

Adsorption of W on W(110): Work-Function Reduction and Island Formation

K. Besocke and H. Wagner

Institut für Technische Physik der Kernforschungsanlage Jülich, 517 Jülich, Germany

(Received 28 February 1973)

Work-function changes up to 0.6 eV were observed during the adsorption of W on a (110) W single-crystal surface for coverages below one monolayer. It is concluded that this is due to a varying structural arrangement of atoms in the outermost surface layer. Atoms in adpositions and ledge positions on their own lattice exhibit electric dipole moments causing work-function reductions with respect to the ideally flat surface.

I. INTRODUCTION

The electron work function of a clean single-crystal surface depends on the crystallographic orientation of the surface. Densely packed surface planes exhibit a higher work function than planes with a more open lattice structure.¹ Adsorption of atoms and molecules may cause work-function changes where, in general, electropositive adsorbates give rise to a work-function reduction and electronegative adsorbates to a work-function increase, respectively.

Several investigations have shown that the structural arrangement of atoms or molecules on a single-crystal surface can also have an effect on the work function. For impurity adsorption, e.g., Adams and Germer² found a decrease in work function upon a temperature anneal of a nitrogen-covered tungsten surface. A similar behavior was observed by Park and Farnsworth³ for oxygen on nickel. Besocke⁴ reported a marked work-function increase for a molybdenum-covered tungsten surface. In all these cases the coverage of the adsorbate did not change during the temperature anneal. Medvedev *et al.*⁵ have recently shown for the case of lithium adsorption on tungsten (112) that the short-range order in the adatom arrangement rather completely determines the work-function behavior whereas the long-range order as observed by low-energy electron diffraction (LEED) inserts a minor influence.

For clean single-crystal surfaces work-function changes were also observed when the structural arrangement of the atoms in the outermost layer deviates from the ideally periodic surface structure. Farnsworth and Madden⁶ found a work-function reduction after argon-ion bombardment of a (100) nickel surface. Erbudak and Fischer⁷ and Mönch⁸ reported a drastic decrease of the work-function of a (111) silicon surface in the transition region between the ordered (7×7) and (2×1) surface structures as observed by LEED. The latter two investigations on clean single-crystal surfaces show only qualitatively a relationship between the work function and some kind of surface disorder.

The following paper describes work-function measurements for the (110) tungsten surface for which deviations from the ideally periodic surface structure were produced by evaporation of W atoms. The results obtained show that the observed work-function changes can be understood in terms of electric dipole moments resulting from single atoms sitting on their own lattice as well as atoms in ledge positions. Quantitatively it is deduced that a single W adatom exhibits a dipole moment of about 1 D and a ledge atom an average dipole moment of about 0.3 D on (110) W. These results can be regarded as an experimental verification of the Smoluchowski¹ hypothesis that any deviation from an ideally flat-surface structure causes a reverse electric double layer by a "smoothing effect" of the electron distribution near the microscopic roughness.

II. EXPERIMENTAL

The experiments were carried out in a LEED-AES apparatus at a total pressure of 2×10^{-10} Torr. The W sample (6-mm diam 1.5-mm thickness) was cut by spark erosion from a high-purity (99.999%) MRC single-crystal rod. The sample was oriented within less than 0.5° to the [110] direction by Laue back reflection, ground and polished with diamond paste, electropolished and cleaned ultrasonically. To prevent contamination from the sample holder the sample was suspended by a pure W wire and mounted on a small heating box enabling the sample to be heated up to 2500 °C. The sample was degassed in the ultra high vacuum system for 8 h at 2000 °C. Carbon was removed from the sample by an anneal at an oxygen pressure of 5×10^{-8} Torr for 12 h at 2000 °C. After this treatment the oxygen was flashed off at a temperature above 2500 °C. This cleaning process was controlled by LEED and AES. The LEED pattern showed the perfect (110) structure and the Auger spectra did not indicate any traces of contamination. W was deposited on the sample from a high-purity (99.999%) filament source using a flash evaporation technique. The W filament

was degassed for several hours at 2000 °C. The Auger spectra taken after the successive evaporation steps did not show any contamination. The deposition rate was calibrated with a quartz microbalance and amounted to 0.02 monolayer per evaporation flash. After each evaporation step the resulting work-function change was measured by the contact potential difference between the sample and the suppressor grid of the LEED optics as derived by the cutoff of the secondary electrons. This method was checked with the retarding field technique in the case of molybdenum adsorption on W(110).⁴ Both methods yielded identical results.

III. RESULTS

Figure 1 shows the work-function change as a function of the amount of deposited W on W(110). The amount of deposited W is given in equivalent monolayers of a (110) plane, i. e., θ equals one monolayer corresponds to 1.42×10^{15} atoms/cm.² The three different curves were obtained for three different substrate temperatures, room temperature T_1 and elevated temperatures T_2 and T_3 . No provisions were made to determine the temperature exactly so that only a rough estimate can be given with $T_1 = 20^\circ\text{C} < T_2 < T_3 < 100^\circ\text{C}$. The work-function change for a given coverage shows a very strong dependence on substrate temperature. For the room-temperature curve work-function changes of up to 0.6 eV are observed. For coverages of more than one monolayer no further change in work function was found for the three different temperatures. The LEED patterns obtained for increasing coverage did not reveal any other structure besides the one for W(110) but the spots became more and more diffuse and the background intensity increased. For $\theta < 0.2$ no marked changes were recorded. Raising the temperature of the W sample from any state as shown in Fig. 1 to about 700 °C for 10 min caused the work function to increase again to its starting value and the LEED spots became sharp. This observation shows that the structural arrangement of the atoms in the surface layer exerts a strong influence on the work function.

IV. DISCUSSION

Work-function changes caused by the adsorption of foreign atoms are usually explained in terms of an electric dipole moment per adsorbed atom. Dipole moment μ and work-function change $\Delta\phi$ are related by the Helmholtz equation $\Delta\phi = 4\pi\mu n$ where n stands for the number of adsorbed atoms per cm.² Applying the same argumentation to the present results leads to the conclusion that a W atom adsorbed on the (110) plane gives rise to an electric dipole moment and hence a work-function

reduction. This may phenomenologically be understood by considering Smoluchowski's¹ smoothing effect of the electron density distribution, especially for an adatom sitting on a close-packed lattice plane like the (110) plane of a bcc lattice.

Considering the effect of substrate temperature and the nonlinear dependence of work-function change on coverage (even for small coverages) in Fig. 1 implies that the experimental results cannot be explained by a single-atom adsorption model alone. For in this model the substrate temperature should not have a strong influence because the reevaporation rate is negligible. Furthermore, the work-function change should, at least for small coverages, be proportional to the number of adsorbed atoms according to the Helmholtz equation.

The following model is consistent with the experimental results and is supported by field-ion-microscope (FIM) observations on the mobility of W atoms on the W(110) plane.^{9,10} According to Tsong,⁹ single W atoms do combine to form multi-atomic clusters even at room temperature. This cluster formation depends strongly on substrate temperature. We therefore assume that the same type of cluster formation occurs after the first deposition step. The number n_i of clusters formed will be a function of the substrate temperature, i. e., at lower temperatures more clusters will be formed than at higher temperatures owing to the temperature dependence of the mean displacement of a single adatom. The W atoms deposited by the subsequent evaporation steps will migrate to these clusters or islands and increase their lateral dimensions. For a given coverage θ the total circumference of islands L is proportional to the square root of the number of islands formed and hence a function of substrate temperature,

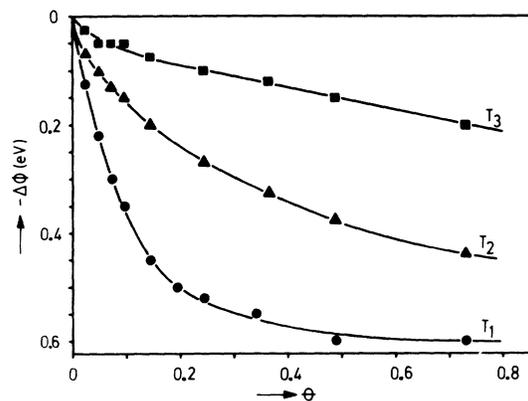


FIG. 1. Work-function change $\Delta\phi$ vs coverage θ for various substrate temperatures $T_1 = 20^\circ\text{C} < T_2 < T_3 < 100^\circ\text{C}$.

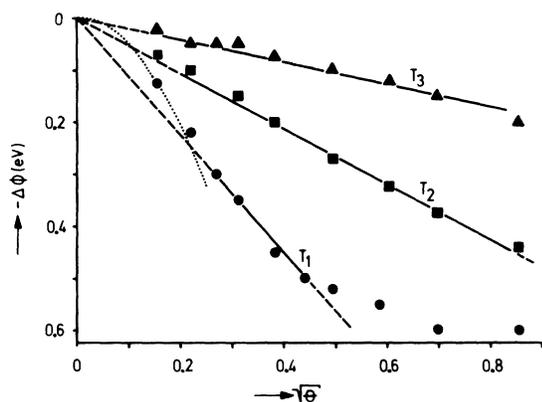


FIG. 2. Work-function change $\Delta\phi$ from Fig. 1 as a function of the square root of coverage θ .

$$L = s \sqrt{n_i} \sqrt{\theta} \text{ (cm/cm}^2\text{)}.$$

The factor s depends on the shape of the islands. If one assumes circular islands of equal diameter, s attains a value of $2\sqrt{\pi}$. For a given number of islands n_i per cm^2 , i. e., for a given substrate temperature, the total circumference length will be proportional to the square root of coverage.

The influence of island formation on the work function can readily be understood if one attributes an electric dipole moment to an edge atom. The smoothing effect again provides the physical understanding as in the case of a single adatom. Different edge structures which are consistent with the underlying substrate structure will give rise to different dipole moments. Atoms in the interior of the islands will not contribute to a work-function change because their structural arrangement is the same as for a perfect (110) plane.

In order to test this concept we plotted in Fig. 2 the work-function change shown in Fig. 1 as a function of the square root of coverage θ . The expected linear dependence is observed for all three substrate temperatures. Also the extrapolations of the linear portions of these curves go through zero as is to be expected if the work-function decrease is only caused by edges. The slope shows the expected decrease with increasing temperature according to the decreasing number of islands formed. For the room-temperature curve deviations from the linear dependence occur for very small and higher coverages. This is understandable because for very small coverages only single adatoms exist on the surface due to their small mobility at this temperature. From this deviation a first estimate of the dipole moment per single adatom can be given. The dotted curve represents a parabolic work-function change which corresponds to a linear change with coverage according to single-

adatom adsorption. For higher coverages the room-temperature curve deviates from linearity due to the mutual interference of nearly spaced edges of neighboring islands. In general, all three curves level off for high coverages according to some kind of equilibrium surface structure which is caused by the interplay of island coalescence and new island growth. The observation that the work function increases again to its starting value after a temperature anneal at 700°C is explained as follows: at this high temperature the islands formed at the lower deposition temperatures will coalesce to large areas causing a smooth surface structure with a very small amount of monoatomic steps like the original surface structure before the deposition started. This is consistent with the observed sharp LEED pattern taken after the 700°C anneal.

V. CONCLUSIONS

From the present experimental results and model considerations the following conclusions can be drawn. W atoms in adpositions and ledge positions exhibit an electric dipole moment on the W(110) plane. Preliminary estimates of these dipole moments are: 1 D for an adatom and an average value of 0.3 D for an atom in a ledge position. For more open surface structures such as the (100) or (111) plane these values will presumably be lower. In general, any deviation from an ideally flat-surface structure will cause a work-function decrease. Mueller¹¹ and Plummer and Rhodin¹² investigated this problem by field emission measurements and found a strong dependence of the emission current on the perfection of the surface. Because of the specific influence of the local field distribution with this measuring technique a proper evaluation in terms of a change in work function could not be given.

Observations by Farnsworth and Madden⁶ on the work-function change of a (100) nickel surface after argon ion bombardment can be explained according to our findings. Work-function measurements can therefore provide additional information on the ordering state of a crystal surface. As shown for W on W(110) the work function may respond to changes in surface atom arrangement more sensitively than the LEED pattern.

It would be interesting to compare our values for the dipole moment with the results of model calculations for the adsorption of W and other 5d transition elements on W,¹³ which up to the present time have been solely tested by experimental values of the binding energy.¹⁴ The dipole moment may, however, show a stronger dependence on substrate orientation and the chemical nature of the adsorbate than the binding energy as known from alkali adsorption on transition metals.¹⁵

- ¹R. Smoluchowski, *Phys. Rev.* **60**, 661 (1971).
²D. L. Adams and L. H. Germer, *Surf. Sci.* **27**, 21 (1971).
³R. L. Park and H. E. Farnsworth, *J. Chem. Phys.* **43**, 2351 (1965).
⁴K. Besocke, in *Proceedings of the Third International Conference on Thermionic Electrical Power Generation*, Jülich, 1972 (Zentralstelle für Atomenergie-Dokumentation, Leopoldshafen, W. Germany, 1972), Vol. 3, p. 1385.
⁵V. K. Medvedev, A. G. Naumovets, and T. P. Smereka, *Surf. Sci.* **34**, 368 (1973).
⁶H. E. Farnsworth and H. H. Madden, *J. Appl. Phys.* **32**, 1933 (1961).
⁷M. Erbudak and T. E. Fischer, *Phys. Rev. Lett.* **29**, 732 (1972).
⁸W. Mönch (private communication).
⁹T. T. Tsong, *Phys. Rev. B* **6**, 417 (1972).
¹⁰G. Ehrlich and F. G. Hudda, *J. Chem. Phys.* **44**, 1039 (1966).
¹¹E. W. Mueller, *Z. Phys.* **126**, 642 (1949).
¹²E. W. Plummer and T. N. Rhodin, *Appl. Phys. Lett.* **11**, 194 (1967).
¹³B. J. Thorpe, *Surf. Sci.* **33**, 306 (1972), and references contained therein.
¹⁴E. W. Plummer and T. N. Rhodin, *J. Chem. Phys.* **49**, 3479 (1968).
¹⁵J. W. Gadzuk, J. K. Hartman, and T. N. Rhodin, *Phys. Rev. B* **4**, 241 (1971).