DETERMINATION OF THE BOND ENERGY IN TWO-DIMENSIONAL CRYSTALS OF ZIRCONIUM ADSORBED ON TUNGSTEN AND NIOBIUM

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Abstract

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DETERMINATION OF THE BOND ENERGY IN TWO-DIMENSIONAL CRYSTALS OF ZIRCONIUM ADSORBED ON TUNGSTEN AND NIOBIUM

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A detailed study of two-dimensional crystallization and sublimation is important not only because of the growing interest in surface phenomena in general. Two-dimensional crystals of one and the same composition, depending on the structure of the substrate, may have different intrinsic structures. In such a case, measuring the bonding forces is a way of studying the interaction of adsorbed particles at short distances (characteristic of the solid phase). By investigating two-dimensional crystals on crystallographically different regions of different substrates, we can arbitrarily vary the packing density of the adsorbed particles and their mutual arrangement. Both of these are usually rigidly fixed in a three-dimensional crystal.

In the work described below, the processes of growth and disappearance of two-dimensional Zr crystals on the surface of W and Nb single crystals were observed with the aid of a field-emission microscope (electron projector). From the temperature dependence of these processes it was possible to determine the bond energy of Zr in a two-dimensional lattice for four physically different substrates (two regions on each material*). Monoatomic Zr films on both W and Nb provide sufficient emission contrast. Therefore, growing two-dimensional Zr crystals, as their dimensions approach the resolution limit (practically even earlier), appear as bright spots against the background of their surroundings.

* The first region, designated in Table 1 as {225}, contains the nearest neighborhoods of the {112} face, encompassing the region of the [110] zone from {338} to {7 7 16}. The second region, designated in Table 1 as {119}, is located in the neighborhood of the cube face (001) and contains the region of the [110] zone from {117} to {1 1 1}.

Fig. 1. Field-emission images of a W single crystal (*a*–*g*) ($r_0 \approx 8000$ Å at a resolution $\delta \approx 80$ Å) and Nb (*d*–*k*) ($r_0 \approx 5000$ Å, $\delta \approx 60$ Å), and various stages of formation and disappearance of two-dimensional Zr crystals on their surfaces. All photographs were taken at room temperature of the tips.

Fig. 1

Figure 1: Fig. 1

a –standard Zr layer deposited on W at $T = 295°$K. W was cleaned of the previous layer by annealing at $T = 2450°$K for 3 min. The atomic Zr beam is incident normally to the (211) face. $1 \cdot 10^{14}$ atoms/cm^2 of Zr were deposited on it. The mean degree of coverage (referred to the entire surface) $\theta \approx 0.1$. Arrows indicate the regions of measurement of Q_M and Q_{sub}.

b –standard layer after annealing at $T = 988°$K for 90 sec. Spots appeared in region (252). In studying the growth, the final moment is somewhat earlier; it corresponds to the first spot that appears, less noticeable than in the figure.

v –after annealing at $T = 1313°$K for 60 sec. The spots in region (252) disappeared (but islands appeared in regions closer to (010)). The first spots appeared in region (119), where Zr migrated.

g –after annealing at $T = 1428°$K for 20 sec. The spots around (001) disappeared, but are still present in the neighborhood of (010).

d –Nb after deposition of Zr and a standard "flash" (1213°K, 10 sec). In appearance it resembles pure Nb, but contains Zr in the form of a "frozen" two-dimensional gas with $\theta \approx 0.1$, distributed over the entire surface.

e –annealing at 688°K for 23 min. Appearance of Zr islands in the neighborhood of $\{112\}$. The final stage in the growth study corresponds to the appearance of the first, still barely noticeable islands.

zh –annealing at 757°K for 10 min. Growth of many two-dimensional crystals in region $\{225\}$ and its neighborhood. The initial stage in the study of two-dimensional evaporation is somewhat earlier.

z –annealing at 803°K for 10 min. The islands in region $\{225\}$ have dissolved (but appeared in neighboring regions closer to the poles [001]).

i –annealing at 851°K for 7.5 min. Formation of islands around [001]. The standard initial state in measuring the dissolution time in these regions corresponds to the appearance of a few first islands.

k –annealing at 983°K for 6 min. Complete disappearance of islands near the poles [001].

Fig. 1

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Table 1

Crystallographic face	System	Growth of two-dimensional crystals: initial conditions	Growth of two-dimensional crystals: final conditions	Growth of two-dimensional crystals: temperature interval, T, K	Q_{m}, eV	Growth of two-dimensional crystals: graph no. in Fig. 2	Two-dimensional sublimation: initial conditions	Two-dimensional sublimation: final conditions	Two-dimensional sublimation temperature interval, T, K	Q_{sub}, eV	Two-dimensional sublimation: graph no. in Fig. 2	Binding energy Q_{b}, eV
{225}	Zr – W	Fig. 1a	Fig. 1b	898 – 1278	0.99± 0.07	1	Fig. 1b	Fig. 1v	1263 – 1338	3.65± 0.12	2	2.66± 0.19
{225}	Zr – Nb	Fig. 1d	Fig. 1e	663 – 783	0.87± 0.06	3	Fig. 1zh	Fig. 1z	803 – 903	2.75± 0.04	4	1.88± 0.10
{119}	Zr – W	Fig. 1a	Fig. 1v	1088 – 1328	1.37± 0.05	5	Fig. 1v	Fig. 1g	1408 – 1510	4.42± 0.10	6	3.05± 0.15
{119}	Zr – Nb	Fig. 1d	Fig. 1i	708 – 818	1.31± 0.12	7	Fig. 1i	Fig. 1k	923 – 993	4.20± 0.12	8	2.89± 0.24

against the background of the substrate. For Zr spots on W, their two-dimensional, rather than three-dimensional, nature was experimentally demonstrated twice, by different methods ([1,2])*. Figure 1 shows how the various stages of growth and dissolution of the spots appear on the projector screen.

The most reliable method for measuring the activation energies of thermally activated processes is to calculate them from the slope of curves of the form $\lg t = f(1/T)$—the so-called Arrhenius plots (t is the time of some characteristic process, T is the absolute temperature). In this case, the very fact that a straight line is obtained experimentally in the indicated coordinates testifies with high probability that the observed phenomenon is based on an elementary process described by the formula of Ya. I. Frenkel ([3])

$$\tau = \tau_0 \exp(Q/kT) \tag{1}$$

(where τ is the mean waiting time for an elementary displacement associated with overcoming, by thermal excitation, a barrier of height Q; τ_0 is the period of oscillation of the particle in the potential well).

Judging from the plots in Fig. 2 (for measurement details see Table 1, the explanations to Fig. 1, and note **), both the process of dissolution of bright spots and the process of their growth proved to be activated. By itself, the growth of any crystal should proceed with the release of energy. In our case the growth process is associated with the peculiarities of the motion of particles of a two-dimensional gas in the adsorbed layer, with an activated process: surface migration. Therefore the energies Q_{m}, calculated from the slope of straight lines 1, 3, 5, 7 in Fig. 2, we attribute to the migration of Zr on W and Nb in the corresponding regions. During the transition of atoms from the two-dimensional crystalline state to the state of a two-dimensional gas (dissolution of islands), Q_{m} must again be expended. Consequently, the pure binding energy Q_{b} in the two-dimensional Zr crystal can be obtained as the difference between the two-dimensional sublimation energy (Q_{sub}, measured from the slope of plots 2, 4, 6, 8 in Fig. 2) and Q_{m}:

$$Q_{\mathrm{b}} = Q_{\mathrm{sub}} - Q_{\mathrm{m}}. \tag{2}$$

* There is also no doubt that the spots are caused specifically by zirconium, and not by some impurity. The spots do not appear on clean W without deposition of Zr. The source (evaporator) of Zr was a drop of iodide Zr melted on a W filament in a vacuum of 10^{-7}–10^{-8} torr. Before deposition of Zr, the filament was heated for a long time in this vacuum to 2500–3000°C. Identical results were obtained with sources of different degrees of training. The experiments were carried out in pumped-out projectors in a vacuum of 10^{-10}–10^{-12} torr with respect to adsorbed gases. Experiments with Zr on Nb were carried out analogously. Nb purified by zone melting was used.

** The temperature was measured by optical pyrometry at $T > 1100^\circ$ K and, at lower T, from the change in resistance of the shank carrying the tip. A pulsed high voltage was used; therefore the electric field had practically no effect on the processes under study.

The main results of the measurements and some of their details are given in Table 1. The principal conclusions following from the measurements are:

1. In all cases $Q_{\mathrm{sub}} \gg Q_{\mathrm{m}}$. The bonding energy in the two-dimensional lattice is a considerable quantity. Two-dimensional crystallization substantially blocks migration.
2. Both Q_{m} and Q_{sub} differ noticeably for all four measurement regions. In this connection, crystallographic differences play the predominant role in comparison with differences in the type of substrate. Q_{m} and Q_{sub} may

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Figure 2: Fig. 2. Arrhenius plots for the growth and two-dimensional evaporation of surface Zr crystals on W and on Nb. (The correspondence of the plots to the processes studied is given in Table 1. Repeated points are indicated by circles.)

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depend on the initial concentration of the adsorbate, but in the present work we used approximately identical concentrations both in the case of the W substrate and in the case of the Nb substrate.

3. Q_b, which should apparently depend only on the distance between Zr atoms and on their arrangement, proves to be much larger near the {001} face, and for the W substrate always larger than for the niobium substrate. Following the arrangement of potential wells on the {001} face of W (lattice constant $a = 3.16$ Å), the Zr atoms pack densely on it. Correspondingly, on {001} Nb ($a = 3.29$ Å) the distances between Zr atoms are somewhat larger. The vicinities of {001} contain "terraces" with a structure of the {001} type. In regions near {112}, the potential wells of the adsorbent impose on the Zr adatoms a looser packing, and a somewhat looser one in the case of Nb. The measured Q_b values agree qualitatively with the considerations given above regarding packing density.
4. If Q_b for the {001} W environment is commensurate with Q_b for the {001} face itself, then one may try to estimate Q_b for the square close-packed lattice realized on it, starting from the known bulk heat of sublimation of Zr, equal to 6.30 eV ([4]). In close packing on {001} W, Zr atoms with a diameter of 3.16 Å are at the same distances as those inherent in the bulk crystal. In the square Zr lattice on {001} W each atom has 4 nearest neighbors; in the bulk β-Zr crystal (body-centered cubic lattice), 8 neighbors. Thus the desired bond energy should amount to half the heat of sublimation, i.e., 3.15 eV. This is close to the measured value $Q_\mathrm{b} = 3.05$ eV.

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CITED LITERATURE

1. V. N. Shrednik, *FTT*, **1**, 1134 (1959).

2. V. N. Shrednik, *FTT*, **3**, 1750 (1961).

3. Ya. I. Frenkel, *Zs. Phys.*, **26**, 117 (1924).

4. A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements*, Publishing House of the Academy of Sciences of the USSR, 1961, p. 373.

Note: Figure translations are in progress. See original paper for figures.