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# Influence of the substrate temperature on the Curie temperature and charge carrier density of epitaxial Gd-doped EuO films

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Rare earth doping is a standard, yet experimentally poorly understood method to increase the Curie temperature ($T_C$) of the ferromagnetic semiconductor EuO. Here, we report on the charge carrier density ($n$) and the $T_C$ of commonly used 4.2 at. % Gd-doped EuO films grown by molecular-beam epitaxy on (110) oriented $YAlO_3$ substrates at various substrate temperatures ($T_{sub}$). Increasing $T_{sub}$ leads to a decrease in $n$ and $T_C$. For high substrate temperatures the Gd-doping is rendered completely inactive: $n$ and $T_C$ drop to the values of undoped EuO. © *2011 American Institute of Physics*. [doi:10.1063/1.3563708]

With its spin-polarization exceeding 90% and its ability to be epitaxially integrated with silicon,[1] GaN,[1] and GaAs,[2] the ferromagnetic semiconductor EuO has a high potential to act as efficient spin-filter and spin-injector for semiconductor-based spintronics. In addition, its outstanding magnetotransport[3] and magneto-optical properties[4] make it an attractive material for magnetoelectronic applications and proof-of-concept devices. Nevertheless, its instability in air and the comparatively low Curie temperature ($T_C$=69 K[5]) strongly limit the application potential of EuO today. Increasing its Curie temperature therefore is one of the key tasks to render EuO attractive for a broader range of applications.

The most commonly applied technique to increase the Curie temperature of EuO is to charge-carrier dope the semiconductor using trivalent rare earth atoms such as lanthanum[1,6,7] or gadolinium.[6,8–13] This approach exploits the additional ferromagnetic exchange interaction, mediated via the conduction electrons, that acts in addition to the direct Heisenberg exchange between the Eu 4$f$ moments.[14–16] Since the first experimental reports in 1968,[6] many doping studies have been performed on single crystals[6,8,9] as well as on films.[10–13] Despite the common approach, the achieved $T_C$ increases vary strongly from experiment to experiment. For example, a maximum Curie temperature of $T_C$=170 K is reported for polycrystalline Gd-doped EuO films;[11] for films with high crystalline quality and near-perfect oxygen stoichiometries, however, the maximum $T_C$ equals 125 K.[12,13] Despite being a common phenomenon, these large differences in the achievable $T_C$ increase are poorly understood and raise the question about the influence of the growth parameters on the doping efficiency and $T_C$-increase in rare earth doped EuO films.

In this letter, we address this question by investigating the influence of the substrate temperature on the charge carrier density ($n$) and the Curie temperature of 4.2 at. % Gd-doped EuO films. Gadolinium was chosen, as it is the most commonly used cationic dopant of EuO and therefore offers the broadest literature for comparison. To perform systematic studies without interfering influences resulting from changes in the film microstructure, thickness, or oxygen stoichiometry, latter parameters were kept constant and only the substrate temperature was changed.

The films were grown using reactive oxide molecular-beam epitaxy on $YAlO_3$ single crystal substrates oriented within ±0.5° of (110).[17] Europium and gadolinium were co-evaporated from effusion cells. The respective fluxes were calibrated using a quartz crystal microbalance and adjusted to result in the desired Eu/Gd ratio. The total metal flux was set to $1.1\times10^{14}$ atoms/cm$^2$ s. The films were deposited in $O_2$ partial pressures $P_{O_2}$ of $1.0\times10^{-9}$ Torr above the vacuum chamber background pressure ($\sim2\times10^{-9}$ Torr). The substrate temperature was set by adjusting the current flow through a resistive substrate heater, resulting in substrate temperatures of $T_{sub}$=300–600 °C.[18] All films were grown in a single batch, one immediately after the other, to thicknesses of 35 nm. The film thickness was corroborated by postgrowth Rutherford backscattering (RBS) measurements on one exemplary sample of the batch. Additional RBS measurements on a reference sample demonstrate the adsorption-controlled growth of the films with $T_{sub}\geq350$ °C, minimizing additional charge carrier doping from oxygen vacancies. To prevent oxidation, the films were protected by a ~20 nm thick capping layer of amorphous silicon. To ensure a constant Gd-doping $x$ in the $Eu_{1-x}Gd_xO$ films, the Eu/Gd ratios of the films grown at the lowest and highest substrate temperatures were determined using x-ray absorption spectroscopy (XAS) using the inverse partial fluorescence yield method.[18] For films grown in the intermediate temperature range, $x$ was assumed to be constant. Four-circle x-ray diffraction (XRD) was used to characterize the structural quality of all films. The scans reveal epitaxial and single-phase films within the resolution limit of XRD.[18] Rocking curves on the 002 Eu reflections show peaks with

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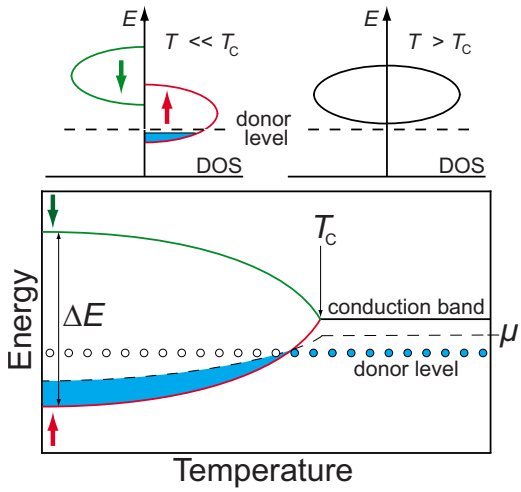


FIG. 1. (Color online) Simplified band structure of doped EuO. Below the Curie temperature the large energy splitting $\Delta E$ of 0.6 eV leads to ionization of the dopants and electron transfer into the lower conduction band. As thermal excitations from the valence band are negligible at these low temperatures, the charge carrier density is almost exclusively determined by the active dopants.

full widths at half maximum of ~0.01°, demonstrating the high and comparable crystalline qualities of all films.[18] The in- and out-of-plane magnetic properties of the $Eu_{0.958}Gd_{0.042}O$ films, including the Curie temperatures, were determined using superconducting quantum interference device magnetometry. To measure $n$ by the Hall effect, bridges were patterned into the samples using an *in situ* combination of ion etching and sputtering. The carrier densities were extracted from the linear magnetic field dependence of the Hall resistance $R_H(H)$ for $\mu_0 H$ exceeding the out-of-plane saturation fields of the $Eu_{0.958}Gd_{0.042}O$ films.[18] All Hall measurements were performed at $T=4.2$ K. Due to the large band energy splitting of 0.6 eV (Ref. 19) of the conduction band in the ferromagnetic state, at low temperatures the shallow dopant states are completely drained into the lower conduction band (Fig. 1). Thermal carrier excitation is negligible at this temperature and $n$ is only determined by the Gd-doping.

Figure 2 shows the influence of the substrate temperature on both the Curie temperatures and the charge carrier densi-

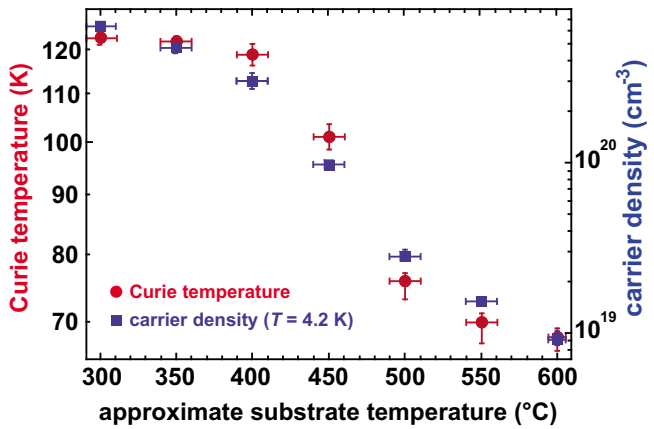


FIG. 2. (Color online) Curie temperatures and charge carrier densities at 4.2 K of the 4.2 at. % Gd-doped EuO films as a function of the approximated substrate temperatures. With increasing substrate temperature both $n$ and $T_C$ are reduced until for $T_{sub} \approx 600$ °C values of undoped bulk EuO are reached.

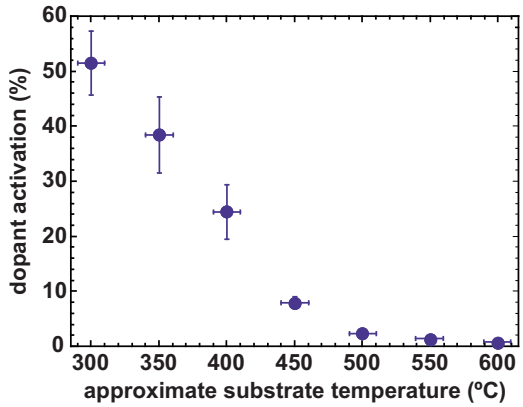


FIG. 3. (Color online) Dopant activation as a function of the approximated substrate temperatures. Starting from an already low activation of 51% at $T_{sub} \approx 300$ °C, the activation drops with increasing substrate temperature until at $T_{sub} \approx 600$ °C all dopants are rendered inactive.

ties of the $Eu_{0.958}Gd_{0.042}O$ films. For substrate temperatures of $T_{sub} \approx 300-350$ °C both quantities are maximized with $T_C \approx 122$ K and $n \approx 5-6 \times 10^{20}$ cm$^{-3}$. Increasing $T_{sub}$ leads to a continuous decrease in $n$ and $T_C$, demonstrating their direct correlation. For $T_{sub} \approx 600$ °C, the Curie temperature and the charge carrier density are reduced to the values of completely undoped EuO, with $T_C=69$ K and $n=9 \times 10^{18}$ cm$^{-3}$.[20] This demonstrates that at high substrate temperatures almost all Gd-dopants are rendered electrically inactive. As the Gd content $x$ in the films stays constant as a function of $T_{sub}$ while $n$ decreases with increasing $T_{sub}$, a $T_{sub}$-controlled decrease in the ability of the Gd atoms to transfer electrons into the conduction band is implied. To asses this behavior we determined the dopant activity $p$ by calculating the expected charge carrier density $n_{ex}$, assuming that every Gd atom donates one electron into the conduction band[14–16] according to $n_{ex}=0.042\ n_{Eu}$, where $n_{Eu}$ designates the density of Eu atoms in EuO. The ratio of the measured charge carrier density $n$ and the expected charge carrier density therefore provides the fraction of active dopants $p=n/n_{ex}$.

Figure 3 shows the dependence of the dopant activity $p$ on the substrate temperature. For $T_{sub} \approx 300-350$ °C, only about 50% of the Gd atoms donate one electron into the conduction band. This low value is further reduced with increasing $T_{sub}$ until at 600 °C, the dopant activity has dropped to $p=0.007$. This is surprising, because the XAS data for the $T_{sub} \approx 600$ °C sample shows that all Gd atoms are ionized to $Gd^{3+}$ and therefore have donated one electron. The small dopant activity thus implies the existence of charge-compensating effects that block the electrons from being transferred into the conduction band, and that become dominant at increasing $T_{sub}$. To assess if this effect can be attributed to a change in growth dynamics at $T_{sub}$, we have grown a $Eu_{0.958}Gd_{0.042}O$ film at $T_{sub} \approx 350$ °C, where high dopant activities and Curie temperatures are achieved. After the deposition and before capping with Si, the film was annealed in vacuum at $T \approx 550$ °C for 30 min. After this anneal, the film showed a low Curie temperature ($T_C=69$ K) and a low carrier concentration ($n=9 \times 10^{18}$ cm$^{-3}$), comparable to those of films grown at $T_{sub} \approx 600$ °C. At 550 °C, low mobilities of the metal ions within the $Eu_{0.958}Gd_{0.042}O$ sample are expected in comparison to a large mobility with respect to oxygen diffusion. We therefore attribute the change in the

$n(T_{sub})$ and $T_C(T_{sub})$ characteristics to changes in the oxygen sublattice of the $Eu_{0.958}Gd_{0.042}O$ films. This is surprising, as all films with $T_{sub} \geq 350$ °C were grown in the adsorption-controlled growth regime, where near perfect oxygen stoichiometries are expected. Nevertheless, this growth regime has only been established for undoped EuO films, and the influence of Gd doping on the adsorption-controlled growth of EuO has yet to be explored.

In summary, we have grown a series of 4.2 at. % Gd-doped EuO films with identical thicknesses and comparable crystalline quality only varying the substrate temperatures. With increasing $T_{sub}$, the charge carrier densities and the Curie temperatures of the $Eu_{0.958}Gd_{0.042}O$ films are increasingly suppressed, until at $T_{sub} \approx 600$ °C no effect of the Gd doping remains observable. This behavior is also reflected in the dopant activity, that drops from already low values of ≈50% at $T_{sub} \approx 300$ °C to about zero at $T_{sub} \approx 600$ °C. A post-growth anneal at $T \approx 550$ °C on a $Eu_{0.958}Gd_{0.042}O$ sample grown at 350 °C led to a Curie temperature of 69 K, the value of undoped EuO. This could indicate that the low dopant activities represent the thermodynamic equilibrium state of Gd-doped EuO. We attribute this behavior to thermally activated changes in the oxygen sublattice. Controlling and engineering the oxygen chemistry might therefore be a way to enhance the dopant activity and with it the Curie temperatures of Gd-doped EuO.

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[1] A. Schmehl, V. Vaithyanathan, A. Herrnberger, S. Thiel, C. Richter, M. Liberati, T. Heeg, M. Röckerath, L. F. Kourkoutis, S. Mühlbauer, P. Böni, D. A. Muller, Y. Barash, J. Schubert, Y. Idzerda, J. Mannhart, and D. G. Schlom, Nature Mater. **6**, 882 (2007).
[2] A. G. Swartz, J. Ciraldo, J. J. I. Wong, Y. Li, W. Han, T. Lin, S. Mack, J. Shi, D. D. Awschalom, and R. K. Kawakami, Appl. Phys. Lett. **97**, 112509 (2010).
[3] Y. Shapira, S. Foner, and T. B. Reed, Phys. Rev. B **8**, 2299 (1973).
[4] K. Ahn and J. C. Suits, IEEE Trans. Magn. **3**, 453 (1967).
[5] T. R. McGuire and M. W. Shafer, J. Appl. Phys. **35**, 984 (1964).
[6] M. W. Shafer and T. R. McGuire, J. Appl. Phys. **39**, 588 (1968).
[7] H. Miyazaki, H. J. Im, K. Terashima, S. Yagi, M. Kato, K. Soda, T. Ito, and S. Kimura, Appl. Phys. Lett. **96**, 232503 (2010).
[8] A. A. Samokhvalov, B. A. Gizhevskii, M. I. Simonova, and N. I. Solin, Sov. Phys. Solid State **14**, 230 (1972).
[9] A. Mauger, M. Escorne, C. Godart, J. P. Desfours, and J. C. Achard, J. Phys. Colloq. **41**, C5-263 (1980).
[10] T. Matsumoto, K. Yamaguchi, M. Yuri, K. Kawaguchi, N. Koshizaki, and K. Yamada, J. Phys.: Condens. Matter **16**, 6017 (2004).
[11] H. Ott, S. J. Heise, R. Sutarto, Z. Hu, C. F. Chang, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B **73**, 094407 (2006).
[12] R. Sutarto, S. G. Altendorf, B. Coloru, M. Moretti Sala, T. Haupricht, C. F. Chang, Z. Hu, C. Schüßler-Langeheine, N. Hollmann, H. Kierspel, J. A. Mydosh, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B **80**, 085308 (2009).
[13] T. Mairoser, A. Schmehl, A. Melville, T. Heeg, L. Canella, P. Böni, W. Zander, J. Schubert, D. E. Shai, E. J. Monkman, K. M. Shen, D. G. Schlom, and J. Mannhart, Phys. Rev. Lett. **105**, 257206 (2010).
[14] A. Mauger, Phys. Status Solidi B **84**, 761 (1977).
[15] N. J. C. Ingle and I. S. Elfimov, Phys. Rev. B **77**, 121202 (2008).
[16] M. Arnold and J. Kroha, Phys. Rev. Lett. **100**, 046404 (2008).
[17] R. W. Ulbricht, A. Schmehl, T. Heeg, J. Schubert, and D. G. Schlom, Appl. Phys. Lett. **93**, 102105 (2008).
[18] See supplementary material at http://dx.doi.org/10.1063/1.3563708 for details.
[19] P. G. Steeneken, L. H. Tjeng, I. Elfimov, G. A. Sawatzky, G. Ghiringhelli, N. B. Brookes, and D.-J. Huang, Phys. Rev. Lett. **88**, 047201 (2002).
[20] J. Schoenes and P. Wachter, Phys. Rev. B **9**, 3097 (1974).