The Electrical Properties of Thin Films of TiN_x and TiC_x

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Thin films of metallically conductive titanium mononitride and carbide were prepared by means of electron beam evaporation. The composition of the samples could be changed over appreciable ranges by introducing nitrogen in the system or adding carbon to the pure starting material, respectively. The transport properties of the resulting compounds were studied as a function of nonstoichiometry and defect structure. A plausible explanation for the different behavior of the films compared to corresponding bulk samples is given and a correlation between the change in electron concentration and the electron transfer theory is presented.

Introduction

During the last two decades, the interest in mononitrides, -carbides and -oxides of the transition metals of group IV to VI of the periodic table has increased substantially because of their unique combination of properties. High hardness[1], melting point[2] and chemical inertness[3], which would classify these materials as refractory compounds, are complemented by high thermal[4, 5] and electrical conductivities[6–8], metallic luster, superconductivity[9] and wide ranges of homogeneity[10, 11]. Throughout this homogeneity region, the compounds also exhibit an extensive defect structure, which can alter the properties of the stoichiometric material considerably[12, 13].

Although it is generally agreed that the cohesive forces in these transition metal compounds involve simultaneous contributions of metallic, covalent and ionic bonding, there are numerous contradictory theories on the extent to which each of these are important. In spite of the considerable amount of theoretical work carried out, no single theory has been totally successful in explaining their properties and experimental evidence is insufficient to permit definite conclusions.

The low specific resistivity and excellent chemical inertness, combined with the high transparency in both the visible and infrared range (for sufficiently thin sections), make these materials especially attractive for possible applications in architecture, solar energy conversion and automotive industries in the form of thin films.

In this paper, the electrical properties of thin films of TiN_x and TiC_x are presented as a function of nonstoichiometry and defect structure together with a possible correlation with the electron transfer theory.

Experimental Procedures

Thin films of TiN_x and TiC_x were prepared by electron beam evaporation. The substrate consisted of simple soda-lime microslide glass. In order to insure sharp x-ray diffraction peaks for the subsequent characterization of the films, a substrate temperature of 300 °C was used. The composition of the samples was altered by respectively introducing nitrogen in the system or adding carbon powder to the starting batch. The stoichiometry of the films was determined by comparison of the lattice parameters obtained from x-ray analysis, with bulk data reported in the literature[2, 14]. The composition was easily controlled between $0.52 < x < 1.15$ for the nitride and $0.70 < x < 0.94$ for the carbide samples. The films had an average thickness of 1500 Å, which has been found to be sufficient in order to eliminate surface scattering effects[15].

While the dependence of the vacancy concentration on stoichiometry is linear for TiC_x, as suggested by several authors[12, 16, 17] and shown in the insert of Figure 1, a slightly different variation was found for TiN_x (Fig. 1) by applying Denker's method[18, 19] to available data[7, 13]. This is mainly due to the presence of vacancies on both the anion and cation sublattices of the NaCl structure of titanium nitride at the stoichiometric composition. This confirms the theoretical contention that, in view of the M.O. energy level diagram of Fig. 2, maximum stability is achieved by that particular crystal structure in which nearly all the bonding orbitals are occupied and the antibonding orbitals vacant. While for TiC no antibonding states are occupied and therefore no

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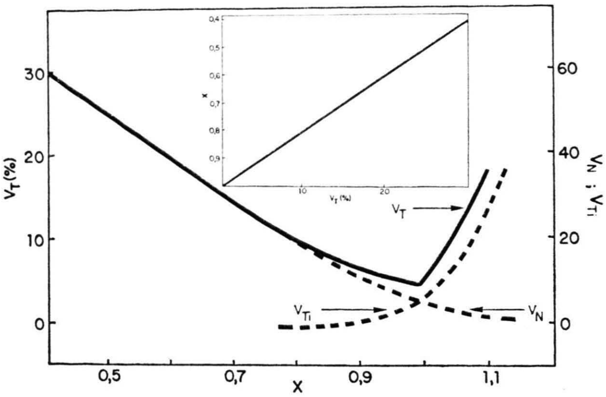

Fig. 1. Variation in the number of vacancies with composition for TiN_x. In the insert, the same variation is shown for the corresponding case of TiC_x.

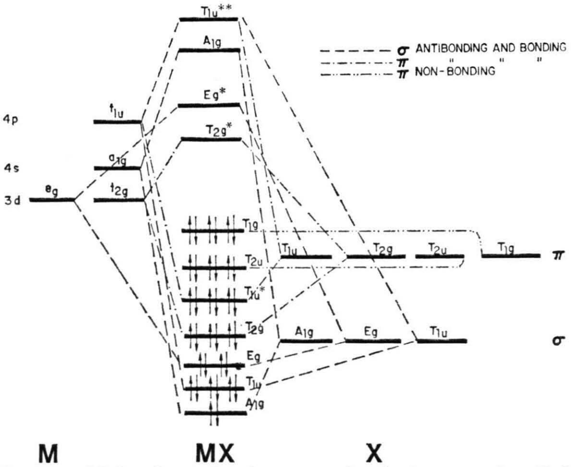

Fig. 2. Molecular orbital energy level diagram for TiC. For TiN add $1e^-$ to T_2^+g (To the upperst A_{1g} add a *.)

vacancies are present, the most stable crystal structure for stoichiometric TiN will have 5% vacant sites on each sublattice [20].

Electrical resistivity values were obtained from four point probe measurements, while information on the number of conduction electrons was obtained from Hall-coefficient studies. The Hall measurements were made on the films by using the D.C. 3-lead technique [21], shown in Figure 3. This method is particularly interesting as it resolves the problem of having a finite voltage drop in the transverse direction even before the magnetic field is applied. Accurate positioning of the leads is therefore no longer necessary.

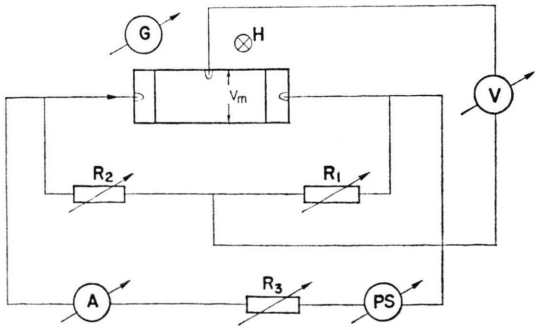

Fig. 3. Block diagram for the circuit measuring the Hall voltage.

Results

A general trend of increasing resistivity with deviations from stoichiometry was found for both compounds. The change was much less pronounced, however, for TiC_x than for TiN_x films, as can be seen from a simple comparison of Figs. 4 and 5.

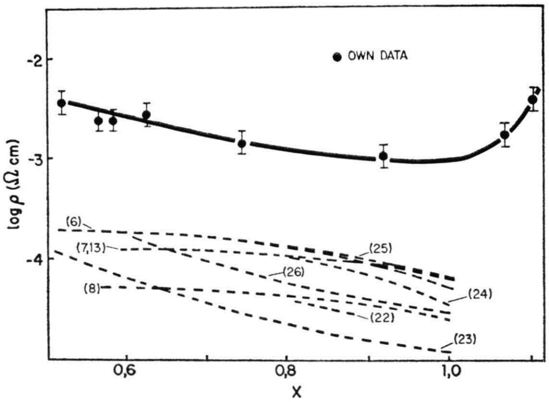

Fig. 4. Variation in the electrical resistivity with deviations from stoichiometry for TiN_x films. (6, 7, 8, 13, 22—26 are footnotes.)

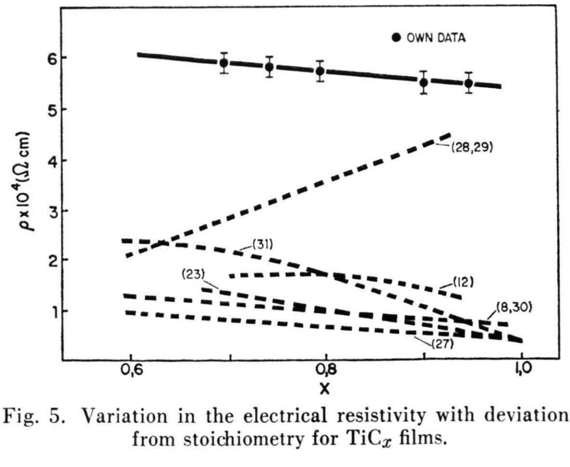

Fig. 5. Variation in the electrical resistivity with deviations from stoichiometry for TiC_x films.

The actual change in resistivity per atomic percent of non-metal added was $2.88 \times 10^{-5}\ \Omega$ cm for the nitride and $3.38 \times 10^{-6}\ \Omega$ cm for the carbide films. The latter were also found to be slightly more conductive than the nitride at equivalent stoichiometries.

The variation for the corresponding bulk samples are shown in the same figures, as reported in the literature. Although qualitatively the change in resistivity for bulk and film is identical, the most outstanding feature is the almost one order of magnitude smaller conductivity of the film samples.

The carrier concentration was obtained from the Hall resistance R_H by the following equation:

$$R_H = -1/n\,e\,. \qquad \text{(I)}$$

Figure 6 indicates how the number of conduction electrons increases with decreasing metalloid content for the carbide samples, but varies in the opposite direction for TiN_x. This is in complete agreement with investigations on bulk samples [7, 8, , ,] although the large disparity in the results obtained by the different authors would make the representation here rather inpractical. While the values reported for the carbide lie in the same order of magnitude as our results, the concentration for the nitride differs by almost a factor of five from the values reported by Aivazov [7, 13]. In our study, the number of conduction electrons n for TiC_x is about twice that of the nitride.

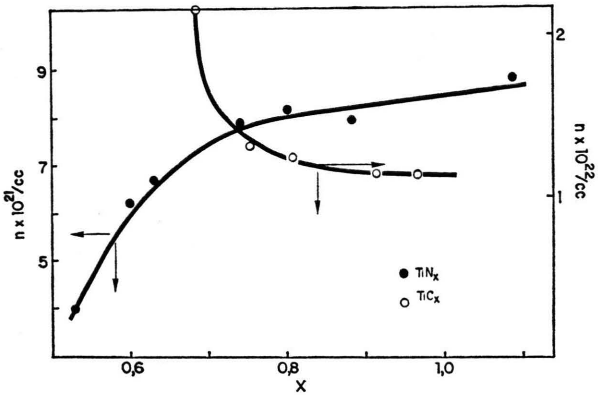

Fig. 6. Change in the number of conduction electrons with composition for both carbide and nitride samples.

Through the combination of Hall coefficient and resistivity measurements one can calculate the electronic mobility from the knowledge of n and the following relation:

$$\varrho = 1/n\,e\,\mu\,. \qquad \text{(II)}$$

with e the electronic charge. It was found in both compounds that the effect of the vacancies introduced is to decrease the mobility. Figure 7 shows indeed how the electronic mobility drops with increasing deviations from stoichiometry. In the case of the nitride the mobilities obtained differ by an order of magnitude from the corresponding bulk samples. For the carbide films the values were of comparable magnitude as for bulk TiC_x. Again the variations found for bulk samples are not represented on the figure because of the large differences between the reported values.

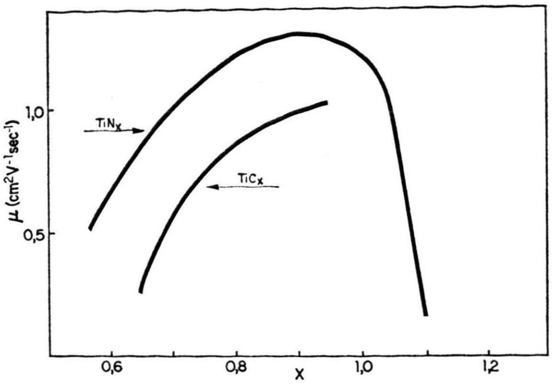

Fig. 7. Variation in electronic mobility with changing stoichiometry of the films.

Discussion

As already mentioned above, the increase in resistivity with deviations from stoichiometry results from an increased scattering of the conduction electrons by the vacancies introduced. The main difference from the bulk values lies in the almost one order of magnitude smaller conductivity of the film specimen, as shown in Figs. 4 and 5. Several reasons for this behavior can be given:

a) The degree of vacancy ordering: This factor is inherent to the preparation process itself. It can indeed be assumed that evaporation of the compounds onto a substrate at 300 °C and keeping it at that temperature for about an hour is sufficient to anneal out most of the stress present (as was proven by annealing studies done on the films), but this temperature is not high enough to produce sufficient diffusion and create a certain degree of order in the vacancy distribution, which can therefore be assumed to more effectively screen the movement of the conduction electrons under the influence of a D.C. field. This is substantiated by the low electronic mobility in the films (0.5 to 1.0 cm^2/V sec) as compared to the bulk values [27] (5 – 20 cm^2/V sec in the specific case of TiN_x).

b) Residual porosity: If the degree of vacancy ordering were the only factor of importance, the difference in electrical resistivities of the film and bulk samples should become smaller when nearing the stoichiometric composition and actually tend to zero in the case of TiC. This however is not the case, the variation with composition actually varying almost parallel for both cases. In view of the substrate temperature of evaporation, analogous studies done by Movchan and Demchishin [32] showed that at this particular temperature relative to the melting point of the compound, the film will have a characteristic domed grain structure, yielding a slightly porous deposit. One observation which substantiates this conclusion is the fact that in the x-ray analysis only the (111) and (222) peaks were observed indicating a strongly oriented crystal structure. As such the electrical resistivity calculated is only an apparent one because the exact cross-section of the sample is not known. By keeping the evaporation variables constant we can at least assume the porosity factor to be constant over the entire range of investigation.

c) Grain size: Although in case of metallic conduction grain boundary scattering can be neglected at room temperature for most materials, the small grain size of our films (±250 Å) and the high Debye temperatures (636 °K in the case of TiN and 848 °K for TiC as compared to 164 °K for Au) might cause the grain size to be of some importance in explaining the differences in behavior between film and bulk.

From the variations in mobility and electron concentration it can be seen that, at least for TiC_x, the differences in transport properties between bulk and film stem from a much smaller electronic mobility in the films, while the comparable magnitude of the number of collectivized electrons indicates the electronic structure of the film not to depart drastically from the bulk. In case of the nitride, however, the mobility was found to be of the same order of magnitude, while the values of the electron concentration differ by almost a factor of five in the most favorable case. The large disparity between the values of n found in the literature, however, makes it inconclusive to compare our results with those for bulk. The values of mobility and electron concentrations found for TiC let us believe that the experimental data obtained in this work are correct, as there is no reason why the values should be very different for TiN_x and TiC_x.

Finally, let us discuss in some more detail the scattering mechanism for TiC_x and TiN_x.

d) Titanium mononitride: It can be seen in Fig. 4 that the electrical resistivity rises much faster at hyperstoichiometric compositions than a substoichiometric ones. This is partly a reflection of the % vacancies versus x curve of Figure 1. However, the fact that the minimum does not lie exactly at the stoichiometric composition indicates that also the scattering power of the N-vacancies is different from that of the Ti-vacancies. The residual resistivity per vacancy can be found from a plot relating the inverse intrinsic mobility to the vacancy concentration. If we express Mathiessen's rule in terms of mobilities, we can write:

$$1/\mu = 1/\mu_i + 1/\mu_v \qquad \text{(III)}$$

where

μ is the effective mobility,

μ_i is the intrinsic mobility (temperature dependant),

μ_v is the mobility associated with the vacancy scattering.

As the intrinsic mobility is usually much larger than the mobility associated with defects, we can simply plot $1/\mu$ versus % vacancies as shown in Figure 8. From the slopes of the appropriate lines we find $\varrho_{V_{Ti}} = 1.98 \times 10^{-4}\ \Omega$ cm and $\varrho_{V_N} = 7.6 \times 10^{-5}\ \Omega$ cm, thus indicating the larger scattering power of the Ti-vacancies. Further, the intrinsic resistivity can be deducted, $\varrho_i = 5.4 \times 10^{-5}\ \Omega$ cm, which is in fairly good agreement with values reported in the literature. The dependence of the residual resistivity on defect structure does not follow the simple linear rule as suggested by Abales [33] and Jongenburger [34]. In fact, Fig. 9 shows a typical exponential behavior in agreement with the observation made by Van Iseghem [35] on thin films of TiO_x.

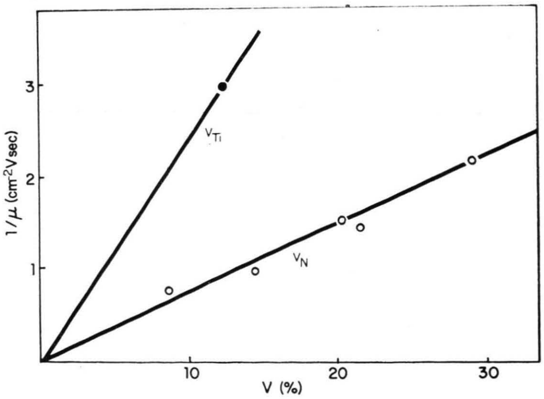

Fig. 8. Inverse intrinsic mobility versus % vacancies for TiN_x films.

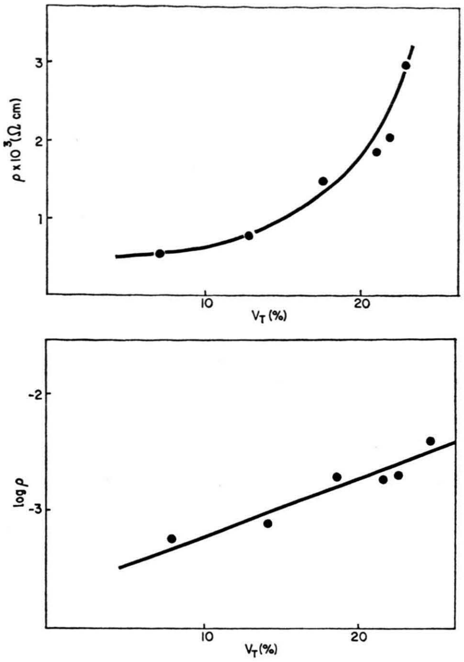

Fig. 9. Dependence of the electrical resistivity of thin films of TiN_x on the vacancy concentration.

The Mathiessen rule is therefore of the form:

$$\varrho = \varrho_{\mathrm{i}} + a\, exp\,(b\, N_{\mathrm{v}})\ . \qquad \text{(IV)}$$

The main reason for this deviation from linearity might be a strong interaction between the vacancies at the concentrations under consideration.

e) Titanium monocarbide: A plot of ϱ versus % vacancies, Fig. 10, gives a straight line for the carbide in contrast with the exponential behavior found for TiN_x and TiO_x. Thus TiC more nearly behaves like an ideal metal and follows Abales' relation. The plot should not be used, however, to determine the intrinsic resistivity, as the introduction of the first initial vacancies has probably a much larger effect than the further addition of defects. This is shown in Fig. 11 by a slight deviation from the linearity predicted by Mathiessen's rule for the relation between $1/\mu$ and the % vacancies and the fact that no stoichiometric TiC can be produced. Therefore, in the homogeneity region of the monocarbide Mathiessen's rule can be written as

$$\varrho = \varrho_{\mathrm{i}} + a\, N_{\mathrm{v}}\ . \qquad \text{(V)}$$

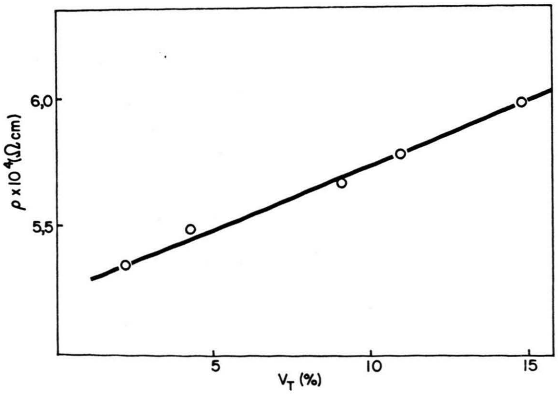

Fig. 10. Dependence of the electrical resistivity of thin films of TiC_x on the vacancy concentration.

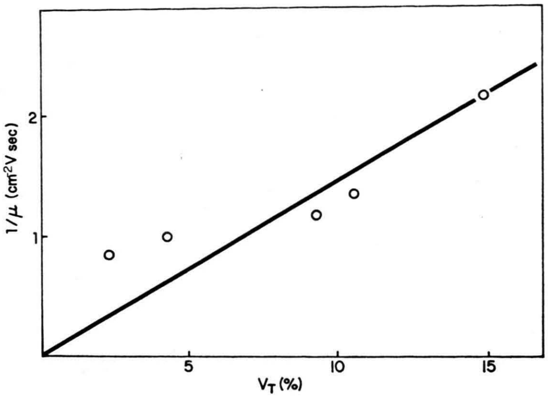

Fig. 11. Inverse intrinsic mobility versus % vacancies for TiC_x films.

Conclusion

From the results of the Hall measurements it can be concluded that the slightly higher conductivity of the carbide samples with respect to the corresponding TiN films does not come from a large difference in scattering cross-section of the vacancies, as the mobilities can be seen to have comparable magnitudes, but rather from an electron concentration which is roughly twice as large for TiC than for TiN. This is in agreement with Tolmacheva's conclusions[36]: the carbides of the transition metals of group IV have more conduction electrons than the corresponding nitrides, because nitrogen has five valence electrons and carbon only four. In case of the nitrides, some of the valence electrons are no longer capable of collectivization and participate in the bonding through the overlap of the electron shells of the ions.

An important observation is the fact that the number of conduction electrons increases with decreasing C-content but decreases in the case of the nitride with decreasing N-content. We may therefore conclude that the charge transfer occurs in the nitride from the nitrogen to the titanium atom, and the electrons freed by the ionization of the N-atom contribute at least partially to the electron cloud. As the n versus x curve of Fig. 6 is almost constant close to the stoichiometric composition it may further be assumed that the change in ionic character mainly occurs in this region, while for more nitrogen deficient compositions the ionic bond becomes saturated and a larger fraction of the electrons gets collectivized. In the carbide, on the other hand, the titanium atom has a predominant donor character. As more C-atoms are added to the structure, they will tend to stabilize their sp^3 electronic configuration by capturing some of the electrons. With decreasing C-content, however, the possibility that Ti gives up electrons to C diminishes and hence the proportion of collectivized electrons decreases. Again this is governed by a saturation phenomenon, resulting in an almost constant value of n in the region close to stoichiometry. With the decrease in metallic bond associated with the decrease in electron concentration, a simultaneous increase in the ionic bonding portion is illustrated by the slight increase in temperature coefficient of resistivity found for TiC_x [37].

Finally, the observation that the variation in resistivity with the % vacancies is much larger for TiN_x than for TiC_x, and more nearly linear for the latter, is a result mainly of the fact that for TiN_x the change in electron concentration and number of vacancies introduced work in the same direction, while in the case of TiC_x one factor will tend to increase the resistivity while the other one decreases it. Apparently the vacancy scattering offsets sufficiently the increase in n with C-deficiency. For the carbide, the vacancies do not seem to interact with one another, while for the nitride the opposite can be deducted from the exponential behavior in Figure 9.

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