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Monolayer Resolution in Medium-Energy Ion-Scattering Experiments on the $NiSi_2(111)$ Surface

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The surface structure of the epitaxial $NiSi_2/Si(111)$ system has been determined applying a new ion-scattering method. Detecting backscattered ions with ultrahigh-energy resolution we resolve the signals from successive atomic layers. From both their intensity and energy, which depends on the specific ion trajectories, we directly deduce the (sub)surface atom coordinates. Applying this new approach, we find that the $NiSi_2(111)$ surface has a bulklike topology, i.e., it is terminated by a Si-Ni-Si triple layer. The outermost Ni-Si and Ni-Ni interlayer distances are relaxed from their bulk values.

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Although the epitaxy of $NiSi_2$ and $CoSi_2$ on Si(111) has been investigated in great detail, relatively little attention has been paid to the $NiSi_2(111)$ surface structure. It has been reported that the $NiSi_2(111)$ surface would be bulklike, with the crystal terminated by a Si-Ni-Si triple layer [1,2]. However, recent reports claim that the surface has an additional Si bilayer on top of the last Si-Ni-Si triple layer [3,4], like the $CoSi_2(111)$ surface in its most stable form [5,6].

We settle this issue employing medium-energy ion scattering (MEIS) in a novel and model-independent fashion. Conventional MEIS is a well-established tool for the crystallography of surface and interfaces. Atomic positions are determined by comparing angular distributions of the total surface backscattering intensity ("blocking patterns") with calculated yields for a variety of structure models [7]. The ion intensity generally contains contributions from several atomic layers, which, in conventional MEIS, are not separated but treated as a whole. This complicates the analysis of, e.g., multilayer relaxations in a crystal surface.

In this experiment we have succeeded in resolving the monolayer contributions in backscattered ion energy spectra taken on the $NiSi_2(111)$ surface using an ultrahigh-resolution analyzer ($\Delta E/E = 9\times10^{-4}$). Angular distributions of the ion yield backscattered mainly from a *single* atomic layer in the surface region ("monolayer blocking patterns") directly yield the surface atomic positions. Furthermore, we observe the trajectory dependence of the energy loss in a single Si surface layer and use it to locate the outermost Si atoms. The data conclusively show that the topology of the $NiSi_2(111)$ surface is bulklike; the presence of a Si double layer on the surface is ruled out.

Epitaxial $NiSi_2$ films of either the type-*A* or type-*B* orientation were grown on clean Si(111) substrates [8,9]. The silicide was checked to be of single orientation (> 92% of the surface area) using ion scattering [2,9]. The data presented here were obtained on type-*B* oriented films; within statistical error, type-*A* oriented silicides yielded identical results. Annealing the silicide films to 600 °C did not affect the surface structure.

In the experiments we used a 100-keV proton beam which was stable to within 10 eV. Energy spectra of the ions backscattered in an angular range of 20° were recorded simultaneously using a modified version of our toroidal electrostatic analyzer (FWHM energy resolution 90 eV at 100 keV). Backscattered yields were normalized with respect to the random height of Ni in $NiSi_2$ [7,10]. The ion energy, energy stability, and resolution were determined by steering the ion beam directly into the analyzer.

Protons backscattered from an atom in the outermost layer of the silicide reach the detector at an energy which is mainly determined by the elastic and inelastic energy losses during the single ion-atom collision. This results in an extremely sharp peak from that layer in the energy spectrum. Ions backscattered from deeper layers additionally lose energy by electronic interactions along the ingoing and outgoing parts of their trajectories through the crystal ("stopping"). These ions show up at lower energies in the spectrum. The statistical spread on the energy losses in the first few atomic layers proves to be rather small, allowing the backscattering contributions from successive layers to be separated.

In conventional lower-resolution MEIS, a channeling direction must generally be chosen for the incident beam in order to reduce the deeper-layer contributions [7]. That restriction is lifted owing to the improved depth resolution; we have deliberately chosen a nonchanneling incident direction in the $(1\bar{1}0)$ scattering plane at an angle of 22.0° with respect to the (111) surface plane [Fig. 1(a)]. Thus the first few atomic layers have about equal hitting probability, giving rise to about equal sensitivity to surface and subsurface layers. These are then separated in the energy spectra, allowing a layerwise structure determination.

Ion intensities were recorded for energies ranging from 95 to 99 keV, and for exit angles with respect to the surface plane between 23° and 63°. In the following we consider different cuts through the resulting two-dimensional data set.

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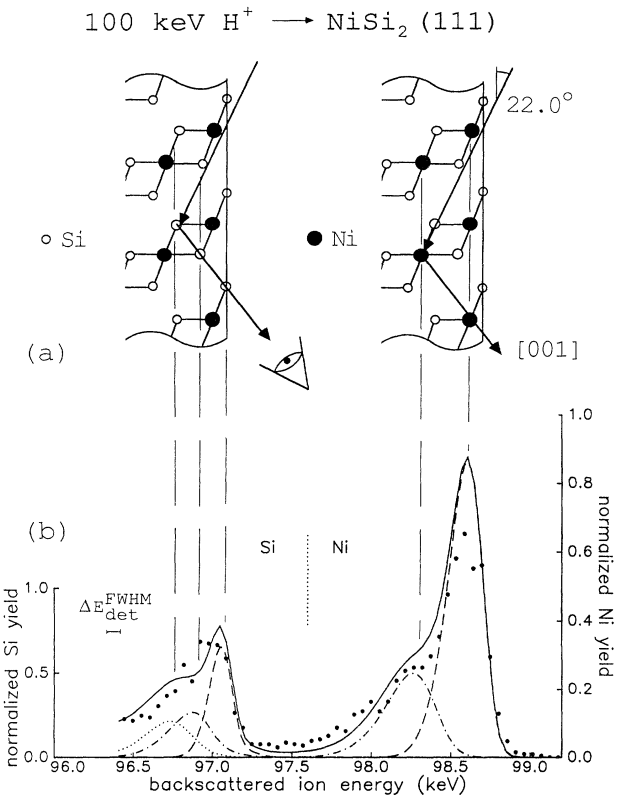

FIG. 1. Monolayer separation by medium-energy ion scattering. (a) Scattering geometry in the $(1\bar{1}0)$ plane for Ni and Si atoms, and (b) energy spectrum (circles) taken under blocking conditions ([001] direction, exit angle 35.03° with respect to the surface (111) plane). The second-layer Ni is visible as a distinct shoulder on the first-layer Ni trailing edge. The result of a Monte Carlo simulation is given (solid curve), together with the contributions from individual layers (broken curves). The FWHM detector resolution is indicated.

The energy spectrum taken in the [001] direction (35.03° exit angle) is shown in Fig. 1(b). Along that crystal axis the signals from deeper layers are attenuated due to surface blocking. The two different peaks are due to backscattering from Si (~97 keV) and Ni (~98.6 keV) surface atoms. The shape of the Ni peak contains the clear signature of the first- and second-layer contributions (Fig. 1). The second-layer signal is shifted by ~300 eV to lower energies and is visible as a shoulder on the trailing edge of the first-layer signal. The observed widths of the layer signals are larger than the 90-eV energy resolution [indicated in Fig. 1(b)] and reflect the intrinsic spreads on the inelastic energy losses.

The angular distributions of the individual monolayer yields were used to perform a layerwise structure determination. On their way to the vacuum, ions backscattered from different layers are blocked in directions which directly reflect the relative atomic positions in the surface region (Fig. 2, top panel). We present a few selected cuts through the Ni part of the two-dimensional data set at constant backscattering depth (A-E) and at constant angle (I-IV) in the bottom panels in Fig. 2. The former were obtained approximating the energy loss to be proportional to the ion path length through the crystal, and will be referred to as "constant depth profiles" (CDP's). The profiles A-E correspond to backscattering depths of 0.50, 1.26, 1.92, 2.56, and 3.43 Ni layers, respectively, using tabulated values for the random stopping power [10]. The absence of blocking features in profile A shows that the signal at the leading edges of the energy spectra is solely due to the first Ni layer of the silicide crystal. An extra Si double layer [3,4] is ruled out since it would unavoidably have resulted in blocking minima in this profile. Profile B has two blocking minima, characteristic of the presence of a second-layer signal at "depth" B in the energy spectra; see Fig. 2, top panel. Profiles C to E probe greater depths in the crystal and the blocking minima increase both in number and in strength.

The blocking minima allow a determination of the interlayer distances. The angular position of the main minimum in profile B is shifted to lower exit angles by 0.4° with respect to the [001] bulk axis, indicating an inward relaxation of the atoms in the topmost Ni layer by 0.05 ± 0.02 Å. The minimum in profile E is observed at the [001] blocking axis direction (35.0° exit angle).

Our layerwise treatment of the data is fully corroborated by fits to each of the angular profiles with linear combinations of simulated monolayer contributions from the first five Ni layers. The simulations were performed using a well-established Monte Carlo technique [11]. In the simulations, we have assumed the outermost Ni-Si and Ni-Ni interplanar distances to be 0.12 Å (see below) and 0.05 Å smaller than in bulk $NiSi_2$, respectively. Values for vibration amplitudes were taken to be identical to those used in Refs. [2,9]. The fits are shown as solid curves in the blocking patterns and energy spectra of Fig. 2. The relative contributions from individual monolayers in the fits are shown for energy spectrum III (broken curves). The fits match the data well, strongly confirming the bulklike surface termination. Residual differences between data and fits are largely a consequence of the approximation of a constant energy loss per unit path length, on which the construction of the CDP's is based.

We have also attempted to describe the data taking into account an inelastic energy loss which does depend on the specific ion trajectory in Monte Carlo calculations. In these simulations the inelastic loss due to a single atom is assumed to decay exponentially with increasing ion-atom impact parameter [9,12,13]. The results were subjected to energy straggling and folded with our detector resolution. In Fig. 1(b) we show the calculated spectrum (solid curve) for the geometry of Fig. 1(a), with its decomposition into the different layer contributions (bro-

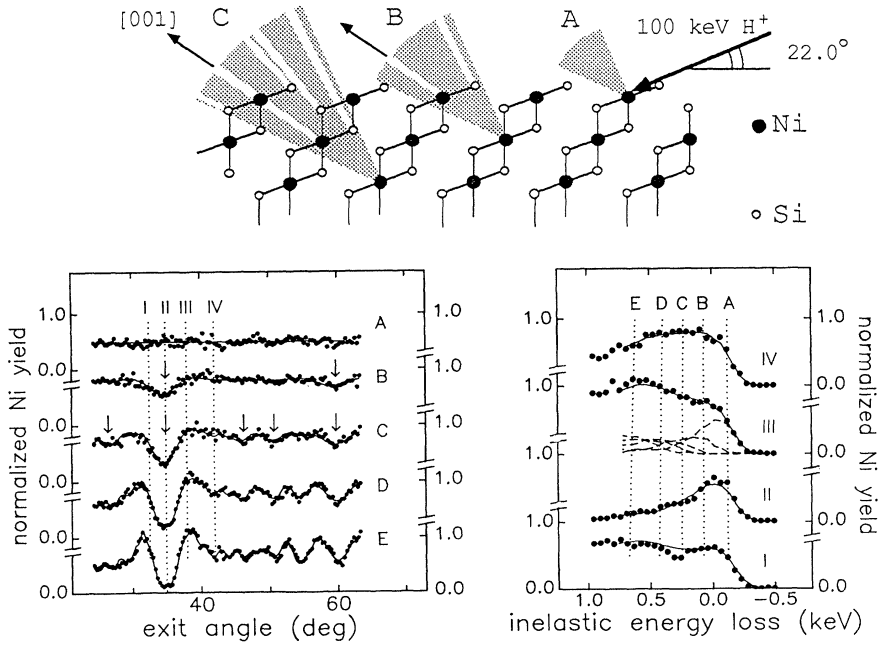

FIG. 2. Layerwise structure determination. Top panel: Scattering geometry; the ion beam is incident at an angle of 22.0° with respect to the surface plane. Bottom panels: Cuts through the two-dimensional data set (Ni signal) at constant angle (energy spectra *I-IV*) and constant backscattering depth (*A-E*). Data are the points; the curves are the result of a fitting procedure (see text). Profiles *A-E* correspond to backscattering depths of 0.50, 1.26, 1.92, 2.56, and 3.43 Si-Ni-Si triple layers, respectively. The blocking minima in the second- and third-layer signals are indicated by small arrows.

ken curves). The agreement with the measured spectrum is rather good, considering that the comparison is made on an absolute scale and does not involve any free parameters.

We have directly observed the dependence of the backscattering energy on the specific trajectory along a single Si surface atom and use it to accurately determine the first Ni-Si interplanar distance. A determination of this distance using conventional channeling and blocking is complicated by the interference of the weak and broad first-layer Ni-Si blocking minimum with narrower minima in the deeper-layer yields. By contrast, the energy-loss measurement is sensitive to the first-layer energies only, allowing an accurate determination. In this experiment, the incident ion beam was aligned with the $[00\bar{1}]$ silicide axis [$(1\bar{1}0)$ scattering plane] at an angle of 35.03° with the surface plane (Fig. 3, inset). The backscattered ions were energy analyzed in a 20° angular range around the $[11\bar{1}]$ direction (dashed line). Ions backscattered from the outermost Si layer reach the detector with a relatively small inelastic energy loss due to electron excitations in the layer itself; on the other hand, ions backscattered from Ni additionally lose energy in the Si surface layer. This inelastic loss is large for ions that pass a Si atom closely, because there the electron density is largest. Additionally, ion deflections away from the Ni-Si internuclear axis to a larger or a smaller

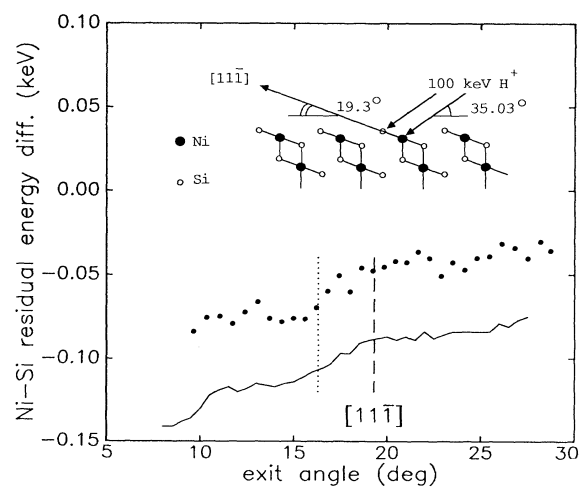

FIG. 3. Energy loss in a single Si monolayer. The residual energy differences (see text) of the Ni and Si first-layer signals have been determined from the leading edges in the energy spectra. Inset: The scattering geometry. The shift of the asymmetric minimum observed at 16.3° (dotted line) with respect to the direction of the $[11\bar{1}]$ bulk axis (dashed line) corresponds to a 0.12-Å contraction of the first Ni-Si interplanar distance. The solid curve is the result of a Monte Carlo calculation (see text).

detection angle cause an apparent energy gain or loss. The small variations in the first-layer Ni backscattering energy are detected using the Si energy as a reference, so that possible angular variations in the detector energy scale cancel out.

We have derived the first-layer backscattering energies from the leading edges of the Ni and Si surface peaks, at which the yield comes from the respective first layers only. Figure 3 shows the angular dependence of the difference of the so-called energy residuals of Ni and Si (circles). The residuals are the differences between the observed leading edges and the (calculated) purely elastic backscattering energies. The negative sign of the energy difference demonstrates the Si termination of the surface. The decrease for smaller exit angles is a natural consequence of the larger energy loss at larger ion path lengths. The inelastic energy losses and ion deflections give rise to a strongly asymmetric minimum at 16.3° exit angle (dotted line). From this angle, we conclude that the outermost Ni-Si interlayer distance is relaxed inwardly from its bulk value by 0.12 ± 0.02 Å. In a LEED analysis Yang, Jona, and Marcus [1] found a relaxation of 0.19 Å; however, they did not specify an error margin. The solid curve represents the result from a Monte Carlo computer calculation using the impact-parameter-dependent inelastic energy loss described above [12]. The simulation accurately reproduces the asymmetric minimum in the data, both in depth and in angular position. The constant-energy difference ($\sim$40 eV) between data and calculation should probably be attributed to the difference in energy straggling between calculated and observed first-layer Ni signals, which effectively gives rise to an apparent energy shift of the leading edge of the experimental Ni peaks. A Si double layer on the surface would have resulted in a residual energy difference larger than 0.2 keV [in an earlier experiment on annealed $CoSi_2(111)$ we have measured a large shift indicative of a Si double layer on top [6]]. In this case, such a shift is not observed.

Both blocking spectra and backscattering energy measurements show that the $NiSi_2(111)$ surface has a bulk-like topology, without an additional bilayer on top [3,4]. The outermost Ni-Ni and Ni-Si interlayer distances are relaxed inwardly by 0.05 ± 0.02 and 0.12 ± 0.02 Å, respectively.

We have demonstrated that MEIS measurements with sufficiently high-energy resolution can be analyzed in a layerwise fashion. This significantly improves the analytical strength of the technique. In addition, energy losses in a single layer of atoms may be used to determine surface structures under circumstances where blocking effects are not strong enough.

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