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# Morphology of Islet Systems Formed During Melting of Continuous Bi Films on Ge and $SiO_2$ Substrates

A.P. Kryshtal*, A.A. Minenkov, S.S. Dzhus

*V.N. Karazin Kharkiv National University, 4, Svobody Sq., 61022 Kharkiv, Ukraine*

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The results of electron microscopic studies of arrays of nanoparticles formed by melting of solid polycrystalline Bi films on amorphous Ge and $SiO_2$ substrates are presented. It has been shown that the islet structure with a small spread of particles' size is formed as a result of self-organization during the melting of bismuth on an inert $SiO_2$ substrate. The connection between the basic characteristics of these particles and the thickness of the initial films was determined. It has been shown that melting of bismuth on the amorphous germanium substrate leads to the formation of disordered arrays of nanoparticles. The morphological structure of these ones depends on the nature of interaction between the components of the film-substrate interface.

**Keywords:** Thin films, Wetting, Film decomposition, Scanning electron microscopy.

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## 1. INTRODUCTION

Thin films find a wide application in modern technology. This, for example, is protective coatings, magnetic layers for data recording, elements of micro- and nanoelectronics. Naturally, the questions of stability of such films are the key ones to provide operability of devices and equipment on their basis. Condensed films, as a rule, are essentially non-equilibrium thermodynamic systems, therefore, over time or with increasing temperature, relaxation processes leading to the decrease in the excess free energy will occur in such a system according to the Le Chatelier's principle. The process of film decomposition which consists in its spontaneous transformation to the system of isolated crystalline islets on the substrate is one of the manifestations of the excess free energy relaxation of a nanodispersed continuous film. It is usually considered that decomposition of a continuous film occurs in two stages [1-3]. Pores formation, mainly, at the triple junctions and grain boundaries takes place on the initial stage [4]. Then, one observes pores growth on account of self-diffusion over the film surface and coalescence leading to the formation of a labyrinthine structure that finally results in the decomposition into isolated islets. The last stage is the most complex for the description; at the same time, formation of the array of isolated islets on the substrate takes place on just this stage [1, 5]. In the literature, there is limited data on the basic characteristics of arrays of nanoparticles formed during decomposition of continuous films and their interconnection with the initial film thickness. These investigations were performed, as a rule, for the films located on the inert substrates [6-8]. At the same time, modern film technology often uses the multilayer and many-component systems. Therefore, it seems reasonable to further investigate the arrays of nanoparticles formed during the decomposition of continuous films including the case when the film substance interacts with the substrate material. Naturally, in the latter case these investigations have a sense only for the systems whose components are partially soluble in the solid state.

Bi films on the $SiO_2$ and Ge substrates were chosen as the object of research. In the first case, substrate is inert with respect to the Bi film; and in the second one – components of the system form the phase diagram of the "simple eutectic" type at complete insolubility of the components in the solid state. Melting temperature of Bi-Ge eutectic almost coincides with the melting temperature of pure bismuth. This choice allows to compare the decomposition behavior of the Bi film on different substrates and estimate the influence of the phase diagram type on the properties of formed islet systems.

## 2. INVESTIGATION TECHNIQUE

According to the task, two series of the samples were formed: $Bi/SiO_2$ and Bi/Ge. $Bi/SiO_2$ system was prepared by thermal evaporation and subsequent condensation of Bi in vacuum of $3 \times 10^{-6}$ mm Hg on the polished plates of monocrystalline silicon with an oxide film of the thickness of 250 nm. Silicon plates were attached by using a special mask to an extensive copper unit with a built-in resistive heater. In this case, evaporator of Bi was located non-symmetrically relative to the substrate that allowed to form in one experiment under the same conditions a set of $Bi/SiO_2$ samples with a continuously changing thickness of the Bi film. During the formation of Bi/Ge samples, 40-50 nm Ge film was condensed on the $SiO_2$ plates directly before deposition of bismuth. All film systems were formed at room temperature of the substrate and then without vacuum failure were heated to the bismuth melting temperature. In this case, heating time was equal to ≈ 30 min; substrate temperature was controlled by chromel-alumel thermocouples. After cooling, the samples were extracted into air and studied by the scanning electron microscope Jeol JSM-840.

Based on the electron-microscopic images, we have determined the basic characteristics of the ensembles of islets formed as a result of the solid state decomposition and further melting of Bi films. Wetting angles by islets of substrates were measured by the oblique observation method in the scanning microscope [9]. Mass thickness of

* aleksandr.p.kryshtal@univer.kharkov.ua

 

bismuth films was determined by the integration of the particle-size distribution histograms under the assumption of the absence of mutual solubility of the components.

## 3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

In Fig. 1 we present the typical electron-microscopic images of the bismuth film after melting on the $SiO_2$ and Ge substrates. It is seen that irrespective of the substrate material, bismuth film after melting is decomposed into isolated islets with the shape of a spherical segment. Contact interaction angle for $Bi/SiO_2$ system was equal to $137 \pm 5$ deg. (Fig. 1c).

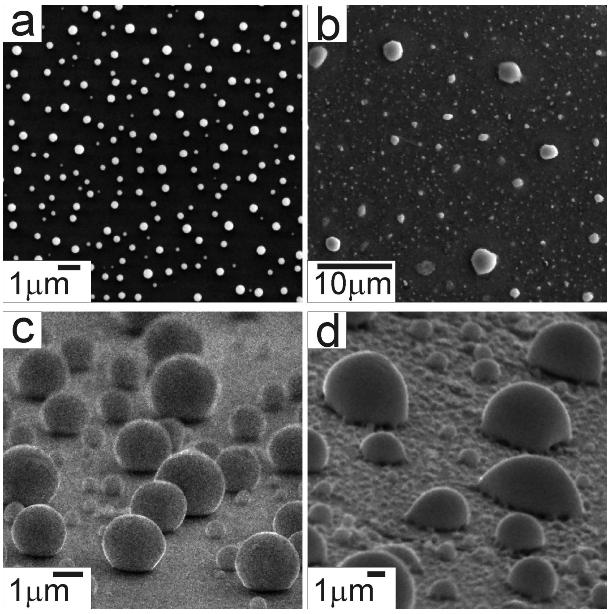


**Fig. 1** – Electron-microscopic images of the islet systems formed as a result of melting of bismuth films on $SiO_2$ (a, c) and Ge (b, d) substrates. Mass thickness of the films: a, b, d – $\approx 24$ nm and c – $\approx 200$ nm

It is difficult to determine the equilibrium wetting angle for the Bi/Ge system: for different particles, and even for the same particle, measuring angle is varied in the range of 60-90 degrees (Fig. 1d). This spread can be partly explained by the effect of wetting hysteresis. Upon melting of the film, formation of islets occurred by the liquid phase running-off from the pre-wetted Ge surface. In this case, elastic deformation of the substrate by the surface tension forces of the liquid leads to a stepwise change of the wetted perimeter and, correspondingly, contact angles. At the same time, difference between the inleakage and running-off angles, as a rule, does not exceed several degrees. Therefore, the observed spread of wetting angles in the Bi/Ge system, probably, besides the effect of wetting hysteresis includes also other mechanisms associated with the features of the interaction between the liquid phase and Ge substrate.

It is necessary to note an absolutely different morphology of islet films formed during the melting of bismuth on the inert and interacting substrates. Thus, in Fig. 1a and Fig. 1b we illustrate the images of $\approx 24$ nm bismuth films melted on the $SiO_2$ and Ge substrates. It is seen that in the first case the film consists of approximately equal islets of the size of $\approx 400$ nm, while the particles whose size more than 100 times exceeds the initial film thickness and achieves 3 μm are present for the Bi/Ge system along with the particles of the size of 500-700 nm. The specified difference is also well seen from the distribution histograms of the particles' surface area NS(R) in sizes (Fig. 2). Thus, one sufficiently narrow maximum is observed for the islet $Bi/SiO_2$ systems and its position does not depend on the type of the distribution functions; maxima of the distribution of the number of particles N(R), area of their surface NS(R) and volume NV(R) coincide. Bimodal particle-size distribution is observed in the Bi/Ge system (Fig. 2b). Here, the main volume of the film is just concentrated in larger particles representing the second maximum.

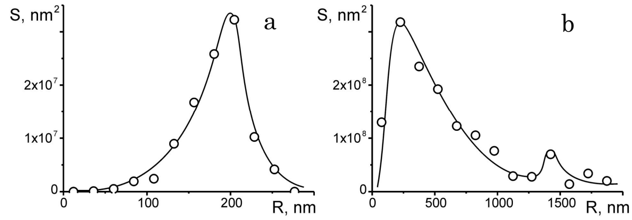


**Fig. 2** – Distribution of the area of islets in sizes in the $Bi/SiO_2$ (a) and Bi/Ge (b) systems for the initial bismuth film thickness of 24 nm

As a result of the performed study, we have plotted the dependences of the substrate fill factor (Fig. 3b) and the most probable particles' size in which film volume is concentrated (Fig. 3a) versus the mass thickness of the bismuth film.

It is seen that the most probable particles' size $R$ for the $Bi/SiO_2$ system increases linearly in the first approximation with increasing mass thickness (Fig. 3a). At that, substrate fill factor $C$ does not almost depend on the initial film thickness (Fig. 3b).

In the case of the bismuth film melting on the Ge substrate, size of the particles, in which main volume of the film $R_v$ is concentrated, non-linearly depends on its thickness. In the range of small thicknesses, coefficient of proportionality between the film thickness and particles' size is equal to $\approx 100$, while for the $Bi/SiO_2$ system it does not exceed 6. At that, fill factor also increases with increasing film thickness (Fig. 3b).

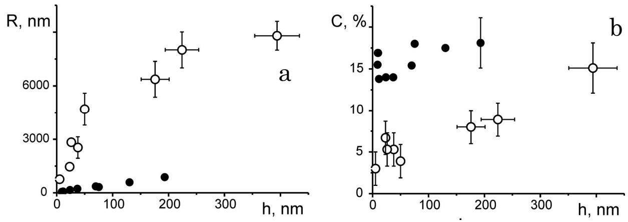


**Fig. 3** – Dependence of the most probable particle size $R$ (a) and substrate fill factor $C$ (b) versus the mass film thickness $h$ (here ● – $Bi/SiO_2$, o – Bi/Ge)

For the description of the observed changes in the morphological structure of the films at melting, it is convenient to use the thermodynamic approach proposed in [10] and later developed in [1]. Under the assumption of decomposition of the film of thickness $h$ into an array of equivalent islets with radius $R$ and contact angle $\Theta$, we have obtained the expression determining the interconnection between the specified quantities:

$$\frac{R}{h} \geq \frac{3 \cdot \sin\Theta}{1 - \cos\Theta + f / \sigma}. \quad (1)$$

Here $\sigma$ is the specific surface energy of the film substance; $f$ is the excess film energy. It was shown in [4] that this expression satisfactorily describes the experimental data on the decomposition of continuous Bi, Sn films on the Si substrates and established that trend to the decrease in the surface energy of the film-substrate system, which is associated with the film-substrate and film-vacuum interfaces, is the determinative one during the formation of islet nanostructures on the substrate at melting-crystallization of the films. If suggest that wetting angle $\Theta$ does not depend on the film thickness, then from the expression (1) we have the functional connection between the islets' radius and the film thickness $R \sim h$ that is observed for the Bi/$SiO_2$ system (Fig. 3a). Functional connection between the islets' radius and the islets' density, namely, $R \sim (1/N)^{1/2}$ also follows from this dependence. Since fill factor is connected with the particles' density by the relation $K \sim NR^2$, then taking into account the connection between $N$ and $R$ it follows that substrate fill factor is a constant value. This result finds the experimental confirmation for the Bi/$SiO_2$ system for which $C$ is not almost changed for all the studied samples (Fig. 3b). The presented estimates show that the decomposition process of a continuous Bi film on the $SiO_2$ substrate is satisfactorily described within the thermodynamic model.

Application of thermodynamics for the description of the characteristics of arrays of particles formed during melting of a continuous Bi film on the Ge substrate is difficult. This is connected, primarily, with the fact that the disordered arrays are formed in the given case especially in the range of small film thicknesses; the particle-size spread achieves several orders of magnitude. At the same time, the obtained experimental data does not contradict the applied model. Thus, decrease in the contact angle, according to (1), leads to the increase in the particles' size at the fixed film thickness. This is clearly evident from the illustrated histograms (Fig. 2) for the Bi film of the same thickness melted on the $SiO_2$ and Ge substrates. With increasing film thickness, the particle-size spread decreases, and for thicknesses more than ≈ 300 nm the arrays of particles can be considered, although very approximately, as monosized. Substitution of the averaged value $\Theta = 75°$ into expression (1) with a glance to the value $f/\sigma$ calculated according the technique [4] at $C = 15$ %, gives the value of $R / h \approx 16$. This estimation satisfactorily correlates with the experimentally measured value for the given film thickness – $R / h \approx 22$.

Non-linearity of the dependence $R(h)$ in the range of small thicknesses is conditioned by the appearance of millimeter particles which, in fact, determine the position of the maximum on the $NV(R)$ histograms. At that, substrate fill factor has an abnormally low value ≈ 5 %. Mechanism of the formation of such particles cannot be explained within the existing film decomposition mechanisms and requires further investigations. However, character of the interaction of components on the film-substrate interfaces plays, probably, the determinative role in this case. During melting of a continuous Bi film on the $SiO_2$ substrate, its decomposition into isolated islets occurs in the solid phase, and subsequent melting of such a film leads only to the formation of a spherical shape of islets facilitating, thus, a correct determination of their integral characteristics. Formation of the liquid phase on the film-substrate interface in the Bi/Ge system is possible at temperatures lower than the eutectic one that intensifies the interaction process and is accompanied by crystallization of amorphous Ge similarly to that observed previously for the Au/Ge system [11] and possessive also the phase diagram of the eutectic type. Therefore, upon reaching the eutectic temperature and complete melting of bismuth particles, difference in the surface energies of the crystalline and amorphous germanium can influence the value of the contact angle in the system and, correspondingly, the formation kinetics of the array of islets on the Ge substrate. The observed spread of wetting angles in the Bi/Ge system serves an indirect confirmation of this fact (Fig. 1d).

Thus, in the work, the formation of islet structures due to the self-organization during melting of Bi films on the Ge and $SiO_2$ substrates has been studied in a wide range of sizes and the connection of the basic characteristics of these structures with the initial film thickness has been determined. It has been established that the substrate fill factor and the most probable size of the particles formed during melting of a bismuth film on an inert substrate are satisfactorily described within the existing thermodynamic model. It has been shown that the interaction behavior of the components cardinally influences the formation of the islet structure during melting of bismuth on the amorphous Ge substrate.

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