Using Metallic Interlayers to Stabilize Abrupt, Epitaxial Metal-Metal Interfaces

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An approach is described for stabilizing metal-metal epitaxial interfaces using a thin metallic interlayer. Rutherford backscattering and channeling techniques along with low-energy electron diffraction and keV He^+ ion backscattering are used to demonstrate that an atomically thin layer of Ti deposited at the Fe-Al interface, a system well known for considerable intermixing at room temperature, forms a thin interface alloy that prevents interdiffusion and improves epitaxial growth of Fe on Al(100). The structure is stable up to about 200 °C.

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Over the past few years, the technology of thin film devices has evolved to the point where individual layers in a multilayer structure may be only a few nanometers thick [1]. Maintaining a well-defined architecture means that the films must be flat on an atomic scale with abrupt interfaces that are at least thinner than the films making up the structure. Various schemes for promoting the growth of flat films, such as using a surfactant [2] or interfactant [3], aim to control the surface or interface energy of the growing film but are not typically designed to prevent interdiffusion at interfaces.

A strategy to limit interdiffusion and to provide a stable template for abrupt, epitaxial metal-metal interfaces is reported here. We show that a single layer of Ti at the Fe-Al(100) interface, a system well known for considerable intermixing at room temperature [4], prevents the interdiffusion of Fe and Al and enables the growth of an epitaxial Fe film. The idea is based on the fact that Ti films grow in a pseudomorphic fcc structure on Al(100) [5] and are stable against diffusion up to nearly 400 °C [6]. The concept of suppressing interdiffusion with an interlayer is not new. Titanium interlayers, 20 nm thick, have been used to promote β-$FeSi_2$ formation on Si(100) by controlling the rate of Fe diffusion through the interlayer to the Si interface [7]. Egelhoff and co-workers have used surface oxidation as a diffusion barrier between Al and several ferromagnetic metals [8]. To our knowledge, however, the current work is the first report of a single metallic monolayer being used as an interlayer to stop diffusion at a metal-metal interface. The concept is expected to be generally applicable for a large class of metal-metal interfaces.

Rutherford backscattering and channeling (RBS/c), along with low-energy electron diffraction (LEED) and low-energy ion scattering (LEIS), were the primary techniques used in the present work. In the channeling geometry 1 MeV He^+ ions are incident along a low-index crystallographic direction. The energy spectrum of backscattered ions exhibits a surface peak (SP) associated with ions backscattered from the topmost layers of the solid [9]. Incident ions missing the target nuclei by more than $\sim$0.1 Å are channeled along the relatively open region between the rows of atoms. A surface atom displaced by $\sim$0.1 Å uncovers the next atom along that row, and the backscattered ion yield from substrate atoms increases. An adatom of a different element sitting directly above a substrate atom reduces the backscattering yield from substrate atoms. Measuring the surface composition with LEIS (1 keV He^+) allows us to investigate interdiffusion with monolayer depth resolution as the interface develops. Electron diffraction (LEED) is used to characterize the long-range order of the surface, while RBS/c provides quantitative information about local order for adatoms above substrate lattice sites.

The Al crystals were cleaned in vacuum by repeated cycles of Ar^+ ion bombardment at room temperature followed by annealing at 500 °C until the LEIS spectrum showed only the Al peak with negligible peaks from any impurities such as oxygen. Metal films were deposited on the Al surfaces at room temperature using resistively heated wires. A deposition rate of about 0.3 monolayer/min was determined using RBS. We use the Al(100) surface density of 1.22×10^{15} atoms/cm^2 to define 1 ML (monolayer) for Fe and Ti coverage. The ultrahigh vacuum target chamber is connected to a 2-MV Van de Graaff accelerator through a differentially pumped beam line [10]. A dose of 3×10^{14} ions/cm^2 was used to collect each channeling spectrum. No increase in ion yield attributed to beam damage during channeling was observed. Coverage measurements with a nonchanneling alignment were also made to avoid errors associated with atom shadowing.

Figure 1 shows the RBS/c spectra obtained for 1 MeV He^+ ions incident on Al(100). The solid circles show a conventional backscattering spectrum with a nonchanneling incident angle for the clean surface. The cutoff

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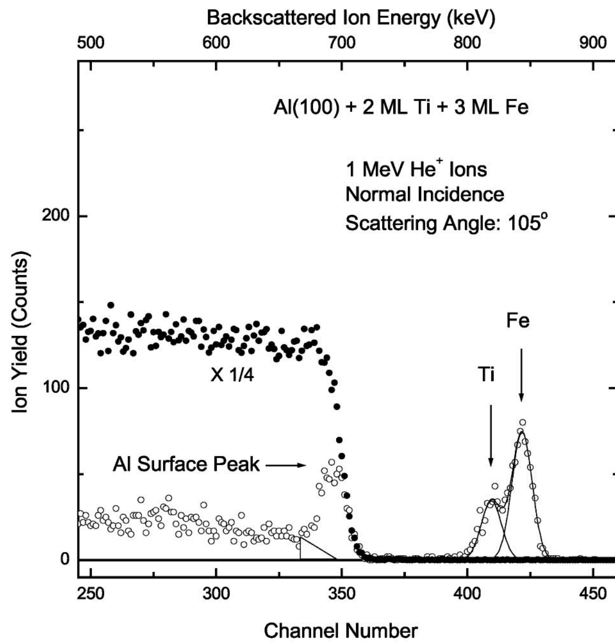

FIG. 1. RBS spectrum for 1 MeV He^+ incident on clean Al(100) in a nonchanneling geometry (solid circles). Channeling spectrum along [100] (normal incidence) for 2 ML Ti followed by 3 ML Fe deposition (open circles). Vertical arrows indicate the energy position for ions backscattered from surface Fe and Ti atoms. The small triangle represents the background area subtracted from the Al peak area.

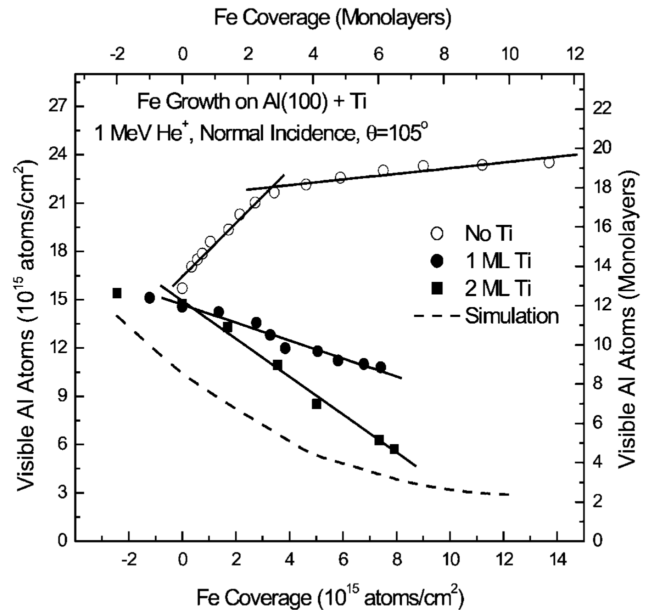

FIG. 2. Number of visible Al atoms for 1 MeV incident He^+ ions as a function of Fe coverage on Al(100) for no Ti interlayer (open circles), and Ti interlayers of 1 and 2 ML. The increase with no interlayer is attributed to alloy formation at the interface. The decrease with Ti interlayers is attributed to shadowing of Al by Fe atoms. The dashed line shows the calculated behavior expected for an epitaxial Fe overlayer.

of the spectrum at 700 keV corresponds to those ions backscattered from Al surface atoms at the set scattering angle of 105°. When the target crystal is rotated to align the [100] direction with the incoming ion beam, the backscattered ion yield (open circles) is reduced due to channeling. Surface atoms now shadow bulk atoms. The measured yield in counts is converted to an effective number of target atoms/cm^2 using the Rutherford cross section and known experimental parameters. The yield for the clean Al surface (not shown) corresponds to 15×10^{15} atoms/cm^2, in reasonable agreement with the value of 14×10^{15} atoms/cm^2 calculated using the simulation code VEGAS [11]. The channeling spectrum shown in Fig. 1 was obtained after the sequential deposition of 2 ML Ti followed by 3 ML Fe. Helium ions backscattered from the deposited atoms at the surface give rise to the two peaks at larger backscattering energies as indicated by the vertical arrows. It is straightforward to extract the areas of the two peaks as shown by the solid lines obtained using standard nonlinear least squares methods. The experiments reported here consist of measurements of these three peaks in the ion yield as a function of Fe and Ti deposition on the surface.

The upper curve in Fig. 2 (open circles) shows the variation of the Al SP area as a function of the Fe peak area for Fe depositions with no Ti interlayer. The curve increases monotonically to about 3 ML Fe coverage, in agreement with previous results [4]. The interpretation is that Fe atoms cause Al surface atoms to move off of substrate lattice sites, making additional Al atoms visible to the incident ion beam. The reaction continues until the thickness of the Fe-Al interface impedes further interdiffusion of Fe and Al atoms at room temperature, at which point an additional 7 ML of Al have become visible.

The lower curves of Fig. 2 show the Al SP area as a function of Fe coverage with 1 ML Ti deposited initially on the clean Al surface (solid circles) and in a later experiment with 2 ML Ti deposited prior to Fe deposition (squares). The effect of the Ti interlayer is remarkable. Now the number of visible Al atoms *decreases* with Fe deposition. Rather than causing Al atoms to be displaced, the Fe atoms cover and shadow the substrate Al atoms and must be growing in an epitaxial structure on the Al-Ti template. For such a reduction in ion yield to occur, the narrow shadow cone created by the Fe atoms (0.11 Å cone radius 4.05 Å behind the Fe atom) must partially overlap a substrate lattice site. That is, the Fe atoms are essentially within a horizontal distance of one shadow cone radius of the substrate lattice sites. A 2 ML Ti interlayer is even more effective in promoting the growth of an ordered Fe overlayer that shadows the Al (squares). Adding a third monolayer of Ti (not shown) does not increase the shadowing significantly beyond that for 2 ML Ti. We interpret this behavior as indicating that Ti adatoms do not grow in a simple overlayer at room temperature, but are instead incorporated into the top 1–2 layers of the substrate. This

conclusion is supported by the LEIS data which show about 50% of the Al peak area remaining at the surface after 2 ML Ti deposition and by the fact that initial Ti deposition does not result in the expected amount of shadowing of the substrate atoms (dashed line in Fig. 2). Quantitative LEED analysis of submonolayer Ti coverage also suggests that Ti atoms may be incorporated in Al surface layers [12]. Adding the second Ti layer apparently improves the performance of the diffusion barrier at the interface, although the effects are already significant after the first Ti monolayer. The dashed line in Fig. 2 shows the behavior expected for the Al SP area assuming 2 ML of Ti atoms on Al lattice sites, followed by Fe deposition. The calculations were done using VEGAS, with an interplanar distance of 1.43 Å for bcc Fe, and the Al vibration amplitude of 0.105 Å for both Fe and Ti atoms. The simulated value for the clean surface (14×10^{15} atoms/cm^2) is positioned at -2 ML coverage so the Al surface with 2 ML of Ti is at zero Fe coverage. In the simulation the Ti atoms also shadow substrate Al atoms and decrease the scattered ion yield, unlike the measurements as noted above. For 7 ML Fe the simulated and measured yields are quite close, suggesting that the order in the Fe overlayer is quite good.

The Ti interlayer effectively stops interdiffusion of Fe and Al atoms, leading to local ordering and shadowing of substrate atoms by Fe adatoms. It also results in improved long-range order for the Fe film growing on the surface, as shown by the LEED patterns of Fig. 3. The diffraction pattern for clean Al(100) [Fig. 3(a)] quickly disappears with Fe deposition, but reappears at higher Fe coverage [Fig. 3(b)] with broadened spots, in agreement with earlier reports [13]. The pattern is attributed to small Fe islands growing on an Fe-Al alloyed interface. With the Ti interlayer, a LEED pattern is obtained for much smaller Fe coverages, and the individual spots are considerably sharper [Fig. 3(c)]. Thus, the interlayer not only stops interdiffusion at the interface, as shown by the shadowing in Fig. 2, but also promotes the growth of larger epitaxial islands. Patterns similar to that shown in Fig. 3(c) were visible for Fe coverages from 3 ML to the end of the experiments at about 8 ML Fe.

For device applications using the interlayer concept, it is desirable to have thermal stability of the structure at the elevated temperatures required for film growth. We studied the Fe/Ti/Al(100) structure as a function of annealing temperature using LEIS to monitor the relative Fe, Ti, and Al surface compositions. Although LEIS is not as quantitative as RBS, because of unknown scattering cross sections and neutralization rates at the surface, when used in the ion detection mode the technique does provide extremely sensitive measurements of relative surface composition [14]. Figure 4 shows LEIS measurements for 6 ML Fe with a 2 ML Ti interlayer, annealed to various temperatures. Up to 150 °C the spectrum is dominated by the Fe peak (heavy dashed line). After

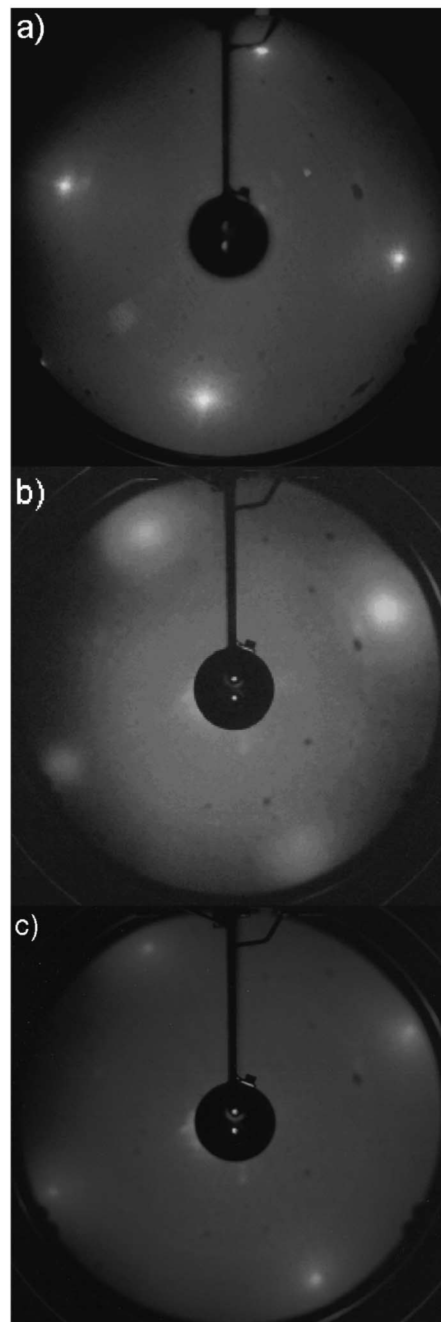

FIG. 3. LEED patterns for Fe deposition on Al(100). (a) Clean Al(100), 52 eV. (b) 9 ML Fe on Al(100) with no Ti interlayer, 52 eV. (c) 5 ML Fe on Al(100) with 2 ML Ti interlayer, 40 eV.

annealing the sample at 200 °C, we observed increased Al yield and decreased Fe yield (light dashed line), indicating that Al atoms were moving to the surface of the sample. After annealing to 300 °C (light solid line), the Fe signal is nearly gone and a small Ti signal remains. Following an anneal at 400 °C (heavy solid line), Ti atoms have also moved into the Al substrate.

Finally, we present a simple model for understanding the effectiveness of the interlayer based on the formation

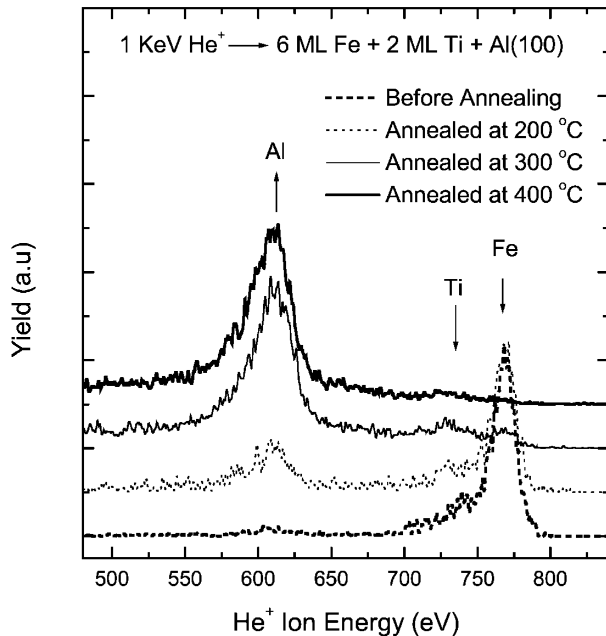

FIG. 4. LEIS spectra following annealing at various temperatures for 6 ML Fe on Al(100) with a 2 ML Ti interlayer. Arrows indicate energy positions for ions scattered from Al, Fe, or Ti atoms on the surface.

energies and associated interatomic bond strengths for the intermetallic compound formed at the interface. First, we note that the (100) surface of bcc Fe has a lattice mismatch of only 0.3% compared to the Al(100) surface [15]. One might then expect ordered growth of Fe on Al(100), but interdiffusion occurs already at room temperature with the negative formation energy (− 25 kJ/mole-atom for FeAl [16]) providing the driving force. Furthermore, bcc FeAl has a volume per atom that is only 74% of that for the relatively open Al lattice. We have used a simple bond model to argue that Fe may diffuse into the Al substrate to occupy interstitial locations with a relatively small residual strain in the Al lattice [17]. Titanium, on the other hand, has a metallic size that is about the same as that of Al, and the volume per atom for TiAl in the face-centered tetragonal structure is about 95% of that for Al. Consequently, diffusion of Ti into Al probably requires Al vacancy formation or an exchange reaction, both of which would occur more readily at elevated temperatures. Although the formation energy for TiAl (− 38 kJ/mole-atom) is larger than that for FeAl, the fact that Ti remains at the Al surface up to 400 °C suggests that there is a large kinetic barrier to Ti diffusion at room temperature. A similar tendency toward intermixing at the surface is seen in first principles density functional calculations for Ti on sapphire where Ti prefers to replace a terminating Al atom rather than occupying a subsurface or atop Al site [18]. In the present case, then, the intermetallic bonds at the interface have been strengthened relative to those of pure Al, and the energy required to exchange an Fe atom with an Al (or Ti) atom has increased. Apparently, the formation energy gained by Fe atoms moving into the lattice is no longer sufficient to drive the exchange reaction at the stiffened interface, and diffusion is greatly reduced at room temperature. Heating the surface to 200 °C enables the Fe atoms to overcome even these stiffened interface bonds, and the effects of the interlayer are compromised.

In summary, we have demonstrated the use of an atomically thin Ti interlayer to stabilize epitaxial growth for Fe films on Al(100) surfaces, a system which exhibits considerable interdiffusion at room temperature. A simple model based on atomic size and intermetallic formation energies is used to explain this behavior and should be useful for identifying other interlayer systems.

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