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The Influence of N-Ion Irradiation on Superconducting TiN*

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The influence of disorder on the properties of the B1 phase superconductive compound titanium nitride has been investigated. Following synthesis and characterization of thin films of TiN, the materials were disordered progressively and uniformly by irradiation with nitrogen ions. The superconducting transition temperature T_c decreased and the low temperature electrical resistivity ρ increased as lattice damage was introduced. The dependence of both T_c and ρ on N-ion fluence Φ could be described by exponentially saturating functions of Φ with similar rate constants. These constants correspond to characteristic damage energy densities of 14 and 12 eV/atom, respectively.

1. INTRODUCTION

A number of transition-metal-based interstitial compounds have very interesting superconductive and physical properties. The class of B1 phase materials, which crystallize in an NaCl structure, includes the well known compounds NbN, VN, and TiN. [1] All are very hard, refractory nitrides; as a group, they are generally considered to be relatively resistant to disordering effects such as those produced by neutron irradiation. [2] The present work is a study of the influence of disorder on TiN, which in bulk becomes superconductive at $T_c = 5.5$ K. [3] This lower-T_c material has been investigated for comparison with earlier results [4,5] on VN. Here we report on the manner in which T_c, the electrical resistivity $\rho(T)$, the resistivity ratio $\Gamma = \rho(300\ K)/\rho(6K)$, and the x-ray diffraction pattern depend on the fluence of damaging ions.

2. EXPERIMENTAL ASPECTS

The materials for investigation were prepared in two steps. First, thin Ti metal films (100 nm thickness) were deposited at a rate of 35 nm/s onto single crystal sapphire substrates by electron beam evaporation from a previously outgassed 99.999 at. % Ti source. Next, the films were transferred to an all-metal cryopumped chamber, where B1 phase TiN was formed by reaction in high purity N_2 gas at 1 atmosphere pressure. This was accomplished by heating to 1250°C the substrates that were contained in an r.f. induction-heated, tubular Mo susceptor. The films as-produced were bright golden, highly reflective, and gave only B1 phase x-ray diffraction peaks. The midpoint of the superconductive transition of one representative sample, resistively measured, was 4.44 K with a 10–90% width of 0.07 K. Very similar results were obtained for other samples prepared separately.

The electrical properties were measured using 4 lead potentiometric methods and spring-loaded contacts to the films. Thermometry was achieved via calibrated carbon glass, germanium, and Pt film resistance thermometers. Prior to irradiation, the value of the resistivity ρ just above T_c was 16.4 μΩ·cm and the residual resistance ratio Γ was 1.78 for the sample described above.

The ion irradiations were performed at the Surface Modification and Characterization Facility at the Oak Ridge National Laboratory. Nitrogen ions were used in order to introduce no foreign chemical species into the samples, which were maintained near room temperature during irradiation. Ion energies of 45 and 340 KeV were employed in a ratio of 1:15 in order to produce an approximately uniform damage energy profile. With this ratio, the average damage energy deposited per unit depth was 640 MeV/cm per ion, which corresponds to 0.122 eV/(TiN unit) for 10^{13} N-ions/cm^2.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Following characterization of the as-prepared TiN thin films, ion irradiation was used to introduce progressively greater amounts of damage energy into the material. The influence of this energy deposition on the superconductive transition temperature is shown in Fig. 1, a plot of T_c (midpoint) as a function of N-ion fluence ϕ. At first, T_c decreased rapidly but then approached a saturation value. The dependence of

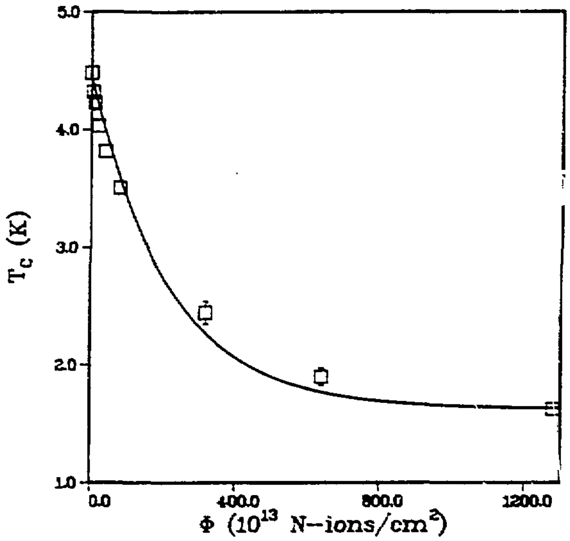

Fig. 1. The T_c (midpoint) of a TiN thin film as a function of N-ion fluence Φ. Experimental data (□); exponentially saturation function, Eq. (1) (solid curve).

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T_c on fluence could be expressed using the empirical relation

$$T_c(\phi) = T_c^s + (T_c^i - T_c^s) \cdot \exp(-\phi/a). \qquad (1)$$

Here T_c^i and T_c^s are the initial and saturation values of T_c, respectively, and (1/a) is a rate constant which characterizes the susceptibility of the material to damage. The continuous curve in Fig. 1 is the result of fitting Eq. 1 to the discrete, experimental data (symbols) in the figure. The least squares fitting procedure yielded the values $T_c^i = 4.48$ K, $T_c^s = 1.62$ K, and $a = 2.16 \times 10^{15}$ N-ions/cm^2, with an rms deviation in T_c of 0.15 K. This value for the rate constant corresponds to the deposition of 14 eV of damage energy per average atom (either Ti or N) in the lattice, which produced about 0.7 displacements per atom.

Other physical properties which are sensitive to disorder include the electrical resistivity ρ and the residual resistance ratio Γ. The dependence of Γ on ion fluence Φ is presented in Fig. 2. This semilogarithmic plot shows that Γ initially decreased rapidly and then asymtotically approached a value of 1.1. Even after high damage ion fluences, a thermal component in the electrical resistivity was still observed, so that $\rho(300\text{ K}) > \rho(6\text{ K}) \equiv \rho_0$. This is unlike the case of VN, in which the thermal component of ρ disappeared altogether at high fluence levels. As discussed below, we find that TiN is more resistant to ion damage than is VN, and it is likely that this accounts for the persistence of a thermal component of ρ.

Accompanying the changes in Γ illustrated in Fig. 2 were substantial increases in electrical resistivity at both room temperature and 6 K, and decreases in the thermal component of ρ. It was found that the residual resistivity ρ_0, which depends on the density and scattering efficiency of different types of defects, also could be described by an exponentially saturating function similar to Eq. 1. A corresponding analysis yielded for the exponential rate constant the value 1.9×10^{15} N-ions/cm^2. This is equivalent to depositing 12 eV of damage energy per average atom, or about 0.6 displacements per atom.

Analyses of the dependences of T_c and ρ_0 on damage ion fluence yielded very similar values, 14 and 12 eV/atom, respectively, for the characteristic damage energies. The similarity of these figures indicates that T_c and ρ are about equally sensitive to the various types of defects created by N-ion irradiation. This is unlike the case of VN, for which the corresponding values were 8.2 eV/atom (from T_c) and 4.2 eV/atom (from ρ_0). For VN, the resistivity was more sensitive to damage than T_c, suggesting that difference types of defects may affect the two properties differently. In contrast, the behavior of TiN was more uniform. Furthermore, the lower-T_c material TiN was more resistant than VN to N-ion damage by roughly a factor-of-two. This difference between the two identically structured B1-phase nitrides, based on transition metals which adjoin in the periodic table, is correlated with stronger interatomic bonding in TiN relative to VN.

Periodically, x-ray diffraction was employed to assess the extent to which the structure of the rocksalt compound was affected by N-ion irradiation. In particular, we wished to establish that the TiN did not become amorphous or severely intermingled with the sapphire substrate via ion-mixing. These diffraction studies showed that the film retained its NaCl (B1) structure at the highest fluence employed, 1.3×10^{16} N-ions/cm^2, after which the four lowest order reflections were still present. Furthermore, the experimentally determined values of the lattice parameter a_0 were constant within experimental uncertainly throughout the experiment. The accumulation of damage in the lattice was apparent, however, as a decrease in height of the diffraction peaks. Qualitatively similar results were found in studies of VN. Relative to VN, less disordering of the lattice was observed in TiN, which is consistent with the values of characteristic damage energy discussed above.

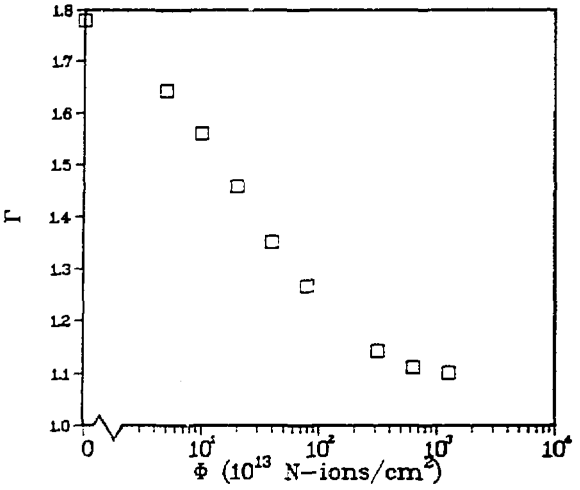

Fig. 2. The residual resistance ratio Γ of a TiN thin film vs. N-ion fluence Φ.

Complementary studies of the upper critical field H_{c2} on virgin TiN have yielded values for the electronic specific heat coefficient γ^* in good agreement with direct measurements on bulk material. After heavy ion damage, γ^* decreased by about 30%. The detailed results of these studies will be discussed in a future publication.

Overall, we find that damage due to N-ion irradiation of TiN leads to a reduction of ~65% in T_c and substantial increases in electrical resistivity. Our analysis indicates that similar levels of ion damage energy density, 14 and 12 eV/atom respectively, characterize the changes in T_c and ρ.

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