Experimental Evidence for Surface Roughening in Two Dimensions

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The heat of two-dimensional evaporation of gold on a tungsten (110) surface is derived from the temperature dependence of the work-function change at constant submonolayer coverage. It shows a temperature dependence as expected for a roughening transition of the island edges at $T_R = 0.57 T_c^{2D}$.

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It has been known for a long time[1,2] that the periphery ("surface") of a two-dimensional (2D) crystal is rough at all temperatures $T \neq 0$ or, in other words, that the roughening temperatures T_R of all surfaces of the crystal are zero.[3] The proofs of this statement assume short-range forces, e.g., nearest-neighbor interactions, and do not exclude that one or several surfaces become rough at $T_R > 0$ if long-range interactions between the atoms exist. A few years ago Abraham[4,5] showed that $T_R > 0$ even in the presence of nearest-neighbor bonds if the bonds of the surface atoms to the interior atoms are weaker than the bonds between atoms in the interior of the crystal. When, in the ferromagnetic Ising model discussed by Abraham, the exchange-interaction energy of the surface spin with the nearest interior spin, $J_s = aJ$, decreases from J to 0, T_R increases monotonically from 0 to the critical temperature of the Ising model, $T_c = 2.27J/k$. A corresponding behavior occurs in the isomorphic lattice-gas model when the bond energy of the surface atom $E_s = (1+a)E/2$ decreases from E to $E/2$, E being the energy per bond in the interior of the 2D crystal.[6]

The Abraham model may be much closer to reality than the original Ising model because a real 2D crystal needs a support which is best realized by a single-crystal surface. The interactions of the edge atoms of this crystal with the substrate are different from the average interactions of the interior atoms, which causes differences in the lateral interactions: Edge atoms have a larger dipole moment than interior atoms[7] and therefore a larger repulsive dipole-dipole interaction contribution to their lateral bonding. As a result of their different neighborhood they have a different (substrate-mediated) indirect electronic interaction[8] with their neighbors. Because of the oscillatory nature of indirect electronic interactions this contribution may increase or decrease the lateral bonding of the edge atoms. Finally, bonding differences between edge and interior atoms may arise from differences in elastic interactions, in particular if there is a misfit between the 2D crystal and substrate. Depending upon the relative magnitude of the various contributions, Abraham's model may or may not have a counterpart in 2D crystals on surfaces of 3D crystals. The purpose of this Letter is to present experimental evidence that it does.

The basic idea of the experiment is simple. If $T_R = 0$ then the roughness of the surface of the 2D crystal should increase monotonically with temperature and concomitantly the average number N_s of neighbors of a surface atom should decrease. If $T_R > 0$ then a slow increase of roughness (decrease of N_s) at $T << T_R$ should be followed by a rapid increase (decrease of N_s) in the neighborhood of T_R. Although the roughness continues to increase above T_R, N_s will rapidly approach an asymptotic value because the roughness increase has a long-wavelength nature and has negligible influence on the local environment of the surface atom. The average number N_s of neighbors determines the heat of 2D evaporation ΔH_{2D} so that a measurement of this quantity as a function of temperature should allow determination of T_R. The magnitude of the difference between ΔH_{2D} above and below T_R can be easily estimated, which will be done here for a hexagonal crystal (see Fig. 1). Sufficiently far below T_R, atoms in the most densely packed 1D surface—which has the highest T_R—have to be removed from the kink positions [three nearest neighbors, Fig. 1(a)], and sufficiently far above T_R, from positions on ledges [two nearest neighbors, Fig. 1(b)]. Overhangs with one nearest neighbor [Fig. 1(c)] may be neglected because they have little chance to form under equilibrium conditions. Thus ΔH_{2D} decreases by 33% from low to high temperatures. This is

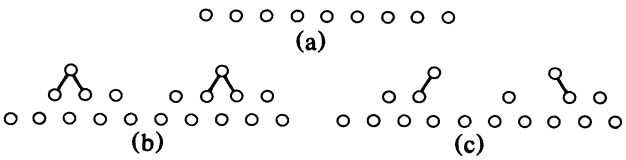

FIG. 1. Surface configurations in a 2D hexagonal lattice. (a) smooth surface ($T << T_R$); (b) rough surface ($T \gtrsim T_R$); (c) overhang on rough surface ($T \gtrsim T_R$). 2D metal islands on a bcc metal (110) surface have a somewhat distorted lattice of this type.

an upper limit because if more neighbors are taken into account the N_s difference becomes smaller.

The measurement of the heat of evaporation of a 2D crystal, as difficult as it may appear, is in fact very simple. We have shown recently[9,10] that information on the state of a 2D phase on a metal surface may be obtained from a study of the coverage (θ) and temperature dependence of the work-function change $\Delta\phi(\theta,T)$. The temperature dependence is caused by the transition of atoms from the condensed phase into the 2D gas phase in which they have a much larger dipole moment than in the condensed phase. In Ref. 8 only the coexistence line between single-phase (gas) and two-phase (gas plus condensate) region and the critical parameters were determined. Here we extract ΔH_{2D} from the $\Delta\phi(T)$ data by a more detailed analysis which is based on the Clausius-Clapeyron equation $d\Pi/dT = \Delta H_{2D}/T\Delta A$. In this analysis it is assumed that the 2D system consists only of condensate and a perfect monoatomic gas so that $\Pi = nRT$ where $n = 1/A$ is the density of the gas phase. With the usual assumption $\Delta A \approx A$, ΔH_{2D} may then be expressed by n

$$\frac{\Delta H_{2D}}{RT} = \frac{dn/dt}{n/T} + 1. \tag{1}$$

As shown in detail elsewhere[11] n can be obtained from the total density N of atoms (in gas plus condensate) and from the work-function change $\Delta\phi(T_0,\theta)$ when all atoms are in the condensed phase (as measured at the lowest temperature T_0), from the work-function change $\Delta\phi_g(T,\theta)$ when all atoms are in the gas phase (extrapolated to the coexistence region from high temperatures), and from the work-function change $\Delta\phi(T,\theta)$ actually measured at T and θ which is due to the mixture of gas and condensate (envelope curve in Fig. 1 of Ref. 8):

$$n(T,\theta) = N\frac{\Delta\phi(T,\theta) - \Delta\phi(T_0,\theta)}{\Delta\phi_g(T,\theta) - \Delta\phi(T_0,\theta)} = N\frac{\Delta(T,\theta)}{\Delta_g(T,\theta)}. \tag{2}$$

The errors made in the extrapolation involved in the determination of Δ_g have little influence on ΔH_{2D} because the Δ_g term resulting from insertion of Eq. (2) into Eq. (1) is small compared to the Δ term. The error in Δ is large at low temperatures because Δ is then of the same magnitude as the experimental error in $\Delta\phi$($\approx$ 1 meV), but small at high temperatures.

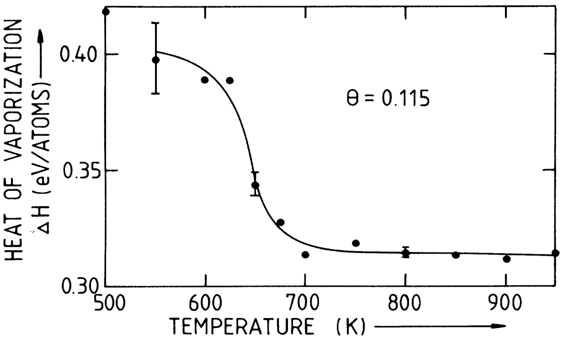

FIG. 2. Heat of 2D evaporation of Au on W(110) as a function of temperature as derived from work-function-change measurements.

Figure 2 shows the ΔH_{2D} results obtained for Au on W(110) by combining Eqs. (1) and (2) as a function of temperature. It is evident that ΔH_{2D} does not decrease monotonically with T but changes rather abruptly between 600 and 700 K from about 0.4 to 0.31–0.32 eV. This is just the behavior expected qualitatively for a roughening transition at a roughening temperature of $T_R = 640 \pm 20$ K. The result that ΔH_{2D} of the rough surface is approximately $\frac{3}{4}$ instead of $\frac{2}{3}$ of the value below T_R indicates that bonding is not only to nearest neighbors. If there were only nearest-neighbor interactions and if the lattice were square instead of the distorted hexagonal one on W(110) then the value of a in Abraham's theory would be 0.84 with use of $T_c = 1130$ K from Ref. 8 and Fig. 1 of Refs. 4 and 5; this corresponds to only an 8% difference between $E_s = (1+a)E/2$ and E. It is interesting to note that the T_R/T_c values obtained for other metals (Cu, Ni, Ag, and Pd) on W(110)[11] differ only slightly from the value 0.57 obtained here for Au (average value 0.55 ± 0.05). The same is true for the ratio $\Delta H_{2D}/\epsilon_{QC}$[11] where ϵ_{QC} is the interaction energy deduced from the experimental T_c values by use of the quasichemical approximation[9] (average value 3.66 ± 0.29). Thus it appears that there is some universal behavior irrespective of the electronic structure of the atom (noble or transition metal) and of the structure of the 2D crystal [commensurate (Ni, Cu, Pd) or incommensurate (Ag, Au)].

It may be argued that the nonmonotonic ΔH_{2D} change is not caused by roughening of the boundary between condensate and gas but rather by structural transitions within the condensate or within the gas phase. The only conceivable change in the gas is a transition from a monomer to a dimer or polymer phase with *de*creasing temperature which would cause a ΔH_{2D} change opposite to the observed one. Structural changes within the condensate can be ruled out because of the large magnitude of the change and because low-energy electron diffraction shows no evidence of melting or any other structural change.

In conclusion, a roughening transition, as predicted by Abraham[4,5] for the planar Ising model, is indicated by a detailed but straightforward analysis of work-function-change measurements of W(110) surfaces covered with submonolayers of Au and other metals. The 2D metal crystals are probably bounded by densely packed $[\bar{1}11]$ and $[1\bar{1}1]$ edges in which the lateral bonding is weakened by dipole-dipole repulsion. For better comparison with theory it would be desirable to extend the measurements to fcc (100) surfaces or to do calculations for the centered rectangular lattice of the bcc (110) plane.

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