Magnetic and structural properties of EuS for magnetic tunnel junction barriers


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In view of potential applications as a spin filter in spintronic devices, we systematically studied the growth by sputtering of ferromagnetic EuS barriers. The relationship between growth and magnetic and transport properties, also in combination with magnetic and nonmagnetic materials, was investigated. We demonstrate that growth at lower substrate temperatures (200 °C), followed by an anneal step at elevated temperatures (430 °C), leads to improved magnetic and transport properties of the barrier layer. We tentatively attribute the observed low-temperature magnetoresistance of high-resistive Al/PbS/EuS/PbS/Gd devices to spin filtering. © 2004 American Institute of Physics.

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The most important obstacle for efficient spin injection from a metal into a semiconductor is the large difference in resistivity, the so-called impedance mismatch. This will mask the spin-dependent resistivity of the metal due to the large resistivity of the semiconductor. To avoid the problem of impedance mismatch, it was suggested that a high-resistive tunnel barrier should be introduced at the metal-semiconductor interface. One possible approach is to replace the ferromagnetic metal and nonmagnetic tunnel barrier with a so-called spin-filter barrier: a semiconductor with different barrier heights for electrons of both spin orientations.

In principle a spin filter can be created using a ferromagnetic semiconductor, since below the Curie temperature the magnitude of the band gap depends on the spin orientation. The spin-filter efficiency of a ferromagnetic semiconductor tunneling barrier depends exponentially on the relative difference in barrier heights for the two spin directions and on the barrier thickness. Therefore the efficiency can be tuned to any desired value, allowing near 100% (pseudo-half-metallic) efficiency of spin filtering. Another advantage of these spin filters is that they probably do not suffer from interface effects, in contrast to the standard tunnel junctions.

A well-studied ferromagnetic semiconductor is EuS (Ref. 4) \((a = 5.97 \text{ Å}, T_C = 16.8 \text{ K}, E_C - E_F = 1.65 \text{ eV})\), which exhibits a spin splitting of the conduction band of up to 0.36 eV below \(T_C\). The splitting of the conduction band was observed in field emission experiments (Fowler-Nordheim tunneling) and was also determined using superconducting electrodes. Recently we used EuS as a spin filter in a magnetoresistance (MR) device by combining it with a single magnetic electrode. A MR ratio of 130% at a temperature of 2 K was obtained, corresponding to a spin-filter efficiency of close to 100%.

For spin injection from EuS into a semiconductor, PbS might be a suitable candidate, due to the close lattice matching \((a_{\text{PbS}} = 5.94 \text{ Å})\). However, growth of these materials is not well established and suffers from problems as interdiffusion and misfit dislocations. Here we report on recent progress in controlling the structural and magnetic properties of EuS spin filters in combination with PbS and (magnetic) metallic electrodes. We will conclude that the best EuS films are obtained by growing at 200 °C and afterwards annealing at a higher temperature (430 °C). Finally, a small magnetoresistance effect is observed based on EuS/PbS/Gd suggesting spin injection from EuS into the PbS semiconductor.

For the characterization of the EuS thin films, both tunnel junctions \((0.5 \times 0.5 \text{ mm}^2)\) and planar samples have been produced using conventional ultrahigh vacuum sputtering techniques with \textit{in situ} shadow masks. Oxidized Si(100) wafers were used as substrates. The EuS layers had thicknesses from 50 Å to 500 Å and the growth rate was kept constant for all samples at 0.26 Å/s while growth temperatures were varied.

X-ray-diffraction measurements have been performed to check the crystalline quality of the EuS layers; see Fig. 1. The strongest EuS peak that is observed is the (200) peak, and was also determined using superconducting

![FIG. 1. X-ray-(Cu Ka) diffraction spectrum of a 500 Å thick EuS layer grown at 400 °C on an oxidized silicon substrate. The substrate was tilted 1° in order to attenuate the silicon peaks. Positions of Si and EuS peaks are indicated, although no EuS(220) peak is present. The inset shows the rocking curve for the EuS(200) reflection, with a silicon reflection on top.](image-url)
while also the higher-order (400) and (600) peaks can be discerned. We do not observe an EuS (220) peak and the relative intensity of the EuS (111) peak is only 3% of the (200) peak, which is 20 times lower than what would be for a completely polycrystalline EuS sample. This suggests a predominantly (100) textured growth. The width of the EuS(200) peak in the spectrum is 0.40°, and corresponds, using the Scherrer formula, to an out-of-plane coherence length of 210 Å, roughly half the film thickness. The rocking curve has a width of about 6.5°, indicating a mosaic structure comparable to the one obtained by Keller et al.10

In order to check the stoichiometry of the EuS layers and to characterize their structure, in situ x-ray photoemission spectroscopy (XPS) was performed on the core level 3d states of the europium ions,11 from which both Eu$^{2+}$ and Eu$^{3+}$ can be detected due to their different charges. From the XPS data on SiO$_x$/PbS/EuS/PbS structures (see Fig. 2), in which PbS has been introduced as a buffer layer, we conclude that the Eu$^{3+}$ content of the EuS layers decreases with increasing growth temperatures. However, based on x-ray diffraction and resistivity measurements, which showed electrical shorts in the EuS barrier layer, we concluded that the EuS layers became very rough when grown at high temperatures. Therefore also layers were grown at 200 °C and afterwards annealed in situ at 430 °C; see Fig. 2. These showed a strong decrease of the Eu$^{3+}$ ion and increase of the Eu$^{2+}$ peak intensities. Since annealing is unlikely to reduce the europium content and to cause a change in stoichiometry this way, the presence of Eu$^{3+}$ ions is probably due to defects, and not to the presence of chemically stable nonmagnetic Eu$_2$S$_3$/Eu$_3$S$_4$. By annealing, the number of defect states is reduced to a level comparable to that of the sample grown at a temperature corresponding to the anneal temperature.

To address the magnetic behavior of EuS, we have measured magnetization loops below $T_C$, shown in Fig. 3. The observed properties are well correlated with the XPS spectra. When a sample is grown at temperatures close to room temperature, the magnetization is much lower than expected, based on the saturation Eu$^{2+}$ moment. Increasing the growth temperature increases the total magnetic moment and remanence, which can also be achieved by annealing at comparable temperatures. However, in contrast to what is observed in the XPS spectra, the magnetic moment is the largest for samples grown directly on the Si/SiO$_x$ substrate, without the addition of an extra PbS layer. This discrepancy can be explained if interdiffusion between the PbS and EuS layers takes place. Interdiffusion does not change the Eu charge state, and therefore does not strongly affect the XPS spectra, but it decreases the remanent magnetic moment of the structure. At 5 K and 30 mT, the 60 Å thick EuS layer grown directly on the Si/SiO$_x$ substrate has a magnetic moment of 5.9$\mu_B$ per europium atom, which is not completely saturated yet. This moment is 84% of the value prediction from the spin quantum number $S=7/2$, and is still increasing towards lower temperatures, as can be observed from the inset of Fig. 3. This behavior is comparable to that of MBE-grown EuS thin films.10,12,13

Devices were prepared with an EuS layer acting as a tunnel barrier between two orthogonal metallic stripe electrodes, one of which was chosen to be ferromagnetic, in order to also study magnetoresistive effects. The actual structure consisted of Al and Gd electrodes and a PbS/EuS/PbS trilayer as the barrier, in which the PbS serves both as a buffer layer to prevent interdiffusion between the EuS and the metals and as a spacer between the ferromagnetic EuS and Gd. Devices with EuS barriers grown at 400 °C showed low resistances ($<100 \Omega$) for barriers below 100 Å, followed by an abrupt jump to resistances above $10^5 \Omega$ for thicker barriers, a sign of a high barrier roughness. In contrast, barriers grown at 200 °C show this resistance jump at lower thicknesses of 60–80 Å, suggesting a lower roughness. More specifically, without annealing the resistance is typically 10–100 kΩ for layers that are 100 Å thick, and
with annealing at 430 °C the resistances rise to the order of 100 MΩ at 5 K. This corresponds to “area resistances” $R \times A$ of the order of $2 \times 10^7$ Ω mm$^2$ for annealed EuS layers of 100 Å. Devices containing only PbS (1000 Å) showed resistances below 100 Ω at 5 K, indicating that the high resistance is due to the EuS barrier layer. As it can be seen in the inset of Fig. 4, the current through the EuS layer is nonlinear with the applied voltage, which is characteristic for tunneling. The resistivity of EuS, exceeding $10^9$ Ω m, was too high for a direct in-plane Hall and resistivity measurement.

Finally, Fig. 4 shows the magnetoresistance of an Al/PbS/EuS/PbS/Gd device with a 120 Å EuS barrier layer grown at 400 °C. When decreasing the magnetic field from positive high fields, the junction resistance rises abruptly at a negative field of a few millitesla suggesting a change in magnetization orientation of the magnetic layers from parallel to antiparallel, and, later, at a negative field of 0.8 T, to parallel directions again. The switching at low fields may be ascribed to the EuS layer, and the one at 0.8 T to the Gd. The switching is better defined than was observed earlier by LeClair et al., although the value of the Gd switching field remains still high and is not yet understood completely. The presence of a clear transition in the resistance related to the magnetization orientation of both layers (similar to a spin valve device) indicates that EuS is acting as a spin-filter layer. We believe that the low value of the magnetoresistance is due to the low value of the PbS resistance compared to the one of the barrier layer, which is currently investigated in more detail. We tentatively ascribe the observed linear background in the magnetoresistance to the modulation of the barrier conductance by the Zeeman effect. Although much smaller than the exchange splitting, the Zeeman energy modifies the absolute height of the tunnel barrier for each spin subband to which the transmission probability of the barrier layer is extremely sensitive.

In conclusion, we observed that growing EuS films at 200 °C and annealing afterwards at 430 °C leads to improved magnetic and transport ($R \times A = 2 \times 10^7$ Ω mm$^2$) properties of the barrier layer. A modest magnetoresistance ratio of 1.5% has been obtained for a PbS/EuS/PbS/Gd sample, suggesting that the tunnel current through EuS is spin polarized and that it persists across the PbS. Future experiments are planned to improve the spin-filter and injection efficiency.

14. The low resistivity of PbS is due to the low gap of 0.4 eV and the location in the conduction band of the electrically active vacancies; see R. Dornhaus, G. Nimtz, and B. Schlicht, Narrow Gap Semiconductors (Springer-Verlag, Berlin, 1983).