

Temperature Dependence of Angles of Silicon Wetting with Tin–Barium Melts

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Abstract—Experimental data on polytherms of the angle of silicon surface wetting with tin–barium melts are presented. It is found that the polytherms are linear in the temperature range between the melting point and 900 K, exhibiting a negative slope coefficient.

DOI: 10.3103/S1062873811080119

INTRODUCTION

The data on the angles θ of the solid surface wetting with metal melts allow us to elaborate adhesion theory, along with the adhesion of metal films in relation to silicon [1, 2] or silicon oxide, as the wetting angles define the strength of interaction between melts and solids. Adhesion energy W_A is represented by the Young equation given by

$$W_A = \sigma(1 + \cos \theta), \quad (1)$$

where σ is the surface tension.

We can exert control over the wetting angles and, consequently, the adhesive energy as well, using minor admixtures of surface-active elements. The minimum angles of the wetting of Si and SiO₂ have been gained by adding titanium with concentrations of up to 6 at % in tin [3].

Barium provides a highly active admixture in tin [4]; in this connection, it is of interest to study the phenomenon, when minor admixtures of barium exhibit an effect upon the angles of the silicon surface wetting with tin melts.

EXPERIMENTAL

Sn–Ba system alloys were fabricated at the Verkin Institute for Low-Temperature Physics and Engineering in Kharkov; they were prepared in glass ampoules positioned in a helium atmosphere; OVCh-000-type tin containing 99.9995 wt % of the base material and 3N barium were taken as initial products. Before the experiments began, solid solution ingots and specimens made from the ingots were stored in VM-1 vacuum oil.

The wetting angles were measured on a high-temperature unit in a helium atmosphere by the lying drop method; the measurement error was under 2%.

KES-001-type silicon(111) wafers were used as substrates.

A melt drop was applied on the substrate through a quartz funnel equipped with an extended capillary; the drops were photographed with a digital camera having a resolution of 6.1 MP. The drop image obtained in the experiment was processed using the CorelDraw software.

RESULTS AND DISCUSSION

The obtained temperature dependence of the wetting angle was shown in Fig. 1.

The measurements were performed at temperatures ranging between the melting temperature and 900 K. In contrast, the measurements of θ for non-

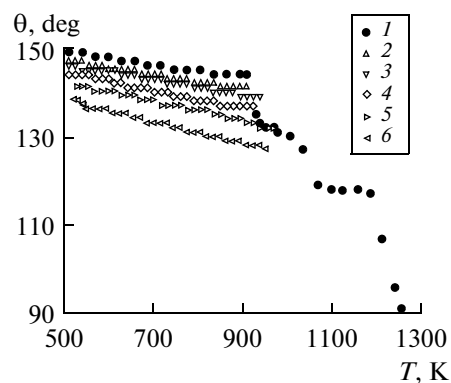


Fig. 1. Temperature dependence of angles of KES-001-type silicon wetting with the following melts: (1) nondoped tin; (2) tin doped with 0.061 at % Ba, (3) 0.097 at % Ba, (4) 0.116 at % Ba, (5) 0.152 at % Ba, and (6) 0.396 at % Ba.

The A and B coefficients from the linear approximation of angle $\theta = A - BT$ for silicon surface wetting with a tin–barium system melt in the range between the melting point and 900K

| C , at % Ba | A , deg | B , deg/K |
|---------------|-----------|-------------|
| 0 | 155.755 | 0.014 |
| 0.061 | 155.028 | 0.016 |
| 0.067 | 154.927 | 0.017 |
| 0.116 | 154.395 | 0.020 |
| 0.152 | 152.540 | 0.021 |
| 0.396 | 150.038 | 0.024 |

doped tin were performed at temperatures of up to 1250 K.

As can be seen from Fig. 1, the polytherms of θ are linear in the range of up to 900 K. The coefficients A and B in the linear approximation of the wetting angle given by $\theta = A - BT$ were found by means of RMS (see table). As can be seen from Fig. 1 and the table, the wetting angles show a decline in a value with increasing barium concentration in tin, but within the investigated temperature range, $\theta > \pi/2$.

In the case of nondoped tin, there are three temperature wetting thresholds: one at ~ 900 K, one at ~ 1050 K, and one at ~ 1200 K. When $T > 1200$ K, $\theta < \pi/2$ and silicon wetting with tin comes into play. It is not improbable that the first two wetting thresholds are associated with the disruption of tin oxides, and the third is associated with the disruption of SiO_2 .

At barium concentrations C ranging from 0.1 and 0.15 at % in tin, there are knees in the isotherms of the wetting angles $\theta(C)$ for KES-0.01-type silicon (Fig. 2). The knees are consistent with the peculiarities of the isotherms of the surface tension within the same concentration range.

Using these data on polytherms θ , we can estimate the energy of the melt adhesion with silicon according to the Young formula. By way of illustration, the energy of the nondoped tin adhesion with silicon $W_A =$

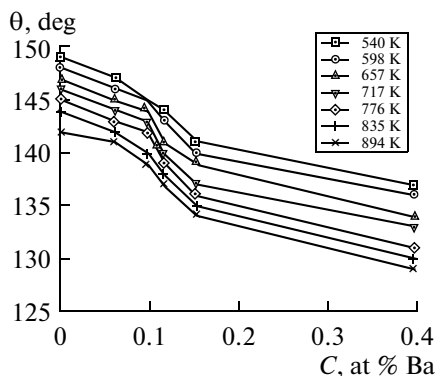


Fig. 2. Isotherms of angles of KES-0.01-type silicon wetting with tin–barium system melts.

70.3 mJ/m^2 at 550K. The adhesion energy is theoretically estimated by invoking various models [4].

When the distance between surface metal and semiconductor atoms is well in excess of lattice spacing and when the exchange processes are not available and the discreet energy levels of outer shell electrons are not perturbed, the interaction between the surfaces displays a molecular nature that is for the most part Van der Waals interwork. The concept of adhesion energy distribution over the bonds of the closest neighbors was used in this case to calculate adhesion. Following this approach, we calculated the Van der Waals component $W_{\text{v-d-w}}$ within the context of the London model:

$$W_{\text{v-d-w}} = n \frac{3 \alpha_1 \alpha_2 I_1 I_2}{2(I_1 + I_2) R^6}, \quad (2)$$

where n is the number of ions per surface area of 1 cm^2 ; α is the atomic polarizability; I_1, I_2 are the first ionization potentials; and R is the distance at which the interaction occurs.

Energies of adhesion with silicon were calculated by Eq. (2) for a number of metals and tin [5]. In the case of the silicon(111) cleavage plane, the number of ions $n_{\text{Si}(111)}$ was taken to be $7.8 \times 10^{14} \text{ at/cm}^2$. The equilibrium distance, at which a metal atom interacts with surface silicon atoms, was defined as a sum of the metal and silicon atom radii. The ionization potential $\text{Sn}I = 7.3 \text{ eV}$, and the polarizability $\alpha = 2.02 \times 10^{-24} \text{ cm}^3$. In our calculations, the SiO_2 ionization potential equal to 11.7 eV was taken as the silicon ionization one [6]. Silicon polarizability α was taken to be equal to $1.63 \times 10^{-24} \text{ cm}^3$ and the atomic radius $R = 11.7 \text{ nm}$. The Van der Waals interaction energy for the tin–silicon system was calculated by Eq. (2) and turned out to be 54 mJ m^{-2} .

As was shown in [1], the Van der Waals component of the adhesion energy can be related to the electron work function ϕ if the semiconductor is considered to be a dielectric.

The metal adhesion with silicon can be calculated as

$$W_{\text{v-d-w}} = -1.175 \times 10^{-13} \frac{(Z\phi)^{3/4}}{D^2}, \quad (3)$$

where Z is a number of the valence electrons in a metal; D is the distance between metal and semiconductor atoms, taken to be equal to a sum of the atomic radii of the contacting objects; and ϕ is the electron work function for the metal. The Van der Waals component estimated with Eq. (3) appears to be 1175 mJ m^{-2} , substantially exceeding the experimental values.

CONCLUSIONS

The polytherms for the angles of KES-0.01-type silicon(111) wafer wetting with diluted tin–barium melts were studied for the first time in the range between the melting point and 900 K. It was shown that in the investigated temperature range, the Sn–Ba melts wet a silicon wafer only partially ($\theta > \pi/2$). Wetting thresh-

olds were observed in our experiments on KES-0.01-type silicon(111) wetting with nondoped tin over a wider temperature range: tin begins to wet silicon at $T \geq 1200$ K. At the concentration $C = 0.01-0.15$ at % Ba, the isotherms of the wetting angles correlate well with the features in the isotherms of surface tension.

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