Temperature Dependence of the Work Function of Adsorbate-Covered Metal Surfaces: A New Method for the Study of Two-Dimensional Phase Transitions

J. Kołaczkiewicz[(a)] and E. Bauer
Physikalisches Institut, Technische Universität Clausthal, D-3392 Clausthal-Zellerfeld, Federal Republic of Germany
and Sonderforschungsbereich 126, Göttingen-Clausthal, Federal Republic of Germany

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Submonolayer coverages of gold on tungsten (110) surfaces cause only a minor work-function *increase*. Heating such a surface produces a large reversible work-function *decrease* which depends on coverage and temperature and which can be attributed to a two-dimensional phase transition.

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The temperature dependence of the work function ϕ of a clean metal surface has long been the subject of experimental and theoretical study with the result that ϕ increases approximately linearly with temperature, with a temperature coefficient $d\phi/dT$ of the order 1×10^{-5} eV K.[1] This is also true for adsorbate-covered surfaces provided that the coverage and the location of the adatoms *normal* to the surface do not change with temperature. There has been the theoretical prediction that ϕ should change significantly with T also when the *lateral* distribution of adatoms changes in an order-disorder transition,[2] a prediction which is in disagreement with experiment.[3,4] This is not surprising because the work function is determined by short-range order, which does not change significantly during the transition because of the repulsive interaction between the atoms.

In this paper we report work function changes with temperatures as large as 0.6 eV at constant coverage without changes in the normal distribution, and give an explanation of this phenomenon. The surface on which these large changes are seen is a W(110) surface with submonolayer coverages of Au. The experiments were performed at a pressure of 5×10^{-11} Torr; the crystal surface had less than a 0.05° deviation from the (110) plane and less than 0.1% of a monolayer C contamination as determined by Auger electron spectroscopy (AES). AES was also used to determine the Au coverage θ, which was calibrated via the break at one monolayer in the AES signal versus deposition time curve.[5] In addition, the adsorbate was characterized by low-energy electron diffraction and thermal-desorption spectroscopy (TDS). The coverages derived from TDS agree, within the limits of error of the TDS monolayer determination ($\pm3\%$), with those obtained by AES. The work function change was measured with the retarding-field electron-beam method in the constant-current mode. In this mode the voltage necessary to maintain a constant current to the crystal—typically $\frac{1}{10}$ of the saturation current—is monitored continuously. Its change ΔV gives directly the work function change $\Delta\phi=-e\Delta V$. By proper shielding an accuracy of ±1.5 meV was obtained for $\Delta\phi$. The temperature was measured with a W 5%Re/W 26%Re thermocouple to ±5 K. The uncertainty in the absolute value of the Au coverage as determined by AES is $+0.015$ monolayers; for a series of small identical Au doses this amounts to only several thousands of a monolayer.

All Au depositions were made at 300 K but the $\Delta\phi(T)$ data reported here refer only to the reversible ϕ changes seen after the first temperature cycling. Before heating, the work function decreased initially very slightly with coverage due to the formation of many small two-dimensional Au islands as indicated by the low-energy electron diffraction (LEED) spot broadening. Cooling to 350 K after heating led to large Au islands as seen by sharp LEED spots and a slight irreversible ϕ increase due to the smaller number of atoms at the periphery of the islands. This number is, however, still large enough to reduce $\Delta\phi$ at submonolayer coverages far below the value expected from $\Delta\phi=+200$ meV at one monolayer. For example, $\Delta\phi=+7$ meV at $\theta=\frac{1}{4}$ and $\Delta\phi=+30$ meV at $\theta=\frac{3}{4}$.

The temperature dependence of ϕ was measured during cooling and is illustrated for several small coverages in Fig. 1. Zero for each curve is the respective $\Delta\phi_\theta=\phi(\theta)-\phi(0)$ at $T=425$ K shown together with θ as curve parameter. $T=425$ K was chosen in order to avoid excessive cooling times. All curves consist of a curved part common to all θ and a θ-dependent linear part. At $\theta\gtrsim0.3$ only the

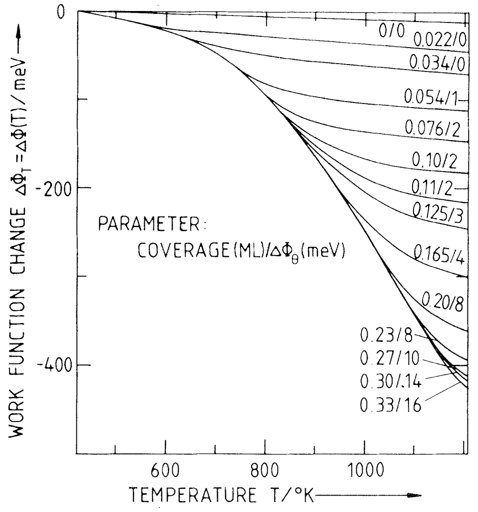

FIG. 1. Work function change $\Delta\phi_T$ of a Au-covered W(110) surface with temperature for several coverages shown as curve parameter together with the work function change $\Delta\phi_\theta$ relative to the clean surface at 425 K.

curved part is observed in the temperature range accessible without excessive desorption.

This general behavior of $\phi(T,\theta)$ can be explained easily by assuming (i) that the adsorbate consists of two-dimensional Au islands surrounded by a two-dimensional gas of Au atoms (and molecules) and (ii) that the dipole moment of a Au atom in the condensed phase is negligible compared to that of a Au atom in the gas phase. At sufficiently low temperature practically all Au atoms have condensed out and the work function change $\Delta\phi_\theta$ relative to the clean surface is nearly zero (see $\Delta\phi_\theta$ values in Fig. 1). With increasing T, the Au islands evaporate into the two-dimensional gas, thereby producing a θ- and T-dependent number of dipoles until all islands have disappeared. This terminates the rapid θ-decrease. The further decrease at low coverage is caused by the T-dependence of the dipole moments of the adsorbed atoms and by the contribution of the substrate; at high coverage it is caused by the dissociation of dimers, and possibly polymers, with increasing T.

A more quantitative description can be given in several ways. If the intersection of the extrapolated θ-dependent straight line segments with the θ-independent curved segment (see Fig. 1 for $\theta = 0.073$) is plotted as a function of θ, the coexistence line between single phase (gas) and two phase (gas + condensate) regions is obtained (Fig. 2). The scatter of the points is not so much due to the $\Delta\phi$, θ, and T errors but mainly caused by the difficulty in determining the intersection. Fits to the coexistence curves of various equations of state (Van der Waals, Dieterici, Guggenheim,[6] Bragg-Williams, and quasichemical approximation[7]) were made with the surprising result that the van der Waals equation gave the best fit. Only the quasichemical approximation allowed comparable fit. The curves shown in Fig. 2 are van der Waals coexistence curves with critical parameters $T_C = 1130$ and 1140 K and $\theta_C = 0.26$.

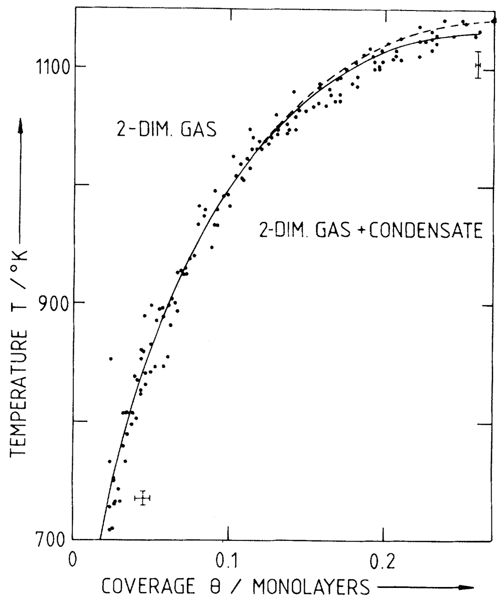

FIG. 2. Coexistence curve between single-phase and two-phase region of Au on W(110) as obtained from the data of Fig. 1. The data points are from four series of experiments, including those obtained from Fig. 1. The curve is the van der Waals coexistence curve for $T_C = 1130$ K and $\theta_C = 0.26$.

The order parameter of a real gas is the density difference $\rho_C - \rho_G$ between condensate and gas[8] or, in two dimensions, $\theta_C - \theta_G$. The critical exponent β of the order parameter of the van der Waals gas is $\frac{1}{2}$, that of the Guggenheim equation $\frac{1}{3}$, which is close to the three-dimensional Ising value 0.31. Guggenheim's equation describes the critical properties of three-dimensional real gases well; the van der Waals equation not only those of Au but also of Ag, Cu, Pd and Ni adsorbates on W(110).[9] This is in marked contrast to the condensation behavior of physisorbed layers as observed by adsorption isotherm measurements.[10,11] For the second layer of Ar on $CdCl_2$, $\beta = 0.16$ was obtained, i.e., a value close to the two-dimensional Ising value $\beta = \frac{1}{8}$, and coexistence curves similar to that from which $\beta = 0.16$ was derived were reported for the first layer of Ar on $MgBr_2$ and $FeCl_2$.[11] Thus, chemisorbed and physisorbed layers seem to differ in their two-dimensional condensation behavior.

The critical quantities T_C and θ_C allow the determination of the lateral interaction parameters if a two-parameter interaction potential such as the Lennard-Jones potential $U(r)=4\epsilon_2[(\sigma/r)^{12}-(\sigma/r)^6]$ is used. The parameters σ (hard core-diameter) and ϵ_2 (depth of potential well) are related to the van der Waals constants $a,b,$ via

$$b=\tfrac{1}{2}\int_0^\sigma d^2r=\tfrac{1}{2}\sigma^2\pi$$

and

$$a=-\tfrac{1}{2}\int_\sigma^\infty U(r)d^2r=-\tfrac{3}{5}\epsilon_2\sigma^2\pi.$$

With $kT_C=(8/27)(a/b)$ and $n_C=N_1\theta_C=1/3b$ [$N_1=$ monolayer density $\approx 14\times 10^{14}$ atoms/cm^2 for Au on W(110)] one obtains

$$\epsilon_2=-(45/16)kT_C=-0.274\text{ eV}$$

and

$$\sigma=[(3\pi/2)N_1\theta_C]^{-1/2}=2.414\text{ Å}.$$

These values are significantly smaller than those for Au-Au interactions in bulk Au as obtained by describing bulk properties with pairwise interaction potentials: $\epsilon_3=-0.451$ eV,[12] or $\epsilon_3=-0.441$ eV,[13] and $\sigma=2.637$ Å.[12,13] This is not surprising because the Au 6s electron contributes significantly to the bonding to the substrate, thus reducing lateral dimensions and bonding of the atoms.

The use of the Lennard-Jones potential for the lateral interactions of chemisorbed atoms is, of course, a very rough approximation. Certainly, just as in the bulk,[14] three-body forces also play an important role in the lateral interactions as demonstrated for many chemisorption systems with repulsive first-neighbor interactions. In view of the limited understanding of the lateral interactions on an atomic level, a phenomenological analysis appears more appropriate. Such an analysis is usually made on the basis of the Clausius-Clapeyron equation with the simplifying assumption of an ideal gas for the gaseous phase. This leads to the equation $E_v/k=T^2d\ln n/dT+T$ for the heat of vaporization per atom, n being the density of gas atoms. If, as in the case of Au on W(110), the dipole moment p_0 of the Au atom in the condensed phase is negligibly small, then the work function change is given by $\Delta\phi(\theta,T)=-4\pi epn(\theta,T)$. Here p is the dipole moment of the gas atoms and it is assumed that Au molecules may be neglected. Thus, an evaluation of $\Delta\phi$ in this manner not only gives the coverage dependence of E_v but also its temperature dependence which contains important information on the specific heat of the condensate. In general, p_0 may not be neglected and the gas also contains a θ- and T-dependent number of molecules which makes the analysis more involved. Such an analysis is in progress at present.

In conclusion, we have shown: (i) On a Au-covered W(110) surface large reversible work function changes with temperature can occur, in spite of constant coverage and the absence of T-dependent displacements of atoms with different electronegativity normal to the surface. (ii) The work function changes are caused by a two-dimensional phase-transition condensate vapor in the Au layer. (iii) The gas-condensate coexistence curve of the two-dimensional system can be obtained easily. (iv) This curve can be fitted well by the van der Waals equation of state which suggests that the critical exponent of the order parameter is $\frac{1}{2}$. When compared to the recently reported He atomic-beam scattering technique for the study of similar phase transitions[15] the present method has the advantage of being much simpler. Furthermore, a detailed analysis of (θ,T)[9] gives direct information on microscopic quantities such as dipole moments and molecular composition of the two-dimensional gas as well as phenomenological quantities such as two-dimensional vapor pressure and heat of vaporization.

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[a] Permanent address: Institute of Experimental Physics, University of Wrocław, 50 205 Wrocław, Poland.

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