

Initial stage of room-temperature metal-silicide formation studied by high-energy He⁺-ion scattering

T. Narusawa and W. M. Gibson

Department of Physics, State University of New York at Albany, Albany, New York 12222

A. Hiraki

Department of Electrical Engineering, Osaka University, Suita, Osaka, 565 Japan

(Received 27 October 1980)

Room-temperature reactivities of Au, Ag, and Pd deposited on clean Si(111) substrate surfaces have been studied by MeV He⁺-ion scattering. It is directly shown that there exists an average threshold film thickness of about three monolayers for gold or silver silicide formation. However, palladium interacts with silicon even at submonolayer coverage to form an amorphous PdSi-like film.

Numerous experimental results have been accumulated about silicide formation due to the reaction of silicon substrates with deposited metal films. As reviewed by Ottaviani,¹ for couples of Si and noble or near-noble metals (M), metal-rich silicides (M_2Si) are first formed at low temperatures ($\leq 200^\circ\text{C}$). Since it is hard to believe that the covalent back bondings of Si surface atoms are broken at such low temperatures to form silicides, several models have been proposed. The model of Walser and Bene² postulates a "glassy membrane" (Si- M mixed phase) at the interface in which Si has no covalent bonding. Silicon can be released easily from this phase, but it is not clear in this model why such a mixed phase is formed. Tu's model³ postulates a diffusion of M into the interstitial sites of Si which transforms Si atoms at the interface from covalent bonding to metallic bonding. A recent model by Hiraki⁴ postulates electrostatic screening by free electrons in the metal overlayer. Such a screening can disturb the electron distribution responsible for the covalent bonding, then qualitatively have a possibility to release Si atoms from the crystal lattice.

In order to elucidate the mechanism of silicide formation, it is of a great significance to investigate the atomic structure at the Si- M interface in the initial stage of reaction. This paper describes an application of the displacement-sensitive MeV He⁺-ion scattering technique⁵ to Si- M (Au, Ag, and Pd) interface studies. The results show that there exists a threshold film thickness to induce the silicide formation in the Si-Au and Si-Ag systems. The measured threshold coverage of ~ 3 monolayers (ML)

for the room-temperature silicide formation can be regarded to correspond to the formation of metallic bonding in the overlayer rather than the diffusion of M atoms into the Si lattice. In contrast, the Si-Pd system shows apparently no threshold but "PdSi"-like phase formation in the initial stage. This suggests a slight invasion of Pd atoms into Si surface region.

The Si(111) substrate, mounted on a UHV three-axis goniometer, was cleaned by Ohmic heating up to $\sim 1100^\circ\text{C}$. The cleanliness of the surface was measured by *in situ* Auger electron spectroscopy (AES) and backscattering before thin film deposition. AES and backscattering revealed the residual impurity carbon of ~ 0.2 at. % and a trace ($\sim 10^{12}$) atoms/cm² of heavy impurity elements, respectively. The *in situ* electron diffraction [5 keV, medium-energy-electron diffraction (MEED)] showed a sharp 7×7 pattern characteristic of the clean Si(111) surface after the cleaning process. Gold, silver, and also germanium for a reference were evaporated from tungsten helical baskets, and palladium was sublimated from a resistively heated pure Pd wire to obtain a deposition rate of ~ 0.5 ML/min on the target surface. The substrate temperature during deposition and measurements was kept at room temperature. AES and backscattering measurements showed clean thin-film growth. MEED did not show any specific diffraction features but only a fading of the 7×7 pattern with the increase of the film thickness over ~ 1 ML. This indicates the amorphous film growth in agreement with other electron diffraction studies.⁶⁻⁸ Backscattering and channeling spectra were mea-

sured in the course of deposition aligning a 1-MeV He^+ -ion beam in the normal $\langle 111 \rangle$ axial channeling direction. The fluence of ion beam was $2\mu\text{C}$ for each spectral measurement. Scattered particles were analyzed by a surface-barrier-type Si detector [resolution ~ 20 keV, full width at half maximum (FWHM)] located in the direction of $\sim 95^\circ$ scattering angle and subtended a solid angle of ~ 2 msr. In this arrangement we can detect the so-called surface peak (SP) as typically shown in Fig. 1.

The SP arises from scattering of projectiles by the surface layer of the target, and its intensity is directly related to the surface atomic structure.⁹ Using this technique, Culbertson *et al.*¹⁰ have shown that the Si(111) (7×7) surface structure is essentially bulklike when investigated in the normal direction, i.e., the lateral displacements of surface atoms from the normal (bulklike) sites are small and confined to one to two monolayers at most. If Si atoms are displaced from the normal sites the SP intensity increases depending upon the magnitude of the displacement.^{11,12} In the present case, a displacement of the topmost layer by ~ 0.2 Å is enough to increase the SP intensity by the amount corresponding to the scattering yield by 1

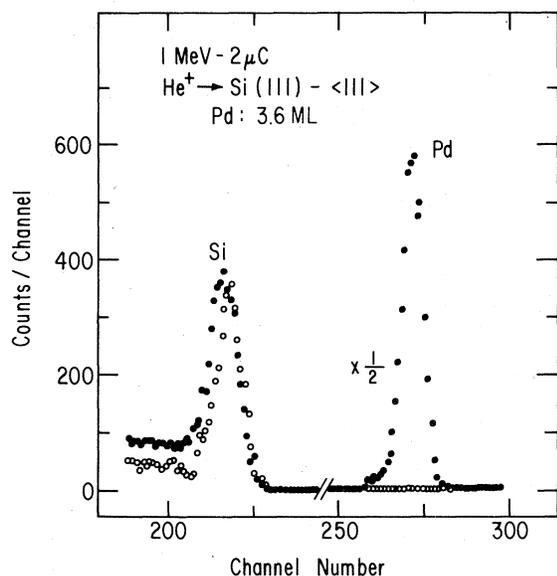


FIG. 1. Typical aligned backscattering spectra from clean (open circles) and Pd-deposited (filled circles) Si(111) surfaces. Note that the surface peak intensity (peak area) of Si increases due to Pd deposition. The Pd peak intensity gives the average Pd-film thickness of 3.6 ML (1 ML = 7.8×10^{14} Pd/cm²). The background pressure during deposition and measurements was lower than 1×10^{-9} Torr.

ML of Si. Displacements of the subsequent layers play the same role unless there exists correlation between the displaced layers. Therefore, assuming the displacements greater than ~ 0.2 Å, we can directly relate the increase of SP intensity to displaced monolayers. Possible effects by multiple scattering of projectiles passing through the overlayer and the shadowing of Si atoms by the overlayer were examined by a computer simulation method.¹² The results showed that, when the overlayer structure is not in register with the substrate the shadowing effect can essentially be ignored in our film thickness region, and the multiple scattering is more important especially in case of heavy element overlayers. This effect is subtracted from raw data in Fig. 2, which shows the relation between the number of displaced Si monolayers and deposited overlayer thickness for each system.

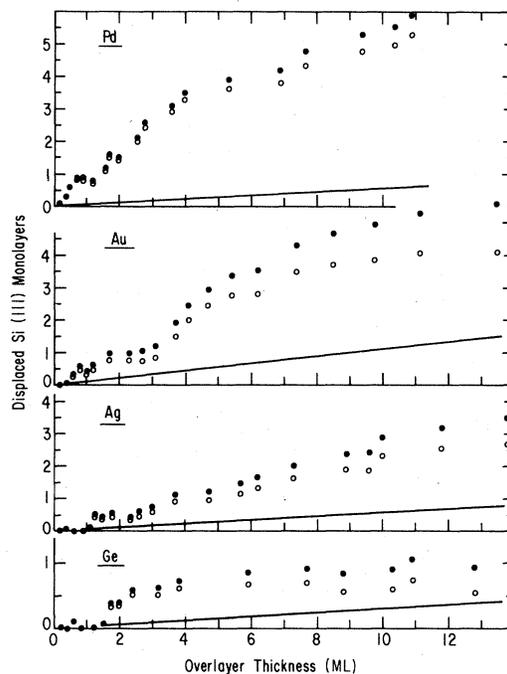


FIG. 2. Displaced Si monolayers vs average overlayer thickness. Filled circles: raw data, open circles: after correction of the multiple scattering effect. Calculated increase in Si surface peak intensity due to the multiple scattering effect is indicated in a solid curve for each system. The average overlayer thickness measured simultaneously by backscattering is expressed in units of equivalent monolayers of Si(111) plane (1 ML = 7.8×10^{14} atoms/cm²). The data plots were collected from 3 to 5 runs for each system. The uncertainty of relative measurements in each run was estimated to be $\pm 3\%$, but error bars are not indicated for clarity.

In the Si-Ge system, about 3 ML of Ge displace ~ 0.5 ML of Si,¹³ but there is no further displacement due to thicker layers. We are most likely to consider this displacement as small in view of the pseudomorphism. Assumption of some Si-Ge and Ge-Ge interactions through their dangling bonds seems quite reasonable in the initial stage of deposition, which result in a formation of pseudomorphic system in a short range. This can displace Si atoms from the normal sites and increase the SP intensity of Si.

In the Si-Au and Si-Ag systems, too, the atoms deposited on the clean 7×7 surface apparently seem not to react substantially with Si atoms until the average film thickness reaches ~ 3 ML. This has been investigated in detail for Si-Au and has been interpreted in terms of tight bonding of the first few ML of the metal to the surface satisfying the dangling bonds.¹⁴ Small displacements of Si at this stage are considered similar to the Si-Ge system. In fact, the stability of 1 ML or less of Au on the clean (111) surface was ascertained by AES (Ref. 4) and backscattering¹⁴ even at high temperatures (500–800°C) well above the eutectic point. After saturation of dangling bonds further gold or silver added to the surface appear rather free to migrate and then to agglomerate into islands or microcrystalline grains. This is the characteristic of the "layer-plus-island" growth of thin films to which both of the present systems belong.^{7,15} When the thickness of grains exceeds a critical value, a spontaneous M -Si reaction takes place as shown by the increase of displaced Si monolayers in Fig. 2. The threshold corresponds to an average film thickness of ~ 3 ML in both Au and Ag cases. This agrees with AES measurements of the Si-Au system^{4,6,15} and the Si-Ag system.⁷ The ratio of displaced Si monolayers to deposited Au or Ag monolayers is slightly deficient in relation to the reaction products with a composition of M_2 Si. This may be due to either unreacted M atoms present on the film or too small displacements of reacted Si atoms. The increase of displaced Si monolayers tends to saturate at a coverage of ~ 10 ML in the Au case, but appears to continue up to a coverage of ~ 14 ML in the Ag case.

In the Si-Pd system, displacements of Si atoms take place at the initial stage of deposition in contrast to the Si-Au or -Ag system. The increase of displaced Si monolayers is linear with the overlayer thickness, and the slope is rather steep in the first stage up to the Pd deposition of ~ 4 ML. Compounds apparently formed at the first and the next

stages are PdSi and Pd₂Si, respectively. The formation of the PdSi "phase" at the first stage is in disagreement with Ho *et al.*⁸ and Freeouf *et al.*¹⁶ However, their claim of the first Pd₂Si phase formation in the Si-Pd system is based upon rather indirect evidence. The AES calibration of Ho *et al.* of the composition and the thickness of the reacted layer was done only in the thickness range greater than 4.5 Å, i.e., ~ 4 ML. The evidence of Freeouf *et al.* came from a similarity of the ultraviolet photoemission (UPS) spectral shape (but the d -band peak shift is different until the deposition of 4–8 Å of Pd) between the low (submonolayer) coverage spectra and the Pd₂Si spectrum. Figure 2 indicates directly that there exists a PdSi-like phase at the low-coverage region before formation of the Pd₂Si phase. This may correspond to a strong interaction between deposited Pd atoms or slight invasion of Pd atoms into the Si surface region which displaces Si atoms from the normal sites. It should be noted that this PdSi-like phase is definitely not the palladium-mono-silicide (PdSi) existing in the bulk phase diagram as a stable silicide up to $\sim 1100^\circ\text{C}$, because at $\sim 500^\circ\text{C}$ our PdSi-like phase is very unstable, i.e., a remarkable indiffusion of Pd atoms into Si takes place readily. The PdSi-like phase is changed to Pd₂Si at an average coverage of ~ 4 ML. This is the threshold in the Si-Pd system in a sense that conversion starts to take place from the PdSi-like to the Pd₂Si phase which is reported to be the most stable between room temperature and $\sim 700^\circ\text{C}$.^{8,16,17} In fact, our UHV annealing experiments¹⁸ of the Si-Pd system as a function of Pd overlayer thickness has shown that the phase formed at the coverage thicker than ~ 5 ML is stable at $\sim 600^\circ\text{C}$.

The reactivity of Au and Ag films with SiO₂ was also examined. When either Au or Ag was directly deposited on a native SiO₂ film of 5–6 ML in thickness, there was no indication of interface reaction, i.e., the SP intensity of Si stayed constant throughout deposition of up to ~ 15 ML. This result agrees with Cheung's observation for the Si-Ag system.¹⁹ It is clear that even very thin oxide layers can strongly impede the interface reaction.

We have shown the following:

(a) Au and Ag films of ≤ 1 ML bond strongly with clean Si(111) surfaces and this is stable without further interaction or diffusion into the substrate at temperatures well above the eutectic point. Formation of this stable Si- M structure may be related to saturation of surface dangling bonds.

(b) For Au and Ag film thickness of ≥ 3 ML a

spontaneous reaction occurs at room temperature with formation of amorphous metal silicide films of composition $M_x Si$ ($x = 2-4.5$). This film grows in thickness with further metal deposition. The thickness saturates at about ~ 10 ML of deposited metal for Au and continues to grow for Ag up to the thickness (~ 15 ML) studied.

(c) The behavior of Pd is different from that of Au or Ag. For this case interaction between the metal and the Si surface atoms takes place even at submonolayer coverage to form an amorphous

"PdSi" film. This film continues to grow upon further metal deposition until at a threshold of ~ 4 ML further reaction with the substrate occurs resulting in formation of a stable Pd_2Si amorphous film.

(d) Even very thin oxide layers on the silicon surface can block the formation of metal silicides.

This work was supported by the Office of Naval Research under Contract No. N00014-78-C-0616.

¹G. Ottaviani, *J. Vac. Sci. Technol.* **16**, 1112 (1979).

²R. M. Walser and R. W. Bene, *Appl. Phys. Lett.* **28**, 624 (1976).

³K. N. Tu, *Appl. Phys. Lett.* **27**, 221 (1975).

⁴A. Hiraki, *J. Electrochem. Soc.* **127**, 2662 (1980).

⁵L. C. Feldman, in *Surface Science: Recent Progress and Perspectives*, edited by R. Vanselow (CRC, Ohio, 1980).

⁶K. Oura and T. Hanawa, *Surf. Sci.* **82**, 204 (1979).

⁷J. A. Venables, J. Derrien, and A. P. Janssen, *Surf. Sci.* **95**, 411 (1980).

⁸P. S. Ho, T. Y. Tan, T. E. Lewis, and G. W. Rubloff, *J. Vac. Sci. Technol.* **16**, 1120 (1979).

⁹Although the SP intensity always contains the contribution of the thermal vibration, we can neglect its effect in relative measurements assuming that the dynamics of the surface lattice do not change much due to deposition of overlayers.

¹⁰R. J. Culbertson, L. C. Feldman, and P. J. Silverman, *Phys. Rev. Lett.* **45**, 2045 (1981).

¹¹S. T. Picraux, W. L. Brown, and W. M. Gibson, *Phys. Rev. B* **6**, 1382 (1972).

¹²K. Kinoshita, T. Narusawa, and W. M. Gibson, *Surf. Sci.* (in press).

¹³If the displacement is smaller than ~ 0.2 Å the number of displaced layers is larger than ~ 0.5 ML. For instance, the displacement of 1 ML by ~ 0.12 Å is also consistent with our measurements.

¹⁴T. Narusawa, K. Kinoshita, W. M. Gibson, and A. Hiraki, *J. Vac. Sci. Technol.* **18**, 872 (1981).

¹⁵G. LeLay and J. P. Faurie, *Surf. Sci.* **69**, 295 (1977).

¹⁶J. L. Freeouf, G. W. Rubloff, P. S. Ho, and T. S. Kuan, *Phys. Rev. Lett.* **43**, 1836 (1979).

¹⁷W. D. Buckley and S. C. Moss, *Solid State Electron.* **15**, 1331 (1972).

¹⁸A. Hiraki, T. Narusawa, and W. M. Gibson (unpublished).

¹⁹W. N. Cheung, Ph.D. thesis, California Institute of Technology, 1980 (unpublished).