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Effect of implanted metal impurities on superconducting tungsten films

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The superconducting transition temperature of more than 30 thin-film tungsten samples was measured using a dilution refrigerator. The samples were fabricated using a 99.999% pure tungsten target and a dc magnetron sputtering system. Individual films were then doped with metal impurity ions using an accurate ion implantation technique. The effect of the metal–ion doping on the superconducting transition temperature was measured for samples with superconducting transitions in the range of 40–150 mK. Magnetic dopant species including Ni, Co, and Fe resulted in suppressed values of the tungsten $T_c$. The suppression was linear with increasing dopant concentration, for concentrations up to tens of ppm. For higher concentrations of magnetic atoms, the data are consistent with the Abrikosov–Gor’kov theory [Soviet Physics JETP 12, 1243 (1961)] modified by antiferromagnetic impurity–impurity interactions. By contrast, tungsten films implanted with Mg or Cr showed little change in $T_c$ after doping. In this article, we present data from cryogenic experiments on these films. We also present x-ray diffraction (XRD) spectra for a subset of the films. Our XRD data confirm that the observed suppression in $T_c$ for the magnetically doped samples is not due to any structural changes (e.g., lattice distortion or damage) induced by the implantation process. © 2002 American Institute of Physics. [DOI: 10.1063/1.1469690]

INTRODUCTION

Our initial interest in adding magnetic impurity atoms to high-purity superconducting tungsten films was motivated by a need for thin-film phonon sensors with adjustable superconducting transition temperature $T_c$. The phonon sensors are used for experiments in particle astrophysics. The performance of these sensors depends critically on the $T_c$ of the superconducting W film, and also on the width of the superconducting transition. We succeeded in developing $T_c$-tunable tungsten sensors for our applications, and the results of that work have been published. At the time that work was done, we were unaware that other groups had previously published magnetic-impurity data for nontungsten superconducting systems. In this article, we extend our earlier results with implanted iron to include two other magnetic dopant species: cobalt and nickel. We also report on results obtained with nonmagnetic “control” species: magnesium and chromium.

The tungsten films used in the studies described below were deposited using a Balzers 450 dc magnetron sputtering system. The as-deposited tungsten films from this system tend to be predominantly polycrystalline, bcc tungsten; this morphology for tungsten is often referred to as its low $T_c$ phase, or alpha phase. Our films also contain a small amount of the metastable, high $T_c$ phase, or beta phase, of tungsten; this is an A15 structure that tends to form when oxygen is present during the deposition. Our as-deposited films have superconducting transition temperatures of the desired order of magnitude for our work (we aim for $T_c \approx 65$ mK). However, the films often have $T_c$ values closer to 150 mK, which is too high for our present applications. We attribute the observed variability in $T_c$ from one batch of films to the next to differing stress characteristics in the deposited films and/or to minute quantities of various residual impurities present in our vacuum chamber during deposition, and/or to other process parameters not yet identified. Fortunately, although the exact cause of the $T_c$ variability has proven difficult to identify and completely remove, the $T_c$ variability itself is easily corrected for in postprocessing, by magnetically doping our otherwise fully fabricated devices. Moreover, our robust technique for adjusting the sharp $T_c$ of our films using ion implantation of magnetic ions does not broaden the superconducting transition nor degrade device performance.

SAMPLES

The samples used in this work were taken from a 350-Å-thick tungsten film deposited on a 210-Å-thick layer of amorphous silicon, on top of a polished, 76-mm-diam, (100) silicon wafer. The presence of the amorphous silicon layer was not important from the standpoint of these studies; it was included for reasons related to the operation of our actual full-scale devices in applications experiments. The amorphous silicon layer and the tungsten film were deposited sequentially without breaking vacuum in the sputtering chamber. The sputtering target used to deposit all of our tungsten films was purchased from Johnson Matthey. It is a 99.999% pure, vacuum-pressed, tungsten target that contains residual impurity concentrations of 0.07 ppm Mg, 0.3 ppm Cr, 0.9 ppm Fe, 0.0019 ppm Co, and 0.10 ppm Ni.
For each set of experiments described below, at least eight neighboring pieces taken from the central region of a single metallized “test” wafer were used; this allowed us to have one “control” sample from the wafer and seven or more “test” samples. The uniformity of $T_c$ across the metallized wafer was good; $\pm 4$ mK across the 7.6-mm-diam wafer. Each sample was $0.25 \text{ cm}^2$ in area. The test samples were separately implanted with the ions of choice, using a Varian ion implanter which has been modified to accommodate nontraditional ion sources. The ion beam energies used were 25 and 47 keV for $^{56}\text{Fe}^+$, $^{58}\text{Ni}^+$, and $^{59}\text{Co}^+$, respectively, and 50 keV for $^{56}\text{Fe}^+$, $^{59}\text{Co}^+$, and $^{58}\text{Ni}^+$. Doses ranging from $1.00 \times 10^{12}$ to $5.00 \times 10^{13}$ ions/cm$^2$ ($\pm 0.01\%$) were used in the studies presented here. All implants were performed with a 7° wafer tilt with respect to the incoming beam. The beam energies were chosen so that the peak of the implanted ion distribution would appear approximately 40% of the way into the 350-Å-thick tungsten film. For reference, the superconducting coherence length in our tungsten films is $\xi_0 \approx 0.3 \mu\text{m}$, which is much greater than the film thickness $\approx 350 \text{Å}$. 

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### TABLE I. Values of the magnetic coupling parameter $\alpha$, the critical concentration $x_c$, and the superconducting transition temperature corresponding to zero impurity atoms of a specific impurity species $T_{c,0}$. The values given correspond to three thin-film systems studied: iron-doped tungsten, cobalt-doped tungsten, and nickel-doped tungsten.

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha$</th>
<th>$x_c$ (ppm)</th>
<th>$T_{c,0}$ (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–W</td>
<td>$-0.060$</td>
<td>69</td>
<td>136</td>
</tr>
<tr>
<td>Co–W</td>
<td>$-0.020$</td>
<td>38</td>
<td>144</td>
</tr>
<tr>
<td>Ni–W</td>
<td>$-1.00$</td>
<td>72</td>
<td>107</td>
</tr>
</tbody>
</table>

### TABLE II. Calculated values of the Abrikosov–Gor’kov and Ruderman–Kittel–Kasuya–Yosida spin-flip relaxation parameters $\tau_{AG}$ and $\tau_{RKKY}$ for our ion-doped samples of thin-film tungsten.

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_{AG}$ (x_c)</th>
<th>$\tau_{RKKY}$ (x_c, T_{c,0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–W</td>
<td>7.6</td>
<td>$-130$</td>
</tr>
<tr>
<td>Co–W</td>
<td>6.5</td>
<td>$-325$</td>
</tr>
<tr>
<td>Ni–W</td>
<td>12</td>
<td>$-12$</td>
</tr>
</tbody>
</table>

### $T_c$ RESULTS AND ANALYSIS—Fe, Ni, AND Co

In Fig. 1, we plot the measured $T_c$ of our 350-Å-thick tungsten films versus dopant concentration for three different magnetic ion species: $^{56}\text{Fe}^+$, $^{59}\text{Co}^+$, and $^{58}\text{Ni}^+$. Three differ-
ent wafers were used for this study, one for each implanted ion species. Thus, the three different unimplanted "control" samples (one from each wafer) had different values of $T_c$.

The curves shown in Fig. 1 correspond to a fit based on the theoretical prediction of Abrikosov and Gor’kov (AG) for the general dependence of $T_c$ on magnetic-impurity concentration. In our analysis, the AG model is modified at high dopant concentrations by the inclusion of a term corresponding to antiferromagnetic ordering between nearest-neighbor magnetic impurities introduced by implantation. The "high dopant-concentration limit" corresponds to $T_c \ll T_{c0}$, where $T_{c0}$ is the superconducting film $T_c$ corresponding to 0 ppm of a specific impurity. Including these effects, the theoretical prediction of the behavior of $T_c$ with magnetic ion doping concentration $x$ is given by

$$\ln (T_c / T_{c0}) = \Psi \{1/2\} - \Psi \{(1/2) + (1/4)(e^{-\gamma})(x/x_c)\} \times \left( T_{c0} / T_c \right) \left[ 1 + \alpha(x/x_c)(T_{c0} / T_c) \right],$$

where $\Psi$ is the digamma function and $\gamma$ is the Euler–Mascheroni constant. In this equation, $\alpha$ is a magnetic coupling parameter which is defined in terms of the Abrikosov–Gor’kov and Ruderman–Kittel–Kasuya–Yosida (RKKY) spin-flip relaxation parameters $\tau_{AG}$ and $\tau_{RKKY}$:

$$\alpha = \tau_{AG}(x_c) / \tau_{RKKY}(x_c, T_{c0}).$$

The relaxation parameters give the relative strengths of the impurity atom–host atom (e.g., Co–W) and the impurity atom–impurity atom (e.g., Co–Co) interactions, respectively. Values of $\alpha \geq 0$ correspond to ferromagnetic ordering (parallel spins) in a film; values of $\alpha < 0$ correspond to antiferromagnetic ordering (antiparallel spins). Magnetic ordering in superconductors is discussed in depth in Refs. 6–10.

The critical concentration $x_c$ is evaluated from the slope of the $T_c$ versus $x$ curve in the low concentration limit

$$\left. \frac{dT_c}{dx} \right|_{x=0} = -\frac{\pi^2 T_{c0}}{8 e^{\gamma} x_c}.$$ 

In Table I we present values of $\alpha$, $x_c$, and $T_{c0}$ determined from our data for each of the three systems studied in this work.

Using the data summarized in Fig. 1 and Table I, we can readily calculate $\tau_{AG}$ and $\tau_{RKKY}$ for the Fe–W, Co–W, and Ni–W systems studied. In the dilute dopant limit

$$\left. \frac{dT_c}{dx} \right|_{x=0} = \frac{\pi}{4 \tau_{AG}^x}.$$ 

Thus, the results of Table II are obtained.

**$T_c$ RESULTS AND ANALYSIS—Mg AND Cr**

In a followup series of experiments, we fabricated and tested tungsten samples implanted with nonmagnetic ions of...
Mg and Cr. These samples were used to confirm that the \( T_c \) suppression effect evident in Fig. 1 was not simply a result of lattice damage induced by the ion implantation process itself. For these studied, 25 keV \( ^{24}\text{Mg}^+ \) ions or 47 keV \( ^{52}\text{Cr}^+ \) ions were implanted into high-purity 350-Å-thick tungsten films. The beam kinetic energies and ion doses were chosen so that the resulting implanted impurity distributions would be quantitatively similar to the distributions used in the magnetic ion experiments. For the Mg work, the impurity concentration at the peak of each implanted ion distribution was netic ion experiments. For the Mg work, the impurity concentration at the peak of each implanted ion distribution was in the range of 3–40 ppm. For each Cr-implanted sample, the peak impurity concentration had a value between 7 and 350 ppm. The measured \( T_c \) values of the Mg–W and Cr–W samples are presented as a function of dopant concentration in Fig. 2.

FILM STRUCTURE MEASUREMENTS

X-ray diffraction (XRD) analysis was performed for several of our tungsten thin-film samples. In Fig. 3, we show the XRD results for a 350-Å-thick tungsten film both before (lower curve) and after (upper curve) implantation with \( ^{56}\text{Fe}^+ \) at 50 keV. The measured \( T_c \) values of these samples were 135 mK (before implantation) and 95 mK (after implantation).

In Fig. 4, we show an XRD spectrum of an “as-deposited,” unimplanted tungsten film with \( T_c \)=95 mK (upper curve), and an XRD spectrum obtained using an immediately adjacent sample from the same metallized wafer after the sample was implanted with the nonparamagnetic dopant \( ^{52}\text{Cr}^+ \) (lower curve). The data shown in this figure were filtered using a Stineman smoothing function before plotting. The Cr implantation was performed at 47 keV, with a dose of \( 5 \times 10^{13} \) ions/cm\(^2\). The poorer signal-to-noise ratio obtained with the Cr-implanted sample was a result of that sample’s smaller size, which was comparable to the collimated x-ray beam profile (=2.5 mm×1 mm) used for the XRD measurements. The continuous background that rises toward small scattering angles in the spectra of Fig. 4 originates from x rays scattering off an amorphous (glass) backing plate used to mount the small samples in the diffractometer.

The XRD data can be used to calculate the lattice spacing of our tungsten films before and after implantation. Our measurements were made using a Philips MRD diffractometer in the parallel-beam configuration. Assuming an incident x-ray source wavelength \( \lambda = 1.5418 \) Å, corresponding to a weighted average of the \( K_a \) lines of Cu, and identifying the crystallographic peaks as shown in Figs. 3 and 4, we get for the lattice parameter of our thin-film samples the values shown in Table III. Our results are in good agreement with the reported value of 3.165 Å for bulk \( \alpha \)-phase tungsten.\(^{11}\)

ACKNOWLEDGMENTS

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