Soviet Physics – Doklady, 1990, V. 35, No.10, pp. 907–908

Effect of an electric field on coalescence in gallium island films

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(Presented by Academician N. G. Basov, February 27, 1990)
(Submitted March 2, 1990)
Dokl. Akad. Nauk SSSR 314, 863-865 (October 1990)

It was found that the external longitudinal electric field stimulates coalescence in gallium island films with different particle sizes on a poorly conducting carbon substrate, which can be considered as a manifestation of the particle mutual-charging effect.

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According to theoretical studies,[1-3] mutual-charging forces arise between particles of different sizes in a group of small metallic particles (of size $r \le 10$ nm) as a result of dimensional dependence of the density of their electronic levels, which causes the Fermi energy of the particles to depend on the radii.

As a model of such a system we can consider an island metallic film obtained on a poorly conducting substrate by vapor—liquid vacuum condensation. By virtue of the anomalies of their formation and growth, island films are characterized by the size distribution of the particles, which depends on the condensation conditions. The mutual-charging forces between particles of different sizes in such films are therefore, an additional factor determining their coalescence on the substrate. Since the mutual-charging forces are electrical in nature, their appearance should depend on the value of the applied external electric field. The appearance of these forces can probably be detected experimentally by studying the size distribution of the microparticles as a result of isothermal holding of island films in an external, longitudinal, constant electric field of different values.

In order to detect the mutual-charging effect experimentally in a system of ultradisperse metallic particles on a poorly conducting substrate, we carried out studies on vacuum-condensed island films. The size of the islands and the conductivity of the substrate, which can be controlled directly during the growth of the films by using the vacuum condensation method, are the main parameters determining the mutual-charging forces in such films.

The experiments were carried out as follows. Carbon films with a thickness of up to 30 nm were condensed on glass plates with previously deposited silver contacts, with a wedge-shaped gap between them. The resistivity of such films (the resistance of a square portion of the film) was determined by their thickness and was varied in a controlled manner over the range from 0.1 MΩ to 10 MΩ. A gallium film, whose mass thickness was checked with a quartz resonator, was deposited by thermal vapor-liquid evaporation onto a substrate so prepared, which was held at 50°C. Since the liquid gallium does not wet the carbon substrate, an island film with spherical particles was formed (Fig. 1). The average size of the gallium particles ranged from 3 to 10 nm in different experiments and was determined, on the one hand, by the possibility of examining the films in an electron microscope and, on the other hand, by the fact that, according to our earlier study,[3] the mutual-charging effect should manifest itself at particle sizes under 10 nm. After condensation the films were held at 50°C in a longitudinal electric field of 2000 V/cm. The wedge-shaped gap between the contacts made it possible to obtain, in a single experiment, samples corresponding to isothermal holding in a field of different strengths. At the same time, in the same experiment in a similar manner we prepared control films, which were held under the same conditions without applying an external electric field. The resulting samples were studied in an EVM-100BR electron microscope. On the basis of the electron micrographs we constructed histograms reflecting the size distribution of the gallium particles in the island film. The measurements were carried out on a 500 × 500-nm portion. To make allowance for the possible error in the determination of the electron-microscopic magnification, the histograms were normalized to a constant mass thickness of the gallium film, which was prescribed by the conditions of the experiment. These studies yielded the following results.

When the samples are prepared in an apparatus with oil pumps in a vacuum of 10^{-4} Pa, the histograms for films held in the electric field do not

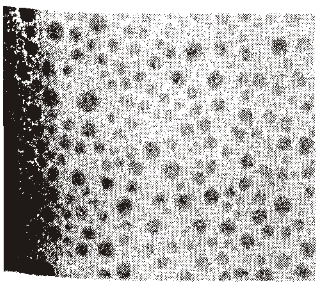

FIG. 1. Electron micrograph of a gallium island film on a carbon substrate; 200 000 × .

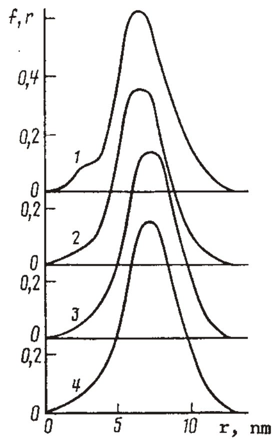

FIG. 2. Size distribution of gallium islands upon condensation in an electric field of strength 50 (1), 100 (2), 300 (3), and 500 B/cm (4). $f(r) = 4\pi r^3 N(r)/3$, nm.

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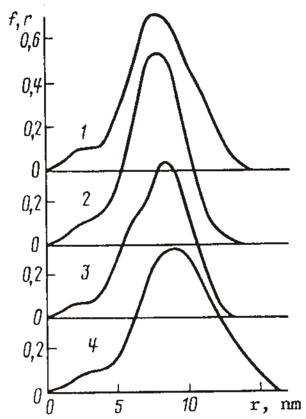

FIG. 3. Size distribution of gallium islands after 1-h hold in an electric field with a strength of 100 (1), 200 (2), 280 (3), and 1100 V/cm (4). $f(r) = 4\pi r^3 N(r)/3$, nm.

have anomalies in comparison with the histograms for the control films held without a field. The curves obtained for the size distribution of the particle volumes $4\pi r^3 N(r)/3 = f(r)$ are characterized by one (at $r_{max} < 10$ nm) or several (at large sizes) maxima, whose position does not correlate with the strength of the applied electric field. The quantity $4\pi r^3 N(r)/3$ is the volume of particles of radius $r \pm 0.5$ nm in a unit area of the film and in the first approximation have the connotation of the effective thickness of a film formed by particles of a given range of sizes. The absence of the effect may be attributed to the film being overgrown by decomposition products of vacuum oils, which stabilizes the film and prevents coalescence of the particles. When gallium was condensed on carbon substrates in an external electric field under the same vacuum conditions, then as soon as the condensation stopped without isothermal holding we observed a displacement of the maximum on the histograms with the growth of the field strength in the region of larger particle size (Fig. 2). For example, the displacement of the maximum for an island film on a carbon substrate with a resistivity of 3 MΩ at a field strength of 500 V/cm was roughly 10% in comparison with samples obtained without an external field. An unambiguous interpretation of these results is difficult, however, since the external electric field may affect not only the coalescence but also the nucleation and growth of the island film.[4] The effect of the longitudinal electric field on the size distribution of the microparticles manifests itself most distinctly on island films prepared in a vacuum of 10^{-5} Pa in a setup with a fluid-free pumping system. Figure 3 shows the distograms of gallium island films on carbon substrates with a resistivity of 4.2 MΩ, held after the end of condensation in an external electric field for 1 h at 50°C. We see that an increase in the field strength causes the maximum to shift to the region of large sizes. For films with an average particle size of the order of 10 nm, for example, the drop size corresponding to the maximum on the histograms is observed to increase by roughly 20% at a field strength of 1000 V/cm.

In summary, the results suggest that an external longitudinal electric field stimulates coalescence in gallium island films with different particle sizes on a poorly conducting carbon substrate, which can be considered as a manifestation of the particle mutual-charging effect predicted in Refs. 1-3.

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Translated by Eugene Lepa

Temperature dependence of the physicomechanical properties of TiB_2–Fe composites

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(Presented by Academician Yu. D. Tret'yakov, January 25, 1990)
(Submitted January 26, 1990)
Dokl. Akad. Nauk SSSR **314**, 1130–1132 (October 1990)

Materials based on refractory compounds (carbides, borides, nitrides, oxides, etc.) are distinguished by high strength, hardness, and elastic characteristics, but at the same time are characterized by brittle fracture over a considerable range of temperatures, i.e., very considerable values of brittle–plastic transition temperatures T_{br} (Ref. 1). Boride composites have recently attracted increasing attention because of their many outstanding characteristics that allow them to be used as tool, wear-resistant, and structural materials (e.g., Refs. 2-4). It was of interest to study the effect of the temperature on the strength, hardness, and elastic modulus of titanium diboride with additions of iron as a binding phase, after having revealed the nature of the fracture of such materials and the value of T_{br}. According to the data of Ref. 5, the TiB_2–Fe system is pseudobinary

