yield is reduced after irradiation and the silicon edge has moved to higher energies due to the sputtering during Ar^+ bombardment. Fig. 2 shows clearly a well-defined step on the front edge of silicon and the whole range of palladium, which represents the formation of a uniform Pd_mSi_n layer by IBM at room temperature. The stoichiometry of Pd_mSi_n compound formed by IBM can be determined from the spectrum heights and atomic numbers of palladium and silicon [15]. From this calculation, the ratio of m/n is found to be 2.13 which can be considered to be 2 within experimental error. Thus it can be easily concluded that the initial compound formed by Ar^+ bombardment will be Pd_2Si. Considering the fact that Pd_2Si is normally formed at elevated temperature, above 200° C, in the conventional furnace annealing method [16], the formation of this equilibrium compound at room temperature by IBM is

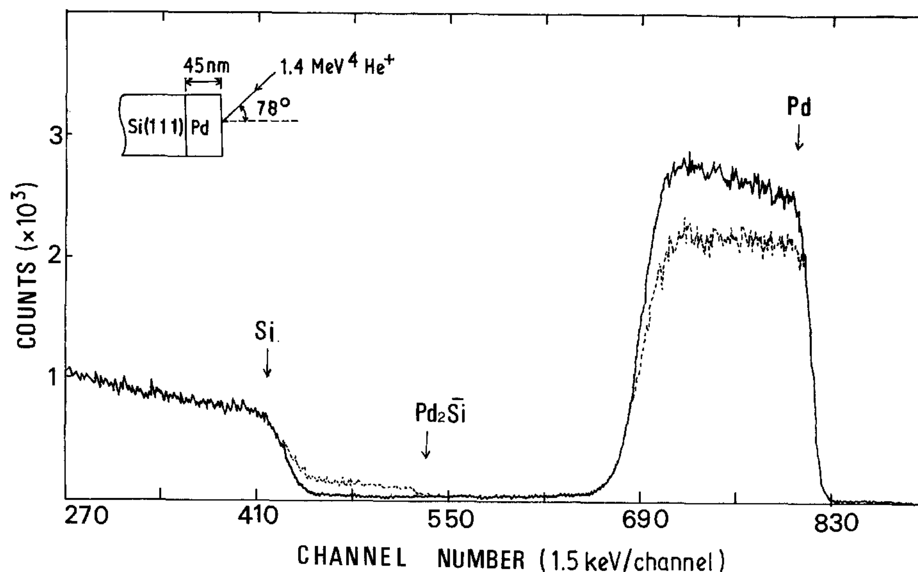

Figure 2 RBS spectra (——) before and (– – –) after irradiation with 1×10^{16} Ar^+ cm^{-2} showing the silicide formation (48 nm thick) at room temperature.

interesting. This result coincides with the results of Hung and Mayer [17] and Horino [18]. Furthermore, this initial compound in the mixed layer is identical with the first phase formed by thermal annealing. This implies that the Walser–Bene rule [19], describing the first thermal phase deduced from the phase diagram, still holds in the IBM process even though this process is a non-equilibrium method. From the viewpoint of thermodynamics, the Gibb's free energy of the mixed layer of palladium and silicon (which has a higher energy state) is decreased by the formation of compound Pd_2Si from this mixed layer. In addition to this thermodynamic consideration, the mobilities of palladium and silicon are greatly enhanced by the vacancy formation during irradiation [20]. Both of these factors are thought to lead the formation of a compound, even at room temperature, under Ar^+ bombardment.

The thickness of Pd_2Si was determined from the energy loss of He^+ in traversing the Pd_2Si layer and the bulk density for Pd_2Si. A simple surface approximation ([15] p. 145) was used for thickness calculation, which was adequate because the total film thickness is relatively thin (less than 100 nm). The thickness of Pd_2Si in Fig. 2 is calculated to be 48 nm. The reacted thicknesses of palladium and silicon to form a Pd_2Si film 48 nm thick are calculated to be 32.7 and 22.2 nm, respectively.

The mixing variances were determined from the consideration of energy straggling and system resolution. The total variance of RBS spectra is

$$\Omega_t^2 = \Omega_s^2 + \Omega_r^2 + \Omega_{mix}^2 \qquad (1)$$

where Ω_s is the Bohr energy straggling ([15] p. 119) associated with the statistical fluctuation in energetic particles moving through a thickness, and Ω_r represents the system resolution, which was found to be 7.5 keV calculated from the range of 16 and 84% of the palladium front edge signal height. Thus the real mixing variance Ω_{mix} can be deduced from the subtractions both of Ω_s and Ω_r from the RBS spectra. The same method was employed for silicon spectra. From this approach, we found that the palladium penetrates 3 nm depth into silicon from the Pd/Si interface while the silicon moves 14 nm across the interface during deposition as shown in Fig. 3b. Taking into account the reaction of palladium with silicon to produce Pd_2Si as before, it was found that a Pd_2Si layer 4.4 nm thick was already formed in the as-deposited state as shown in Fig. 3c. The present finding of phase formation during the deposition stage again coincides with the results of Coulman *et al.* [21] and Hung and Mayer [17]. However, the thickness of Pd_2Si (4.4 nm) in our experiment is thinner than that of Coulman *et al.* (15 nm) possibly because of the different experimental conditions used.

A thin interfacial layer of Pd_2Si under unirradiated conditions indicates that interfacial reaction may occur during deposition as suggested by Hung and Mayer [17]. However, this fact cannot explain all the reactions involved in our experiment. Because only 2 nm of silicon is consumed from the total 14 nm which penetrated across the interface for the formation of 4.4 nm Pd_2Si, the rest of the silicon residing on the palladium side should produce the solid solution $Pd_{1-x}Si_x$ within this region as schematically shown in Fig. 3c. Thus it is thought that the diffusion is a dominant process for the Pd/Si system, so that the whole reaction is controlled by an interfacial reaction as mentioned above. Furthermore, the silicon atoms are considered to be the dominant diffusing species both in furnace annealing and irradiating conditions for the Pd/Si system. This strongly supports the above arguments. Thus the thickness of Pd_2Si might be increased by further irradiation due to the cascade mixing or radiation-enhanced diffusion as shown in Fig. 3d.

To investigate the dominant diffusion of silicon atoms into palladium, the depth distributions of vacancy and implanted Ar^+ concentrations are shown in Fig. 4. These distributions were obtained by a computer simulation program which was adapted from TRIM [22] with 1000 ions at an energy of 78 keV. Both of the vacancy and ion distributions for Ar^+ irradiation

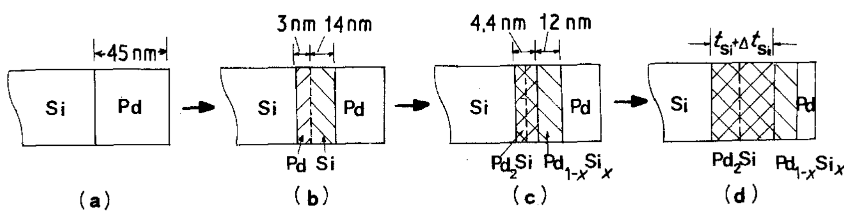

Figure 3 A schematic sequence diagram for silicide formation in Pd/Si bilayer (a). Interdiffusion of silicon and palladium as-deposited (b) resulted in 4.4 nm Pd_2Si during deposition (c). (d) Silicide growth with irradiation.

extend across the Pd/Si interface; the Ar^+ irradiation produces a nearly flat damage and concentration profile on the palladium side, but a decrease on the silicon side which arises from the lower atomic mass and larger lattice parameter of silicon than that of palladium. The mean projected range (36 nm) is represented by an arrow. As shown in Fig. 4, most of the vacancies are produced within the palladium side of the Pd/Si thin film, which indicates that the silicon atoms can easily exchange their lattice sites with vacancies generated during irradiation. Thus it can be concluded that the interpenetration of silicon and palladium atoms across the Pd/Si interface occurs by some mechanism which has a close relation to vacancy production.

The intermixing parameter was determined from the measured variances Ω_{mix} in the backscattering spectra, converted to units of depth

$$\sigma^2 = \Omega^2_{\text{mix}}/[N(\varepsilon)]^2 \tag{2}$$

and

$$\Omega^2 = \sigma^2(\phi) - \sigma^2(0) \tag{3}$$

where $\sigma(\phi)$ and $\sigma(0)$ are the measured variances after and before irradiation fitted to the rear edge of the palladium signal from the target, and N and (ε) are the atomic number density and the stopping cross-section factor of palladium for backscattering, respectively. The results for palladium at various doses, ϕ, are plotted in Fig. 5. These experimental results clearly show that mixing is increased with dose.

These results can be compared with the predictions of models based on the isotropic cascade mixing; a theoretical expression relating the increment of mixing variances to ion dose, ϕ, and the energy loss in nuclear collision $(Sn(x))$, or vacancy production rate can be obtained using Andersen's model [23] and the Kinchin–Pease relation [24]

$$\Omega^2 = 2Dt = \tfrac{1}{3}\Gamma_0 \frac{Sn(x)}{N} \xi_{21} \frac{R_c^2}{E_d} \phi \tag{4}$$

where $\Gamma_0 = 0.608$, N is the atomic density of palladium ($6.8 \times 10^{22}\,\text{cm}^{-3}$) $\xi_{21} = [4M_1M_2/(M_1 + M_2)^2]^{1/2}$, M_1 and M_2 are the atomic mass number of incident ion and target atom, respectively, E_d is the effective displacement energy, and R_c is the r.m.s. separation for a vacancy–interstitial pair. By choosing reasonable values for various parameters ($Sn(x) = 1030\,\text{eV}\,\text{nm}^{-1}$ ([22] p. 53) $E_d = 47\,\text{eV}$ [25], $R_c = 1\,\text{nm}$ [24]), Equation 4 is plotted against dose in Fig. 5. As shown in Fig. 5, the experimental values are in good agreement with an isotropic cascade mixing model. We also compared our results with a radiation-enhanced diffusion model and a fixed sink diffusion model [26]; these are not shown in this paper. These calculations are higher than our experimental results by factors of 3 and 100, respectively. Thus we conclude that the interfacial mixing of the Pd/Si system would be contributed to dominantly by isotropic cascade mixing.

4. Conclusions

Evaporated thin palladium films 45 nm thick, on Si(1 1 1) substrate were irradiated to various doses by 78 keV Ar^+ at room temperature. This study showed that intermixing occurs across the Pd/Si interface. The absence of deep RBS tails for palladium and the small area of the silicon spectra show that short-mixing is the dominant process. The calculated damage profile computed with TRIM code also showed that the vacancies were produced within the palladium side of the Pd/Si bilayer by irradiation. Both of these results support the fact that silicon is the dominant moving

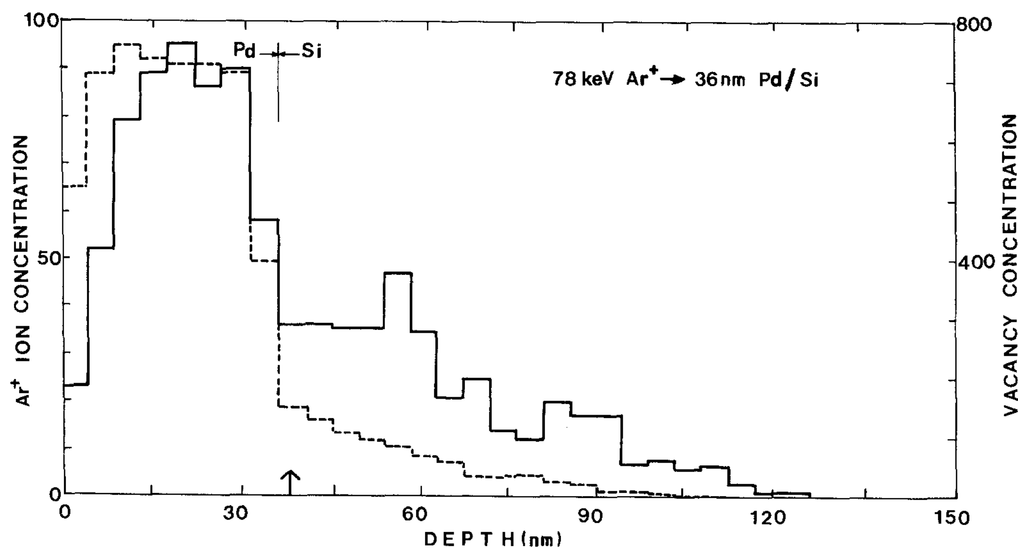

Figure 4 The computer calculation for the depth distribution of (– – –) vacancies and (——) implanted Ar^+ concentration after irradiation with 1000 Ar^+ at 78 keV (TRIM code).

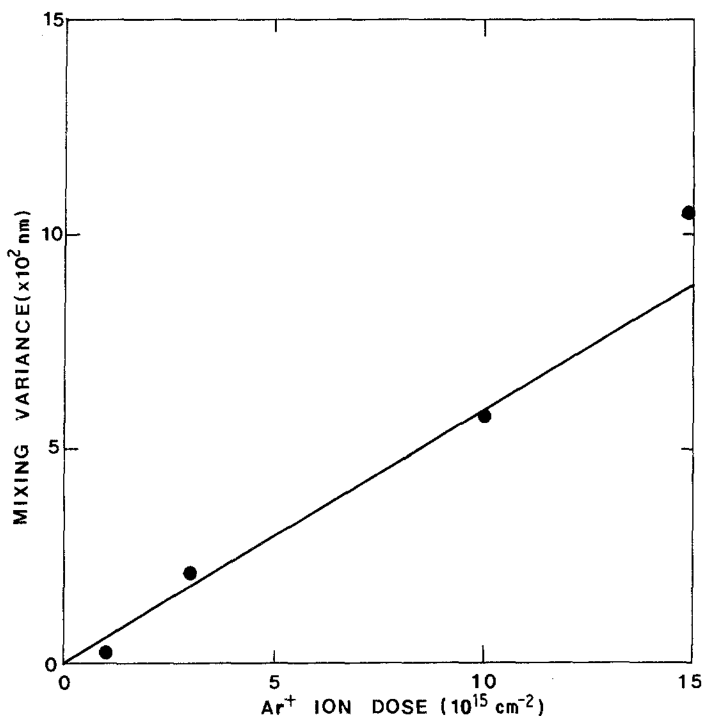

Figure 5 Comparison of dose dependency of palladium mixing in the Pd/Si system between (●) experimental and (——) theoretical cascade mixing.

species via a mechanism-related vacancy production in the Pd/Si system. Furthermore, the mixing behaviour is increased with dose which coincides well with the isotropic cascade mixing model. It was also found that Pt_2Si (4.4 nm thick) and solid solution $Pd_{1-x}Si_x$ should be formed during deposition. Thus the thickness of Pd_2Si is increased with dose. At a dose of 1×10^{16} Ar^+ cm^{-2}, a 48 nm thick layer of Pd_2Si was formed by ion-beam mixing at room temperature. Thus it can be concluded that the metal-rich silicide Pd_2Si can easily be formed with ion-beam mixing at room temperature.

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