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Ni-Si(111) interface: Growth of Ni_2Si islands at room temperature

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E. J. van Loenen, J. W. M. Frenken, and J. F. van der Veen

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dyn cm^{-2} of *a*-Si:H.[12] The low-temperature thermal dehydrogenation has been proposed[13] on infrared evidence to occur, in part, via loss of molecular hydrogen. The occlusion of hydrogen at the interface has been argued[8] to arise from differences in diffusion rates between the amorphous layer and substrate. Notwithstanding the origin of molecular hydrogen at the interface, the evidence supports an explosive mechanism for the macroscopic release of H_2.

The evidence in this letter shows that *a*-Si:H/*c*-Si interfacial regions act as nucleation centers since the formation of micro bubbles and, ultimately, circular craters were only formed at unoxidized positions.[14] Clearly lateral diffusion of H atoms or H_2 is relatively fast, at elevated temperatures, compared to occlusion at the SiO_2 layer.

To summarize, the present technique enables the encoding of information to be realized in *a*-Si:H films using conventional technology, although further developments using localized laser oxidation[15] are envisaged.

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Ni-Si(111) interface: Growth of Ni_2Si islands at room temperature

E. J. van Loenen, J. W. M. Frenken, and J. F. van der Veen
FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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Ultrathin films (0–20 Å) of Ni have been deposited on atomically clean Si(111) surfaces at room temperature. The composition and morphology of the films have been determined, employing the high depth resolution obtainable in medium energy ion scattering. Disordered Ni_2Si islands are formed, which grow laterally and in thickness with increasing Ni coverage. The silicide formation ends when the islands coalesce into a continuous film, at a Ni coverage of $\approx 8 \times 10^{15}$ Ni atoms/cm^2. During the silicide growth, the surfaces of the islands are rich in Si.

Knowledge of the stoichiometry, morphology, and growth mechanisms at the initial stages of metal film formation on silicon are of great importance in understanding silicide growth and Schottky barrier formation. Walser and Bene[1] have predicted the initial formation of a "glassy membrane" between the metal film and the Si substrate, with a composition close to that of the deepest eutectic in the binary phase diagram. For Ni on Si this would be $Ni_{1.2}Si$.[2] However, from photoemission work[3–5] the formation of a mixed layer with a graded composition near the silicide/Si interface is concluded, whereas a recent SEXAFS study[6] reported the direct formation of the stable $NiSi_2$ phase at room temperature (RT). To help settle this issue, experimental techniques are required that directly probe the composition of the interface region with high depth resolution.

In this letter we report medium energy ion scattering results which show that initially clusters of Ni_2Si are formed. No evidence is found for a Si-rich layer at the interface with Si. Instead, Si enrichment is observed on top of the Ni_2Si islands.

The experiments were performed in an UHV chamber with a base pressure of 7×10^{-11} Torr. Si(111) 7×7 surfaces were prepared by mild sputtering (RT) and annealing at 1400 K. Backscattered He^+ ions were energy analyzed with a toroidal electrostatic analyzer,[7] which simultaneously measures a 20° range of scattering angles. A depth resolution of 3 Å results from the exceptionally good energy resolution of this analyzer (700 eV for 175 keV ions), as compared to the inelastic energy loss of the projectiles in the solid, being ≈ 210 eV/Å for the experimental conditions used here.[8] Details of the experimental setup and sample cleaning procedure have been published elsewhere.[7,9] Ni was deposited at a rate of 0.1–0.2 monolayer per minute by direct sublimation from a 99.997% pure Ni wire, placed at a distance of ≈ 20 cm from the sample.

Figure 1 shows two backscattering energy spectra taken from clean and Ni covered Si(111). The 175-keV He^+ beam was aligned with the $[00\bar{1}]$ direction in the Si(111) substrate. Due to shadowing of deeper atoms, the ion beam only hits the first atoms of every $[00\bar{1}]$ string, whereby the backscattering yield from below the surface is strongly reduced. The toroidal energy analyzer was set such that a range of scattering angles θ around the $[11\bar{1}]$ direction was accepted. This particular direction was then selected for further analysis ($\theta = 54.8°$). In this "double alignment" geometry, the backscattered yield from below the Si surface is still further reduced, due to blocking of ions on their way out by atoms along the $[11\bar{1}]$ atomic rows. For the clean Si(111) 7×7 sur-

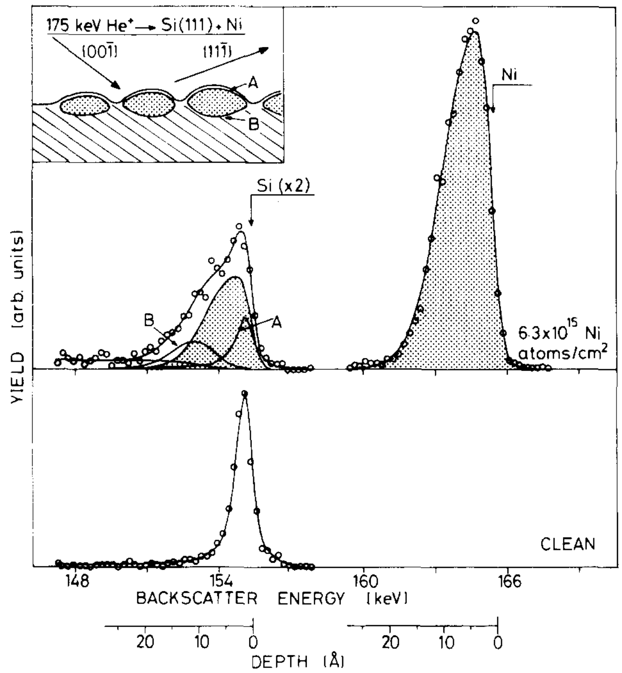

FIG. 1. Backscattering energy spectra for a clean and Ni covered Si(111) surface, for the coverage indicated. The curves shown are explained in the text. The shaded areas correspond to backscattering from the mixed Ni-Si islands, as shown in the inset.

face this results in the sharp Si surface peak with low background, shown in Fig. 1.

Upon deposition of Ni on this surface a second peak appears, at the energy expected for backscattering from Ni surface atoms,[10] as indicated by the arrow in Fig. 1. The total Si peak area increases with coverage, indicating that Si atoms are displaced from their positions in the [00$\bar{1}$] atomic rows and now become visible to the ion beam and detector. Thus mixing occurs between Ni and Si at room temperature. The absence of significant shadowing and blocking effects in the Ni spectra shows that the compound is highly disordered, i.e., polycrystalline or amorphous.

The composition of the mixed layer has been determined by converting the Ni and Si peak areas to the respective numbers of atoms/cm^2. Details of such conversions have been published elsewhere.[11] The results are shown in Fig. 2, where the number of visible Si atoms/cm^2 is plotted versus Ni coverage. For the clean Si(111) 7×7 surface, 2.8×10^{15} atoms/cm^2 are visible to beam and detector in the present scattering geometry. This is two monolayers more than expected for a bulk-terminated Si(111) surface (marked BULK in Fig. 2). These extra Si atoms are already displaced from lattice positions in the 7×7 reconstruction.[12] This puts a lower limit on the sensitivity for Ni induced displacements in this scattering geometry, as is reflected by the essentially constant total Si yield at coverages below 2×10^{15} Ni atoms/cm^2. For higher coverages the number of displaced Si atoms increases at a rate of one per two deposited Ni atoms, showing that Ni_2Si is being formed. This composition is in agreement with photoemission results in this coverage range,[4] but contradicts the recent SEXAFS results by Comin *et al.*[6,13] Finally, above $\approx8\times10^{15}$ Ni atoms/cm^2 the rate of Ni_2Si formation slows down significantly.

In order to be more sensitive to possible Ni induced atomic displacements in the coverage range below 2×10^{15} Ni atoms/cm^2, the ion beam was aligned along the [$\bar{1}\bar{1}\bar{1}$] axis normal to the surface. Viewed along this direction, the clean 7×7 reconstructed Si(111) surface shows only minor atomic displacements.[12] After deposition of 1.7×10^{15} Ni atoms/cm^2, the Si peak area was found to be increased above the clean surface value by 0.8×10^{15} atoms/cm^2, which shows that Si atoms are displaced, and do not simply remain at their positions in the reconstructed Si surface. Note that again the ratio of displaced Si to Ni atoms is 1:2. The latter result is in good agreement with MeV ion channeling measurements.[14]

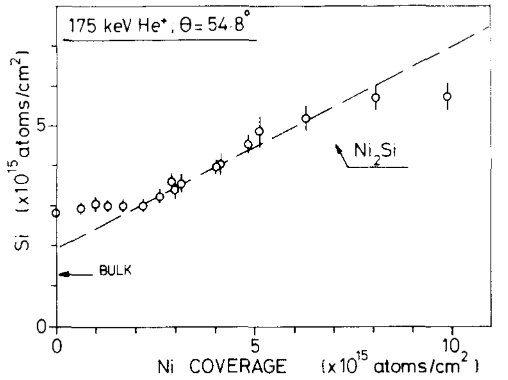

FIG. 2. Total number of Si atoms/cm^2 visible to beam and detector as a function of the Ni coverage, for the scattering geometry shown in the inset of Fig. 1.

The morphology of the film directly follows from the average width (full width at half-maximum) of the Ni spectra. For a continuous Ni_2Si film the inelastic energy loss has been calculated,[8,10] and the result is shown by the broken line in Fig. 3. The experimental widths, corrected for the detector resolution and small Ni isotope shifts, are also shown in Fig. 3, and are, for the highest coverages, in good agreement with the expected values. For the lower coverages however, the widths are much larger than expected for a continuous film, showing that Ni_2Si clusters are formed in the initial stage of silicide formation. The percentage of the substrate surface covered by islands is readily obtained from the ratio of expected to measured Ni peak widths. The data points approach the line slowly, showing that the clusters grow lat-

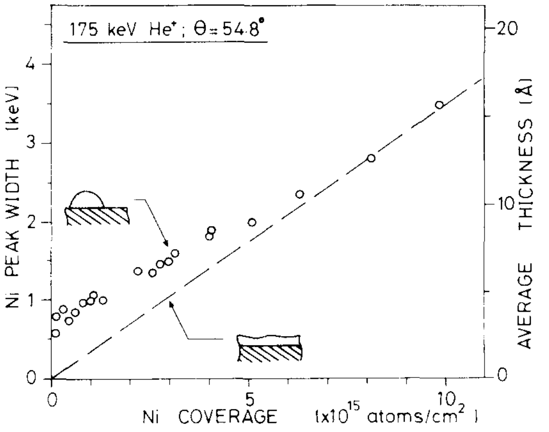

FIG. 3. Experimental Ni peak widths, as a function of Ni coverage. Ni_2Si is shown dotted in the insets. The widths expected for a continuous film are indicated by the broken line.

erally, and coalesce into a continuous film at a coverage of $\approx 8\times 10^{15}$ atoms/cm^2, where the film has an average thickness of about 14 Å. This is just the coverage at which the reaction slows down dramatically.[15]

Extrapolation of the Ni_2Si line in Fig. 2 to zero coverage shows that an extra amount of 0.6×10^{15} Si atoms/cm^2 remains visible, above the amounts incorporated in the "silicide." In order to determine the location of these extra Si atoms, a deconvolution of the Si spectra has been made. The contribution from the Si atoms incorporated in the mixed Ni_2Si film can be subtracted, since it results in a peak, having the same shape as the observed Ni peak, with an area determined from the known stoichiometry. This is shown shaded in Fig. 1. Then two other contributions remain: one from below the mixed film (B) and one from the surface (A). Surface peak A in Fig. 1 originates from $\approx 5\%$ of the Si surface (1.5×10^{14} atoms/cm^2) being bare and from Si enrichment of the island surfaces ($\approx 5\times 10^{14}$ atoms/cm^2). The latter contribution almost disappears after closure of the film, which suggests that these Si atoms have come on top of the islands by diffusion over the edges. The area of peak B corresponds to the value expected for a bulklike terminated Si(111) surface, which indicates that the Si-silicide interface is not significantly enriched in Si. For the very thin islands formed below $\approx 2\times 10^{15}$ Ni atoms/cm^2, the distinction between mixed and surface Si in the islands becomes somewhat ambiguous. Since furthermore these islands reside on or in the Si substrate, the Ni atoms will effectively be in a Si-rich environment, which may explain the photoemission and SEXAFS results mentioned in the introduction.

From these results we suggest that the initially clustered form of the film plays an important role in the high reactivity of Ni and Si at room temperature. As has been suggested by Zunger[16] the energy released upon metal cluster formation can be sufficient to overcome activation barriers for reaction and diffusion. Furthermore, Si is available between and on top of the islands, allowing for a rapid reaction until the islands coalesce into a continuous film.

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