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Smart Interfacial Bonding Alloys

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Smart Interfacial Bonding Alloys

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ABSTRACT

The goal of this LDRD was to explore the use of the newly discovered strain-stabilized 2-D interfacial alloys as smart interface bonding alloys (SIBA). These materials will be used as templates for the heteroepitaxial growth of metallic thin films. SIBA are formed by two metallic components which mix at an interface to relieve strain and prevent dislocations from forming in subsequent thin film growth. The composition of the SIBA is determined locally by the amount of strain, and therefore can react "smartly" to areas of the highest strain to relieve dislocations. In this way, SIBA can be used to tailor the dislocation structure of thin films.

This project included growth, characterization and modeling of films grown using SIBA templates. Characterization will include atomic imaging of the dislocations structure, measurement of the mechanical properties of the film using interface force microscopy (IFM) and the nanoindenter, and measurement of the electronic structure of the SIBA with synchrotron photoemission. Resistance of films to sulfidation and oxidation will also be examined. The Paragon parallel processing computer will be used to calculate the structure of the SIBA and thin films in order to develop ability to predict and tailor SIBA and thin film behavior.

This work will lead to the possible development of a new class of thin film materials with properties tailored by varying the composition of the SIBA, serving as a buffer layer to relieve the strain between the substrate and the thin film. Such films will have improved mechanical and corrosion resistance allowing application as protective barriers for weapons applications. They will also exhibit enhanced electrical conductivity and reduced electromigration making them particularly suitable for application as interconnects and other electronic needs.

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Smart Interfacial Bonding Alloys

Introduction

The goal of this LDRD was to explore the use of the newly discovered strain-stabilized 2-D interfacial alloys as smart interface bonding alloys (SIBA). These materials will be used as templates for the heteroepitaxial growth of metallic thin films. SIBA are formed by two metallic components which mix at an interface to relieve strain and prevent dislocations from forming in subsequent thin film growth. The composition of the SIBA is determined locally by the amount of strain, and therefore can react "smartly" to areas of the highest strain to relieve dislocations. In this way, SIBA can be used to tailor the dislocation structure of thin films.

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Our project to investigate these new film materials was broken into three sub projects. The first sub-project was to investigate the atomic structure of thin film alloys grown on Ru(0001). The second was to apply the newly developed interfacial force microscope (IFM) to study local mechanical properties of materials. This was done on A(111) surfaces. The third sub-project was to perform atomistic calculations of the IFM experiments using atomic potential on the Sandia Paragon machine. Each of these sub-projects will be described in separate sections below.

Scanning Tunneling Microscopy Measurements of Ag-Cu Alloys on Ru(0001)

The alloys we studied consisted of mixtures of Ag and Cu. Strain induced by the substrate plays a central role in this new alloying mechanism which overcomes the traditional size barrier to alloy formation between metals with large lattice mismatches. This is demonstrated in the scanning tunneling microscopy (STM) study of sub-monolayer Ag and Cu films on Ru(0001). The large lattice mismatch between Cu(111) ($2.56\text{\AA}$) and Ag(111) ($2.89\text{\AA}$), which is approximately 13%, leads to a wide miscibility gap which exists in their bulk binary phase diagram up to the liquid phase boundary. The Ru(0001) substrate, with its lattice constant ($2.71\text{\AA}$) between those of Cu and Ag, mediates this mismatch and the mixing of Ag and Cu in the first layer results in a structure of lower strain and higher commensurability with the substrate. The dispersion of the smaller Cu atoms within the Ag film leads to the formation of a two dimensional alloy phase with a specific stoichiometry. This new phase is observed to segregate with respect to Ag and form domains which are determined by local strain considerations in the Ag layer. The role of strain in determining the phase diagram of alloy thin film systems is unique from the case in three-dimensions. Understanding these relationships and their effects on phase transitions and stability of 2-D systems will be vital to the physics of thin film and superlattice systems and provide a platform for the study of binary phase diagrams in two-dimensions. This mechanism of alloy formation also leads to the possibility of fabricating new thin film materials with novel physical properties.

The experiments were performed in a UHV chamber with a base pressure less than 10^{-10} Torr. The Ru sample was oriented to within 0.1° of the (0001) direction and mechanically polished with standard techniques. In vacuum, the sample was cleaned by a brief sputtering with 500 eV Ar ions followed by approximately 200 O_2 adsorption-desorption cycles. Cleanliness was verified by Auger electron spectroscopy and low-energy electron diffraction. The final sample condition was determined by STM. Ag and Cu were deposited by evaporation from resistively heated tungsten baskets. Chamber pressures remained below 10^{-10} Torr during depositions. All depositions were performed at room temperature with subsequent annealing as described in the text. All STM imaging was performed at room temperature. STM images are displayed in gray-scale representation with brighter areas corresponding to higher corrugation amplitude.

The single component systems of Cu/Ru(0001) and Ag/Ru(0001) have been studied by a variety of spectroscopic and topographic techniques [4-10]. Individually, the first atomic layer of Cu and Ag are known to wet the Ru(0001) surface. Recent work by Schick et al. [11] using thermal desorption spectroscopy indicates that co-deposited Ag and Cu on Ru(0001) desorb from a mixed state. However, the mechanisms which drive the mixture of these immiscible metals could not be concluded.

The first atomic layer of Ag on Ru(0001) displays a range of structures determined by the local density of Ag in the layer [12]. At full saturation of the layer, an uniaxially expanded structure is formed that consists of an ordered array of misfit dislocation stripes running along the [120] direction, as shown in Figure 1a. This strain relief structure has been observed in several other (111) orientation overlayer systems [13,14] as well as on the reconstruction of the (111) faces of Au [15,16] and Pt [17,18]. The stripes of the structure correspond to domain walls separating regions of hcp and fcc stacked Ag. In the walls, the Ag atoms occupy bridge sites and allow the lattice to relax along the close packed [100]

direction. Below saturation of the first Ag layer, the Ag film relaxes further to form a different network of dislocations shown in Figure 1b. The details of this structure can be seen in Figure 1c, which displays an atomically resolved image of the unit cell. The dark regions of the surface contain the cores of two surface edge dislocations. The extra rows of atoms which originate at these cores are marked by the crossed lines in Figure 1c. The insert in Figure 1c clearly shows the core structure of the dislocations. In the vicinity of these dislocations, the Ag lattice is highly distorted. The existence of these extra rows results in a local densification of the Ag lattice in this area which decays gradually in the direction leading between the extra rows, (region marked A in Figure 1c), and more abruptly in the opposite direction, (region marked B in Figure 1c). This strain results in a better match of the Ag lattice to the Ru substrate and thus can be accommodated in higher symmetry hollow-like sites which accounts for the darker appearance of the atoms in this region. As this strain is relaxed away from the dislocations, the misfit of the Ag overlayer with the substrate results in occupation of lower coordination atop-like sites which appear higher in the image. In the region opposite to the extra rows (area B), this occurs within a few lattice constants since the density of Ag in this area is reduced. In the region between the extra rows (area A), the relaxation is more gradual and the transition to the atop regions is more gradual and requires 7 lattice spacings. It is the regions of relaxed Ag residing on low symmetry atop-like sites that correspond to the array of bright areas in the larger scale image of Figure 1b. This interpretation of the data is corroborated by measurements of the local atomic separations that reveal a smaller local lattice spacing in the darker regions as compared to the brighter areas [12]. It was this Ag structure, Figure 1b, that formed the starting point of all the experiments discussed here. A detailed discussion of the Ag strain relaxation mechanisms will be contained in a forthcoming paper [12].

For the purposes of this discussion, it is important to note that the local elevation of the film corresponds to the degree to which the atoms in that region reside in Ru hollow sites. This correspondence is not immediate and recent calculations by Mottet et al. [19] and Foiles [20] have shown that substrate relaxation can result in overlayer atoms which reside in atop sites as having a lower elevation relative to the surface than those in hollow sites. In addition, electronic effects can also lead to corrugations which do not relate to local topology [14]. H. Brune et al. have determined that Ag overlayer atoms residing in hollow sites on Pt(111) are imaged higher due to an increased electron density at regions of higher Ag atomic density. As mentioned above, for Ag/Ru(0001), we find the opposite correspondence. The dark areas in Figure 1b contain a higher density of atoms [12]. Furthermore, relaxation in the refractory Ru(0001) substrate are expected to be much smaller than those of the Cu(111) of ref 19 and 20. We therefore believe that in the case of Ag/Ru(0001), the correspondence of corrugation height and binding site can be made.

Small amounts of Cu added to the Ag film of Figure 1b mix upon deposition at room temperature to bond directly with the Ru substrate. This mixing is not simply due to kinetic limitations at room temperature as may be expected in a phase segregation system. This is demonstrated in Figure 2 which displays a film with a concentration ratio of Cu to Ag of $X_{\text{Cu}}/X_{\text{Ag}} = 0.19$, that has been annealed to 550°C. The Cu atoms and clusters appear as dark features with a corrugation of approximately 0.15Å below the Ag layer, consistent with the size difference between the two elements. (Our assignment of these features to Cu is corroborated by comparison of the deposited amount of Cu with the amount observed in these features. Other groups have already shown the ability of STM to distinguish different

metallic constituents within the same layer although the exact nature of the observed contrast is still unclear [21-23].) The Cu and Ag do not phase segregate as would be the case in the bulk. Instead, the Cu atoms preferentially occupy regions in-between the corrugation maxima of the pure Ag film pattern, resulting in a rough grid pattern of Cu (Figure 2). With further deposition of Cu, the dislocation pattern of the Ag layer is disrupted. This can be seen in Figure 3 which displays an image of a film with $X_{\text{Cu}}/X_{\text{Ag}} = 0.25$ following a 550°C anneal. Two types of Cu-Ag domains have formed possessing roughly triangular shapes and are separated by raised stripes of Ag. These two domain types are rotated 60° relative to one another. The domain formation becomes more defined as the concentration of Cu increases. Figure 4a shows a film with $X_{\text{Cu}}/X_{\text{Ag}} = 0.42$. The film now consists of two dimensional Ag-Cu mixed domains separated by pure Ag domain walls. The detailed structure of the Ag-Cu domains can be seen in Figure 4b. The Cu and Ag mix primarily through the interweaving of chain-like clusters. The stoichiometry within the triangular domains is consistent at $X_{\text{Cu}}/X_{\text{Ag}} \approx 0.5$, indicating that a true 2-D alloy phase has been formed. Phase separation between the alloy and the pure Ag occurs via the formation of the domain walls. As $X_{\text{Cu}}/X_{\text{Ag}}$ increases and the fraction pure Ag decreases, the width of the domain walls remains intact and the decrease is accounted for by reduction in overall wall length. These domain walls are approximately $20\text{\AA}$ wide and appear $0.1\text{\AA}$ higher than the Ag within the alloy phase. These features are identical, within experimental uncertainty, to the domain wall structures found in the uniaxially expanded structure of the pure Ag film (Figure 1a). In the pure Ag case, the walls separated regions of hcp and fcc stacking, and an analogous assignment is made for the alloy film. This identification is corroborated by the different average heights between the two types of alloy domains. The larger upward pointing triangular structures of Figure 4a, (marked A), are imaged $0.05\text{\AA}$ lower than the other. This difference is attributed to the occupation of the two types of hollow sites, hcp and fcc. Therefore, the Ag domain walls connect alloy regions of different hollow stacking as in the pure Ag situation.

As can be seen in Figure 4a, one type of alloy domain occupies a larger fraction of the surface. This is due to the binding energy difference between the two types of hollow sites. The larger domains are likely to be hcp stacked alloy, since in the pure Cu film, this is the preferred site. As the concentration ratio between Cu and Ag increases to 0.5, the energetically favorable alloy domain grows at the expense of the other, until a uniform Ag-Cu two-dimensional alloy covers the surface at $X_{\text{Cu}}/X_{\text{Ag}} \approx 0.5$. Throughout our experiments, no long range ordering within the alloy was observed.

The data described above can be understood on the basis that the alloying of Cu and Ag in this system is driven by the strain relief of the Ag lattice by the incorporation of the smaller Cu atoms. In their bulk states, the large size difference between Cu and Ag hinders their formation of a solution. However, a simple hard sphere model of Cu and Ag would lead to an average lattice constant of a mixed film much closer to the $2.71\text{\AA}$ spacing of the substrate. The atoms in the alloy phase therefore experience an energy reduction via two related effects : 1) reduced strain energy as compared to the pseudomorphic single component films, and 2) the atoms in the alloy phase can be accommodated in Ru hollow binding sites thereby eliminating misfit dislocations. At low Cu concentrations, the first effect leads to preferential incorporation of the Cu in the regions between the Ag corrugation maxima (Figure 2). As discussed above, the Ag atoms in these lower regions reside in higher coordination hollow-like sites. By sitting in lower portions of the potential corrugations, the

compressive stress due to the substrate in these areas is larger than that applied to the Ag atoms in the nearly atop sites at the maxima regions. This is confirmed by the smaller local lattice spacing in these areas [12]. Modulations in the local lattice spacing of overlayer systems has also been predicted theoretically both in the modeling of lattice mismatch accommodation within the Frenkel-Kontorova model [24, 25] and in embedded atom method simulations of the coincidence lattice structure of Ag on Cu(111) [26]. Incorporation of Cu into these highly strained areas of the Ag film results in the largest strain relief.

Strain relief also determines the film structure and local composition as the Cu concentration increases. Within the alloy domains, the atoms reside in hollow binding sites and are locally strain relieved. The existence of two types of alloy domains (Figure 4b) corresponds to the two types of hollow sites available for occupation, the fcc and the hcp. Energetically, only type of hollow is preferred, (which most likely is the hcp domain since Cu is known to reside in Ru hcp sites [10]), as is indicated by only one domain existing as the Cu-Ag mixture reaches 1 to 2 composition. The question remains as to why the minority alloy domain forms, (region B of Figure 4a), for $X_{\text{Cu}}/X_{\text{Ag}} < 0.5$. Below this saturation composition, there remains unaccommodated Ag. The film phase segregates into regions of the alloy and regions of pure Ag. In order to minimize the total energy of the system, this phase segregation results in the formation of the two types of alloy domains separated by Ag domain walls. The Ag in the walls occupy transition sites between the hcp and fcc hollows. These sites are of lower coordination and, following the arguments above, allow a greater degree of strain relaxation as compared to hollow sites. Therefore, the energy gain in reducing the strain in the Ag phase overcomes the cost of forming the minority alloy domain and the interfaces between the two phases.

In conclusion, we have demonstrated that the reduction of strain can be the driving mechanism in the formation of alloys in multi-component thin film systems. This has been shown for the case of monolayer films of Ag and Cu on Ru(0001). Although Ag and Cu are immiscible in their bulk phases, their lattice mismatches with the Ru substrate leads to the formation of a strain relieved Ag-Cu alloy with near 2:1 stoichiometry. We have also observed that strain relief also plays a dominant role in the nucleation and growth of the Ag-Cu domains. This phenomena is expected to be important in superlattice systems in which stresses of opposite signs are applied to the constituents of the film. It also may be a mechanism by which novel materials can be produced.

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Figures Sub-Section 1:

Figure 1(a)

Figure 1(b)

Figure 1(c)

Figure 1. Dislocation structure of Ag/Ru(0001). a) $170\text{\AA} \times 50\text{\AA}$ STM image of uniaxially expanded structure observed at saturation of first atomic layer. Bright stripes represent transition regions of Ag acting as domain walls between fcc and hcp occupied regions. b) Misfit dislocation structure of sub-monolayer Ag/Ru(0001) films ($400\text{\AA} \times 400\text{\AA}$). c) Atomically resolved image of structure in 1b. Surface edge dislocations are marked by crossed line segments. Details of the dislocation structure shown in inset.

Figure 2. 300Å X 300Å STM image showing film of Figure 1b following deposition of Cu and annealing to 550°C. $X_{\text{Cu}}/X_{\text{Ag}} = 0.19$. Dark areas are Cu atoms and clusters.

Figure 3. 400Å X 400Å STM image of a film of $X_{\text{Cu}}/X_{\text{Ag}} = 0.25$ after annealing to 550°C. Initial formation of Ag-Cu domains is imaged.

Figure 4(a)

Figure 4(b)

Figure 4. a) 1000Å X 1000Å image of film with $X_{\text{Cu}}/X_{\text{Ag}} = 0.42$ following annealing to 550°C. Two domains of the alloy can be seen and are separated by domain walls made up of pure Ag phase. Details of the alloy domain structure and domain walls can be seen in 4b. (200Å X 200Å).

Interfacial Force Microscopy Investigations of Au(111) Surface Properties

Nanometer-scale indentation is now widely applied to measure mechanical properties on a local scale. The technique has proven most valuable in quantifying the properties of small-scale structures such as thin films. However, because of the inherent nature of nano-scale indentation, it also provides an unprecedented opportunity to understand the physics and chemistry of how local structure is linked to observed mechanical properties. Though progress has been made, no clear picture of this link at the nanometer level has as yet been developed. To this end, we have studied a model system with controlled atomic-level structure (i.e., individual steps) in order to determine their influence on detailed mechanical behavior.

It has long been recognized that mechanical properties are controlled by the density of defects that act as heterogeneous nucleation sources for dislocations. The effects of pre-existing dislocations [1], inhomogeneities [2], grain boundaries [3] and surface scratches [4] on mechanical properties have been well documented. Recent nanoindentation studies on well-prepared Au single crystals in regions free of surface defects also give measured yield strengths comparable to the predicted ideal strength of the lattice [5-7]. Surface defects, in the form of surface steps, have been observed to affect the yield stress measured by nanoindentation [7], but the effect of a single surface defect has not been explored. By performing indentation tests in the vicinity of a single surface defect, we have measured its affect on heterogeneous nucleation and by controlling the position of the probe with respect to the defect we are able to gain some understanding of the processes controlling the onset of plastic yield.

Mechanical measurements were performed using the Interfacial Force Microscope (IFM). This instrument, which has been described in detail elsewhere [8], is distinguished by its use of a novel electrostatically-driven, force-feedback sensor to ensure rigid displacement control during a loading experiment. This characteristic of the sensor will be exploited to quantify different sample responses arising from differences in surface morphology. In addition, the IFM has the capability to perform constant-force imaging, similar to other scanning force techniques. Imaging at a low force (0.2 μN) allowed us to locate surface steps and to characterize the permanent deformation after indentation.

The force sensor and piezo actuators were calibrated using a standard laboratory electronic balance and a displacement indicator, respectively. Both calibrations are necessary for quantitative measurements. Probes used in this study were electrochemically etched 100 μm tungsten wires with tip radii and parabolic shape determined by field emission Scanning Electron Microscopy (four probes were used with radii of 250, 720, 1000 and 2300 $\text{\AA}$). Single-crystal Au samples with (111), (001), and (110) orientations were Ar-ion sputtered and annealed at 950°C. Immediately after cleaning, samples were immersed in a 0.5 mM ethanolic alkanethiol ($\text{CH}_3(\text{CH}_2)_{15}\text{SH}$) solution for 24 hr to develop a self-assembled monolayer (SAM) of hexadecanethiol to passivate the probe-sample interaction. Without the SAM, a strong adhesive interaction occurs between the Au and W tip and the material is plastic on contact [9, 10]. Passivation eliminates this adhesion [9, 11] and allows us to analyze elastic force profiles using Hertzian theory [12, 13], which predicts the elastic behavior of a parabolic tip and planar sample using continuum elasticity. If the applied stress exceeds the elastic limit of Au, plastic deformation is observed through a deviation from the Hertzian response and a hysteresis loop in the loading cycle. With the probe radius (R)

known, we can quantify the mean applied stress at yield (σ_y) from the measured force (F) and depth of deformation (δ) using the relationship [12],

$$\sigma_y = \frac{F_y}{\pi R \delta_y}, \quad (1)$$

where the subscripts refer to values at the yield threshold.

Sputter-annealing cycles produced surfaces in which the only observed defects were surface steps. A typical portion of this surface is shown in Figure 1a in a repulsive-force image covering an area 7500x7500 Å. Two steps can be seen; a single step having a height of 2.5 Å and a double step with a 5.0 Å high step. Intra-step separations within multi-step defects were smaller than the lateral resolution of the imaging technique (in this case $\approx$ 100 Å), such that step bunches appeared as single step edges. Loading data were taken as a function of the position of the tip with respect to its step neighbors as illustrated in Fig. 1b.

As a demonstration of the effect of surface defects on loading cycles, Fig. 2 presents results from indentations acquired far from and near to a step edge. In both cycles, the force rises nonlinearly with depth of deformation following the Hertzian relationship until plasticity begins. The deviation from Hertzian behavior, indicated by the open arrows in Fig. 2, takes the form of relaxation “events” where the load suddenly drops to some percentage of its threshold value. Loading was continued until the repulsive force reached 21.5 μN, at which point the probe was retracted. The loading cycle of Fig 2a was obtained with the indenter centered between the edges of a terrace that was wider than 5000 Å (far from a step). In this case, yield occurred at approximately ~19 μN. The load drop during the initial yield event was nearly 100% and further plasticity also occurred in smaller, but significant, relaxation events. The depth of the residual indentation was 150 Å. In Fig 2b, the indenter was positioned on a 1550 Å-wide terrace, with the indenter axis approximately 300 Å from the 28 Å-high step edge. In this case, the yield event occurred at a force of ~10 μN, which corresponds to a reduction in σ_y by almost 50%. The load relaxation was only a few percent and further plasticity occurred through a similar series of smaller events. The depth of the residual indentation was 210 Å.

To quantify the influence of a single defect, threshold yield-stress values near straight, isolated steps were measured on Au (111) surfaces. From a series of loading cycles performed using probes of various radii at various distances from steps of various heights, σ_y was calculated using Eq. 1, the results of which are presented in Fig. 3. A positive distance from the step edge (d) corresponds to indenting on the high side of the step, and negative values correspond to the low side. An error bar is shown on one of the data points to illustrate a typical contact diameter at yield ($2a_y$) relative to the step/probe separation, estimated from the relation [12]:

$$a_y = \sqrt{R \delta_y}. \quad (2)$$

The horizontal broken lines on the upper portion of the ordinate axis identify the range of σ_y found for Au (111) on wide, defect-free terraces [5]. When the indenter is positioned directly above the edge of the step ($d = 0$), σ_y is only 60-70% of the σ_y found on defect-free terraces. It is important to point out that a decrease in σ_y is observed not only when the contact area and step overlap, but even when the two are considerably separated. This indicates that there is some interaction between the step and the stress field outside the contact area:

To quantify the spatial dependence of the reduction in σ_y , we have re-plotted the data of Fig. 3 in Fig. 4 as a function of $|d/a_y|$ instead of d . Whenever $|d/a_y| < \sim 3$, lower σ_y values were observed and whenever $|d/a_y| > \sim 3$, σ_y was no different from that found on wide, defect-free terraces. The transition between the two regimes is not distinct and occurs somewhere in the range $2 < d/a_y < 3$. These results suggest that a step does not affect σ_y when it is a distance greater than $\sim 3a_y$ away from the indenter, but that it *does not* have to be within the contact area to affect plastic yield.

The spatial extent of plasticity was quantified by measuring the dimensions of the pile-up for indentations on defect-free terraces. In an effort to isolate the plasticity due to the initial yield event, loading was immediately reversed when the instrument identified a drop in load of 10% within one 0.5 Å displacement increment. From 20 topographs, the mean periphery of the pile-up, identified as the extent of the region disturbed by the indentation, was found to be $\sim 3.2a_y$ (with a standard deviation of 0.45). Taking the radius of pile-up to be the plastic zone radius (R_{pl}) we find that $R_{pl} \approx 3.2a_y$, which is in agreement with previous nanoindentation studies [14, 15].

The processes involved in initiating yield include the nucleation of dislocation loops occurring at the position where the shear stresses are maximum [6, 7, 16]. The point of maximum shear is below the probe tip and well within the contact area, yet we see that a defect at some distance outside the contact area can reduce σ_y significantly. Based on continuum mechanics [12], stresses outside the contact area fall off as $(a_y/r)^2$ and are principally tensile in nature. Thus, shear stresses at $r = 3a_y$ can be expected to be more than an order of magnitude lower than the maximum values. Still, dislocation nucleation could be precipitated by the step's presence if the step acts as a significant stress concentrator. The continuum-level stress concentration factor is approximately $\sqrt{h/\rho}$, where h is the step height and ρ is the radius of the step at its base [17]. While we did see a scaling effect with h , to achieve shear-stress levels at the step that equal the shear stresses under the indenter would then require $h/\rho > 100$, meaning that ρ must assume subatomic values. The continuum approach is an inadequate approximation for this case, since a step is by its very nature an atomic-level feature. Paradoxically, the lateral size scale of the effect is orders of magnitude larger than the atomic scale. The solution to the problem, including a full understanding of the detailed processes responsible, will have to await calculations which are able to handle the dimensions of the experiment while including the atomic-level details in the neighborhood of the step boundary.

In summary, we have performed nanoindentation experiments to quantify the effects of surface defects on the initiation of plastic yield. Indenting near a step reduced σ_y by 30-45 % and reduced the magnitude of yield-relaxation events. In addition, we have identified a characteristic length within which surface defects affect indentation processes and this length $\approx 3a_y$. These observations indicate that processes that initiate yield are not localized to the point of maximum shear, but can be influenced by the concentration of stress due to inhomogeneities. The results of this study not only identify the effect of surface defects on indentation, such that we have a better idea of how to correlate results from atomically smooth and rough surfaces, but they also give an indication that yield processes are less localized than previously appreciated.

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Figure 1. a) Constant-force $7500\text{\AA} \times 7500\text{\AA}$ image of the Au (111) surface, depicting a monatomic step ($2.5\text{ \AA}$ high) and a double step ($5\text{ \AA}$ high). The double step consists of two monatomic steps with a separation smaller than the lateral resolution of the probe ($\approx 100\text{ \AA}$). b) shows the same surface (different location) after several indentations.

Figure 2. Indentation loading cycles demonstrating the effect of steps on plasticity. Open arrows identify yield thresholds. a) Loading cycle when the terrace width is greater than $5000\text{ \AA}$ and indenter is centered between the terrace edges. a) Loading cycle when the indenter is on a $1550\text{ \AA}$ -wide terrace, $300\text{ \AA}$ from one terrace edge.

Figure 3. Measured mean stress at yield as a function of step-indenter separation (d) for steps having heights ranging from 5 to 30 Å. Positive d values indicate that the indenter is on the high side of the step, while negative values refer to the low side. An error bar is shown on one data point to represent typical diameters of the contact area at the yield threshold relative to the probe/step separation.

Figure 4. Measured mean stress at yield as a function of $|d/a_y|$ (absolute value of distance from the step normalized by elastic contact radius prior to yield). When $|d/a_y| < 2$, the yield stress is reduced by a neighboring step, while for $|d/a_y| > 3$ the yield stress is unaffected. The average size of the plastic zone (R_{pl}) for an undefected surface is indicated by the dashed line.

Modeling of IFM Indentation of Au(111)

Mechanical deformation, fracture, and friction of solids and thin films pose some of the most interesting computational challenges for atomistic calculations of materials properties. The fundamental goal is to establish connection between atomic scale processes and measurable mechanical properties of materials. The development of nanoindentation techniques [1], atomic force microscopy [2], and the interfacial force microscope (IFM) [3,4] has generated considerable interest in the detailed mechanisms of deformation during indentation at a very small scale. Indentation techniques measure the mechanical properties of thin films and other materials (e.g., elastic constants, yield stress, and hardness) by measuring the force or load on the indenter tip as a function of the tip displacement during indentation and retraction.

The classical problem of an isotropic elastic material filling a half space and indented by a spherical frictionless indenter was first solved by Hertz [5] and has been extended to anisotropic media and to a variety of indenter shapes [6]. However, real indentation experiments also involve plastic deformation, i.e., plastic flow and the creation of defects, which can be studied with atomistic calculations. In this Letter, we present a new computational model that couples a frictionless indenter, represented here by a repulsive potential, with atomistic calculations to study the elastic and plastic deformation during indentation on a passivated surface. Combined with a new approach for imaging defects, this provides insight into the initial stages of plastic deformation which had previously been unavailable.

Previous atomistic calculations have studied indentation and retraction using the embedded atom method (EAM) [7,8], or other semi-empirical techniques [9], as well as first principles methods [10]. These calculations showed strong bonding between the indenter tip and the surface due to the large energy of adhesion between two clean surfaces. This leads to a jump to contact upon approach and necking between the tip and surface during retraction [7,11].

In experiments, the tip-surface adhesive interaction will be dramatically reduced if the tip and surface are not atomically clean. Surfaces in ambient atmospheres, for example, often have passivating layers of oxide [12]. In other experiments, surfaces are passivated by the addition of an alkanethiol layer which prevents bonding between the tip and the surface [4,13]. The model discussed here is tailored to address these thiol passivated surfaces, as well as to reproduce the salient features of displacement-controlled indentation experiments [3,4]. Interpretation of force vs. displacement curves requires understanding the atomistic structures of dislocations and other defects created during indentation. Such understanding will help resolve disagreement in the literature regarding yield stresses and mechanisms leading to plastic flow under indentation.

We model the effect of a passivation layer by using a strong repulsive potential to represent the indenter tip. Each atom in the indented material interacts with the idealized indenter via the potential $V(r) = A \theta(R-r) (R-r)^3$, where A is a force constant, $\theta(R-r)$ is the standard step function, R is the indenter radius, and r is the distance from the atom to the center of the indenter sphere. We chose this particular potential in order to avoid the numerical problems during energy minimization caused by a perfectly hard sphere potential. There is no force in the direction tangent to the tip sphere. The model is therefore analogous

to the Hertzian indenter in that it is frictionless, similar to the lubricant effect of the thiol passivating layer [13].

Minimum energy calculations were performed for indentation on a Au(111) surface, using a repulsive potential with $A = 5.3 \text{ nN/\AA}^2$ to model a spherical indenter with an 80 Å radius. (Related experiments [14] used indenter tips with radii as small as 250 Å, but atomistic calculations for these are still prohibitive.) The gold surface was represented by a slab of dimension 240 x 210 x 160 Å containing 470,000 atoms. Periodic boundary conditions were used parallel to the surface, and the bottom layer was held fixed. In order to ensure that these boundary conditions did not affect the results, calculations were also run on smaller rectangular slabs and on a threefold symmetric triangular slab with fixed boundaries on the sides and bottom layer. Results for such cases are qualitatively identical. The indenter displacement, d , was changed in small steps (0.1 to 1 Å) and at each step the total energy was minimized at 0 K, using a conjugate gradient algorithm and an EAM potential for Au [15]. In the vicinity of plastic yield points, smaller steps (0.01 Å) were used to verify that the resulting dislocation structure did not depend on the step size. We chose this approach to mimic the quasi-equilibrium IFM experiments [3,4]. In addition, we performed short molecular dynamics (MD) runs to study dislocation nucleation, as described later in this Letter. All calculations were run with the ParaDyn code [16].

The force vs. displacement curves for indentation and retraction are shown in Figure 1. Initially, the indentation curve follows the Hertzian solution for elastic deformation where $F = Kd^{3/2}$ [5]. The indentation modulus derived from the fitting constant, K , is in good agreement with experiment. The force, F , on the indenter decreases abruptly when the elastic stress under the indenter is partially relieved by plastic deformation in the thin film. The shape of the indentation curve in the vicinity of the yield points is in excellent agreement with experimental results [17]. When the indenter tip is retracted after reaching the first yield point in Fig. 1, the force at small displacements matches that during indentation. This indicates that the plastic deformation created at the first yield point has healed during retraction. In contrast, the force profile during retraction from the second yield point indicates permanent deformation after retraction.

In order to study the structures of the plastically deformed thin film in detail, the location and type of defects present must be reliably identified. Separating the defects from the extensive elastic deformation in the thin film is not a trivial problem. Techniques relying on the electron density, the potential energy, the dislocation density tensor [18], or the atomic level stress tensor [19] for each atom often identify regions of elastically deformed material in addition to the defected material. Therefore, we have exploited the fact that a centrosymmetric material (such as gold or other fcc metal) will remain centrosymmetric under homogeneous elastic deformation. In a centrosymmetric material, each atom has pairs of equal and opposite bonds to its nearest neighbors. As the material is distorted, these bonds will change direction and/or length, but they will remain equal and opposite. When a defect is introduced nearby, this equal and opposite relation no longer holds for all of the nearest neighbor pairs. Thus we can define a centrosymmetry parameter which is zero for a centrosymmetric material under any homogeneous elastic deformation and nonzero for any plastic (i.e., non-elastic) deformation of the material.

The centrosymmetry parameter for each atom is defined as follows:

$$P = \sum_{i=1,6} |\mathbf{R}_i + \mathbf{R}_{i+6}|^2$$

where $\mathbf{R}_i$ and $\mathbf{R}_{i+6}$ are the vectors or bonds corresponding to the six pairs of opposite nearest neighbors in the fcc lattice. The twelve nearest neighbor vectors for each atom are first determined in an undistorted bulk fcc lattice, with the orientation of the slab. The analogous set of twelve vectors for each atom in the distorted lattice, $\mathbf{R}_i$, is then generated by finding those neighbors in the distorted lattice with vectors closest in distance to the undistorted nearest neighbor vectors. It is possible that this set will contain duplicates or non-nearest neighbors if a given atom has fewer than twelve nearest neighbors or a very distorted local environment. Each "equal and opposite" pair of vectors is added together, then the sum of the squares of the six resulting vectors is calculated. This final number is a measure of the departure from centrosymmetry in the immediate vicinity of any given atom and is used to determine if the atom is near a defect.

For reference, the centrosymmetry parameter is zero for atoms in a perfect Au lattice, $24.9 \text{ \AA}^2$ for surface atoms, $8.3 \text{ \AA}^2$ for atoms in an intrinsic stacking fault, and $2.1 \text{ \AA}^2$ for atoms halfway between fcc and hcp sites (i.e., in a partial dislocation). These values assume that the gold nearest neighbor distance does not change in the vicinity of these defects. We find in practice that the centrosymmetry parameter can readily distinguish between these three types of environments.

Figure 2 shows three views of the dramatic defect structure after the first plastic deformation event (at the circle in Fig. 1). The atoms are colored according to the value of the centrosymmetry parameter with red for partial dislocations ($P = 0.5 - 4.0$), yellow for stacking faults ($P = 4.0 - 20$), and white for surface atoms ($P > 20$). These ranges were chosen based on the values for the different environments given above. Note that Fig. 2 does not allow identification of the Burgers vectors. The stacking faults are bounded by the partial dislocation loops, which start at the surface and reach a depth of $85 \text{ \AA}$ into the thin film. All of the defects in this system lie on $\{111\}$ planes which are the energetically-preferred slip planes in the fcc lattice. From the (111) surface, there are three unique $\{111\}$ planes extending into the bulk. In this structure, defects can be seen parallel to only two of these three planes.

The structure shown in Fig. 2 is complex and it is beyond the scope of this paper to catalog the many dislocation lines and Burgers vectors involved. A simpler, but fundamental question regards the nucleation of this defect structure. By using MD and the centrosymmetry parameter, we were able to image the nucleation of the partial dislocation loops. The starting geometry for the MD run was that at label 1 in Fig. 1, and the tip displacement was held to that at the circled point in Fig. 1. We found that 2-fold symmetric partial dislocation loops first appear at approximately half of the contact radius beneath the surface. Figure 3 presents two different views of these initial partial dislocation loops. The dislocation lines and Burgers vectors of the nucleating dislocation loops were obtained by examining appropriate Burgers circuits on the $\{111\}$ planes containing the partial dislocations. These dislocation loops grow rapidly into the solid, emerge at the surface, and interact to produce the structure shown in Fig. 2. The MD run was continued long enough for the loops to equilibrate (on the order of picoseconds).

The nucleation of dislocation loops off the indenter axis was not expected when we began these calculations. A commonly used empirical criterion for dislocation nucleation is that the maximum resolved shear stress (MRSS) on the shear plane exceed the critical shear stress for the indented material [20]. From continuum elasticity theory [21], the MRSS is on the indenter axis and on a plane at 45° from the axis. Hence it has generally been assumed

that dislocations nucleate on the indenter axis. However our simulation results show unequivocally that this is not the case. This occurs because the $\{111\}$ slip planes are at an angle of 71° from the indenter axis. Reexamination [22] of the elasticity solution for the shear stress off-axis [23] shows that the MRSS on the $\{111\}$ planes occurs off-axis, in agreement with our predictions. This significant consequence of the continuum elasticity solution had not been appreciated previously.

The MRSS just before the first yield point in our calculations was 7 GPa. By modeling simple shear along a $\{111\}$ slip plane using the same EAM potential, we predict a critical shear stress of 2 GPa for bulk Au. Clearly the usual empirical criterion for plastic yield mentioned above is not a good approximation at these very small length scales. As the indenter size decreases to the nearly atomistic scale, the volume having a maximum shear stress decreases until it is comparable to the dislocation line width. At this small length scale, the average shear stress over the nucleating dislocation loop will be less than the maximum shear stress. This explains the discrepancy between the maximum resolved shear stress at yield (7 GPa) and the predicted critical shear stress of Au (2 GPa).

This loss of the (111) surface's threefold symmetry upon indentation appears to be a fundamental property of the glide process along two of the three $\{111\}$ planes. The orientation of the dislocation structure can vary with the initial conditions of the simulation such as the indenter aiming point and the symmetry (2-fold or 3-fold) of the boundary conditions, but we never obtain a 3-fold symmetric defect structure.

In summary, this work provides the first atomistic imaging of dislocation nucleation in a passivated surface under displacement controlled indentation. Our computational model probes both the elastic deformation regime of the Hertzian indenter and the plastic deformation regime of mechanical testing on passivated surfaces. The method we have developed to identify the defects clearly distinguishes between elastic and plastic deformation. In another paper we will discuss similar calculations for the Au (001) and (110) surfaces [24]. Each surface produces unique dislocation structures, and force vs. displacement curves, due to the orientation of the $\{111\}$ slip planes relative to the surface. These detailed structures provide a basis for understanding plastic deformation during the indentation and retraction processes and therefore the mechanical properties of the thin film.

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Figure 1. Force vs. displacement curve for Au(111) during indentation (solid line) of a spherical tip with 80 Å radius and during retraction (dashed lines) after the first (1) and second (2) plastic yield points. The circle marks the point where the structure in Fig. 2 was obtained.

(a)

(b)

(c)

Figure 2 (color). Defect structure at the first plastic yield point during indentation on Au(111), (a) view along $[11\bar{2}]$, (b) rotated 45° about $[111]$, and (c) rotated 90° to $[1\bar{1}0]$. The colors indicate defect types as determined by the centrosymmetry parameter: partial dislocation (red), stacking fault (yellow), and surface atoms (white). Only atoms with $P > 0.5$ are shown.

(a)

(b)

Figure 3 (color). Snapshot during dislocation nucleation at the first plastic yield point on Au(111), (a) same view and colors as Fig. 2(a), (b) a 2-layer thick cross-section of a $(\bar{1}11)$ plane containing the partial dislocation loop on the right in Fig. 3(a), where all atoms are now shown ($P < 0.5$ in blue) and the partial dislocation line and stacking fault Burgers vector are marked. The Burgers vector lies along $\langle \bar{1}\bar{2}1 \rangle$ and is $1.67 \text{ \AA}$ long.

Conlcusion

Our work has clearly demonstrated that surfaces and interfaces have distinctly differing structure that greatly impacts the growth and mechanical properties of thin films. This work has been extremely promising and the technical continuation of the project has been achieved by a BES funding.

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