Normal and reversed tunable magnetoresistance in a NiO$_x$/p-doped silicon diode

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Nonstoichiometric NiO$_x$ thin films fabricated by heating in air nickel thin films sputtered on p-doped silicon substrates show a superparamagnetic magnetization and frustrated magnetism with transition temperatures of 200–300 K. Transport measurements across the magnetic/semiconductor bilayer have a rectifying I-V and voltage dependent magnetoresistance, with maximum ratios at 77 K and 2 T of 70% and −17%. The effect is explained in terms of field dependent polarization in granular NiO$_x$ and highly efficient spin filtering/injection. © 2009 American Institute of Physics.

To fabricate hybrid spintronic devices compatible with current semiconducting technologies, one needs to be able to either have spin dependent transport in a semiconductor, i.e., a magnetic semiconductor, or to use semiconductors as effective spin carriers between magnetic materials. However, although high spin polarization has been measured in photo-currents from ferromagnet/semiconductor and ferromagnet/insulator/semiconductor structures, pure electrical current measurements of spin polarized transport through ferromagnet/semiconductor interfaces have not given good results. This may be due to interface or resistivity mismatch at the ferromagnet/semiconductor interfaces or to an excessive contribution to the transport by the unpolarized s electrons. It has also been suggested that some measurements involving polarized light can include optical effects intrinsically due to the ferromagnet, reducing the real polarization by one order of magnitude from that measured. The best results in the electrical measurement of spin currents in hybrid devices are obtained when using an insulator spacing layer between the ferromagnet and the semiconductor. However, these tunnel junctions usually require interfaces of atomic quality deposited by molecular beam epitaxy, which is slower, more expensive, and technically difficult than sputtering, the deposition technique used in the semiconducting industry.

Thermally oxidized NiO$_x$ on the other hand is an easy to deposit material with potential for high spin polarization applications due to the absorbance of nickel s electrons by the surrounding oxygen atoms. If enough s electrons are bonded while keeping a net ferromagnetic moment, the current will be carried by spin polarized d electrons, increasing the resistivity and polarization relative to pure Ni. Here we show that it is possible to fabricate a NiO$_x$/p-doped silicon diode with voltage-dependent normal/reversed magnetoresistance (MR). We explain this effect as due to band splitting and high spin polarization.

Ni thin films 5–15 nm thick were deposited on p-doped silicon substrates (nominal resistivity of 1 Ω cm, native SiO$_2$ thickness of 1–3 nm) by sputtering and later oxidized by heating on air at 200–300 °C from 30 min to 2 h. The density of the films, related to the oxygen and vacancies content, decreases with the oxidation time, varying from 6.5 g cm$^{-3}$ (Ni-rich) to 5.2 g cm$^{-3}$ (oxygen/vacancies-rich). We find that films with higher density than these are metallic, whereas films with lower density are insulating, green colored and do not show magnetism. The stoichiometry however cannot be asserted due to the presence of vacancies and the density variation with film depth, with nickel rich regions near the substrate. In-plane resistivity for the NiO$_x$ films is of the order of 1–10 Ω cm.

The NiO$_x$ films have ferro/superparamagnetic nickel rich regions within the antiferromagnetic NiO$_x$ lattices and both competing via exchange and superexchange interactions.

The magnetization of the films shows frustrated magnetism, with transition temperatures between 200 and 300 K. The transition peak becomes broader and displaces toward lower temperatures as the magnetic field is increased, until fields of the order of several 100 mT are applied and the peak disappears (Fig. 1). Below the transition the films are superparamagnetic (coercivity of order 1 mT or less), with magnetization slopes of up to 500 Am$^2$/kg T (see Fig. 1 inset), and a saturation magnetization from 0.4 to 1 μ$_B$ per nickel atom.

The deduced particle size is of the order of 10–15 nm.

FIG. 1. (Color online) (a) Normalized magnetic moment vs temperature at different fields for an oxygen rich NiO$_x$ film. Inset: Low field hysteresis loop below the transition temperature before (open squares) and after (full circles) further oxidation at 100 °C (MR data in Fig. 3). Reduced magnetization is likely due to oxygen diffusion.

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In our NiO$_x$/p-Si diodes the current in NiO$_x$ may be carried via the remaining free $s$ electrons, the weakly localized magnetic $d$ electrons (effective mass of order $20m_e$) (Ref. 12) and mobile polaron holes at the $t_{2g}$ orbitals corresponding to the high spin configuration, with their relative contributions dependent on the oxidation state. For all the films we prepared the reversed current at low voltage is at least one order of magnitude smaller than the forward current, so the contribution to the conductance of hopping holes films we prepared the reversed current at low voltage is at least one order of magnitude smaller than the forward current, so the contribution to the conductance of hopping holes present in crystalline NiO (Ref. 14) and hole carriers generation can be observed in the increased reversed current when exposing nickel rich diodes to yellow light ($h\nu$ of order of 2–2.5 eV) [Fig. 2(a)]. We also find that the breakdown voltage of these diodes is quite low, of the order of 1.5 V, which points to a very narrow depletion layer and/or the presence of a thin SiO$_2$ insulating barrier of similar height. These diodes do not show significant magnetic field dependent transport from 77 to 290 K (positive MR $\pm 1\%$).

The diodes with low density NiO$_x$ (5.2 g cm$^{-3}$) on p-silicon do not show breakdown voltage 3 V (above 3 V heating effects dominate the transport) and the I-V characteristic can be fitted to a Schottky characteristic with a deduced barrier height of 0.55 eV at room temperature and 0.15 eV at 77 K [Fig. 2(b)], similar to previous measurements of Ni on p-Si. A lower barrier height at lower temperatures is an effect due to film inhomogeneities, as the temperature is lowered, the carriers tend to cross the interface through the lower energy barrier points. However, the resistance increases due to the reduction in the cross section and increased semiconductor series resistance.

These diodes show normal and reversed MR as function of the applied voltage at temperatures below some 120 K. The maximum magnetoresistive values at 77 K are 72% and –17% at fields of 2 T [see Figs. 3(a) and 3(b)]. This MR is the average of the magnetoresistance throughout all the film, but the contribution may not be uniform in all regions. As the temperature is decreased, we observe that the MR is constant for resistances above a certain value; i.e., as the low barrier regions increase their contribution to the resistance and the magnetic domain size increases, so does the MR [Fig. 3(c)]. The MR would also be higher if we took into consideration the resistance in series offered by NiO$_x$ and doped silicon films, which do not contribute significantly to the magnetotransport.

We also find the MR dependent on NiO$_x$ magnetization, with a reduction in the MR by a factor of 2 when the magnetization slope is reduced by a factor of 3 by diffusing oxygen atoms (heating the sample to some 100 °C), although the diode resistance and the MR varies with temperature. The line is the fit to a $-32\%$ constant MR over the resistance in excess of 190 $\Omega$. Positive MR above 120 K is due to the Lorentz effect. (d) MR at 2 T and 77 K for this sample before (MR multiplied by a 1/2 factor, open squares) and after (MR not modified, full circles) the NiO$_x$ film magnetization has been reduced by a factor of 3 by heating at 100 °C.

We explain this tunable MR as due to the dominant contribution of the spin polarized $d$ electrons and the band splitting in the NiO$_x$ film. At high temperatures or low magnetic fields, the magnetic configuration of the material will be composed of nanometer-sized grains with random magnetic orientation. These grains are smaller than the spin diffusion length of the semiconductor and the spin injection/filtering cancel out over the film. As the magnetic field $B$ increases and the magnetization of the islands align, the averaged transport becomes spin dependent. The spin up $d$ band will be full and lower in energy, whereas there will be two or three electrons in the high energy $t_{2g}$ spin down band (see schematic in Fig. 4).

Considering only the contribution of the $d$ electrons, the forward current density depends on the energy gap between the $d$ band and the conduction band in the p-Si as

$$J_{B=0} \propto \exp(-q\phi_{B=0}/kT),$$

with as the $\phi_{B=0}$ zero voltage barrier height, $q$ as the electron charge, $k$ as the Boltzmann’s constant, and $T$ as the temperature. After the field is applied the $d$ band is split and the transport becomes spin dependent. Taking ANiO$_x$, as the energy band split, instead of having $8d$ electrons at an energy...
level of $q\phi_0$ (relative to the conduction band of the semiconductor), we have five (spin up) electrons at an energy of $q\phi_0-\Delta\text{NiO}_2$ and three (spin down) electrons at an energy of $q\phi_0+\Delta\text{NiO}_2$. Their relative contribution to the current density will be different, so Eq. (1) becomes

$$J_{[B=\pm 0]} = \frac{5}{8} \exp\left(-q\phi_0 - \Delta\text{NiO}_2/kT\right) + \frac{3}{8} \exp\left(-q\phi_0 + \Delta\text{NiO}_2/kT\right).$$

The proportionality factor is the same in Eqs. (1) and (2). From here we see that $J_{[B=\pm 0]}$ can be larger than $J_{[B=0]}$, i.e., the MR can be negative. In our measurements, the maximum $J_{[B=\pm 0]}/J_{[B=0]}$ is 1.17 at 1.5 V, so from Eqs. (1) and (2) the deduced $\Delta\text{NiO}_2$ at 77 K would be 6 meV ($\phi_0=0.15$). However, the exchange splitting should be similar or higher than the Curie temperature ($-25$ meV). This underestimation is probably due to additional effects from the magnetic field that reduce the negative MR, such as spin accumulation at the semiconductor near the interface and the Lorentz effect, and to the contribution to the resistance of the $s$ electrons.

When the voltage is reversed, the current is due to the minority carriers, with the semiconductor injecting electrons into the $\text{NiO}_2$ film. When a magnetic field is applied, the spin up $d$ band in $\text{NiO}_2$ will be full, therefore allowing only the spin down electron current from the semiconductor, resulting in $J_{[B=0]}/J_{[B=\pm 0]} < 1$ and a positive MR. Considering other effects as negligible, if the $s$ electrons do not contribute to the conductivity and all the spin up electrons are filtered, $J_{[B=\pm 0]}/J_{[B=0]}$ would be equal to 0.5. The minimum coefficient (at $V=0$) for our samples is 0.58, very similar to the theoretical minimum. We can therefore conclude that the polarized $d$ electrons are indeed the main contributors to the electronic transport in these $\text{NiO}_2$ films resulting in a high spin polarization.

Our nonstoichiometric $\text{NiO}_2$ films on $p$-doped silicon substrates act as magnetic rectifying diodes without the need for a third magnetic spin collector layer. The change in polarization with the magnetic field varies with the temperature and the magnetization slopes, giving rise to lower MR at higher temperatures or lower magnetizations. By controlling the level of oxidation, it may be possible to increase the temperature of operation and reduce the magnetic field required to obtain a significant effect, which would open many possibilities for the use of $\text{NiO}_2$ in spin filtering/injection devices and magnetic transistors.

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