SUBSTRUCTURAL STEP TRANSITIONS AT THE INITIAL STAGES OF EPITAXIAL GROWTH OF PbTe ON NaCl

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SUBSTRUCTURAL STEP TRANSITIONS AT THE INITIAL STAGES OF EPITAXIAL GROWTH OF PbTe ON NaCl

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Thin condensed films, especially at the initial stage of growth, are nonequilibrium systems (^1). Their transition to an equilibrium state with increasing thickness or upon annealing may proceed with the participation of phase transitions, for example by replacement of nonequilibrium crystalline modifications by more stable ones (^2). For systems that do not undergo phase transformations, a series of structural transitions has been observed that obey an intraphase rule of steps (^3).

In the present work a successive change of nonequilibrium states has been found at the initial stages of epitaxial growth of PbTe films on NaCl. The specimens were prepared by condensing PbTe onto a (100) cleavage of NaCl crystals heated to temperatures $T_{\text{sub}} = 90\text{–}160^\circ$, in a vacuum of $5 \cdot 10^{-5}$ torr. The condensation rate ω was varied from 0.8 to 7 Å/sec. In one experiment 100 specimens were prepared, for which the rate ω and the condensation time t were varied, while the remaining process parameters were kept identical. The specimens were separated by carbon films, which were deposited immediately after the completion of condensation, and were examined in a UEMV-100V electron microscope.

At $\omega = 4.7$ Å/sec and $T_{\text{sub}} = 150^\circ$, at the initial stage of growth of the epitaxial PbTe film, very thin bounded crystals are formed (Fig. 1a, $t = 2$ sec). Such crystals are nonequilibrium, since they have too large a store of specific surface energy and of the energy of distortions of the crystal lattice arising during epitaxial coalescence of crystals with different lattice parameters ($a_{\text{PbTe}} = 6.34$ Å; $a_{\text{NaCl}} = 5.628$ Å (^4)). Upon further condensation the PbTe crystals lose stability, are destroyed, and pass into particles free from crystal-lattice deformations and possessing a smaller specific surface (Fig. 1b, $t = 5$ sec). Each flat crystal that has lost stability should, under the action of surface-tension forces, collect into one most compact particle, as particle 1 in Fig. 1b. However, in most cases this process arises simultaneously at several points of a single crystal: at one or two central points, while several small droplets are formed at the periphery. This can be seen in Fig. 1b, where a dashed line marks the region which at the

Fig. 4

Figure 1: Fig. 4

preceding stage was one flat crystal and turned into several droplets. Figs. 1–3, see insert to p. 79.

At low condensation rates the destruction is weakly expressed and is reduced to the formation of holey crystals (Fig. 2, $\omega = 0.8$ Å/sec, $t = 30$ sec).

The subsequent stages of growth of a PbTe film are shown in Fig. 3, for $\omega = 2.7$ Å/sec. In Figs. 3a, b ($t = 3$ and 5 sec) the stages of fragmentation are visible.

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Fig. 1

Fig. 2

Fig. 3

and partial contraction of flat crystals. The process of contraction into a more compact shape, developing within a single crystallite, may be regarded as autocoalescence. Autocoalescence is most fully expressed at the time of 7 sec (Fig. 3c), when droplet-shaped particles 1 are observed. Autocoalescence of particles prevents strong-bond sites with the substrate, which appear as black dots 2 on the contours of the lighter particles. The density of these dots is $7 \cdot 10^{10}$ cm^{-2}, which corresponds to the density of accumulations of point defects that are nucleation centers in ionic crystals (^{5}).

The next stage of growth, shown in Fig. 3g, is growth according to the usual scheme with coalescence of several neighboring particles, which, on coming into contact, merge by the mechanism of liquid flow and give rounded, droplet-like growth forms (^{6}). Subsequently (Fig. 3d, e; $t = 20$ and 30 sec), faceting is observed in the growing particles, and their gradual transition to the equilibrium cubic growth form.

Thus, the sequence of stepwise processes in the initial stages of epitaxial growth of PbTe on NaCl appears as follows: 1) growth of flat nonequilibrium crystals; 2) subsequent transition by means of autocoalescence to a more equilibrium bulk state, accompanied by the removal of distortions of the crystal lattice; 3) overgrowth of rounded particles into faceted crystals, which, both in form and in the state of the crystal lattice, are already closer to the equilibrium state than the crystals at the very first stage.

Fig. 4

The appearance and duration in time of each growth stage at constant temperature depend on the condensation rate, as can be seen in the diagram of Fig. 4. In region I, flat deformed particles grow, as shown in Fig. 1a. In region III, faceted particles grow, corresponding to Fig. 3e. In region II, the processes of destruction of unstable particles, autocoalescence, and coalescence take place. The extent of region II is indicated by horizontal lines of different types, which correspond to four batches of specimens prepared in different experiments. The shift of interval II from one experiment to another is associated with changes in the substrate temperature within $150 \pm 10^\circ$, and also with inaccuracies in controlling the condensation time. The open circle at the beginning of the lines corresponds to the beginning of destruction of PbTe crystals (Fig. 1b), and the dark circle to the state of Fig. 3d. The tilde sign means that the initial or final moments were not fixed precisely.

Experiments carried out at $T_s = 90^\circ$ showed the presence of the same growth stages as at 150°, but with changes of the same type as those observed when the condensation rate is increased.

To estimate the growth kinetics of PbTe particles, the dependence of the substrate coverage coefficient β (the ratio of the area occupied by the condensate to the total area of the substrate) on the condensation time t was determined. From a series of electron-microscope images of PbTe condensates, for which ω and t were known, the coefficient β was measured, and then the particle thickness h was calculated from the formula $h = \omega t/\beta$. Knowing h and determining from the images the length l of the base side of tetragonal PbTe particles, one can find the shape coefficient $k = h/l$.

The experimental data for these quantities at $\omega = 4.7$ Å/sec are given in Table 1. It is seen from the table that by the moment of destruction (5 sec) the crystals are very thin and have $k = 0.035$. At the stage of autocoalescence and coalescence, β decreases appreciably. Afterward, a rapid increase of k up to a value of ~ 0.2 is observed.

Table 1

t, sec	β	h, Å	l, Å	$k = h/l$
2	0.46	20	700	0.028
5	0.64	35	1000	0.035
7	0.62	55	930	0.059
10	0.54	85	930	0.091
20	0.62	150	860	0.175
40	0.76	250	1200	0.210

Electron-diffraction studies show that at the growth stage corresponding to the destruction of the initial PbTe crystals and their detachment from the substrate, their orientation is disturbed. Subsequently the orientation is restored. The microelectron diffraction patterns obtained from the films shown in Fig. 1*a* and 3*d*, *e* are spot patterns; for Fig. 1*b* and 3*b*, *c*, they consist of arcs.

The sequence of transitions observed on PbTe condensates in the initial stages of epitaxial growth, representing a stepwise approach to the equilibrium state (cf. (7)), is more complete and varied in comparison with other studied cases of epitaxial growth. This sequence should be characteristic of a large number of substances for which there is a considerable mismatch between the lattice parameters of the condensate and the substrate. If it has not previously been observed in full, this is only because the manifestation of the various growth stages is very sensitive to the experimental conditions—the type of substrate, the ratio of the bonding forces of the substrate and the condensing substance, the substrate temperature, the condensation rate, and so on.

Some growth stages may proceed so rapidly, or at such small particle sizes, that they cannot always be recorded experimentally. For example, in the case of PbTe growth on NaCl at a condensation rate > 7 Å/sec, the first stage that can be recorded is the stage of autocoalescence, corresponding to Fig. 3*b*. When the condensation rate is reduced to 0.8 Å/sec, surface-migration processes gradually bring the crystal closer to its equilibrium shape, so that it does not reach an unstable state and its destruction is not observed.

Special cases of the general scheme considered by us can be found in many works on the study of epitaxial growth ([6,8]). Thus, during the condensation of Ag on MoS_2, an initial stage of formation of flat faceted crystals is observed, but autocoalescence and destruction of the initial particles are absent. At the same time, during contact of flat Au particles, a related process occurs—coalescence of particles with detachment from the substrate and loss of faceting ([6]).

Taking into account that the processes of destruction of the initial crystals affect the orientation of particles, while the course of autocoalescence is associated with interaction with defects of the crystal surface, the phenomena observed on PbTe condensates prove important for understanding the mecha-

the mechanism of crystal decoration. At subsequent stages of epitaxial growth, new stepwise structural transitions to a more equilibrium state are possible.

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