DYNAMICS OF A METAL OVERLAYER ON METALLIC SUBSTRATES - HIGH TEMPERATURE EFFECTS

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ABSTRACT

We have explored the structure and the dynamics of a bimetallic system consisting of a hexagonal (almost) overlayer of Ag on a square lattice (*Ni*(100) and *Cu*(100)), as a function of the surface temperature. In each case the structure is "nearly" incommensurate giving rise to a low frequency Goldstone mode. Also, the overlayer atoms slosh back and forth over the substrate in a corrugated fashion. The calculated dispersion of the Ag/metal vertical mode, at room temperature, is in excellent agreement with experimental data. At higher temperatures floater atoms appear on top of the overlayer displaying a variety of cluster formations and also exchanges with the substrate atoms leading to surface disordering, interdiffusion and melting.

I. INTRODUCTION

An interesting question in surface alloy formation is how one type of metal atoms arrange themselves over the other because of the obvious differences in the lattice constants and the electronic structures. If these surface bimetallics lead to a commensurate or a nearly incommensurate structure then a related question is the stability of the interface as a function of surface temperature. Apparently, a commonly occurring combination is a hexagonal surface layer on a substrate with square symmetry.¹ Our interest here is in two such systems, i.e. a monolayer of Ag on *Ni*(100) and on *Cu*(100). For Ag/*Ni* the lattice mismatch is 16% while for Ag/*Cu* it is 13%. On forming a hexagonal arrangement on the (100) substrate, however, the overlayer becomes almost stress free. These structures have already been the subject of several experimental studies using low energy electron diffraction^{2,3} (LEED), electron energy loss spectroscopy³ (EELS) and scanning tunneling microscopy⁴ (STM), which point to the presence of a $c(2 \times 8)$ surface unit cell^{3,4} for Ag on *Ni*(100) and a $c(2 \times 10)$ structure^{2,3} for Ag on *Cu*(100), i.e. Ag atoms are row-aligned with the substrate atoms in the ratio of 7 Ag to 8 *Ni* and 9 Ag to 10 *Cu*, respectively. Apart from structure, the dispersion of the Ag vertical mode along a high symmetry direction has also been measured.³

Our interest here is in the dynamics and the stability of these nearly incommensurate structures, particularly at higher temperatures. The earlier theoretical studies of these structures were based on pair potentials and the role of the rigid substrate was to provide surface corrugation.^{3,5,6} Our approach here is to use many-body potentials of the embedded atom (EAM) type for a molecular dynamics simulation in which all substrate and adsorbate atoms are dynamic. Starting with a row-aligned configuration at room temperature of the type predicted from data, we first calculate the structure factor and the dispersion of the Ag/metal vertical mode whose agreement with EELS data would test the reliability of the interatomic potential. Next we look for the Goldstone mode which is to be expected in incommensurate or nearly incommensurate structures.⁵ This is a mode localized in the surface layer and polarized along the incommensurate direction/plane whose frequency $\omega \Rightarrow 0$ as $\vec{Q}_{||} \Rightarrow 0$ ($\vec{Q}_{||}$ is the wave vector polarized parallel to the surface plane), for a totally incommensurate structure, and $\omega \Rightarrow$ finite value as $\vec{Q}_{||} \rightarrow 0$, for a nearly incommensurate structure. We then analyze the mean square displacements of the atoms and the dispersion of the surface phonon along several high

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symmetry directions and compare these quantities made with those on the bare substrate. Finally, the simulations are extended to higher surface temperatures to observe anharmonic effects and to monitor the process of surface disordering.

Fig. 1a. The Lattice

Fig. 1b. The Surface Brillouin Zone

Fig. 2. Fluctuations in coordinates of 16 equivalent Ag atoms at 300K

In the next section we describe the model system and some details of the calculations. Section III contains the results and is followed by some discussions in Section IV.

II. MODEL SYSTEM AND CALCULATIONS DETAILS

For clarity we will discuss mostly the $Ag/Ni(100)$ system and report on results for $Ag/Cu(100)$ only when appropriate. The surface unit cell shown in Fig. 1a consists of 7 Ag atoms arranged on top of 8 Ni lattice spacing. Note that we have chosen $[\bar{1}10]$ as the incommensurate direction and an equally favourable domain orientation would have the nearly incommensurate structure along $[110]$. In an experiment both types of domains exist and have to be accounted for in the analysis of the data. The Brillouin Zone for the hexagonal Ag layer together with that of the substrate is presented in Fig. 1b.

The molecular dynamics cell consists of 112 Ag atoms arranged as in the Fig. 1a (4 units along the x -axis and 2 units along the y -axis) over 9 layers of Ni with 128 atoms/layer. Periodic boundary conditions are applied in the directions parallel to the surface. Classical equations of motion for all 1264 atoms are solved numerically using standard techniques. After the system has been equilibrated at the desired temperature, statistics are accumulated over longer runs of 50–200 ps at each temperature. The mean square vibrational amplitudes, the layer-by-layer structure factor and the surface phonon spectral densities are then calculated. The details of these calculations will be presented elsewhere.^{7,8}

The interaction potential is obtained from the embedded atom method.⁹ The main virtue of this form for our purposes here is that it is many-body, albeit empirical, in nature and parameters do not have to be adjusted to reproduce surface phenomena.

III. RESULTS

We present here some of the results for Ag on $Ni(100)$ at 300K and at 1200K–1700K. At lower temperatures the main emphasis is on the dynamics of the $c(2 \times 8)$ structure, which persists even at 1200K, while the high temperature studies examine the approach to surface disordering and melting. Note that the bulk melting temperature for Ni using EAM potentials is 1740K (experimental value is 1726K).

a. Sliding/Sloshing Motion and the Goldstone Mode

An interesting conclusion from the analysis of the mean square displacements of the atoms is that at 300K the Ag overlayer slides back and forth over the Ni substrate along the nearly incommensurate direction. The center of mass of the Ni layers move in the

opposite direction to keep the net center of mass of the system stationary. Also, as each Ag atom moves a distance of about 3.4 Å from a bridge site to a hollow site it does so in a corrugated manner as shown in Fig. 2. It lies low above Ni(100) at the hollow site and rides higher at the bridge position.

The calculated phonon spectral densities near the zone center ($\vec{Q}_{||} \rightarrow 0$) exhibits a very low frequency mode (1.5 cm^{-1} at 300K) which is polarized along the y -axis (the nearly incommensurate direction). This is the Goldstone mode for Ag on Ni(100). Its finite frequency corresponds to the lock-in energy for the translation of the overlayer along the nearly incommensurate direction. For Ag on Cu(100) the frequency of this mode is 1.3 cm^{-1} at 300K.

Fig. 3a. Phonon spectral density of top layer Ni atoms at $\bar{X}$ at 300K.

Fig. 3b. Phonon spectral density of top layer Ni atoms at $\bar{Y}$ at 300K.

b. Surface Phonon Dispersion

We have calculated the dispersion of the surface phonons at 300K and 1200K along three high symmetry directions in the substrate Brillouin Zone: $\bar{\Gamma}-\bar{M}$, $\bar{\Gamma}-\bar{X}$, and $\bar{\Gamma}-\bar{Y}$. While for the bare substrate $\bar{X}$ and $\bar{Y}$ are equivalent, with the hexagonal overlayer they are not and $\bar{Y}$ is no longer at the overlayer zone boundary (see Fig. 1b). Also, the $\bar{\Gamma}-\bar{M}$ direction is significant because it is equivalent for the two domain orientations, thereby facilitating experimental measurements of the surface modes along this particular direction. Along this direction our calculated dispersion of the Ag/Ni and the Ag/Cu vertical mode^{8,10} is in excellent agreement with the EELS data.³

In Fig. 3, we present the spectral densities for the Ni atoms, in the layer directly below the Ag overlayer, at $\bar{X}$ and $\bar{Y}$ points in the two-dimensional Brillouin Zone. In each figure the “longitudinal” and the “shear horizontal” modes lie in the surface plane, polarized, respectively, parallel to the wave-vector and normal to it. The “vertical” mode is polarized along the surface normal. At $\bar{X}$ the shear horizontal mode is softer than the corresponding one at $\bar{Y}$, and it is also split into several modes. This is a result of the nearly incommensurate (1×8) arrangement along the y -axis along which the shear horizontal mode at $\bar{X}$ is polarized. The shear horizontal mode at $\bar{Y}$ is polarized along the x -axis which is the commensurate direction for the Ag overlayer. Thus, there is no splitting in this mode or a softening in the frequency. At $\bar{Y}$, the shear horizontal mode resembles more the same feature¹¹ on bare Ni(100). The Rayleigh wave at 3.9 THz on the bare surface, appears prominently at a slightly higher frequency at $\bar{X}$ (Fig. 3a) and not at $\bar{Y}$ (Fig. 3b). Additionally, two other vertical modes are present at ~ 6 THz and 6.8 THz at both $\bar{X}$ and $\bar{Y}$ for the bimetallic system.

The richness in the phonon spectral densities at $\bar{X}$ and $\bar{Y}$ call for experimental measurements to validate the claims made here. However, a word of caution is that the presence of the other domain orientation would cause considerable mixing in the signals from the two inequivalent symmetry points.

The spectral densities for the *Ag* atoms at $\bar{X}$ and $\bar{Y}$ and for both *Ag* and *Ni* atoms at $\bar{M}$ further reveal the nature of the bonding between *Ag* and *Ni* atoms and the pronounced directional asymmetry. At 1200K all modes broaden but not all to the same extent. These details can be found in Ref. [7].

Mean Square Displacement (<i>Ag</i>) (In Units of $10^{-2} \text{ \AA}^2$)			
T	$\langle u_x^2 \rangle$	$\langle u_y^2 \rangle$	$\langle u_z^2 \rangle$
3K	.004	.011	.014
300K	.830	1.600	2.300 (1.3)
1200K	5.500	10.500	8.300
<i>Ag</i> (111) 300K	1.096	1.173	1.590

c. Mean Square Vibrational Amplitudes

The variation of the mean square vibrational amplitude of atoms with temperature is a measure of the anharmonicity of the interaction potential. For harmonic systems this scaling is linear. The numbers in Table I illustrate that even at 300K the *Ag* vibrations are anharmonic and the anharmonicity is largest along *x* – the commensurate direction. More significant is the enhanced vibrational amplitude at all temperatures along the *y*-axis resulting from the nearly incommensurate arrangement. Note that the *y* motion of the center of mass of the *Ag* layer has been already subtracted. The value 1.3×10^{-2} for $\langle u_z^2 \rangle$ results when the slow vertical oscillation between bridge and hollow sites is subtracted out. Comparison of the mean square vibrational amplitude of the *Ag* atoms on *Ni*(100) with those of the top layer *Ag* atoms on *Ag*(111) shows that $\langle u_x^2 \rangle$ for the former is in fact smaller than that of the latter. The vibrational amplitudes of the *Ni* atoms in the layer directly below the *Ag* are also anharmonic and anisotropic.⁷

d. Surface Disordering

We now turn to the atomic trajectories in the high temperature range, i.e. 1200K to 1700K. At 1200K the first 50 ps run after equilibration was rather quiet as only one *Ag* atom left the overlayer to float over it for about 26 ps and then to settle back into the layer. Subsequent runs for a total of 150 ps exhibited much more activity with several floater atoms wandering, dimerizing, clustering, unclustering, and so forth. There were also exchange processes in which *Ni* atoms would move into the overlayer and *Ag* atoms would move into the top substrate layer. A snapshot of a trajectory at 1200K is shown in Fig. 4. Note that at this temperature the structure is on the average $c(2 \times 8)$ although large distortions are present.

At 1300K, the disordering of the surface was more pronounced than at 1200K. Occasionally a silver atom would be trapped even in the second layer of the *Ni* substrate and several *Ni* atoms found their way into the overlayer. There were also clustering of *Ni* and of *Ag* atoms. As the temperature was raised to 1500K, all these processes became more frequent making the surface pretty disordered. At 1300K, and even more so at 1500K, there were a large number of *Ni* atoms in the overlayer and also floating above the overlayer. Similarly some *Ag* atoms penetrated into the third substrate layers while most floated above in clusters. Despite the increased activity in the surface layers, the layers below second *Ni* layer were relatively calm even at 1500K. The situation changed completely at 1700K, which is close to the bulk melting temperature of *Ni*. *Ag* and *Ni* atoms were intermingled everywhere, the surface was completely disordered (melted)

and there was a large outward vertical expansion of the system. These characteristics are presented below in Fig(s). 5–8, which show a side view of the system of 9 *Ni* layers and 1 *Ag* overlayer. Here we have two free surfaces but the *Ag* overlayer has been placed at the top surface only. The lighter atoms are *Ni*. Note the dramatic change in the ordering at 1700K at both the lower and the upper surface. In Fig. 8 the lower most atom is an *Ag* atom that has gone down 9 layers. In Fig. 9 the average linear density of the *Ag* atoms as a function of the height above the *Ni* substrate is given. The averaging was done over 50 ps. At 1300K, there is only a trace of *Ag* in the first substrate layer and some have become “floaters” with an average height of 5Å, while most *Ag* most are at $\sim 3\text{\AA}$ from the starting configuration of the top layer substrate atoms. At 1500K, there is still a concentration of these atoms around 3.5Å, but at 1700K the curve loses its peaks at *Ag* atoms diffuse everywhere.

Fig. 4. Top view of *Ag/Ni*(100) at 1200K.

IV. DISCUSSION

We have found the *Ag/Ni*(100) system very dynamic at all temperatures here. At 300K, the sliding/sloshing of the overlayer on the substrate along the incommensurate axis, the presence of the Goldstone mode and the richness in the surface phonon spectral densities offer several opportunities to understand the characteristics of such bimetallic systems both experimentally and theoretically. At higher temperatures, the approach to surface disorder indicates the interdiffusion of *Ag* and *Ni* atoms with the rate increasing with temperature. Since in our simulations one free surface behaves like clean *Ni*(100), Fig(s). 6–8 also contrast the relative calm of that surface compared to the other, except at 1700K when both surfaces are disordered.

It will be interesting to follow these atomic trajectories over much longer times and also study the effects of the finite size of the system, but such work will be meaningful when coupled to similar experimental studies.

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Fig. 5. Initial configuration of Ag/Ni(100) at 1700K

Fig. 6. Side view of Ag/Ni(100) at 1300K after 50 ps.

Fig. 7. Side view of Ag/Ni(100) at 1500K after 50 ps.

Fig. 8. Side view of Ag/Ni(100) at 1700K after 50 ps.

Fig. 9. Ag atom height distribution.

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