

Low-temperature diffusion of dopant atoms in silicon during interfacial silicide formation

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It has been recently reported that the formation of transition-metal silicides induces a strong enhancement of dopant diffusion in silicon at low temperatures ($\sim 250^\circ\text{C}$). However, the mechanism which is responsible for the enhanced diffusion has not been addressed. We have undertaken a systematic study to clarify the mechanism. Our results show that diffusion enhancement occurs only as a result of advancing silicide-silicon interfaces. We also find that diffusion enhancement is a unique feature of the interfacial formation of near-noble-metal silicides, but not refractory-metal silicides. By correlating these observations with the interstitial diffusion of near-noble-metal atoms in silicon, we propose that during silicide formation a large number of point defects is generated in the silicon near the silicide-silicon interface, and that these point defects are responsible for the enhanced diffusivity of substitutional dopants at low temperatures.

I. INTRODUCTION

Diffusion of substitutional dopant atoms in silicon normally occurs at high temperatures ($\sim 1000^\circ\text{C}$), but the formation of transition-metal silicides has been reported recently to induce a strong enhancement of dopant diffusion at low temperatures ($\sim 250^\circ\text{C}$). Surface analytical techniques^{1,2} as well as electrical measurements³⁻⁹ were used to verify the low-temperature diffusion of dopant atoms. It is found consistently that a fraction of the dopant atoms have been pushed into silicon by the advancing silicide-silicon interface. We refer to these atoms as being redistributed. A large fraction of the redistributed dopant atoms has been found to occupy substitutional lattice sites and to be electrically active. This is inferred from Hall measurements³ and the reduction of both the barrier height of Schottky diodes⁴⁻⁶ and contact resistance of Ohmic contacts.⁷⁻⁹

Thus far only near-noble-metal silicides and no refractory-metal silicides have been studied. Therefore, it is not clear whether the effect is general to all silicides.

In this paper we report a set of systematic studies with an aim to elucidate the mechanism responsible for the enhanced diffusion of dopant atoms at low temperatures. We find that diffusion enhancement occurs only as a result of an advancing silicide-silicon interface, as is the case during an interfacial reaction to grow silicides, but not when the silicide is formed by coevaporation of metal and silicon. We also find that diffusion enhancement occurs only during interfacial formation of near-noble-metal silicides, such as PtSi, Pd₂Si, and NiSi, but not refractory-metal silicides such as TiSi, TiSi₂, VSi₂, and TaSi₂. On the basis of these observations, a mechanism of enhancement of dopant diffusion at low temperatures is proposed.

II. EXPERIMENTAL

The silicon substrates used in this work were commercially available *n*-type wafers of 10- Ω cm resistivity and $\langle 100 \rangle$ orientation. Following standard cleaning, the

wafers were implanted with 40-keV As to a dose of $7.2 \times 10^{15} \text{ cm}^{-2}$. We have chosen a low implantation energy to simulate processing conditions used in submicron device technology. The implantation damage was removed by annealing the wafers at 900°C for 45 min in flowing O₂ gas. The oxygen formed a thin SiO₂ layer during annealing to prevent loss of As. The wafers were then dipped in buffered HF to remove the oxide layer before they were loaded into the evaporator for metal film deposition. After pumping down the system to about 2×10^{-8} Torr, thin films of Pt, Ta, Ti, or V were evaporated onto the wafers with an electron gun at pressures in the low 10^{-7} -Torr range. For the refractory metals, prior to deposition a sufficient amount of the metal was evaporated onto the walls of the evaporator to getter residual oxygen and water vapor contained in the system. After deposition small samples were cleaved from the wafer and annealed in a furnace flushed with He, which was purified by a hot Ti sponge filter. Analysis of the samples was performed with Rutherford backscattering (RBS) spectrometry and ion-channeling measurements.¹⁰ The silicide phases formed were identified by x-ray diffraction in a Seeman-Bohlin thin-film diffractometer.

The thickness of the silicide layers was calculated from the corresponding RBS spectra by assuming bulk density for the silicide compound and by use of the surface-energy approximation for the evaluation of the stopping cross section.¹⁰ Since an overlap between arsenic and metal signals in the RBS spectra would impair a careful analysis of the dopant redistribution, we have selected the thickness of the silicide layer and the scattering angle in order to optimize the RBS analysis. The thickness of the deposited metal film was chosen such that the amount of silicon consumed during silicide formation corresponded to a thickness of at least 2 times the depth of the 40-keV As implant in Si in order to probe the As redistribution. A backscattering angle of $\theta = 130^\circ$ was selected, which yielded improved depth resolution over the standard $\theta = 170^\circ$ setting but still prevented overlap between the arsenic and metal signals in the RBS spectra.

In the case of PtSi formation, where we have observed a redistribution of As, the amount of substitutional As in front of the silicide layer was determined from high-resolution ion-channeling measurements. For that purpose we have etched off the silicide and the unreacted Pt layer in aqua regia. This etchant does not attack silicon. A trace amount of Pt was always found at the surface of the etched samples, which corresponded, however, to less than a monolayer. Swift $^4\text{He}^+$ particles of 2.3-MeV energy were used for the channeling measurements, and the silicon surface barrier detector was set at an angle of $\theta=98^\circ$ with respect to the impinging $^4\text{He}^+$ beam. This geometry yields a backscattering depth factor of 5.2 Å/keV for As in Si. In order to reduce the spread in scattering depth of the $^4\text{He}^+$ particles in Si, an aperture with a rectangular slit 2 mm wide and 8 mm high was placed in front of the detector. For a high-resolution spectrum a total charge of 40 μC was accumulated to compensate for the reduced detector acceptance angle and to obtain a good signal-to-noise ratio. For the measurement of the substitutional amount of As by ion channeling, the major crystal axis of the Si sample was aligned with the impinging beam. For the measurement of the total amount of As in the Si, the sample was misoriented (i.e., the major crystal axis was offset by 5° from the beam and the sample was continuously rotated around that axis).

It has been reported that the bombardment of single-crystal silicon with megaelectronvolt He ions may induce a movement of impurity atoms of lattice sites.¹⁰ However, this beam-induced disorder has only been observed when the crystal was randomly aligned with respect to the analysis beam. For channeled alignment the number of impurities pushed off lattice sites is several orders of magnitude smaller and can be neglected in our case. To minimize beam-induced effects we moved the beam to a fresh spot after alignment of the sample and analyzed the sample in random alignment subsequently. Since all samples were analyzed in the same manner we obtained a true comparison of the As distribution in these samples.

III. RESULTS

A. The Pt-Si system

A Si wafer implanted with arsenic and post-annealed at 900°C for 45 min as described above was coated with 900 Å of Pt. The RBS spectra of samples of that wafer before and after isothermal anneals at 350°C for 10, 40, and 80 min are shown superimposed in Fig. 1(a). We find from Fig. 1(a) that the Pt signal decreases in height and increases in width with annealing time. Simultaneously, a step develops at the leading edge of the Si signal. Both facts show that the Pt and the Si have mixed. From the relative height of the Pt and Si signals after the 80-min anneal, we calculate a Pt-to-Si atom ratio in the mixed layer of $1.0\pm 10\%$. This indicates that the compound PtSi has been formed, which is confirmed by x-ray analysis. The fast drop in the height of the Pt signal for the 10-min anneal is due to the transformation of the Pt layer into Pt_2Si , the silicide phase that forms prior to the PtSi phase.

This has been confirmed by both RBS and x-ray analysis. The silicide phase Pt_2Si forms very rapidly at 350°C .¹¹

The signal of the implanted As, which is barely visible at 1.84 MeV in Fig. 1(a), is displayed separately in Fig. 1(b). Note that both the energy scale and the backscattering yield scale have been enlarged. The As spectra of Fig. 1(b) are found to be displaced to lower energies after prolonged heat treatments. This can be interpreted by a deeper distribution of As in the Si bulk, which means that some As atoms have diffused into the silicon during PtSi formation. The entire amount of As seems unchanged, but some As atoms have also been accumulated in the silicide as indicated by the peak at 1.93 MeV in Fig. 1(b).

It is difficult to extract information on the exact depth of the As redistribution from Fig. 1(b) because the stopping cross section of $^4\text{He}^+$ particles in the overlaying silicide layer changes with increasing thickness of the silicide. The best solution to this problem is to etch off the silicide and to investigate the As profile in the Si with a high-resolution channeling experiment, with the use of the scattering geometry described above. The As profiles are shown in Fig. 2(a) for samples misaligned with the impinging $^4\text{He}^+$ beam (random spectra) and in Fig. 2(b) for samples where the $\langle 100 \rangle$ axis has been aligned with the beam (aligned spectra). Three profiles are shown in each case: before silicide formation (0 min), after 10 min, and after 80 min of silicide formation at 350°C . These profiles are displayed versus their relative position with respect to the original silicon surface. This position is determined by the location of the silicide-silicon interface, which can be accurately calculated from the thickness of the silicide as measured with RBS. By assuming the bulk density for the silicide we can find the amount of Si consumed to form the silicide. This gives us the depth of the silicide-silicon interface beneath the original silicon surface. This depth is marked by the vertical arrows in Fig. 2 and can be read from the x axis. Note that the peak of the As profile before silicide formation is shallower than the projected range of the implant ($R_p = 270$ Å) because a thin oxide layer has been purposely formed during the post-implantation anneal.

The As profile after implantation and Pt deposition, but prior to silicide formation, is shown by the open circles in Fig. 2(a). Annealing for 10 min at 350°C consumed about 320 Å of Si for silicide formation, and the As profile beneath the silicide-silicon interface is given by the open squares in Fig. 2(a). After an 80-min anneal at 350°C the entire Pt layer has been transformed into PtSi, and the interface is located about 600 Å below the original Si surface. The As profile for this case is displayed by the triangles in Fig. 2(a). We can deduce the following from these profiles: First, As atoms have diffused into the silicon bulk during platinum-silicide formation at a low temperature of 350°C ; second, the amount of redistributed As atoms decreases with increased thickness of the silicide; and third, the redistributed As atoms extend over a depth of 100–200 Å.

The profiles shown in Fig. 2(a) represent the total amount of As since the samples were misaligned with respect to the $^4\text{He}^+$ beam. In the case of $\langle 100 \rangle$ alignment of the samples we obtained the channeling spectra shown

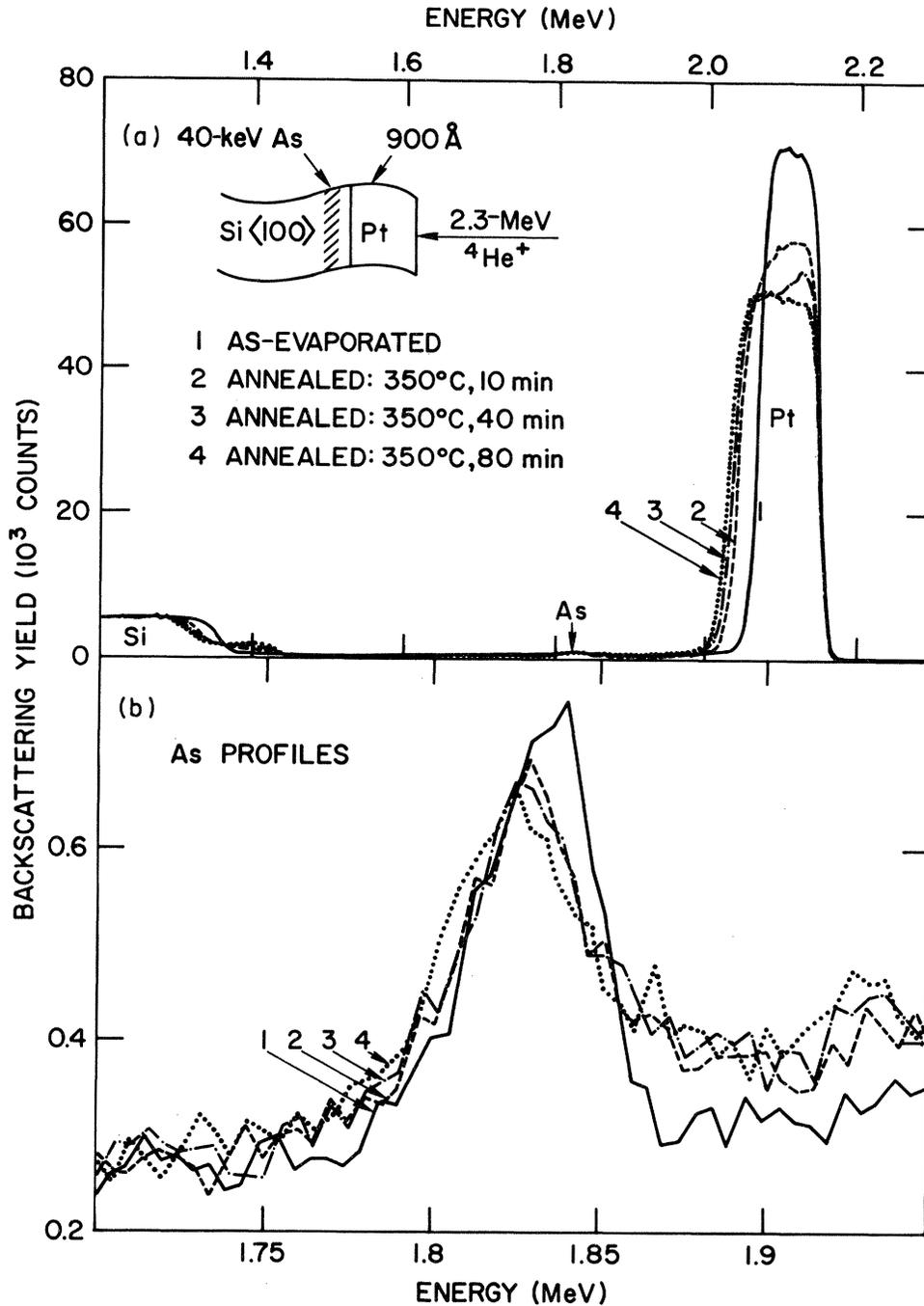


FIG. 1. (a) 2.3-MeV $^4\text{He}^+$ RBS spectra of an arsenic-implanted Si sample after evaporation of 900-Å Pt and subsequent annealing at 350°C for 10, 40, and 80 min. (b) Corresponding profiles of the arsenic displayed on enlarged scales.

in Fig. 2(b), which represent the profiles of interstitial As. We deduce from Fig. 2(b) that part of the redistributed As is interstitial. A comparison of the backscattering yields of Figs. 2(a) and 2(b) shows that the interstitial part of the redistributed As amounts to about 50%. Then, the difference between the total amount of As and the corresponding amount of interstitial As, corrected for the minimum yield in Si,¹⁰ equals the amount of As which is substitutional. Since the minimum yield in Si is about 3%, the

amount of substitutional As is also around 50%. We note that only those arsenic atoms which are located on Si lattice sites are electrically active. Hence, the substitutionality of part of the redistributed As atoms provides direct evidence for the observed lowering of the Schottky barrier height^{4,5} and contact resistance⁷ following PtSi formation.

Redistribution of As also occurs during Pt₂Si formation,¹² but the effect is not as strong as during PtSi formation. Fortunately for technological applications the phase

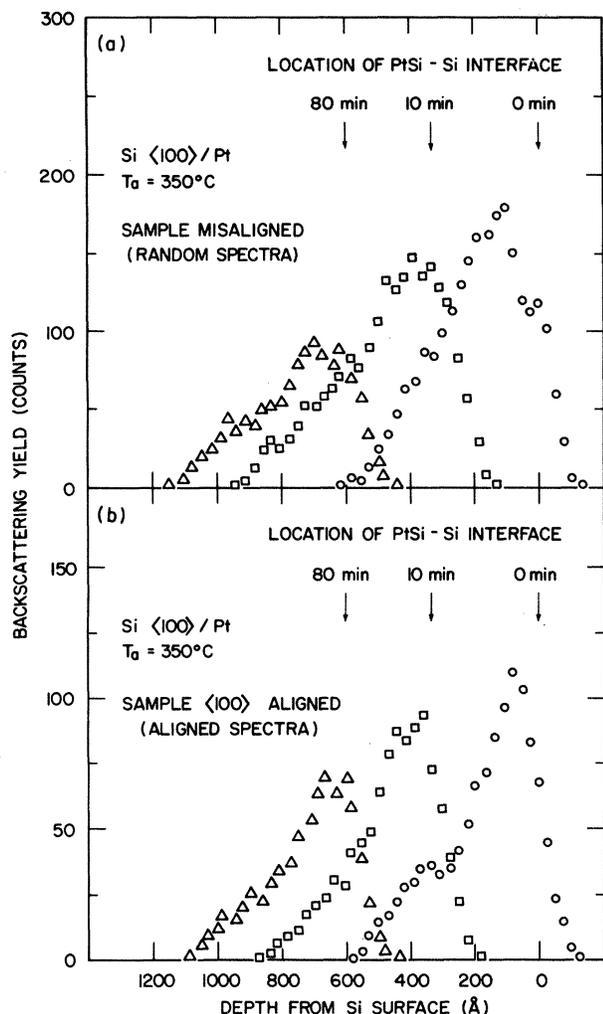


FIG. 2. Arsenic profiles at various stages of silicide formation as found with high-resolution ion channeling. The spectra are superimposed by taking into account the location of the silicide-silicon interface with respect to the original silicon surface. (a) Random spectra, (b) $\langle 100 \rangle$ aligned spectra.

PtSi is the important one because it is the thermally stable end phase in the Pt-Si binary system.

B. The Ta-Si system

To investigate the generality of dopant redistribution during interfacial silicide formation we have chosen as the first refractory silicide the compound TaSi_2 from the Ta-Si system. An arsenic-implanted Si wafer was coated with 550 Å of Ta and samples thereof were annealed at 700°C for 20 and 50 min. The RBS spectra of an as-deposited sample and heat-treated samples are shown in Fig. 3(a). The signal from the silicon has been omitted in this figure in order to simplify matters, and the arsenic signals have been magnified by a factor of 50. The change of the Ta signal reflects the intermixing of Ta with Si. One-half of the Ta has been consumed by silicide formation after the 20-min anneal and the entire Ta layer is transformed into a silicide following the 50-min anneal. From RBS as well

as x-ray analysis we determined that the compound formed is TaSi_2 , which is known to be the first phase to form in a thin-film couple of Ta and Si.¹¹

The As profiles in Fig. 3(a) reveal that there is no shift to lower energies upon annealing. Rather, the height of the As signal at its original position of 1.82 MeV decreases with annealing, and a new As peak at 1.90 MeV appears. This new As peak is close to the surface position of As, as marked by the vertical arrow labeled As. We can conclude from this result that the implanted As atoms have not been redistributed into the silicon during TaSi_2 formation; instead, some of them have been incorporated into the growing silicide layer and have accumulated near the surface of the sample. This is also evident from a computer simulation of the RBS spectra,¹³ as shown in Fig. 3(b). The computer program simulates RBS spectra in the Gaussian approximation. Spectrum 1 is a simulation of the RBS spectrum from the as-evaporated sample. Spectrum 2 simulates the case where one-half of the Ta layer has been transformed into TaSi_2 together with the assumption that 50% of the As atoms have been redistributed into the silicon and 50% have been accumulated in the silicide. The As in the silicides has been modeled as a peak near the surface, in correspondence with the experimental findings. The split of the As signal into two peaks illustrates this situation. The case of complete silicide formation is shown by the spectra 3 and 4, wherein two possible As profiles have been simulated, demonstrating 0% redistribution (spectrum 3) and 100% redistribution (spectrum 4) of the As into the silicon. The difference between these last two cases is clearly visible by the large energy separation of the two corresponding As peaks. By comparing the simulated spectra of Fig. 3(b) with the actual measured spectra of Fig. 3(a) it is apparent that during TaSi_2 formation a redistribution of As has not taken place. This result is in clear contrast to the cases of near-noble-metal silicides investigated to date. The area under the As peak of 1.90 MeV is smaller than that under the as-implanted As signal at 1.82 MeV. This indicates that some As has diffused out of the TaSi_2 layer and has been lost during the heat treatment at 700°C .

C. The Ti-Si system

The absence of As redistribution is not unique to the Ta-Si system; we will show that it is also true for the Ti-Si system. In Fig. 4(a) we present the RBS spectrum of an arsenic-implanted sample with an evaporated layer of 370-Å Ti and the spectra obtained after subsequent annealing at 600°C for 10, 35, and 150 min. The silicon signal has again been omitted in Fig. 4. Silicide formation is indicated by the change of the Ti signal. The phase formed is TiSi as identified with x-ray analysis. The As signals are enlarged by a factor of 10. Again, the height of the As signals at the implant position decreases with annealing and a new As peak develops at 1.93 MeV. This refers to an absence of As redistribution.

Computer simulation of RBS spectra are again used to interpret the experimental results. In Fig. 4(b) we show two simulations, one for the as-evaporated sample and the

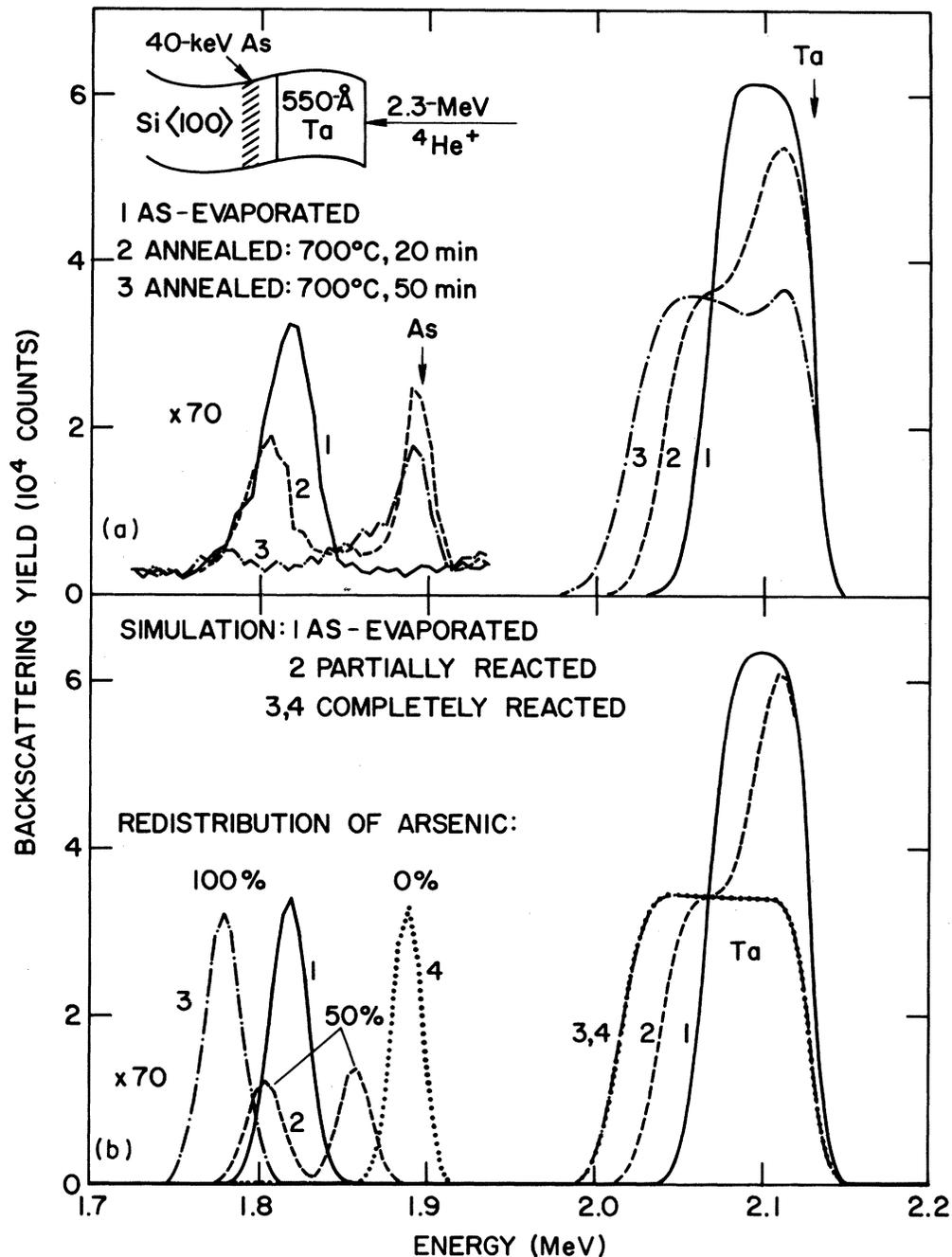


FIG. 3. (a) 2.3-MeV ${}^4\text{He}^+$ RBS spectra of arsenic-implanted Si samples with an evaporated Ta layer of 550 Å thickness and subsequently annealed at 700°C for 20 and 50 min. The Si signal is omitted. Vertical arrows indicate surface positions of the corresponding elements. (b) Computer simulation of the spectra of (a), illustrating the cases of 0%, 50%, and 100% As redistribution during interfacial silicide formation.

other for complete TiSi formation without As redistribution into the silicon. The comparison of the simulated and measured spectra demonstrates clearly that As redistribution is absent during TiSi formation.

The same observation is also true for TiSi₂ formation at higher temperatures. The results are given in Fig. 5. Two RBS spectra are displayed in Fig. 5; one for the as-evaporated sample and the other for TiSi₂ formed at

700°C for 30 min. The shift of the As signal to higher energy upon annealing demonstrates again that most of the As atoms have accumulated near the silicide surface. Since the silicide-silicon interface has penetrated beyond the depth of the original As implant, we conclude from Fig. 5 that As redistribution into the silicon did not take place. Note from the different areas under the As peaks that some As escaped during the high-temperature anneal.

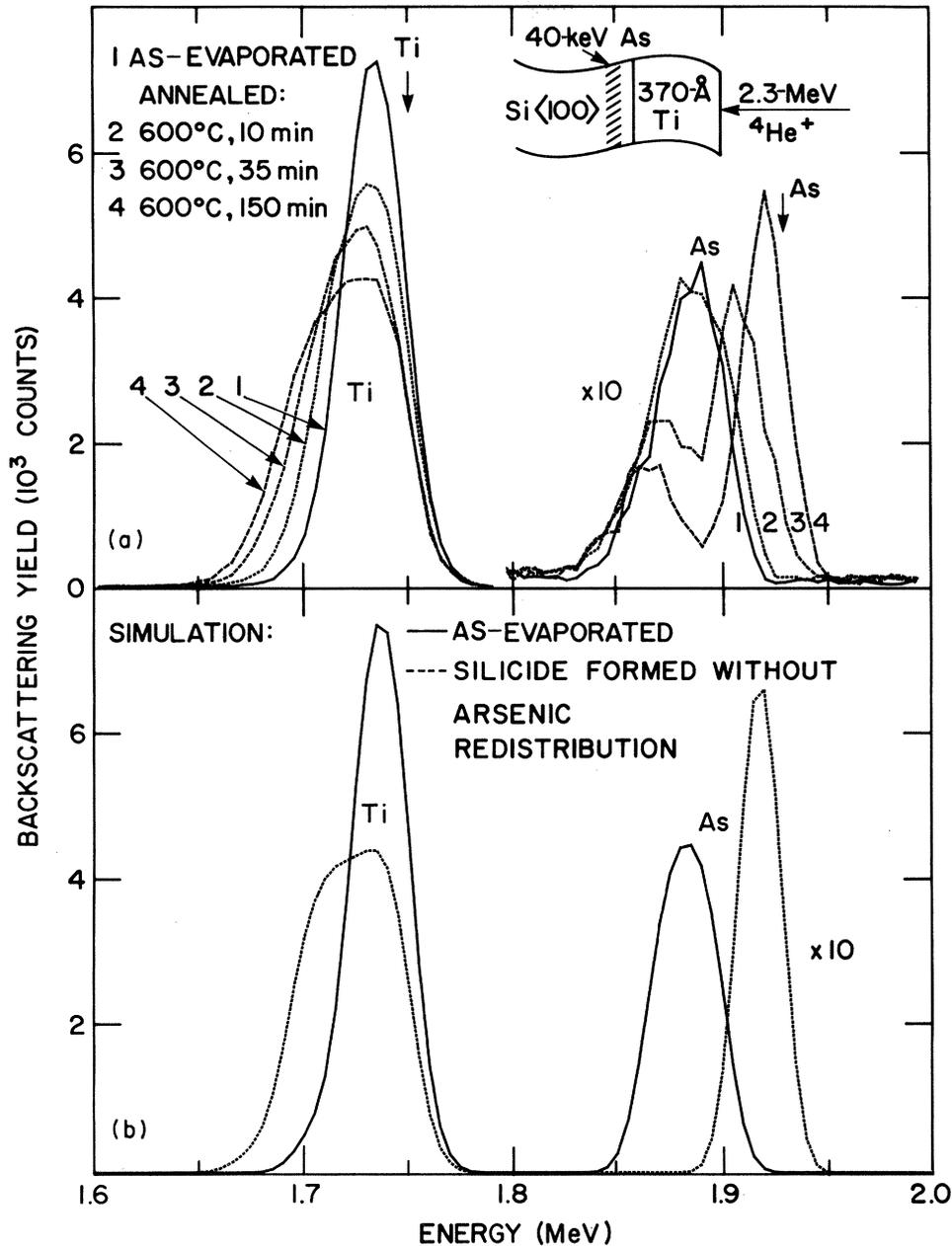


FIG. 4. 2.3-MeV $^4\text{He}^+$ RBS analysis of arsenic-implanted Si samples coated with 370-Å Ti and subsequently annealed at 600°C for 10, 35, and 150 min. The Si signal is not shown. The silicide formed is TiSi. Surface positions of Ti and As are shown by the vertical arrows. (b) Computer simulation of the spectra of (a) for the as-evaporated sample and the sample with complete TiSi formation but without As redistribution.

D. The V-Si system

The third and last case of the refractory-metal-silicon system that we have investigated is the V-Si system. The thickness of the V film was 440 Å and the annealings were performed at 550°C for 20, 80, and 200 min. The corresponding RBS spectra are shown in Fig. 6(a). From RBS and x-ray analysis we found that the compound formed at 550°C is VSi_2 . The As signals shift to higher energies upon annealing as in the previous refractory-metal-silicon cases. Simulated RBS spectra are given in Fig. 6(b) for the as-evaporated sample and for the sample

with complete silicide formation but without As redistribution into the silicon. The comparison of Fig. 6(a) with 6(b) shows that As redistribution does not take place during VSi_2 formation.

E. The coevaporated Pd-Si system

To investigate whether a moving silicide-silicon interface is responsible for the low-temperature dopant redistribution, we formed the silicide by coevaporation of its constituents rather than by interfacial reaction of a metal film with Si to exclude a moving interface. We selected

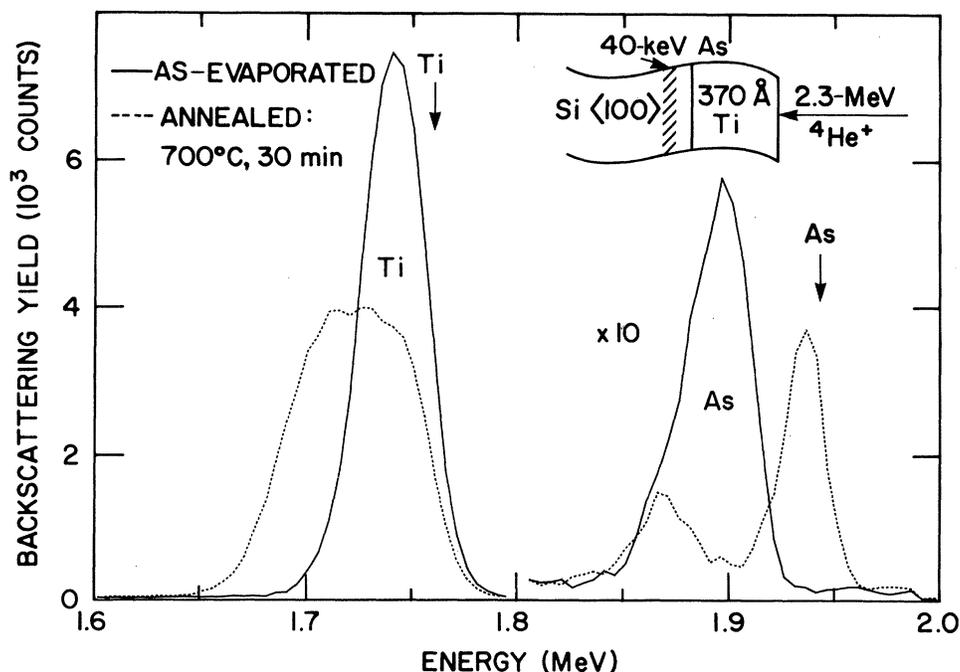


FIG. 5. 2.3-MeV $^4\text{He}^+$ RBS spectra of an as-evaporated Ti/Si(As) sample and a sample subsequently annealed at 700°C for 30 min. The silicide formed is TiSi_2 .

the Pd-Si system because redistribution of As into the silicon by Pd_2Si has been studied in detail,^{2,6} and also because it is unlike the Pt-Si system where both Pt_2Si and PtSi can form since the compound Pd_2Si is extremely stable.

The Si wafers used were the same as reported above. The coevaporation rates of Pd and Si were carefully adjusted to yield a thin film with the stoichiometry of the compound Pd_2Si . The RBS spectrum of such a coevaporated sample is shown in Fig. 7. From the heights of the Pd and Si signals (the Si signal is omitted in the figure for simplicity), we calculate that the composition of the coevaporated layer corresponds to the phase Pd_2Si within the accuracy of RBS ($\pm 5\%$). A heat treatment of the coevaporated sample should not result in a movement of the silicide-silicon interface. A minor displacement is possible if the composition of the coevaporated film departs slightly from exact Pd_2Si stoichiometry. The Pd signal in Fig. 7 of the sample annealed at 250°C for 5 h proves that the interface did not move.

The signals of the As are enlarged by a factor of 20 in Fig. 7. It is evident that the As profile has not been altered by the heat treatment. On the other hand, when Pd_2Si is formed in the conventional way by a moving silicide-silicon interface, a significant redistribution of the implanted As has been observed.² We can therefore conclude that the redistribution of As is correlated to the growth of near-noble-metal silicides; in other words, the mechanism which enables the silicides to grow at low temperatures is essential to the low-temperature redistribution of dopants.

IV. DISCUSSION

We have summarized in Table I all results known to date on the redistribution of dopant atoms during silicide

formation.¹⁻⁸ The result published by Wittmer and Seidel¹ for NiSi is at variance with those reported by Ohdomari.⁹ However, Wittmer and Seidel mentioned that both overlap between nickel and impurity signals and the limited resolution of RBS could impede the detection of impurity atoms at the silicide-silicon interface. For this reason Ohdomari used differential Hall measurements and neutron activation analysis, which have a much better resolution than RBS, to probe the As profile. Indeed, he observed a redistribution of As into the silicon following Ni_2Si and NiSi formation.

The general picture from Table I concerning dopant redistribution is that it is a unique feature of near-noble-metal silicides and does not occur during refractory-metal silicide formation. The extensive electrical measurements performed with PtSi and Pd_2Si contacts and Schottky diodes⁴⁻⁸ indicate that the dopant redistribution is independent of the dopant species. Our result from the coevaporated Pd-Si system proves that the redistribution of dopant atoms is correlated to the growth mechanism of the silicide. Therefore it is of great interest to know why only near-noble-metal silicides are capable of redistributing dopant atoms at low temperatures. We shall discuss this question in the following.

We start by discussing two possible explanations which we can rule out. First, the formation temperatures of near-noble-metal silicides, which are listed in Table I, range from 200 to 400°C. Thus dopant redistribution during silicide formation is truly a low-temperature process. At such low temperatures the diffusion of dopant atoms via intrinsic equilibrium defects in Si can be ruled out.

Second, we can also rule out equilibrium segregation effects. Generally speaking, equilibrium segregation at grain boundaries occurs only over a distance which is

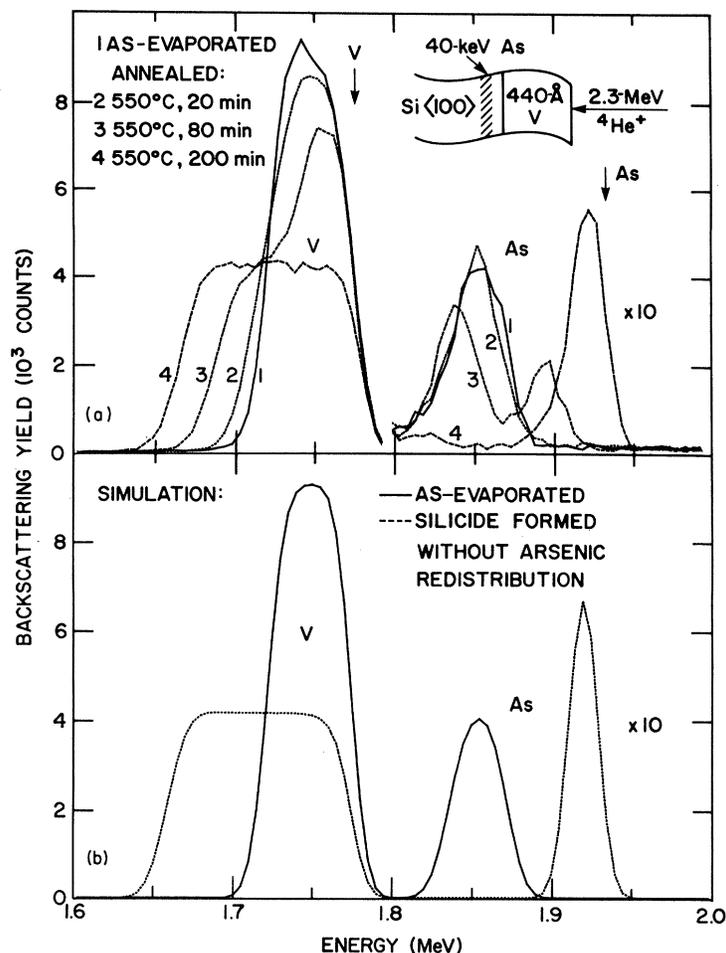


FIG. 6. (a) 2.3-MeV $^4\text{He}^+$ RBS spectra of arsenic-implanted Si samples evaporated with 440-Å V and subsequently annealed at 550°C for 20, 80, and 200 min. The Si signal is omitted. Vertical arrows indicate surface positions of the corresponding elements. (b) Computer simulation of the spectra of (a) for the case of the as-evaporated sample and the sample with complete VSi_2 formation but without As redistribution.

equal to the separation of neighboring grains (e.g., over the width of about one atomic layer). An analogy between grain boundary and interface segregation exists because lattice imaging studies have shown that transition-metal-silicide-silicon interfaces are structurally as sharp as grain boundaries.¹⁴⁻¹⁷ Thus the width of a possible interface segregation should be much smaller than the observed dopant redistribution depth of 100–200 Å. Furthermore, no redistribution was observed at the silicide-silicon interface of the coevaporated silicide, which cannot be explained on the basis of segregation. We can therefore conclude that equilibrium segregation cannot account for the redistribution of dopant atoms during interfacial silicide formation. Nevertheless, whether the low-temperature redistribution of dopant atoms near the silicide-silicon interface can be regarded as a nonequilibrium segregation phenomenon is unclear.

The low-temperature dopant redistribution is most likely due to an enhanced diffusion mechanism. From our data we find an effective diffusivity of arsenic of 7×10^{-15} cm²/sec during the redistribution by Pd_2Si at 250°C and of 2.5×10^{-15} cm²/sec during the redistribu-

tion by PtSi at 350°C. This corresponds to an enhancement of over 5 orders of magnitude if the high-temperature diffusivity of As in Si is extrapolated to 300°C.¹⁸ Obviously, in our case only excess defects could be responsible for the enhancement of the dopant diffusivity. Since the metal silicides are formed on a highly perfect crystal we must assume that excess defects are generated during the near-noble-metal silicide formation. In addition, these defects should not be generated during the growth of refractory-metal silicides because dopant redistribution is absent.

Lattice images of cross sections of transition-metal-silicide-silicon interfaces showed no extended defects such as dislocations, stacking faults, or defect clusters in the Si layer neighboring the interface.¹⁴⁻¹⁷ Hence the type of defect we should consider for the enhanced diffusion is the point defect. Point defects that can be generated in the silicon during interfacial silicide formation are vacancies, silicon self-interstitials, and solutes of metallic atoms. If, on the basis of an order-of-magnitude estimate, we assume that on the average one point defect is needed to redistribute one arsenic atom during interfacial

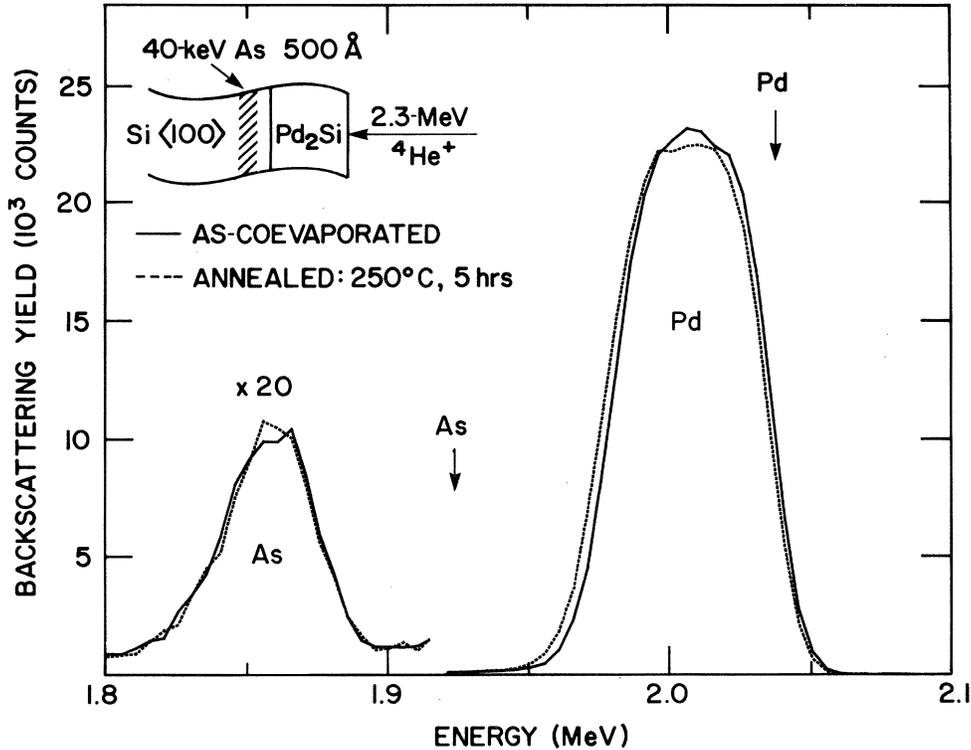


FIG. 7. 2.3-MeV $^4\text{He}^+$ RBS analysis of a coevaporated Pd_2Si layer on arsenic-implanted Si. Spectra are shown prior to and after an anneal at 250°C for 5 h. The Si signal is not shown. Surface positions of Pd and As are shown by the vertical arrows.

silicide formation, the observed redistribution of over 8×10^{14} As atoms per cm^2 over 100 Å of Si during Pd_2Si formation² implies that the excess point-defect concentration is about 10^{21} cm^{-3} at 250°C. From an investigation of the silicon self-diffusion coefficient it has been proposed that the maximum thermal equilibrium point-defect concentration near the melting point of silicon is about $5 \times 10^{16} \text{ cm}^{-3}$.¹⁹ Assuming an activation energy of 2.4 eV for the formation of a vacancy in silicon,²⁰ we estimate an equilibrium point-defect concentration of around 10^3 cm^{-3} at 300°C. The comparison shows that near-noble-metal silicide formation requires the generation of an excess point-defect concentration on the order of 10^{18} cm^{-3} . This raises the question about which mechanism is able to create such a large amount of point defects near the silicide-silicon interface.

Large volumetric changes are involved when silicides are formed by reacting a metal film with silicon. These volumetric changes create a high tensile-stress level at the silicide-silicon interface.²¹ As a result, point defects could be generated in the silicon near the interface to relieve some of the tensile stress. However, these point defects would give rise to dopant redistribution during near-noble-metal silicide as well as refractory-metal silicide formation, in contradiction to the experimental findings. We must therefore look for a mechanism of point-defect generation that is unique to near-noble-metal silicides.

The growth of metal silicides demands a continuous supply of silicon and metal atoms to the silicide-silicon interface. Metal atoms can be supplied by diffusion of atoms through the growing silicide layer. On the other hand, silicon atoms must be supplied by a process which

TABLE I. Redistribution of dopants during silicide formation.

Metal	Silicide	Formation temperature	Redistribution of		
			P	As	Sb
Ni	Ni_2Si	200°C		Yes	
	NiSi	400°C		Yes	
Pd	Pd_2Si	250°C	Yes	Yes	
Pt	Pt_2Si	250°C		Yes	
	PtSi	350°C	Yes	Yes	Yes
Ta	TaSi_2	700°C		No	
Ti	TiSi	600°C		No	
	TiSi_2	700°C		No	
V	VSi_2	550°C		No	

releases atoms from the silicon lattice.²² Generally, for the growth of transition-metal silicides one of these two processes dominates. In the case of near-noble-metal silicides the diffusion of metal atoms, which are the predominant diffusing species,^{23–31} determines the growth rate, resulting in a parabolic law. On the contrary, the predominant diffusing species in refractory-metal silicides are silicon atoms.²² A characteristic of near-noble-metal silicides is the low temperature at which they form. The low-temperature silicide formation implies that there exists a low-energy process that enables Si lattice atoms to break bonds and react with these metals. Since the activation energy for interstitial diffusion of near-noble-metal atoms in Si is low [e.g., 1.2 eV for Ni in Si (Ref. 32)], it has been suggested that near-noble-metal atoms can diffuse into Si at a low temperature and soften the Si covalent bonds to weaker metalliclike bonds. This reduction in bond strength will generate the flux of silicon atoms needed to form near-noble-metal silicides at low temperatures. Recent ion-channeling^{33,34} and photoelectron spectroscopy^{35,36} studies of the Ni-Si interface provide support for the interstitial model of near-noble-metal silicide formation. On the other hand, the formation of refractory-metal silicides necessitates the release of silicon atoms at the silicide-silicon interface, since the interstitial diffusivity of these metals in silicon is negligible. The loosening of silicon atoms at steps and ledges of the interface requires a higher energy and occurs typically at temperatures around 600°C, which is also the crystallization temperature of amorphous Si. Therefore, refractory-metal silicides form at higher temperatures.

From the above discussions we conclude that during the growth of near-noble-metal silicides there is a continuous supply of metal atoms to the silicide-silicon interface and these atoms diffuse into interstitial voids of the silicon lattice. This leads to a dissociation of silicon atoms from their lattice sites and the formation of point defects such as vacancies and/or self-interstitials. Because the number of tetrahedral voids in Si is large and the observed silicide growth rate is fast, the concentration of the generated point defects is large too. These point defects could enhance the diffusivity of substitutional dopants in silicon and cause a dopant redistribution near the interface during near-noble-metal silicide formation. It follows from the above discussion that this process of point-defect generation does not occur during the growth of refractory-metal silicides or without a moving silicide-silicon interface.

The low-temperature diffusion phenomenon of dopant atoms during interfacial silicide formation should be distinguished from the known dopant redistribution that occurs during thermal oxidation of silicon.^{37–39} The oxidation-induced redistribution of dopant atoms occurs at high temperatures, typically between 1000 and 1100°C. In this case, the growth of the silicon dioxide perturbs the point-defect concentration in the vicinity of the SiO₂-Si interface. This causes an enhancement or reduction of the diffusivity of substitutional impurities. Dopants which have a low solubility in SiO₂ (such as boron, phosphorus, and arsenic) are found to be enriched in the silicon by the advancing SiO₂-Si interface.

V. CONCLUSION

We have investigated the dopant redistribution during transition-metal silicide formation and found that arsenic atoms are redistributed during the growth of PtSi but not during the growth of TaSi₂, TiSi, TiSi₂, and VSi₂. Also, no redistribution was found with coevaporated Pd₂Si. A comparison with our earlier results on the arsenic redistribution during Pd₂Si formation and other results published in the literature^{1–8} shows that dopant redistribution during interfacial silicide formation is a rather unique feature of near-noble-metal silicides. We have discussed various mechanisms that could be responsible for this effect. We suggest that point defects are responsible for an enhancement of the diffusion of dopant atoms, which is observed at the low temperature. Based on an interstitial defect model of diffusion of near-noble metals for their silicide formation, we propose that this process creates a large number of point defects, which in turn enhances the diffusivity of dopant atoms. This enables the dopant atoms to redistribute during the low-temperature near-noble-metal silicide formation. Our experiments and current theoretical understanding of diffusion mechanisms do not allow us to determine the nature of the point defects whose generation is responsible for the dopant redistribution.

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¹M. Wittmer and T. E. Seidel, *J. Appl. Phys.* **49**, 5827 (1978).

²M. Wittmer, C.-Y. Ting, I. Ohdomari, and K. N. Tu, *J. Appl. Phys.* **53**, 6781 (1982).

³I. Ohdomari, K. N. Tu, K. Suguro, M. Akiyama, I. Kimura, and K. Yoneda, *Appl. Phys. Lett.* **38**, 1015 (1981).

⁴J. B. Bindell, W. M. Moller, and E. F. Labuda, *IEEE Trans. Electron Devices* **ED-27**, 420 (1980).

⁵A. Kikuchi and S. Sugaki, *J. Appl. Phys.* **53**, 3690 (1982).

⁶A. Kikuchi, *J. Appl. Phys.* **54**, 3998 (1983).

⁷M. Wittmer, C.-Y. Ting, and K. N. Tu, *J. Appl. Phys.* **54**, 699 (1983).

⁸S. S. Cohen, P. A. Piacente, G. Gildenblat, and D. M. Brown, *J. Appl. Phys.* **53**, 8856 (1982).

⁹I. Ohdomari, of Waseda University, Japan (private communication).

¹⁰W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).

¹¹K. N. Tu and J. W. Mayer, in *Thin Films—Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer, (Electrochemical Society, Princeton, 1978), p. 359.

¹²M. Wittmer, C.-Y. Ting, and K. N. Tu, *Thin Solid Films* **104**, 191 (1983).

- ¹³J. F. Ziegler, R. F. Lever, and J. K. Hirvonen, in *Ion Beam Surface Layer Analysis*, edited by O. Meyer, G. Linker, and F. Käppeler (Plenum, New York, 1976), Vol. I, p. 163.
- ¹⁴H. Föll, P. S. Ho, and K. N. Tu, *J. Appl. Phys.* **52**, 250 (1981).
- ¹⁵H. Föll, P. S. Ho, and K. N. Tu, *Philos. Mag. A* **45**, 31 (1982).
- ¹⁶L. J. Chen, J. W. Mayer, K. N. Tu, and T. T. Sheng, *Thin Solid Films* **93**, 91 (1982).
- ¹⁷R. T. Tung, J. M. Poate, J. C. Bean, J. M. Gibson, and D. C. Jacobson, *Thin Solid Films* **93**, 77 (1982).
- ¹⁸D. L. Kendall and D. B. DeVries, in *Semiconductor Silicon*, edited by R. R. Haberecht and E. L. Kern (Electrochemical Society, Princeton, 1969), p. 358.
- ¹⁹H. J. Mayer, H. Meher, and K. Maier, in *Weak Interaction Physics—1977 (Indiana University), Proceedings of the Conference on the Present Status of Weak Interaction Physics*, edited by D. B. Lichtenburg (IOP, London, 1977), p. 186.
- ²⁰J. A. van Vechten and C. D. Thurmond, *Phys. Rev. B* **14**, 3551 (1976).
- ²¹J. Angilello, F. d'Heurle, S. Peterson, and A. Segmüller, *J. Vac. Sci. Technol.* **17**, 471 (1980).
- ²²K. N. Tu, *Appl. Phys. Lett.* **27**, 221 (1975).
- ²³W. K. Chu, K. Kraütle, J. W. Mayer, H. Müller, M.-A. Nicolet, and K. N. Tu, *Appl. Phys. Lett.* **25**, 454 (1974).
- ²⁴W. K. Chu, S. S. Lau, J. W. Mayer, H. Müller, and K. N. Tu, *Thin Solid Films* **25**, 393 (1975).
- ²⁵R. Pretorius, C. L. Ramiller, S. S. Lau, and M.-A. Nicolet, *Appl. Phys. Lett.* **30**, 501 (1977).
- ²⁶T. G. Finstad, J. W. Mayer and M.-A. Nicolet, *Thin Solid Films* **51**, 391 (1978).
- ²⁷R. Pretorius, C. L. Ramiller, and M.-A. Nicolet, *Nucl. Instrum Methods* **149**, 629 (1978).
- ²⁸R. Pretorius, J. O. Olowolafe, and J. W. Mayer, *Philos. Mag. A* **37**, 327 (1978).
- ²⁹J. E. E. Baglin, F. M. D'Heurle, W. N. Hammer, and S. Petersson, *Nucl. Instrum. Methods* **168**, 491 (1980).
- ³⁰J. E. E. Baglin, F. M. D'Heurle, and C. S. Petersson, *J. Appl. Phys.* **52**, 2841 (1981).
- ³¹F. D'Heurle, S. Petersson, L. Stolt, and B. Strizker, *J. Appl. Phys.* **53**, 5678 (1982).
- ³²G. L. P. Berning and L. L. Levenson, *Thin Solid Films* **55**, 473 (1978).
- ³³N. W. Cheung, R. J. Culbertson, L. C. Feldman, P. J. Silverman, K. W. West, and J. W. Mayer, *Phys. Rev. Lett.* **45**, 120 (1980).
- ³⁴N. W. Cheung and J. W. Mayer, *Phys. Rev. Lett.* **46**, 671 (1981).
- ³⁵P. J. Grunthaner, F. J. Grunthaner, and J. W. Mayer, *J. Vac. Sci. Technol.* **17**, 924 (1980).
- ³⁶Y.-J. Chang and J. L. Erskine, *Phys. Rev. B* **26**, 4766 (1982).
- ³⁷A. S. Grove, O. Leistiko, Jr., and C. T. Sah, *J. Appl. Phys.* **35**, 2695 (1964).
- ³⁸M. M. Atalla and E. Tannenbaum, *Bell System Tech. J.* **39**, 933 (1960).
- ³⁹D. A. Antoniadis and I. Moskowitz, *J. Appl. Phys.* **53**, 6788 (1982).