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Abstract

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THE INFLUENCE OF OXYGEN ON THE ELECTRICAL PROPERTIES OF TITANIUM NITRIDE

(Presented by Academician G. V. Kurdyumov, 14 IX 1961)

Among the nitrides of the transition metals, titanium nitride TiN is one of the most interesting not only from a practical point of view (^{1}), but also theoretically (^{2}), since titanium is characterized by a high acceptor ability, expressed in the easy addition to it of valence electrons of other atoms, while nitrogen has a high ionization potential (14.51 eV), which accounts for the known difficulties in transferring its valence electrons to a bond. The influence of the nitrogen content in the titanium nitride lattice (within its homogeneity range) on the electrical properties has been examined in detail in (^{3}), where it was shown that a decrease in the nitrogen content in titanium nitride leads to the appearance of an energy gap between the *s*- and *d*-states of titanium and the *p*-states of nitrogen, as a result of which titanium nitride with a deficiency of nitrogen atoms in the lattice acquires semiconductor properties.

It is obvious that a substantial change in the electrical properties of titanium nitride may be expected not only when the nitrogen content in its lattice is decreased, but also when nitrogen atoms are replaced by atoms of other nonmetals differing from the nitrogen atom both in size and in polarization properties. In this connection, the present work investigates the character of the influence on the electrical properties of titanium nitride of oxygen atoms, which is also important for studying the properties of alloys of the TiN—TiO system, and also for assessing the properties of titanium nitride contaminated with oxygen, often obtained in industrial production processes for this technically widespread product.

It should be noted that the nature of the influence of oxygen on the properties of titanium nitride was observed in the work of Münster and Sagel (^{4}), who studied the temperature dependence of the electrical conductivity of thin layers of titanium nitride deposited on substrates of tungsten, aluminum oxide, and quartz. They found that on substrates of tungsten and difficultly reducible aluminum oxide, titanium nitride retains the metallic properties characteristic of it in the state of limiting content of nitrogen atoms in the lattice, whereas titanium nitride deposited on a quartz substrate shows a negative temperature coefficient of electrical resistivity; moreover, the transition to the region of a negative temperature coefficient depends on the thickness of the nitride film, beginning for a film 7 μ thick at 500°, and for a film 12 μ thick at 800°. Münster and Sagel attributed this effect to reduction of SiO_2 during deposition of titanium nitride from the gas phase on the surface of quartz glass, with transfer of some of the oxygen atoms into the nitride lattice. Work (^{5}) confirms these results, and the data obtained in it are given in Table 1.

In the present work, alloys of the TiN—TiO system were obtained by two-stage treatment in a stream of ammonia of mixtures of $TiO_2 + Ti$; in the first stage, carried out for 4 hr at 800°, TiO_2 was reduced predominantly to TiO, and in the second—for 4 hr at 1300°—nitride and solid solutions TiN—TiO were formed. Metallographic and X-ray analyses showed the single-phase character of the formed .

Table 1

Electrical properties of titanium nitride films obtained by deposition from the gas phase on various substrates

Substrate material	TiN layer thickness, µ	Specific electrical resistivity, ohm • cm, at 20°	Specific electrical resistivity, ohm • cm, at 801°	Temperature coefficient of resistance in the interval 700–800°	Hall coefficient, cm^3/C
Tungsten	–	$1.65 \cdot 10^{-5}$	$5.82 \cdot 10^{-5}$	$+3.2 \cdot 10^{-2}$	–
Al_2O_3	7	$4.6 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$+2 \cdot 10^{-2}$	$-1.2 \cdot 10^{-4}$
SiO_2 (quartz)	3	$1.4 \cdot 10^{-2}$	$1.8 \cdot 10^{-4}$	$-2 \cdot 10^{-2}$	–
SiO_2 (quartz)	9	$3.9 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$-4 \cdot 10^{-4}$	$-1.3 \cdot 10^{-4}$

of alloys, and their chemical composition is given in Table 2, where the results of measurements of specific electrical resistivity, thermoe.m.f., and the Hall constant of these alloys at room temperature are also shown.

Table 2

Composition and results of measurements of the electrical properties of TiN—TiO alloys

Content, mol. % TiN	Content, mol. % TiO	Specific electrical resistivity, μohm·cm	Hall coefficient, $R \cdot 10^4$, cm^3/C	Thermoe.m.f. coefficient, μV/deg	Content, mol. % TiN	Content, mol. % TiO	Specific electrical resistivity, μohm·cm	Hall coefficient, $R \cdot 10^4$, cm^3/C	Thermoe.m.f. coefficient, μV/deg
100	0	26	−0.67	−9.3	62.7	37.3	12.7	−1.36	−8.6
90	10	17.9	−0.4	−7.1	47.6	52.4	14.2	−1.64	–
79.6	20.4	13.1	−0.17	−6.4	46.7	53.3	–	−1.70	−13.4
73.1	26.9	11.3	−0.48	−0.75	46.0	54.0	14.3	−2.02	–
65.0	35.0	12.1	−0.82	–	41.8	58.2	27.0	−2.64	–

As follows from the data on the change in electrical resistivity in the TiN—TiO section of the system (Fig. 1), the addition of TiO to TiN initially causes a rather sharp decrease in electrical resistivity up to a TiO content of 25-30 mol. %, after which the resistance again slowly increases up to 50–55 mol. % TiO, when this increase becomes abrupt. Such a course of the change in properties is usually characteristic of cases involving the mutual influence of two competing factors, which in the present case are evidently the atomic radius and the ionization potential of oxygen. With small additions of oxygen, the principal role is played by its lower ionization potential (13.57 eV) compared with that of the nitrogen atom (14.51 eV), which facilitates the transfer of electrons from the oxygen atoms into the conduction band and reduces the total negative polarization of the energy complexes of the lattice, consisting of nitrogen and oxygen atoms. At the same time, however, the influence of the geometrical factor increases—the larger radius of oxygen atoms compared with nitrogen atoms—which causes a gradual decrease in the overlap of the energy bands, accompanied by an increase in the period of the solid-solution lattice. Beginning at 30 mol. % TiO, this factor becomes increasingly important, causing a gradual rise in resistance, and in the region of 50 mol. % TiO there is a sharp increase in resistance due to the predominance of oxygen atoms in the solid-solution lattice and a kind of "phase reversal,"when titanium monoxide becomes the solvent rather than the dissolved component. In this, an important role is apparently played by the ability of the oxygen atom to contribute only 2 electrons to the bond, in comparison with 3 electrons for the nitrogen atom.

The curves for the concentration dependence of the thermoe.m.f. (Fig. 2) and the Hall constant (Fig. 3) have an analogous character; for them, however, the minimum in the region of a TiO content of about 20 mol. % is more clearly expressed.

The minimum of the thermoelectric power for a TiO content of 20 mol.% and its coincidence with the minimum on the electrical resistivity-composition curve are in good agreement with the views set forth in work (6), namely that the thermal e.m.f. decreases in absolute magnitude with increasing degree of overlap (smearing) of the energy bands. From the data on the concentration variation of the Hall coefficient up to 20 mol.% TiO, one may assume a relative increase in the hole component in the process of electrical conductivity, which agrees with the decrease in the absolute value of the negative

[Figure 1 and Figure 2]

Fig. 1. Concentration dependence of the electrical resistivity of alloys of the TiN—TiO section

Fig. 2. Concentration dependence of the thermoelectric power of alloys of the TiN—TiO section

[Figure 3 and Figure 4]

Fig. 3

Fig. 3. Concentration dependence of the Hall coefficient of alloys of the TiN—TiO section

Fig. 4

Fig. 4. Temperature-concentration dependence of the specific electrical resistivity of alloys of the TiN—TiO section.
1 –46% TiN + 54% TiO; 2 –65% TiN + 35% TiO; 3 –62.7% TiN + 37.3% TiO; 4 –73.1% TiN + 26.9% TiO; 5–79.6% TiN + 20.4% TiO

value of the thermoelectric power. Conversely, after 20 mol.% TiO the hole contribution to the electrical conductivity decreases.

Figure 4 shows the temperature-concentration dependence of the electrical resistivity of TiN—TiO alloys, from which it follows that all the alloys studied, upon reaching a certain temperature, change the sign of the temperature coefficient of electrical resistivity to negative; moreover, this temperature generally increases with increasing nitride content in the solid solution, with a simultaneous decrease in the absolute value of the maximum electrical resistivity. An earlier temperature

The passage through a maximum for alloys rich in TiO is evidently associated with the role of a geometrical factor—the larger size of the ionic radius of oxygen, which leads to a reduction in the smearing of the energy bands. Also noteworthy is the different character of the maxima on the curves: apparently, sharp maxima correspond to the predominant influence of one of the nonmetals (oxygen or nitrogen), while relatively flat ones correspond to their mutual influence, close to one another in the final result.

On the basis of the data obtained, one may suppose analogous changes in the electrical properties with composition in the systems ZrN—ZrO and HfN—HfO. However, owing to the lower acceptor capacity of zirconium and hafnium atoms compared with the titanium atom, the role of oxygen in them should be manifested more weakly, and the maxima on the temperature-concentration dependence curves should occur at higher temperatures than for the TiN—TiO system, because of the greater overlap of the energy bands.

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