

A vitrifying structure transition in the Dy/Mo(112) adsorption system

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Annealing-driven irreversible structural transitions are studied by low energy electron diffraction in submonolayer Dy films adsorbed on the Mo(112) surface. In a wide coverage range $\theta > 0.07$, Dy overlayers deposited at low temperatures ($T \approx 100$ K) are ordered and keep their structure upon annealing up to 350–600 K. Near $\theta = 0.68$, the overlayers are stable to high-temperature annealing ($T_a = 1000$ K) as well, whereas the denser films are metastable and transform to more stable ordered structures. An unusual annealing effect is found for $\theta < 0.58$: the initially ordered metastable phases are replaced by phases having no extended order, which are assumed to be two-dimensional glasses.

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Introduction

The glassy state of matter attracts an abiding great interest from both the basic and practical standpoints (see, e.g., Ref. 1). There are a lot of methods of producing various kinds of glasses. Among them, special attention is paid at present to preparation and studies of thin glassy and amorphous films, which combine a number of useful properties provided by the disordered structure and low dimensionality. In this communication, we report on a new method allowing one to obtain ultrathin (submonolayer) films which, in contrast to the usual amorphous films, are stable against annealing and retain their disordered structure in a broad temperature range.

Our results have been obtained with Dy submonolayers on the Mo(112) surface. The adsorbed Dy atoms possess an appreciable positive electrical charge, and their interaction with one another is of complex nature including both dipole–dipole and substrate-mediated interactions. The energy of such interactions can reach 10^{-2} – 10^{-1} eV for nearest neighbors, so the adsorbed films are usually ordered below $T = 100$ – 1000 K [2,3]. Owing to the considerable dipole moment associated with the adsorp-

tion bond (above 1 D at low Dy coverage), the adsorbate strongly reduces the work function of the surface. The work function and structure of Dy/Mo overlayers were studied earlier [4], but the annealing-driven structural transitions and work function changes have not been revealed. Specifically, the $c(2 \times 2)$ lattice was reported to exist up to $\theta = 0.5$, which is followed by uniaxially compressed lattices at $\theta > 0.5$ in the submonolayer coverage range. The coverage is defined as the ratio of adsorbate to substrate surface atom concentrations. We have investigated the structure of Dy adlayers both as-deposited at a low temperature ($T = 100$ K) and successively annealed in the range of $100 \text{ K} < T_a < 1200 \text{ K}$, with recording of the resulting structures at the low temperature. The rate of temperature decrease after each annealing step did not exceed -5 K/s . In such experiments, we have found a strong effect of annealing on the character of the order.

Results and discussion

To carry out this study, we have used the UHV system and the experimental setup described earlier [5–7]. Briefly, a SPECTALEED instrument

equipped with a charge-coupled device (CCD) camera was used for studying surface structure. The stored video records of the low energy electron diffraction (LEED) patterns were utilized to measure the peak intensities for the particular spots. The contact potential difference method was applied for monitoring the work function changes. The same molybdenum specimen as in our previous work [6,7] was used for the substrate. Its surface consists of (112) terraces as broad as $350 \text{ \AA} \times 550 \text{ \AA}$ along the $[\bar{1}\bar{1}1]$ and $[1\bar{1}0]$ axes, respectively. The atomic beam of Dy was obtained from a piece of dysprosium metal spot-welded to a tantalum ribbon serving as a heater. Auger electron spectroscopy was used to check the cleanliness of the substrate and the adsorbate. The coverage θ was determined from the deposition time and work function measurements, which were calibrated by means of LEED in the coverage range $\theta = 0.68\text{--}0.75$. This range is specific for the existence of a single-phase incommensurate structure undergoing uniaxial compression and therefore is not likely to contain other phases which might be overlooked by LEED.

At annealing temperatures below $T_a = 350\text{--}600 \text{ K}$, a set of ordered overlayer structures is found with increasing coverage from $\theta = 0.07$, till the formation of a close-packed physical monolayer at $\theta = 0.77$. These structures in their majority are different from those reported in Ref. 4. Intending to discuss in detail the phase transitions for the

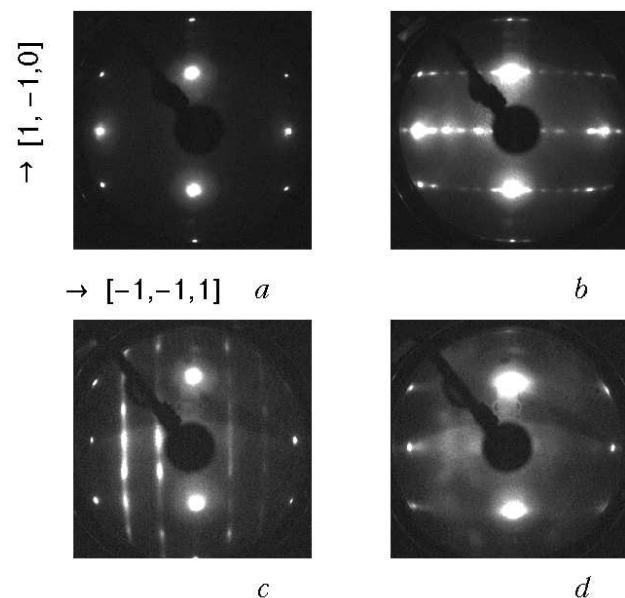


Fig. 1. Low energy electron diffraction patterns from Dy/Mo(112) overlayers. The pattern from the clean substrate (a) is presented for a reference, with the principal axes indicated. Coverage (monolayers): 0 (a); 0.25 (b); 0.68 (c); 0.45 (d). Annealing temperature, K: 200 (b); 800 (c, d). Electron energy, eV: 67 (a, b); 55 (c, d).

Dy/Mo(112) system in a separate paper, we will not present here the whole series of ordered film structures observed in this work but will focus on the annealing-driven irreversible order-disorder transition.

In general, the periodicity of an ordered film structure differs from that of a substrate. Therefore LEED usually reveals an order in the adsorbed overlayer via extra (fractional-order) diffraction beams which are absent in the cases of a clean substrate or a disordered adsorbed layer. For example, Fig. 1, b demonstrates a LEED pattern from an ordered (6×1) Dy overlayer which is observed in the coverage range $\theta = 0.07\text{--}0.3$. The pattern differs from that of the clean substrate (Fig. 1, a) by five extra beams between the integer-order beams along the $[\bar{1}\bar{1}1]$ direction. Figure 2 shows a possible model of the (6×1) structure which is consistent with the LEED pattern and the coverage value. It should be mentioned that the (6×1) structure is one of those transforming into a glassy phase in the progress of annealing. Patterns with fractional-order LEED spots are indeed observed in the whole submonolayer coverage range at the low annealing temperatures mentioned above. A full list of the ordered structures found will be given in the diagram of annealed states presented below.

The increase of annealing temperature exerts a different effect on the order in Dy adfilms depending on their coverage. As a measure of the degree of order we use the peak intensity of LEED. Above $\theta > 0.6$, the annealing results in a usual effect of improvement of the order. This is illustrated in

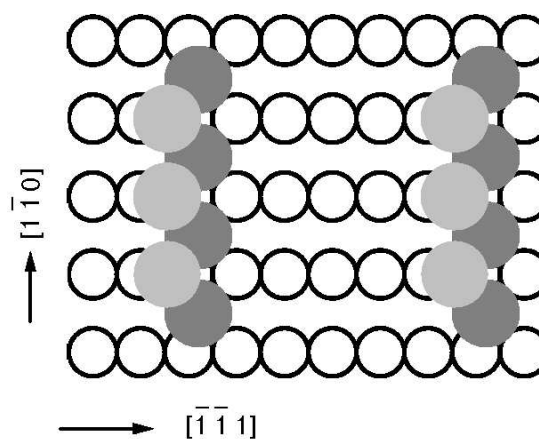


Fig. 2. A hypothetical hard-sphere model for an ordered dysprosium overlayer (6×1) corresponding to $\theta = 0.3$. The unfilled circles show the topmost substrate layer, grey disks show the adsorbate layer, with heavier darkness corresponding to greater vertical depth. The principal axes are indicated.

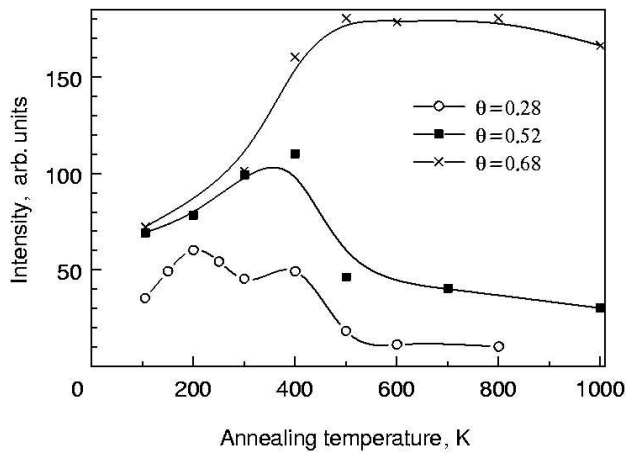


Fig. 3. Annealing-driven changes in intensity of fractional-order LEED beams specific to the structures observed at different Dy coverages. The beam intensity after annealing is always measured at $T = 100$ K.

Fig. 3 for $\theta = 0.68$: the fractional-order beam intensity gradually increases and then levels off. The relevant LEED pattern from the eventually annealed overlayer is shown in Fig. 1,c. The steady growth of the order starting from the lowest annealing temperature is indicative of considerable mobility of adatoms already at 100 K. Designating as T_{mob} a certain minimum temperature at which adatoms can move over neighboring adsorption sites during the time of an experiment, we conclude that T_{mob} is < 100 K. According to this designation, T_{mob} can be expressed in terms of the parameters of surface diffusion as $T_{\text{mob}} \approx E_d / 30k_B$, where E_d is the activation energy, and k_B is Boltzmann's constant [2,8]. Besides promoting adatom mobility, an increase of temperature can also cause an order-disorder transition if the temperature reaches some critical value T_c specified by the interaction energy of adatoms E_i as $T_c \approx E_i / k_B$ (see Ref. 8). Ordering is realized in the time of an experiment (10^{-10} s) if

$$T_{\text{mob}} < T_c, \text{ or } E_d < 30 E_i; \quad (1)$$

otherwise, upon the cooling that follows each annealing step, a frozen disorder is observed instead of order. The overlayer under consideration ($\theta = 0.68$) is apparently what results when inequality (1) is fulfilled. It should be noted that the lattice retains its original symmetry under annealing only in a narrow coverage range close to $\theta = 0.68$. The denser films (from $\theta = 0.68$ up to the close-packed monolayer at $\theta = 0.77$) are metastable and undergo irreversible transitions to the more stable ordered structures. In this case, LEED records the replacing of one pattern of superstructure spots by another.

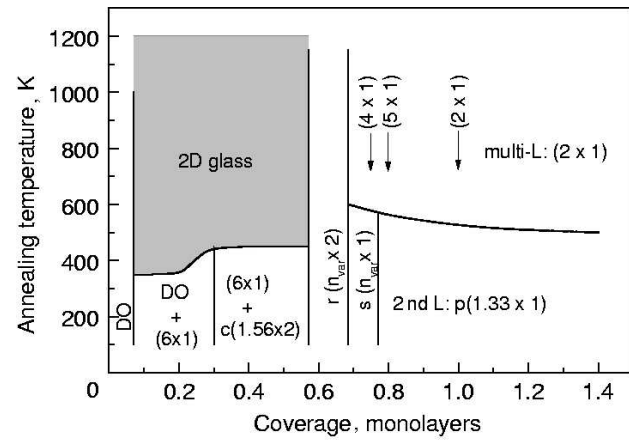


Fig. 4. Diagram of annealing-driven changes in structure of Dy overlayer on Mo(112). DO: disordered phase; 2D glass: two-dimensional glass (shaded area); $r(n_{\text{var}} \times 2)$ and $s(n_{\text{var}} \times 1)$: rectangular (diatomic) and skew-angle (primitive) structures, respectively, having lattice spacing varying with θ ; 2nd L: second layer; multi-L: multilayer structure. The other notations of ordered structures are conventional. The arrows show the coverages at which the specified structures form.

For the coverages $0.07 < \theta < 0.58$ the annealing results in an unusual effect: firstly, only a limited improvement of the order occurs, which is followed by decay of the previous order without transition to any other ordered phase. This peculiarity is illustrated qualitatively by an irreversible disappearance of the fractional-order LEED features in pattern (d) of Fig. 1 and quantitatively by intensity curves with local maxima followed by virtual fading of intensity (see Fig. 3). At low temperatures ($T_a < 200-400$ K), inequality (1) seems to be valid. However, at a later stage, annealing evidently causes an irreversible change in the overlayer properties (such as the diffusion parameters and adatom interaction energy), so that inequality (1) reverses its sign:

$$T_{\text{mob}} > T_c. \quad (2)$$

The irreversible transitions are summarized in Fig. 4, which shows a wide area (shaded and designated as 2D glass) of annealing temperature in the submonolayer coverage range at which the overlayer loses an extended order. The notations of the all ordered structures found are also listed in Fig. 4. Though Fig. 4 resembles a phase diagram, that is not the case: here the overlayer state is presented at a standard temperature of 100 K, contrary to a phase diagram, which shows the state at a current temperature.

To prove that the effect of high-temperature annealing on LEED patterns at low coverage is not

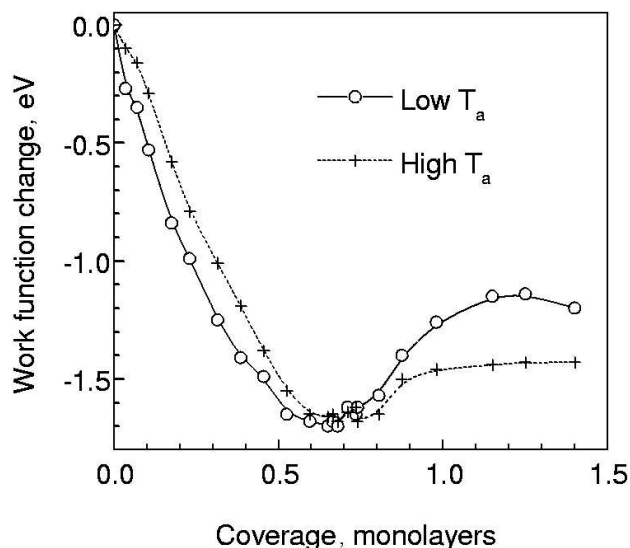


Fig. 5. Coverage dependence of the work function changes obtained after low- ($T_a < 350\text{--}600$ K) and higher-temperature annealing.

a trivial result of the removal of Dy adatoms from the surface, the work function changes caused by annealing have been monitored. The coverage dependences of these changes taken after low- ($T_a < 350\text{--}600$ K) and higher-temperature annealing are presented in Fig. 5. It is seen that at none of the coverage, high-temperature annealing returns the work function to its value specific for the clean surface.

One of possible interpretations of the described annealing irregularity might be a transition to another more stable phase which is characterized by too low a disordering temperature, unavailable in our experiment, so that $T_{\text{mob}} < T_c < 100$ K. However, the quite small variation of the work function (and thereby of the adatom dipole moment) due to high-temperature annealing indicates that no essential weakening of at least dipole-dipole adatom interactions happens. Therefore, taking into account the rather wide coverage range in which the order is lost, we consider that even this interaction only can provide a sufficiently high T_c at medium coverages where the inter-adatom distances become very short.

Though some decrease of T_c should not be ruled out, especially at low coverages, another possibility seems to be more realistic: a poor order can be explained by an annealing-driven change of adatom mobility, which becomes insufficient to ensure equilibration. Direct experimental investigations of surface diffusion show evidence that the mobility of Dy atoms adsorbed on Mo(112) in the discussed range of coverage and subjected to high-tempera-

ture annealing is indeed low [9]. The diffusivity equals $10^{-9}\text{--}10^{-8}$ cm²/s at $T = 700\text{--}800$ K. It is lower by two order of magnitude than that, e.g., for strontium films adsorbed on the same substrate at comparable coverages [10]. An estimate of the time necessary for diffusion over the path of an inter-adatom distance, which is obtained by extrapolation of the diffusivity data to the temperature range $T_a = 200\text{--}300$ K optimal for the ordering of metastable phases, results in $10^5\text{--}10^3$ s. This value is apparently distinct from the much shorter diffusion time providing rapid equilibration of metastable phases at low temperatures. Hence this fact corroborates our suggestion about the dramatic drop of adatom mobility in the range $\theta = 0.07\text{--}0.58$ upon high-temperature annealing. Not only the low-temperature ordering of Dy phases such as (6×1) described above is significant. Precovering of the Mo(112) surface with a dilute Dy film ($\theta \approx 0.1$), with its subsequent high-temperature annealing, suppresses strongly the Sr and Li overlayer ordering, whereas without high-temperature annealing, the same Dy dope to the Sr or Li overlayer even improves the ordering process, indicating a high adatom mobility.

We suggest that the origin of hindering the adatom mobility by high-temperature annealing may consist in adsorption-induced surface reconstruction. The Mo(112) surface is close-packed in the direction along the channels (see Fig. 2). However, adsorption succeeded by high-temperature annealing can induce a reconstruction of its topmost layer into some loose-packed structure, and the ordering is known to advance very slowly on the rough surfaces [2]. The roughness of the reconstructed surface means that adatoms are mixed with surface substrate atoms and one actually obtains a kind of two-dimensional alloy. For example, such a carbon-induced reconstruction to a rough «checkerboard» structure is detected for Mo(112) both by LEED and STM techniques [11]. Contrary to this, the mobility of Dy adatoms on the original (non-reconstructed) surface Mo(112) seems to be high enough to provide some ordering for all coverages even at temperatures as low as 100 K. Some suggestion concerning the mechanism of formation of a rough surface can be deduced from data on the work function changes (Fig. 5). Up to at least 0.5 monolayer, the curves corresponding to low-temperature and high-temperature anneals are seen to run almost in parallel, as if 5 to 10% of the adsorbate monolayer is no longer contributing to the work function change after the high-temperature anneal. It seems that approximately this amount of dysprosium must

have «reacted» with the surface upon high-temperature annealing (as a random process), so that this fraction is leveled down from the position of an adatom, protruding into the vacuum, to a position within the two-dimensional alloy incorporated in the surface substrate layer. The result is that it makes little contribution to the surface potential barrier. This reaction obviously happens already with the first few percent of the monolayer, and after completion of the surface reaction (limited presumably by buildup of surface stress due to incorporation of Dy into the Mo layer), nothing more happens. Since the surface has now a random and more rough corrugation, Dy adsorbed on top of this two-dimensional alloy cannot order at low coverage. However, at high coverages ($\theta > 0.58$), the situation seems to differ due to domination of direct lateral interactions of adatoms, which are strong at short inter-adatom distances and switch on a more intense driving force of ordering.

Thus, the high-temperature annealing of low-coverage Dy submonolayers ($0.07 < \theta < 0.58$) results in their transition to a disordered state. At $T > 600$ K, Dy adatoms possess a high mobility in this state [9], so this is actually a melted phase. However, while the temperature is lowered, the mobility seems to dramatically reduce before the overlayer manages to order. This is just what is typical for a vitrifying transition.

A peculiarity of the submonolayer vitrification is a strong influence of the substrate potential corrugation on the behavior of an overlayer. At an arbitrary coverage, a disordered film has generally an incommensurate structure. A lack of overlayer mobility implies the pinning of adatoms to the wells of the Peierls relief (the substrate potential corrugation modified by adatom lateral interaction [8]). For incommensurate structures, the pinning means transformation into a phase termed chaotic [12]. In this phase, the potential wells have no standard depth due to a random distribution of the adatoms over the adsorption sites, and consequently, the random value of interaction energy between neigh-

boring adatoms. Besides poor mobility, this is a fundamental property of an amorphous state.

It is worth noting that a low-coverage glassy overlayer of Dy and other similar adatoms which possess an appreciable magnetic moment may show properties of ultrathin (actually two-dimensional) amorphous magnetic materials.

Conclusion

To conclude, we have found a set of metastable ordered states in two-dimensional Dy overlayers deposited onto Mo(112) at low temperatures. Upon high-temperature annealing, they are irreversibly replaced by stable ordered structures at high coverages and by a glassy state at low and medium coverages.

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1. J. M. Ziman, *Models of Disorder*, Cambridge Univ. Press, London (1979).
2. A. G. Naumovets, *Sov. Sci. Rev. Phys.* **A5**, 443 (1984).
3. O. M. Braun and V. K. Medvedev, *Usp. Fiz. Nauk* **157**, 631 (1989) [*Sov. Phys. Usp.* **32**, 328 (1989)].
4. F. M. Gonchar, V. K. Medvedev, T. P. Smereka, and G. V. Babkin, *Fiz. Tverd. Tela* **32**, 1872 (1990) [*Sov. Phys. Solid State* **32**, 1092 (1990)].
5. D. Jürgens, G. Held, and H. Pfnür, *Surf. Sci.* **303**, 77 (1994).
6. A. Fedorus, D. Kolthoff, V. Koval, I. Lyuksyutov, A. G. Naumovets, and H. Pfnür, *Phys. Rev.* **B62**, 2852 (2000).
7. A. Fedorus, G. Godzik, V. Koval, A. Naumovets, and H. Pfnür, *Surf. Sci.* **460**, 229 (2000).
8. I. Lyuksyutov, A. G. Naumovets, and V. Pokrovsky, *Two-Dimensional Crystals*, Academic Press, New York (1992).
9. A. T. Loburets, A. G. Naumovets, and Yu. S. Vedula, *Surf. Sci.* **399**, 297 (1998).
10. A. T. Loburets, N. B. Senenko, A. G. Naumovets, and Yu. S. Vedula, *Phys. Low-Dim. Struct.* **10/11**, 49 (1995).
11. T. McAvoy, C. Waldfried, J. Zhang, P. A. Dowben, O. Zeybek, T. Bertrams, and S. D. Barrett, *Europhys. J.* **B14**, 747 (2000).
12. P. Bak, *Rept. Progr. Phys.* **45**, 587 (1982).