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Microscopic Observation of the Kirkendall Effect in Ti/Si and Ni/Si Systems

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The formation of silicides via the thin-film deposition of transition metals Ti and Ni onto Si substrates has been investigated by a slow positron beam. In the case of the Ti/Si, the formation of the silicides did not induce the shortening of positron diffusion length in Si substrate. On the contrary, the diffusion length of positrons in formed silicides was very short indicating the presence of a great number of positron traps in silicides. The diffusion of Si atoms as a dominate diffusion species during $TiSi_2$ formation could not be recognized by the present experiment. On the other hand, in the case of Ni/Si, the silicidation induced a very short diffusion length of positrons in the Si substrate. On the contrary, the diffusion length in the formed silicide is long to a comparable extent expected defect-free metals. The diffusion of Si during $NiSi_2$ formation was observed by the present experiment.

1. INTRODUCTION

There is much interest in the interaction of metal films with Si. Interest in the metal silicides lies in their usefulness in integrated circuits as Schottky barriers, ohmic contact, and low resistivity gate interconnects.[1] In materials science, it is also interesting that the silicide formation between two solid phases in direct contact to form ordered intermetallic compounds at temperatures well below the formation of any liquid phase. It is the central problem that what is the moving mechanism of metal atoms and Si atoms during the silicide formation.

The aim of the present work is to investigate the formation mechanism of silicides in Ti/Si and Ni/Si systems from the point of view of vacancy condensation by means of a slow positron beam.

2. EXPERIMENTAL

The Ti film in the thickness of 30 nm was deposited on *p*-type Cz-Si with the (100) face orientation and the resistivity of 5 Ω·cm by a DC magnetron sputtering method with a deposition rate of 52 nm/min. After the deposition, one specimen was annealed at 850°C for 60 min and the other at 1000°C for 30 min. By the annealing, $TiSi_2$ layer in the thickness of 75 nm was formed.[2]

The Ni film in the thickness of 100 nm was deposited in the same way as the Ti/Si specimen with a deposition rate of 33 nm/min. The annealing at 850°C for 60 min induced the formation $TiSi_2$ film in the thickness of 360 nm.[2]

The present experiment was performed by using the ultra-high vacuum slow positron beam line constructed at University of Tsukuba. The lineshape of the spectrum was characterized by a lineshape S parameter. All the as-deposited specimens and the annealed one were characterized by positron experiment before and after the removal of the epilayers on Si substrate by chemical etching. The details of the measurement system was described in the previous paper.[3]

3. RESULTS AND DISCUSSION

Figure 1 shows the lineshape parameter S as a function of incident positron energy, i.e., the S(E) response, for the as-deposited Ti/Si specimen, annealed one at 850°C and annealed one at 1000°C. The solid lines in company with the data plots indicate the best fits of model equation incorporating the positron diffusion to the experimental data, as explained later. The plots for the 850°C annealed $TiSi_2$/Si and 1000°C annealed one are displaced upwards by 0.02 and 0.04, respectively, for clarity. The relationship between the incident positron energy E and the mean positron penetration depth $\bar{x}$ is given by

$$\bar{x}(\mathrm{nm}) = 40E^{1.6}(\mathrm{keV})/\rho(\mathrm{g/cm^3}) \qquad (1)$$

where ρ is the specific density of the specimen. The energy corresponding to the position of the

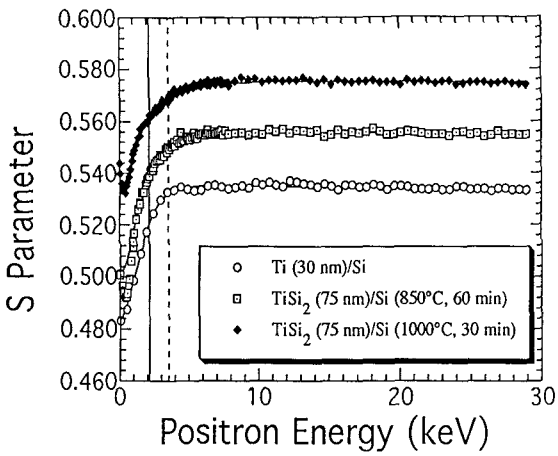

Figure 1. S(E) plots for the as-deposited Ti(30 nm)/Si specimen and annealed ones at 850°C and 1000°C, respectively. For clarity, plots are displaced by 0.02 between each other.

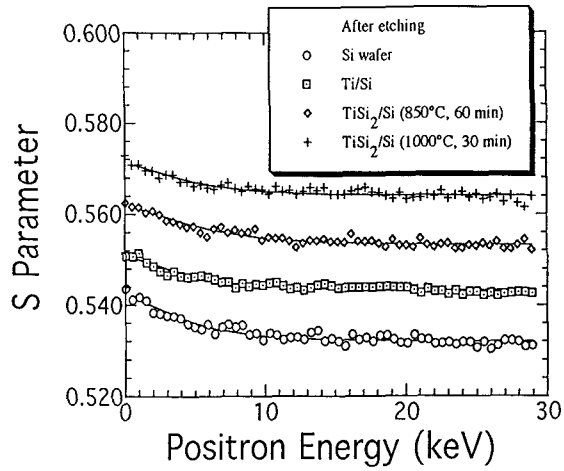

Figure 2. S(E) plots for Ti(30 nm)/Si and $TiSi_2$ (75 nm)/Si specimens after etching out epilayers. For clarity, plots are displaced by 0.02 between each other.

interface for the as-deposited Ti/Si specimen is expected to be about 2.2 keV according to Eq. (1) as indicated by the solid vertical line. The vertically dashed line indicates interface position of $TiSi_2$/Si in the same way. The lower value ($\sim$0.48) at the surface indicate the positron annihilation at the Ti. From the previous study,[4] it is known that the S value of Ti is about 0.48 for this specific apparatus. The annealing treatment for the silicidation modifies the S(E) relation a little bit. The S values in the epilayer of 1000°C annealed $TiSi_2$/Si are higher than that of 850°C annealed one. The higher temperature might lead to the introduction of higher concentration of defects, causing the increasing of S parameter. When the incident positron energy increase the S parameter increase drastically, implying the increase of annihilation in the bulk Si. The interesting point to be investigated here is the effect of the silicidation on the diffusion length of positrons in Si substrate together with the diffusion length in the formed silicide epilayer. In order to determine the diffusion length, the S(E) relation for each specimen before and after the etching out of the epilayers was measured. From the S(E) relation before the etching, we can determine the diffusion length L_{epi}, L_{Si} in the silicide and Si substrate, respectively. After the etching, we can also determine the diffusion length L_{Si} in the Si substrate. The S(E) relation can be given by

$$S(E) = S_{epi}F_{epi}(E) + S_iF_i(E) + S_bF_b(E) \qquad (2)$$

where S_{epi} is the S parameter for the annihilation in the epilayer, S_i that for the annihilation at the interface and S_b that for the annihilation in the Si substrate.[5] The F_{epi}, F_i and F_b denote the fraction of positron annihilation in the epilayer, at the interface and in the Si substrate. When the surface of specimen is etched, the S(E) response can be simply given by

$$S(E) = S_sF_s(E) + S_b[1 - F_s(E)], \qquad (3)$$

where S_s is the S parameter for the annihilation at the surface and F_s the fraction of positrons annihilating at the surface. Figure 2 shows the S(E) plots for Ti/Si and $TiSi_2$/Si system after etching. The plot of wet-etched Si wafer is also included as a reference. The determined values of diffusion length of positron in epilayer and in Si substrate are summarized in Table 1. The diffusion length

Table 1
Summary of parameters obtained by fitting one-dimentional diffusion model of positron for Ti/Si, Ni/Si specimens and wet-etched Si wafer.

Specimens	S_{epi}	S_i	S_{Si}	L_{epi} (nm)	L_{Si} (nm)
Ti (30 nm)/Si	0.4820	0.5369	0.5343	25	293
After etching			0.5332		229
$TiSi_2$ (75 nm)/Si (850°C, 60 min)	0.4575	0.5666	0.5373	65	268
After etching			0.5331		310
$TiSi_2$ (75 nm)/Si (1000°C, 30 min)	0.4807	0.5569	0.5363	57	265
After etching			0.5340		244
Ni (100 nm)/Si	0.5070	0.5376	0.5346	66	267
After etching			0.5334		317
$NiSi_2$ (360 nm)/Si	0.5284	0.4474	0.5337	102	86
After etching			0.5347		105
Wet-etched Si Wafer			0.5320		225

of positrons in the Si substrate after various treatment was found to be longer than 200 nm. These values for the Si substrate are comparable to that in defect-free Si.[6] On the other hand, the diffusion length in the formed silicide epilayers is very short, ranging around 60 nm. The well annealed metals usually shows the diffusion length longer than 100 nm. This fact clearly shows that the silicidation introduces defects in formed silicide epilayer, but not in the Si substrate. It is known that the diffusing species in the Ti/Si during silicidation of $TiSi_2$ is Si atoms.[7–9] Chu *et al.*[8] investigated the silicide formation by using implanted noble gas atoms as diffusion marker and indicated that Si is the dominant moving species in $TiSi_2$. However, vacancy accumulation should occur in the Si side if Si is the diffusing species. No evidence was found that the Si substrate was degraded by the silicidation in the present experiment.

Figure 3 shows the S(E) plots for the as-deposited Ni/Si specimen and for the annealed one. The vertically solid and dashed lines indicate the interface positions of Ni(100 nm)/Si and of $NiSi_2$ (360 nm)/Si, respectively. Table 1 also summarizes the determined values of various quantities in the Ni/Si system. Fig. 4 shows the S(E) plots for the as-deposited Ni/Si specimen and for the annealed one, both after the etching out of epilayers. By the silicidation, the diffusion length in the Si substrate became very

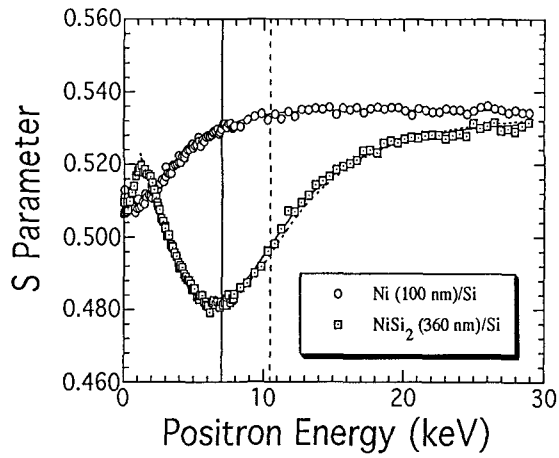

Figure 3. S(E) plots for the as-deposited Ni(100 nm)/Si and $NiSi_2$ (360 nm)/Si specimens.

short. The value of diffusion length around 100 nm clearly means that a great number of vacancies are introduced into Si substrate. On the other hand, the diffusion length in the formed silicide epilayer is very long to a comparable extent expected for the defect-free metals. The lower S parameter at the interface (~0.503) indicates that the silicide epilayer is coherent with the Si substrate and indicates the lack of defects at the interface. Studies[8, 10] showed the initial formation phase is Ni_2Si and the formation of NiSi is

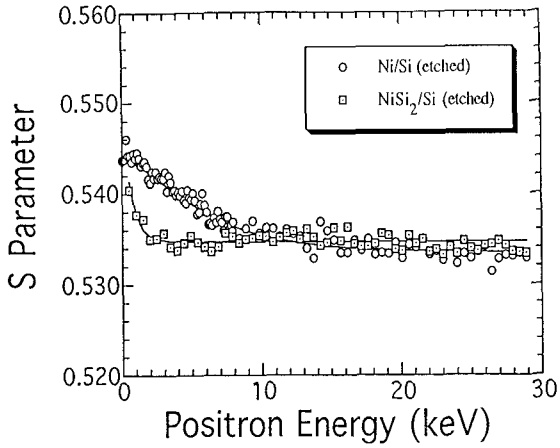

Figure 4. S(E) plots for the as-deposited Ni(100 nm)/Si and $NiSi_2$ (360 nm)/Si specimens after etching out epilayers.

very fast at temperature above 350°C which is stable up to 750°C. The diffusion species in the Ni_2Si and NiSi is already recognized as Ni atom by noble gas marker experiment.[11] At temperature higher than 750°C, epitaxial growth of $TiSi_2$ has been found on crystalline Si substrate.[12] In such a case, the disilicide $NiSi_2$ has a close lattice match with Si. Our results coincide well with the previous conclusion in such an aspect. However, the shortened diffusion length of positrons in Si substrate indicate that the Si diffusion also occurs during $TiSi_2$ formation regardless of diffusion of Ni atoms. In such an aspect, our results are discrepant from the noble gas marker experiment performed by d'Heurle *et al.*[11]

4. CONCLUSION

This experiment for the first time reports the successful use of a slow positron beam to the microscopic observation of the Kirkendall effect in the metal/Si system. In the case of the Ti/Si, the formation of the silicides did not induce the shortening of positron diffusion length in Si substrate. The diffusion of Si atoms as a dominate diffusion species during $TiSi_2$ formation could not be recognized by the present experiment. On the other hand, in the case of Ni/Si, the silicidation induced a very short diffusion length of positrons in the Si substrate. However, the diffusion length in the formed silicide is long to a comparable extent expected defect-free metals. The diffusion of Si, regardless of the diffusion of Ni atoms, during $TiSi_2$ formation was observed by the present experiment.

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