Electronic phase coherence in normal metals is incredibly sensitive to magnetic scattering. As a result, the weak localization magnetoresistance and time-dependent universal conductance fluctuations are powerful probes of magnetic impurities. We report measurements of these effects in Au and Ag nanowires with a 1.5 nm thick Ti adhesion layer underneath the deposited metal. The results indicate an anomalously large magnetic impurity concentration due to the Ti layer. Results suggest that this magnetic scattering and its evolution are related to the oxidation state of the Ti.

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Electronic phase coherence in normal metals gives rise to many conductance effects in mesoscopic architectures. These effects include the weak localization (WL) magnetoresistance, time dependent (TD) and magnetic field dependent (MF) universal conductance fluctuations (UCF), and the Aharonov-Bohm effect. This coherence is typically limited by three types of interactions, electron-electron scattering, electron-phonon scattering, and spin-flip scattering from magnetic impurities. At temperatures much below ~10 K, the electron-phonon scattering is usually negligible. It was suggested as early as 1984 [1] that the WL magnetoresistance could be used as a probe of magnetic scattering at such temperatures. It has been shown experimentally that magnetic impurity concentrations down to a few parts per million cause observable changes in many of the quantum transport phenomena [2,3]. Clearly, quantum transport phenomena are incredibly sensitive to even trace quantities of magnetic impurities.

There have also been recent reports that ordinarily nonmagnetic oxides such as HfO$_2$ [4] and TiO$_2$ [5] can exhibit strong magnetic properties when oxygen defects are present. In this paper we report WL and TDUCF measurements on Au and Ag nanowires that demonstrate anomalous magnetic properties of the TiO$_x$ adhesion layer and strongly indicate that the oxidation state of the Ti is responsible. These results again show quantum transport phenomena as a quantitative probe of magnetic impurities.

All the samples were patterned on undoped GaAs substrates by standard electron beam lithography. All metal depositions were performed in a cryopumped electron beam evaporator that has never been used to evaporate magnetic materials. The evaporations were all done as near a chamber pressure of 7.5 × 10$^{-7}$ Torr as possible. The Ti layer (when present) was deposited at a controlled rate ≤0.15 nm/s, with the total thickness as detected by quartz crystal monitor kept between 1-1.5 nm. The Au or Ag evaporation was then performed immediately (within minutes) without ever removing the sample from the vacuum chamber of the evaporator. The Au was 99.9999% pure while the silver was 99.99% pure. Because of the affinity of Ti for oxygen, the adhesion layer is TiO$_x$, with the oxygen fraction determined in part by the Ti deposition rate. Without the adhesion layer, neither Au or Ag samples exhibit signatures of magnetic scattering, as discussed below.

Once samples were fabricated, they were placed in a $^4$He cryostat and cooled within an hour. Once cooled to 2 K, the WL magnetoresistance measurements were performed. These measurements were made using the standard ac four terminal resistance technique. The magnetoresistance data was acquired by changing the applied field in steps between ~.39 and .39 T in Au and between ~.33 and .33 T in Ag. The resultant magnetoresistance curves were analyzed using [2]:

$$\Delta R/R|_{\text{1d}} = -\frac{e^2}{2\pi h L} \left[ 3 \left( \frac{1}{L_\phi^2} + \frac{4}{3L_{SO}^2} + \frac{1}{12} \left( \frac{w}{L_B} \right)^2 \right)^{-1/2} \right] - \left( \frac{1}{L_\phi^2} + \frac{1}{12} \left( \frac{w}{L_B} \right)^2 \right)^{-1/2}$$

The value $\Delta R/R$ in this equation is defined as $R(B) - R(B = \infty)/R(B = \infty)$ while $L_{SO}$ is the spin-orbit scattering length, $w$ is the sample width, and $L_B = \sqrt{\hbar/2eB}$. Both the coherence length, $L_\phi$, and the spin-orbit scattering length, $L_{SO}$, are left as free parameters while fitting. The typical $L_{SO}$ value was ~290 nm in Ag and ~10 nm in Au.

Samples cooled immediately after fabrication systemically showed smaller coherence lengths and larger magnetic impurity concentrations. In one test, a 70 nm Au sample was made with a 1.5 nm thick Ti adhesion layer and cooled to 2 K within an hour of finishing the fabrication process. The WL magnetoresistance was measured, and then the sample was warmed to 305 K and left in the cryostat under low vacuum (5 Torr of helium with some air contamination). The sample was then cooled and the WL remeasured. This whole process was then repeated one more time. The results are shown in Figure.1. The lines show the Nyquist scattering length[2], the expected $L_\phi$ if decoherence is dominated by electron-electron scattering.

Next, a similar test was performed on a 75 nm wide Au sample with a 1.5 nm thick Ti underlayer to observe how ambient lab conditions affected the WL suppression.
adhesion layer was present, and no suppression without the Ti layer. Similar annealing tests were attempted with Ag, but the oxidation of the Ag films themselves made the test impossible over the same time scale. The coherence lengths of Ag with Ti did not show any noticeable change after 24 hours of air exposure.

The Au samples clearly show a reduction in the total dephasing rate after exposure to air for an extended period. In light of Ref. 8, we show below that the TiO$_x$ layer’s approach to TiO$_2$ stoichiometry is likely the culprit. The change in the base resistance of the sample due to annealing was only $\sim$ -10%, far too small to explain the observed change in $L_\phi$. Identically prepared Au samples lacking Ti adhesion layers exhibit similar annealing of the overall resistance, but with no sign of suppressed $L_\phi$ before or after annealing. At higher temperatures where electron-phonon scattering dominates dephasing, little change is observed in the samples with Ti layers. A reduction in the spin-flip scattering is left as the only likely cause of the coherence length increase upon annealing.

The TDUCF measurements provide strong evidence that the suppressed $L_\phi$ prior to annealing results from magnetic scattering. TDUCF are an enhanced $1/f$ noise at low temperatures$^8$ due to quantum interference and mobile scatterers. Much like WL magnetoresistance, the $1/f$ noise amplitude is altered in the presence of a perpendicular magnetic field. Over some field scale related to $L_\phi$, the noise power will drop by a factor of 2$^9$. A second field-dependent change occurs in the presence of magnetic impurities. At sufficiently large fields, Zeeman splitting of the impurities suppresses the spin-flip scattering, leading to an increase in measured noise power. This upturn at high fields is observed in the samples with Ti, and is reduced upon the annealing described above, while no such upturn is seen in samples without an adhesion layer. This is demonstrated in Figure 3.

The $L_\phi$ data before annealing allow a quantitative examination of the magnetic impurity concentration. For the initial data in Fig. 2, $L_\phi(T)$ looks nearly saturated at 2 K. This saturation should continue until the temperature is well below the Kondo temperature of the magnetic impurities. The Nagaoka-Suhl formula relating the spin-flip scattering rate to the concentration of magnetic impurities can be used to estimate the this impurity concentration. By assuming the saturated $L_\phi$ is dominated by spin-flip scattering, the relation should be$^7$:

$$\tau_\phi^{\text{saturated}}[\text{ns}] \simeq 6 / c_{\text{mag}}[\text{ppm}] \quad (2)$$

Here coherence time is related to $L_\phi$ via the classical diffusion constant, $L_\phi \equiv \sqrt{D\tau_\phi}$. In this sample this gives an effective bulk magnetic impurity concentration of $\sim$16 ppm, much higher than the expected total impurity concentration of the source gold (1 ppm) or Ti (8 ppm). Assuming spin-flip scatterers reside at the TiO$_x$/Au interface, we can estimate the surface density of impurities at 14000 impurities/µm$^2$. Attempts to examine the direct magnetic signal from these moments via SQUID
FIG. 3: The resistive noise power of two Au samples normalized to the zero field noise power. The closed shapes are data from a 70 nm wide sample with a Ti layer, before and after 48 hours of annealing. Open symbols are data from a 75 nm wide sample with no Ti layer.

magnetometry and low temperature electron spin resonance measurements were unsuccessful.

To further confirm the important role of oxygen, an examination of the coherence length suppression as a function of the Ti evaporation rate was performed. With the chamber vacuum near $7.5 \times 10^{-7}$ Torr when the Ti evaporation begins, much of the Ti adhesion layer is actually TiO$_x$ by the time the Ag or Au is deposited over it. Lower evaporation rates of the Ti should yield layers with higher oxygen content, closer to TiO$_2$, and presumably with a decreased magnetic response. Table I shows the WL magnetoresistance suppression at 2 K as a function of the Ti evaporation rate. Since both $L_\phi(T)$ and the predicted Nyquist time depend on the diffusion constant of the metal, properly comparing different samples must be done with care. We compared the ratio of the measured $\tau_\phi$ to the expected Nyquist scattering time for that particular sample. The clear correlation between the Ti evaporation rate and the coherence suppression supports the hypothesis that the oxygen content of the Ti layer strongly affects that layer’s magnetic scattering properties.

The role of metallic Ti as a magnetic scatterer has been examined previously in the limit of extremely dilute coverage, with an observed suppression of the weak localization magnetoresistance. The proposed mechanism in that case was local spin fluctuations, with a dephasing rate proportional to $T$. Such a temperature dependence is not compatible with our observations of a weakening dependence of $L_\phi$ on temperature as $T \to 0$.

In summary, measurements of quantum corrections to the conduction in Au and Ag nanowires prepared with adhesion layers confirm strong magnetic effects in nonstoichiometric TiO$_x$. Although standard SQUID and ESR measurements failed to detect a magnetic signature in Ti/Au films, it may be possible to detect a signal with scanning SQUID microscopy. Such studies would give important information about the microscopic nature of magnetic defect centers in ordinarily nonmagnetic oxides.

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| Material | Ti rate [Å/s] | $\tau_\phi / \tau_{\text{e-e}}$ |
|----------|--------------|------------------|
| Ag       | .82          |                  |
| Ag       | .5           | .36              |
| Ag       | 1.5          | .14              |
| Au       | -            | 1.14             |
| Au       | .3           | .71              |
| Au       | 1            | .19              |

[1] G. Bergmann, Phys. Rep., 107, 1 (1984).
[2] G. Bergmann, J. of Magnetism and Magnetic Materials, 54-57, 1433 (1986).
[3] F. Pierre and N. O. Birge, Phys. Rev. Lett. 89, 206804 (2002).
[4] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature 430, 630 (2004).
[5] S.D. Yoon, Y. Chen, A. Yang, T.L. Goodrich, X. Zuo, D.A. Arena, K. Ziener, C. Vittoria, and V.G. Harris, J. Phys: Cond. Matt. 18, L355 (2006).
[6] G. Bergmann and H. Beckmann, Phys. Rev. B, 52, R15687 (1995).
[7] F. Pierre, A. B. Gougam, A. Anthore, H. Pothier, D. Esteve, and N. O. Birge, Phys. Rev. B 68, 085413 (2003).
[8] S. Feng, P. A. Lee, and A. D. Stone, Phys. Rev. Lett. 56, 1960 (1986); 56, 2772(E) (1986).
[9] A. D. Stone, Phys. Rev. B 39, 10736 (1989).
[10] J. S. Moon, N. O. Birge, and B. Golding, Phys. Rev. B 56, 15124 (1997).
[11] B. W. Gardner, J. C. Wynn, P. G. Björnsson, E. W. J. Straver, K. A. Moler, J. R. Kirtley and M. B. Ketchen, Rev. Sci. Inst., 72, 2361 (2001).
