

Layer-by-layer growth of lithium films on tungsten and molybdenum (011) faces: manifestations in the work function

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Some structural features which are evidence of a layer-by-layer film growth have been observed for the first time in the behavior of the work function upon the formation of Li polylayers on W and Mo (011) faces. It is suggested that films with a (011) bcc orientation form at 300 K, while films with the (0001) orientation of a rhombohedral Li lattice form at 77 K. The difference is explained in terms of a polymorphism of Li.

The phase changes which occur in adsorbed films during the growth of a coating are manifested in several characteristics, in particular, the concentration dependence of the work function. The basic changes in the work function ϕ are known to terminate at the formation of the first monolayer of the adsorbate.¹

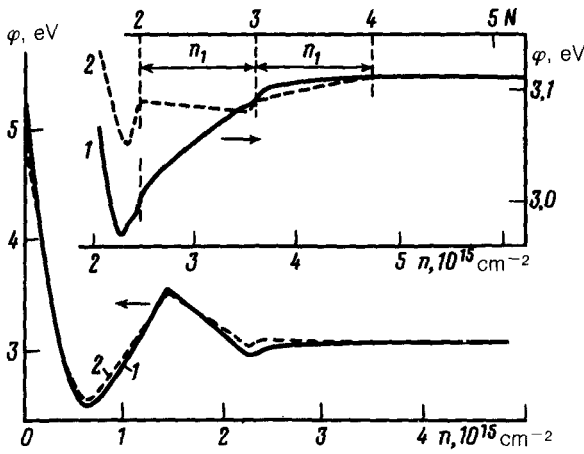


FIG. 1. Concentration dependence of the work function for (1) the Li-W (011) system and (2) the Li-Mo (011) system. Shown at the top are curves recorded beginning with the filling of the second layer [N is the number of layers; $n_1 = (1.17 \pm 0.02) \times 10^{15} \text{ cm}^{-2}$]. The substrate temperature is 300 K.

Our purpose in this study was to detect structural features in the behavior of ϕ during the growth of adsorbed supermonolayer films by improving the measurement accuracy. We studied the Li-W (011) and Li-Mo (011) systems. In this version of the contact-potential-difference method, the apparatus automatically records curves of the behavior of the value of ϕ of the surface during adsorption²: $\phi(t)$. The sensitivity of the procedure was a few millielectron volts. The flux of lithium atoms was strictly calibrated, so that the data on $\phi(t)$ could be used to construct curves of $\phi(n)$, where n is the surface concentration of lithium atoms (Fig. 1). This calibration was carried out over the time taken to reach ϕ_{max} during the formation of the first layer.³ As the initial work function of the clean substrates we adopted values of 5.35 eV and 5.0 eV for the tungsten and the molybdenum, respectively.⁴ The behavior $\phi(n)$ during the formation of the first and second lithium layers is described in Refs. 3 and 5, and we will not discuss it here.

During the formation of supermonolayer coatings at $T = 300 \text{ K}$, the work function ϕ undergoes changes up to $n \approx 5 \times 10^{15} \text{ cm}^{-2}$ (the top part of Fig. 1), i.e., up to the formation of essentially four atomic layers, on both substrates. The curves reproduced from the diagram recordings reveal changes in slope, which repeat after the deposition of each portion $n_1 = (1.17 \pm 0.02) \times 10^{15} \text{ cm}^{-2}$, starting at the second layer. This concentration is extremely close to the concentration of atoms on the (011) face of bcc bulk lithium, which is $1.15 \times 10^{15} \text{ cm}^{-2}$, according to the lattice constant of lithium at $T = 300 \text{ K}$ ($a = 3.502 \text{ \AA}$; Ref. 6). It can be concluded on this basis that the deposition on these substrates involves a layer-by-layer formation of single-crystal films with the (011) orientation. The layer-by-layer growth of the film on molybdenum proceeds to at least four layers, and that on tungsten to slightly more than three layers; then the changes in ϕ halt. The value found for ϕ for the lithium film at $n \approx 5 \times 10^{15} \text{ cm}^{-2}$, $3.11 \pm 0.05 \text{ eV}$, refers to a close-packed (011) lithium face. We know of no other experimental data on ϕ_{hkl} for lithium. We simply note that the value found agrees with the value for polycrystalline lithium.⁴

During the deposition of lithium on the (011) face of molybdenum at 77 K,

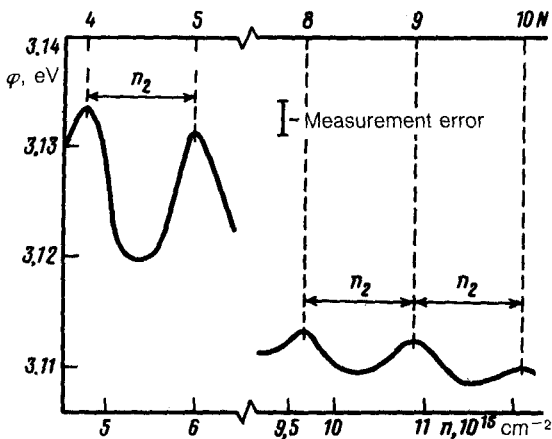


FIG. 2. Time evolution of ϕ during the formation of the fifth and subsequent layers of lithium on the (011) face of molybdenum at 77 K [N is the number of layers; $n_2 = (1.22 \pm 0.02) \times 10^{15} \text{ cm}^{-2}$].

changes in ϕ are observed even after the deposition of the fourth layer (Fig. 2). The strict periodicity of this dependence is interesting. The amplitude of the changes in ϕ , which starts at ~ 0.015 eV, falls off progressively with increasing film thickness, and after nine or ten layers the changes in ϕ cease, within the resolution of the method. The period of this dependence corresponds to a concentration $n_2 = (1.22 \pm 0.02) \times 10^{15} \text{ cm}^{-2}$, which differs from the value found at 300 K. In explaining this fact we need to take into consideration the circumstance that at $T < 80$ K, according to recent results,⁶⁻⁸ a polymorphic conversion occurs in a lithium crystal, from a bcc structure to a close-packed rhombohedral phase, with lattice constants $a = 3.0986 \text{ \AA}$ and $c = 22.735 \text{ \AA}$ (Ref. 6). It is quite probable that this conversion is also occurring in our case. The value of n_2 agrees within $\sim 2\%$ with the concentration of atoms on the close-packed (0001) face of the rhombohedral lithium lattice ($1.203 \times 10^{15} \text{ cm}^{-2}$). This result is evidence for the formation at 77 K of a single-crystal lithium film with this face oriented parallel to the surface of the substrate. With regard to the decrease in ϕ between the fourth and tenth layers (≤ 0.02 eV; Fig. 2), the apparent reason is a very slight decrease in the structural quality of the surface layers of the film in the course of the film growth.

Although the processes by which the films grow on tungsten and molybdenum at 300 K are of the same nature, the curves of $\phi(n)$ in the vicinity of the second and third layers are quite different for these two substrates. During the formation of the second layer, for example, the change in ϕ on tungsten is $\sim 20\%$ greater than that on molybdenum, and in the third layer the magnitude of the change in ϕ differs by nearly an order of magnitude. Furthermore, during the formation of the third layer on tungsten, we observe a monotonic increase in ϕ , while on molybdenum there is a linear decrease. The atomic structure of the substrates which were used in these experiments was essentially identical (the lattice constants differ by only 0.018 \AA), so that this structure should play no significant role in the observed differences. The results found here can be explained in terms of a particular feature of the adsorption binding of lithium to tungsten and molybdenum: different contributions of the ionic and covalent components of the binding. This conclusion follows from the fact that the heats of adsorption

of lithium on these substrates are essentially identical, but the dipole moment of the bond on molybdenum is $\sim 20\%$ smaller than that on tungsten. In general, it can be concluded that the effect of the substrates on the electronic properties of the lithium films grown at 300 K extends to a depth of about four layers of the adsorbate. A study of diffusion in lithium polylayers on the (011) faces of tungsten and molybdenum has also revealed substantial differences between these substrates.^{5,9}

In summary, this increase in the accuracy of ϕ measurements has made it possible to obtain some qualitatively new physical results which are evidence of a layer-by-layer growth of single-crystal films of the alkali element lithium and of an effect of the temperature on the structure of the films that form in the course of adsorption.

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