Island size distribution under different substrate temperatures and film mass thickness

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Introduction

The ultradispersion systems, of which the vacuum-deposited island films are part, make it possible, due to their nature distinguished by minute characteristic dimensions, to change various properties within so wide limits which are, in principle, unattainable for usual massive materials. It is thanks to this feature that they are widely applied in most diverse fields of science and technology (catalysis chemistry, materials science, microelectronics, etc.), and arouse a great interest among researchers and industrial engineers working in different spheres. Notably, knowledge of characteristic size corresponding either to the greatest particle surface area or its greatest volume, and the size correlation with the production conditions are vital for any application. A considerable number of papers [1-5] focused on the island size distribution, however, t.ɛ main results have been obtained for crystalline condensates in which the particles can only roughly be characterized by one size. In formation of island condensates, especially on amorphous neutral substrates, at the temperature much lower than the melting temperature, condensation into a liquid phase is observed [6]. Their crystallization can yield arrays of single-crystal particles of either an unbalanced spherical shape or a balanced cut which are rather promising for the development of nanotechnology. Therefore, we deemed it expedient to study distribution in the condensates-produced via liquid phase, and establish the relationship between the distribution, mass thickness, and temperature under preset condensation conditions.

Experimental method

The study of particle size distribution has been conducted for island films condensed onto amorphous carbon substrates in a 10^{-4} Pa vacuum. To investigate the correlation between distribution and mass thickness gallium condensates have been used, treated according to the vapour-liquid mechanism at a temperature of 320 K. Choice of this metal was caused by the fact that due to its low melting point (299 K), gallium preserves its liquid state even under room temperatures (because of supercooling). This made it possible to examine size distribution of the islands in liquid phase, excluding potential variations of particle shape and size distribution due to crystallization. Use of gallium for investigating the size distribution temperature dependence in proximity of the maximum supercooling temperature is inexpedient, as in this case, samples would have to be condensed and studied using electron microscope under low temperatures (according to [6], the maximum supercooling temperature T_g makes up about two thirds of the melting temperature T_s ($T_g = 2/3T_s$), i.e., for gallium condensates $T_g \approx 200$ K), which would present technical problems. Therefore, tin films condensed on carbon substrate have been used for studying island distribution temperature dependence. Of the metals examined earlier [6], tin was the best in terms of preserving its shape characteristic of a liquid phase during crystallization from the supercooled state. Besides, gallium and tin have low vapour pressures under the given temperatures, which allows to disregard re-evaporation.

To minimize side effects, samples have been prepared in both cases so as to obtain a series of samples with different mass thickness (Ga/C system: $1 < t_m < 20$ nm) or temperatures (Sn/C: $250 < T < 400$ K) under identical conditions, i.e., in one experiment. To this end, condensation was carried out on a substrate with a temperature gradient within 250

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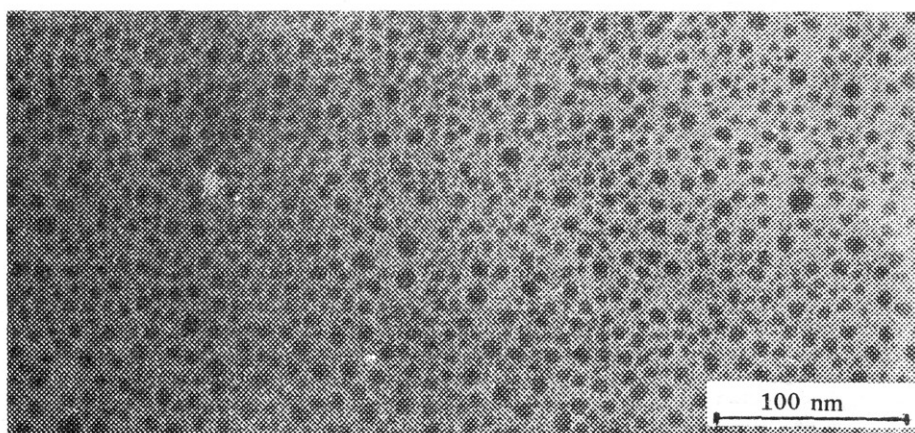
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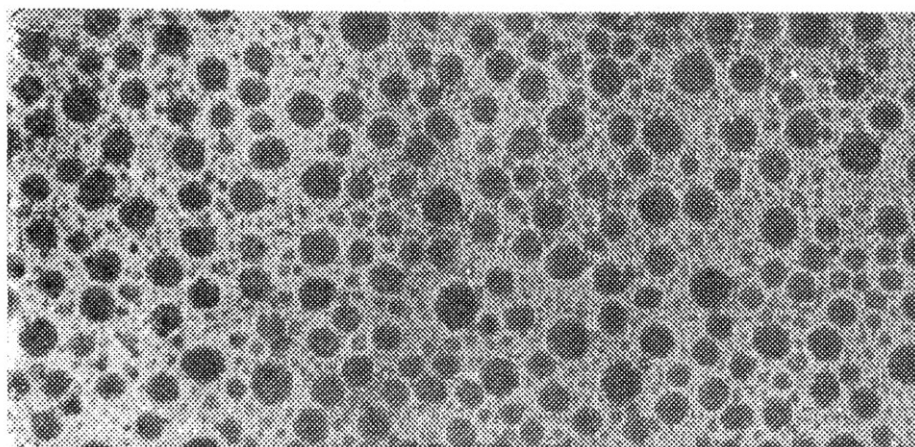
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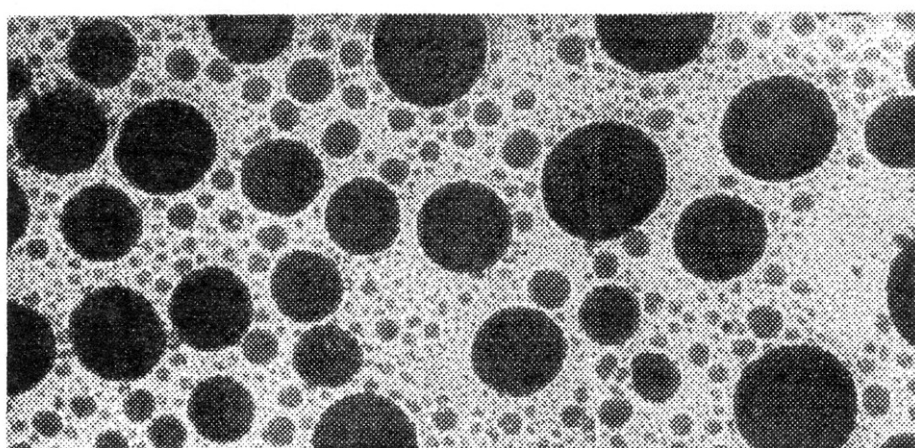
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Fig.1. Photomicrographs of different mass thickness gallium films on carbon substrates. Film thickness: a) 2 nm; b) 5 nm; c) 14 nm.

through 400 K for temperature dependence study, whereas in studying the dependence of distribution on thickness a metal evaporator was located asymmetrically with respect to an elongated substrate, which has allowed to obtain a continuous set of mass thickness over its length within the above interval. Film thickness were monitored in the process of condensation by a quartz vibrator, and refined subsequently by the results of histogram study. After the condensation, films were cooled in vacuum to room temperatures, isolated from substrate, and then examined by transmission electron microscopes ЭМВ-100БР and ЭМ-125.

Photomicrograph analysis was used to determine particle distribution over their radii in films of different mass thickness $N(R, t_m)$. Such distributions for the films condensed according to vapour-liquid mechanism are distinguished for an extremely great number of minimum sized particles Fig.1. Notably, the smallest particles are not recorded quite often due to limited resolution of an electron microscope. Usually, in investigating integral properties of island films, it turns out that it is not the number of given size particles which is important, but their total volume $\sim N(R)R^3$ (in studying the processes wherein the whole particle volume is involved, for example, particle coalescence, in structural study of island films), surface area or cross-section $\sim N(R)R^2$ (adsorption, catalytic power of island films, and optical studies). Fig.2 shows size
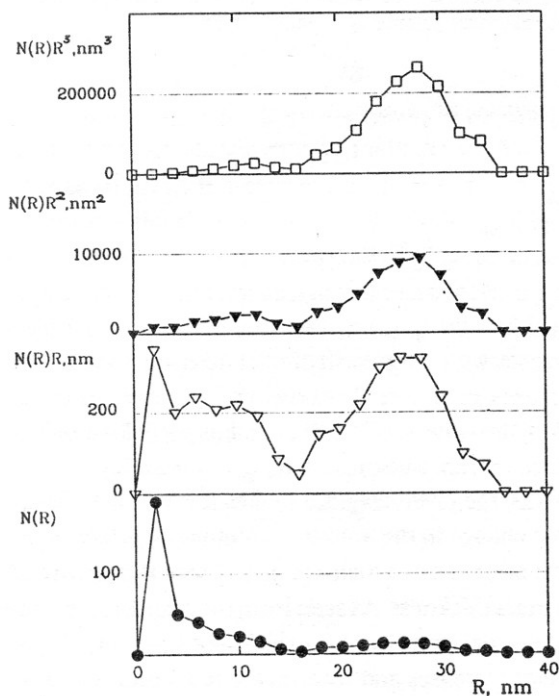
distribution for island tin film on carbon substrate presented in different coordinates which illustrate the importance of proper choice of distribution function type for studying respective properties.

To determine relationship between the distribution and mass thickness of island films, this work used the volume distribution functions which were standardized by an area of measured region (S) and range of sizes applied (ΔR):

$$t(R) = A \cdot N(R) \cdot R^3 / (S \cdot \Delta R) \qquad (1)$$

Factor A accounts for a particle shape, i.e., the kind of its volume dependence on the characteristic size. For the islands shaped as spherical segments with an edge wetting angle Θ (this particle shape is typical of the island films obtained by condensation according to the vapour-liquid scheme) the A factor is determined by the relation

$$A = \frac{\pi}{3}(2 + \cos\Theta) \cdot (1 - \cos\Theta)^2 \qquad (2)$$

$t(R)$ is a non-dimensional quantity equal numerically to the mass thickness of film which is formed by unit interval islands surrounded by R. It can be assumed for convenience that $\Delta R = 1$ nm, then $t(R)$ will acquire the dimension of length. Should we integrate the function $t(R)$ from zero to R_{max}, or, actually, sum up the $t(R)$ value through a unit interval, we would directly determine the mass thickness of film for each sample.

2. Correlation between island size and film mass thickness

Fig.3 illustrates the study of island size distribution in gallium films of different mass thickness on carbon substrate. The plots show the kinetics of particle distribution variation as the film thickness grows. A specific feature of histograms obtained is presence of the first fixed maximum at $R \sim 3$ nm, and appearance of the second maximum starting with $t_m \sim 3$ nm which increases with the growth of mass thickness, and is shifted to the region of larger-sized particles.

The above method of histogram implementation is a generally accepted one, and can be applied when it is necessary to determine characteristics of a specific film. However, quite an inverse problem often arises in practice, i.e., to obtain a film with the maximum amount of preset size particles. In this case, it is necessary to examine volume variation of the desired size particles. To this end, it would be expedient to exchange places of the variable (R) and parameter (t_m), and represent the obtained distributions $N(R, t_m)$ in the coordinates "$t_m - t(R, t_m)$".

Fig.4 shows a series of dependences $t(R, t_m)$ as a function of t_m for the examined system. As is shown,

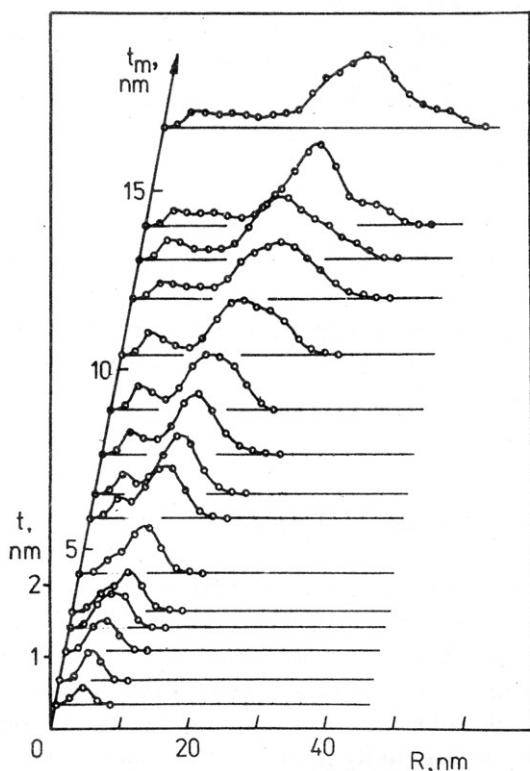Fig.2. Particle size distribution for island tin film represented in different coordinates.

Fig.3. Gallium island size distribution in films of different mass thickness.
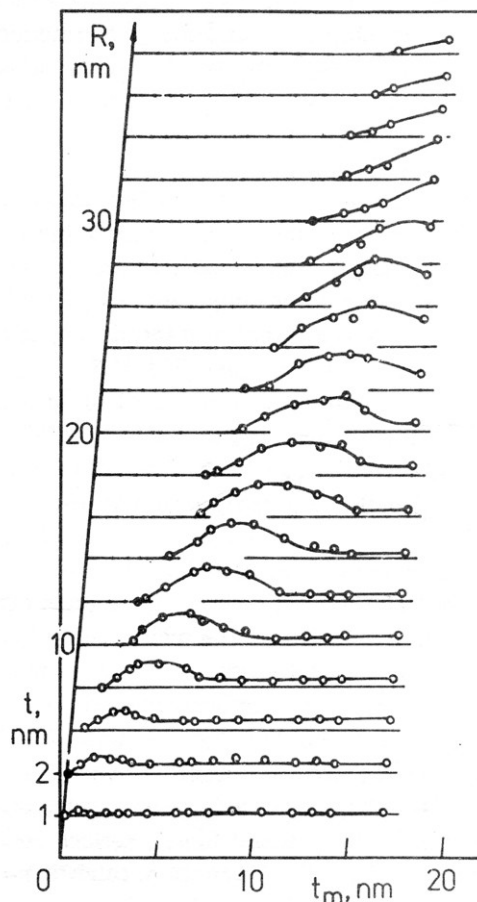

Fig.4. Variation of volume of different size particles against mass thickness of gallium film.

nonmonotonic variation of the fixed size particles number is observed within the studied interval of gallium film mass thickness (1 to 20 mn) as the thickness grows. In this case, three characteristic values of mass thickness can be isolated in dependence $t(R, t_m)$ for a fixed radius particle: $t_{m1} \sim 0.25R$ is the thickness before which the given size particles are nonexistent; $t_{m2} \approx 0.5R$ is the thickness corresponding to the maximum number of particles with the radius $R \pm \Delta R/2$; and t_{m3} is the thickness at which the volume of given radius particles reaches some constant value preserved within a wide interval of thickness $t_m > t_{m3}$ (up to $t_{m3} \approx 20$ nm) amounting to some 20% of the maximum value. Generalization of these results allows to plot a diagram in the coordinates "$t_m - R$" which reflects regularities of island size variation against film growth (Fig.5). Shown in this diagram are plots of characteristic thickness t_{m1}, t_{m2}, and t_{m3} as a function of radius of the particles separating the regions in which the fixed size particle volume behaviour becomes different with the growth of film mass thickness. There are

no particles of preset size in the A region (below t_{m1} line): $t(R, t) = 0$. Plot t_{m1} corresponds to the moment when particles of the given radius R begin to appear, and plot t_{m3} shows the stabilization of their amount. In between these lines the volume (amount) of the given size particles passes through its maximum value determined by plot t_{m2}, i.e., the total volume of particles increases with the growth of thickness in region B, and decreases in region C. Above the t_{m3} line, in the D region, the volume of the given radius particles does not depend on film thickness: $t(R, t_m) = const(R)$.

Thus, the given diagram makes it possible to easily locate change in the amount (volume or surface area) of the preset size particles (e.g., R') with the growth of film mass thickness. As seen from the graph, this radius particles occur at the film thickness t_{m1}', then their amount increases and reaches the maximum value on the line t_{m2}'; amount of the given size particles keeps diminishing up to the thickness t_{m3}', and at $t_m > t_{m3}'$ their number becomes constant, and makes up an insignificant fraction of the total film volume. Conse-
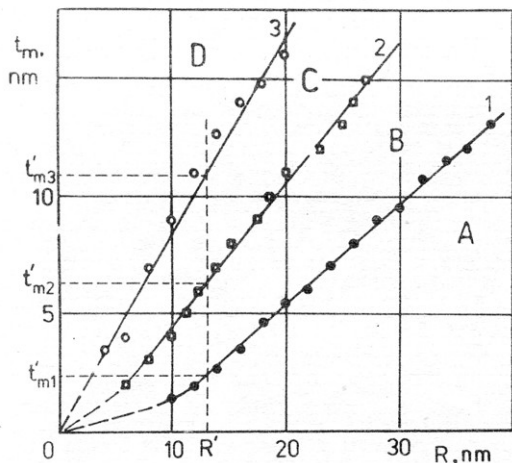
Fig.5. Island gallium film growth diagram. Plots 1, 2 and 3 correspond to critical thickness t_{m1}, t_{m2}, and t_{m3}.

quently, if a film with the maximum amount of preset size particles is to be produced according to experiment conditions, the mass thickness of such film should correspond to the value located on the line $t_{m2} = t_{m2}(R')$. Actually, this value corresponds to the histogram maximum, that is, particles of the given size make the greatest input into the total film volume. Notably, about a half of the total volume is accumulated within an interval corresponding to a 20% deviation from R': $(0.8-1.2)R'$.

In the cases, when the surface area of preset size islands is chosen as a governing parameter, the dependence families shown in Figs.3,4 can be remade for respective coordinates. In this case, the diagram will not undergo qualitative changes, and can also be used for selecting optimal conditions for preparing island films with the preset degree of dispersion.

It should be noted that the distributions obtained apply to the given conditions of film preparation. To purposely change the microparticle size distribution either the film fabrication parameters could be varied: substrate temperature, condensation rate, samples annealing temperature and time, or else, additional external factors could be introduced. So, for example, application of a longitudinal electric field during film condensation or after its cessation stimulates coalescence, which provokes increase of particle characteristic size [7].

3. Substrate temperature effects on island size distribution

The study in temperature effects on microparticle size distribution in proximity of the maximum supercooling temperature has been performed for three

series of island tin film samples with different mass thickness (2, 5 and 15 nm) condensed onto a substrate with temperature gradient. Fig.6 shows the photomicrographs illustrating the change of morphological structure with change in the condensation mechanism from vapour-crystal to vapor-liquid. As is seen, a considerable change in the shape of particles condensed above and below the limit temperature T_g is observed for thick tin films ($t_m \approx 15$ nm). As the mass thickness is reduced, the difference in the film microstructure becomes hardly noticeable ($t_m \approx 5$ nm), and at $t_m \approx 2$ nm, it is practically impossible to positively determine the mechanism of film condensation judging from its appearance. The visual appraisal of temperature T_g from these graphs gives a value of 295 K which is well coordinated with the data of other authors [8,9].

It is clear from comparing the distributions corresponding to different t_m and the fixed temperature above T_g that the island tin films retain the regularities noticed in studying the Ga/C system. As the mass thickness increases, the principal maximum is shifted to the region of great R values, and the histogram characteristic points come to coincide with the values determined by the plots t_{m2} and t_{m1} in the island film growth diagram according to the vapour-liquid mechanism (Fig.5).

Within one sample series, i.e., under constant mass thickness, particle size distribution is a function of two variables (particle radius and temperature) which is presented as a surface in a three-dimensional coordinate system «R - T - t(R)». Such a surface can be plotted using computer processing of measurements. Presented in Fig.7 are island size distributions as a function of substrate temperature for tin condensates of different mass thickness. All curves in the figure display the principal maximum shift with the growth of temperature into the region of larger particle sizes in passing the temperature T_g. The results obtained for the principal maximum position as a function of temperature are shown in Fig.8. The observed shift occurs within a narrow temperature interval (~ 10 K), and corresponds to the temperature T_g determined from the morphological structure of condensates (its location is marked with arrows in Fig.7). The shift value δR depends on the film mass thickness, and increases with the latter's growth both in absolute value, and with respect to the principal maximum position. So, films with the thickness $t_m \approx 15$ nm will have the shift of $\delta R \approx 5$ nm or 20% of the size corresponding to the maximum particle volume; with the thickness $t_m \approx 5$ nm the shift $\delta R \approx 1.5$ nm or 14%, and for the thinniest films studied of $t_m \approx 2$ nm the shift
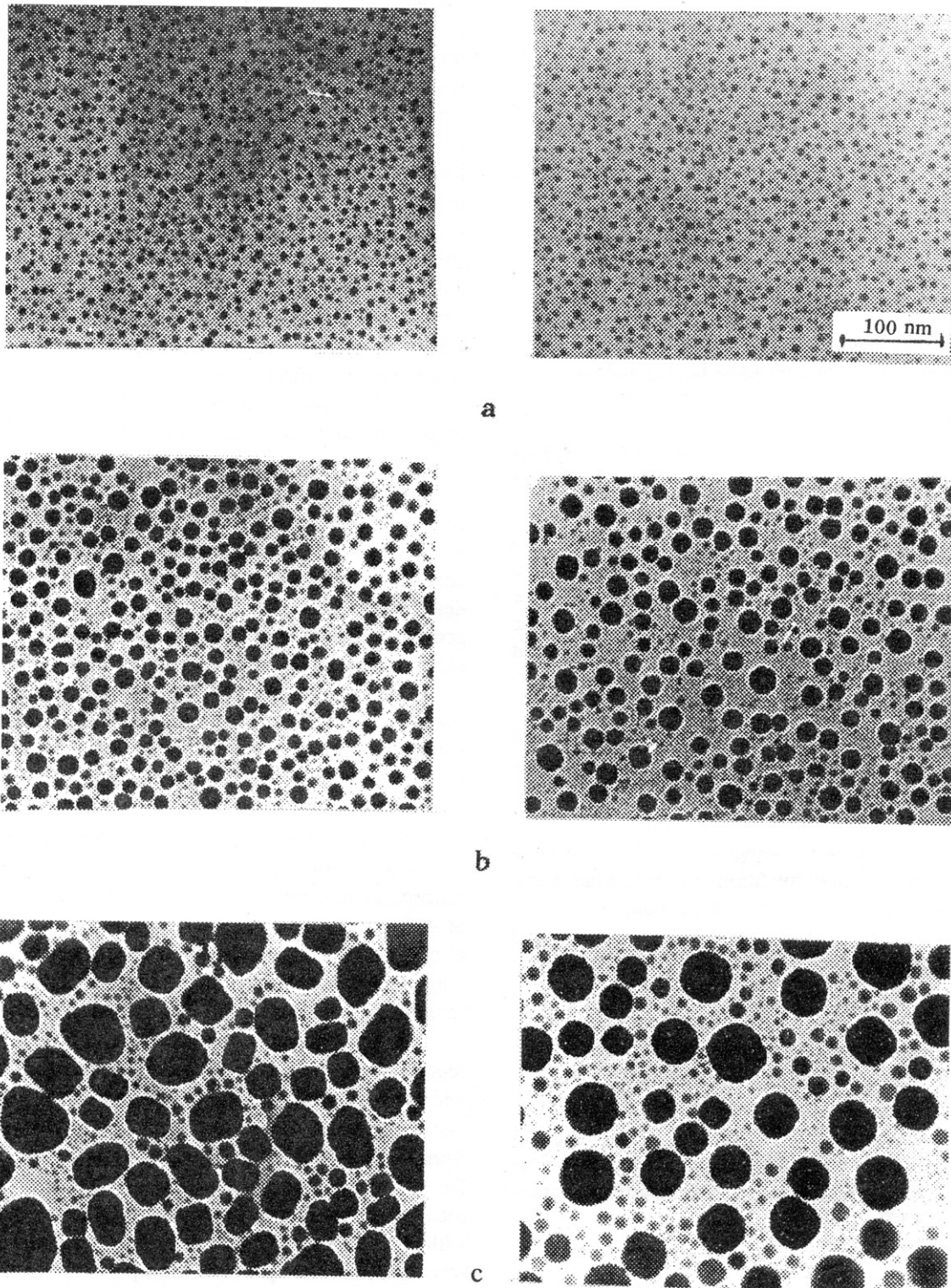
Fig.6. Photomicrographs of different mass thickness tin films on carbon substrates condensed according to the vapour-liquid mechanism (T = 310 K)(right), and vapour-crystal mechanism (T = 280 K)(left). Film mass thickness: a) 2 nm; b) 5 nm; c) 15 nm
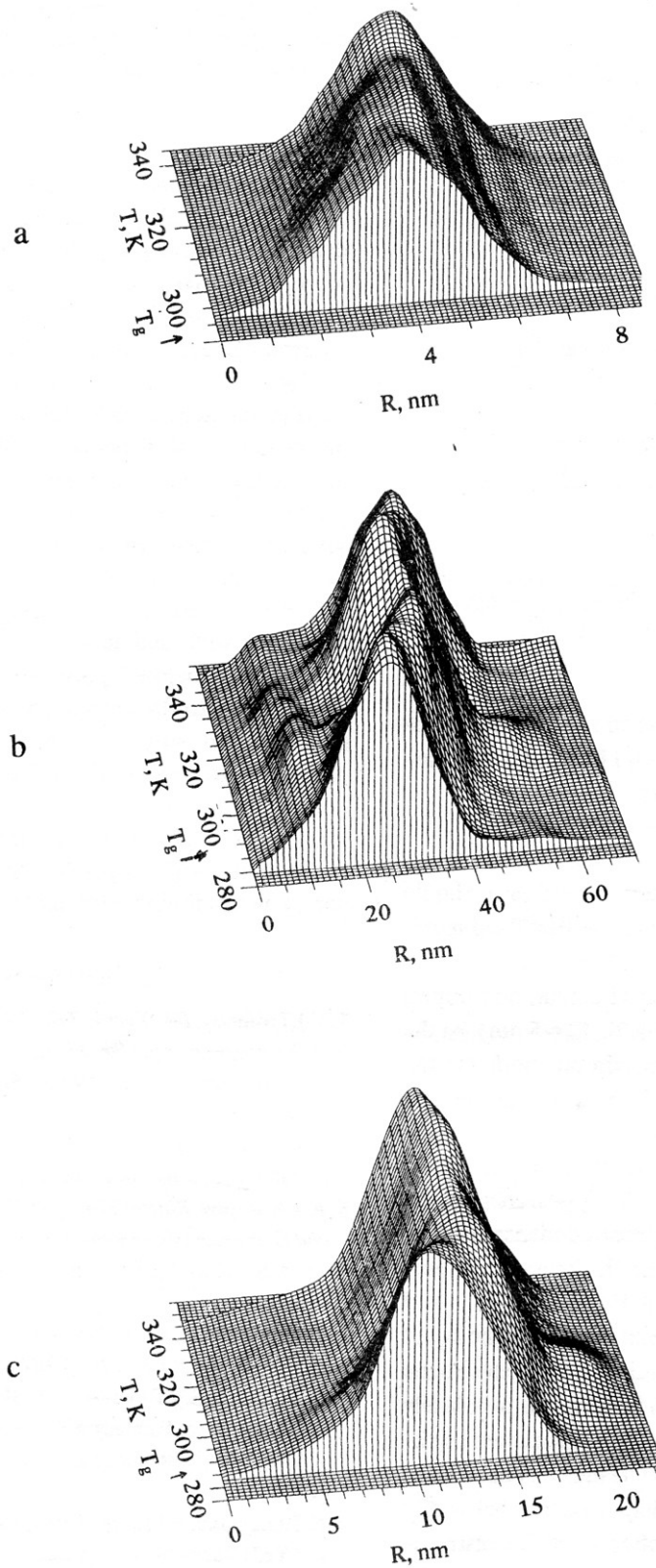
Fig.7. Temperature dependence of island size distribution in tin films of different mass thickness: a) 2 nm; b) 5 nm; c) 15 nm.
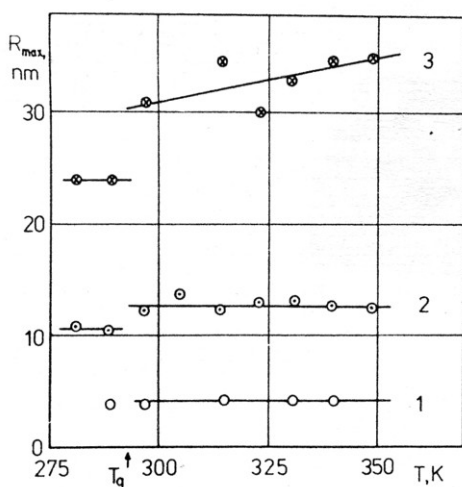
Fig.8. Temperature dependence of distribution function principal maximum position for thin tin films of different mass thickness: 1) 2 nm; 2) 5 nm; 3) 15 nm.

$\delta R \approx 0.4$ nm or 10%. There will be no principal maximum shift altogether for island tin films with the mass thickness below one nanometre.

Another important distinction of distributions for the films fabricated according to the vapour-crystal mechanism from the distributions typical of the liquid phase condensation is absence of the first fixed maximum. It is especially expressed on "thick" films (Fig.7c, $t_m \approx 15$ nm), and, to some extent, on samples with smaller mass thickness (Fig.7b, $t_m \approx 5$ nm). At the same time, there is no first maximum both for the crystalline and liquid state of islands on the thinnest films (Fig.7a, $t_m \approx 5$ nm).

It should be noted that distributions for the films produced at $T < T_g$ are similar in appearance to the distributions typical for liquid phase condensation, but correspond to smaller film mass thickness when particle coalescence is insignificant. Besides, as the island growth due to lower melting point starts with the liquid phase and below T_g^*, the distributions correspond to the liquid phase condensation, and, thus, are absolutely identical up to a certain value of t_m. As the mass thickness increases, crystallization of islands and their transition from spherical to flat shapes occurs below T_g. Simultaneously, coalescence effects on size distribution grow, and, thus, difference in histograms for the films produced above and below the transition temperature becomes more pronounced. Consequently, the differences observed in histograms, and the nature of their dependence on the film mass thickness are due, primarily, to the change in particle growth shapes, and their impeded coalescence under condensation according to the vapour-crystal mechanism.

Conclusions

Thus, a technique of studying the island size distribution depending on different factors on films condensed via liquid phase has been developed in this work. Study has been carried out of the distribution variation during growth of island gallium film on an amorphous carbon substrate. The data obtained helped to plot a diagram in the coordinates "$R-t_m$", which diagram could be used for fabrication of films with the preset degree of dispersion. Effects of the substrate temperature on microparticle size distribution in proximity of the maximum supercooling of tin condensates on carbon have been examined. It was proved that the observed changes of histogram type in transition via the crystallization temperature, such as the principal maximum shift, and absence of the first maximum at temperatures below T_g are caused by transition from the spherical to flat growth shapes of the islands, and their impeded coalescence in the crystalline state. Shift of the principal maximum in histogram during transition via the temperature of changing condensation mechanism can be used for its determination, especially when the differences in film microstructure can hardly be discriminated visually.

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