Increasing Magnetoresistance Using Magnetic-Field-Tunable Interfaces

Andreas Schmehl, Darrell G. Schlom, and Jochen Mannhart*

The ferromagnetic semiconductor europium monoxide (EuO) displays outstanding electronic properties, such as colossal magnetoresistive effects (CMR),[1,2] metal-to-insulator transitions (MIT),[3,4] and close to 100% spin-polarization in the ferromagnetic state.[5,6] Its structural and electronic compatibility with silicon make EuO a promising candidate for silicon-based spintronics. Using rare earth doping, the Curie temperature (T_C) of EuO can be increased from 69 K[7] to ~170 K.[8] This increase, however, comes at the cost of drastically reduced resistance ratios, both for the CMR effect and the MIT.[5] Here, we show how this intrinsic predicament can be overcome. We report a drastic increase of the magnetoresistance and the MIT resistance ratios of bulk $Eu_{0.99}La_{0.01}O$ achieved by interfacing this semiconductor with niobium. The transparency of this interface critically depends on the large Zeeman splitting of the $Eu_{0.99}La_{0.01}O$ conduction band,[9,10] allowing for the temperature and magnetic field induced switching between non-linear and linear current-voltage characteristics, associated with tunnelling-dominated and metallic transport across the interface.

Interfaces between transition metal oxides can exhibit outstanding physical properties, by far surpassing those of the bulk materials encompassing them. The spontaneous creation of a highly conducting and even superconducting two-dimensional electron liquid at the interface between the band insulators $SrTiO_3$ and $LaAlO_3$,[11,12] or the strong enhancement of the magnetoresistance at grain boundaries in CMR manganites[13,14] are just two examples of how interfaces can improve existing physical properties or generate completely new behavior. These effects arise from the sensitivity of transport properties in the vicinity of interfaces to the band structures and compositions of the abutting materials. In this work we demonstrate how this dependence can be exploited to drastically enhance the magnetoresistance of lanthanum-doped europium monoxide by interfacing it with niobium. In doing so, one can reconcile the conflicting objectives of simultaneously achieving high Curie temperatures and enhanced magnetoresistance ratios.

Dr. A. Schmehl, Prof. J. Mannhart
Experimentalphysik VI
Elektronische Korrelationen und Magnetismus
Institut für Physik
Universität Augsburg
Augsburg D-86135, Germany
E-mail: andreas.schmehl@physik.uni-augsburg.de
Prof. D. G. Schlom
Department of Materials Science and Engineering
Cornell University
Ithaca, NY, 14853 – 1501, USA

DOI: 10.1002/adma.201003999

Europium monoxide (EuO) is one of the few known ferromagnetic semiconducting oxides (Curie temperature T_C = 69 K).[7] Doping the system with donors, either by introducing oxygen vacancies, or by substituting Eu with rare earth atoms (e.g., La or Gd, refs. 1 and 2), induces metal-to-insulator transitions (MIT) associated with up to 13 orders of magnitude change in resistance.[3] Applying external magnetic fields substantially shifts T_C, creating a colossal magnetoresistive (CMR) effect comparable to that of the CMR manganites.[15] These dramatic changes of the transport properties are attributed to charge transfer from the donor states, which in the paramagnetic state are located below the conduction band edge, into the lower conduction band. This transfer is caused by the large Zeeman splitting of the conduction band of ΔE_Z = 0.6 eV,[9,10] which leads to an overlap of the lower conduction band with the donor level (**Figure 1**a).[15] Due to the large splitting and the low charge carrier density, the carriers only occupy the lower conduction band, generating close to 100% spin-polarization.[5,6] Large doping concentrations (~1–2% La or Gd in EuO) mediate an additional ferromagnetic exchange mechanism, increasing T_C up to 170 K in 8% Gd-doped films grown on MgO,[8] and up to 200 K in 1000 Gauss magnetic background field in 10% La-doped EuO grown on $SrTiO_3$.[16] At these high doping levels, however, the magnitude of the CMR and the MIT are significantly reduced, making it challenging to benefit from these effects at elevated temperatures.[5]

A possible route to circumvent this dilemma is to create an interface between highly doped EuO and a metal. As we show, interfaces can be grown with transport properties that are not only altered by the change of charge carrier density n below T_C, but which are also sensitive to the energy splitting of the conduction band. In the related ferromagnetic semiconductor system EuS (T_C = 16 K) it has been demonstrated that the interface to a gold contact creates a Schottky diode, the properties of which are modulated by the change of the Zeeman splitting of the conduction band.[17] We expand this mechanism to exploit phase-transition induced changes of the EuO carrier-density and band structure to induce large CMR effects above 69 K. To achieve this goal, we tune the transport behavior of an $Eu_{1-y}La_yO$/Nb interface by adjusting the doping level y, until the interface transparency changes at T_C, driven by both the change in n and ΔE_Z. At these doping levels high Curie temperatures are obtained.

Using the Schottky-Mott approximation,[18,19] the semiconductor side of the $Eu_{1-y}La_yO$/Nb interface can be described as a charge carrier depleted, insulating region (Figure 1b). The width w of the insulating zone depends on the built-in potential Φ_B and on the semiconductor charge carrier density n. It is given by: $\omega = \sqrt{(\phi_B \cdot 2 \cdot \varepsilon_0 \varepsilon_s)/n}$, with ε_s being the dielectric constant

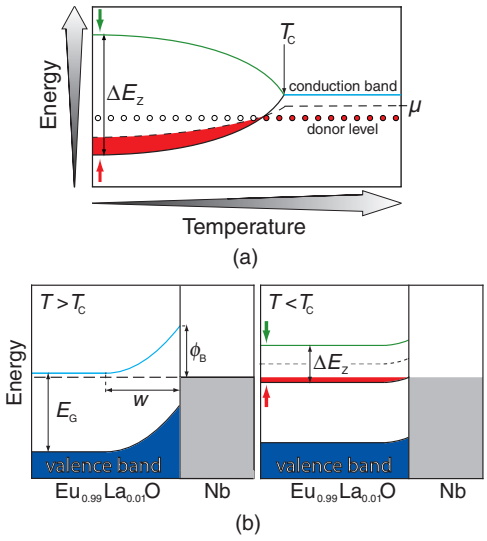

Figure 1. Simplified band structures of electron-doped EuO and of the $Eu_{0.99}La_{0.01}O$/Nb interface. Below T_C, the large Zeeman splitting ΔE_Z of the conduction band leads to an intersection of the lower conduction band with the donor level, inducing a metal-to-insulator transition with a 100% spin-polarized metallic lower conduction band (a). At the semiconductor/metal interface, the energy splitting and the charge carrier transfer causes a reduction of the semiconductor energy gap E_G and of the barrier width (w) and height (Φ_B). These changes switch the contact between tunnelling-dominated ($T > T_C$) and metallic transport behavior ($T < T_C$) (b).

of the semiconductor. As Φ_B is determined by the difference of the work functions of the metal and the semiconductor, the Zeeman splitting of the conduction band of $Eu_{1-y}La_yO$ below T_C lowers Φ_B by ~0.3 eV and thus reduces the depletion width w (Figure 1b). In addition, n is drastically increased below T_C. Accordingly, w is reduced even further. Because the charge carrier density n is determined by the dopant concentration y, one can tune the range of change of the barrier width w by appropriately adjusting y, with the aim to maximize the corresponding change in interface transparency. In the paramagnetic state, the optimized doping concentration generates interface barriers across which the current predominantly flows by tunneling. In this regime, the transparency of the interface depends exponentially on w and therefore is very sensitive to small changes in n and Φ_B. In the ferromagnetic state, however, the Zeeman splitting and the increase in the charge carrier density are so large that the barrier height and width are reduced to such an extent that the interface becomes metallic. The temperature or external magnetic field driven changes in Φ_B and n are therefore expected to result in a transport behavior of the interface, which is switchable between tunnelling-dominated and metallic transport regimes. The associated MIT and CMR effects are substantially enhanced with respect to the bulk material, and are accessible at the desired elevated temperatures. As both the band structure and the chemical potential in doped EuO show strong temperature dependence around T_C, simple tunneling models with static barriers do not allow the quantitative analysis of the derived transport properties of the interfaces. A full quantitative description of the $Eu_{1-y}La_yO$/Nb interface is subject of further experimental and theoretical studies.

Following this approach to obtain high magnetoresistances at high temperatures, we fabricated ramp-type junctions between $Eu_{1-y}La_yO$ (y = 0.005 and 0.01) and niobium. The films were grown on (110) $YAlO_3$ substrates using reactive molecular-beam epitaxy. To protect the EuO from oxidation in air, the films were capped in situ using 100 Å of Si. An in situ structuring technique was employed to define the contacts and to pattern device structures.[20] The contact pattern used allows independent four-point measurements of the transport properties of the $Eu_{1-y}La_yO$ film, of the niobium film, and of their contact on the same bridge.[21] Using such a sample geometry, the individual contributions to the measured transport behavior of the interface are determined.

Figure 2 shows the temperature dependent transport properties of an optimized $Eu_{0.99}La_{0.01}O$/Nb interface. In the paramagnetic state above the Curie temperature, the transport across the interface shows diode like, non-linear voltage–current ($V(I)$) characteristics. With the onset of the ferromagnetism at

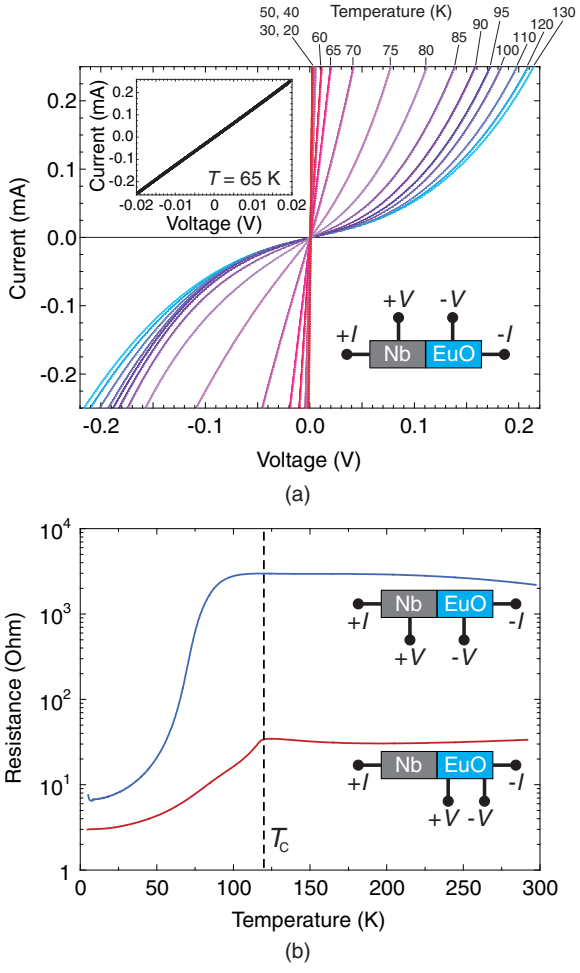

Figure 2. Temperature dependent transport properties of the $Eu_{0.99}La_{0.01}O$/Nb interface. Below T_C = 120 K, the non-linearity of the voltage-current characteristics is progressively suppressed with decreasing temperature (a) leading to linear $V(I)$ behavior at $T \leq 65$ K (inset of a). For bias currents of 10 μA this corresponds to strongly enhanced resistance changes at the MIT with respect to bulk $Eu_{0.99}La_{0.01}O$ (b).

T_C = 120 K (measured independently using superconducting quantum interference device (SQUID) magnetometry) the non-linearity of the $V(I)$ curves starts to be suppressed until at 65 K linear (Ohmic) $V(I)$ characteristics are found. Further reduction of the temperature decreases the interface resistance while maintaining linear $V(I)$ characteristics (Figure 2a). For a measurement current of 10 μA the temperature dependent resistance ($R(T)$) behavior displayed in Figure 2b is obtained. Upon cooling the $Eu_{0.99}La_{0.01}O$/Nb interface through T_C, the $R(T)$ characteristic shows a pronounced insulator-to-metal transition with a resistance change of almost three orders of magnitude ($(R_{125K} - R_{10K})/R_{10K} \approx 440$). For comparison, the contribution of the bulk $Eu_{0.99}La_{0.01}O$ to the measured device resistance is also plotted. As expected from highly doped europium oxide, the MIT is substantially suppressed and widened, with a resistance change of only about one order of magnitude ($(R_{125K} - R_{10K})/R_{10K} \approx 10.5$). The contribution of the $Eu_{0.99}La_{0.01}O$ to the total device resistance is small (~1% at T_C), which demonstrates, that the resistance of the complete structure as well as the large resistance change at the MIT is controlled by the $Eu_{0.99}La_{0.01}O$/Nb interface. Consequently the ratio between the interface resistance and the resistance of the bulk $Eu_{0.99}La_{0.01}O$ decreases with decreasing temperature. The temperature range of the transition from non-linear to linear transport behavior is controlled by the temperature dependence of the Zeeman splitting ΔE_Z of the conduction band and the associated changes in the chemical potential μ (Figure 1).[9]

A corresponding behavior is obtained by applying external magnetic fields. To asses the magnetoresistance of the $Eu_{0.99}La_{0.01}O$/Nb interface, $R(T)$ curves were measured with 10 μA bias current in zero magnetic field and at $\mu_0 \cdot H = 8$ T in-plane field. From these curves, the temperature dependence of the magnetoresistance ratio $MR(T) = (R_{0T}(T) - R_{8T}(T))/R_{8T}(T)$ was calculated. For comparison, the same measurements were performed on the bulk $Eu_{0.99}La_{0.01}O$. The results, acquired on the same sample as discussed above, are depicted in **Figure 3**a. The magnetoresistance ratio of the $Eu_{0.99}La_{0.01}O$/Nb interface surpasses that of the bulk $Eu_{0.99}La_{0.01}O$ over the complete temperature range measured (5 K–295 K). The maximum value of $MR_{interface} \approx 31$ at $T = 87$ K exceeds that of the bulk $Eu_{0.99}La_{0.01}O$ semiconductor by a factor of ~15 ($MR_{bulk} \approx 2.1$ at $T = 120$ K). At $T = 87$ K, $MR_{interface}$ exceeds MR_{bulk} by a factor of 43. Correspondingly, the $V(I)$ characteristics show substantial changes under applied magnetic fields (Figure 3b). These changes are again maximized at $T = 87$ K. With increasing in-plane magnetic field, the non-linear $V(I)$ characteristics are progressively suppressed. For $\mu_0 \cdot H \geq 6$ T linear transport behavior is achieved (inset Figure 3b), demonstrating that the interface can be switched using magnetic fields. Notably, these optimized magnetotransport properties are accessible at temperatures exceeding the Curie temperature of undoped EuO (69 K) and the boiling temperature of liquid nitrogen.

Both the temperature- and the field-dependent transport properties of the $Eu_{0.99}La_{0.01}O$/Nb contact are strongly enhanced with respect to bulk $Eu_{0.99}La_{0.01}O$, benefiting from the switching of the interface. Similar, but not as pronounced results are obtained at $Eu_{0.995}La_{0.005}O$/Nb interfaces.[21] This demonstrates that high electron doping levels are required to tune the interfaces to become critical. At these doping levels one can exploit high MIT and CMR ratios at elevated temperatures.

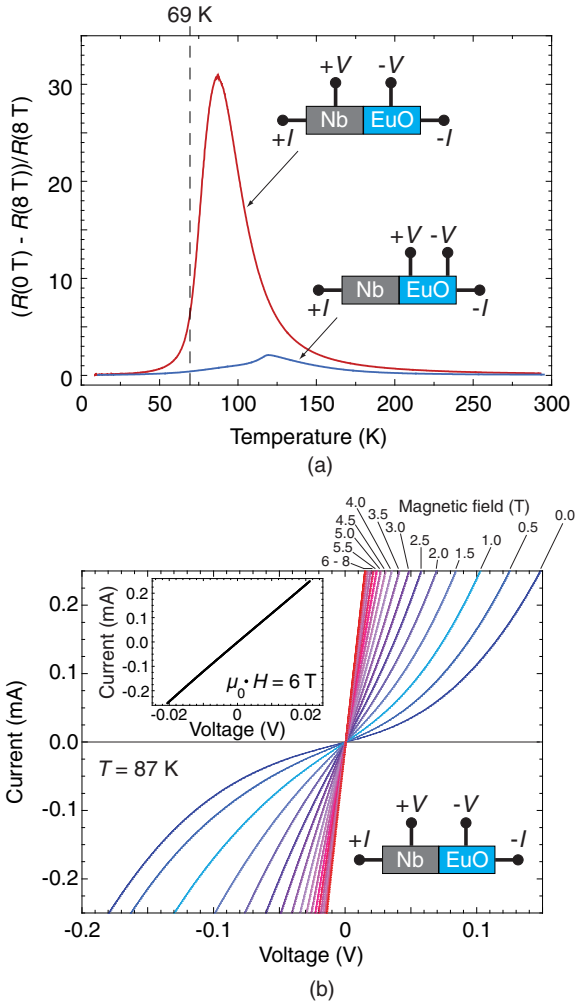

Figure 3. Magnetic field dependent transport properties of the $Eu_{0.99}La_{0.01}O$/Nb interface and bulk $Eu_{0.99}La_{0.01}O$. The magnetoresistance ratio (MR) of the interface exceeds that of the semiconductor over the complete temperature range (a). The MR of the interface shows a maximum at 87 K, surpassing that of bulk $Eu_{0.99}La_{0.01}O$ by a factor of 43. At $T = 87$ K, the non-linearities of the $V(I)$ characteristics are progressively suppressed with increasing field (in-plane), leading to linear behavior for $\mu_0 \cdot H \geq 6$ T (b). The drastically improved magnetoresistance ratios of the interface are accessible above 69 K, the T_C of undoped EuO.

In summary, we have enhanced the magnetoresistance and the metal-to-insulator transition in highly electron-doped europium monoxide by interfacing it with niobium. By optimizing the rare earth doping level, the interface properties are tuned to the point, at which changes of the band structure and of the charge carrier density cause a transition of the interface between tunneling-dominated and metallic transport. The doping levels necessary for achieving these improved properties are high enough to benefit from the carrier-mediated increase in Curie temperature. The principles laid out here are applicable to any metal/semiconductor interface where the semiconductor shows large Zeeman splitting under magnetic field, e.g., dilute magnetic semiconductors.

Supporting Information

Supporting Information is available from the Wiley Online Libray or from the author.

Acknowledgements

The authors acknowledge fruitful discussions with Prof. Hans Kroha. The work at Augsburg was supported by the EU (oxIDes) and by the DFG (TRR80). The work at Cornell was supported by the AFOSR (FA9550–10–1–0123).

Received: October 29, 2010
Published online: January 21, 2011

[1] F. Holtzberg, T. R. Mc Guire, S. Methfessel, J. C. Suits, *Phys. Rev. Lett.* **1964**, *13*, 18.
[2] A. Mauger, M. Escorne, C. Godart, J. P. Desfours, J. C. Archard, *J. Phys. Colloq.* **1980**, *41*, C5-263.
[3] G. Petrich, S. von Molnár, T. Penney, *Phys. Rev. Lett.* **1971**, *26*, 885.
[4] The term metal-to-insulator transition will be applied throughout this letter to describe the resistance drops that occur during cool-down through the ferromagnetic phase transition of EuO, even if at high electron doping levels these transitions are rather between two metallic states with largely different conductances.
[5] A. Schmehl, V. Vaithyanathan, A. Herrnberger, S. Thiel, C. Richter, M. Liberati, T. Heeg, M. Röckerath, L. Fitting Kourkoutis, S. Mühlbauer, P. Böni, D. A. Muller, Y. Barash, J. Schubert, Y. Idzerda, J. Mannhart, D. G. Schlom, *Nat. Mater.* **2007**, *6*, 882.
[6] R. P. Panguluri, T. S. Santos, E. Negusse, J. Dvorak, Y. Idzerda, J. S. Moodera, B. Nadgorny, *Phys. Rev. B* **2008**, *78*, 125307–1.
[7] T. R. McGuire, M. W. Shafer, *J. Appl. Phys.* **1964**, *35*, 984.
[8] H. Ott, S. J. Heise, R. Sutarto, Z. Hu, C. F. Chang, H. H. Hsieh, H.-J. Lin, C. T. Chen, L. H. Tjeng, *Phys. Rev. B* **2006**, *73*, 094407–1.
[9] J. Schoenes, P. Wachter, *Phys. Rev. B* **1974**, *9*, 3097.
[10] P. G. Steeneken, L. H. Tjeng, I. Elfimov, G. A. Sawatzky, G. Ghiringhelli, N. B. Brookes, D.-J. Huang, *Phys. Rev. Lett.* **2002**, *88*, 047201–1.
[11] A. Ohtomo, H. Y. Hwang, *Nature* **2004**, *427*, 423.
[12] N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, J. Mannhart, *Science* **2007**, *317*, 1196.
[13] A. Maignan, Ch. Simon, B. Raveau, *Sol. Stat. Comm.* **1995**, *96*, 623.
[14] A. Gupta, G. Q. Gong, G. Xiao, P. R. Duncombe, P. Lecoeur, P. Trouilloud, Y. Y. Wang, V. P. Dravid, J. Z. Sun, *Phys. Rev. B* **1996**, *54*, R15629.
[15] Y. Shapira, S. T. Foner, T. B. Reed, *Phys. Rev. B* **1973**, *8*, 2299.
[16] H. Miyazaki, H. J. Im, K. Terashima, S. Yagi, M. Kato, K. Soda, T. Ito, S. Kimura, *Appl. Phys. Lett.* **2010**, *96*, 232503.
[17] C. Ren, J. Trbovic, P. Xiong, S. von Molnár, *Appl. Phys. Lett.* **2005**, *86*, 012501–1.
[18] W. Schottky, *Naturwissenschaften* **1938**, *26*, 843.
[19] N. F. Mott, *Proc. Cambr. Philos. Soc.* **1938**, *34*, 568.
[20] Details of the growth procedure and the patterning technique are described in the Supporting Information section of reference 5.
[21] Details of the device geometry used and additional transport data are described in the Supporting Information section.