NO-assisted molecular-beam epitaxial growth of nitrogen substituted EuO

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We have investigated a method for substituting oxygen with nitrogen in EuO thin films, which is based on molecular beam epitaxy distillation with NO gas as the oxidizer. By varying the NO gas pressure, we produce crystalline, epitaxial $EuO_{1-x}N_x$ films with good control over the films' nitrogen concentration. *In situ* x-ray photoemission spectroscopy reveals that nitrogen substitution is connected to the formation $Eu^{3+}4f^6$ and a corresponding decrease in the number of $Eu^{2+}4f^7$, indicating that nitrogen is being incorporated in its 3^- oxidation state. While small amounts of Eu^{3+} in over-oxidized $Eu_{1-\delta}O$ thin films lead to a drastic suppression of the ferromagnetism, the formation of Eu^{3+} in $EuO_{1-x}N_x$ still allows the ferromagnetic phase to exist with an unaffected T_c, thus providing an ideal model system to study the interplay between the magnetic f^7 ($J = 7/2$) and the non-magnetic f^6 ($J = 0$) states close to the Fermi level. © *2012 American Institute of Physics*.
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The key to producing novel spintronic devices is to find magnetic materials that can be combined with conventional semiconductors. One class of materials being considered is that of the dilute magnetic semiconductors (DMSs). In this case, standard semiconductors are doped with magnetic impurities, leading to spin-dependent electron transport phenomena which stem from the conduction-electron-mediated ferromagnetic coupling.[1,2] Another promising class of materials is that of the ferromagnetic semiconductors (FMSs) from the rare earth pnictide and chalcogenide families. Despite currently having lower Curie temperatures (T_c) than the DMSs, the rare earth compounds are interesting because of their spectacular properties arising from the interplay between the large magnetic moments due to the atomic-like f-orbitals and the electrons in the wide conduction bands. Arguably the archetypical FMS is EuO, with its $J = 7/2$ moment from the $Eu^{2+}f^7$ ions, a T_c of 69 K, with a spin-split conduction band which allows for spin tunneling with up to 100% spin polarization.[3–5] It exhibits a metal-insulator transition as a function of applied magnetic field and temperature with a resistivity jump of 6 and 8 orders of magnitude, respectively;[6–8] this is even higher than what is observed in the colossal magneto-resistance manganites.[9,10] Furthermore, EuO was grown successfully on Si, GaN, and GaAs[4,11–13] and could thus be readily incorporated in conventional semiconductor technology. Similarly GdN, which is isoelectronic

and isostructural to EuO, exhibits many of the same interesting properties with a T_c of about 60 K.[14,15]

In the search for new compounds in the area of FMSs and based on the promising properties of EuO and GdN, another system that has attracted some attention is EuN. At first glance, this might appear surprising, due to the non-magnetic, $J = 0$ character of its $Eu^{3+}f^6$ ions. However, recent band structure calculations seem to indicate that the $J = 0$ state can be spin polarized, giving rise to ferromagnetism with an unoccupied f band located close to—or even right at—the chemical potential.[16–18] This would lead to the realization of half-metallic ferromagnetic behavior. Ruck *et al.* have investigated this possibility in EuN films grown by molecular beam epitaxy (MBE). However, by studying the magnetic properties by x-ray magnetic circular dichroism, they found no evidence for a ferromagnetic state.[19]

In this work, in search of half-metallic ferromagnetic behavior associated with nominally non-magnetic Eu^{3+} ions, we follow a different approach. Rather than pure EuN, we grow thin films of $EuO_{1-x}N_x$ aiming at embedding the $Eu^{3+}f^6$ ions induced by nitrogen substitution in the well-defined ferromagnetic lattice of EuO. This is in accordance with the above-mentioned rationale that the magnetization provided by the EuO lattice on non-magnetic $Eu^{3+}f^6$ might lead to the formation of a spin-polarized conduction band, whose filling is directly controlled by the nitrogen concentration. As a result of the narrow bandwidth of the f-derived band, these carriers would have a large effective mass.

Since $EuO_{1-x}N_x$ has not been synthesized before, we must first determine if such a system can be grown. It is widely known that it is difficult to grow pure EuO thin films. EuO is extremely unstable in air, and even in UHV environment—if it is grown with too much supply of oxygen—it will form Eu_2O_3 and/or Eu_3O_4 phases. On the other hand, if it is grown with too little supply of oxygen, Eu metal clusters
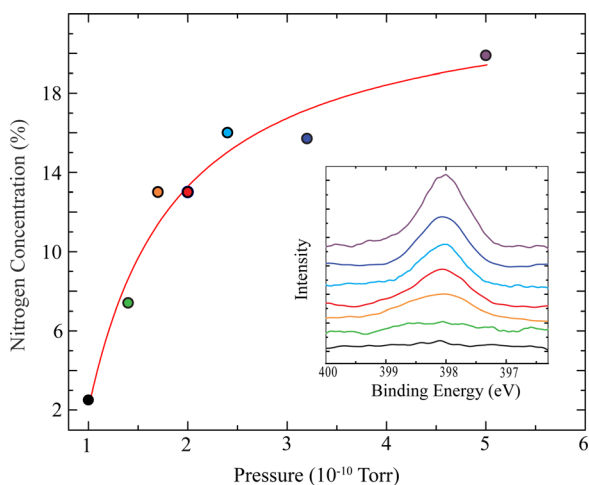
FIG. 1. Increase in nitrogen concentration in the $EuO_{1-x}N_x$ films as a function of NO partial pressure. These concentrations were measured using the ratio of the background-subtracted nitrogen and oxygen $1s$ core level areas in XPS, corrected for their corresponding photo-ionization cross-sections. The inset shows the increase in the nitrogen $1s$ core level peak with increasing NO pressure as measured by XPS. The red line is a guide to the eye, based on a fit to the Langmuir adsorption equation, see Ref. 26.

may form.[20] Both of these situations will deteriorate the extraordinary properties of EuO. These problems can be overcome to successfully grow high-quality EuO thin films by the MBE distillation method, which involves evaporating europium metal onto a hot substrate in a low pressure of oxygen.[3,21–23] The low oxygen pressure prevents the formation of Eu_2O_3 and/or Eu_3O_4, while any unreacted metal is re-evaporated from the hot substrate surface thus maintaining the well-proven europium distillation growth technique.[23–25] This is the approach we have chosen to grow our $EuO_{1-x}N_x$ films; however, instead of pure oxygen, we used NO gas, and during the course of the work, we also discovered that the oxygen-nitrogen substitution can be tuned.

The choice of NO gas as both the oxidizer and as a means of substituting nitrogen in EuO was inspired by earlier NO_2-assisted epitaxial growth of Fe_3O_4, $Fe_{1-\delta}O$, and CrO.[27,28] There, NO_2 gas was used because it is a very efficient oxidizer; as a side effect, it was found that, in addition to the desired amount of oxygen, nitrogen was also being incorporated into the films. Since the nitrogen concentration in the films was decreasing upon increasing NO_2 pressure, it was hypothesized that the probability of nitrogen substitution was higher when there was insufficient oxygen to form a stoichiometric material. Since the conditions in MBE distillation are always oxygen deficient by design, this technique can be used as a general approach to incorporate nitrogen into oxide films. For the case of EuO, since NO_2 is far too aggressive an oxidizer, we chose NO gas instead, following the work on nitrogen substituted SrO by Elfimov *et al.*[29] In that work, by keeping the rate of metal evaporation constant and changing the background pressure of NO gas in the UHV growth chamber, it was shown that the amount of nitrogen taken up by the film can be tuned.

The $EuO_{1-x}N_x$ samples were grown on yttria-stabilized zirconia (YSZ) substrates, whose 5.142 Å lattice constant is very close to one of bulk EuO, 5.144 Å. These substrates, purchased from SurfaceNet GmbH., were annealed in the

growth chamber for 2 h at 600 °C in 1×10^{-6} Torr of oxygen (the chamber base pressure is in the 10^{-10} Torr range). This procedure removes surface contaminants, re-oxygenates the substrate, and gives defects on the surface enough mobility to aggregate into step edges, producing an atomically flat surface. After annealing, the substrate temperature was set to 450 °C. Europium metal was evaporated from a Knudsen cell at a rate of 8.2 Å per minute; the rate was measured with a quartz crystal monitor. The chamber was backfilled with NO gas through a precision leak valve and the NO partial pressure was measured with a MKS Instruments residual gas analyzer. While Eu evaporation rate and substrate temperature were kept constant for all growths, the amount of NO gas used to oxidize and dope the films was adjusted for each growth. The range of gas pressures was between 1×10^{-10} and 5×10^{-10} Torr. The choice of substrate temperature, evaporation rate, and NO pressure range determine if the conditions are favourable for MBE distillation; starting parameters were chosen based on earlier work.[23,30]

Fig. 1 demonstrates how the amount of nitrogen incorporated into the $EuO_{1-x}N_x$ films varies by changing the background pressure of the NO gas. The concentration of substituted nitrogen was estimated from the photo-ionization cross-section[31] corrected ratio of nitrogen and oxygen $1s$ core level peaks measured by x-ray photoemission spectroscopy (XPS).[28] The XPS measurements were performed *in situ* with monochromatized Al $K\alpha$ radiation and a VSW 150 electron analyzer. As shown in the inset of Fig. 1, the nitrogen $1s$ peak grows with the NO pressure (the spectra were normalized to the oxygen $1s$ peak area, not shown).

We note that the non-linear increase of nitrogen concentration in the $EuO_{1-x}N_x$ films with increasing NO pressure is
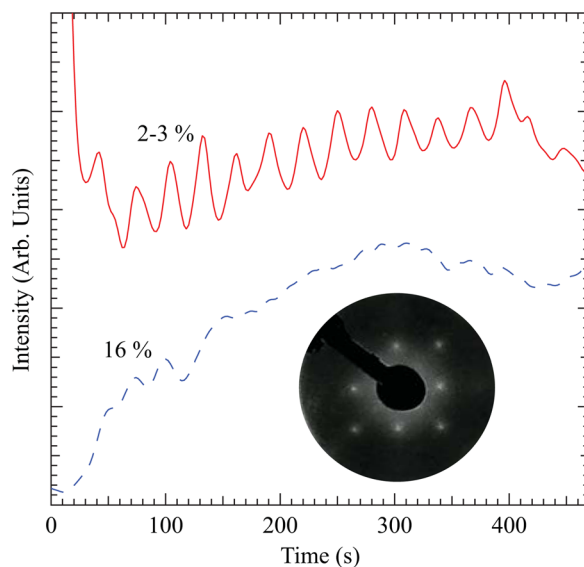

FIG. 2. RHEED spot intensity oscillations for 2%–3% and 16% nitrogen concentration, respectively. The inset shows a LEED diffraction pattern for a 13% N substituted sample. The initial three oscillations in the 16% nitrogen substitution case are consistent with a layer-by-layer growth process enabled by oxygen being donated to the film by the YSZ substrate. The 2%–3% substitution film exhibits in addition RHEED oscillations that continue well past the thickness where oxygen donation from the substrate could have an effect, indicating that these prolonged oscillations are due to sustained layer-by-layer growth of $EuO_{1-x}N_x$. The LEED diffraction pattern indicates that even after 100 min of growth, the film remains crystalline.

very different from the previously reported linear decrease with increasing gas pressure,[27,28] observed in the NO_2-assisted growth of Fe_3O_4, $Fe_{1-\delta}O$, and CrO. In these latter cases, the metal-to-NO_2 flux ratio was approximately 1, setting the growth far outside of the MBE distillation regime used here. One could then envision that the NO_2 oxidizes first the available Fe or Cr, leaving behind an equal number of NO molecules that can react with the remaining metal; since the number of these remaining metal sites is inversely proportional to the initial NO_2 pressure, one obtains the observed linear decrease in nitrogen concentration with increasing NO_2 pressure. For the present case of NO-assisted growth of EuO, we can conclude that the increase of the N-to-O ratio with increasing NO pressure stems specifically from the MBE distillation conditions, although further research will be needed for the accurate quantitative modeling of the adsorption kinetics under these conditions.

In addition to providing a method for introducing nitrogen into EuO films, MBE distillation with NO gas also produces films with excellent crystalline quality. All of the films exhibited low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) patterns, with well-defined diffraction spots after growth. The films also exhibited layer-by-layer growth under certain conditions, as indicated by the presence of typical RHEED oscillations (see Fig. 2 for representative RHEED data from 2% to 3% and 16% nitrogen substituted $EuO_{1-x}N_x$ and crystalline LEED data from a 13% substituted sample). The 16% substitution level does exhibit three RHEED oscillations at the beginning of growth but they quickly disappear. These initial RHEED oscillations are seen in all the films, regardless of the substitution level; however, the lower pressure growths exhibit RHEED oscillations that continue for several 10's of monolayers. The difference between high and low pressure regimes is most likely due to a too high concentration of defects in the heavily nitrogen-substituted films; these defects act as nucleation sites, initiating three-dimensional island growth and destroying the two-dimensional, layer-by-layer growth. Initially, however, the growth is primarily controlled by oxygen being donated to the film by the YSZ substrate, rather than by the NO gas:[23] this allows the observation of layer-by-layer growth independent of the NO gas pressure. RHEED oscillations that continue beyond 4-5 monolayers cannot be due to the substrate donating oxygen, because the film is at that point too thick for oxygen from the substrate to diffuse to the surface.[23] Therefore, these additional oscillations must originate from $EuO_{1-x}N_x$ growing in a truly layer-by-layer mode, as in the case of the 2%–3% substitution level shown in Fig. 2.

The results discussed above demonstrate that MBE distillation with NO gas is a suitable approach for producing high crystallinity, epitaxial $EuO_{1-x}N_x$ films, with tunable nitrogen-oxygen substitution. To establish the oxidation state of the substituted nitrogen and provide a more detailed characterization of the films' electronic structure, we performed XPS valence band measurements *in situ* (Fig. 3). The spectra evolution indicates that as the nitrogen concentration increases so does the amount of Eu^{3+} spectral weight, while the Eu^{2+} intensity decreases. We also note that the oxygen 2p intensity does not increase with increasing NO-pressure,
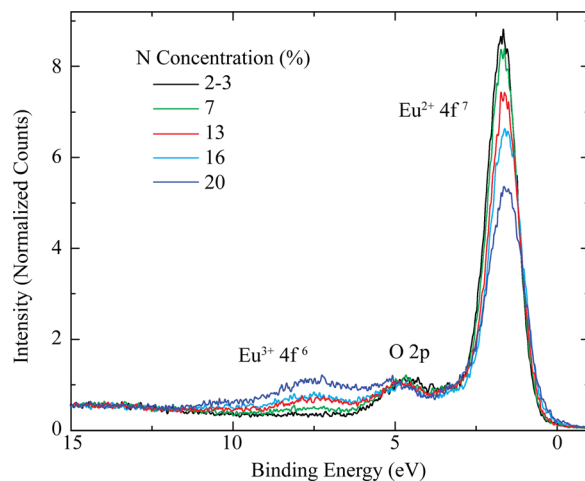

FIG. 3. Valence band XPS spectra of $EuO_{1-x}N_x$ as a function of nitrogen concentration. The increase of spectral intensity in the Eu^{3+} peak and the corresponding decrease in Eu^{2+} spectral weight suggest that nitrogen is being incorporated in its 3^- oxidation state. The XPS spectra were normalized to the total number of counts.

establishing that the increase of Eu^{3+} is due to the substitution of O^{2-} with N^{3-}, thus with nitrogen being incorporated in its 3^- oxidation state. Whereas these XPS results match those from over-oxidized $Eu_{1-\delta}O$ films, the electronic/magnetic properties of $EuO_{1-x}N_x$ are remarkably different. In particular, at variance with the behavior observed for $Eu_{1-\delta}O$ where small amounts of Eu^{3+} lead to a drastic suppression of the ferromagnetism,[23] over-oxidation in $EuO_{1-x}N_x$ still produces a lineshape of the magnetization curve which is Brillouin-like, suggesting an appreciable preservation of the ferromagnetic phase. Important is that the T_c of about 69 K, as in pure EuO, is observed over a wide range of nitrogen substitution. This is demonstrated by magnetization measurements performed *ex situ* with a Quantum Designs MPMS-XL7 SQUID magnetometer in a 10 G field (after capping the samples with a thick aluminum layer to protect them from further oxidation when removed from the MBE system) and here shown in Fig. 4.
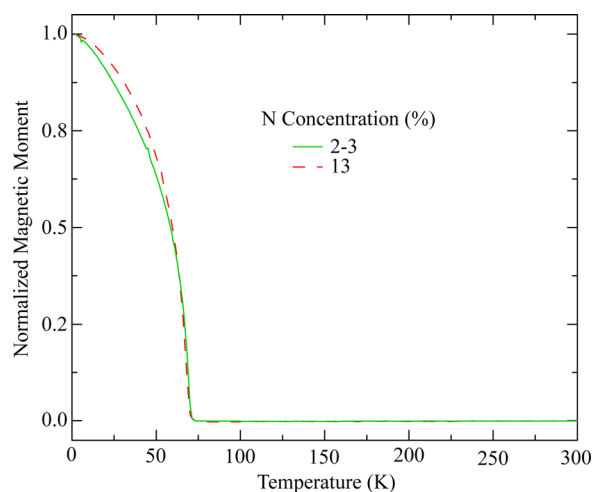

FIG. 4. Magnetization curves for two different $EuO_{1-x}N_x$ samples at 10 G. The transition temperature remains unchanged from the EuO value of 69-70 K, even at high levels of nitrogen substitution.

In conclusion, by substituting nitrogen for oxygen in EuO, we have made a Eu^{2+}/Eu^{3+} system that remains ferromagnetic despite the inclusion of $Eu^{3+}4f^6$ sites, something not possible in the more extensively studied $Eu_{1-\delta}O$. In addition, $EuO_{1-x}N_x$ is also the ideal system for the specific purpose of studying the hopping between the f^7 ($J = 7/2$) and f^6 ($J = 0$) levels located in proximity of the chemical potential. In this respect, $EuO_{1-x}N_x$ is also better than Eu_xGd_{1-x} N—in which such f^6/f^7 mixing is also achieved—since in the latter case, the $4f^7$ levels of Eu and Gd are split in energy by several eVs,[30] preventing an efficient hopping within the f band. More generally, the MBE NO-assisted distillation technique described here provides a means to tune the oxygen-nitrogen substitution in other binary oxides.

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