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Epitaxial growth of EuS on InAs(100) and InP(100)

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ABSTRACT

We studied the growth of thin europium sulfide films on InAs and InP substrates. The EuS layer thickness varied from 2 to 20 nm. The substrates were chosen due to a close matching with the EuS lattice constant and because of the zinc-blende structure compatible with GaAs technology. Deposited films were characterized by means of low-energy electron diffraction (LEED) and atomic force microscopy (AFM). The measurements provide evidence for epitaxial growth of EuS. A high crystalline order is present in the EuS layer. Islands are formed on both substrates. They are larger on InAs than on InP for the same EuS film thickness. The size of the islands decreases for both substrates from several hundred to around 50 nm beyond thicknesses of 4 and 20 nm on InP and InAs, respectively. AFM measurements corroborate these findings revealing more details about the morphology of the EuS layers. The islands are denser on InP completely covering the underlying substrate. On InAs, the islands are more widely spaced, forming broad terraces. Analysis of the terrace edges revealed a minimum step height in accordance with a monolayer of EuS along the 〈100〉 direction.

1. Introduction

The semiconducting Europium chalcogenides EuX (X═O, S, Se, Te) exhibit very interesting magnetic properties. Ever since the discovery of ferromagnetism in europium oxide [1] (EuO) and europium sulfide [2] (EuS) in 1962, these two materials have been the target of many investigations and calculations. They are ferromagnetic semiconductors and the only known examples of pure Heisenberg ferromagnets with localized spins. For a long time they have been promising candidates for possible spintronic applications and the realization of a spin polarized current within a semiconductor. The setback, however, is their low Curie temperature of only 65 K (EuO) and 16.5 K (EuS). While there was a lot of effort to increase the ordering temperature [3,4] especially in EuS, until recently, the Curie temperature could not be raised above room temperature (RT). A more recent approach includes the use of multilayers of ferromagnetic *3d* transition metals and EuS showing promising results at room temperature with clear evidence of spin polarization of the EuS electrons [5,6].

In their ferromagnetic state, EuO and EuS exhibit a spin-orbit splitting of the 5d conduction band of about 0.60 and 0.36 eV, respectively, making them good candidates for spin filtering applications [7,8].

While EuS and EuO are ferromagnetic with Eu^{2+} in the divalent state, the trivalent state Eu^{3+} found in compounds such as Eu_2S_3 (Eu_2O_3) and Eu_3S_4 (Eu_3O_4) exhibits only paramagnetism. Thus, the formation of these compounds during, or after evaporation is unwanted. Although being the ferromagnetic semiconductor with the lower Curie temperature, EuS is stable in air as opposed to EuO and easier to handle for evaporation. For this reason, EuS was used in this work instead of EuO.

Although EuS is known for over 50 years now, the exact band structure has still not been measured by modern detection methods, such as photoemission spectroscopy. In fact, early theoretical models of the magnetic exchange mechanisms in the Eu chalcogenides relied on absorption and reflectivity measurements [9]. If a high quality EuS film can be grown on a suitable substrate, it would be possible to measure the exact band structure which might provide further insight into the magnetic exchange mechanism at hand. With the use of EuS/Co multilayers it was possible maintain a ferromagnetic Eu signal at RT. The thickness of EuS used in those multilayers was below 10 nm (i.e. 4–6 nm) and the layers were entirely amorphous [5]. Recent polar magneto-optical Kerr rotation measurements on samples having less repetitions have also shown a ferromagnetic Eu signal at RT which suggests that the effect does not entirely depend on the number of layer repetitions [10]. So, an epitaxial layer of EuS topped with Co could show a larger enhancement of EuS T_C.

Epitaxial growth of EuS has been investigated for a long time and a wide range of substrates has been used with varying results. In an early attempt in 1964, Chen and Zeitman claimed to have achieved epitaxial growth of EuS on NaCl, NaBr, MgO and CaF_2 while apparently the use of Cu, Ge, Si or mica as substrates led to the formation of polycrystalline films [11]. A few years later, Reichelt and Viehweg reported on the epitaxial growth of EuS on mica [12] and in the early 80's Zinn et al. reported epitaxial growth of EuS on Si [13,14,15]. Though the results are

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different and appear contradictory or unplausible, especially regarding the rather large misfits for MgO (42%) and Si (10%), the growth temperature is mentioned as an important parameter in all works and is always in the same range. Good growth is achieved between 300 and 400 °C. Zinn uses a growth temperature of 900 °C and claims that lower temperatures would lead to polycrystalline growth on Si. More recent works have focused on the growth of EuS on PbS [16] and BaF_2 [17]. The two substrates, InAs and InP, of our experiments were not used for EuS growth before. They crystallize both in the zinc-blende structure and their lattice constants are 6.058 Å and 5.869 Å respectively. Compared to the lattice constant of bulk EuS of 5.968 Å this gives an absolute misfit of merely 1.5% and 1.7% for InAs and InP, respectively, qualifying both as good candidates for epitaxial growth.

2. Experimental

The substrates and films were prepared in a molecular-beam epitaxy (MBE) system with a base pressure better than 1×10^{-9} mbar. The InAs(100) and InP(100) substrates were sputtered in cycles of 30 min. The substrate surface cleanliness was checked by Auger-electron spectroscopy (AES) afterwards. If needed, the procedure was repeated. Following the sputtering, the substrates were annealed at 300 °C for about 20 min. Crystalline order along with the development of the characteristic 2 × 4 and c(2 × 8) reconstructions were checked in situ by spot-profile-analyzing low-energy electron diffraction (SPA-LEED).

Electron-beam evaporation is a technique best suited for EuS evaporation because of the high sublimation temperature (~2400 °C) of EuS. Powder was chosen as target material because it is easy to handle. The EuS powder was evaporated from a tungsten crucible at rates between 0.3 and 2.0 Å/s. Thickness of the films ranged between 2 and 20 nm. It was monitored by a quartz balance. The substrate temperature was varied between room temperature (~25 °C) and 400 °C. After deposition, the films were annealed again at 300 °C for 20 min and checked by AES and SPA-LEED to ensure the presence of EuS and to check the crystallinity. AFM measurements were performed ex situ in air.

3. Results

3.1. Thickness control

AES was not only used to verify the presence of EuS on the substrate but also to estimate the thickness of the deposited films and thus verify the nominal thickness provided by the quartz balance. It is well known that the intensity of a peak measured with any kind of spectroscopy is related to the amount of material observed [18]. In the case of the deposition of EuS on InAs and InP, the intensity of the indium peak at 404 eV of both substrates can be used to estimate the film thickness. For this we propose two models:

$$I_{In} = I_{In\infty}\left[exp\left(-\frac{d}{\lambda_{In,EuS\ cos(\theta)}}\right)\right]. \quad (1)$$

$$I_{In} = I_{In\infty}\left[(1-x)\ exp\left(-\frac{d}{\lambda_{In,EuS\ cos(\theta)}}\right) + x^{*}\ exp\left(-\frac{d+h}{\lambda_{In,EuS\ cos(\theta)}}\right)\right] \quad (2)$$

Here, $I_{In\infty}$ is the intensity of the pure bulk In, d is the homogeneous thickness of the film, x the percentage of substrate area covered with islands, h the island height, Θ is the emission angle of the electrons with respect to the surface normal and $\lambda_{A,B}$ is the attenuation length of Auger electrons in material B when emitted by material A. For the experiment considered, the electrons are emitted quasi perpendicular to the surface, so that $\cos(\theta) = 1$. $\lambda_{In,EuS}$ was calculated by free software from the NIST [19] using parameters of bulk europium sulfide for the film, giving $\lambda_{In,EuS} = 1.123$ nm.

Model 1 (Eq. (1)) assumes a constant thickness d of EuS on top of the substrates with no islands. Model 2 (Eq. (2)) assumes layer plus island growth (i.e., Stranski-Krastanov-like growth). In this model a homogeneous thickness is assumed to cover the entire substrate area and the fraction area x is covered with islands with constant height h. The overall deposited material as measured by the quartz balance adds a restriction to the values that x, d and h can assume:

$$d_{Quartzbalance} = d + x * h \quad (3)$$

Fig. 1 shows the normalized In intensities measured for EuS films deposited at substrate temperatures of 100 °C on InP with different thicknesses. For model 1 the film thickness was set to the thickness given by the quartz balance. For model 2 the values of d and x were linearly increased with the amount deposited (i.e. $d = 0.43 * d_{Quartzbalance}$ and $x = 0.13 * d_{Quartzbalance}$). With these values the homogeneous thickness for the thickest films (i.e. 4 nm deposited amount) was 1.76 nm and the amount of film covered with additional islands 52%. The height of the islands would amount to 4.4 nm for these values. This was motivated by AFM measurements on a 4 nm EuS film on InP (see section below).

From Fig. 1 one can deduce two things. First, the model assuming only layer growth and a constant thickness does not fit the measured intensities well. This makes a pure layer-by-layer growth improbable. Second, Model 2 fits the measured data better, suggesting a mixed growth mode with islands. This is still a very simple model and it is possible to reproduce the same curve with a variety of values for d and x.

The black strips on the left side are instrumental artifacts.

3.2. Surface ordering

The SPA-LEED patterns obtained were used to determine the crystalline order at the surface. A typical SPA-LEED picture is shown in Fig. 2. The pure InAs and InP substrates showed typical 2 × 4 and c(2 × 8) surface reconstructions before EuS deposition. For small nominal EuS thicknesses this structure was still visible. This indicates that the substrate surface was not fully covered by an entire layer of EuS for small thicknesses, in agreement with the assumptions made in model 2 in the previous section. Increasing the EuS film thickness beyond 2 nm led to the disappearance of the reconstructions, meaning that now the entire substrate was covered with at least one monolayer of EuS.

According to the Scherrer formula [20], the sharpness of diffraction spots is related to the size of the islands formed on the substrate:

$$\Lambda = \frac{K\lambda}{\beta\ \cos(\theta)}, \quad (4)$$

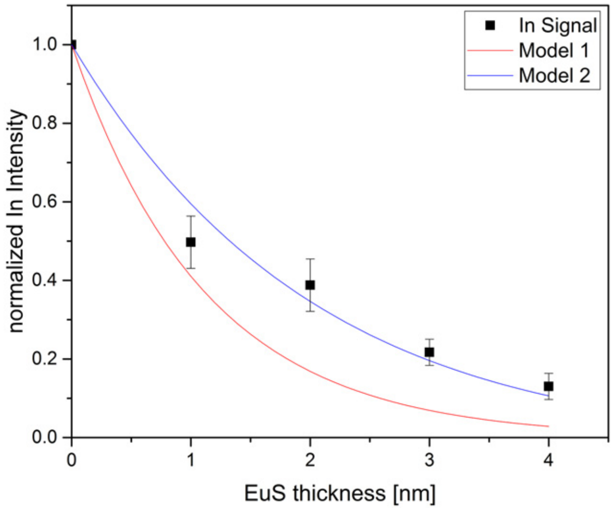

Fig. 1. Normalized In intensity for EuS films on InP substrates deposited at 100 °C. Model 1 assumes a homogeneous film thickness. Model 2 assumes a homogeneous thickness with additional islands with constant height covering part of the area.