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Calculation of ion-scattering yields from simulated intermetallic surfaces: Ni-Al(110)

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A recently developed formalism for calculating ion-scattering yields from simulated crystal surfaces has been extended to the case of bimetallic surfaces. MeV He^+ scattering yields are calculated for thin Ni films reacting with Al(110) surfaces. Interatomic potentials based on the embedded-atom method are used in a Monte Carlo approach to simulate the evolution of the Ni-Al interface as a function of Ni coverage. The calculated ion-scattering yields are in good quantitative agreement with the measured yields, showing two distinct stages of reaction and overlayer growth. Limitations of the simulation and measurement methods are discussed.

There is considerable interest in understanding the reaction between transition metals and aluminum because of the potential for using the aluminides as metallization layers on semiconductors,[1] and as structural materials.[2] High-energy ion scattering (HEIS) is an effective tool for probing the structure of Al–transition-metal interfaces. In our previous work, HEIS and x-ray-photoemission spectroscopy (XPS) were used to investigate the early stages of aluminide formation at the Ni-Al interface.[3] In this paper we report, to our knowledge, the first use of atomistic simulations to characterize the Ni-Al interface reaction, *coupled with an experimental check on the accuracy of the simulations.* We used interatomic potentials based on the embedded-atom method (EAM) in a Monte Carlo scheme to generate snapshots of the atomic coordinates at the interface. Ion-scattering yields were calculated using these snapshots, and compared with measured ion-scattering yields for the reacted interface. In the first application of this formalism the effective-medium theory was used to describe the interactions between Al atoms in a study of surface melting.[4] Medium-energy ion-scattering yields (100 keV H^+) were calculated using snapshots of the disordered surface, and compared with measured yields. The present study extends this effort in three important ways: (1) use of EAM potentials; (2) application to a bimetallic, reactive interface; and (3) extension to higher ion energies (1 MeV He^+). In this paper we compare the simulated and measured results, comment on possible limitations of the simulations, and note a potential problem area associated with dechanneling, in interpreting ion-scattering yields from reacting solid/solid interfaces.

Recently we performed ion-scattering and photoemission experiments to determine the interface reaction for thin Ni films deposited on Al(110) surfaces at room temperature.[3] The number of Al atoms visible to the incident He^+ ion beam, integrated over the sampling depth in the crystal (number of atoms/cm^2), was measured as a function of Ni coverage, as shown in Fig. 1. These results are evidence of a strong Ni-Al reaction. For the first 2.2 monolayers (ML) of deposited Ni atoms, we observed an increase in the number of Al atoms visible to the ion beam, at a rate of 1.9 Al atoms per deposited Ni atom. For Ni depositions between 2.2 and 8.1 ML, the number of visible Al atoms continued to increase, but at a slower rate of about 1:3. In a conventional interpretation of the results in Fig. 1, the slope for the ion-scattering yield vs Ni coverage would be used to determine the average stoichiometry of the reacting interface region. In the present case the slope of about 2:1 would indicate a stoichiometry of Al_2Ni. This would be particularly interesting since no stable compound with this stoichiometry occurs in the bulk Ni-Al phase diagram.[5] To understand why the yield increases at this rate, and to further understand why the reaction rate changes as a function of coverage, it is extremely useful to develop an atomic viewpoint of the early stages of the interface formation.

In our Monte Carlo (MC) computer simulations of the reacting interface, we use the Metropolis scheme for determining which trial atomic displacements are accepted.[4,6] The interactions between Ni and Al atoms are determined using EAM potentials.[7] Since EAM has been shown to reproduce portions of the Ni-Al bulk phase diagram,[8] various relaxations and reconstructions on metal surfaces,[9] and composition profiles for alloys exhibiting surface segregation,[10] it is reasonable to investigate whether or not the outcome of the simulations will agree with the experimental results. The comparisons will at least provide an important test case for the utility of particular EAM potentials, and valuable input for further development of the EAM approach to simulating the properties of metal surfaces and interfaces.

We first performed MC simulations for the clean

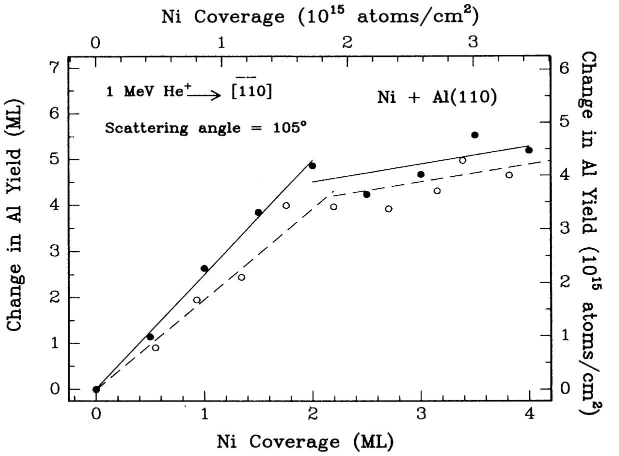
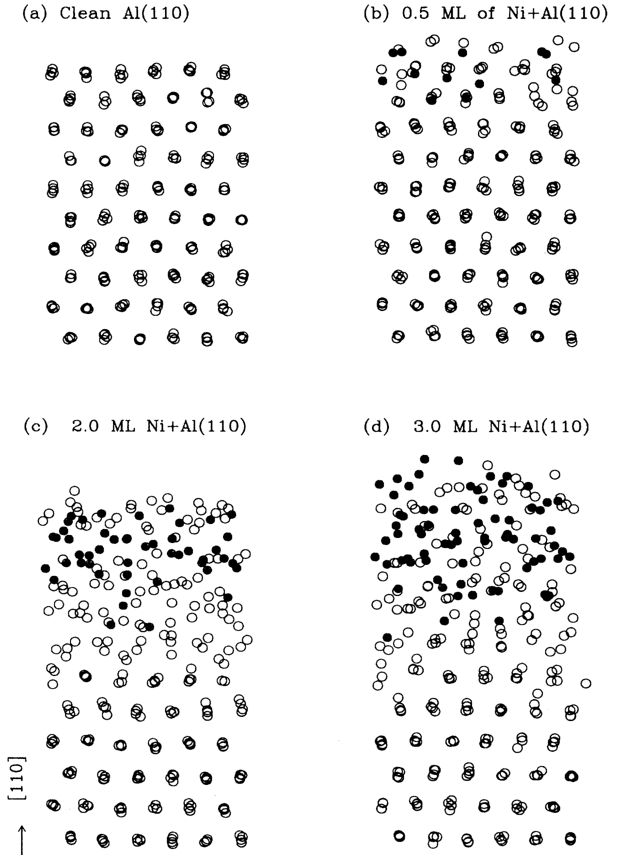


FIG. 1. Change in ion-scattering yield from Al atoms, relative to the value for the clean surface, plotted as a function of Ni coverage on the Al(110) surface. Experimental (simulated) values for the yield are shown by open (closed) circles. The dashed and solid lines are the results from least-squares fits to the measured and simulated data, respectively.

Al(110) surface. The crystal contained 48 layers of rectangular Al(110) planes, each with 24 atoms (4×6). The bottom six layers were frozen at the bulk Al lattice positions, while the upper 42 layers were free to move. Periodic boundary conditions were applied parallel to the surface. The crystal was initially evolved for 5000 cycles at room temperature. We define one "cycle" as one attempted move for each free atom in the Metropolis scheme. The ratio of accepted-to-attempted moves was about 54%. While evolving the crystal for an additional 500 cycles, we periodically stored the atomic configuration of the atoms after every ten cycles, generating 50 snapshots. A typical snapshot of the clean Al(110) surface is shown in Fig. 2(a). Ion-scattering simulations were then performed on these snapshots. A stationary state in the evolution of the crystal was achieved after 5000 cycles, in that neither the total energy of the crystal nor the calculated scattering yield changed significantly with additional cycles. We refer to this process as equilibration, although we do not claim that the crystal is in thermodynamic equilibrium. The crystal was evolved for 5000 more cycles, and another independent set of snapshots was generated. A total of 150 snapshots were generated in this manner for ion-scattering simulations.

The calculated ion-scattering yield from the snapshots of the Al(110) crystal, using 1-MeV He$^+$ ions at normal incidence, was about 15% higher than the experimental yield. Most of this disagreement can be attributed to an artifact of the MC simulations. The simulated crystal (4×6×48 atoms) tends to wave back and forth in a direction parallel to the surface. Although the amplitude is small, it is sufficient to uncover atoms in the deeper layers, making them visible to the high-energy ions. This phenomenon is understood and can be reduced by enlarging the simulated crystal.[4] Since we calculate the ion-scattering yield for each layer, contributions to the yield from deeper layers, associated with the waving motion, can be distinguished from contributions to the yield originating near the surface and associated with reaction and disorder. In this work we reduced the waving contribution to the yield in the deeper layers by uniformly shifting those layers in the snapshot so as to restore the center of mass for each layer to its starting position. Since this correction is made only *after the snapshots have been generated,* it has no effect on the future evolution of the crystal, which continues to wave unrestricted. The shift simply has the effect of restoring the shadowing known to exist in real crystals along the rows of atoms. The uppermost layers were shifted as a block in the direction required to restore the center of mass in layer 10, since the visibility of these layers to the ion beam is not significantly altered by the waving motion. After this correction the calculated ion-scattering yield for the clean Al(110) surface (14.2 ML) agreed with the experimental value (12.9±0.7 ML) within statistical and experimental errors.

We next simulated the overlayer experiment by placing Ni atoms on the already evolved Al(110) surface. Initial-


(a) Clean Al(110)

(b) 0.5 ML of Ni+Al(110)

(c) 2.0 ML Ni+Al(110)

(d) 3.0 ML Ni+Al(110)

FIG. 2. Snapshots of simulated Al(110) surfaces for different coverages of Ni. (a) Clean Al(110). (b) 0.5 ML of Ni. (c) 2 ML of Ni. (d) 3.0 ML of Ni. The positions of the atoms are projected onto the (001) plane. Al (Ni) atoms are indicated by open (solid) circles. Only the top ten Al layers of the simulated crystal are shown.

ly, 12 Ni atoms (0.5 ML) were placed at random coordinates above the surface. The system was then evolved for 15 000 cycles. After each 5000 cycles, 50 snapshots of the evolved system were created in the manner described earlier, resulting in a total of 150 snapshots. A snapshot for Al(110)+0.5 ML of Ni is shown in Fig. 2(b). Surprisingly, a significant number of Al atoms have already been displaced by Ni adsorption. The ion-scattering yield calculated from such snapshots was again used first to check for equilibration of the system, and ultimately to compare quantitatively with the measured scattering yields. The Ni/Al(110) system achieved a steady state after 5000 cycles, to the extent that neither the total energy nor the calculated yields changed significantly. To further check for equilibration we evolved the crystal for another 25 000 cycles. There were no significant changes in the ion yield or number of Ni atoms in each layer between 5000 and 40 000 cycles. We next deposited another 0.5 ML of Ni atoms randomly on the already evolved Ni/Al(110) system. The same procedures were used to evolve the crystal and then simulate the ion-scattering yields. We continued deposition of Ni atoms, in increments of 0.5 ML, up to 4-ML total Ni coverage. The snapshots for 2 and 3.0 ML of Ni on the Al(110) surface are shown in Figs. 2(c) and 2(d), respectively.

In Fig. 1 we show the experimental (open circles) and simulated (solid circles) ion-scattering yields from Al atoms as a function of Ni coverage. The values of the yields at zero coverage have been suppressed. The measured number of Al atoms visible to the incident ion beam increases at two different rates, depending on Ni coverage. It is remarkable that the simulations also show a break around 2 ML of Ni coverage. For the experimental yield, the initial slope is 1.9 Al atoms per Ni atom up to a Ni coverage of 2.2 ML, followed by a slope of 0.39 Al atoms per Ni atom at higher coverages. From the simulations we obtained an initial slope of 2.5 Al atoms per Ni atom up to a Ni coverage of 2 ML, followed by a slope of 0.39 Al atoms per Ni atom at higher coverages. We conclude that the simulations are in surprisingly good quantitative agreement with the measured yields. The constant offset between the calculated and measured yields, which has been suppressed in the figure, is 1.3 ML, i.e., the difference in the simulated and measured values for clean Al(110).

As mentioned above, a conventional interpretation of the measured yield shown in Fig. 1 would attribute the slope of 1.9 Al atoms per Ni atom to the formation of a compound with a stoichiometry of Al_2Ni. However, our XPS measurements are more consistent with the initial formation of NiAl up to a Ni coverage of 2.2 ML, and Ni_3Al thereafter.[3] This discrepancy can be explained by looking at the layer-by-layer results for the simulated ion yield. From the simulations we conclude that the presence of disordered Al atoms and relatively heavy Ni atoms near the surface leads to significant deflections of some of the incident ions, and ultimately to increased dechanneling 10–20 layers below the surface of the crystal. The energy resolution of the solid-state detector (20 keV) is insufficient to discriminate between these dechanneled ions, and ions backscattered from the top ten layers where the disordered atoms reside. From the simulations we conclude that *almost half* of the increased Al yield in the initial Ni coverage regime is associated with dechanneling. Thus both the scattering yield in the surface region and the XPS results are consistent with the formation of a NiAl-like compound. The contribution of multiple scattering and dechanneling to the surface peak area has been discussed in the past.[11] However, the typical contribution in that case was much smaller than that seen in our simulations. Thus our results should raise a caution flag on the future use of the slope to infer compound stoichiometry, at least for high-energy measurements where energy resolution is insufficient to distinguish between the two contributions. In this context, the MC simulations are very important for fully understanding the experimental ion-scattering results.

Finally, we comment on the utility of the snapshots in understanding the Ni-Al reaction as measured by ion scattering. The normalized layer occupancies, i.e., the number of atoms in layer *i* divided by the number of lattice sites in the Al(110) layer (24), are plotted in Fig. 3 as a function of Ni coverage. Al layer occupancies, Ni layer occupancies, and total layer occupancies are shown in Figs. 3(a), 3(b), and 3(c), respectively. We label the surface layer of clean Al(110) as the zeroth layer, while the

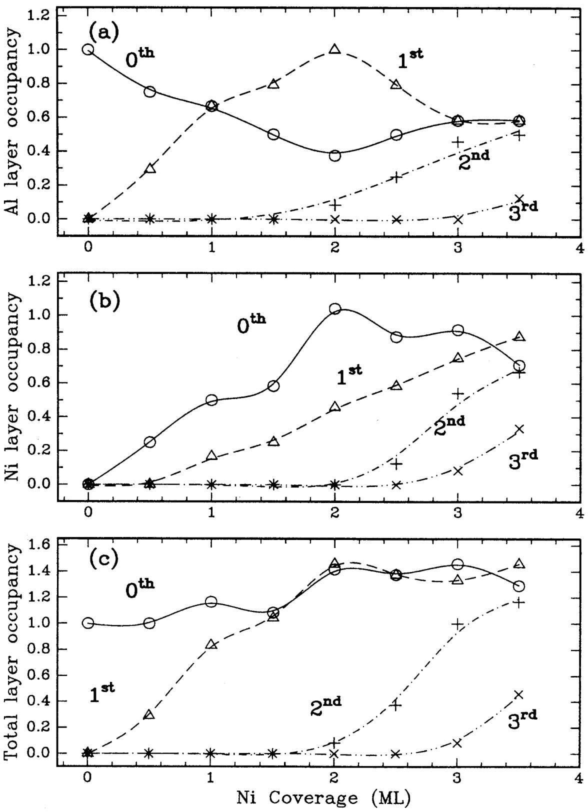


FIG. 3. Normalized layer occupancies [number of atoms in a layer divided by the number of sites in an Al(110) layer] as a function of Ni coverage, for (a) Al occupancies, (b) Ni occupancies, and (c) total occupancies in each layer. The surface layer of clean Al(110) is labeled as the zeroth layer. Added layers above the surface are labeled as first layer, second layer, etc.

added layers above the surface are denoted as first, second, and third layers, respectively. A number of points can be made based on the figures. First, in Fig. 3(b) it can be seen that, as the Ni coverage increases up to 2 ML, the occupancy of Ni atoms in the zeroth layer increases immediately, while the Ni occupancy in the first layer becomes nonzero only after 0.5 ML of Ni deposition. This indicates that initially the deposited Ni atoms move down into the Al substrate, causing Al atoms to move off their lattice sites. These displaced Al atoms move up into the first layer above the surface, as shown in Fig. 3(a). That is, the occupancy of Al atoms in the zeroth layer decreases up to 2 ML of Ni coverage, while the first-layer Al occupancy increases. In fact, for 1 ML of Ni coverage, about 0.3 ML of Ni occupies the layer *below* the zeroth layer (layer -1). Second, Al atoms do not move into the second layer until a coverage of 2 ML of Ni is achieved. Thus Al atoms, piling up in the first layer, and Ni atoms, accumulating in the zeroth layer, contribute to an overall increase of layer occupancies for layers 0 and 1, as seen in Fig. 3(c). Saturation of the total layer occupancies for layers 0 and 1 seems to occur after 2 ML of Ni deposition. This increased density at the Ni-Al interface appears to be associated with the reduced reaction rate, and corresponding decreased slope for Al ion yield, seen in Fig. 1 after 2 ML of Ni coverage. Consistent with the increased density in these layers, we find that the average nearest-neighbor distance (2.56 Å) between atoms in these simulated layers is comparable to the NiAl (2.50 Å) and Ni_3Al (2.54 Å) nearest-neighbor distances, and significantly less than that for Al (2.86 Å). Finally, looking again at Figs. 3(a) and 3(b), we see that after 2 ML of Ni coverage the occupancy of Al atoms in layer 1 starts decreasing. At the same time the Ni occupancy in layer 1 is still increasing. Thus after 2 ML of Ni deposition we see the evolution of the interface toward a more Ni-rich composition, such as Ni_3Al, as suggested by the reduced slope for ion yield in Fig. 1 and the Ni 2*p* line shape in XPS.[3]

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