Structure of thin films on surfaces of single crystals

L. A. Bol'shov, M. S. Veshchunov, and A. M. Dykhne
(Submitted 29 September 1980)
Zh. Éksp. Teor. Fiz. **80**, 1997–2003 (May 1981)

We consider a film model which makes it possible to describe from a unified point of view the structure of monatomic films on transitions to an incommensurate phase, the structure of epitaxial single-crystal films of finite thickness and intergrain boundaries of polycrystals. In particular, we describe the transition of a monatomic film to an incommensurate structure on a deformable substrate. We show that in a homogeneous film of finite thickness significant stresses may arise if the substrate and the film are close in periodicity. We note the advantages of diffusion methods for investigating phase transitions to an incommensurate structure in adsorption films.

PACS numbers: 68.55. + b

1. One of the most interesting questions in surface physics concerns the structure and phase transitions in thin (including monatomic) films formed on single-crystal substrates during adsorption, oxidation, crystal growth from the liquid or gas phase, etc. In the last twenty years the structure and properties of monatomic films adsorbed on carefully prepared crystalline substrates have been studied intensively. It has developed that the structure of the films depends substantially on the nature of the intersection of the adsorbed particles with the substrate and with one another. In the case of a deep (compared with the interaction energies within the film) potential relief in the substrate, the absorbed films from structures which are commensurate with the substrate and ordered (at sufficiently low temperatures) The two-dimensional crystallography has proven to be exceptionally rich. In a number of adsorption systems, about twenty crystal modifications are observed, differing in the periodicity of the structure and the arrangement of the adsorbed atoms in the unit cells.

Investigations of the structural transitions in such films (see, for example, the review in Ref. 1) have shown that with a change in the average film concentration (by sputtering definite amounts of material on a cold substrate of sufficiently large dimensions), the transition between the two closest simple structures (with periodicities on the order of the interatomic separation) occurs through a succession of structures with longer periods. The intermediate structures consist of a succession of unit cells of simple structures with microscopic breaks between them. The distance between breaks is determined by the film concentration.

The picture of structural transitions described in Ref. 1 was based on consideration of the ground state of the film with long-range interaction in the one-dimensional and the two-dimensional case.[2] Subsequently, Pokrovskii and Uĭmin[3] obtained rigorous evidence for such a picture for a one-dimensional chain of atoms at absolute zero temperature.

At a finite temperature, obviously the breaks are disordered, spaced far apart, and the transition between ordered structures which are closest in concentration occurs through a succession of structures with disordered breaks, the concentrations of which vary continuously with a change in film concentration.[4] How-

ever, rigorous results at $T \neq 0$ have not yet been obtained, and at the present time the complete pattern of the phase diagram for a film with long-range repulsive interaction on a substrate with a deep potential relief is not even qualitatively clear.

2. Recently, considerable attention has been focused on the theoretical and experimental investigations of ordered structures of monatomic films which are not matched with the substrate. Unmatched or incommensurate structures are formed in systems with particle interactions within the film which are large compared with the depth of the potential relief. This situation is typical for films with repulsion at concentrations greater than that required for a monolayer, and also for films with strong attraction at submonolayer concentrations.

In particular, a number of theoretical papers[5-8] are devoted to the description of the phase transition from a structure commensurate with the substrate to an incommensurate structure. In these papers it is shown that under certain conditions a transition occurs from an ordered structure which is matched with the substrate to an incommensurate structure consisting of large sections of the matched structure and macroscopic breaks between them. We note that in the case of widely separated breaks[5-10] the structures of films with weak interaction with the substrate differ from the structures of films with strong interaction[1-3] only in the dimensions and the structure of the breaks.

In this paper, we consider a film model which makes it possible to describe from a unified point of view that structure of monatomic films in the course of transitions to an incommensurate phase, the structure of epitaxial single-crystal films of finite width, and the integrain boundaries of polycrystals. In particular, we describe the transition of a monatomic film to an incommensurate structure on a deformable substrate. We show that in a homogeneous film of finite width, significant stresses might arise if the periods of the substrate and film are close. We show that certain differences between the results of a large number of papers[5-10] on these topics are due not to the difference in physical models but rather to the variety of external conditions (the average concentration or the chemical potential is specified as in equilibrium growth from the

0038-5646/81/051038-04$02.40   1038

gas phase).

3. We consider a model that makes it possible to describe the structure of monatomic films on a periodic substrate, single-crystal epitaxial films, and intergrain boundaries of a polycrystal.

Let us first assume that the interaction within the layers is greater than the interaction between layers. Then the relative displacements within the layers are small and their energy can be written in the harmonic approximation. The interaction between layers should take into account the possibility of significant relative displacements of atoms in the different layers, as in a model of the Peierls–Nabarro type. We need only take into account the possibility of a smooth variation of the period of the poyential created by adjacent layers. To simplify the exposition, it is convenient to consider a system of one-dimensional chains ($\partial u / \partial n \ll c$):

$$H = \sum_{n,k} \left[\frac{m_k}{2} \left(\frac{\partial u_n^{\,k}}{\partial t} \right)^2 + \frac{\varkappa_k}{2} (u_{n+1}^{\,k} - u_n^{\,k})^2 \right. \tag{1}$$
$$\left. + V_k \cos \frac{2\pi}{c_{k,k-1}} (n c_k + u_n^{\,k} - s_{k-1}(n) c_{k-1} - u_{k-1(n)}^{\,k-1}) \right];$$

here m_k and $\varkappa_k$ are the mass and rigidity in the k-th chain of atoms; $u_n^{\,k}$ is the displacement along the chain; the choice of the period $c_{k,k-1}$ of the chain, from which the displacement in the k-th and $(k-1)$-th chains is reckoned, is described below: $s_k(n)$ is the number of the atom in the $(k-1)$-th chain closest to the n-th atom in the k-th chain; V_k is the interaction between the $(k-1)$-th and the k-th chains.

In the rigorous derivation of the Hamiltonian in Eq. (1), in the quasiclassical approximation we have used the fact that for $\partial u / \partial n \ll c$ the structure of each chain is locally periodic, but generally speaking with its own period. In the interaction potential produced by one chain, we should write its own local period $c_k(n)$. The analyses that follows shows that at close (initiating (at $V = 0$) periods of the chains, the equilibrium state proves to be almost periodic with an general period $c_{k,k-1}$, subject to determination. For simplicity we took this fact into account in writing the Hamiltonian in Eq. (1).

The structure of a film described by the Hamiltonian (1) depends essentially on the ratio of the interaction parameters within the chains and between the chains.

4. We consider first the limiting case in which the interaction between the adsorbed films and the substrate is much greater than the interaction between layers of the substrate. In this case, it is sufficient to consider the equilibrium between the two upper chains that model the absorbed film and the upper layer of the substrate. It is convenient to choose the period c of the chain, from whose nodes the atomic positions in both chains are reckoned, in such a way that the interaction energy within the chains be a minimum when the periods of the chains coincide (strong interaction between chains). In fact, for sufficiently close initiating periods a and b (at $V = 0$) for both chains, even a weak interaction V is sufficiently strong to lead to agreement of the periods

(see Ref. 7). Then

$$c = (\varkappa_1 + \varkappa_2) a b / (\varkappa_1 b + \varkappa_2 a).$$

At $|a - b| \ll a$, the displacement of atoms in both chains have rather long wavelengths and the quasiclassical approximation may be used. The Hamiltonian in Eq. (1) for the two chains has the form

$$H = \sum_{n,m} \left[\frac{m_1}{2} \left(\frac{\partial u_n^{\,1}}{\partial t} \right)^2 + \frac{m_2}{2} \left(\frac{\partial u_m^{\,2}}{\partial t} \right)^2 + \frac{\varkappa_1}{2} (u_{n+1}^{\,1} - u_n^{\,1})^2 \right.$$
$$\left. + \frac{\varkappa_2}{2} (u_{m+1}^{\,2} - u_m^{\,2})^2 \right] + \sum_n V \cos \frac{2\pi}{c} (n a + u_n^{\,1} - m(n) b - u_{m(n)}^{\,2}); \tag{2}$$

here the function $m(n)$ has a discontinuity at unity, and the separation between discontinuities is much greater than unity.

Below we shall see that close to the transition to an incommensurate phase, large regions of commensurability arise which are separated by small smooth breaks. Then, going to the continuous limit

$$a = c(1 + \delta_1), \qquad b = c(1 + \delta_2), \qquad x = 2\pi n \delta_1,$$
$$\varphi(x) = 2\pi n \delta_1 + 2\pi u_n^{\,1}/c, \qquad \psi(x) = 2\pi m(n) \delta_2 + 2\pi u_{m(n)}^{\,2}/c,$$
$$h = (\varkappa_1 c^2 \delta_1^2 / V)^{1/2} \qquad (\delta_{1,2} \ll 1),$$

we obtain for the potential energy of the system

$$U = \text{const} \int dx \left\{ \frac{1}{2} \left(\frac{\partial \varphi}{\partial x} - h \right)^2 + \frac{1}{2} \frac{\varkappa_2}{\varkappa_1} \left(\frac{\partial \psi}{\partial x} + h \frac{\varkappa_1}{\varkappa_2} \right)^2 + \cos(\varphi - \psi) \right\}. \tag{3}$$

It turns out that taking into account the dependence $m(n)$ in the considered first approximation with respect to $\delta_{1,2}$ is an exaggeration of the accuracy.

Minimizing Eq. (3) leads to the equilibrium solutions

$$\varphi_0 = 2 \frac{\varkappa_2}{\varkappa_1 + \varkappa_2} \, \text{am} \left(\left(1 + \frac{\varkappa_1}{\varkappa_2} \right)^{1/2} x, k \right), \qquad \psi_0 = -\frac{\varkappa_1}{\varkappa_2} \varphi_0, \tag{4}$$

here am is the elliptic Jacobi amplitude, k is the modulus of the elliptic functions and is connected with h by the relation

$$h = \frac{4}{\pi} \left(\frac{\varkappa_2}{\varkappa_1 + \varkappa_2} \right)^{1/2} \frac{E(k)}{k}. \tag{5}$$

A solution to Eqs. (4), (5) exists in the region

$$h > h_c, \qquad h_c = \frac{4}{\pi} \left(\frac{\varkappa_1 + \varkappa_2}{\varkappa_2} \right)^{1/2}.$$

For $h < h_c$, the minimum of the potential energy corresponds to a constant value for the functions φ and ψ, and $\varphi - \psi = \pi(2m + 1)$, i.e., the periods of the chains coincide at $h < h_c$. At $h = h_c$, a phase transition occurs to an incommensurate structure from a commensurate structure, and the relative arrangement of atoms in the chains (accurate to within renormalization of the rigidity) agrees with the position of the atoms in the chain on the substrate with the fixed potential relief found earlier.[7,8]

Relative to deeper layers of the substrate, the two layers considered are in neutral equilibrium (to zero-order approximation in the interaction between the substrate layers). Of course, allowance for the last interaction lifts this degeneracy.

We emphasize that when minimizing U we have re-

garded the parameter h or (which is the same thing the quantities $\delta_{1,2}$ or a and b as fixed. We recall that a and b are the initiating periods of the chains without taking into account the interaction V. Retaining them when the interaction is included, we keep the stress or the chemical potential μ in the adsorbed film constant. This situation is characteristic for films in thermodynamic equilibrium with a large volume of gas (equilibrium adsorption, condensation from the gas phase). In the situation involving cold-condensed films or films sputtered in fixed doses, it is physically correct to set the average concentration of the film at $\theta = \partial F / \partial \mu$, when F is the free energy of the films. Since there is a break in the free energy F at a second-order phase-transition point, on going from μ to θ the entire region of chemical potentials $|\mu| < \mu_c \sim h_c$ corresponds to a single point $\theta = \theta_c$; i.e., a commensurate structure exists at a single average concentration θ_c. When θ deviates from θ_c, periodic dislocations arise, the concentration of which depends on $|\theta - \theta_c|$.

Qualitatively, both situations are realized on adsorption of a monatomic film on a substrate with a fixed potential relief ($\varkappa_2 \to \infty$).

5. We now proceed to a consideration of the more general question concerning the behavior of a film of finite width on a deformable substrate. It is clear that a very thick film is equivalent to a semi-infinite crystal, having its equilibrium periodicity far from the interface. If this period does not coincide with the period of the substrate, then the boundary region is deformed. In van der Merwe's work[10] and subsequent papers (see, for example, Ref. 11) the structure of the boundary region was studied for two semi-infinite crystals within the framework of elasticity theory, which is applicable if the periods of the crystals are close. In the limiting case of a monatomic film, for rather strong interaction with the substrate, the film duplicates the structure of the top layer of the substrate (see Sec. 4). To determine the structure of a film of finite width in the case of close crystal periods, we can use elasticity theory, but the boundary conditions must be determined in a self-consistent manner from the microscopic model, assuming significant relative displacements of atoms in adjacent layers.

Let us first determine the equilibrium structure of a film of finite width on a substrate with a fixed potential relief. Going to the deformable substrate leads only to renormalization to the answers considered previously for the case of two chains.

If the interaction between layers in the film is sufficiently strong (not weaker than the interaction of the top layer with the substrate), dislocations do not arise within the film; therefore in the Hamiltonian of Eq. (1) we may assume that the periods of all the layers of the film coincide but are not equal to the period of the substrate. In this case, the relative displacements of atoms of adjacent layers are small and the harmonic approximation is adequate to describe their interactions.

In the limit that is continuous with respect to both coordinates, the equation for the displacements along the layers $\varphi(x, y)$ (x is along the interface, y is perpendicular to the interface) which we obtained from the Hamiltonian in Eq. (1) agrees with the equation of elasticity theory ($\Delta \varphi = 0$). The boundary conditions should be determined by minimizing the total energy after solving the problem with boundary conditions calling for continuity of the stresses at the interface and the absence of external forces on the free surface. As a result, for sufficiently thick films (compared with the distance l between dislocations) we obtain

$$\varphi(x, y) = \text{Arctg} \frac{\text{sh}(2\pi y/l)\sin(2\pi x/l)}{1+\text{ch}(2\pi y/l)\cos(2\pi x/l)}. \tag{6}$$

From Eq. (6) it follows that the breaks arising penetrate right through the film. The separation between the breaks and the instant at which they appear are found by substituting Eq. (6) into a continuous analog of Eq. (1).

As is evident from Eq. (6), for $y \gg l$ the displacements $\varphi \to 2\pi x/l$, i.e., deep within the film the layers then are periodic. In the case of a very thick film $l = 2\pi$, the period established coincides with the initiating period. For finite thicknesses, l varies from 2π to ∞ depending on the ratio of V and $\varkappa c^2 \delta^2$. In this case, the period of the film differs from the initiating period by $\Delta a = a\delta(1 - 2\pi/l)$. At $l = \infty$, the film is commensurate with the substrate.

It is essential that in some range of initiating periods, a structure of a film of finite thickness exists which is just commensurate with the substrate. The meaning of the results is explained rather simply. In an infinite crystal the period deep within the crystal is rigorously defined; therefore the separation between breaks is determined only by the difference between the periods of the crystals, and commensurate structures appear only in crystals whose periods coincide. In the case of epitaxial films of finite thickness, at a small difference in initiating periods, a homogeneous stress arises ($\sim h\partial \varphi/\partial x$) along with a modulation in the film, stretching or compressing the film. Under the action of this stress ($\propto V$), the period of the film changes and if the initial difference between the periods is small the period of the film may coincide with the period of the substrate.

The effective rigidity of the film increases with the number of layers; therefore the region of initial periods for which the period of a homogeneous film coincides with the period of the substrate shrinks with increasing film thickness d. For $d \sim V/\varkappa c\delta^2$, the transition described above from a commensurate to an incommensurate structure occurs, and the dislocation breaks penetrate the entire thickness of the film (cf. Ref. 5). This situation is quite similar to the evolution of a monatomic film as its chemical potential changes.

Now it remains only to consider the deformability of the substrate. This is easily handled in complete analogy to the case of two chains. If two crystals of finite thickness have different lattice periods a and b, then they will have a common period

$$c = \frac{ab(E^{(1)}b + E^{(2)}a)}{E^{(1)}b^2 + E^{(2)}a^2},$$

where $E^{(1)}$ and $E^{(2)}$ are the Young's moduli of the corresponding crystals. Accordingly, it is necessary to modify the obtained solutions, as was done for two chains.

We now note that in the Hamiltonian of Eq. (1) we have completely neglected the displacements along the y axis. To take these displacements into account, it is sufficient to solve the elasticity-theory problem for a film of finite width, in which in contrast to the semi-infinite film the period is renormalized and is itself dependent on the film thickness. The form of the solution agrees with the solution for the semi-infinite film[10,11]

$$u_x = \sum_{n=1}^{\infty} \sin k_n x \sum_{j=1}^{2} A_{nj} \exp(\gamma_j k_n z),$$

$$u_y = \sum_{n=1}^{\infty} \cos k_n x \sum_{j=1}^{2} B_{nj} \exp(\gamma_j k_n z);$$

here $k_n = \pi n/l$, and the parameters γ_j, A_{nj}, and B_{nj} are definite combinations of the elastic constants of the crystal. In the case under consideration, the displacements are reckoned from the lattice points of the structure with the new period. Accordingly, we must redefine the parameters k_n. The procedure for determining the new period is described above: but even in the case of three layers numerical methods are necessary to carry out the calculations.

It is interesting to note that for anisotropic crystals, for which $\mathrm{Im}\,\gamma_j \neq 0$, the dislocation breaks penetrate the film at an angle to the interface.

6. One of the most interesting physical deductions of the consideration of the equilibrium of a film of finite thickness on a substrate with close periodicity is the possibility of creating a macroscopic single-crystal film in a strongly stressed state. Indeed, for a commensurate structure the relative strain of the film along the interface is equal to δ. In this case the stresses arising in the film are smaller by only a factor δ times than the atomic ones, i.e., they could reach a value on the order of 10 kbar. Such high stresses are usually achieved only under nonequilibrium conditions (high-pressure techniques). A material in such a stressed state may have a number of unusual properties. A change in the period and in the symmetry of the lattice in the film may lead to a metal-dielectric transition, to rearrangements of the electronic spectrum, to a change in or to the appearance of superconducting properties, etc. It is especially interesting that material in this case is in an equilibrium state and does not need to be maintained by external forces. The thickness of such layers may reach $d \sim V/\kappa a \delta^2$, i.e., it increases with a decrease in the incommensurability δ. Of course, the stresses in the film decrease in this case. We can increase the sample size by preparing a multilayer film and by alternating film material and substrate layers. In any case, the possibility of obtaining the material in such a state merits additional theoretical and experimental investigation.

7. In conclusion, we would like to call attention to the advantages of diffusion methods for investigating phase transitions in an incommensurate structure in adsorbed films. We have in mind experiments of the type in Ref. 12, in which diffusion was studied in Na films on tungsten. As shown in a previous work,[13] when a steady-state diffusion flux

$$j = -D \frac{\partial \mu}{\partial \theta} \nabla \theta$$

is established in an adsorbed film containing sections with the aforementioned commensurate-phase concentration θ_c, macroscopic regions of commensurate phase are formed with dimensions $\propto l/j$. In fact, there is a break in the film free energy F at the point $\theta = \theta_c$, and the chemical potential $\mu = \partial F/\partial \theta$ is discontinuous. It is easy to see that the δ-function character of $\partial \mu/\partial \theta$ leads to formation of a plateau ($\nabla \theta \to 0$) on the diffusion front. A similar correlation between the structural phase transition and the presence of a plateau in the diffusion distribution was apparently observed in the experiment referred to above.[12]

[1]L. A. Bol'shov, A. P. Napartovich, A. G. Naumovets, and A. G. Fedorus, Usp. Fiz. Nauk 122, 125 (1977) [Sov. Phys. Usp. 122, 432 (1977)].

[2]L. A. Bol'shov, A. M. Dykhne, and A. P. Napartovich, in: Abstracts, 15th All Union Conf. on Emiss. Electronics 1973, Vol. 1, pp. 6–8, Akad. Nauk Ukr. SSSR, Inst. Fiz., Kiev.

[3]V. L. Pokrovskiĭ and G. V. Uimin, J. Phys. C11, 3535 (1978).

[4]G. Ertl and J. Küppers, Surface Sci. 21, 61 (1970).

[5]S. C. Ying, Phys. Rev. B3, 4160 (1971).

[6]V. L. Pokrovskiĭ and A. L. Talapov, Zh. Eksp. Teor. Fiz. 75, 1151 (1978) [Sov. Phys. JETP 48, 579 (1978)].

[7]V. L. Pokrovskiĭ and A. L. Talapov, Zh. Eksp. Teor. Fiz. 78, 269 (1980) [Sov. Phys. JETP 51, 134 (1980)].

[8]P. Bac, D. Mucamel, J. Villain, and K. Wentowska, Phys. Rev. B19, 1610 (1979).

[9]F. Frank and J. H. Van der Merwe, Proc. Roy. Soc. (London) A198, 205 (1949).

[10]J. H. Van der Merwe, J. Appl. Phys. 34, 117 (1963).

[11]A. I. Gubanov, Fiz. Tverd. Tela (Leningrad) 17, 1089 (1975) [Sov. Phys. Solid State 17, 692 (1975)].

[12]A. T. Loburets, A. G. Naumovets, and Yu. S. Vedula, Zh. Eksp. Teor. Fiz. 77, 773 (1979) [Sov. Phys. JETP 50, 391 (1979)].

[13]L. A. Bol'shov, Proceedings IV International Seminar on Surface Physics, Wroclaw, Poland, 1979. Wroclaw University, 1980, p. 42.

Translated by C. Flick

1041   Sov. Phys. JETP 53(5), May 1981

Bol'shov et al.   1041