Diffusion layers and the Schottky-barrier height in nickel silicide–silicon interfaces

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New experimental results are presented which suggest that a diffusion layer is always present after forming nickel silicide interfaces at Si surfaces. This layer is a distinct ordered metallic phase having a silicon-rich ($NiSi_2$) stoichiometry which occurs when Ni atoms occupy alternate tetrahedral interstitial voids in the Si lattice. Evidence of this layer is obtained with the use of low-energy electron diffraction, transmission-electron microscopy, and photoelectron emission from interfaces produced at room temperature and higher temperatures at which Ni_2Si and NiSi compounds form by selective growth. The invariance of the Schottky-barrier height for Ni silicide interfaces is attributed to this ordered stoichiometric layer. In addition, this interfacial structure appears to have important bearing on planar selective growth processes which occur during the formation of nickel silicide interfaces.

I. INTRODUCTION

The first model attempting to describe the barrier height of metal-semiconductor contacts was proposed in 1939.[1,2] This model (the Schottky-Mott model) is based on general thermodynamical principles which lead to a simple expression ($\phi_B = \phi_M - \chi_s$) relating contact barrier height (ϕ_B) to the difference between the metal work function (ϕ_M) and the semiconductor electron affinity (χ_s). This model necessarily neglects surface and interface chemical effects; however, it does correctly predict general trends observed for ionic, large-band-gap materials. Observations departing significantly from the predicted trends for covalent materials such as silicon have led to a number of other considerations.[3] Models based on surface states,[4] interface states,[5] band-gap narrowing,[6] dipole layers,[7] image forces,[8] and various chemical-bonding arguments[9] have been suggested. Recent review articles[10,11] summarize the present situation. Simply stated, there is currently no unified description of the Schottky-barrier height for metal-Si contacts, and present efforts are focused primarily on selected classes of metal-Si interfaces which exhibit attractive characteristics.

Two particular features of reactive-metal–silicide interfaces appear central to the problem of understanding their barrier height. First, the barrier height is related to the type of metal used in forming the silicide.[10,11] Second, when more than one silicide phase can be formed as the "metallic" contact of the metal-Si interface, the barrier height does not strongly depend upon the stoichiometry of the compound in several important cases.[12,13] Table I summarizes some relevant results for Ni silicides. Additional important and related characteristics of silicides include selective planar growth of stoichiometric compounds,[14,15] the formation of several stoichiometric phases,[15] and epitaxial growth.[16]

In relation to the first of these features, a number of attempts have been made to correlate the barrier height with

TABLE I. Formation temperatures, work functions, and Schottky-barrier heights for Ni and silicide contacts on *n*-type Si(100). Work functions were measured by photoemission in this experiment. Barrier-height references: (1) G. Ottaviani, K. N. Tu, and J. W. Mayer, Ref. 17; (2) E. H. Rhoderick, *Metal Semiconductor Contacts* (Clarendon, Oxford, 1978); (3) P. E. Schmidt, P. S. Ho, and T. Y. Tan, J. Vac. Sci. Technol. 20, 688 (1982).

Silicide phase	Formation temperature of bulk silicide	Work function (eV)	Schottky-barrier height ϕ_B (eV) (1)	(2)	(3)
Ni (Thin film)	~25 °C	5.10	0.66	0.70	
Ni_2Si (Polycrystal)	~200 °C	4.94	0.66	0.71	0.63
NiSi (Polycrystal)	~430 °C	4.82	0.66	0.69	0.65
$NiSi_2$ (Epitaxial)	~800 °C	5.03		0.70	0.63

a specific silicide compound parameter. One example associates the barrier heights with heats of formation of various silicides.[9] The correlation fails for several specific cases, but a very encouraging trend is apparent for most silicide compounds. A second attempt to correlate barrier heights with a compound parameter involves the compound eutectic temperature.[17] This correlation holds up even better than that for heats of formation; however, the eutectic-temperature model lacks an explanation founded on basic physical principles. A third approach assumes that the Schottky model is still applicable, but that a specific value of the silicide work function, based on the actual interface stoichiometry, must be used.[18]

The second feature, the constancy of the Schottky-barrier height of silicide-Si interfaces of different stoichiometries formed from the same metal, must also be explained in terms of atomic-level properties of the interfacial region. Both issues must be addressed in a comprehensive model even if the model only applies to a small class of interfaces. Considerably less attention appears to have been directed toward understanding the constant-barrier-height issue, and it is this specific problem which we primarily address in this paper.

In a previous paper,[19] we reported experimental evidence which indicated that the initial state of interface formation of Ni-silicon interfaces at higher temperatures is characterized by a diffusion layer of nickel atoms at Si(100) surfaces. Low-energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS) were used to argue that nickel atoms occupy tetrahedral interstitial voids in the Si lattice after low-coverage Ni-film evaporation ($0.25 \geq \Theta \geq 25$ Å) and annealing to 800 °C. Ion-channeling experiments[20] have also detected a similar diffusion-layer structure on "as-deposited" thin nickel films. We found previously that the postulated diffusion layer exhibits several characteristics which appear to be relevant to the barrier-height problem: (1) Prolonged annealing at 800 °C does not deplete the diffusion layer, (2) the stoichiometry of the diffusion layer is $NiSi_2$ or perhaps slightly more silicon rich (this is based on the measured *d*-state binding energy of Ni atoms at several stoichiometries[19,21] and on calculations[22] which relate density of states to stoichiometry), (3) the postulated crystal structure of the diffusion layer is not the same as epitaxial $NiSi_2$, and (4) the diffusion layer appears to be a key factor in selective growth.

In this paper we present direct evidence for an ordered interfacial layer based on transmission-electron diffraction (TED) and, in addition, demonstrate using TED and UPS that the ordered layer exists at the interface between planar films of Ni_2Si and NiSi stoichiometry (formed by selective growth) on the Si(100) substrate. The experimental techniques and sample preparation details for the UPS work have been described in previously reported work.[19] Our new results, in conjunction with other pertinent experimental results, lead us to conclude that an ordered silicide layer exists at all practical interfaces between nickel silicide phases grown on silicon surfaces, and appears to be an important factor in selective growth and the constancy of the Schottky-barrier height of Ni-silicon interfaces.

II. PHOTOELECTRON-EMISSION STUDIES

Figures 1 and 2 display angle-integrated UPS energy-distribution curves (EDC's) for sequential deposition of Ni onto Si(100) followed by annealing. The annealing temperature for EDC's in the two figures were, for Fig. 1, 200 °C, and for Fig. 2, 430 °C. Annealing thick Ni films at these temperatures produce distinct stoichiometric silicide layers by selective growth, specifically, Ni_2Si (200 °C) and NiSi (430 °C). It is well established that the epitaxial $NiSi_2$ phase requires higher temperatures (800 °C) to nucleate from an existing planar structure.

The lower EDC of Fig. 1 corresonds to a clean Si(100) (2×1) surface. The other EDC's correspond to Ni deposition followed by annealing at 200 °C. Annealing time was approximately 1 min for each angstrom of deposited Ni. Surface states on the clean Si (2×1) surface and the LEED (2×1) patterns are both destroyed by any coverage of Ni atoms greater than 0.25 Å. In this paper, we describe Ni coverages in angstroms, where 1 Å corresponds to 9.17×10^{14} Ni atoms/cm^2. Also, 1 Å of Ni reacted with Si to form $NiSi_2$ yields approximately 3.6 Å of silicide. Subsequent annealing at 200 °C reestablishes the surface-state peaks and the (2×1) LEED pattern for low coverages (approximately 0.5 Å or less) but does not reestablish the surface-state peaks. As shown in Fig. 1, annealing at 200 °C does reestablish the LEED (2×1) structure for coverages up to about 4 Å. The fact that the

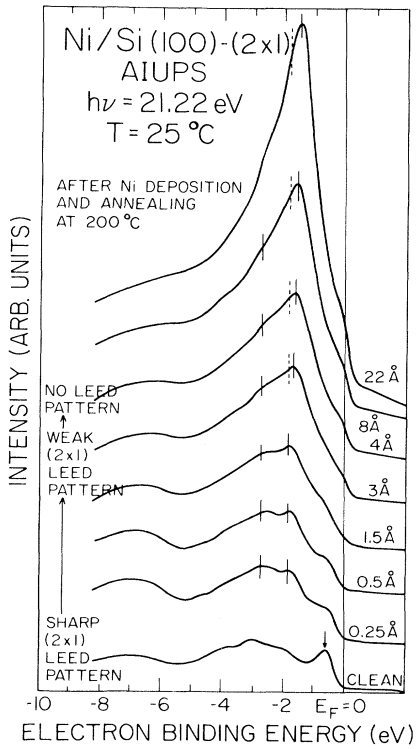


FIG. 1. Angle-integrated EDC's for sequential coverage of Si(100) by Ni atoms followed by annealing at 200 °C. Energy resolution approximately 100 meV, statistical error less than 5%. (1-Å Ni $=9.17\times10^{14}$ Ni atoms/cm^2.)

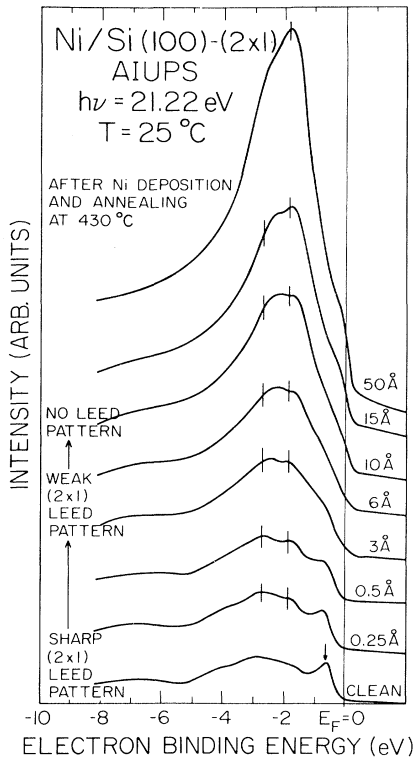


FIG. 2. Angle-integrated EDC's for sequential coverage of Si(100) by Ni atoms followed by annealing at 430 °C. Energy resolution approximately 100 meV, statistical error less than 5%. (1-Å Ni $=9.17\times10^{14}$ Ni atoms/cm^2.)

(2×1) LEED pattern can be observed after annealing at 200 °C for Ni coverages greater than a monolayer suggests that some interstitial diffusion has occurred. This possibility is consistent with our previous observations at higher annealing temperatures[19] and with channeling studies of room-temperature-deposited Ni atoms.[20]

The Ni-layer EDC's in Fig. 1 exhibit two principle peaks. One peak has a fixed binding energy of -2.78 eV (measured from the Fermi level E_F), and its amplitude is observed to decrease rapidly with increasing coverage. The second peak consists of two structures, one at -1.9 eV which also exhibits a decrease in amplitude as Ni coverage increases, and another peak at -1.4 eV which increases in amplitude with coverage. Vertical lines in Fig. 1 identify these peaks.

We attribute the peak at -2.78 to d-state emission from Ni atoms diffused into the Si lattice. This assignment is based on the (constant) measured binding energy of the peak and the results of our previous work on the diffusion layer[19] which has shown that this layer is characterized by a d-state binding energy of -2.78 eV. The attenuation of this peak with increasing Ni coverage is consistent with an electron escape depth of about 12 Å.

We attribute the peak at -1.9 eV at very low coverage (less than approximately 1.0 Å) to a surface-chemisorbed species of Ni. As coverage is increased beyond 3 Å the Ni_2Si phase is able to nucleate as a stoichiometric compound, and the peak at -1.4 eV binding energy begins to dominate the spectra. This accounts for the apparent shift in the main peak as coverage increases. The binding energies of the dominant peak in stoichiometric phases of Ni_2Si, NiSi, and $NiSi_2$ have been determined in our previous work[19] and by others.[21] Even after there is clear evidence that the Ni_2Si phase has been established (at 8 Å coverage, for example), the diffusion-layer peak persists. This shows a Si-rich phase ($NiSi_2$) exists at the interface. Persistence of the LEED pattern at low coverage, ion-channeling results,[20] and the fact that selective growth[12] apparently depends on Ni atoms in interstitial voids of the Si lattice[19] all support the existence of the diffusion layer. Transmission-electron-diffraction studies, described later, support this conclusion, and also support the proposed structure model for this layer.

We have considered other possible origins of the -2.78-eV peak, but must conclude that it can only be explained in terms of emission from interstitial Ni atoms. Our experimental studies of nickel silicides and thin nickel films on Si surfaces have shown that the photoemission cross section for Ni d states is large, and new peaks in EDC's, even at very low Ni coverage, clearly arise from d-state emission. Our room-temperature LEED and UPS studies of low-coverage films of Ni on Si(100) (2×1) have established that in the coverage range 0.25—0.75 Å, the same two peaks occur, i.e., at -1.9 and -2.78 eV. Annealing at 200 °C increases the strength of the -2.78 eV peak, decreases the strength of the -1.9-eV peak, and reestablishes the (2×1) LEED pattern. We conclude that annealing permits surface Ni atoms to diffuse to interstitial voids, just as our results obtained at 800 °C suggest. At 800 °C, nearly all of the surface atoms are able to diffuse into the interstitial voids. Thus an 800 °C anneal not only reestablishes the (2×1) surface reconstruction, but also reestablishes the surface states.

Similar trends are apparent in Fig. 2. The primary difference in this case is that at 430 °C, NiSi nucleates and the low-coverage chemisorbed phase which exhibits the same d-state binding energy as NiSi cannot easily be distinguished from this bulk phase which is also present. There are only two peaks, one due to the diffusion layer (again at -2.78 eV) and one due to NiSi (at -1.9 eV). The diffusion-layer peak is attenuated as the NiSi layer grows, and the NiSi peak grows with coverage as expected.

Close inspection and comparison of Figs. 1 and 2 reveal that more Ni atoms diffuse into the Si lattice for a fixed number of deposited Ni atoms at the higher temperature. This conclusion is based on the fact that the 430 °C annealing temperature permits the (2×1) LEED patterns to be observed at Ni atom coverages a factor of 2 higher than those which quench the (2×1) reconstruction at lower annealing temperatures. This suggests higher initial solubility of Ni atoms in the Si lattice at higher temperatures.

One can legitimately argue that assignment of the peak at -2.78 eV to the diffusion layer may not be unique. Close inspection of EDC's for bulk Ni_2Si and NiSi taken at photon energies of 21 eV (Ref. 21) reveals a similar weak structure in the neighborhood of -2.78 eV. Our own high-resolution EDC's for thick films of Ni_2Si and

NiSi produced by selective growth on Si(100) surfaces are in good agreement with the data for bulk stoichiometric silicides. However, our high-resolution EDC's and difference curves obtained from them permit us to distinguish easily between the peaks produced by bulk features and peaks produced by the diffusion layer.

Figures 3 and 4 illustrate decomposition of difference EDC's based on our previously established spectra for the diffusion layer and the compounds Ni_2Si and NiSi. The dotted lines are the result of subtracting the clean-surface EDC from the nickel-coverage EDC's in Figs. 1 and 2. We have attempted to suitably normalize each pair of spectra before subtracting them by equating the emission of the bulk Si peak at -7 eV taking into account the electron escape depth. This procedure is unnecessary at higher coverages. Features produced by Ni $3d$ states have overwhelming cross sections compared with Si valence-band features, and this characteristic renders unimportant any errors introduced by our normalization technique. Other factors which could have bearing on peak structures such as band bending and surface segregation can also be considered negligible. The main point we wish to make in relation to the difference curves and the synthesized difference curves based on established bulk spectra is that in all cases where compound film thickness was of the order of the electron escape depth or less, it was necessary to include a contribution from the diffusion layer to obtain an acceptable fit to experimental results. We have obtained similar results for Ni-Si interfaces formed at room temperature.[23]

Figures 3 and 4 also show that the diffusion-layer peak at -2.78 eV occurs at a significantly higher binding energy than either of the weak structures observed in the bulk Ni_2Si and NiSi EDC's. Our data placed the various bulk d-state peaks at the following values: For NiSi, the main peak is at -1.90 eV and the weaker peak is at -2.50 eV; for Ni_2Si, the main peak is at -1.40 eV and the weaker is at -2.40 eV. The diffusion-layer peak lies at a significantly higher binding energy and is not observable in films having nickel coverage greater than about 10 Å.

We can also effectively argue that our results do not represent a special case which occurs only at 21.22 eV photon energy. Our previous studies of $NiSi_2$ epitaxial crystals[24] have shown that there is very little dispersion of Ni d bands in the Si host lattice, and that photon energy ($21 \leq \hbar\omega \leq 48$ eV) and emission angle do not significantly affect the position or relative strengths of Ni d-state peaks. We obtain the same conclusions from angle-resolved spectra at $\hbar\omega = 21.2$ eV and angle-integrated spectra at $\hbar\omega = 26.85$ eV. We note here also that all of the UPS spectra reported here were obtained using the same experimental configuration to avoid changing the electron-escape angles probed. We found no evidence of significant peak shifts which could be attributed to the analyzer geometry.

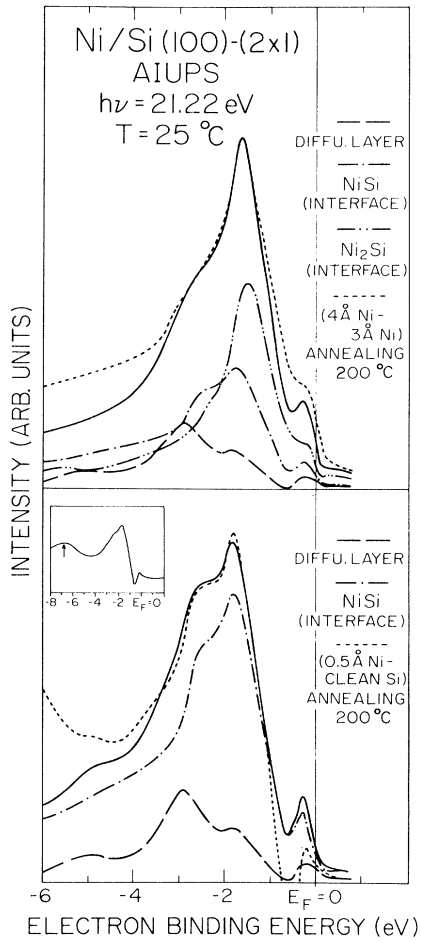


FIG. 3. Difference spectra (from Fig. 1) and "best-fit" synthesis of difference spectra (solid lines) based on known spectra for diffusion layer, and stoichiometric silicides. Inset: Difference curve (same as dotted curve) over broader energy range. Arrow shows effect of surface segregation, i.e., bulk states of accumulated Si at surface. Similar effects can be produced by prolonged annealing of bulk silicides. Ni d states' energies are not changed when Si segregates.

III. TED STUDIES

Finally, because our LEED studies have not produced direct structural evidence of the diffusion layer, we conducted TED studies of some of the thin-film structures which were used in our photoemission experiments. It is not unexpected that LEED appears unable to identify the ordered diffusion layer which we postulate. Our UPS studies show a nearly simultaneous occurrence of diffusion, chemisorption, and silicide formation. The latter two processes produce disordered layers at the surface and therefore do not yield a LEED pattern. In addition, according to the simple dimer model of the Si(100) (2×1) surface reconstruction, the diffused Ni atoms must occupy interstitials below the top two Si layers in order not to disturb the reconstruction. This places the diffused atoms out of the region where LEED is most sensitive.

The samples were prepared for TED studies by jet thinning using a mixture of 70 mol% HNO_3 and 30 mol% HF, and TED patterns were obtained using a Japan Electron Optics Laboratory (JEOL) microscope. We studied

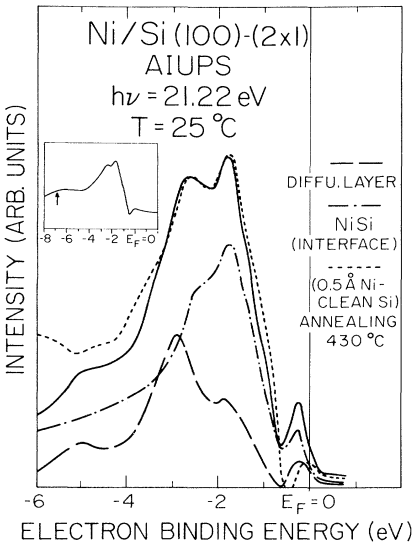


FIG. 4. Difference spectra (from Fig. 2) and "best-fit" synthesis of difference spectra (solid line) based on known spectra for diffusion layer and stoichiometric silicides. Inset: See caption for Fig. 3.

transmission along the ⟨100⟩ axis of pure Si(100) crystals, Si(100) crystals with a saturated diffusion layer (produced by 50-Å Ni deposition followed by annealing at 800 °C), and samples corresponding to selected EDC's of Figs. 1 and 2 with Ni coverage in the (0.5—20)-Å range.

Figure 5 displays representative results for three selected cases. The first diffraction pattern corresponds to a Si(100) surface after a saturated diffusion layer had been established [Fig.5(a)]. TED studies of clean Si(100) targets yielded a pattern similar to that shown in Fig. 5(a) except all weaker spots [i.e., (020), (200), (060), etc.] were missing as expected from diffraction selection rules for the diamond lattice. LEED and photoemission studies of saturated diffusion layers identified surface states and the (2×1) reconstruction as reported previously. TED of the diffusion-layer sample clearly shows superlattice spots characteristic of an ordered array of diffused atoms. Identical patterns were obtained for well-ordered crystals of $NiSi_2$.

Our proposed model[19] for the diffusion layer consists of Ni atoms in tetrahedral sites of the silicon lattice. This structure is not a Bravais lattice and must be described as a lattice with a basis. The underlying lattice is fcc and the basis can be taken to be $d_1=0$, $d_2=\frac{1}{4}a(\hat{x}+\hat{y}+\hat{z})$, and $d_3=\frac{1}{2}a(\hat{x}+\hat{y}+\hat{z})$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along the cube axes and a is the side of the cube cell [see Fig. 6(b)]. The reciprocal lattice is bcc with a conventional unit cell of side $4\pi/a$. The basis contains three atoms; therefore, the structure factor does not in general vanish at arbitrary points in k space and one would therefore expect to observe superlattice spots for an ordered diffusion layer as shown in Fig. 5(a).

We note that $NiSi_2$ has the cubic CaF_2 structure, which can be described by an fcc Bravais lattice plus a basis consisting of $d_1=0$, $d_2=\frac{1}{4}a(\hat{x}+\hat{y}+\hat{z})$, and $d_3=-\frac{1}{4}a(\hat{x}+\hat{y}+\hat{z})$. Again, the reciprocal lattice is bcc. The mismatch of the lattice constants for $NiSi_2$ and our proposed diffusion-layer structure model is less than 0.5% and therefore these two structures are not distinguishable easily from TED measurements without extensive analysis of the intensities.

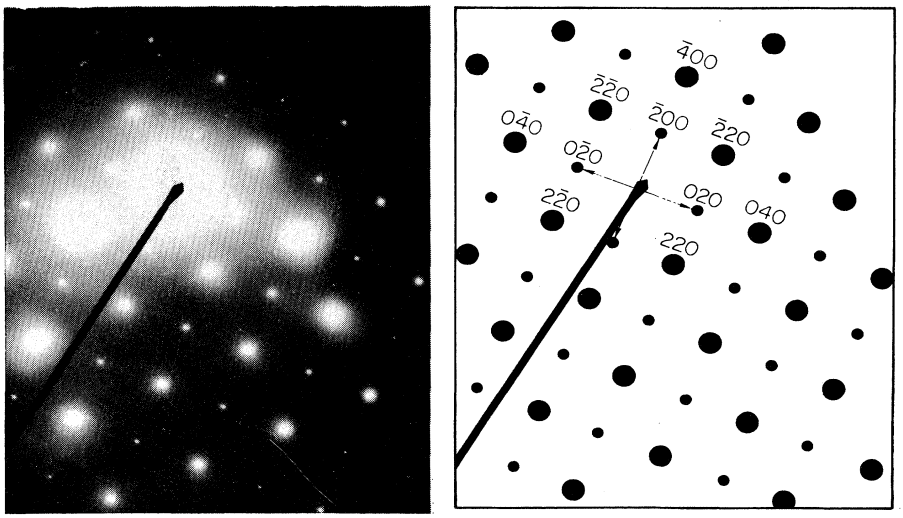
The other two diffraction patterns in Fig. 5 correspond to Si(100) surfaces after deposition of 20-Å Ni films followed by annealing at 300 °C [Fig. 5(b)] and 400 °C [Fig. 5(c)]. These TED patterns exhibit the Si lattice rings which we have identified as resulting from formation of polycrystalline Ni_2Si (200 °C) and NiSi (400 °C). In addition, weak superlattice spots can again be seen which correspond to the Ni atoms in registry with the Si substrate, i.e., the diffusion layer. Note that the only diffraction features observed corresponding to $NiSi_2$ stoichiometry are the new spots which indicate the presence of an fcc structure reflecting Ni atoms in registry with the Si lattice.

IV. DISCUSSION

Physical characteristics and composition of Ni-silicide—Si interfaces have been studied in other UPS experiments[24–28] and by x-ray-photoemission spectroscopy[29–33] (XPS). These studies have established the reactive nature of Ni- (and other metal-) silicide—interface formation, and have generally shown that graded composition from Si-rich to metal-rich compounds are characteristic of the interface. This feature and other considerations discussed in the Introduction have presented considerable difficulty in arriving at an appropriate approach to understanding the Schottky-barrier height. In the present paper, we have demonstrated that the established characteristics of photoelectron spectra for stoichiometric silicides[19,25–33] and the diffusion layer[19] permit identification of distinct phases which constitute the interface.

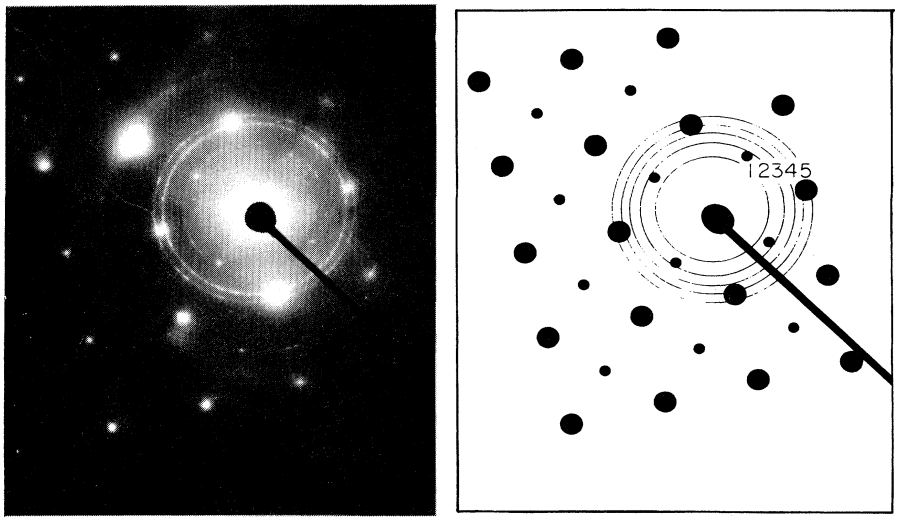
Our TEM and UPS results clearly show $NiSi_2$ and NiSi form by selective growth on Si(100) at the appropriate temperatures. In addition, our results indicate the simultaneous presence of a shallow ordered silicon-rich ($NiSi_2$) phase. The depth of the layer depends on the formation temperature but the stoichiometry and structure do not appear to be affected by annealing temperature or the silicide phase (or phases) present above the interface. Recent work by Tung *et al.*[34] on the formation of ultrathin single-crystal silicide films on Si indicates it is possible to form well-ordered structures having $NiSi_2$ stoichiometry at temperatures below 800 °C which are generally regarded as necessary to form thick (1000-Å) epitaxial films of $NiSi_2$. These results support our primary conclusion which is that an ordered phase having $NiSi_2$ stoichiometry exists at the interface.

We believe, however, that the actual structure of the interfacial layer remains in question. Both crystal structures (our diffusion layer and $NiSi_2$) have Ni atoms on an fcc lattice which differ in lattice constant by less than 1%. Our TED studies cannot differentiate between the two models shown in Fig. 6. We do have indirect evidence based on photoemission that the interface structure is different from the $NiSi_2$-CaF_2 crystal structure. Figure 7 compares photoemission spectra for $NiSi_2$ with a differ-



(a)

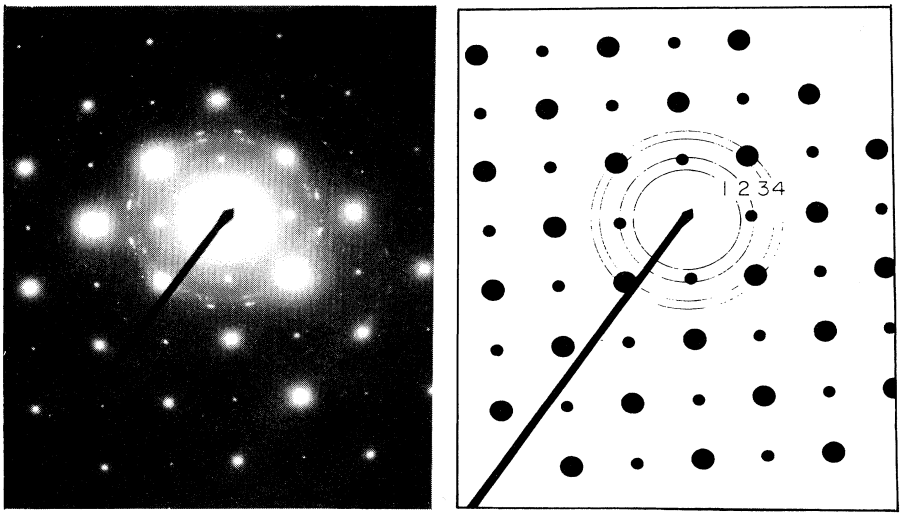
SATURATED DIFFUSION LAYER
Si(100) + 50 Å Ni
ANNEALED 800 °C



(b)

Si(100) + 20 Å Ni
ANNEALED 300 °C 30 MIN

RING	hkl	COMPOUND
1	(011)	Ni_2Si
2	(200)	NiSi
3	(112)	Ni_2Si
4	(202)	Ni_2Si
	(210)	NiSi
5	(113)	Ni_2Si



(c)

Si(100) + 20 Å Ni
ANNEALED 400 °C 10 MIN

RING	hkl	COMPOUND
1	(011)	Ni_2Si
2	(200)	NiSi
3	(210)	NiSi
	(202)	Ni_2Si
4	(113)	Ni_2Si

FIG. 5. TED results for (a) saturated diffusion layer (see text), (b) 20-Å Ni on Si(100) interface annealed at 300 °C, and (c) 20-Å Ni on Si(100) interface annealed at 400 °C. Left panels: description of sample and identification of TEM rings from known structure of NiSi and Ni_2Si. Center panel: TED photo. Right panel: accurate reproduction of TED photo. Large spots correspond to spots seen for clean Si(100) lattice. Smaller spots represent superlattice spots which occur when Ni atoms enter the Si lattice.

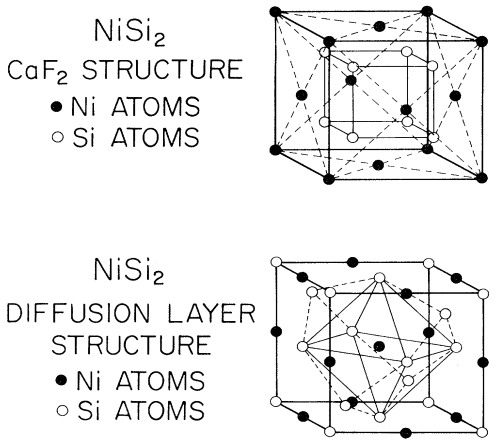


FIG. 6. Structure models for diffusion layer and $NiSi_2$.

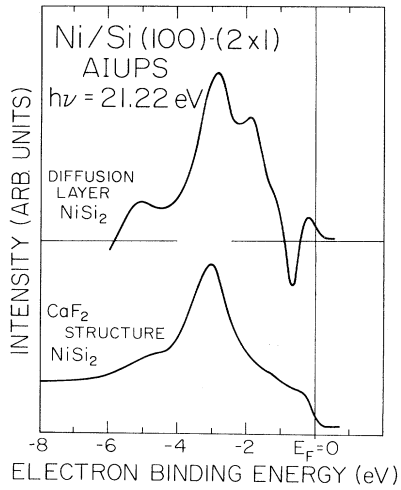


FIG. 7. Photoemission spectra for $NiSi_2$ (lower curve) and difference spectra for diffusion layer (upper curve).

ence spectra obtained by subtracting EDC's obtained from the diffusion layer. There is a slight difference in the binding energy associated with the major peak and an additional peak in the diffusion-layer spectra. This additional structure could be associated with splitting of the antibonding d states produced by the different Si atom coordination.

The diffusion-layer structure presents other features which lead us to favor it over the $NiSi_2$ structure at the interface. If the CaF_2-structure $NiSi_2$ phase forms initially at the interface, the traditional selective growth process in nickel silicide growth ($Ni_2Si \rightarrow NiSi \rightarrow NiSi_2$) is bypassed, and the first-phase rule[35] which correctly predicts first-phase nucleation in a broad range of silicides (including nickel silicide) is violated. The diffusion-layer phase does not correspond to a stable crystal structure which appears in the bulk nickel silicide phase diagram and the first-phase rule does not apply. Finally, the nucleation and growth of twin CaF_2-structure $NiSi_2$ islands on Si(100) and Si(111) (Refs. 34 and 36) surfaces can be explained[37] based on the two possible domains for the diffusion layer. The two diffusion-layer domains are identical except one is the rotational twin of the other, and is obtained by a 180° rotation of the fcc Ni sublattice around the ⟨111⟩ direction. The appearance of a twin-domain (CaF_2-structure) $NiSi_2$ silicide layer as the final phase in the selective growth sequence in the nickel silicides can be qualitatively explained by nucleation and growth at the interface where rotational twins of the diffusion layer exist.[37] This process would also account for the sharp silicide interfaces produced on Si(111) surfaces and the faceted interfaces on Si(100) surfaces.[36]

We have determined the work function of the (100) and (111) surface of $NiSi_2$ and found both values to be approximately 5 eV. [$\phi(111)=5.03\pm0.10$ eV.] The electron affinity of Si(111) is approximately $\chi_s(111)\sim3.85$ eV.[18] It is clear from these experimental values that the Schottky model is inadequate for describing the barrier height for $NiSi_2$ phases in contact with a silicon crystal surface. We are unable to measure the work function of the diffusion layer, but believe that the value for $NiSi_2$, which has the same stoichiometry, is approximately correct. Therefore the diffusion layer does not account for the measured barrier height with the Schottky model.

V. CONCLUSIONS

We have presented evidence that an ordered silicon-rich phase having $NiSi_2$ stoichiometry exists at interfaces formed by depositing Ni onto Si(100) surfaces followed by annealing. The layer depth increases with annealing temperature, but the stoichiometry and structure appear to be independent of temperature. Our transmission-electron-spectroscopy (TEM) studies have clearly identified this diffusion layer in cases where polycrystalline Ni_2Si and NiSi phases have begun to nucleate. UPS studies of the interfaces lead to the same conclusions. The formation energetics associated with this layer are not yet understood. However, recent work[34] on ultrathin epitaxial films of $NiSi_2$ have demonstratèd that an ordered Si-rich phase can indeed form before Ni_2Si and NiSi phases nucleate. Two distinct crystal structures are consistent with direct experimental evidence for the layer. The model we favor is characterized by Ni atoms in voids of the Si lattice. This model provides a basis for accounting for selective growth (the interstitial-defect model). The presence of a distinct ordered diffusion layer at Ni-silicon interfaces formed under a variety of conditions also constitutes an important new interface model which can serve as a basis for accounting for the barrier-height behavior shown in Table I.

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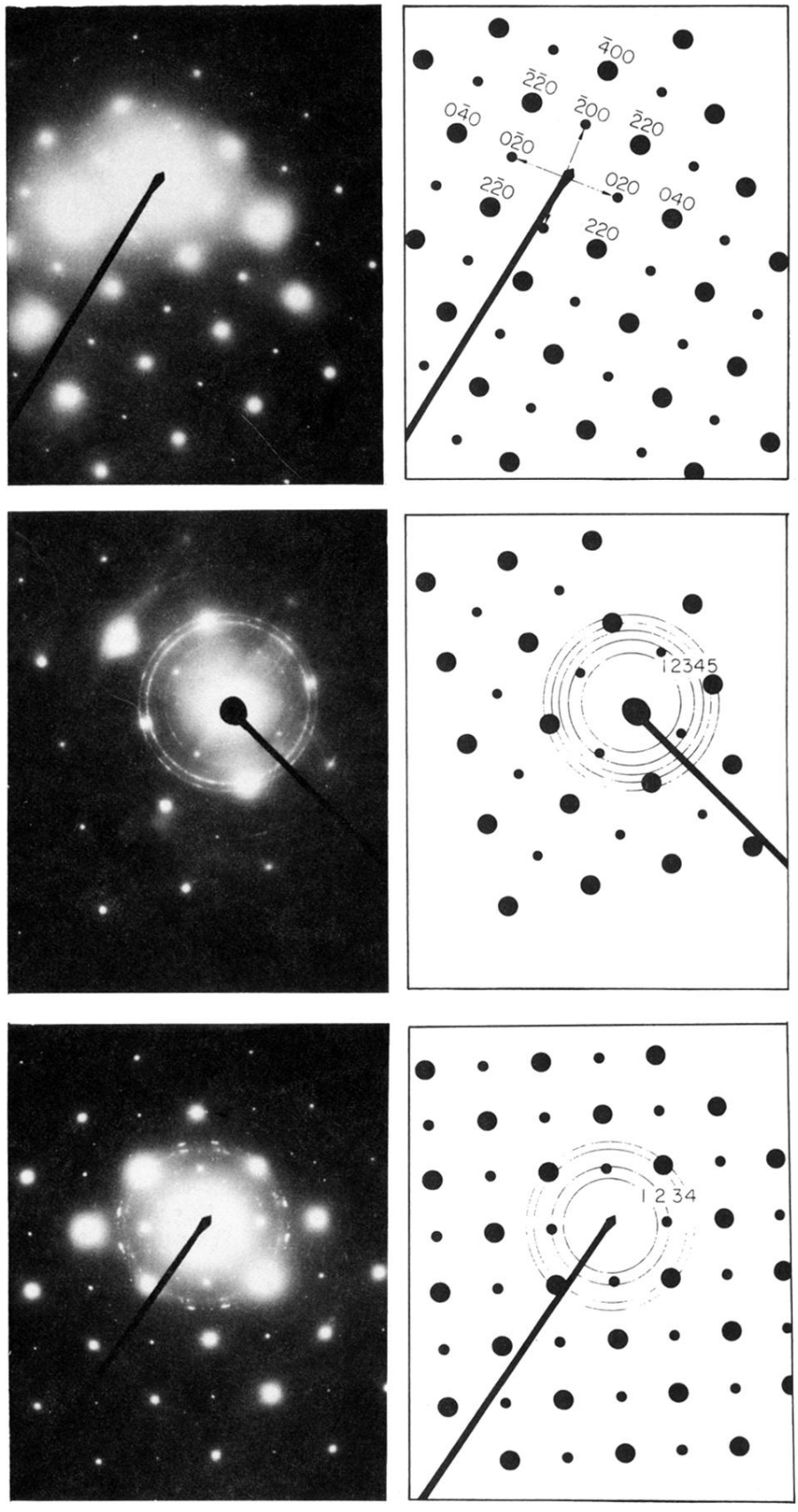

FIG. 5. TED results for (a) saturated diffusion layer (see text), (b) 20-Å Ni on Si(100) interface annealed at 300 °C, and (c) 20-Å Ni on Si(100) interface annealed at 400 °C. Left panels: description of sample and identification of TEM rings from known structure of NiSi and Ni_2Si. Center panel: TED photo. Right panel: accurate reproduction of TED photo. Large spots correspond to spots seen for clean Si(100) lattice. Smaller spots represent superlattice spots which occur when Ni atoms enter the Si lattice.