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SIZE and TEMPERATURE EFFECTS in WETTING in ISLAND FILMS

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Research in wetting island films permits to study the properties of surface phenomena in high dispersion systems and to obtain the parameters of a solid body surface that are important for applications. The vacuum condensation technique permits to keep the influence of various impurities and adsorbed layers at a low level and also to control the dispersive state of contacting phases easily.

This paper is devoted to studies of wetting in metal island films on different substrates in the broad ranges of temperature (from 0.6 to 1.5 of the melting temperature), island size (from 3 nm to 10 μm) and thickness of films serving as substrates (from 0 to 100 nm).

Size effect in wetting. Wetting in a liquid-solid system is characterized by the equilibrium wetting angle θ related to surface energies σ_s , σ_l and σ_{sl} of contacting phases according to Young's equation

$$\cos \theta = (\sigma_s - \sigma_{sl}) / \sigma_l$$

Here indices s, l and sl relate to solid, liquid and interphase surfaces, respectively.

With the inclusion of size dependences of the drop surface energy σ_l and of the interphase energy of the drop-substrate boundary σ_{sl} in the form

$$\sigma_l = \sigma_l^\infty (1 - \alpha/R) \quad \text{and} \quad \sigma_{sl} = \sigma_{sl}^\infty (1 - \beta/r)$$

one obtains the following expression for the microdrop wetting angle [1]

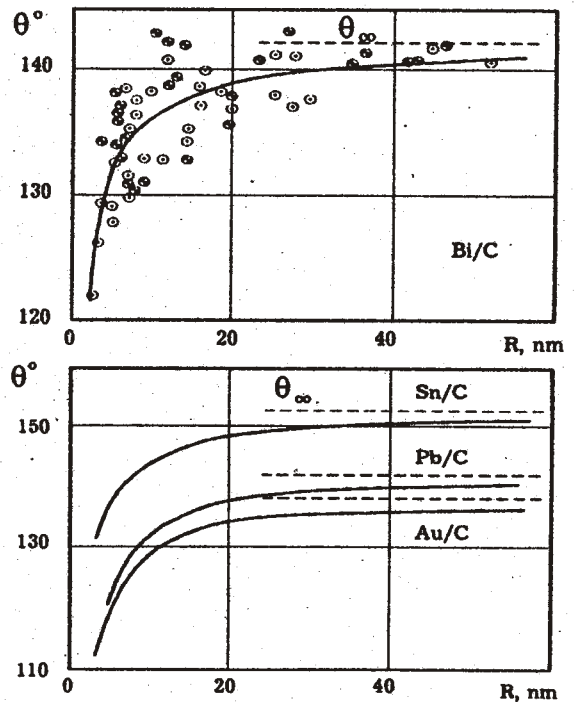
$$\cos \theta = \cos \theta_\infty - \frac{\alpha}{R} + \frac{\beta}{2R \sin \theta} \frac{\sigma_{sl}^\infty}{\sigma_l^\infty}$$

We have obtained the wetting versus drop size for a number of contact systems (Sn/C, Bi/C, Au/C, Pt/C and Pb/Si) [1,2]. We have studied the island metal films condensed in vacuum $10^{-5} - 10^{-7}$ Pa according to the "vapour-liquid" mechanism.

The wetting angles have been measured on crystallized drops. The techniques applied [3] are the modifications of the well-known sessile-drop method. The drop parameters are found by straightforward measurements of drop profiles on micrographs (cleavage and convolution methods for visible light and electron microscopies, respectively), or by photometric measurements of electronmicroscopic images of microparticles (photometry technique).

In the systems studied the wetting angles do not depend on microdrop size for particles with $R > 30$ nm. For particles with sizes $R < 30$ nm the size effect is observed, i.e., wetting is improved with R decreasing so that at $R \approx 5$ nm the change of the angle θ comprises approximately 20° to 25° (see figure). The observed behaviour is related to the size changes of surface and interface energies.

Using measured data, we have found the quantities σ_{sl}^∞ and β characterizing the size dependence of the interphase energy with the inclusion of the known values α and $\sigma_s = 120 \pm 30$ mJ/m² [1,2].



Wetting angle versus radius of metal drops on the amorphous carbon substrate.

System	σ_l^∞ , mJ/m ²	α , nm	σ_{sl}^∞ , mJ/m ²	β , nm	θ_∞
Au/C	1130	0.48	970	2.2	138.8
Sn/C	531	0.52	592	1.0	152.7
Pb/C	450	0.58	474	2.1	141.7
Bi/C	376	0.60	414	1.3	141.4

Parameter β is positive indicating the decrease of the interphase energy on decreasing the radius.

Wetting of free thin films. In high dispersion systems liquid particles may wet the surface of free films. Then the particle size and film thickness are such that the size dependence of surface energy does not manifest itself. However, one also observes specific phenomena related to the film deformation under a liquid particle.

One has prepared the specimens for studies condensing indium, tin and lead in vacuum 10^{-4} Pa onto free carbon films of various thicknesses (from 4 to 30 nm) at the temperature somewhat above the metal melting point. Wetting angles and film thicknesses have been measured on electron micrographs of convoluted pieces of the film with crystallized particles.

For systems under study the contact angle θ is observed to decrease by 20° to 25° with the film thickness t decreasing for $t < 30$ nm [2]. The change of the contact angle is due to film sagging under the liquid drop. Assuming that only elastic deformation of films occurs, the theoretical description of free film wetting has been made [4]. From the comparison between measured values and calculations for the limiting cases of bending and tension we have determined the Young modulus ($3.8 \cdot 10^{10}$ H/m) and the surface energy (120 mJ/m²) of the thin carbon film.

Wetting of thin films on a solid substrate. We have studied the wetting of films with variable thickness deposited onto solid substrates for different kinds of interaction between liquid drops, film and substrate (Sn/C/KCl, Sn/Al/NaCl, Pb/Ni/NaCl, Pb/Ni/Si, Pb/Ni/GaAs, Bi/Fe/KCl) [2]. In this case the contact angle depends on the intermediate layer thickness and changes from the value corresponding to the wetting of pure substrate (for $t \rightarrow 0$) to one for the wetting of film material in massive state (for $t > t_c$). Limiting thickness t_c is determined by a type of components interaction and amounts to 50 - 100 nm for systems with solution and(or) chemical interaction of components. If these factors do not work the value t_c is not more than 10 nm. The dependences observed are attributed to the heterogeneous wetting surface.

Wetting in supercooled condensates. For In/C and Sn/C we have studied wetting in a wide range of temperatures (from 300 up to 800 K), including a region of supercooled state of metals [5]. Specimens have been prepared condensing a metal in vacuum on a substrate with the temperature gradient. Then the substrate has been cooled to room temperature and wetting angles have been measured from electron-micrograph profiles of crystallized particles obtained at different temperatures. The cooling of drops and changing of their volume during solidification do not lead to noticeable changes of wetting angles. Therefore, the angle values obtained from crystallized particles relate to the temperatures at which the latter were formed under condensation.

Below melting point the contact angle reduces significantly (from 130° up to 80°) with the supercooling increasing. The transition from nonwetting to wetting is observed near the temperature of maximal supercooling for tin (320 K). The $\theta(T)$ dependence is established to be sensitive to pressure and composition of a residual gas. On decreasing the residual pressure from 10^{-3} to 10^{-6} Pa the dependence $\theta(T)$ for supercooled tin condensates shifts to the region of lesser angles by 20° to 30° .

Above 700 K the wetting angle in the Sn/C system exhibits the behaviour typical for non-interacting systems: $d\theta/dT = -0.01$ deg /K.

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