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## Features of island nanostructures formed by melting Sn, Bi and Sn–Bi thin films on C substrates

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### ABSTRACT

We report the results of studying the morphological structure of island systems formed by melting Sn, Bi and eutectic Sn–Bi polycrystalline films 2–70 nm thick deposited on carbon substrates. Substrate coverage with a film is found to be non-uniform against film mass thickness after its melting and crystallization. The interval of film thickness is determined where the island systems with narrow enough particle size distribution are formed under melting.

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### 1. Introduction

For solving fundamental and applied problems we need to produce ensembles of almost identical nanosize particles on various substrates. During the last years this problem became of crucial importance in view of nanotechnology development. One of the ways for solving this problem is the employment of various deposition techniques for island systems formation with required size on substrates. However, a single maximum histogram of particle size distribution is observed only at small mass thickness both during deposition directly onto the solid state, and through an intermediate liquid state with the subsequent crystallization.

Besides, the authors [1] report on the spontaneous formation of island systems with unimodal particle size distribution as a result of melting and the subsequent crystallization of continuous polycrystalline Bi films. At the same time, there are only few papers devoted to the variation of morphological structure of continuous films on a substrate under their melting and crystallization, whereas the studies on the spontaneous formation of island systems by melting and crystallization of discontinuous solid films to our knowledge are actually not carried out.

Taking into account, that this way can be promising for producing systems consisting of ensemble of almost identical particles on

a substrate, it seems to be expedient to study morphological structure variation of discontinuous films of a various mass thickness as a result of their melting and crystallization.

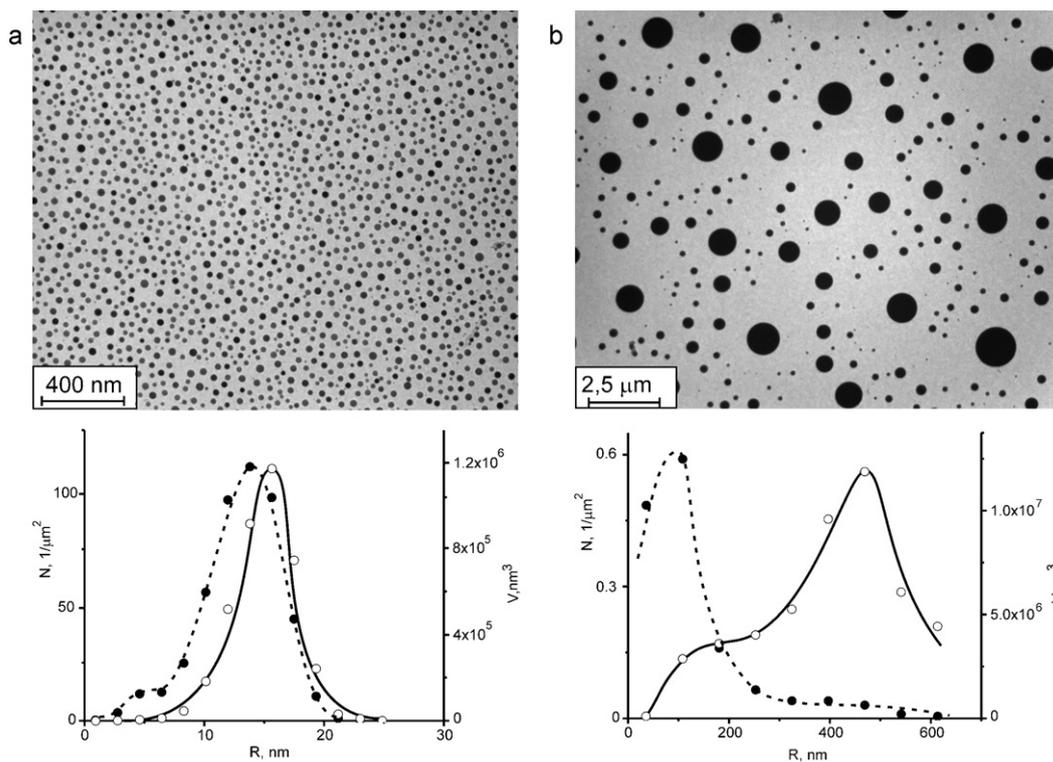
The vacuum deposits of tin, bismuth and Sn–Bi of eutectic composition on the amorphous carbon substrate were chosen as the objects of study. This choice was caused by the available experimental data on morphological structure of island condensates of tin and bismuth generated through the liquid phase, depending on their mass thickness and temperature of C-substrate [2–4]. Moreover, it is convenient to work with the deposits of these metals due to their low melting temperatures, and also because of the fact that in films of bismuth the oriented growth of particles with distinctly shown faceting is easily observed owing to its strongly pronounced anisotropy [5–7].

### 2. Experimental details

The experiments were carried out in hand-made vacuum vessel with base pressure  $2 \times 10^{-8}$  mbar. The Sn, Bi and Sn–Bi eutectic alloy films were prepared by evaporating 99.999% purity metals from resistively heated molybdenum boats with subsequent condensation on the substrate kept at room temperature. The extended massive copper substrate with  $\sim 10$  cm length was supplied with an internal resistive heater, located on its axis along its whole length. NaCl fresh cleavage crystals 0.5–0.8 mm thick were fastened to the substrate by means of a special copper mask. A metal evaporator was placed under one end of the substrate. Such layout enables

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**Fig. 1.** Bright-field TEM images of the molten Sn films and corresponding distributions of particles size (●) and volume (○) at different film mass thickness (*a*–4 nm, *b*–47 nm).

us to obtain up to 25 samples of different thickness during a single experiment. Sn–Bi eutectic films were prepared by consecutive deposition of components from separate sources. The geometry of a relative positioning of evaporators was chosen such as to provide the eutectic composition between the deposited quantities of tin and bismuth along a substrate. The mass thickness of the deposits was monitored by 4.2 MHz quartz crystal oscillator, whereas the temperature of the substrate was measured by calibrated K-type thermocouples. The NaCl crystals were covered by 20 nm layer of carbon evaporated from an arc discharge just before preparation of films under study. Mobile shutters were positioned between the evaporators and the substrate holder on which initial portions of metal for the formation of the stationary mode of evaporation were condensed.

The studies of the samples were carried out directly after deposition on the C-substrate at room temperature, and after heating above the melting temperature and subsequent cooling. The films on a carbon substrate were separated from NaCl crystals by their dissolution in the distilled water and poured out on the copper grids for transmission electron microscope (Selmi TEM-125K) investigation. Images were registered with CCD camera and analyzed on personal computer using specially developed software.

### 3. Results and discussion

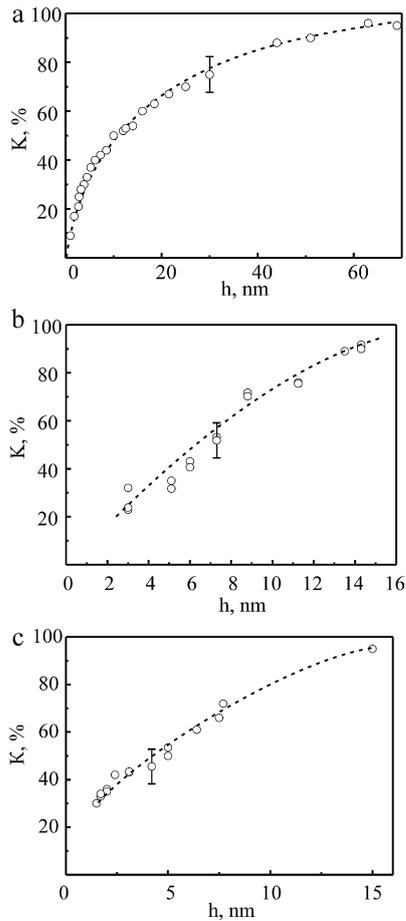
The electron-microscope investigations have shown that in full agreement with the data accumulated in the scientific literature [e.g. 5] in the as-deposited state (vapor–crystal condensation mechanism) the morphological structure of the films is determined by their mass thickness. With the increase of thickness a consecutive transition is observed from the structure consisting of isolated islets, which are close in form to the spherical ones, to the system of contacting platelets with the subsequent transition to labyrinth-like structure and finally to continuous polycrystalline films.

The isolated particles with the truncated sphere shape are spontaneously formed after melting–crystallization of all investigated films irrespective of their thickness. However, the arrangement pattern of particles on the substrate and of their size distribution during the growth of mass thickness of the films undergo essential qualitative changes (Fig. 1). The coverage, that is the ratio of the projection area of the particles to the total substrate area, is known to be rather sensitive to the change of their morphological structure. Therefore, this paper deals mainly with the dependence of the coverage against mass thickness of as-deposited films and those after melting.

We observe the uniform growth of the coverage with the increase of film mass thickness in the as-deposited state for Sn, Bi and Sn–Bi films (Fig. 2), this growth being correlated with available theoretical calculations [8]. Moreover, the coverage for Sn films grows much slower with film thickness than Bi one, that is Sn films became solid at larger mass thickness as compared with Bi films.

The coverage for Sn–Bi films prepared by consecutive deposition of components seems to be a sum of coverage values for Sn and Bi films at small mass thickness due to minute solubility of components at room temperature. For example, the coverage for Sn and Bi films 7.5 nm thick amounts to ca. 40% and ca. 60% respectively (Fig. 2a and b). The Sn–Bi eutectic film 15 nm thick consists of Sn and Bi films 7.5 nm thick each. Therefore the coverage for such Sn–Bi film has to approach 100% in agreement with the measured value (Fig. 2c).

The behavior of the coverage against mass thickness changes substantially after melting for all investigated films with simultaneous reduction in absolute value (Fig. 3). It grows rapidly from 10 to 20% at the minimum investigated thickness to the maximum ~30–40% at some intermediate thickness  $h_1$  and further it decreases with the increase in thickness, and approaches the approximately constant value in 5–15% interval for different systems. The electron-microscope images show that  $h_1$  thickness corresponds to the thickness value when contacts appear between

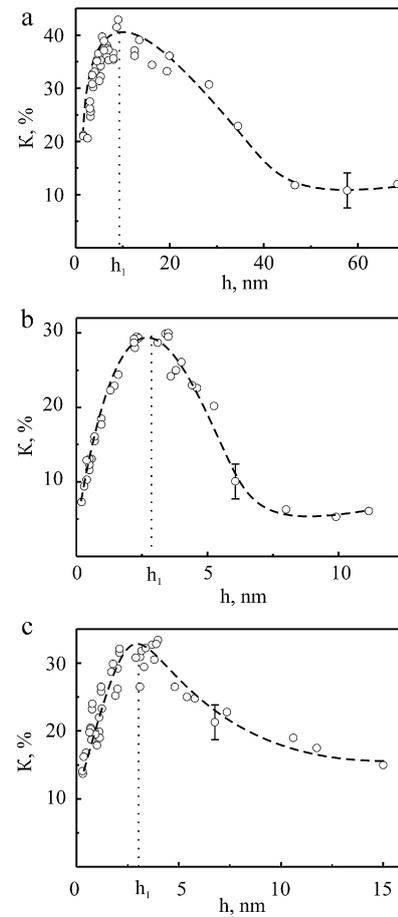


**Fig. 2.** Variation of the substrate coverage versus film mass thickness for as-deposited Sn (a), Bi (b) and Sn-Bi films (c).

isolated islets and the labyrinthic film structure starts to form. This thickness amounts to  $\sim 3$  nm for Bi/C and Sn-Bi/C systems and  $\sim 9$  nm for Sn/C one as follows from Fig. 3. The particle size distribution histograms calculated for this film thickness show a rather narrow distribution of both number and volume of islands over size (Fig. 1a). Moreover, melting of solid films within the  $0-h_1$  thickness range enables one to form the particles arrays with unimodal distribution of particles over size, but the sharpest histograms are the ones relating to  $h_1$  thickness, i.e. the thickness of initiation of labyrinthic structure formation in the solid films.

With a further increase in thickness, the picture changes essentially and the coverage decreases approximately 3 times (Fig. 3). Such films are characterized by disordered particle size distribution, and in electron-microscope images there are considerable quantities of small particles among big ones which, possibly, were generated as a result of coalescence under melting and disintegration of the thick film (Fig. 1b).

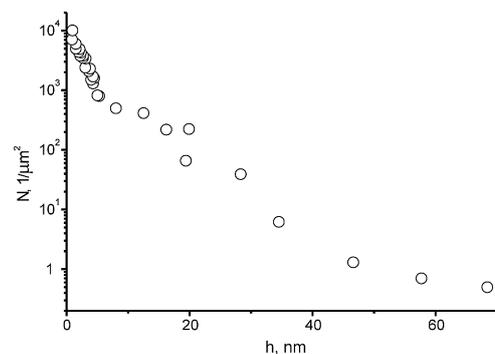
The changes of character of the particle size distribution are well coordinated with the change of the substrate coverage (Fig. 3) and particles number density (Fig. 4). As it was already mentioned, after having reached  $h_1$  thickness the coverage decreases approximately three times. The similar situation is observed for the number density of particles. With the increase in thickness the particle density for Sn/C system smoothly decreases, and having achieved the thickness of more than 40 nm it does not vary practically. The range of thickness from 10 to 40 nm for Sn/C films corresponds to the transition from the island structure to the almost continuous film through labyrinthic one.



**Fig. 3.** Size dependence of the coverage for Sn (a), Bi (b) and Sn-Bi films (c) after their melting.

The outlined data indicate that the evolution of the morphological structure of the investigated films with thickness as a result of their melting-crystallization has qualitatively various patterns at different thickness values. These changes can possibly be explained taking into account known laws of growth and melting of metal nanosystems on a neutral amorphous C-substrate in a following way.

According to existing conceptions [7,9] the formation of Sn and Bi films occurs according to Vollmer-Weber mechanism at room temperature of the carbon substrate. The nuclei of the condensed phase formed at the initial stage of film growth are liquid owing to size dependence of the melting temperature and have the form of a spherical segment with the contact angle  $\Theta > 90^\circ$  for Bi and Sn. When growing particles reach the size corresponding to the



**Fig. 4.** Number density of the molten Sn films of different mass thickness.

size dependence of the melting temperature, their crystallization occurs and further condensation proceeds directly into the crystal phase. Upon crystallization of spherical Bi particles they get a strongly pronounced facet [5–7], whereas Sn particles keep the form close to the spherical one [9]. Under subsequent condensation the crystallized particles flatten, the contacts appear between them, and the labyrinthic structure starts to form which consequently evolves into the structure of a continuous polycrystalline film with the corresponding relief. The formation of flattened particles and the appearance of contact between them in the case of bismuth takes place at smaller mass thickness, than for tin [5,6]. The coverage in this case grows continuously from 0% to 100%, which means that one can achieve any coverage by varying film thickness, whereas in the case of condensation directly into liquid state only the island growth occurs and the coverage cannot exceed ~55% due to coalescence of particles [2–4].

Melting of isolated particles and subsequent crystallization clearly lead to the reduction of the substrate coverage only due to the acquisition of the particles' form close to spherical one. The specified change will be more expressed for more flattened as-deposited particles. Hence, the decrease in the coverage is related to the reduction of the particles surface area and the respective reduction of the area occupied by them on the substrate, without any significant change of their quantity. Under the occurrence of contacts between the crystal particles during melting the capillary forces merge contacting particles leading to reduction of their total quantity under crystallization and accordingly to the reduction of the coverage. Reduction in coverage for very small thickness values is possibly related to the speedy liquid-phase coalescence of such small particles [10].

The results of research into the particle size distribution in the films on the carbon substrate, generated through the liquid phase [2,3], also point in favor of our consideration. According to the above papers the characteristic feature of the particle size distribution of such systems is the occurrence of the second maximum (starting from the thickness ~3 nm) which is displaced into the range of bigger size particles with the mass thickness growing.

Sharp reduction in coverage starting from some thickness value corresponding to transition to continuous films might be caused (cf. [11]) by disintegration features of thick continuous films below the melting temperature of bulk samples. This disintegration possibly occurs through the supercooled liquid phase which is formed owing to the reduction of surface energy of a film on the neutral,

not wetted amorphous substrate at the expense of its splitting into islets [11].

#### 4. Conclusion

We have demonstrated that the morphology of island films formed by melting of crystalline Sn, Bi and eutectic Sn–Bi films on the amorphous carbon substrate is determined directly by the formation of initial condensates according to Vollmer-Weber mechanism.

After film melting the non-uniform dependence of the coverage on film mass thickness has been revealed. The maximum value of coverage is attained after melting of 9 nm thick Sn and 3 nm thick Bi and Sn–Bi films. We observed the spontaneous formation of island structures possessing a unimodal size distribution up to the thickness values corresponding to the transition from island to labyrinthic structure of as-deposited films.

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