Real-Space Determination of Atomic Structure and Bond Relaxation at the $NiSi_2$-Si(111) Interface

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The atomic structure at the interface of a 180°-rotated single-crystal $NiSi_2$ film on Si(111) has been determined by a new thin-film ion-channeling method, using ultrahigh depth resolution. The Ni atoms at the interface are found to be sevenfold coordinated. The bonds across the interface are slightly contracted.

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Heteroepitaxial systems are of considerable interest in solid-state physics, from both a fundamental and a technological point of view. Although the epitaxial growth and crystallographic structure of a number of single-crystal films have been investigated extensively,[1,2] until now the atomic structure of lattice planes adjacent to a heterojunction interface could not be determined unambiguously for lack of a suitable probe for in-depth analysis. Yet, knowledge of the interface structure is crucial for an understanding of other interface properties such as, in the case of metal-semiconductor junctions, the Schottky barrier height.

In this Letter we present a new "real-space" method for the determination of atomic positions at interfaces. The method is based on Rutherford backscattering spectrometry combined with ion channeling. Different with respect to previous channeling work[3,4] is the use of an ion focusing effect which occurs in crystal channels. In epitaxial structures the focused ion fluxes can be directed onto specific substrate atoms at the interface, provided that the overlayer is thin enough (typically ≈ 25 Å). The additional use of ultrahigh depth resolution (≈ 4 Å) then permits in-depth structural characterization of single atomic planes at interfaces. The atomically abrupt interface of the $NiSi_2$-Si(111) bicrystal will serve as an illustration of the method.

The silicide $NiSi_2$ has the cubic CaF_2 structure with a bulk lattice parameter 0.46% smaller than that of Si. Tung, Gibson, and Poate[2] have shown that uniform and pseudomorphic (111)-orientated films of single-crystal $NiSi_2$ can be grown on Si(111) with a high degree of perfection. The film may grow on the substrate in different epitaxial arrangements. By following the method for growth described by Tung, Gibson, and Poate,[2] we have selected "*B*-type" films for our purpose, i.e., films with a lattice orientation rotated 180° about the Si(111) surface normal. This still leaves two possibilities for the registry of the overlayer with respect to the substrate: one with fivefold- and one with sevenfold-coordinated Ni atoms at the interface, as depicted in Fig. 1. Though the latter structure is favored by cross-section transmission-electron-microscopy (TEM) lattice imaging,[5,6] definite structure assignments are hampered by uncertainties in sample thickness and other input parameters for TEM image calculations.[5,7] Furthermore, the bond lengths across the interface may be relaxed because of the lowered symmetry at the interface. Detection of such relaxation effects falls outside the resolution of TEM. The present high-resolution ion-scattering results show unambiguously that the interface has the "sevenfold" structure. The bond lengths across the

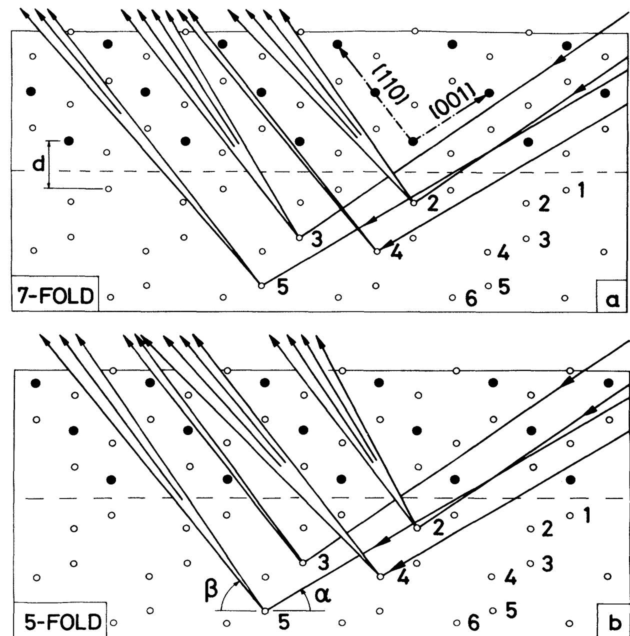

FIG. 1. Scattering geometry for interface structure determination, showing $(1\bar{1}0)$ planes with (a) sevenfold- and (b) fivefold-coordinated interface structures. Open circles denote Si atoms; filled circles denote Ni atoms.

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interface are found to be slightly contracted.

Experiments were performed in a UHV system equipped with LEED and Auger apparatus and a metal-evaporation source by which Ni can be deposited at a rate of ~ 0.2 monolayer/min. The UHV system is coupled to a 200-keV accelerator for ion-scattering analysis. Backscattered ions (H^+ or He^+) are energy analyzed with a toroidal electrostatic analyzer which simultaneously measures a 20° range of scattering angles with an angular resolution of better than 0.3°. A depth resolution of 4–7 Å results from the good energy resolution of the analyzer ($\Delta E/E = 4\times10^{-3}$) as compared to the inelastic energy loss of the ions traveling through the silicide film [53 eV/(Å depth interval) for 100-keV H^+ in the scattering geometry of Fig. 1 and 165 eV/(Å depth interval) for 175-keV He^+ in the scattering geometry used for the relaxation measurements].

The Si(111) sample was cleaned by a standard method.[8] After cleaning a sharp (7×7) LEED pattern was observed and no impurities were detected by either Auger or ion scattering. *B*-type $NiSi_2$ films were formed by deposition of 6.7×10^{15} Ni atoms/cm^2 on the surface at 300 K and subsqequently heating to 770 K for 5 min. The resulting $NiSi_2$ film exhibits a (1×1) LEED pattern and has a thickness of 25 Å, as determined by ion scattering.

The interface was probed by directing a 100-keV H^+ beam into the [00$\bar{1}$] channels of the $NiSi_2$ film. These channels make an angle of 34.9° with the (111) surface plane in the strained, pseudomorphic film. The ion flux, focused in the silicide channels, may hit the susbtrate Si atoms marked 2, 3, 4, and 5 in Fig. 1. Deeper substrate atoms are shadowed by these first substrate atoms, while atom 1 is shadowed by the atomic rows in the silicide. Therefore, only atoms 2 to 5 contribute to backscattering in the interface region. All four atoms are simultaneously visible to the beam for an incidence angle $\alpha = 35.1°$. By choosing slightly different incident beam directions within the [00$\bar{1}$] channels, it is possible to direct the focused ion flux onto particular atoms of this group. For $35.3° < \alpha < 35.8°$ atoms 2 and 3 are hit while 4 and 5 are shadowed, whereas for $34.3° < \alpha < 34.9°$ atoms 4 and 5 are hit while 2 and 3 are shadowed (Fig. 1). This holds for both the fivefold and the sevenfold structure. The backscattered ions can reach the vacuum again through the $NiSi_2$ [110] channels and emerge from these within a well-defined range of exist angles β. For the sevenfold structure the location of atoms 4 and 5 with respect to these channels is such that this angular range is very narrow, whereas atoms 2 and 3 backscatter ions through these channels over a much wider range [Fig. 1(a)]. For the fivefold structure the situation is the reverse. Thus the registry of the overlayer follows immediately from measurement of the angular distribution of emerging ions for different incidence angles of the beam around the [00$\bar{1}$] axis. For such a measurement to succeed it is necessary that the interface backscattering signal can be distinguished from the surface and substrate signals. Here the use of high depth resolution is essential. Furthermore, intensity variations of the interface signals within an angular range of typically 1° have to be measured, which requires high angular resolution.

Figure 2 shows a typical energy spectrum, exhibiting backscattering peaks (labeled *A*) from the nonshadowed Ni and Si surface atoms, a well-resolved peak (*B*) from the exposed substrate atoms at the interface, and a dechanneling background (*C*) from the substrate bulk. The integrated yield of the interface peak (*B*), approximated by the shaded area in Fig. 2, can be converted into the effective number of monolayers visible to beam and detector.[8] Though generally no more than two interface layers are actually hit, the above number can be as high as 7, because the ion flux is concentrated in the ingoing and outgoing channels. Figure 3 shows measured angular distributions of the interface yield, expressed in monolayer units, for three different incident beam directions: $\alpha = 34.5°$, 34.9°, and 35.1°. The distribution is extremely narrow for the lower incidence angles of the beam and widens dramatically as the incidence angle is increased. This is exactly the behavior expected for the sevenfold interface [Fig. 1(a)].

In order to determine the interface structure quantitatively, Monte Carlo computer simulations of the scattering process were performed for the specific structure models. Typically, some 10^5 ions were tracked through the pseudomorphic thin-film structure for each incident and outgoing direction. In calculating the tracks, a Molière ion-atom scattering potential was used. The atoms were assumed to vibrate isotrop-

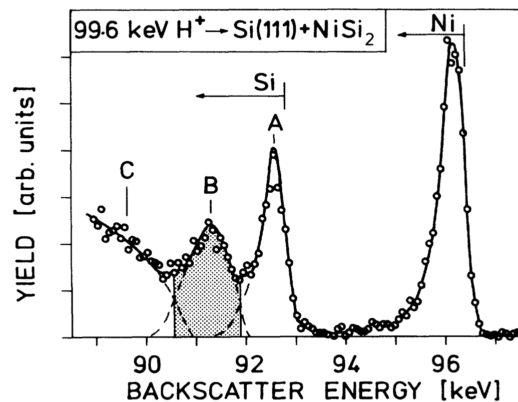

FIG. 2. Example of backscatter energy spectrum, with (*A*) Si surface peak, (*B*) Si "interface" peak, and (*C*) substrate dechanneling signal; $\alpha = 34.5°$, $\beta = 54.1°$.

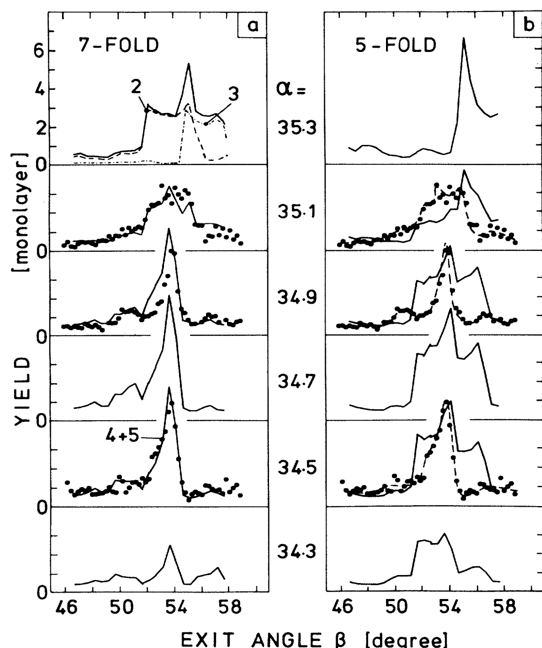

FIG. 3. Interface peak area as a function of exit angle β for different incidence angles α within the $[00\bar{1}]$ channels. Full lines are results of Monte Carlo simulations and dots are experimental data points (99.6-keV H^+). Broken lines in (b) are meant to guide the eye.

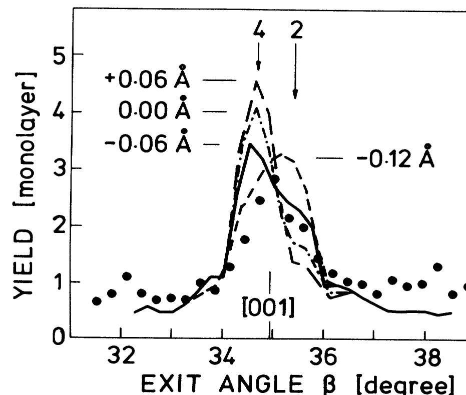

FIG. 4. Interface peak area as a function of exit angle β in the bond relaxation measurement. The 175-keV He^+ beam is incident along the $[\bar{1}\bar{1}1]$ direction. Curves are results of Monte Carlo simulations and dots are experimental data points.

ically with one-dimensional rms thermal displacements of 0.09 Å and 0.11 Å for the Ni and Si atoms in $NiSi_2$[9] and 0.078 Å for the substrate Si atoms. With use of the nuclear-encounter probability approach combined with the concept of time reversibility,[10] the effective number of visible interface layers was computed and compared with experiment. The solid curves in Fig. 3 represent the simulated angular distributions. For the sevenfold structure they agree very well with the data as regards angular positions, shapes, and absolute intensities. For the fivefold structure none of the curves fit the data. The rich structure in the distributions can, with the aid of Fig. 1 and the simulations, be traced back to contributions from single atomic planes. For example, the peculiar shape in the top-left panel of Fig. 3 is the sum of two partially overlapping emission cones from atoms 2 and 3, while the weak shoulder in the asymmetric line shape measured for $\alpha = 34.5°$ can be traced back to atom 5. Thus backscattering contributions from single atomic planes are close to being resolved.

Finally, we have searched for relaxation effects at the interface. For this purpose a 175-keV He^+ beam was aligned with the $[\bar{1}\bar{1}1]$ direction in the silicide. Then only atoms 2 and 4 are visible. The detector was set around the [001] direction (previously the direction of the incoming beam). In the following we consider variations in the distance d as defined in Fig. 1. The unrelaxed distance d (3.12 Å) is composed of one bulk Si-Si distance (2.35 Å) and one Ni-Si interplanar distance in the pseudomorphic silicide (0.77 Å). At this stage no attempt was made to determine these two distances separately. As d increases, atom 2 becomes invisible since it moves in line with the atomic rows of the overlayer. On the other hand, as d becomes smaller, atom 4 is obscured. Since the emission cone from atom 2 into the [001] channels is slightly shifted in angle with respect to that of atom 4, the sign and magnitude of the relaxation follows directly from the angular distribution of backscattered projectiles. The distribution is derived from a collection of energy spectra similar to the one shown in Fig. 2. Figure 4 shows the result in comparison with Monte Carlo computer simulations performed for different relaxation values. Note in these simulations the rapid switching of backscattered intensity from atom 2 to atom 4 as the relaxation of d is changed from -0.12 Å to $+0.06$ Å. The d values have been varied in steps of 0.02 Å and the best fit to the data is obtained for a contraction of 0.06 Å. The error in the determination of d is estimated to be ± 0.08 Å, resulting mainly from the uncertainty in beam alignment with respect to the $[\bar{1}\bar{1}1]$ direction in the silicide.

In summary, we have demonstrated the use of ion focusing in thin epitaxial films for in-depth crystallography of interfaces. The $NiSi_2$-Si(111) interface structure has been solved by this method. The data obtained from this interface show particularly its sensitivity for detection of bond relaxation effects at the interface.

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