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Effects of variations of silicide characteristics on the Schottky-barrier height of silicide-silicon interfaces

P. E. Schmid,* P. S. Ho, H. Föll,† and T. Y. Tan
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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One basic question concerning Schottky-barrier formation at the silicide-Si interface is whether the barrier height is influenced by the material characteristics of the silicide. This question was investigated by studying the barrier formation at Pd-Si and Ni-Si interfaces over a range of parameters, including the silicide stoichiometry, microstructure, substrate orientation, surface preparation and annealing after silicide formation. The barrier was formed by evaporating metal on chemically cleaned and atomically cleaned [ultrahigh-vacuum- (UHV-) prepared] Si surfaces. The photoresponse technique was used to measure the barrier height and results are compared with *I-V* measurements. Rutherford ion backscattering and transmission electron microscopy were used to characterize the silicide phase, microstructure, and interface morphology. Within the experimental accuracy, the barrier height was found to be unaffected by variations in the silicide characteristics with the exception of surface preparation. The results can be qualitatively understood by classifying the interface to be either extrinsic or intrinsic. The barrier height for the extrinsic interface is mainly controlled by defects and contaminants induced during the praparation of the interface. For the intrinsic interface it is determined by some interfacial characteristics originating from metal-silicon interaction at the interface. We propose that one such characteristic is the metal-silicon bond at the interface.

INTRODUCTION

The study of Schottky-barrier formation at metal-semiconductor interfaces has been of long-standing scientific and technological interest. Recently considerable attention has been focused on the transition-metal—silicon contact because of its potential applications for large-scale integrated circuits.[1] One characteristic distinguishing this type of interface from the others is the strong chemical reactivity which induces formation of silicide compounds at moderate annealing temperatures, e.g., formation of Pd_2Si below 250 °C.[2] Silicide formation requires mass transport of the metal or silicon atoms, or both, across the interface. As reaction proceeds to form a silicide layer, a silicide-silicon interface is established beneath the initial metal-silicon interface. The stoichiometry and atomic structure of the silicide-silicon interface are basically different from the metal-silicon interface, which in turn is expected to alter its electronic and electrical properties.

The kinetics and phase stability of silicide formation have been extensively investigated.[3] In general, the formation of a specific phase and its microstructure depend on the annealing conditions and on the silicon-substrate orientation. A large range of variation has been observed for the phase stoichiometry, i.e., from metal-rich to silicon-rich silicides, and in the microstructure, i.e., from microcrystalline to epitaxial structures. The structure of the epitaxial interfaces has been studied in detail using the lattice-imaging technique of transmission-electron microscopy (TEM).[4] The result revealed the structure to be abrupt with a sharp transition region of one to two atomic layers. Ion-scattering measurements[5] confirmed the existence of silicidelike compounds in the first few monolayers of the interface although ion-channeling experiments also detected the presence of metal atoms in the Si substrate, e.g., in the Ni—Si system.[6]

Surface-electron-spectroscopy techniques, such as uv, x-ray, and synchrotron-radiation photoemission and Auger spectroscopy, have been used to investigate the electronic structure of silicide and silicide-silicon interfaces.[7,8] Chemical bonds responsible for silicide formation were found to originate from hybridization of the metal *d* and silicon *p* valence states. Silicide formation was observed to dominate the electronic structure of the interface, with spectral features of the hybrid states reflecting a silicon-rich environment. In addition true interface states have been observed at Pd (Ref. 9) and Pt (Ref. 10) interfaces, indicating specific bonding characteristics between metal and silicon at the interfaces.

In spite of the progress in understanding the bonding and structural characteristics, their correlation to the interfacial electrical property, particularly the Schottky-barrier height (SBH), remains elusive. A fundamental difficulty lies in that most of the spectroscopy techniques are only capable of detecting a small fraction (~ 0.1 ML) of a monolayer of electronic states with an energy resolution not better than 0.2—0.5 eV. Both factors are insufficient for detecting the presence of a small amount of band-gap states (10^{13}—10^{14} e/eV cm^2) (Ref. 11) and their energy position which would be enough for pinning the Fermi level to determine the barrier height.

Nevertheless, the strong chemical reactivity indicates that the barrier formation at the silicide-Si interface may be fundamentally different from the usual models developed for the metal-Si interface assuming weak metal-Si interactions.[12] This was first realized by Phillips and Andrews[13] who stressed the importance of chemical bonding by correlating the SBH to the heat of formation of bulk silicides. Based on the spectroscopy observation[14] of a Si-rich environment at the interface, Freeouf[15] proposed a correlation between the SBH and an interfacial characteristic, namely, the effective work function of an interface of the metal-Si_4 stoichiometry. Later, Ottaviani, Tu, and Mayer[16] suggested the interfacial characteristic in the correlation to be the metal-Si eutectic temperature. We chose to investigate this problem experimentally. Based on the dominant role observed for silicide formation in determining the microstructure and electronic properties of the interface, we raised a fundamental question: To what extent is the SBH determined by the silicide characteristics? To answer this question, we investigated the effect of variations in the silicide characteristics on the SBH. The Ni and Pd silicide-Si interfaces formed on Si(111) and Si(100) substrates were selected for our study because together they provide a large variety of stoichiometries and lattice structures of silicides for checking the correlation.

In addition, we measured the dependence of SBH on the method of Si-surface preparation and the extent of annealing after silicide formation. The former was used for studying the effect of interface defects and contaminations and the latter for studying the effect of diffusion of metal atoms into Si.

SAMPLE PREPARATION

The Si(111) and Si(100) substrates used were all *n* type with (2—10)-Ω cm resistivity. Two types of interfaces were prepared, one on chemically cleaned substrates and the other on atomically cleaned [ultrahigh-vacuum-(UHV-) prepared] substrates. The first had an initial metal layer of about 300 Å which was evaporated in an oil-diffusion-pump system in a vacuum of 10^{-6}—10^{-7} Torr. The second contained about 30—50 Å of metal film evaporated by sublimation in an UHV atmosphere on surfaces prepared by heat cleaning at about 1300 °C or by sputtering plus heat cleaning at about 900 °C. The sputter cleaning was carried out using 1-keV Ar ions. The Si surface after either cleaning showed no detectable C and O contaminants when examined by Auger-electron spectroscopy (AES).

After metal evaporation the sample was annealed in a constant-flow purified He atmosphere under appropriate conditions to form the desired silicide phases. The silicide phases used in our study included the three Ni silicides, Ni_2Si, NiSi, and $NiSi_2$, and one Pd silicide, Pd_2Si. To minimize sample-to-sample variations the SBH was measured on diodes prepared on the same wafer after each heat treatment.

CHARACTERIZATION OF SILICIDES

Silicide compounds were characterized by Rutherford backscattering (RBS) and TEM techniques. RBS was used to examine the interfacial reaction and the silicide stoichiometry while TEM was used to observe the microstructure and morphology of the interface. A set of the RBS spectra observed in Ni-Si(100) samples after various anneals are shown in Fig. 1. The relatively flat plateaus observed for Ni and Si peaks indicate the formation of Ni silicides. The changes in the shape and magnitude of the Ni and Si peaks show the formation of Ni_2Si, NiSi, and $NiSi_2$ after 250, 425, and 725 °C anneals, respectively. Moreover, the relatively sharp Ni profiles on the low-energy side at about 1.6 MeV for 250 and 425 °C anneals reveal well-defined Ni_2Si-Si and NiSi-Si interfaces. In contrast, the extended low-energy tail of the 725 °C spectrum indicates the possibilities of a rough interfacial morphology, formation of isolated silicide clusters, and/or extensive interdiffusion of Ni into Si substrates. These possibilities cannot be discerned by RBS data alone and will be discussed later together with TEM observations.

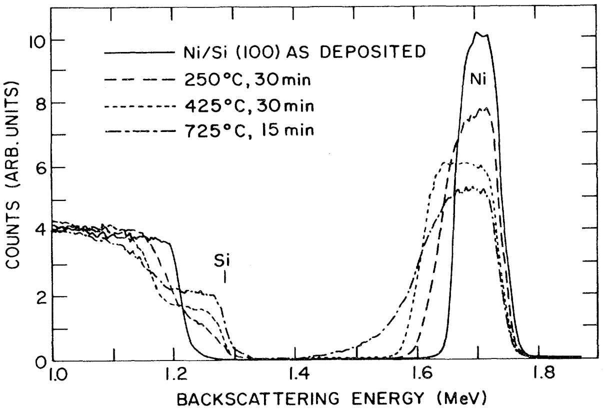

FIG. 1. RBS spectra observed at the Ni-Si(100) interface showing the formation of the three Ni silicides after different anneals.

RBS spectra for the Ni silicide formed on the Si(111) substrate are very similar to those of Si(100) shown in Fig. 1 except that the Ni_2Si on Si(111) was found to form at a slower rate and the tail of the low-energy profile after 725 °C annealing was less extended. This can be attributed, to a lesser extent, to the factors mentioned above in influencing the interfacial stoichiometry. Results of the Pd-Si system were as expected in that annealing at 215—250 °C formed well-defined Pd_2Si layers and further annealing at 400 °C did not degrade the Pd_2Si-layer profile. The interface morphology of these silicides will be discussed later in connection with TEM observations. For simplicity, the RBS spectra of these observations will not be shown.

TEM observations were made with the use of the "flat-on" mode with the electron beam normal to the interface and the "cross-sectional" mode with the electron beam parallel to the interface. The former was useful for observing the grain structure of the silicide, e.g., the size and preferred orientation, the lateral uniformity, and the possible occurrence of mixed-silicide phases. The cross-sectional mode was particularly suited for examining the interface morphology. When it is used with high-resolution lattice-imaging technique, structural details can be observed to a resolution of the lattice distance, about 2—3 Å.[4] However, the technique in general does not have sufficient sensitivity for determining the stoichiometry deviation of the compound or the diffusion of metal atoms into the Si substrate.

These TEM techniques have been employed to study the microstructure and interfacial morphology of the Ni (Ref. 17) and Pd (Ref. 18) silicides. For the three Ni silicides a major portion of the results has been reported previously.[17] In this study additional flat-on TEM was carried out on samples prepared together with those used for SBH measurements. The microstructures observed were in agreement with the previous study. For Pd_2Si its microstructure and morphology formed at 250 °C on Si(111) and Si(100) have also been reported previously.[18] Here further flat-on and cross-sectional TEM observations have been carried out; including new observations on samples after 200, 300, and 400 °C anneals. We summarize the results of these silicide microstructures in Tables I and II and describe the interface morphology below.

Cross-sectional TEM carried out for Ni_2Si and NiSi formed on Si(111) revealed a relatively flat silicide surface but a rather rough interface. The rough interfacial morphology manifests the difficulty of maintaining uniform reaction at the interface during silicide formation. Observation for $NiSi_2$ on Si(111) showed a similar morphology except that the $NiSi_2$ phase is epitaxial on Si(111), so its interface is composed of facet planes instead of random modulation. The morphology of this interface is shown in Fig. 2(a). On the scale of RBS observation (about 1 mm), the profile of this interface would appear extended, displaying a tail in the spectra consistent with that shown in Fig. 1. However, an extended RBS-profile tail can also be due to nonuniform surface coverage, e.g., island formation and/or diffusion of metal atoms into the Si substrate. While flat-on TEM showed no island formation of silicide, the possibility of metal in-diffusion cannot be eliminated, particularly since a high-temperature (725 °C) anneal was used to form $NiSi_2$. However, by comparing the tail length of the RBS spectrum and the extent of faceting, the latter seems to be the main contribution to the interface roughness as observed by RBS.

On a finer scale of about 100 Å, i.e., within the dimension of one facet plane, the $NiSi_2$-Si(111) interface is atomically smooth with an abrupt structural transition from $NiSi_2$ to Si. The lattice image of this interface, as shown in Fig. 2(b), reveals almost perfect twin orientation of $NiSi_2$ with respect to the Si matrix.

The morphologies of Ni_2Si and NiSi on Si(100) are similar to those on Si(111) regarding the interface roughness and grain structure. The $NiSi_2$ is epitaxial on Si(100), and similar to the Si(111) case, it is characterized by a heavily faceted interface morphology.[2] The faceting of this interface is more extensive than Si(111), as evidenced by a longer tail observed in the RBS profile. Compared with the Si(100) interface, the structure of Si(111) appears to be equally abrupt as seen in the high-resolution lattice image [Fig. 2(c)]. The microstructures of other Ni-silicide interfaces on the Si(100) substrate can be found in Ref. 17, so they will not be shown here.

TABLE I. Values of SBH's for Pd-silicide—Si interfaces. (PR denotes photoresponse measurement.)

Substrate type	Annealing condition	Silicide phase and structure	Method of measurement	Barrier height (eV)
Si(111) UHV	None	Pd	*I-V*	0.63
sputter cleaned			PR	0.63
	200 °C	Pd_2Si	*I-V*	0.71
	1 h	epitaxial	PR	0.70
Si(111) UHV	None	Pd	PR	0.73
heat cleaned				
	150 °C			
	30 min	Pd_2Si	PR	0.71
Si(111)	None	Pd	*I-V*	0.77
chemical cleaned			PR	0.73
	215 °C	Pd_2Si	PR	0.73
	2 h	epitaxial		
	+250 °C	Pd_2Si	PR	0.71
	2 h	epitaxial		
	+400 °C	Pd_2Si	PR	0.71
	1 h	epitaxial		
Si(100)	None	Pd-Si	PR	0.75
chemical cleaned				
	215 °C	Pd_2Si	PR	0.73
	2 h	polycrystalline		
	+250 °C	Pd_2Si	PR	0.73
	2 h	polycrystalline		
	+400 °C	Pd_2Si	PR	0.72
	1 h	polycrystalline		

TABLE II. Values of SBH's for Ni-silicide—Si interfaces. (PR denotes photoresponse measurement.)

Substrate type	Annealing condition	Silicide phase and structure	Method of measurement	Barrier height (eV)
Si(111) heat cleaned	150 °C 30 min	Part Ni_2Si	PR	0.64
Si(111) chemical cleaned	None	Ni	PR	0.57
	250 °C 40 min	Ni_2Si textured	PR	0.67
	+425 °C 15 min	NiSi textured	PR	0.66
	+720 °C 20 min	$NiSi_2$ epitaxial	PR	0.65
Si(100) chemical cleaned	None	Ni	PR	0.55
	250 °C 40 min	Ni_2Si polycrystalline	PR	0.63
	+425 °C 15 min	NiSi polycrystalline	PR	0.65
	+720 °C 20 min	$NiSi_2$ epitaxial	PR	0.63

The structure of Pd_2Si formed by annealing within 200—400 °C is epitaxial on Si(111) and polycrystalline on Si(100). The morphologies of the Pd_2Si-Si(100) interface after 200, 300, and 400 °C anneals are shown in Fig. 3. Compared with the Ni silicides, the Pd_2Si layer is rougher on the surface but smoother at the interface. Annealing at 300 and 400 °C after formation of Pd_2Si at 200 °C does not increase the interfacial roughness. This is consistent with the small variation in the Pd_2Si profiles observed by RBS. As mentioned already, although diffusion of metal atoms into Si during annealing subsequent to the silicide formation is to be expected, this cannot be identified in our TEM observations.

The Pd_2Si-Si(111) interface has been examined in detail using high-resolution cross-sectional TEM.[18] Lattice-image contrast revealed a structurally abrupt interface with the $(22\bar{4}0)$ basal plane of the hcp Pd_2Si matching to the Si (111) planes. The transition region was observed to be as sharp as one lattice spacing, about 3 Å. It contain structural defects in the form of atomic steps and misfit dislocations. The degree of abruptness of this interface is very similar to the two $NiSi_2$ epitaxial interfaces on Si(111) and Si(100).

In addition to all these interfaces prepared on chemically clean Si surfaces, the Pd_2Si interface on sputter-cleaned Si(111) surface with UHV metal deposition was examined. Upon deposition at room temperature, spontaneous formation of Pd_2Si up to 10—15 Å coverage was observed but its structure was microcrystalline with a grain size of 10—20 Å. The contrast of this structure to the epitaxial Pd_2Si formed on a chemically clean Si(111) surface is shown in Fig. 4. Annealing at 200 °C caused the grains to grow in size to several hundred Å. Further annealing at 400 °C restored the epitaxial growth of Pd_2Si but not to the same extent as the 250 °C annealed Pd_2Si on chemically cleaned surfaces.

BARRIER HEIGHT MEASUREMENT

The SBH was measured mostly by the internal photoemission method[19,20]; *I-V* measurements have also been carried on some samples for comparison. This photoelectron-injection technique is convenient to set up and the result is accurate and independent of the diode geometry. Since the measurement is carried out essentially without voltage biasing it is particularly suited for our study where many measurements were made on diodes with very thin metal coverage. In addition, it is capable of detecting the presence of different barrier heights in a mixed diode.

The source of monochromatic light consisted of a 100-W tungsten-halogen lamp imaged on the entrance slit of a 0.4-m monochromator equipped with a 75-line/mm grating. A silicon low-pass filter was placed in front of the entrance slit. The outgoing beam was passed through a chopper and the output slit was imaged on the semiconductor side of the diode. The useful range of the light source was 0.65—1.1 eV and its photon flux was calibrated with a PbS detector. With the use of a Ge filter the range of the source can be shifted to 0.48—0.70 eV. The diode was connected to a low-impedance lock-in amplifier synchronized on the chopper. The photocurrent spectrum was stored on a computer, normalized with respect to the photon flux, and its square root was plotted versus photon energy. The straight portion of this curve extrapolated to zero photoyield gives the barrier height. Examples of the results obtained for Pd and Ni silicides formed on Si(111) surfaces are plotted in Figs. 5 and 6. The photoyield

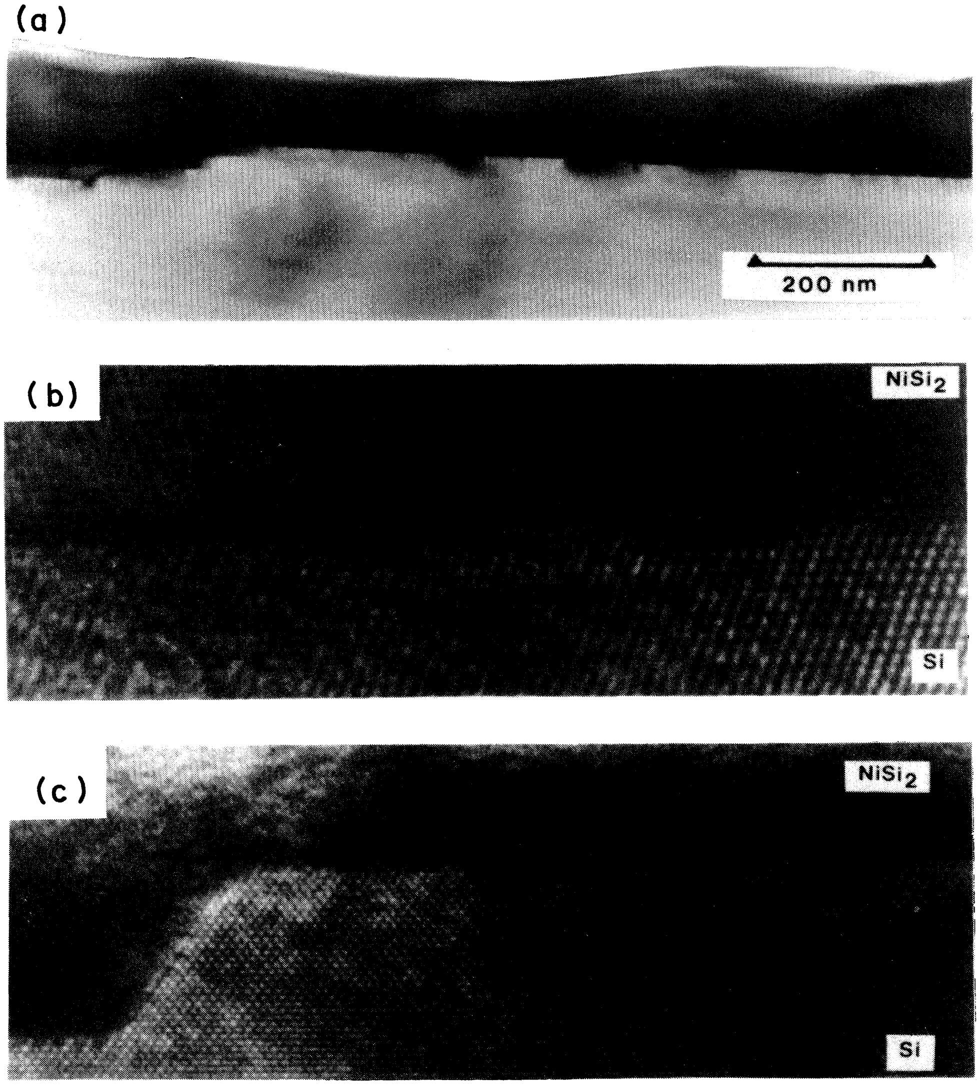

FIG. 2. Cross-sectional TEM micrographs showing (a) the overall morphology of the $NiSi_2$-Si(111) interface, (b) the high-resolution lattice images of $NiSi_2$ on Si(111) (the $NiSi_2$ is twinned with respect to the Si matrix), and (c) the lattice images of $NiSi_2$-Si(100) interface. A large facet on a Si (100) plane and a small facet on a Si (111) plane are visible. Scale for (b) and (c) can be seen by noting that the lattice spacing in Si is 3.1 Å (from Ref. 17).

curve also displays features associated with the transition inside the semiconductor so that the portion of the curve that related to the carrier injection at the barrier is the dominant contribution only up to about 0.98 eV for a Si diode. When the barrier height is larger than about 0.75 eV the linear portion of the plot becomes so short that the extrapolated barrier energy must be corrected.[21] Data for SBH are summarized in Tables I and II.

DISCUSSION

In this paper we investigate the effect on SBH due to variations in the silicide characteristics with the aim to find the factors controlling Schottky-barrier formation at silicide-silicon interfaces. For this purpose we study the Ni and Pd systems over a range of parameters, including the stoichiometry, microstructure, substrate orientation, annealing after silicide formation, and surface preparation. Data in Tables I and II indicate that the effect of the first three parameters on SBH is insignificant with the variations within the estimated error limit of 30 meV in our measurements.

The independence of the SBH on the silicide stoichiometry has also been observed in two previous studies on chemically cleaned substrates; Iwami *et al.*[22] reported a SBH of 0.7 eV measured by the *C-V* method for the three Ni silicides and Ottaviani *et al.*,[23] using *I-V* measurements, found a SBH of 0.66 eV for Ni_2Si and NiSi on

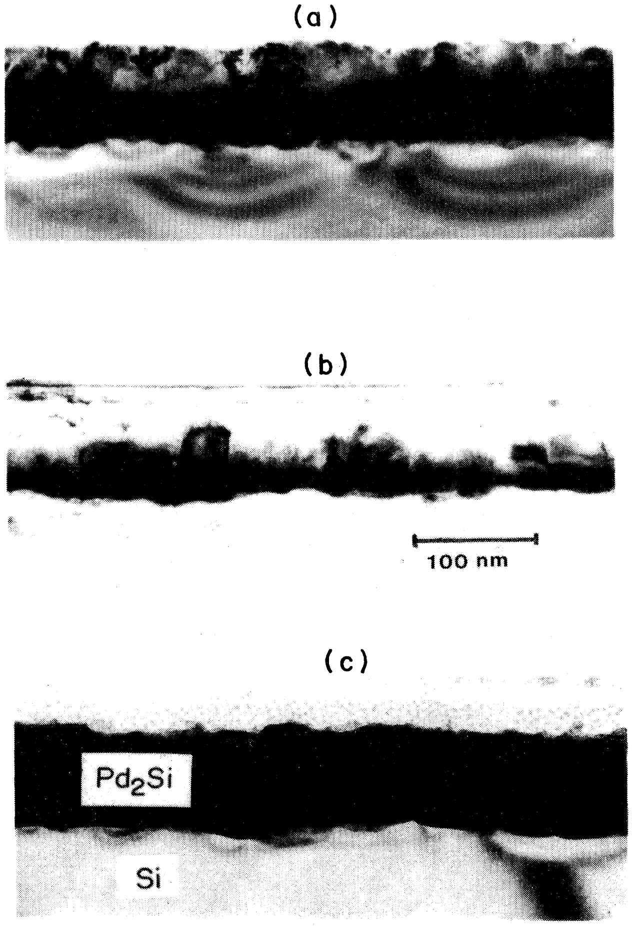

FIG. 3. Cross-sectional TEM micrographs showing the morphologies of the Pd_2Si-Si(100) interface after annealing at (a) 200 °C, (b) 300 °C, and (c) 400 °C for 1 h each.

Si(100), 0.75 eV for Pd_2Si on Si(111), and 0.85 eV for Pt_2Si and 0.87 eV for PtSi. Results of these previous and the present studies show that the material characteristics of the bulk-silicide phases are not prime factors in determining the SBH at the silicide-silicon interface. Therefore, there seems to be no basis to support models which correlate the SBH to bulk-silicide characteristics.

The effect of annealing after completing silicide formation is also small, with barely a detectable (10—20)-meV drop in SBH with increasing annealing temperatures. The cross-sectional TEM micrographs in Fig. 3 reveal that the annealing condition used in our experiments has little effect on the overall morphology of the Pd_2Si-Si interface although the observed tail in the RBS profile indicates the possibility of some Pd atoms diffusing into Si. This result suggests two possibilities: (a) The diffusion of Pd into Si does not significantly change the barrier height, or (b) a relatively small number of Pd atoms in Si is sufficient for establishing the barrier height, and since that already exists upon initial silicide formation, a further increase has little effect.

In contrast, changes in the barrier height with surface preparation are clearly observed. However, the effect is complicated. While chemically cleaned and sputter-plus-heat-cleaned surfaces show barrier heights different from the well-reacted interface, the heat-cleaned surfaces do not. This naturally leads to the question concerning the effect of surface contaminations and defects. Spectroscopy studies on Pd (Ref. 14) and Ni (Ref. 24) found spontaneous formation of silicidelike compounds upon room-temperature deposition of 10—20 Å on the two UHV-prepared surfaces and TEM observation[13] showed the reacted layer of Pd on Si(111) to consist of microcrystalline Pd_2Si [Fig. 4(b)]. Therefore the SBH data show that even with silicide formation, the electrical property of the interface can be affected by the presence of contaminants and defects. Moreover, a small amount of defects, such as those present in sputter-plus-heat-cleaned surfaces, is sufficient to influence the barrier height. These results, plus the fact that the effect can be eliminated by increasing the amount of silicide formation clarify the role of material reaction in Schottky-barrier formation. Its function seems important not so much for inducing the formation of specific silicides, but rather in establishing an interface and in controlling its electrical characteristics.

At this point, it is pertinent to mention the results of related studies on initial barrier formation at the Pd,[25] Ni, and Pt (Ref. 26) interfaces with Si using synchrotron-radiation photoemission spectroscopy. By measuring the shift of the Si 2*p* core level in the bulk to monitor the band bending at the interface, the change of the SBH from a clean Si surface can be measured as a function of metal coverage. Results showed that coverages of 3—4 Å for Pd and about 2 Å for Ni and Pt are sufficient to establish the barrier height. In addition, by tuning the photon energy to measure the valence structure of the surface, it was found that at these coverages the metal characteristics of the Fermi-Dirac cutoff edge is not fully developed, indicating that a complete metal coverage is not required for establishing the barrier height.

These results on initial Schottky-barrier formation together with those of the present study establish the true interfacial character of Schottky-barrier formation at the transition-metal—silicon interface. On this basis the effect of interfacial reaction can be understood by specifying the interface to be either extrinsic or intrinsic, depending on the extent of the reaction. The extrinsic interface is one formed with a limited amount of reaction where the initial interface contaminants and defects, even after dispersing throughout the reacted layer, still exist in sufficient number to affect the barrier height. As the reaction continues, the reacted layer can expand into Si sufficiently to establish an interface free of contaminants and defects. This is called an intrinsic interface and its electrical property is not affected by external defects.

The amount of reaction required for establishing an intrinsic interface depends on the kinetics of the interfacial reaction and on the amount of defects in the initial interface. For near-noble metals Pd and Ni the kinetics is fast, so silicide formation occurs under moderate annealing conditions, such as those used in this study. In such cases, an intrinsic interface can be readily established. In contrast, the refractory metal V-Si (Ref. 27) and Ti-Si (Ref.

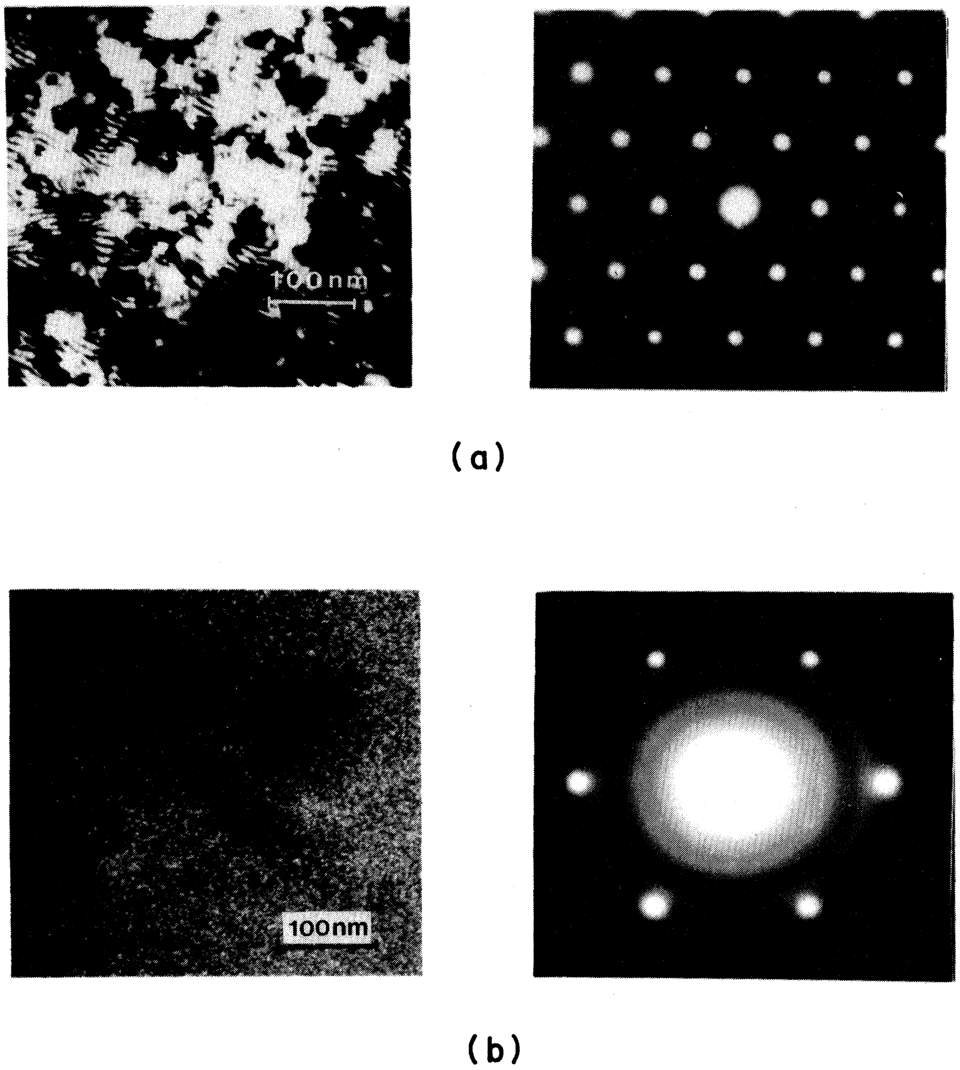

FIG. 4. TEM micrographs showing the microstructure and diffraction pattern for (a) epitaxial Pd_2Si formed on Si(111) and (b) microcrystalline Pd_2Si formed by room-temperature deposition of 10—20 Å Pd on UHV clean Si(111) surface.

28) interfaces are less reactive, annealing under similar conditions (about 200—400 °C) does not completely convert to silicides, so an intrinsic silicide-silicon interface is more difficult to establish. Nevertheless, it has been observed that by annealing at temperatures below silicide formation, a metal-silicon intermixed layer with stoichiometry different from equilibrium silicide phases can be formed at the refractory metal-Si interface. Interestingly, the SBH of such an interface is similar to the well-reacted silicide-silicon interface. Therefore, silicide formation is not prerequisite for establishing an intrinsic electrical interface; instead the amount of reaction should be sufficient to leave the defects behind the interface to ensure intrinsic electrical properties.

In this regard, it is pertinent to ask the effect of diffusion, or interatomic mixing, on the nature of the interfacial layer. As pointed out in the discussion of the annealing effect on the SBH of Pd_2Si, increasing the diffusion of metal atoms into Si after silicide formation has only a small effect on the barrier height. Furthermore, the intrinsic SBH can be established by reacting a few monolayers of metal on a clean Si surface. It seems clear that the extent of diffusion or interfacial mixing is not of prime importance in barrier formation, instead its role is to establish an atomic configuration where metal and Si atoms can intimately interact. Such a configuration can be formed with isolated metal atoms or in a metal-silicon cluster, and since a relatively small amount of such complexes is needed to establish the barrier, diffusion can effectively shift the electrical interface into Si below the structural silicide-Si interface. This raises an interesting question regarding the distinction between the structural and the electrical interfaces.

Summarizing all these results we infer that for intrinsic

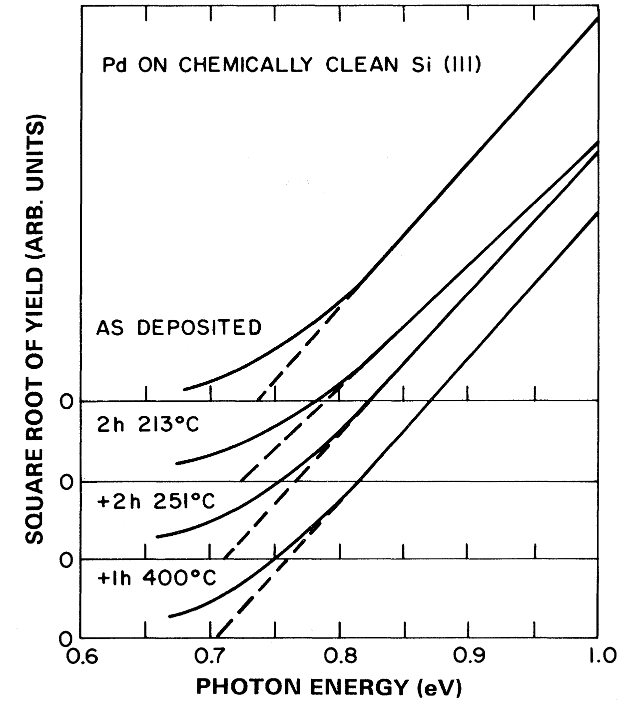

FIG. 5. Examples of results of photoresponse measurements for Pd on chemically clean Si(111) surface. Silicide phase is identified as Pd_2Si after annealing. Straight portion of the curve extrapolated to zero photoyield gives the barrier height.

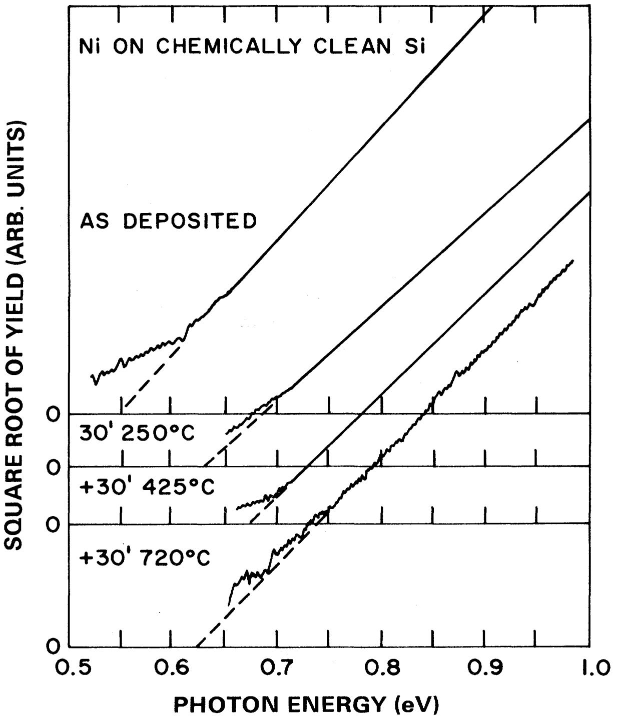

FIG. 6. Examples of results of photoresponse measurements for Ni on chemically clean Si(111). Silicide phases are identified as Ni_2Si for 250 °C, NiSi for 425 °C, and $NiSi_2$ for 720 °C. Straight-line extrapolation to zero photoyield gives the barrier height.

interfaces the barrier height is determined by the metal-silicon interaction at the interface or some interfacial characteristics originating from this interaction. On this basis, the invariance of the SBH of the Ni silicides can be understood by suggesting a common interfacial characteristic for the three Ni silicides which determines the SBH. At present, the atomistic nature of the metal-Si interaction at the interface and the mechanism by which this interaction generates the interface states to establish the barrier height are not yet understood. Nevertheless, the interaction definitely depends on the metal species, e.g., different for Ni vs Pd, and its variation shows a chemical trend with the number of *d* electrons, e.g., low SBH for refractory metals and high SBH for near-noble metals. Moreover, its range is confined to atomistic dimensions, i.e., 2—3 Å at the interface, as evidenced by the fact that a monolayer amount of metal coverages is sufficient to establish the barrier. One parameter fulfilling these characteristics is the metal—silicon bond at the interface formed as a result of interfacial reaction. We propose this as one of the prime factors in determining the SBH. These bonds are specific to the transition-metal—silicon interface and based on surface-spectroscopy studies, they originate most probably from a hybridization of the metal *d* and Si *p* states. Their nature has to be modified from that in bulk silicide to reflect the structural and chemical environment at the interfaces. Thus they are distinct from those suggested by Phillips and Andrews.[11] The true interface states observed at Pd-Si (Ref. 9) and Pt-Si (Ref. 10) interfaces have already provided some evidence for the existence of distinct chemical bonds at transition-metal—Si interfaces. The configuration of such interfacial bonding has yet to be studied since even the TEM lattice-imaging technique does not have sufficient resolution to reveal the atomic arrangement at the interface.

Finally, it is important to realize that the material reaction leading to interface formation inevitably involves movement of point defects. Their presence changes the local stoichiometry and atomic configuration of the interface. This may alter the nature of the metal—silicon bond at the interface. Such questions are important to resolve for understanding barrier formation at the silicide-Si interface.

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[*] Present address: Ecole Polytechnique de Lausanne, CH-1015 Lausanne, Switzerland.

[†] Present address: Siemens AG, München, Federal Republic of Germany.

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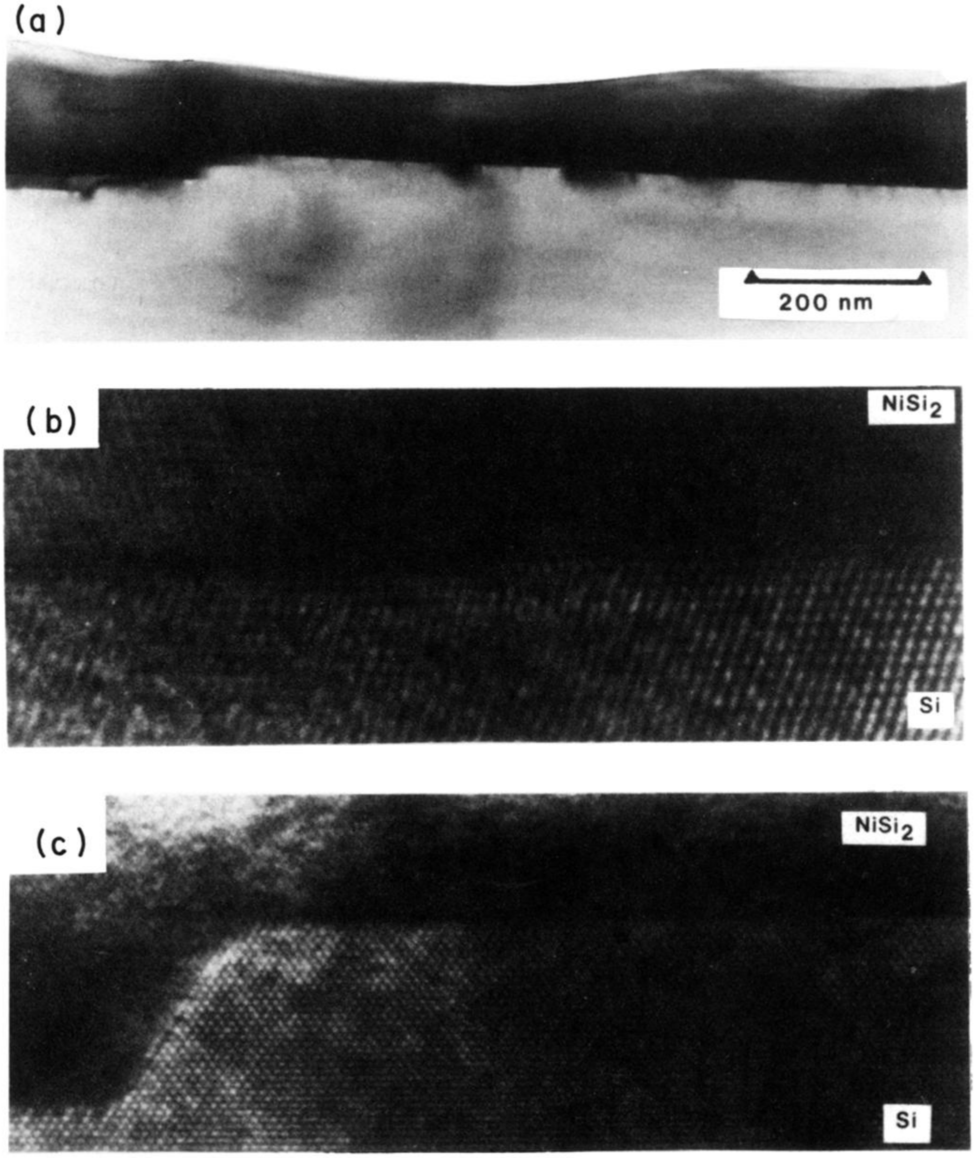


FIG. 2. Cross-sectional TEM micrographs showing (a) the overall morphology of the $NiSi_2$-Si(111) interface, (b) the high-resolution lattice images of $NiSi_2$ on Si(111) (the $NiSi_2$ is twinned with respect to the Si matrix), and (c) the lattice images of $NiSi_2$-Si(100) interface. A large facet on a Si (100) plane and a small facet on a Si (111) plane are visible. Scale for (b) and (c) can be seen by noting that the lattice spacing in Si is 3.1 Å (from Ref. 17).

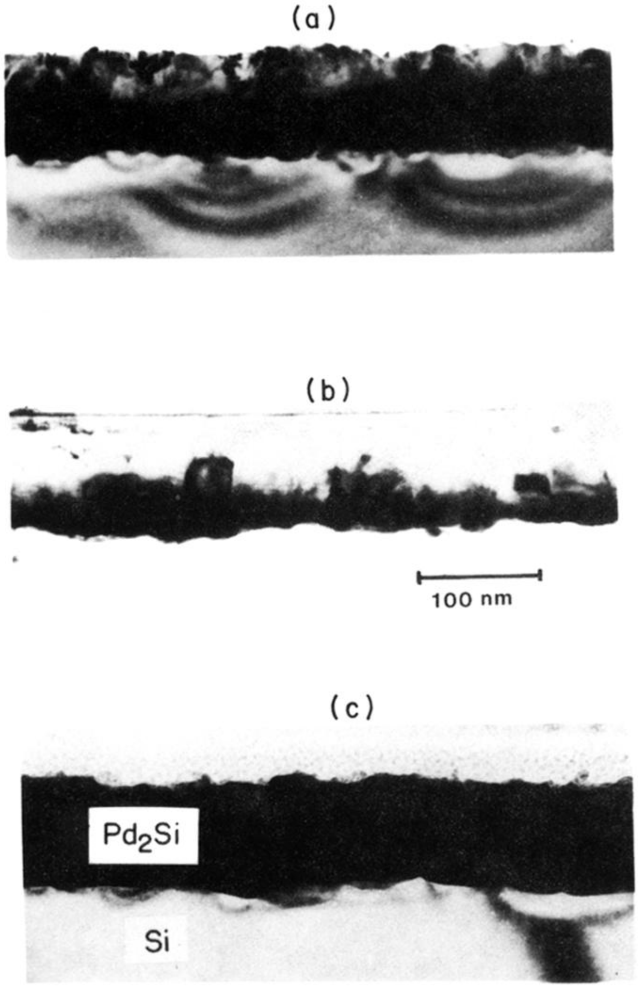
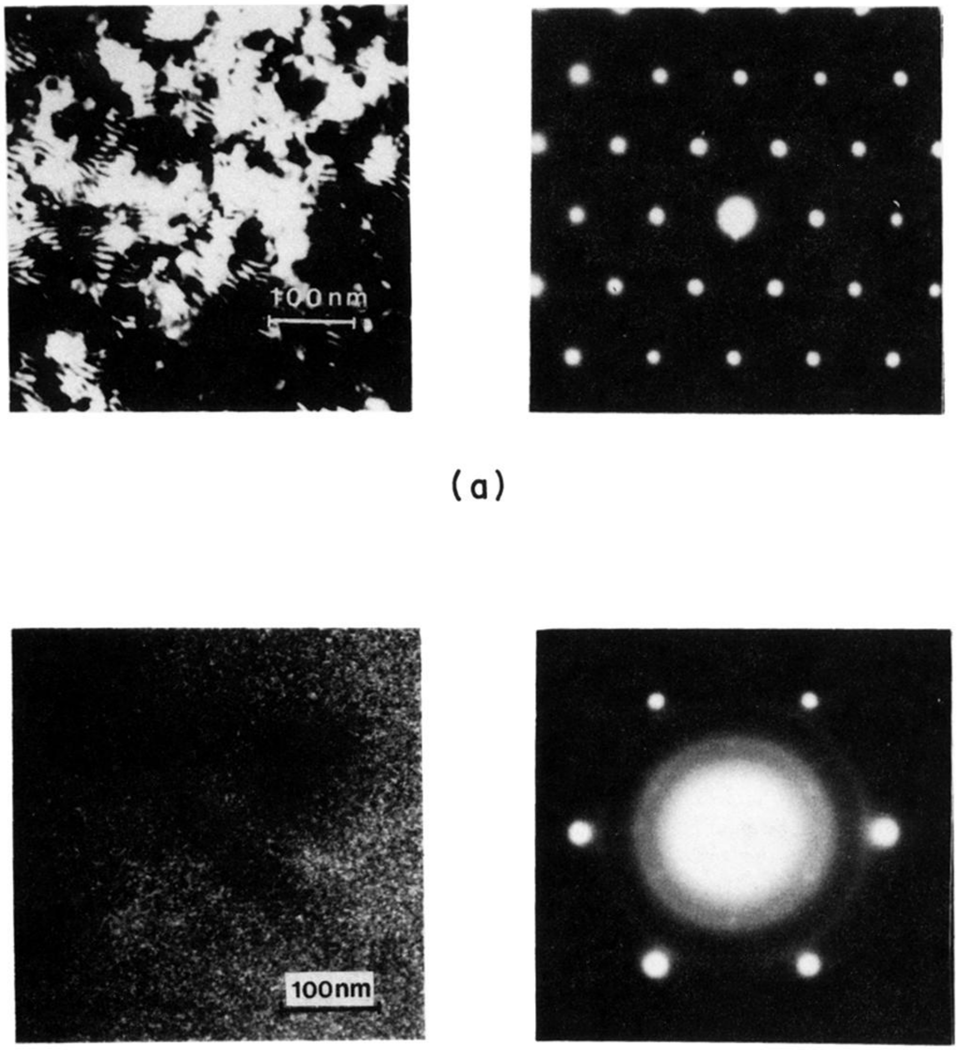


FIG. 3. Cross-sectional TEM micrographs showing the morphologies of the Pd$_2$Si-Si(100) interface after annealing at (a) 200 °C, (b) 300 °C, and (c) 400 °C for 1 h each.



(b)

FIG. 4. TEM micrographs showing the microstructure and diffraction pattern for (a) epitaxial Pd_2Si formed on Si(111) and (b) microcrystalline Pd_2Si formed by room-temperature deposition of 10—20 Å Pd on UHV clean Si(111) surface.