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Effects of Gd Doping and Oxygen Vacancies on the Properties of EuO Films Prepared via Pulsed Laser Deposition

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We have successfully prepared EuO films on Si(100) wafers via pulsed laser deposition (PLD). It is well recognized that EuO grows with texture growth along (100) but the addition of 4% Gd changes the lattice constant and the texture growth to (111) as well as having a profound influence on the magnetic properties. The differences in the effects between Gd doping and oxygen vacancies, both expected to be n-type (donor state) dopants in EuO, are discussed.

Index Terms—**Doping, EuO, Gd, magnetic semiconductors, oxygen vacancies, pulsed laser deposition.**

I. Introduction

EUROPIUM oxide is a well known ferromagnetic semiconductor, and is a good candidate for spin filter barrier materials [1], [2]. Stoichiometric EuO has a Curie temperature $(\mathrm{T_C})$ of 69 K. There is a strong enhancement of the ferromagnetic $\mathrm{T_C}$ by electron doping via rare-earth atoms [3]–[6] or oxygen vacancies [4], [7], [8]. Furthermore, the conductivity of EuO can be tuned to match that of silicon by doping EuO with oxygen vacancies or with rare-earth elements [3], [9], [10].

Epitaxial or very strongly textured EuO(100) films can be grown on Si (100) wafer with high quality interface [11]. The known complication is that the presence of a high oxygen partial pressure at the initial stages of the EuO film growth leads to formation of Eu^{3+} (indicative of Eu_2O_3) at the Si/EuO interface [3], [10]. Generally, the investigation and understanding of the properties of europium oxide films may have been hindered by the difficulty in preparing controllable and stable films [4]. Methods for preparing EuO films reported so far include reactive thermal evaporation of Eu and molecular beam epitaxy (MBE) under ultra-high vacuum condition in the presence of oxygen gas [3], [10], [12]–[14].

In this work, we have successfully prepared the high quality europium oxide films on Si(100) wafer via pulsed laser deposition (PLD) and investigated the magnetic properties of the resulting films. There are changes in the texture growth and lattice constant seen with just a small number of either oxygen vacancies or the inclusion of a small amount of Gd in the PLD grown EuO films. The combination of oxygen vacancies and Gd doping leads to a dramatic change not only in the $\mathrm{T_c}$ of EuO, but unusual heterostructure device characteristics with Si(100) that are sensitive to an in-plane applied field at room temperature, well above the EuO Curie temperature $(\mathrm{T_c})$.

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II. Sample Preparation

The Si wafers were cleaned with diluted HF acid and acetone, and then immediately placed in the vacuum chamber. Before the deposition, the Si wafers were annealed at 750°C in vacuum of 10^{-5} Torr under pure-H_2 gas in order to further remove the native SiO_2 surface layer from the wafers. The annealing times of 30 and 50 min resulted in stoichiometric and oxygen deficient films, respectively. The EuO and Gd doped EuO films were grown using pulsed laser deposition (PLD) in a vacuum of 10^{-5} Torr with H_2 on these prepared Si(100) wafers at room temperature. The PLD targets were either Eu (99.9%) metal or a mixture of Eu (99.9%) and Gd (99.9%) metals, and the purity of H_2 gas used during the deposition is 99.995%. To prevent the degradation of $\mathrm{EuO_{1-x}}$ films when exposed to air, the film were protected in situ by a Pt capping layer, except those films used for device fabrication.

X-ray diffraction (XRD) data were collected using a Philips X'Pert diffractometer using Cu $K\alpha$ radiation. The magnetic properties were measured with a physical properties measurement system (PPMS) from Quantum Design. The heterojunction devices were constructed using Al/Au contacts, sputtered under a base pressure in the order of 10^{-7} Torr at room temperature. The I–V curves were obtained using a Keithley 236 Source Measure Unit and an Oxford DC low noise voltage supply and the magnetic field was applied in the plane of the film.

III. Structural Properties

The XRD provides an excellent indication that both the EuO and Gd doped EuO films are high quality europium oxide films. Fig. 1 shows the XRD patterns of both $\mathrm{EuO_{1-x}}$ and $\mathrm{Eu_{0.96}Gd_{0.04}O}$ films. No impurity phase was observed in either the EuO or the $\mathrm{Eu_{0.96}Gd_{0.04}O}$ films, where the substrates were annealed at 750°C for a shorter time. For $\mathrm{EuO_{1-x}}$ and $\mathrm{Eu_{0.96}Gd_{0.04}O_{1-x}}$ films, there is evidence of silicide formation

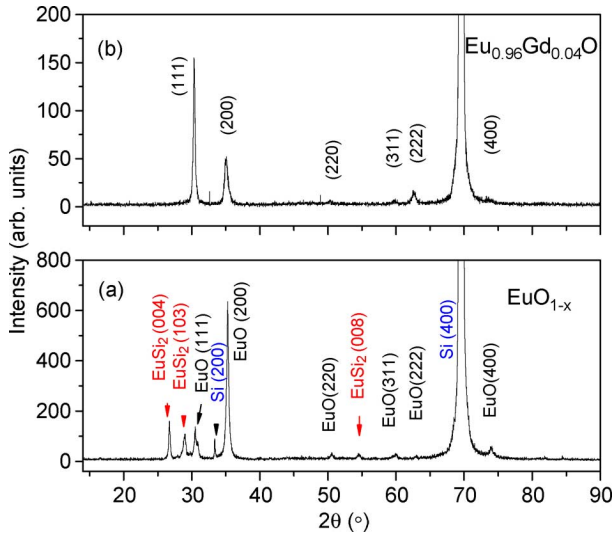

Fig. 1. XRD patterns of EuO_{1-x} and $Eu_{0.96}Gd_{0.04}O$ film. A change in the textured growth from the (100) for EuO_{1-x} to (111) for $Eu_{0.96}Gd_{0.04}O$ is evident.

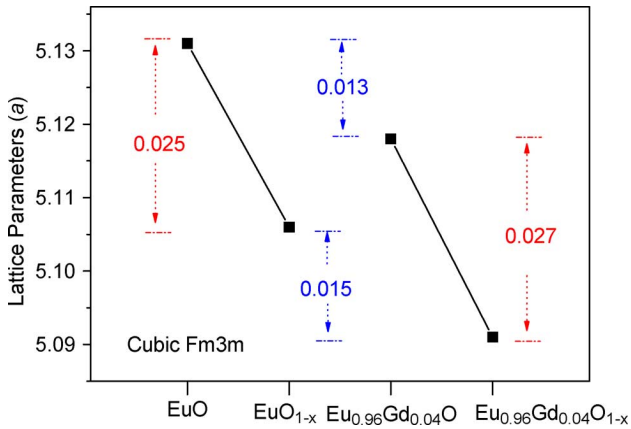

Fig. 2. Lattice parameter a (in Å) of the stoichiometric EuO, reduced EuO_{1-x}, Gd doped unreduced $Eu_{0.96}Gd_{0.04}O$ and $Eu_{0.96}Gd_{0.04}O_{1-x}$, determined from (200) and (111) diffraction peaks.

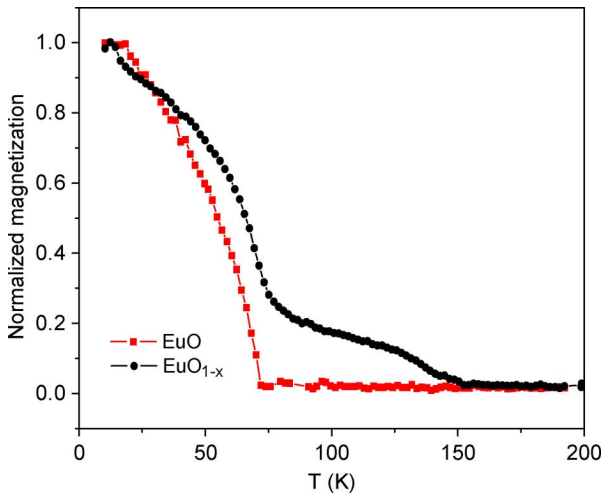

Fig. 3. Magnetization as a function of temperature of EuO films grown by PLD in vacuum and under H_2 flow. The latter shows the characteristic double-dome curve of an oxygen deficient EuO (see text).

as peaks of $EuSi_2$ were observed in some films [see Fig. 1(a)]. The substrates were annealed at 750°C for a longer time for these oxygen deficient films. Eu in the laser-induced plume tends to react with Si to formation $EuSi_2$ in this case because it is less likely to have residual SiO_2 on the surface of the substrates that prevents the reaction of Eu and Si.

As can be seen, for the EuO_{1-x} films, the XRD is dominated by the (200) diffraction line as expected from prior work [3], [11]. For the $Eu_{0.96}Gd_{0.04}O$ films the dominant XRD feature is (111) indicating that the preferential texture growth has altered with just this small amount of Gd doping.

The lattice constants a determined from the (200)/(111) peaks for the Gd-doped, oxygen deficient, and stoichiometric EuO are consistent with the presence of Gd and O vacancies. While $a = 0.5131$ nm for EuO, this lattice constant decreases to 0.5106 nm for EuO_{1-x}. Upon Gd doping, the unreduced sample $Eu_{0.96}Gd_{0.04}O$ has a lattice constant of $a = 0.5118$ nm because of the smaller Gd radius, but this value decreases further to 0.5091 nm for $Eu_{0.96}Gd_{0.04}O_{1-x}$ when the film is oxygen deficient. Evidently 4% Gd doping induces a 0.0013–0.0015 nm reduction in the lattice parameter while oxygen vacancies independently result in a reduction of 0.0025–0.0027 nm. Fig. 2 illustrates the changes in lattice constant a with an increase oxygen vacancies and Gd doping.

While the changes in lattice constant are expected from lattice change, the changes in texture growth are a little unusual, but could be the result of a change in interfacial strain, although small. Although we do not believe these changes are a result of a crystallographic phase change, as with the inclusion of 4% of Gd in the cubic (Fm3m) lattice EuO is expected to remain a soluble random alloy of the same crystal structure [15], such a possibility cannot be ruled out. Our results suggest PLD is an applicable method for growing doped and undoped EuO films and opens a new simple route to prepare this interesting material. This may be very valuable for spintronic device applications as EuO and doped films are good candidates for barrier materials in spin filters and for injectors in spin injection devices.

IV. Magnetic Properties

Fig. 3 shows the magnetization versus temperature M(T) curves of EuO and EuO_{1-x} films measured at 100 Oe, where the magnetization curves are normalized to unity at 10 K. The ferromagnetic transition of the stoichiometric EuO is at about 70 K, but the reduced EuO_{1-x} has a T_C as high as 150 K. Fig. 4 shows the magnetic hysteresis curves for the oxygen deficient EuO at 10 K. Open hysteresis loops were apparent over the whole temperature range though the coercivity of the films decreases with increasing temperature from 70 Oe at 10 K to 20 Oe at 100 K. For stoichiometric grown EuO, the match to the expected transition temperature (69 K [16]) as well as the XRD results suggest that high quality stoichometric EuO film can be prepared using PLD with metal targets. Our results also demonstrate that we have obtained stoichiometric or oxygen deficient europium oxide films by using PLD through alterations in the conditions for pretreatment of the Si wafer and during the deposition.

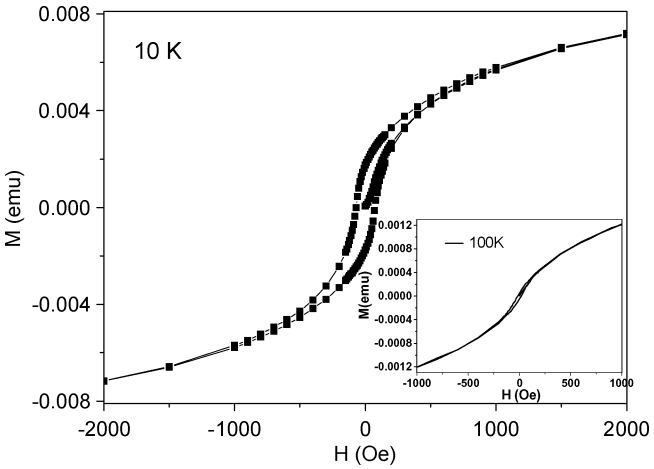

Fig. 4. Magnetic hysteresis curve at 10 K for the oxygen deficient EuO. Insets show the magnetic hysteresis at 100 K.

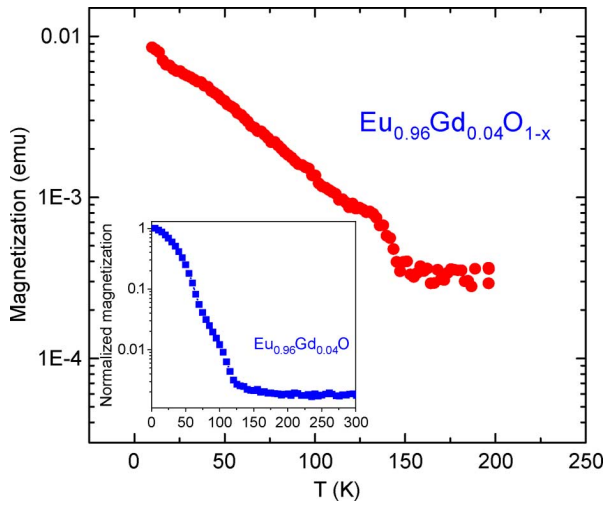

Fig. 5. Magnetization as a function of temperature for $Eu_{0.96}Gd_{0.04}O_{1-x}$, and inset shows the same magnetization plot for $Eu_{0.96}Gd_{0.04}O$. The magnetization is plotted on a logarithmic scale. The T_C of Gd-doped un-reduced $Eu_{0.96}Gd_{0.04}O$ is about 120 K, while that of the reduced sample $Eu_{0.96}Gd_{0.04}O_{1-x}$ is about 145 K.

It is clear from our results (Fig. 3) and those of others [4], [7], [8] that EuO_{1-x} exhibits a very much enhanced Curie temperature of about 150 K with a distinct shape in magnetization versus temperature, i.e., M(T). A drop in magnetization in the vicinity of 70 K, with an more complete quenching of the magnetization at high temperatures is also observed with temperature dependent magnetization M(T) of $Eu_{0.96}Gd_{0.04}O$ films, as seen in Fig. 5, inset.

The "double-dome" feature in M(T) and higher T_C are characteristic of EuO_{1-x} and are not the result of impurities. Other than Eu, no appreciable quantities of other rare earth impurities were present in our EuO_{1-x} films. It appears, nonetheless, that either the doping by O vacancies or the addition of large local moment impurities (Gd) enhances the Curie temperature. It may well be that existence of impurity levels [17], [18] inside the semiconducting gap or an increase in the number of carrier electrons result in the distinct shape of the magnetization M(T).

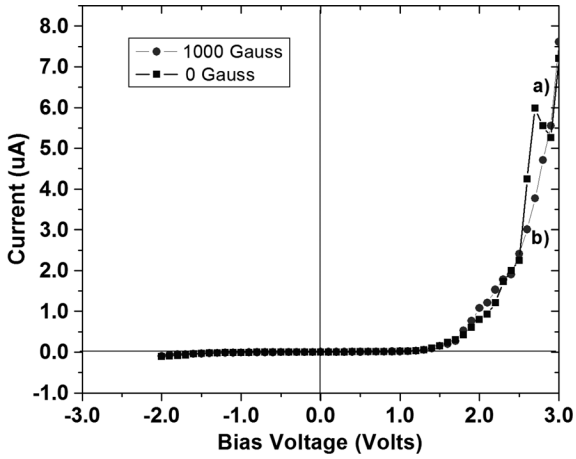

Fig. 6. The magnetization dependent Esaki tunnel diode like behavior for an $Eu_{0.96}Gd_{0.04}O$ on Si(100) heterostructure. The I–V curve (a) for zero applied magnetic field exhibits negative differential resistance at room temperature at less than 3 V forward bias. The negative differential resistance is not evident in an applied magnetic field as shown in (b).

The high magnetization below 69–70 K is likely the result of the large Eu moments, as this is the Curie temperature of stoichiometric EuO. It is expected that the magnetization of EuO arises from the $4f^7$ electron configuration of Eu^{2+}. This appears to dominate the magnetization below 69 to 70 K.

At 69 to 70 K, there is a drop in magnetization. Above 70 K, the magnetization may be dominated by the on site polarization of conduction electrons as the carrier densities may be enhanced by oxygen vacancies or Gd doping. While Matsumoto *et al.* has suggested that the donor levels might be different for Gd doping and oxygen vacancies [4], the overall effect on the temperature dependent magnetization has similarities for both Gd-doped and oxygen deficient films.

Both oxygen deficiencies and the addition of Gd are expected to be n-type donors in EuO, i.e., both add donor states. Both impurities may well act in concert, although differently. While the T_C of Gd-doped unreduced $Eu_{0.96}Gd_{0.04}O$ is 120 K (Fig. 5, and inset, magnetization shown on a logarithmic scale), it increases to 145 K when the Gd-doped sample is oxygen deficient $(Eu_{0.96}Gd_{0.04}O_{1-x})$. There are evident complexities. The combination of Gd doping and oxygen vacancies may degeneratively dope $Eu_{0.96}Gd_{0.04}O$ across the nonmetal to metal transition. Such degenerative doping of the EuO is suggested by the negative differential resistance in the forward bias of $Eu_{0.96}Gd_{0.04}O$, with both Gd doping and oxygen vacancies, reminiscent of an Esaki tunnel diode. Fig. 6 shows the magnetization dependent Esaki tunnel diode like behavior (for zero applied field, at room temperature) for an $Eu_{0.96}Gd_{0.04}O$ on Si(100) heterostructure even with very few oxygen vacancies. The negative differential resistance disappears under the application of a large magnetic field indicating that the electronic structure at the interface due to the local moments may be a key component in the interfacial band alignments either with the contacts or the Si(100). The magnetic field was applied in the plane of the films and the measurements shown here were done at room temperature.

V. Conclusion

We have prepared high quality europium oxide EuO films on Si(100) wafers via PLD. Both stoichiometric and oxygen deficient films of EuO have been fabricated with and without the addition of Gd as a dopant. The resulting films exhibit changes in lattice constant, texture growth, and T_C. In spite of alteration of the film by a combination of both oxygen vacancies and Gd doping, the films remain single phase as determined by XRD. The increase in the T_C may be attributed to the enhanced magnetic coupling by donor states and/or conduction electrons. In spite of the similarities in the enhancement of T_C, we do expect some differences as a result of Gd doping and oxygen vacancies and suggest that the properties of the carriers induced by Gd doping and oxygen vacancies are different. Due to the exchange splitting of either the conductance band edge or the addition of a defect donor state impurity level, EuO_{1-x} is believed to have a high spin polarization [3], [10], [12], [13] but the states introduced by oxygen vacancies may not be identical to those introduced by the inclusion of a large local moment impurity like Gd.

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