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"SOLITON HETEROEPITAXY" IN THE FORMATION OF EPITAXIAL FILMS OF II – VI COMPOUNDS UNDER HIGHLY NONEQUILIBRIUM CONDITIONS

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Abstract. Initial stages of the epitaxial growth of CdTe and CdS film on substrates cooled to the temperatures below 0 °C are experimentally investigated. Electron diffraction patterns corresponding to the early stages of growth and photographs of the surface are presented. The experimentally revealed features (island size 20-25 nm, a δ-function size distribution of the islands, and a monotonic orientation process of the islands) are explained in the framework of a phenomenological theory of heterophase fluctuations and nucleation with the use of migration of solitons initiated by the misfit dislocations of crystal lattices.

1. INTRODUCTION

The broad spectrum of optical-electrical properties of the II – VI compounds has motivated a great interest to epitaxial films of these compounds. However, there still remains a field that has scarcely been included in the investigations: film formation from the vapor phase onto cooled substrates. It has been believed that epitaxial growth of II–VI films is possible only on substrates heated to several hundred degrees centigrade [1]. The present investigation, whose results have been previously discussed in [2], demonstrates the possibility of epitaxy on substrates cooled to negative temperatures. The work concerns the initial stages of epitaxial growth of cadmium telluride and sulfide under the above-mentioned conditions.

2. EXPERIMENTAL DETAILS

The films were prepared in a quasi-enclosed volume [3] on a substrate cooled by liquid nitrogen [4]. The reactor containing the powder heated to the sublimation point and the cooled substrates were brought together by a manipulator only during the time of film formation (only a few seconds). The temperatures of the reactor and the substrate were monitored by Chromel-Alumel and Copper-Constantan thermocouples, respectively. The cadmium telluride film was formed from CdTe powder at the sublimation temperature of 500 °C and the cadmium sulfide film from CdS powder at 650 °C, both under 10^{-3} Pa vacuum. By this method we were able to obtain epitaxial film of cadmium telluride at a substrate temperature in the range from 228 to 233K and cadmium sulfide film between 212 and 218K. The thickness of films was within hundredth part of micron.

To reduce the effect of the residual atmosphere and substrate contamination the substrates were heated at 400 °C in vacuum prior to the film deposition and the vacuum chamber was flushed out with pure agron.

As a substrate, we used muscovite with (0001) surface orientation.

To estimate the sticking coefficient and determine the nature of the flux reflected from the substrate we carried out special control experiments by the arrangement shown in Fig.1. A mica ring was disposed over the substrate and a mica sheet with a narrow slot was laid above it. Molecular flow was directed from evaporator to the slot at a certain angle. When the film has deposited, we examined the surface of the slotted sheet facing the substrate.

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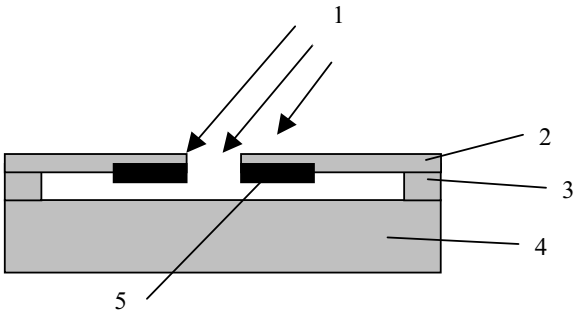

Fig. 1. Experimental arrangement for investigating the flux reflected from the substrate. 1 – flux of condensing material; 2 – sheet with a slot; 3 – mica ring; 4 – substrate; 5 – "halo".

The effect of the evaporator radiation on the substrate temperature was studied during the preliminary runs. Low-melting material ($T \cong 320$K) was placed in front of the reactor, which was not filled with powder. As seen from the relief on thin layer formed by the low-melting material, the effect of the evaporator radiation on the substrate temperature was negligible.

The film thickness was estimated with an MII-4 microinterferometer. The structural investigations were carried out by means of a PEM-100 (TEM) electron microscope and a model EMR-100 electron diffraction unit.

The main results of the investigations are shown in Figs. 2 and 3. Fig. 2 presents electron microscope images of a CdTe film on the substrate at various stages of growth. Fig. 2a illustrates that the film begins to grow with the appearance of widely separated islands with linear dimensions of 20-25 nm. No definite regularity is apparent in their arrangement. During the growth process the substrate surface is covered by islands of the same size (Figs.2b and 2c). At a certain stage of the growth the film becomes continuous (Fig. 2d), and then its relief remains essentially unchanged.

In Fig.3 we present the electron diffraction patterns of a CdTe film at the different stages of growth.

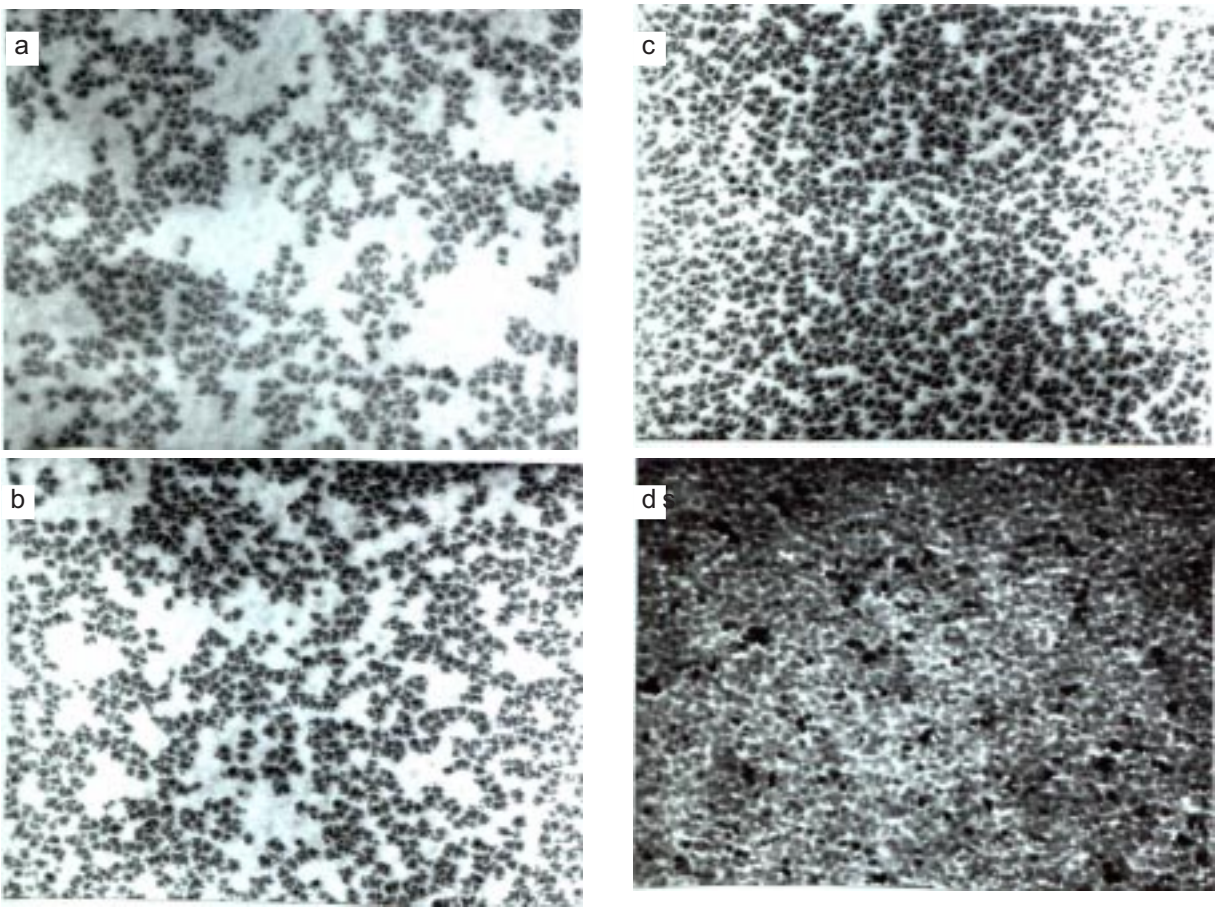

Fig. 2. Morphology of CdTe films on a cooled substrate. Figures a-d correspond to different stages of film growth.

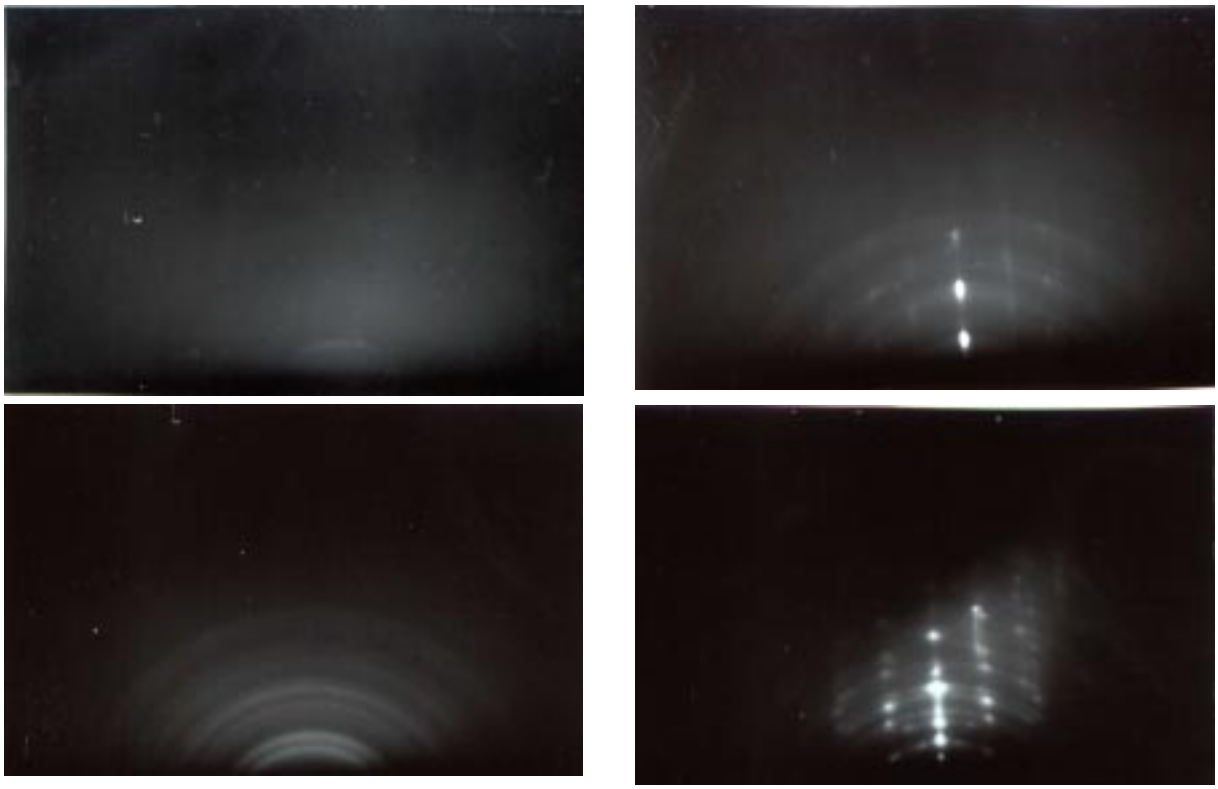

Fig. 3. Electron diffraction patterns of a CdTe film on a cooled substrate. Figures a-d correspond to different stages of film growth.

The same letter designations correspond to the same film in Figs. 2 and 3.

The films were of the cubic modification with the (111) plane oriented parallel to the substrate surface.

Fig. 3a shows that at the initial stage of growing the film is nearly amorphous. Then it becomes polycrystalline with azimuthal misorientation (Fig. 3b). This misorientation decreases with the growth time (Fig. 3c), and at the point when the islands merge together, the film becomes epitaxial (Fig.3d). The electron microscope pictures and the electron diffraction patterns registered during the formation of the epitaxial films of cadmium sulfide were similar to those for the cadmium telluride films.

Examination of surface of the sheet with the slot showed that in each experiment an uniform “halo” with poorly oriented structure, close to amorphous, was formed on the surface facing the substrate during all stages of the film growth.

The presence of the halo indicates that the sticking coefficient α differs from unity. According to our estimations, $\alpha \cong 0.1$. This latter result indicates that the substrate temperature is different from that of the islands formed. As is known from the theoretical results [5], the desorption of an individual adatom from the substrate without diffusion over the surface requires the incident flux temperature above 6000K.

Thus, the investigations of the formation of CdTe and CdS films on the muscovite substrate showed that the epitaxial growth of II–VI films under highly nonequilibrium conditions is characterized by the following behavior:

1) the islands with size of about 20-25 nm are formed with the temperature higher that that of the substrate;
2) the density of islands on the substrate increases at the initial growth stage, while the island size remains constant;
3) the islands on the substrate become oriented monotonically during the growth.

3. DISCUSSION

Let us consider reasons for this behavior.

It is a well-known fact that an individual atom or molecule incident on the substrate quickly dissipates its excess kinetic energy. A characteristic relaxation time is $\approx 2/\omega_o$ [6], where ω_o is the natural oscillation frequency of atoms of the substrate lattice ($\omega_o \cong 10^{14} \cdot s^{-1}$). In addition, it is known that because

of the relatively low energy of the incident molecular flux (T_v < 650 °C), the adatom vapor cannot change substantially the substrate temperature [7]. Therefore, the individual atoms and molecules on the substrate remain nearly immobile. Hence, the formation of the nuclei of a new phase is unlikely because it requires the delivery of a large number of atoms or molecules into a very narrow region of the surface where the relatively short-range interatomic forces operate.

In addition, the microstructures shown in Fig. 2 cannot be formed via nucleation and growth processes taking place on the substrate. The island size is highly uniform, and there is no known process which would produce the same result. This can be only due to the deposition of the completely formed islands, which are then able to move over the substrate to a considerable extent [8]. For example, if we assume that open area seen in Fig. 2a captures adatoms or molecules, then the islands at the edges of the region should be more dispersed and vary in size. There is no indication of this situation. Thus, It is likely that these islands are formed in the vapor phase.

The interaction of the nuclei formed by heterophase fluctuations in the molecular flux with the substrate differs from those of atoms and molecules. The time required for these nuclei to dissipate their excess energy will be considerably higher, since it will be given by the equation [9]

$$\frac{\partial T}{\partial t} = \chi \Delta T, \qquad (1)$$

The rough estimation of characteristic time is then $\tau \sim r^2/\chi \approx$ 1ns. Here χ is the temperature conductivity, Δ is the Laplacian operator and r is the linear size of a nucleus.

In addition, the discussed nuclei will have a surface that absorbs radiation from the evaporator, and this surface is much larger then the surface of contact with substrate through which the excess internal energy is taking away (for half-spherical nucleus this difference is two times). The combination of the above factors determines the island temperature higher than that of substrate.

We believe that the delta-function nature of the size distribution of the islands is an additional argument in favor of the model. The Volmer theory of heterogeneous nucleation assumes the existence of nuclei of various sizes in the vapor phase, up to the critical size. However, the contribution of the subcritical nuclei to the nucleation rate is small. Most of the subcritical nuclei break up again, and a favorable sequence of fluctuations occurs only accidentally. In the present case, for the reasons mentioned above, even the stable islands on the substrate are at a higher temperature than the substrate. Since the relaxation time is finite, one can consider that this difference in the temperatures is finite too.

Under these conditions most of the subcritical nuclei will break up, the support for this assumption follows also from the experimentally observed low sticking coefficient and the nature of the island size distribution function, which is similar to a delta function.

Let us examine the possible mechanisms for the experimentally observed monotonic azimuthal orientation of the islands in the film.

A similar process is usually assumed to proceed during the diffusion coalescence [10], but this assumption seems to be unlikely here due to the low substrate temperature and the short time of the orientation formation. On the other hand, it is known that the matching of the film and substrate lattice constants is a very important factor in heteroepitaxial growth. Variations of the crystalline lattices lead to the rise of elastic forces. This in turn results in the forced reconstruction of the lattice in the diffusionless way. In particular, Kukushkin and Osipov [10] have considered the migration of the crystalline islands over a crystalline substrate of a different phase due to misfit dislocations. The theoretical justification of a sharp increase in the island mobility at a certain relation between the lattice parameters of the island and the substrate was proposed in this work, which can be written as [10].

$$\varepsilon = \frac{(a-b)}{b} > (2\pi)^{3/2}\sqrt{\frac{f}{\lambda a}}, \qquad (2)$$

Here a is the lattice parameter of the substrate, b is the same for an island in the plane of the substrate, f is a constant characterizing the force due to the substrate acting on an atom of the island, and λ is a parameter that characterizes the force of interaction among the atoms of the island.

In the derivation of Eq. (2) the influence of the temperature was not taken into account. The initial Lagrangian was used in the form

$$L = \int \left\{ \frac{m}{2}\left(\frac{\partial y}{\partial t}\right)^2 - af\left[\frac{\lambda a}{2f}\left(\frac{\partial y}{2f} - \varepsilon\right)^2 + \frac{1}{2\pi}\left(1 - \cos\frac{2\pi y}{a}\right)\right]\right\}\frac{dx}{a}, \qquad (3)$$

where *m* is the mass of atoms constitute the island, *y* is a variable that characterizes the displacement of an atom of the island from the corresponding minimum in the substrate potential at the time *t*, and *x* is the coordinate along the substrate.

As can be seen from Eq. (3), the simplest way to take the temperature into account is to introduce the temperature dependence of the lattice parameters. In this case, all the results obtained in [10] will be correct, but the parameter ε in the final expression (see Eq. (2)) should be considered as a function of the temperature.

From these results we can conclude that the temperature dependence of ε will be especially strong when a film is formed on a cooled substrate, since the temperature gradient between the islands and the substrate should be accounted for in addition to the different linear thermal expansion coefficients. This gradient also depends on the substrate temperature. Thus, according to Eq. (2) we can select the conditions at which the islands become highly mobile by varying the substrate temperature. As demonstrated in [9], this mobility is due to solitons that arise due to the lattice mismatch between the island and the substrate. In the case of the formation of a crystalline island on an orienting substrate, the minimum of the potential energy will correspond to an oriented substrate and it is reasonable to assume that the formation of solitons will favor the orientation.

This soliton heteroepitaxy model is supported by the experimental results. While for the CdTe film, which has a lattice constant of 0.648 nm, the temperature of epitaxial growth is $T \cong 230$K, for the CdS film the lattice constant is 0,582 nm and the temperature of epitaxial growth is $T \cong 215$K. Moreover, all temperature ranges of the oriented growth that we have found for the films of CdS_xTe_{1-x} solid solutions lie from 215 to 230K depending on the composition.

The absence of diffraction reflexes from the substrate at the initial growth stages can be considered as a result of the formation of the thin adatoms layer. Note that due to the diffusion of some atoms to islands this layer is not formed on the hot substrates.

4. CONCLUSIONS

The following conclusions may be done from our results:

1) the heteroepitaxial growth of II-VI films on cooled substrates occurs through the formation of individual islands of 20-25 nm in size, the concentration of these islands steadily increases and they have a common direction of orientation, while the size of the islands remains nearly constant;
2) the size of islands and their delta-function size distribution can be explained in the framework of Volmer's nucleation theory with the account of the heterophase fluctuations;
3) the nature of the orientation of the islands on the cooled substrate correlates with the temperature-induced variation in the lattice mismatch between the deposited material and the substrate;
4) the heteroepitaxial growth under highly nonequilibrium conditions can be explained and theoretically described via migration of solitons initiated by the misfit dislocations of crystal lattices.

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REFERENCES

[1] L.S. Palatnik and I.I. Papirov, *Epitaxial Films* (Nauka, Moscow, 1971), in Russian.
[2] A.P. Belyaev, V.P. Rubets, I.P. Kalinkin and M.Yu. Nuzhdin, In: *Second international workshop «Nucleation and non-linear problems in first-order phase transitions" (NPT 2002)* (St.Petersburg, 2002) P.62.
[3] I.P.Kalinkin, V.P.Aleskovskii and A.V.Simashkevich, *Epitaxial Films of II-VI Compounds* (LGU, Leningrad, 1978), in Russian.
[4] K.K.Murawjeva, V.P.Rubets, Ya.S.Smirnov and I.P.Kalinkin // *Prib. Tekh. Eksp.* **5** (1991) 188, in Russian.
[5] B.McCarroll and G.J.Ehrlich // *J.Chem.Phys.* **38** (1963) 523.
[6] *Handbook of Thin Film Technology*, ed. by L.I.Maissel and R.Glang (McGraw Hill Hook Company, New York, 1970).
[7] J.P.Hirth and G.M.Pound, *Condensation and Evaporation: Nucleation and Growth Kinetics* (Pergamon Press, Oxford, V.2, 1963).
[8] V.P. Rubets and S.A. Kukushkin // *Thin Solid Films.* **221** (1992) 267.
[9] L.D.Landau and E.M.Lifshitz, *Theory of Elasticity* (3rd English edition, Pergamon Press, Oxford, 1986).
[10] S.A.Kukushkin and A.V.Osipov // *Phys. Solid State.* **36** (1994) 799.