

## Formation and structure of epitaxial nickel silicide on Si {111}

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(Received 9 September 1983)

A LEED (low-energy electron diffraction) study of the reaction of very thin Ni films on Si {111} suggests the existence of a threshold coverage of Ni for the formation of NiSi<sub>2</sub>. If the initial Ni coverage is 6 monolayers or less, high-temperature anneals at 900–1200 °C for times of a few seconds up to a few minutes produce a 1×1 structure. The LEED spectra from this structure are practically identical to those of the quenched “1×1” phase that can be obtained by quenching from high to room temperature the 1×1 phase of clean Si {111}. If the initial Ni coverage is higher than 6 monolayers then the above high-temperature anneals produce epitaxial NiSi<sub>2</sub>. The top layer of the NiSi<sub>2</sub>{111} film contains only Si atoms; the second layer contains only Ni atoms. The first interlayer spacing is contracted approximately 25% with respect to the bulk value.

Nickel silicide NiSi<sub>2</sub> is one of four silicides (Ni, Co, Pd, and Pt) that is known to form epitaxially on silicon. It crystallizes in the cubic CaF<sub>2</sub> structure with lattice parameter  $a_0 = 5.406 \text{ \AA}$  (as compared with  $a_0 = 5.4282 \text{ \AA}$  for silicon, hence with 0.41% mismatch) and has been shown to grow epitaxially on all low-index planes ({111}, {001}, and {110}) of silicon.<sup>1</sup> The surface of NiSi<sub>2</sub>{001} at the vacuum interface was reported to be reconstructed and partially disordered, but the surface of NiSi<sub>2</sub>{111} was found to have bulk periodicity parallel to the surface,<sup>2</sup> i.e., to produce a 1×1 LEED (low-energy-electron diffraction) pattern. Tung, Gibson, and Poate<sup>3</sup> have recently studied the formation of epitaxial NiSi<sub>2</sub> films in ultrahigh vacuum starting from very thin Ni films deposited on Si {111} and subsequently annealed to about 500 °C. They made the interesting observation that the epitaxial NiSi<sub>2</sub> films have the same orientation as the Si {111} substrate (type A) if the initial Ni deposits are large (13–16 monolayers), but are rotated 180° with respect to the substrate (type B) if the initial Ni deposits are small (1–7 monolayers). At very low Ni coverages (< 6 monolayers) the orientation of the epitaxial films was stated to be “hard to identify,” but the corresponding LEED patterns were always 1×1, and further growth of the same films was always found to be of type B.<sup>3</sup>

Much attention has been devoted to the nature of the silicide-silicon interface<sup>4,5</sup> and to the process of silicide formation,<sup>3,6</sup> while relatively few studies have been concerned with the silicide-vacuum interface. Questions such as whether the top atomic layer of the silicide films consists of Si or Ni, or both, whether NiSi<sub>2</sub> is formed immediately after deposition and anneal of the Ni film on the Si surface or other intermediate phases form first, whether the NiSi<sub>2</sub> surface is bulklike and/or relaxed, etc., are still unanswered. We address these questions in the work reported here. We have used LEED (low-energy electron diffraction) and AES (Auger electron spectroscopy) to examine the reaction of Ni with a Si {111}7×7 surface, and obtained several novel and interesting results, to be described below.

The substrate was cut from a large Si {111} wafer (10 Ω cm, *n*-type, 0.2 mm thick), cleaned *in situ* by a sequence

of argon-ion bombardments and anneals to produce a sharp 7×7 LEED pattern. Nickel was deposited onto the Si {111}7×7 surface by heating a Ni wire to about 1300 °C with electric current. The rate of deposition was estimated subjectively from the time required to obliterate the LEED pattern to be approximately 1 monolayer/min. We will base our estimates of the surface coverage on this deposition rate in the following, but we note that such estimates may possibly be in error by as much as a factor of 2 in absolute magnitude. A typical experimental procedure was to deposit 1–2 monolayers of Ni, then anneal the sample at high temperatures (900–1200 °C) for periods of time varying from a few seconds to several minutes and finally observe the LEED pattern with the sample at room temperature.

For any amount of Ni between about 1 and 8 monolayers (the maximum coverage attained in this study) the LEED pattern was always 1×1. However, at low coverages, up to about 6 monolayers (whether achieved in one or in several cumulative depositions), the LEED spectra (diffracted intensity versus electron energy) were found to be different from those at high coverage (> 6 monolayers). We distinguish therefore between a Si {111}1×1-Ni(LC) (for low coverage) and a Si {111}1×1-Ni(HC) (for high coverage) phase. Once the LC phase was obtained we could form the HC phase by adding more Ni. Conversely, by annealing the HC phase at high temperature (thereby presumably reducing the Ni concentration in the surface region) we could return to the LC phase. The LC phase is associated with higher background in the LEED pattern than the HC phase. The latter was identified as nickel disilicide, as discussed below, but the former is characteristic of the silicon surface. We have found, in fact, that the LEED spectra for all beams of the 1×1-Ni(LC) phase that we have measured (5 at normal, 8 off-normal incidence) are almost identical to the corresponding spectra of the quenched “1×1” phase which is obtained by quenching to room temperature the high-temperature 1×1 phase of Si {111}.<sup>7</sup> This observation is striking because the quenched 1×1 phase occurs on an allegedly clean surface, whereas the 1×1-Ni(LC) phase involves up to 6 monolayers of Ni (or about  $6 \times 10^{15}$  Ni

atoms/cm<sup>2</sup>) distributed in the top few atomic layers of the Si {111} surface. At this point we can make no statements about the structure of this phase other than to say that it is probably close to being bulklike and is associated with strain or disorder. The latter statement is based on the observation of high background in the LEED pattern; the former statement is related to the fact that the quenched  $1 \times 1$  structure is similar (although not identical<sup>7</sup>) to that of impurity- or laser-stabilized Si {111} surfaces, both of which have relaxed bulklike structures.<sup>8,9</sup> Further suggestions about the possible atomic structure of the  $1 \times 1$ -Ni(LC) phase are discussed below.

The HC phase involves higher concentrations of Ni in the surface region than the LC phase. Figure 1 allows an estimate of the difference in Ni concentration from the magnitudes of the AES line intensities of Ni (at 61 eV) and Si (at 92 eV). The figure represents the dependence of the ratio of these AES lines upon the angle of incidence of the primary exciting electron beam. We note a few features of interest: (i) The relative Ni concentration in the HC phase is about three times that in the LC phase. This ratio is among the largest observed in the present study. Different preparation conditions (higher annealing temperatures, longer annealing times, etc.) can produce concentration ratios as low as 1.5. However, the HC phase is always more Ni rich than the LC phase. (ii) The Ni/Si ratio in the LC phase is almost independent of the exciting incidence angle. We interpret this fact to mean that the Ni atoms are uniformly distributed over the atomic layers interrogated by the AES beam. (iii) The Ni/Si ratio in the HC phase varies with exciting incidence angle. This variation (the decrease at small angles) is consistent with the assumption that the Ni atoms reside *below* the top surface layer. Hence the incidence-angle dependence of the AES response (a dependence that, as far as we know, has not been discussed in the

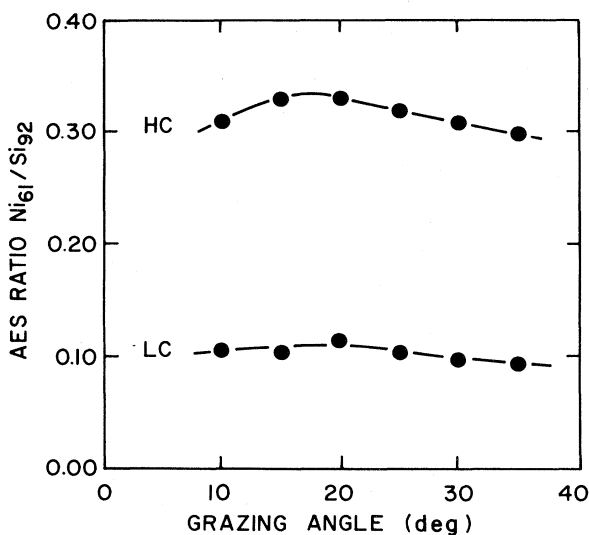


FIG. 1. Dependence of the intensity ratio of Ni to Si AES lines upon grazing angle of incidence of the primary electron beam. HC, high-coverage phase; LC, low-coverage phase. The concentration ratio shown here (3:1) is among the largest observed in this study. The average ratio is closer to 2:1.

literature heretofore) indicates that the top layer of the HC phase contains only Si atoms.

We note that if the HC phase is indeed NiSi<sub>2</sub> then 6 or more monolayers of Ni on the Si substrate give rise to 18 or more layers of NiSi<sub>2</sub>, hence the LEED electrons "see" essentially a semi-infinite crystal of NiSi<sub>2</sub> with a {111} surface exposed. Thus we proceeded to calculate the LEED spectra expected from such a sample assuming a top layer of Si atoms and varying initially only the first interlayer (Si-Ni) spacing  $d_{12}$ . We found that for a contraction of  $d_{12}$  of 25% with respect to the bulk value the calculated LEED spectra are in excellent agreement with the experimental spectra *but only if we assume that the second layer of the silicide (Ni in this case) is rotated by 180° (or 60°) with respect to the position of the second layer (Si) of the silicon substrate.*<sup>10</sup> Hence we have the type-B orientation discussed by Tung *et al.*<sup>3</sup> Figure 2 shows the 10 and 01 spectra at normal incidence and the 00 and 01 spectra at  $\theta = 15^\circ$ ,  $\phi = 180^\circ$  (curves labeled S in the figure). For the normal-incidence case we have also calculated the intensities expected from a NiSi<sub>2</sub>{111} surface with a top layer of Ni atoms (curves labeled N in Fig. 2). The results confirm the information provided by the incidence-angle dependence of AES (see above) that the top atomic layer contains only Si atoms.<sup>11</sup> We expect that a refinement of the LEED analysis will modify the values of the lower interlayer spacings of the silicide structure and improve the fit

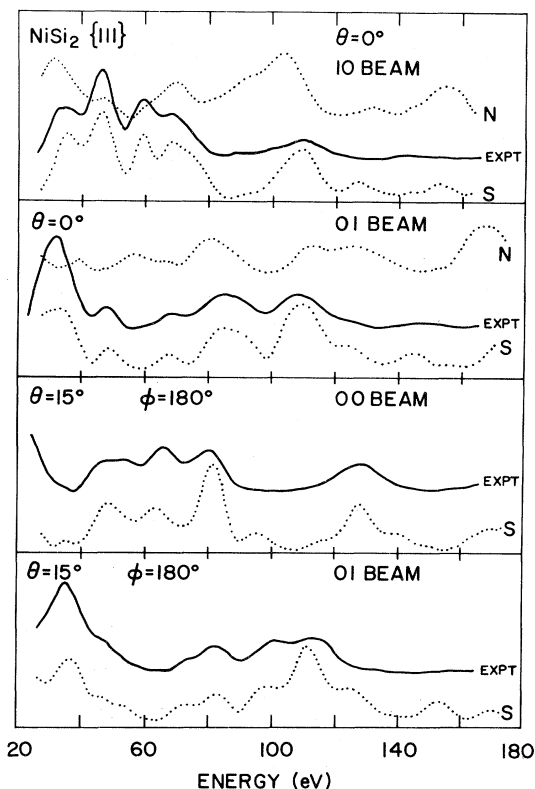


FIG. 2. Experimental and theoretical LEED spectra for a NiSi<sub>2</sub>{111} surface. Curves labeled S were calculated for a Si top layer relaxed 25% with respect to bulk. Curves labeled N were calculated for a Ni top layer relaxed 25% with respect to bulk.

to experiment further.

Figure 3 compares the diamond structure as seen from our Si{111} surface (left in the figure) with the calcium fluoride structure as seen from our NiSi<sub>2</sub>{111} surface. Assuming bulk values for the interatomic distances we see that the constitutions of the first two atomic layers are very similar in the two structures, with the proviso that the second layer consists of Si in the silicon structure and of Ni in the silicide structure, and the orientations of the second layers are different by 180° (or 60°) in the two structures. It is tempting to speculate that in the LC phase the Ni atoms lie in the interstitial sites of the Si lattice, and when their concentration is high enough the silicide structure is formed by switching the bonds from Si to Ni in the second layer. The existence of a presilicide phase with Ni in interstitial sites of the Si lattice has also been proposed by Chang and Erskine<sup>12</sup> on the basis of transmission electron diffraction, photoemission, and LEED studies of silicide films on Si{001}. It is improbable, however, that Chang and Erskine's "diffusion layer" with ordered interstitial Ni is the same as our 1×1-Ni(LC) phase because the latter is almost identical with the quenched 1×1 phase of clean Si{111}, which seems to exclude ordered arrangements of Ni atoms.

The existence of a threshold coverage of metal prior to silicide formation has been reported before. Okuno, Ito, Iwani, and Hiraki<sup>13</sup> and Narusawa, Gibson, and Hiraki<sup>14</sup> found that the reaction of Au with Si on {001} and {111} surfaces occurs only if the Au thickness exceeds 4–5 monolayers. But Tromp *et al.*<sup>15</sup> conclude from ion scattering studies of Pd on Si that if there is a critical Pd thickness at which a reaction with Si is induced, it must be less than 2 monolayers of Pd. In the case of Ni on Si{111} discussed here, while we cannot be certain about the absolute magnitude of the critical Ni coverage for silicide formation, we believe that a threshold value exists—the proof is in the LEED evidence for large structural differences between LC and HC phases.

In conclusion, the study reported here has suggested the following conclusions: (1) Reaction of Ni with Si{111} produces two different crystalline phases with different Ni concentrations. Below a threshold value estimated at 6 monolayers of Ni a 1×1 structure is formed that is almost identical to the quenched 1×1 phase of clean Si{111}. Above the threshold coverage, NiSi<sub>2</sub> is formed. (2) The top layer of the NiSi<sub>2</sub>{111} surface thus formed contains only Si atoms,

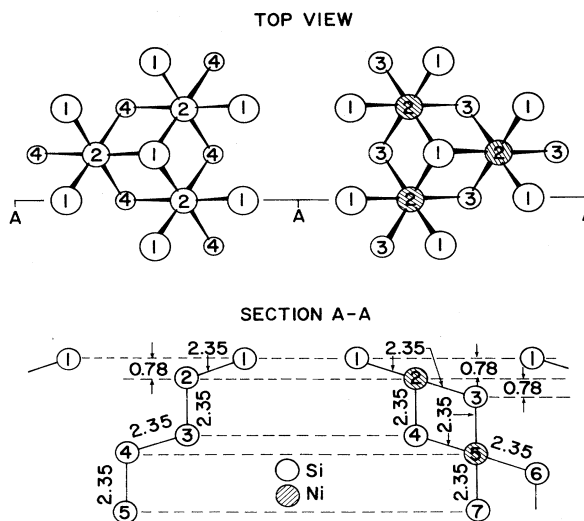


FIG. 3. Schematic top and cross-sectional views of Si{111} (left) and NiSi<sub>2</sub>{111} (right). Circles with 1 represent atoms in the first layer; circles with 2, atoms in the second layer, etc. The numbers in the cross-sectional views are distances in angstroms as encountered in the respective bulk structures. The horizontal dashed lines are meant to help in comparing the two structures. Note the different orientations of the second layers in the two structures. In the 1×1-Ni(LC) structure, Ni atoms may be located in the interstitial sites above atoms in the 4th layer (left). Switching the bonds from atoms 1 to 2 and rearranging the lower layers is required for formation of the silicide.

with Ni in the second layer. (3) The first interlayer spacing is contracted approximately 25% with respect to the bulk value. A refinement of the structure is in progress.

#### ACKNOWLEDGMENT

We are greatly indebted to Dr. K. N. Tu of IBM Research for his suggestions about this work and for his support. Two of us (W.S.Y. and F.J.) were sponsored in part by the National Science Foundation.

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<sup>10</sup>Differentiation between type-A and type-B orientation is simple and unambiguous if LEED intensity spectra are considered. For example, at normal incidence the 10 and 01 spectra calculated for type A, (10)<sub>A</sub> and (01)<sub>A</sub>, are inverted for type B, i.e., (10)<sub>A</sub> = (01)<sub>B</sub> and (01)<sub>A</sub> = (10)<sub>B</sub>. Comparison between calculated and observed spectra immediately shows which orientation is present in the experiment. For a discussion of the relationship between the relative orientation of the second atomic layer and LEED pattern see, e.g., F. Jona, *J. Phys. C* **11**, 4271 (1978).

<sup>11</sup>Further confirmation is provided in the work by O. Nishikawa and

co-workers at the Tokyo Institute of Technology (private communication), in which atom-probe and field-ion-microscope studies of NiSi<sub>2</sub> show that the first layer of atoms to leave the surface is entirely silicon.

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