



Soviet-era science, translated into English

V. B. LAZAREV

1964

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.39840>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Fig. 1

Figure 1: Fig. 1

Abstract**Full Text****PHYSICAL CHEMISTRY****V. B. LAZAREV****STUDY OF ADSORPTION LAYERS ON THE SURFACE OF MOLTEN GERMANIUM***(Presented by Academician I. I. Chernyaev on February 17, 1964)*

It is known that the adsorption of various substances on the surface of a semiconductor changes its electrophysical properties ⁽¹⁾. In connection with this, the study of adsorption layers formed at the outer boundary of a semiconductor by surface-active impurities ^(1,2) is of considerable interest. A particularly interesting case is that in which the surface-active substances include an additive introduced specially into the semiconductor in order to create a specified type of conductivity.

In the present work the task was set of studying the effect on the surface tension of germanium of metals of the third and fifth groups of the periodic system, some of which are used in technology for doping germanium ⁽³⁾, namely: antimony, bismuth, indium, gallium, and thallium.

It is necessary to point out that direct investigation of surface-active properties at the boundary of a crystal is, experimentally, an extremely complicated problem, the solution of which has not yet been fully found. There are indirect studies ⁽⁴⁾, from which it follows that metals possessing definite surface-active properties on a liquid metallic surface retain them on the solid surface of crystals. It is for this reason that we investigated the surface properties of a series of metals on the surface of liquid germanium. For measuring the surface tension σ of metallic solutions, the method of maximum pressure in a gas bubble was used, with two sharply pointed capillaries of different diameters immersed in the melt to the same depth. The measurements were carried out mainly using the procedures described in ⁽⁵⁾. Subsequently, together with A. V. Pershikov, we also constructed an apparatus that made it possible to measure the surface tension of a number of alloys of different concentration without violating the tightness of the apparatus (see Fig. 1). To prepare an alloy with a new concentration in this apparatus, it was sufficient,

Fig. 1

Fig. 2. Surface tension of germanium alloys at different temperatures: 1 –950, 2 –1000, 3 –1050, 4 –1100, 5 –1150°

Figure 2: Fig. 2. Surface tension of germanium alloys at different temperatures: 1 –950, 2 –1000, 3 –1050, 4 –1100, 5 –1150°

moving, by means of siphon 1, holder 2, to drop into crucible 3 with the melt under study a definite amount of the additive metal. The required temperature was attained by heater 4, and measurements of σ were carried out with the aid of two capillaries of different diameters 5, as in work (5).

The preparation of the concentrated master alloy used subsequently to obtain germanium alloys with a specified additive content was carried out in quartz ampoules sealed under vacuum. The germanium used for the investigations had a resistivity of $40 \Omega \cdot \text{cm}$; the additive metals were of the highest purity grade. Measurements of σ for solutions germanium–gallium, germanium–indium, germanium–thallium, germanium–bismuth were carried out in the temperature interval $950\text{--}1150^\circ$ and at concentrations of the second component from 0 to 6 at. %.

Surface tension of germanium–antimony melts was studied in the temperature interval $950\text{--}1100^\circ$. The concentration dependences of the surface tension of all the alloys studied are shown in Fig. 2. All the additives investigated, with the exception of gallium, lower the surface tension of germanium, although quantitatively the surface activity of bismuth, thallium, indium, and antimony on germanium differs greatly.

The greatest surface activity on germanium among the metals studied is possessed by bismuth and antimony, the smallest by indium and gallium. In the case of germanium there is as yet no basis for assuming that donor and acceptor impurities differ sharply in the character of their influence on the surface tension of the solvent, as Shashkov and Kolesnikova indicate for the case of silicon (6). Thus, for example, additives of antimony and bismuth, on the one hand, and thallium, on the other, apparently exert opposite effects on the type of conductivity in germanium, but all these metals lower the surface tension of germanium, although the surface activity of thallium, indium, and gallium is quantitatively less than the surface activity of antimony and bismuth.

Fig. 2. Surface tension of germanium alloys at different temperatures: 1 –950, 2 –1000, 3 –1050, 4 –1100, 5 –1150°

The value of the limiting surface activity

$$G_0 = - \lim_{C \rightarrow 0} \frac{\partial \sigma}{\partial C}$$

for bismuth, antimony, thallium, and gallium decreases with increasing temperature, which is in agreement with the conclusions of the molecular theory of

Fig. 3. Adsorption of various metals on the surface of liquid germanium at 950°

Figure 3: Fig. 3. Adsorption of various metals on the surface of liquid germanium at 950°

Fig. 4. Ideal isotherm of a two-dimensional gas at 950°

Figure 4: Fig. 4. Ideal isotherm of a two-dimensional gas at 950°

surface phenomena in solutions developed by V. K. Semenchenko (7).

Using the Gibbs formula

$$\Gamma = -\frac{1}{RT} C \cdot \frac{\partial \sigma}{\partial C} (1 - C),$$

we calculated the adsorption values (Γ) of gallium, indium, thallium, antimony, and bismuth on the surface of germanium (C is the concentration).

The adsorption isotherms of the indicated metals at 950° are presented in Fig. 3. In the range of concentrations studied, the adsorption did not reach extreme values; with increasing content of the additive metal there was a steady increase in adsorption, which at concentrations below 2 at. % was li-

linear character. This made it possible to determine the number of impurity atoms at the outer boundary of germanium in the region of extremely low additive concentrations. It turned out that bismuth, antimony, thallium, and indium have a tendency toward an increased content in the surface layer.

Thus, calculations carried out on the basis of adsorption data showed that, at a bismuth concentration in the bulk equal to one bismuth atom per million germanium atoms, the concentration of bismuth on the surface of germanium is 7-10 times greater than in the bulk.

Fig. 3. Adsorption of various metals on the surface of liquid germanium at 950°

Fig. 4. Ideal isotherm of a two-dimensional gas at 950°

Consequently, when speaking of adsorption films formed by bismuth on the outer surface of germanium, it must be borne in mind that at additive concentrations of $1 \cdot 10^{-6}$ at. %, the area corresponding to one bismuth particle in the surface layer will be $\sim 1 \cdot 10^7 \text{ \AA}^2$.

Since the adsorption of the other metals studied is less than that of bismuth, for them the area corresponding to one impurity particle in the surface layer will prove still larger.

This result makes it possible to conclude that, in the range of concentrations of alloying additives used in semiconductor technology, even in the case of so-called degenerate semiconductors, the adsorption layer is still very far from saturation. Using our data on the adsorption on germanium of the metals listed above, we calculated the magnitude of the area corresponding to one particle of additive metal in the surface layer of the melt. The data obtained, in the coordinates $\pi - \omega$, where π is the lowering of the surface tension of germanium and ω is the magnitude of the area, are shown graphically in Fig. 4. As can be seen from Fig. 4, the experimental points for bismuth, antimony, and thallium are located rather close to the ideal isotherm, whose equation is $\pi\omega = KT$, where K is Boltzmann's constant and T is the temperature.

This permits the adsorption films of bismuth, antimony, and thallium on liquid germanium to be assigned to the type of the so-called gas-like films. It is interesting to note that analogous results were obtained by Pokrovskii and Thyssen in studying the surface tension of tin solutions ⁽⁸⁾.

Since a number of criteria of surface activity for metals have been discussed in the literature ^(7,9-12), it is of interest to compare them with our experimental data. The opinion has been expressed that, of two metals taken, the surface-active one should be the metal whose melting point is lower ⁽¹²⁾. Cases are known in which this is indeed so; however, the opposite also often occurs: for example, antimony (melting point 630°) lowers the surface tension of indium (melting point 156°) ⁽¹³⁾, all alkali metals lower the surface tension of mercury, etc. ⁽⁷⁾. Of the metals we obtained, gallium had the lowest melting point; however, it was precisely this metal that proved surface-inac...

active on germanium. In work ⁹ it was proposed, in estimating surface activity, to take into account the difference in the atomic volumes of the solvent and the additive, so that the substance with the larger atomic volume should be surface-active.

Taking into account that the surface activity of the metals studied on germanium increases in the series gallium–indium–thallium–antimony–bismuth, one should note the agreement of this sequence with the change in the difference between the atomic volumes of these metals and germanium ($V_M - V_{Ge}$), as is seen from Table 1.

Table 1

Metals	Difference of atomic volumes, $\text{cm}^3 V_M - V_{\text{Ge}}$	Difference of generalized moments, $\text{el}/\text{cmm}_{\text{Ge}} - m_M$	Value of the difference in surface tension $\sigma_{\text{Ge}} - \sigma_M$	Value of the limiting surface activity on germanium at temperature $t = 950^\circ\text{C}$
Gallium	-3.1	$-0.09 \cdot 10^8$		-20
Indium	+2.6	$0.155 \cdot 10^8$	110	250
Thallium	+3.5	$0.203 \cdot 10^8$	188	450
Antimony	+4.1	$0.186 \cdot 10^8$	267	900
Bismuth	+6.2	$0.785 \cdot 10^8$	285	1200

The criterion of Semechenko's statistical generalized moments¹⁰ also agrees satisfactorily, although still somewhat less well, with our data, since the sequence of differences of generalized moments ($m_{\text{Ge}} - m_M$) does not quite precisely coincide with the sequence of increasing surface activity.

Apparently, the best criterion of surface activity is the value of the difference in surface tensions of the solvent and the additive: the greater this quantity, the higher the surface activity; moreover, in calculating the difference one should take the values of the surface tension not at their melting points (since these are different for each metal), but at the temperature for which the surface activity is determined. Surface tension is a thermodynamic quantity which, to a certain degree, characterizes the molecular force field of a substance in the condensed state. Therefore, the difference in surface tensions may be regarded as a characteristic of the degree of difference between molecular force fields.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Received
12 II 1964

CITED LITERATURE

- ¹ V. B. Sandomirskii, *Khim. nauka i prom.*, **2**, No. 2, 167 (1957).
- ² *Surface Phenomena in Semiconductors*, Collection, Moscow, 1963.
- ³ *Germanium*, Collection of Translations, Moscow, 1955.
- ⁴ V. I. Danilov, D. S. Kamenetskaya, *DAN*, **68**, 677 (1949).
- ⁵ P. P. Pugachevich, V. B. Lazarev, *ZhFKh*, **34**, 2607, No. 3 (1960).
- ⁶ Yu. M. Shashkov, T. P. Kolesnikova, *ZhFKh*, **37**, 1397 (1963).
- ⁷ V. K. Semechenko, *Surface Phenomena in Metals and Alloys*, Moscow, 1957.
- ⁸ N. L. Pokrovskii, D. S. Tissen, *DAN*, **128**, 1228 (1959).
- ⁹ A. M. Korol' kov, *Izv. AN SSSR, OTN*, No. 2, 35 (1956).

- ¹⁰ S. N. Zadumkin, *ZhNKh*, **5**, 1892 (1960).
¹¹ V. I. Nizhenko, *Surface Phenomena in Nickel-Based Alloys*, Kiev, 1963.
¹² P. A. Rehbinder, *Zs. phys. Chem.*, **111**, 447 (1924).
¹³ V. B. Lazarev, M. Ya. Dashevskii, *DAN*, **146**, 822 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.