Phase transitions in submonolayer strontium films adsorbed on the (011) face of tungsten

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Phase transitions in submonolayer strontium films adsorbed on the (011) face of a tungsten crystal are investigated by a low-energy electron-diffraction technique at temperatures between 5 and 300°K. At low temperatures there are three regions of homogeneity and two regions of first-order phase transitions in the phase diagram. A polymorphic transformation of the strontium film is observed. From a comparison of the phase diagram and the concentration dependence of the adsorption heat it is concluded that as the coverage increases the interaction forces between the adsorbed strontium atoms reverse sign. The relation between the work function and the observed film structure is also investigated. Data are obtained on the effect of the substrate temperature during film deposition on the film structure, and on the effect of the order-disorder transition in the film on the work function.

1. INTRODUCTION

Interest in the investigation of two-dimensional phase transitions in adsorbed films on solid surfaces has noticeably increased of late[1-5]. This is caused to a considerable degree by the improved facilities for experimentation in this region. For example, the method of diffraction of slow electrons, which is rapidly developing at present, makes it possible to investigate in detail the appended structure of ordered two-dimensional phases.

From the physical point of view, the study of phase transitions in adsorbed films is of particular interest because the interaction of the particles on the surface can have a rather unique character. Thus, in the case of a strongly polar bond between the adsorbed atoms and the substrates, a major role is played by the dipole-dipole repulsion between the adsorbed atoms. One might assume that for this reason, in contrast to films with attraction interaction between the adsorbed atoms, no phase transition of the type of two-dimensional condensation can be realized in films with repulsion even at the lowest temperatures. However, such transitions were indeed observed, albeit in a limited range of surface concentrations[2,6], in adsorbed films of a number of electropositive elements on metals. Bol'shov and Napartovich have shown that this can be attributed to the strong decrease of the charge of the adsorbed atoms with increasing degree of coating, as a result of which their uniform distribution on the substrate becomes unstable when a certain critical concentration is reached[7,8].

The main purpose of the present article was to investigate further phase transitions in submonolayer films with strong polar bond and to obtain on this basis data on the interaction of the adsorbed atoms. The object of the study was a system consisting of strontium and the (011) face of tungsten. The dipole moment of the bond in this case amounts to ≈7 debye at small degrees of coating[9].

A distinguishing feature of the present experiments was that the investigated temperature region was extended to T = 5° K whereas the earlier investigations of similar systems were carried out only at T = 77° K. In the investigation of the nature of the interaction between the adsorbed atoms it is important, in principle, to study the behavior of the system precisely at low temperatures, when the equilibrium structure of the film is determined primarily by the energy factor rather than the entropy factor.

2. PROCEDURE

The structure of the adsorbed films was investigated by diffraction of slow electrons (10–100 eV). The apparatus was made entirely of glass with one of the stubs in the form of a double Dewar vessel. The outer part of the vessel was filled with liquid nitrogen and the inner one with liquid helium. Molybdenum leads sealed into the glass passed through the interior of the vessel. A tungsten-crystal substrate, oriented with the (011) face, was mounted on these leads. The temperature of the crystal was determined with a thermocouple of tungsten–rhenium alloys VR5-VR20. All the parts of the apparatus were thoroughly outgassed, so that the partial pressure of the active components of the residual gases in the apparatus did not exceed $\sim 10^{-11}$ Torr. The strontium evaporator was described in [9], and the remaining details of the procedure in [2,6].

In experiments of one type we followed the variation of the electron diffraction pattern when the strontium was evaporated on a tungsten crystal oriented with the (011) face. The flow of the strontium atoms to the crystal was maintained constant. By fixing the temperature of the crystal, it was possible to register the time variation of the intensity of the appearing superstructure reflections; when necessary, the film could be annealed beforehand. In experiments of another type, after evaporating a certain amount of strontium on the surface, we measured the dependence of the intensity of the diffraction beams on the substrate temperature. The aggregate of these data makes it possible to construct the phase diagram of the adsorbed film[7]. Simultaneously with observing the diffraction patterns, we registered during the strontium-evaporation process also the change in the work function (by the contact potential difference method). Using the dependence of the work function of Sr–W(011) on the surface concentration n of the adsorbed atoms of strontium, which was obtained in [9], we could determine the value of n at each instant of time. The concentration scale was calibrated more accurately by analyzing the electron diffraction patterns, just as described in our earlier paper[11].

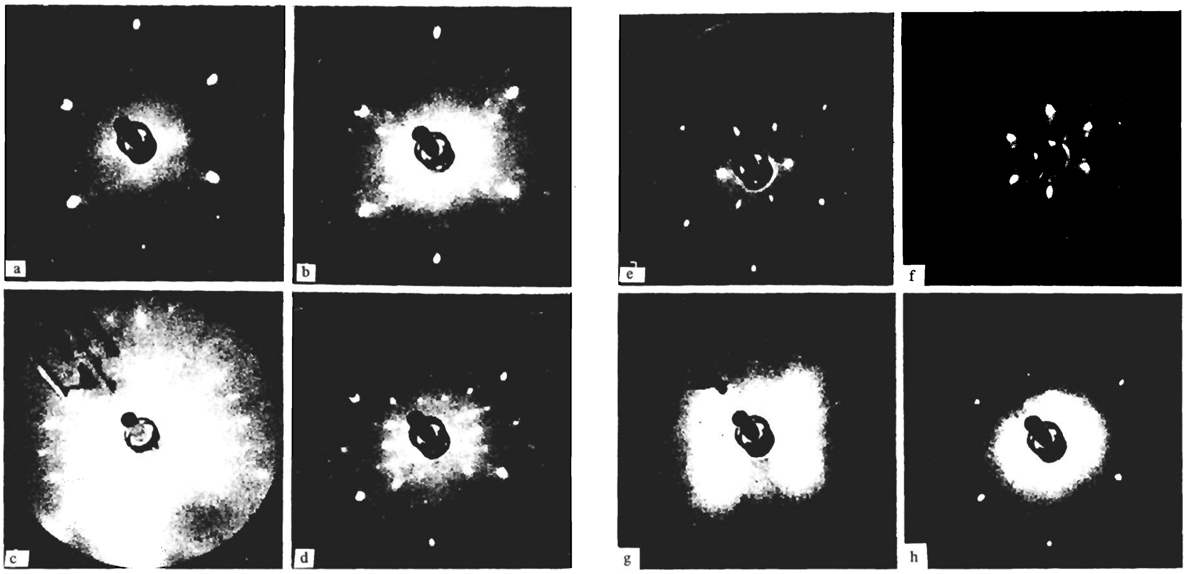

FIG. 1. Diffraction patterns of the system Sr—ω(011) at T = 5° K; a) clean substrate, b) n = 6.67 (n is in units of 10^{14} cm^{-2} throughout); c) 1.2, d) 1.4; e) 4;2; f) 5.0; g) 1.0; h) 5.0; Pictures b—f) are for films annealed at 300—400° K, while g and h are for films that were not annealed. The electron energy was 54 eV, with the exception of g (17.5 eV).

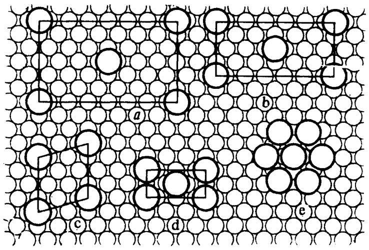

FIG. 2. Models of the structure of the Sr film: a—c) structures of α phase at stoichiometric ratios n:nW equal to: a) 1:21, lattice c (7 x 3); b) 1:12, lattice c (6 x 2); c) 1:10, lattice c (10 x 2); d) β phase, lattice c (3 x 1); e) γ phase, hexagonal lattice.

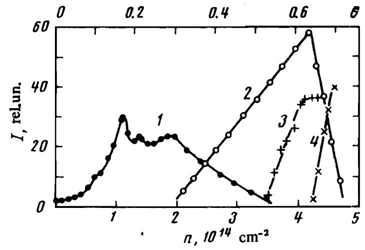

FIG. 3. Dependence of the intensity of the diffraction reflections of different phases on the concentration of the adsorbed atoms: 1—α, T = 77 K, 2—β, T = 77 K, 3—γ, T = 280 K, 4—γ, T = 77 K.

The phase transitions were used only in the submonolayer region, in which the adsorbed film could be regarded as a two-dimensional system.

3. RESULTS AND DISCUSSION

Figure 1 shows the diffraction patterns observed at different stages of the evaporation of the strontium on the (011)W face, while Figure 2 shows the sequence of structures of fundamental phases, produced by the adsorbed atom of the strontium with increasing surface concentration, corresponding to these electron diffraction patterns. Figures 3 and 4 show typical plots of the intensity of the corresponding diffraction beams on the concentration and the temperature, while Figure 5 shows the phase diagram plotted on the basis of these relations.

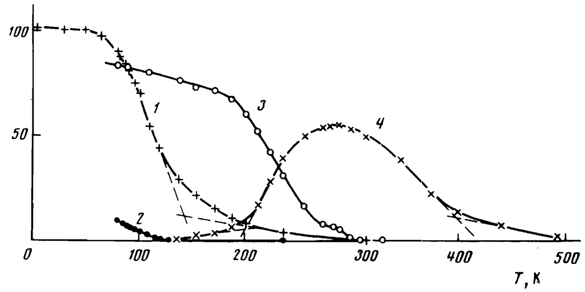

FIG. 4. Temperature dependences of the intensity of the diffraction reflections of the structures α (1) and β (2) at n = 2.2 x 10^{14} cm^{-2} and of β (3) and γ (4) at n = 3.8 x 10^{14} cm^{-2}. The temperatures of the phase transitions were determined from the points of intersection of the dashed lines. The high-temperature "tails" of the curves are due to the presence of short-range order.

The adsorbed strontium atoms on the (011) face have an appreciable mobility even at low temperatures. Thus, in the case of evaporation of strontium on a substrate cooled with liquid helium, at a degree of coating $\theta \gtrsim 0.6$, a long-range order is established in the film without additional annealing (Fig. 1g). At T = 77° K, long-range order is already established practically in the entire region of the submonolayer coatings. To obtain more reliable results, we have additionally stabilized the film structure by annealing at 300—400° K for several seconds, and also monitored the influence of the rate of cooling and the time of maintenance of a given temperature on the formed structure. The aggregate of the data indicates that in our experiments the equilibrium state of the film is reached practically in the entire range of T and θ, with the possible exception of the smallest T and θ (the boundary between the phases and in Figure 5 at T = 77° K).

The two-dimensional structures produced in small coatings (as compared with dense monolayers) are macroscopically homogeneous and are characterized by a large interatomic distances. In the first suffici-

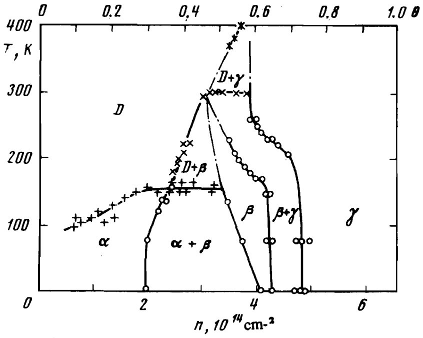

FIG. 5. Phase diagram. D—disordered structure. The degree of coating $\theta = 1$ corresponds to the close-packed monolayer.

ently ordered lattice, there is approximately one adsorbed strontium atom for approximately 20 surface tungsten atoms. The diffraction pattern (Fig. 1b) is characterized in this case by the presence of a large number of additional (fractional) reflections. Owing to their low intensity, it is difficult to interpret the picture reliably. Judging from the geometry of the electron diffraction pattern, the corresponding two-dimensional structure is apparently close to a lattice type c (7 × 3) (Fig. 2a). In this lattice, the shortest interatomic distance is ≈13Å while $n : n_W = 1 : 21$ ($n_W = 1.41 \times 10^{15}$ cm^{-2} is the surface concentration of the tungsten atoms on the investigated face).

With further evaporation of strontium, distinct diffraction patterns are observed in succession, corresponding to the lattices c (6 × 2) and (10 × 2) (Figs. 2b and 2c) and to concentrations $n : n_W$ equal to 1 : 12 and 1 : 10. On going from one stoichiometric concentration to the other, a characteristic shift of the additional reflections is observed, together with a splitting of some of them (see Fig. 1c). According to [12,13], this indicates that at intermediate concentrations the film consists of a statistical mixture of cells corresponding to "stoichiometric" structures.

Thus, the strontium film is homogeneous in a rather wide range of small concentrations (at degrees of coating $\theta < 0.3$). The corresponding region on the phase diagram (Fig. 5) is designated the α phase.

When the critical concentration of the adsorbed strontium atoms is reached (at low temperatures it is equal to $n = 2 \times 1^{-14}$ cm^{-2}), the film is no longer homogeneous and a first-order phase transition, reminiscent of two-dimensional condensation, sets in. During the course of this transition, the evaporation of the strontium leads to a growth of stubs with denser structure on the surface, of type c (3 × 1) (Fig. 2d), but the structure contains an appreciable number of vacancies (≈25% at T = 150–200° K). We call this structure the β phase. In the region α + β (Fig. 5), the adsorption coating has a spotty character, as is manifest on the electron diffraction pattern by the coexistence of reflections corresponding to both phases. After the face transition is completed, the entire surface is coated with phase β. Further increase of the film density following additional evaporation of strontium proceeds first by filling the vacancies present in the β phase (the β region in Fig. 5). In this region, the film is again homogeneous. Then, after a second critical concentration value is reached, the next denser γ phase begins to be separated, and is characterized by a hexagonal structure that does not match the substrate (the two-phase region β + γ in Fig. 5)1). The increased density of this structure after the entire surface is covered is the result of a gradual decrease of the lattice period, with preservation of the hexagonal symmetry, in analogy with the results observed for other analogous systems[2,6,14]. Finally, at $n = 6.6 \times 10^{14}$ cm^{-2}, the maximum packing of the first monolayer is reached ($\theta = 1$), and further deposition of the adsorbate leads to the initiation of the second monolayer.

Thus, complicated phase transformations take place in submonolayer strontium films as they become denser. It should be noted that the change of the electronic state of the adsorbed atom in the phase transitions leads to the appearance of a number of singularities of the dependence of the work function of the Sr–W (011) system on the degree of coating. Figure 6 (curve 2) shows such a dependence, obtained at T = 5° K for a film stabilized by annealing at 300–400° K. It is seen, for example, that in the two-phase region (α + β) the work function varies linearly, as expected of the average value of the work function of a spotty surface on which the area of the spots of one type decreases with increasing θ, and the area of the spots of the other type increases. A linear section of $\varphi(\theta)$, albeit shorter, corresponds also to the region (β + γ). The minimum of the work function correlates with the start of the α → β phase transition, and the transition to the saturation section correlates with the completion of the packing of the first monolayer ($\theta = 1$).

Let us discuss now the factors that can cause so complicated a picture of the phase transitions. Inasmuch as at low temperatures the character of the equilibrium structure is determined principally by the energy factor, it is natural to correlate the data on the phase transitions at T = 5° K with the dependence of the heat of adsorption of strontium on the (011) face of tungsten on the degree of coating (Fig. 6, curve 1)2).

The homogeneities regions of the films α and γ correspond to two steeply drooping sections of the $q(\theta)$ curve, on each of which the total decrease of the heat of adsorption amounts to approximately 1 eV. We see that it is precisely the strong decrease of the heat of adsorption with increasing θ which makes it impossible for the adsorbed atoms to become condensed into a denser phase in the indicated regions even at the lowest temperatures. Indeed, the phase transition temperature is [8] is

$$T_{\text{tr}} = -\frac{1}{k}\theta(1-\theta)\frac{\partial^2 \mathscr{E}}{\partial \theta^2} \qquad (1)$$

(k is the Boltzmann constant, $\mathscr{E}$ is the internal energy of the film). Since $q \sim (-\partial \mathscr{E}/\partial \theta)$, it follows that at $\partial q/\partial \theta < 0$ we obtain formally $T_{\text{tr}} < 0$. The abrupt decrease of the adsorption heat with increasing coating offers evidence of a strong repulsion interaction between the adsorbed atoms, which is apparently due to the presence of a large dipole moment of the adsorption bond, at any rate in the case of small coatings. In the region of large θ, an additional factor comes into play, and contributes to a decrease of the heat of adsorption, namely the film lattices are no longer matched to the substrate. The adsorbed atoms are then forced to leave the energy wise most favored centers on the substrate.

At the same time we should have $\partial q/\partial \theta > 0$ in the region where the first-order phase transition is observed, in accordance with (1). However, the isobar method used in [9] to determine the heat of absorption

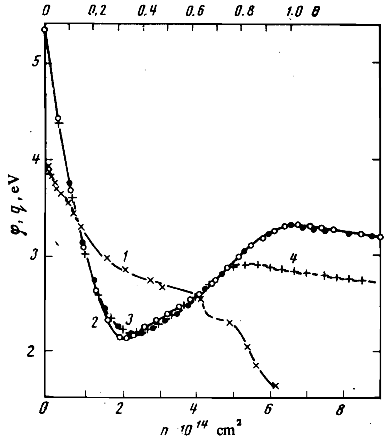

FIG. 6. Concentration dependences of the heat of adsorption (1) and of the work function (2–4) of the Sr–W (011) system. The heat of adsorption was calculated from the adsorption isobar [9]; the dashed curve shows the assumed course of the curve in the region n = (4–5) × 10^{14} cm^{-2}, 2–T = 5° K (annealing at 300–400° K); 3–T = 290° K, 4–T = 5° K (without annealing).

does not make it possible to register a section of the q(θ) curve with positive slope, since in this region it is impossible to realize a stationary state of a film with uniform distribution of the adsorbed atom over the surface. On the isobar we observe practically a jumplike change of the coating, corresponding to a section of the plateau on the q(θ) curve (in this case θ characterizes the average and not the local concentration of the adsorbed atoms).

Thus, an analysis of the phase diagram and of the concentration dependence of the heat of adsorption allows us to conclude that the effective interaction potential between the adsorbed atoms is a function that lies in the positive half-plane and decreases nonmonotonically with increasing distance (the presence of two regions in which a first-order phase transition takes place indicates that this dependence has two maxima). In other words, in certain intervals of distances between the adsorbed atoms there occurs a weakening of the repulsion interaction, which is equivalent to the onset of effective attraction forces. According to the theory of Bol'shov and Napartovich[7,8], which takes into account the Coulomb interaction of the adsorbed atoms via a free half-space, this effect can be due to progressing mutual depolarization of the adsorbed atoms after a certain critical degree of coating is reached. It is also possible, however, that the nonmonotonic variation of the interaction energy between the adsorbed atoms with changing distances due not only to the depolarization effect, but also to an indirect interaction of the adsorbed atoms via the electron gas of the substrate[15]. The role of an interaction of this type, which is oscillatory in character, increases with decreasing dipole moment of the bond.

We note that Einstein and Schrieffer[16] were able, by taking into account the indirect interaction, to explain the experimentally observed symmetry of a number of two-dimensional lattices, while Tsong[17] observed experimentally the oscillatory character of the interaction between the atoms rhenium adsorbed on tungsten. It appears that allowance for the interaction of the adsorbed atoms via the electron gas of the substrate is important also when it comes to describing phase transitions in adsorbed films.

An interesting feature is possessed by the region of the $\beta \rightarrow \gamma$ phase transition. The limits of this region are so located that at certain types of coating the transition from the phase β to the phase γ can be effected by increasing the temperature, i.e., a polymorphic transformation is observed. Insofar as we know, this is the first observation of a polymorphic transformation in submonolayer electropositive films. An estimate of the contribution of various types of entropy to the free energy of the film shows that the main moving force of this transition is the increase of the vibrational entropy of the film when a structure that is not matched to the substrate structure is produced (γ phase, see Fig. 2d). As shown by Ying[18], the phonon spectrum of mismatched two-dimensional lattices extends all the way to zero frequency, whereas for structures that are matched with the substrate (which include the β phase) the spectrum begins with a nonzero frequency. For this reason, the mismatched phase has a larger entropy and becomes stable with increasing temperature.

Let us examine now the data on non-annealed films obtained by evaporating strontium on a tungsten crystal at liquid-helium temperature. The flux of the strontium atoms to the surface was such that ≈15 minutes were necessary to evaporate a complete monolayer. The observations have shown that, starting with coatings having $\theta \approx 0.1$, a diffuse halo is observed on the electron diffraction pattern around the mirror reflection; this halo has a shape different from annular. This is evidence of the presence of an anisotropic short-range order in the arrangement of the atoms. At $\theta \approx 0.6$ the halo breaks up into a number of sufficiently distinct reflections corresponding to the phases β and γ, i.e., long-range order appears in the film.

It must be emphasized that this result is not connected with the action of the beam of electrons on the film. It is also not very likely that the ordering of the film is due to a local increase of the temperature at the surface when energies released in the adsorption act itself. Indeed, experiments in an ion field-emission projector have shown that the dissipation of the energy in a metal at low temperatures occurs so rapidly, that the adsorbed atom does not have time to complete even one migrational jump from the position at which it lands initially[19]. It appears that the establishment of the short-range order is connected with the presence at 5° K of a certain mobility of the Sr atoms on W(011), corresponding to an adsorbed-atom migration activation energy $\sim 10^{-2}$ eV. The unusually small migration activiation energy on going from the random distribution to the short-range order may be due to the fact that strong local stresses are produced around the adsorbed atom occupying a nonequilibrium position on the substrate (relative to the equilibrium ordered structure). These stresses can deform the potential relief, as a result of which the barrier to the transition of the adsorbed atom towards the equilibrium position can be significantly lowered. As the film approaches equilibrium, the role of this factor becomes weaker. It is possible that this is precisely the reason why the establishment of long-range order in the film occurs only at 70 – 80° K. If it is assumed, according to[20], that for long-range order to be established each adsorbed atom must execute 6 – 10 jumps, then the corresponding migration activation energy in this case should amount to $\sim 10^{-1}$ eV. It should be noted that recently a noticeable mobility of surface atoms was observed even for highmelting-point metals at unexpectedly low temperatures (for example, at 50° K for rhodium atoms on Rh(111) with activation energy $\lesssim 0.25$ eV[21]).

We have also investigated the influence of the disordering of films, which occurs with increasing temperature (i.e., the order-disorder transition), on the work function of the system Sr–W(011). As for other metal-film systems[2,6,11], it was established that the disturbance of the long-range order in the film does not lead to noticeable changes in the work function (accurate to several hundreds of an electron volt). We attribute this to the fact that the work function is determined principally by the short-range order. Indeed, owing to the presence of short-range order, the nearest neighbors around a given adsorbed atom are arranged in almost the same manner as in the presence of long-range order. On the other hand, the action of the more remote neighbors depends little on their concrete distribution over the substrate. The net result is that the electronic properties of the adsorbed atoms, which are determined by its interaction with other adsorbed atoms, remain practically unchanged.

A more significant influence of the temperature on the work function is observed only for coatings (see curves 2 and 3 in Fig. 6) at which the film in the low-temperature region is two-phase. Obviously, in this case the increase of the temperature first leads to a redistribution of the adsorbate between the phases and to a change in the short-range order in each of them, and then to a transition of the film to a single-phase state. In the region $\theta > 0.7$, noticeable changes in the work function accompany also the annealing of the films, which leads to a transition from a metastable structure to an equilibrium structure (see curves 2 and 4 in Fig. 6).

Thus, our results show that in submonolayer films of even the simplest adsorbates one can observe a very complicated phase-transition picture. Further investigation of these films promises to yield important information on the nature of the particle interaction on the surface and on those factors which determine the properties of the adsorbed atoms and of the surfaces coated by them.

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1) This transition sets in even before all the vacancies in the c (3 x 1) lattice are filled. Approximately 8% of them remain at T = 5° K.

2) The heat data shown in Fig.6 were obtained in [9] by measuring the rate of desorption in the interval 500 - 1400° K, and pertain to a disordered film. However, they differ from the values of the heat for the ordered film by a negligible amount $\sim kT_{dis} \ll q$ (T_{dis} is the disorder temperature).

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