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CONDUCTIVITY OF MATERIALS MADE OF ALUMINUM
NITRIDE AND SILICON NITRIDE MIXTURES

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CONDUCTIVITY OF MATERIALS MADE OF ALUMINUM
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To establish the possible mechanism for conductivity in aluminum nitride a study was made of the electric conductivity of pure AlN and its mixtures with silicon nitride at different temperatures and partial pressures of nitrogen in the gas phase. The thermoelectromotive force was also measured. The experiments used polycrystalline samples of cylindrical shape 18 mm in diameter made of powders (particle size $5\mu\text{m}$) by hot pressing in graphite press molds at a temperature of 1973-2273°K and pressure $1.47 \cdot 10^6 \text{ n/m}^2$. The items obtained by this method had porosity not over 5%. After pressing the samples were machined to remove carbon from the surface, and were annealed in a stream of dry ammonia for 10 h at a temperature of 1273-1373°K. Chemical analysis did not detect carbon in them.

Electric conductivity was measured according to the bridge scheme on an alternating current of frequency 10 kHz. In order to guarantee close contact of the platinum electrodes with the surface of the samples a thin layer of platinum was sprayed on them.

Experiments were conducted in the temperature interval 1273-1573°K with a half hour delay at each assigned temperature with heating and cooling. The results in both cases corresponded well. To create a controllable gas medium technical nitrogen, ammonia gas, and argon were employed. In the latter the partial pressure of nitrogen was 19.6 n/m^2 . The gases were carefully cleaned of oxygen and moisture.

The results of the electric conductivity measurement (x) of aluminum nitride and its mixtures with small amounts of silicon nitride (up to 3.5 mol %) at different temperatures and partial pressures of nitrogen P_{N_2} are given in fig. 1. The slope of the straight lines confirms the nature of the change in x with temperature that is known from [1]. The activation energy of electric conductivity (ΔE) of aluminum nitride computed from the data in fig. 1 is 3.8 ev. Such an amount of ΔE differs slightly from certain other data [1,2], however there are studies where the width of the forbidden zone is noticeably higher and is 5-6 ev [7]. The absolute values of x in our case are somewhat higher than the known [1] which can be related to the presence of carbon, although it is not detectable by chemical analysis. It can be assumed that this does not have a significant effect on the qualitative discussion of the results.

Comparison of straight lines 1 and 2 for x reveals its dependence on P_{N_2} : with a reduction in the partial pressure the electric conductivity increases

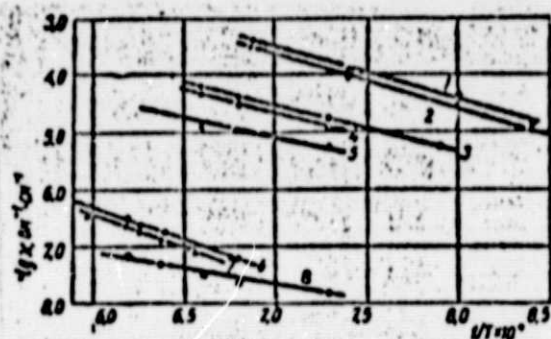
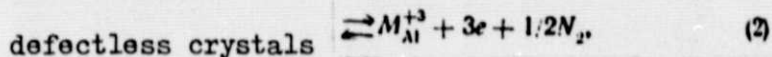
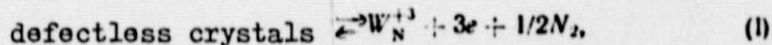


Fig. 1. Dependence of Electric Conductivity of Aluminum Nitride and its Mixtures with Si_3N_4 on Temperature:

1,2--AlN; 3,4--AlN+0.9 mol % Si_3N_4 ;
 5--AlN+3.5 mol.% Si_3N_4 ; 6,7--AlN+1.7
 mol.% Si_3N_4 ; 8--AlN+1.3 mol.% Si_3N_4 .

somewhat. It is known [3] that a similar effect of the partial pressure of metalloid (for example, for oxides and sulfides) is demonstrated on the electron nature of conductivity governed either by an excess of metal, or by a deficiency of metalloid. This is also indicated by the negative sign of the thermo-electromotive force we measured (fig. 2, curve 3).

However, the weak dependence of electric conductivity on the partial pressure of nitrogen does not make it possible to propose a noticeable disorder in aluminum nitride with the participation of the gas phase, for example, according to the schemes



where W_N^{+3} --nitrogen vacancy, M_M^{+3} --aluminum in interstices, e--electron.

In fact for the processes (1) and (2) from the law of active masses follows the proportionality of electric conductivity $p_{N_2}^{-1.8}$ versus $p_{N_2}^{-1.25}$ obtained from the experiment.

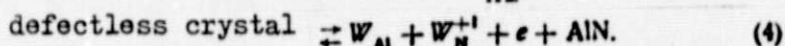
The practical independence of electric conductivity from partial pressure of nitrogen can be observed in the case of the actual conductivity of the semiconductor [4], when disorder results in the simultaneous appearance of the electron e and the "hole" e+, for example:

defectless crystal $\rightleftharpoons e + e^+$.

(3)

However here the thermoelectromotive force must be lacking or be close to zero since the mobility of the electrons and the "holes" are close among themselves. This hypothesis is not confirmed by experiment (fig. 2, curve 3).

If it is considered that the transfer of electricity in aluminum nitride is implemented by electrons (this is indicated by the large negative values of thermoelectromotive force), then such defects of the lattice must compensate for them, those defects whose existence is not affected by the nitrogen pressure. Such a case can be realized with the simultaneous formation of nitrogen vacancy W_N^+ , associated with the "hole" of the neutral aluminum vacancy W_{Al}^0 :



To confirm such a mechanism for the disorder the electric conductivity and thermoelectromotive force of AlN with additions of silicon nitride were measured (fig. 2, curve 1, 2, and fig. 3). For all the temperatures the minimum x is observed with a content of 1.3 mol.% Si_3N_4 .

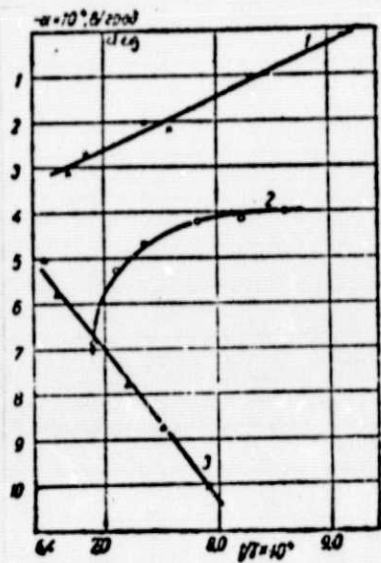
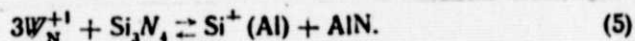


Fig. 2. Effect of Temperature on Thermoelectromotive Force with $P_N = 0.98 \cdot 10^5$ n/m² and Silicon Nitride Content: 1--0.9; 2--1.7; 3--0 mol.%.

With the introduction of the cation Si^{4+} into the sublattice of aluminum an excess positive charge is formed. Having designated such a unit by the symbol $Si^+(Al)$ one can express the process of interaction by the equation:

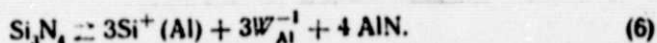


Consequently, the introduction of silicon nitride reduces the amount of anion vacancies whose content is proportional to the concentration of electrons of conductivity. A reduction in the amount of electrons occurs as a consequence of the recombination of the neutral defects associated with the "holes" with the formation of charged cation vacancies W_{Al}^{-1} . The summation of equations (4) and (5) results in a general equation of



Fig. 3. Effect of Additions of Silicon Nitride to AlN on Electric Conductivity at Temperatures: 1--1573, 2--1473, 3--1373°K.

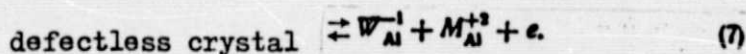
disorder in the nitride mixture:



Thus, small additions of silicon nitride reduce the concentration of the electrons available in pure AlN and liberate the aluminum vacancies. Since the mobility of the electrons is much greater than that for the ion defects the introduction of Si_3N_4 results in a drop in electric conductivity.

Measurements of the thermoelectromotive force in nitride mixtures (fig. 2, curve 1 and 2) confirm the equations of the reactions (5) and (6). In fact, for the sample that contains 1.3 mol.% of Si_3N_4 , i.e., corresponding to the minimum x in fig. 3 the thermoelectromotive force is lower than for pure AlN which indicates the decrease in concentration of electrons of conductivity.

An explanation has also been previously proposed [5] for the conductivity of AlN by the formation of nitrogen vacancies. However the cited results do not exclude another scheme of disorder. For example, in pure nitride it is possible to hypothesize the transition of cations into the interstices M_{Al} with the simultaneous formation of cation vacancies and conductivity electrons:



In this case the reduction in the electron concentration with the addition of Si_3N_4 occurs as a result of the reduction in content of aluminum cations located in the interstices. The summary process for the mixed crystal is expressed by

COMPARISON OF EXPERIMENTAL AND VALUES OF ELECTRIC CONDUCTIVITY OF ALUMINUM NITRIDE COMPUTED ACCORDING TO NERNST-EINSTEIN EQUATION

(a) Temperature, °K	$D_N, \text{cm}^2/\text{sec}$	N, cm^{-3}	E, e	$\tau_{\text{vac}} = -E/E_0 \cdot 10^6$	$\kappa \cdot \tau, \text{cm}^{-1} \cdot \text{cm}^{-1}$	
					(b) расчет	(c) эксперимент
1173	$2,5 \cdot 10^{-13}$	$6,0 \cdot 10^{13}$	0,00011	0,94	$2,0 \cdot 10^{-16}$	$7,9 \cdot 10^{-9}$
1273	$2,0 \cdot 10^{-11}$	$2,0 \cdot 10^{14}$	0,00014	0,94	$5,8 \cdot 10^{-12}$	$3,25 \cdot 10^{-9}$
1373	$6,3 \cdot 10^{-10}$	$7,0 \cdot 10^{14}$	0,00015	1,00	$1,9 \cdot 10^{-10}$	$1,1 \cdot 10^{-7}$

a--Temperature, b--calculation, c--experiment.

equation (6), i.e., in exactly the same way as for disorder according to equation (4). Therefore measurements of electric conductivity do not make it possible to unambiguously judge if disorder occurs in pure aluminum nitride with the transfer of cations into the interstices according to equation (7), or with the formation of anion vacancies according to equation (4).

For a more unambiguous solution to the problems of the mechanism of disorder one can use the Nernst-Einstein equation:

$$\frac{\kappa \cdot \tau}{D} = \frac{Nz^2 \cdot e^2}{kT}, \quad (8)$$

where D--diffusion coefficient, N--number of current carriers (in 1 cm^2), ze--particle charge, k--Boltzmann constant, τ --number of ion transfer.

Since diffusion and electric conductivity are determined by the nature of the disorder, by substituting in equation (8) alternately the diffusion coefficients of nitrogen and aluminum we must for one of the cases obtain the value of electric conductivity close to that found from the experiment. In other words, for such an evaluation it is necessary to know the amounts of the diffusion coefficients (more exactly, the coefficients of self-diffusion) of nitrogen and aluminum in nitride, as well as the number of ion transfer (τ).

Unfortunately, such data are very limited. The quantitative dependence D_N on temperature in the interval 800-900°K, according to the data of work [6] can be expressed by the equation:

$$D_N = 4,2 \cdot 10^{10} \exp(-11850/T). \quad (9)$$

As concerns the diffusion coefficients of aluminum, then as far as we know, there are no such data in the literature. The quantities computed according to formula (9) are given in the table. Here we assume that in our experimental conditions the nature of the temperature dependence D_N is not altered.

To determine the portion of ion conductivity (number of ion transfer) the electromotive force (E) was measured for the concentration of galvanic element with gas electrodes



in which the electrodes were washed with gases with different nitrogen partial pressure. As the latter argon ($p_{\text{N}_2} = 19.6 \text{ n/m}^2$) and dissociated ammonia gas ($p_{\text{N}_2} = 2.44 \cdot 10^4 \text{ n/m}^2$) were selected which were purified of oxygen and moisture. The results of these measurements are given in the table.

Comparison of the obtained data with the thermodynamically possible amount (E_0) computed according to the equation

$$E_0 = \frac{RT}{6F} \ln \frac{p_{\text{N}_2}'}{p_{\text{N}_2}''} \quad (10)$$

makes it possible to find the summary number of ion transfers (τ) in aluminum nitride (see the table). It is apparent that τ_{ion} is extremely small which once again indicates the dominance of electron conductivity of AlN.

From the equations of disordering (4) and (7) follows the equality of equilibrium concentrations of conductivity electrons and ions. By taking the mobility (u) of the current carriers (electrons) $1.0 \text{ cm}^2/\text{v}\cdot\text{sec}$ [7] one can compute their concentration (N) according to the known formula

$$x = zeNu, \quad (11)$$

and then also the values of electric conductivity corresponding to the accepted diffusion coefficients. The quantities x computed according to the Nernst-Einstein equation for the case of electricity transfer according to the nitrogen vacancies are compared to the experimental in the table, from the data of which it follows that x_{calc} differs considerably from x_{exper} . It is necessary to note that the substitution in equation (8) of the amounts x corresponding to the cold-pressed samples, i.e., by 1.5-2.0 orders lower, will not change the significant difference in x_{calc} and x_{exper} . Therefore it is hardly possible to propose the transfer of electricity with the participation of nitrogen, i.e., as a consequence of the formation of anion vacancies. In other words, the cited calculation indicates more the disordering of nitride with the transfer of cations of aluminum in the interstices according to equation (7) than with the formation of anion vacancies according to equation (4).