INCOMPLETE MELTING OF THE Au(100) SURFACE

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ABSTRACT

We study the high-temperature disordering of the reconstructed Au(100) surface by molecular dynamics simulation using a many-body interatomic potential. We find that the surface deconstructs at 0.8T_m in good agreement with experimental data, but proper surface melting does not occur close to the bulk melting point. Instead there is an in-plane disordering of the two topmost layers. The thickness of the disordered region remains constant with increasing temperature, indicating blocked, or incomplete, melting of the (100) crystalline substrate. An analysis of the structure reveals that crystalline and disordered islands coexist on two first surface layers for temperature between deconstruction and bulk melting.

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Possible evidence of weak disordering at high temperatures was also obtained for the Ge(111) surface [8]. The microscopic structure of the high temperature phase on all these incompletely wet surfaces with a limited amount of disorder is not particularly well understood.

We simulate here the Au(100) surface at high temperatures, and predict that it should also exhibit incomplete wetting, following high-temperature deconstruction. Use of a well-established realistic potential yields a uniquely detailed picture of the surface structure as it crosses deconstruction and enters this incompletely disordered state.

The reconstructed Au(100) surface forms at room temperature an incommensurate hexagonal layer on the top of the square bulk lattice [9]. Recently Mochrie et al published a detailed X-ray diffraction study of the structure and phase transitions on the Au(100) surface between 300K and the bulk melting temperature ($T_m = 1337 K$) [9,10]. They found that at low temperatures reconstructed domains rotated by $\pm 0.81^\circ$ with respect to the substrate coexist with fully aligned reconstructed domains. This phase undergoes a transition at 970K into an unrotated "distorted-hexagonal" phase where all domains become aligned with the substrate.

At 1170K there is a disordering, or deconstruction, transition where the diffraction pattern of the hexagonal reconstruction disappears. In the whole experimental temperature range the Au(100) surface remains smooth [9,10]. Therefore, the reconstructed surface structure of Au(100) is completely characterized between 300 and 1170K. However, much less is known about the deconstructed high-temperature phase above 1170K (i.e. $0.88T_m$). It was found that a few topmost layers are disordered, but it was not possible on the basis of the X-ray diffraction data to distinguish between a liquid or a statically disordered surface film. We study here the high-temperature properties of the Au(100) surface by molecular dynamics (MD) simulation. Our results show that up to the bulk melting point only two top layers exhibit lateral disordering. Moreover, these disordered layers are seen to be instantaneously inhomogeneous. In the following, we will first describe our MD simulation method in Section II. The results are presented in Section III. A discussion and the conclusions are given in Section IV.

II. COMPUTATIONAL METHOD

We have done an extensive MD simulation study of the high-temperature properties for the Au(100) surface by heating carefully slab-shaped samples from $T = 0$ up to the bulk melting point. To describe the interparticle interactions, we have used an empirical, but very well-tested many-body interatomic potential for gold [11]. The many-body potentials for noble metals are well known to give a correct description of the metallic cohesion both in bulk, and at surfaces [11,12]. This, of course, a necessary ingredient for a realistic computer simulation of our surface system. All details of our "glue model" potential were fixed in previous bulk calculations [11] and there are no arbitrary parameters in the present simulation. An earlier study of the Au(100) surface with the same potential [13] yielded a very successful description of its long-period reconstruction, including its denser nearly triangular first-layer packing and the associated misfit defects with the square substrate. That study also showed that an optimal geometry at $T = 0$ is $(34 \times 5)$ and that all $(M \times 5)$ structures, $M > 20$, have very similar surface energies [13]. The ex-
experimental surface reconstruction is close to a \((20 \times 5)\) structure \cite{14}. The behavior of the Au(100) surface reconstruction for \(T > 0\) was also studied by MD simulation \cite{15} (using the same potential of Refs. \cite{11,13}). On the other hand, melting and non-melting of fcc metal surfaces were recently studied by MD simulations using various many-body potentials \cite{16-18}. However, there is as yet no detailed MD study of incomplete melting, of which Au(100) happens to provide an example. We therefore concentrate here on the melting properties of the Au(100) surface.

For most of our calculations the MD box consists of 16 layers and a total of 4956 particles. In order to have a large lateral size of the box we put in each bulk layer 20 particles along the \(x = (011)\) direction and 15 particles along the \(y = (011)\) direction of periodically replicated MD slab. We have also done simulations for a smaller system of 8 layers and 1704 particles with a \((20 \times 10)\) cell in each bulk layer. We did not see any substantial difference in the two simulations, and only results for the larger system are presented here. To model the reconstruction of the Au(100) surface at \(T = 0\) we increase the lateral density by putting more particles in the topmost layers of the slabs. The density increment of 26\% corresponds to a hexagonal layer, which was previously found to be optimal for our potential \cite{13}, as well as close to the experimental situation. Our quasi-triangular lattice is contracted 4.76\% along the \((011)\) direction and 3.77\% along the \((011)\) direction relative to a bulk ideal triangular layer. The three bottom layers of the slabs are kept fixed to simulate the bulk of the system. We change the lattice constant of the sample with temperature according to the expansion coefficient of the bulk: both the expansion coefficient and the bulk melting temperature \((T_m \sim 1355 K)\) are known from previous bulk simulations \cite{11}. The temperature of the system is controlled by rescaling the particle velocities. We start from the reconstructed surface at \(T = 0\) and then move on to each successively higher temperature from the well equilibrated sample at the lower temperature, in steps of 100K first and then 50K. Depending on the temperature samples were equilibrated using 10 to \(5 \times 10^6\) MD time steps. Since our MD time step corresponds to \(7.14 \times 10^{-15}\) s, the total simulation time for each run at higher temperatures is typically \(\sim 3.5\) ns.

III. RESULTS

A. Density profiles and potential energies

We present in Fig. 1 the \((z,y)\) averaged density profiles for Au (100) simulated in our larger MD box as a function of temperature. It can be seen that several top layers gradually disorder with increasing \(T\) (i.e. the peak heights decrease and the peak widths of top layers increase), but the solid-like layered structure is preserved up to the bulk melting point (Fig. 1(d)). This behavior should be contrasted with results of MD simulations for (110) surface of exactly the same model crystal, exhibiting pronounced surface melting \cite{18}: in that case, the crystalline layer structure in the density plots is lost at high temperatures and a genuine liquid film forms at the surface. One of the criteria for surface melting is that the average potential energy per atom in a melted layer is higher (liquid-like) than in a typical bulk (solid-like) layer. Fig. 2 shows the potential energy per particle at various temperatures. The minima on the potential energy curve correspond to the maxima
on the density plot. From Fig. 2 (d) is possible to see that the potential energy per particle exhibits the layered structure up to the bulk melting point. On the contrary, for (110) surfaces the flat portion of \( E_p \) corresponds to the surface melted region of MD box, i.e. to the free motion of particles in the liquid region of the slab [17].

B. Orientational order

Figure 3 shows the orientational order parameters \( O_4 \) and \( O_6 \). While the fourfold order parameter \( O_4 \) is well suited for a description of the square bulk lattice, the sixfold order parameter \( O_6 \) describes the nearly hexagonal structure of the reconstructed topmost layer. These order parameters are defined as

\[
O_n = \frac{\sum_{ij} W_{ij} \cos^{n-1} \theta_{ij}}{\sum_{ij} W_{ij}},
\]

where the sums run over the first-neighbor pairs. The angle \( \theta_{ij} \) is defined between \( i-j \) bond (projected on the xy plane) and x axis. We assume a weight function \( W_{ij} = \exp[-(z_i - z_j)^2/2\delta^2] \), where \( \delta \) is the average inter-layer spacing, so as to filter out non-coplanar neighbours. The fourfold order parameter \( O_4 (= 1 \) for the (100) surface of an ideal fcc crystal at \( T = 0 \)) obviously decreases at higher temperatures. In similar way, the sixfold order parameter is defined such that \( O_6 = 1 \) for the (111) surface of an ideal fcc crystal at \( T = 0 \). In our simulation for Au(100), the surface order parameter \( O_6 \) is well established at 0.3\( T_m \) and 0.74\( T_m \) (Fig. 3(a,b)) indicating the presence of hexagonal crystalline order. However, it decreases rapidly with temperature and at 0.81\( T_m \) it has dropped below 0.1. This is in good agreement with the experimental result for a disordering (deconstruction) transition at 1170 K (i.e. 0.88\( T_m \)) [9,10]. At 0.89\( T_m \), as shown in Fig. 3(c), the surface has completely lost the sixfold order parameter. Figs. 3 (c,d) show that at high temperatures only the square symmetry of the (100) bulk planes exists, in agreement with the X-ray diffraction patterns for disordered phase [9,10]. It is possible to see from Fig. 3(d) that \( O_4 \) for few topmost layers does decrease close to the bulk melting point, but does not vanish as \( T_m \) is approached. In particular, the fourfold order parameter for the Au(100) surface does not at all look like the behavior of \( O_4 \) found for the topmost layers on the melting Au(110) surface at high temperatures [18], where it goes especially fast to zero for \( T \rightarrow T_m \).

C. Mean square displacements

Fig. 4 shows how the vertical mean square displacements from the equilibrium positions, \( (u^x)^2 \) (measured for a time evolution of 3.5 ns) increase with temperature. In experiments of Refs. [9,10] it was found that at all temperatures the vibrational amplitudes normal to the Au(100) surface for several top layers are much larger than in the bulk. Since the normal vibrational amplitudes are smaller than the lattice spacing, the layer order is preserved up to the bulk melting point. In our simulation close to the bulk melting point the histogram bar for the vertical mean square displacement of the surface layer is \( \sim 25 \) times higher than for the interior bulk layers (Fig. 4(d)). This ratio falls to \( \sim 10 \) at 0.3\( T_m \) (Fig. 4(a)). The results for the in-plane (i.e. \( x \) and \( y \)) components of the mean square vibrational amplitude for two top layers are presented in Figs. 5 and 6. In-plane mean square displacements at higher temperatures are rather isotropic (i.e. \( (u^x)^2 \sim (u^y)^2 \)) and much larger than vertical components \( (u^z)^2 \), which indicates lateral disordering. A similar kind of unusual "inverted" anisotropy, where the out-of-plane vibrational amplitude at room temperature is 30% smaller than the in-plane vibrational ampli-
tude, was recently found by medium energy ion scattering for the Cu(100) surface [19]. Decreased lateral order for the high-temperature phase of the Au(100) surface was already suggested in order to explain a large decrease of the X-ray reflectivity at the hexagonal disordering transition [9,10]. However, the X-ray data do not give details of this lateral disordering.

D. Particle trajectories

MD trajectories in Figs. 7-10 show lateral disordering at different temperatures. While at 0.3T_m and 0.74T_m (Figs. 7 and 8) there is a little diffusion and the surface is in a solid phase, at 0.89T_m and ~T_m (Figs. 9 and 10) a considerable amount of liquid diffusion exists, but solid-like islands are also present. Disorder is essentially restricted to the two topmost layers. We would like to point out that trajectories in Figs. 7-10 represent the system after a long evolution of ~ 3.5 ns. Using the same potential in a much shorter simulation for Au(110) [18], it was found that surface melting starts already at 0.75T_m. After ~ 0.7 ns, for example, 5.5 (110) layers are melted at 0.99T_m [18]. On the contrary, as shown in Figs. 9 and 10, only two topmost layers of Au(100) exhibit pronounced in-plane disordering and these are stationary, well equilibrated states. Figs. 8(a,e) show a characteristic rectangular monolayer hole in the topmost layer. The hole appears at T ~ 0.65T_m. Since our simulation was carried out with the fixed number of particles, this hole acts to realize a further density increase in the top layer relative to its density at lower temperatures (and itself already higher than that of the ideally terminated bulk). Similar holes, formed as a consequence of a density change in different phases of surface reconstruction, were apparently found by scanning tunneling microscopy on Si(111) and Ge(111) [20]. At the top layer of Au(100) no such increase of lateral density was suggested so far since the X-ray diffraction data did not show any major change in the lattice constants of the hexagonal layer between 300 and 1100 K [9,10]. In our simulation we do instead find evidence of density increase. It remains for future experiments to check whether, as already found for Si(111) and Ge(111), these holes may also appear on the large flat terraces of Au(100), or not. On a real surface, what seems rather more likely is that boundaries may act as a source of atoms and prevent the formation of holes, while the whole top layers goes denser.

In our simulation the hole remains on the surface at higher temperatures because of the lack of extra atoms (Figs. 9(a) and 10(a)). Even so, the rest of our laterally large MD box is a good model for the high-temperature properties of real Au(100). Analysis of the X-ray data for specular reflectivity [10] gives the decrease (from 1.26 to 1) of the average top layer density at deconstruction transition. Our simulation is not precise enough to deal directly with this question, although the order parameters (Fig. 3) clearly demonstrate deconstruction.

IV. DISCUSSION AND CONCLUSIONS

The results of our simulation show that the Au(100) surface does not exhibit surface melting, i.e. complete wetting. Instead there is a limited high-temperature disordering located in the two topmost layers. Chernov and Mikheev studied analytically the structure of liquid films on the solid surface [21]. They found that the substrate induces the layer-type ("smectic") ordering in thin liquid film and as a consequence oscillations of its free energy as a function of the thickness. The free
energy term which corresponds to the quasicrystalline (residual) order in the thin liquid film is \( \sim \exp(-2h/\xi) \), where \( h \) is the film thickness and \( \xi \) is the correlation length in the bulk liquid. The layering effects lead to the quantization of the film thickness in units \( 2\pi/k_x \), where \( k_x \) is the wave number which correspond to the first maximum in the structure factor of the bulk liquid. The structure of the liquid film is determined by the underlaying lattice and that produces (experimentally observed) surface melting anisotropy. Therefore, there is a possibility not only for surface melting, but also for incomplete melting, i.e. only a small number of layers may melt below the bulk melting point and these disordered layers show pronounced quasicrystalline order. Our results for the Au(100) surface are in agreement with this picture of incomplete melting. This is probably also the explanation for results obtained experimentally for Pb(100) and Ge(111) at high temperatures [4-6,8].

In summary, we have studied the high-temperature behavior of Au(100) and found that this surface deconstructs at \( T \sim 0.87T_m \), but does not exhibit surface melting. Previous MD simulations for the same potential have shown that the close-packed Au(111) surface does not melt below the bulk melting point [16]. On the contrary the open Au(110) surface, starting from a \((1 \times 2)\) missing row structure, first deconstructs and then shows well pronounced surface melting which begins already at \( 0.75T_m \) [18]. It was found there that the thickness of the liquid layer grows linearly with \( \ln(1 - T/T_m) \). Parallel experimental results for surface melting of Au(110) and non-melting of Au(111) were obtained by ion shadowing and blocking technique [22]. We expect that future detailed experiments should be able to check our MD simulation results for the high-temperature phase of the Au(100) surface. Recently we also studied the high-temperature behavior of some Au(100) vicinal surfaces and found a similar disordering of top layers [23].

Finally, we remark that the existence of a limited high-temperature disordering in the two top layers on the Au(100) surface, as well as of surface melting on Au(110), is in agreement with a general statistical mechanics analysis of the effect of the roughening transition on the wetting phenomena [3]. For example, if a solid film condenses on a substrate at \( T_w < T_r \), it will exhibit layering, i.e. it is possible to follow the formation of a monolayer, then of the second layer, etc. If \( T_r < T_w \), layering is absent and the film condenses smoothly [3]. In [9,10] was found that the Au(100) surface does not roughen up to \( T_w \). On the contrary, on Au(110), a surface roughening transition is followed by surface melting, i.e. \( T_r < T_w \). It will be interesting also to study in this light the high-temperature disordering of the Pt(100) surface. Recently this surface was also studied by synchrotron X-ray diffraction [24]. Although Au(100) and Pt(100) exhibit similar phases of reconstruction, it was found that the Pt(100) surface roughens at \( 0.89T_m \). Therefore, there is a possibility for \( T_w > T_r \) and the Pt(100) surface may exhibit (very close to the bulk melting temperature) complete wetting, i.e. surface melting.

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Figure 1: The (x,y) averaged density profile at: (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\) (±1%). The three leftmost layers are kept fixed, the Au(100) surface is on the right and the dashed line represents the value for liquid Au surface at \(T_m\). Note that the gradual surface disordering does not spread into the bulk at \(T \sim T_m\) (incomplete melting).

Figure 2: The (x,y) averaged potential energy per particle: (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\). The minima correspond to crystalline layers. Other comments as in Fig. 1.

Figure 3: The (x,y) averaged orientational order parameters, \(O_y\) (dashed line) and \(O_x\) (full line): (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\). The disappearance of \(O_x\) at high temperature is due to the deconstruction between (b) and (c).

Figure 4: The (x,y) averaged vertical mean square displacement: (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\). Note the change of the scale along the vertical axis for all mean square displacement plots (Figs. 4–6).

Figure 5: The x-component (parallel to (011)) of the mean square displacement: (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\).

Figure 6: The y-component (parallel to (0\(\bar{1}1\))) of the mean square displacement: (a) 0.3\(T_m\), (b) 0.74\(T_m\), (c) 0.89\(T_m\), (d) \(\sim T_m\).

Figure 7: MD particle trajectories at 0.3\(T_m\): (a) top view, (b) side view. Trajectories refer to a time span of \(\sim 10\) ps, after an equilibration time of \(\sim 3.5\) ns.

Figure 8: Trajectories at 0.74\(T_m\): (a) top view of the topmost layer, note the "hole" at the bottom, left, (b) top view of the second layer, (c) top view of the third layer.
layer, (d) side view, (e) slice of MD box showing a side view of the hole.

Figure 9: Trajectories at 0.89Tₘ: (a) top view of the topmost layer, (b) top view of the second layer, (c) top view of the third layer, (d) side view.

Figure 10: Trajectories at ~Tₘ: (a) top view of the topmost layer, (b) top view of the second layer, (c) top view of the third layer, (d) side view.