EuNiO$_3$ thin films- growth and characterization

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Abstract. We report on the process formation of EuNiO$_3$ thin films on various substrates, studies of optimization conditions for synthesis process and primary investigation. EuNiO$_3$ thin films were deposited by Radio Frequency Magnetron Sputtering in Ar-O atmosphere using a ceramic target with additional nickel pellets. We used Si, NdGaO$_3$ and SrTiO$_3$ substrates. Afterwards samples were annealed in high pressure and temperature in order to achieve a desired oxygen stoichiometry. Thickness of the film was controlled by deposition time and calculated by X-ray Reflectivity. X-ray diffraction measurements revealed that obtained thin films exhibit EuNiO$_3$ phase on the surface still accompanied by Eu$_2$NiO$_4$ and NiO phases in the bulk. Therefore annealing seems to be a very surface sensitive process. That inhomogeneity was confirmed in X-ray photoemission depth profiling studies for EuNiO$_3$/Si (60nm) thin film. Surface contamination with adsorbed oxygen has been observed with grazing angle analysis. Ni2p photoemission line analysis revealed a possible mixed-valence character of Ni electronic state.

1. Introduction

Rare earth nickelates are a family of transition metal oxides that received a great deal of attention as it exhibits a wide range of properties. Presumably the most important is that RNiO$_3$ compounds undergo different types of phase transitions: metal-insulator and antiferromagnetic-paramagnetic. The temperatures of transitions appear to be related to the size of the rare earth cation, subsequently the Ni-O bond length and Ni-O-Ni superexchange angle.

RNiO$_3$ compounds crystallize in a perovskite-type structure ABX$_3$ of GdFeO$_3$ type. The ideal structure is of cubic symmetry with B cations in the cell corner and A cation in the middle. Each B cation is surrounded by six X anions, forming together so-called BX$_6$ octahedron. In the RNiO$_3$ series the positions of A, B and X atoms are occupied by R, Ni and O ions respectively. This ideal structure is however fairly distorted for most of the nickelates due to small size of the R$^{3+}$ cations, which force the NiO$_6$ octahedra to tilt in order to optimize the R-O distances. The distortion can be described by so-called tolerance factor or Goldschmidt factor.

Depending on the temperature and R radius size, three regimes can be distinguished where RNiO$_3$ crystal is either a paramagnetic metal, an antiferromagnetic insulator or a paramagnetic insulator. Apart from LaNiO$_3$ all nickelates exhibit at least one transition. When the size of rare earth’s radius...
(or the tolerance factor) decreases, the temperature of the metal-insulator transition ($T_{MI}$) increases. It is however different when considering the magnetic phase transition. For less distorted perovskites, like NdNiO$_3$ and PrNiO$_3$, the Neel temperature increases for decreasing tolerance (t) factor, similarly to $T_{MI}$. Yet, when considering medium and small-sized rare earths (R= Sm, Eu, Y, Lu) $T_N$ decreases with diminishing t factor. Such diversity is of top interest and few theories arose in order to explain it from which the most known are Zaanen-Sawatzky-Allen framework and charge disproportionation model.

For many years also Eu mixed valence in various compounds has been investigated. However this effect is not fully understood yet. The phenomenon of mixed valence is related to basic properties of solids like electrical conductivity, magnetic properties, superconductivity, and metal-insulator transition. Eu shows mixed valence in several Eu compounds. For some of them (EuF$_3$, EuS, EuO$_3$, EuCl$_3$) which are characterized by trivalent bulk europium state the surface valence transition was found.

EuNiO$_3$ is a rare earth nickelate of monoclinically distorted perovskite structure in room temperature. Bulk compound has a tolerance factor equal 0.892 and has separated phase transitions with $T_{MI}$=463K and $T_N$=205K [4].

In this work we report the deposition of EuNiO$_3$ thin films of various thicknesses and on different substrates and we describe primary investigation of their structure.

2. Experimental details

EuNiO$_3$ thin films were deposited by RF Magnetron Sputtering using Argon-Oxygen atmosphere. In order to optimize densification, the target was synthesized by a technique derived from Peccini sol-gel method. The resulting powder was pressed in an isostatic press and sintered in air at 1300°C for 12 hours. The target was analyzed by X-ray diffraction and revealed a mixture of Eu$_2$NiO$_4$ and NiO.

The composition of the target and the films was controlled using energy dispersive X-ray analysis in a scanning microscope at 20 kV. The cationic ratio Eu/Ni of target was equal to one but the first thin films exhibited lack of Ni. In order to obtain stoichiometric films three additional nickel pellets of 4mm diameter were added onto the target. Thin films were deposited on Si(100), NdGaO$_3$(100), NdGaO$_3$(110) and SrTiO$_3$(100) substrates.

The residual pressure and working pressure of the deposition process were close for each sample and equal ($4.9\pm0.1)\times10^{-6}$ mbar and ($4.7\pm0.1)\times10^{-2}$ mbar respectively. The films were deposited at the temperature of 600°C. The deposition time was varied in order to obtain films with different thicknesses. The process was followed by annealing at high temperature (800°C) and under high oxygen pressure (180mbar) for 48 hours in order to achieve stoichiometric EuNiO$_3$.

X-ray reflectivity was used in order to measure the film thicknesses. We used a Cu Kα radiation of 1.54Å wavelength.

We have also performed X-ray Photoelectron Spectroscopy measurements at room temperature with Al Kα radiation of 1486.7eV photon energy. In order to study the very top part of the film a grazing geometry was applied. Incident beam of X-rays was irradiating the surface and the photoelectrons were collected under the angle of about 20° with respect to the surface of the film and compared with standard measurements performed with 45° angle between surface and the analyzer. We performed depth profile measurements to investigate the electronic and chemical structure of the sample deeper than few top layers of surface. We used Ar$^+$ ions of energy of 2 keV for gradual sputtering an area of 2.5mm×2.5mm in ten-minute cycles. After each cycle of sputtering the spectra of Ni$_2$p, O$_1$s, Eu$_4$d and valence band were collected from area of 800µm diameter. Some standard room temperatures XPS spectra were taken as well.

3. Results and discussion

EDS measurements revealed that the best atomic composition (Eu/Ni=1) is obtained when using three additional nickel pellets, so the deposition process was continued with this amount. In figure 1 a linear dependence of the Eu/Ni ratio is showed as a function of surface of nickel pellets.
Depending on the deposition time samples of various thicknesses were obtained. To measure the thickness of the sample an electron density gradient’s sensitive technique, the X-ray Reflectivity, was used. It allowed not only to extract information about the free surface and the interfaces, but also to determine the mass density and the thickness of thin layers along the direction normal to the specimen surface. Thickness $t$ was calculated using the dependence on the difference between two consecutive minima of periodicity displayed in equation (1).

$$q t = \frac{\lambda}{\Delta \theta} = \frac{2\pi}{\Delta q}$$

where $q = \frac{4\pi \sin \theta}{\lambda}$

A clear single periodicity identified in the studied samples allowed performing a calculation of the film thickness. Additionally a computation of thickness with MATLAB program was made, and results were in good agreement with experimental data. In figure 2 a spectrum of X-ray reflectivity of sample deposited on silicon is given.

![Figure 1. Eu/Ni ratio in the final EuNiO$_3$ films derived from the EDS data as a function of surface of Ni pellets added to the ceramic target. The best composition is achieved for 33 mm$^2$ of Ni which corresponds to three additional pellets.](image)

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We have studied selected samples with few techniques described in experimental section. Basic properties of those samples are displayed in table 1.

Table 1. Properties of selected samples. Thickness of the sample was estimated on the base of deposition time.

| Sample number | Substrate     | Thickness (nm) | Annealing conditions |
|---------------|---------------|----------------|----------------------|
| ES8           | Si(100)       | 60             | Temperature (°C)     |
|               |               |                | 800                  |
|               |               |                | Oxygen pressure (mbar) |
|               |               |                | 168                  |
| ES15          | SrTiO$_3$(100) | 120            |                       |
|               |               |                | 710                  |
|               |               |                | 182                  |
| ES17          | NdGaO$_3$(110)| 210            |                       |
|               |               |                | 720                  |
|               |               |                | 183                  |

X-ray diffraction investigation revealed several important features of the obtained samples. Before annealing, all thin films have shown diffraction peaks that can be indexed as a mixture of Eu$_2$NiO$_4$ and NiO. The samples were poorly crystallized and strongly oriented although the direct relationship between Si(100) substrate and film is not straightforward. This is probably related to relatively low oxygen pressure of 0.2 bar during film growth. It is in agreement with earlier results received for rare earth nickelate perovskites (e.g. in the work Laffez et al. [5]). After annealing we may obtain thin film of the desired composition EuNiO$_3$ or a film with some oxygen deficiency – EuNiO$_{3-\delta}$. Both compounds can be present in various crystalline forms: polycrystalline randomly oriented EuNiO$_{3-\delta}$ thin film, highly textured EuNiO$_{3-\delta}$ thin film or EuNiO$_3$ film with strong preferential orientation. In diffraction patterns we have found that apart from EuNiO$_3$, some NiO and Eu$_2$NiO$_4$ are still present in the film. In some cases, products of reaction with the substrate were visible.

The XPS survey spectra have shown that beside the elements which were the standard components of the films some contaminations with carbon, silicon and for one sample with chromium were found. The atomic composition derived from the survey XPS spectra indicated to a value of the Eu/Ni ratio much lower than 1. This fact arises mainly from the surface contamination with carbon. In order to verify the composition through the film a depth profile analysis has been performed.

The most prominent XPS lines from all elements were acquired using high resolution analysis. All XPS spectra were normalized with respect to the maximum value of count rate.

The Eu spectra are known to be sensitive to the valence state due the large (up to 9 eV) shift between the lines attributed to 2+ and 3+ valence states. In all investigated EuNiO$_3$ films both Eu 3d and 4d lines have shown the dominant 3+ valence state. A very slight contribution from the 2+ state at lower binding energies were found. Both 2+ and 3+ valence states appear to be of the same intensity for both standard and grazing geometries of analysis indicating to the lack of surface valence transition.

Ni 2p XPS lines have shown a complex multiplet structure (figure 3). No change was observed when changing the surface sensitivity of the measurement by changing the geometry of the experiment. This again, as for Eu, may be ascribed to uniform distribution of nickel 2p states.

In figure 4 a comparison between spectra obtained in standard and grazing analysis is given for oxygen 1s and valence band. In O1s spectrum a change of ratio between the standard perovskite line around 529eV and line at 531.5eV originating from surface contaminants is observed. The ratio is smaller for grazing analysis geometry which indicates that the EuNiO$_3$/Si(100) surface has more contaminants than can be found deeper in the film [6,7]. In the valence band not only small changes in intensity of line around 2eV are observed, but also a shift towards higher binding energies for grazing analysis geometry. Generally a very low photoelectron intensity was observed at the Fermi level. It is in accordance with the most likely insulating state of the film at the room temperature.

The relative intensity of the feature at around 2eV decreases for the more surface sensitive geometry. It can be thus attributed to the bulk states of the film.
Figure 3. Ni2p spectra for standard and grazing analysis angle for EuNiO3/Si (60 nm). In the insets the main lines Ni2p\(_{3/2}\) and Ni2p\(_{1/2}\) are given. No change in the spectrum for various geometries indicates uniform distribution of Ni2p states in the sample.

Figure 4. XPS spectra of O1s (left) and valence band (right) of EuNiO3/Si (60 nm). Some changes in the structure are observable dependent mainly on the concentration of surface adsorbed oxygen.

In figure 5 a depth profile of EuNiO3/Si thin film of thickness 60nm is presented. It contains information of atomic concentration of each element in the film. One can notice that proper for the perovskites structure Eu: Ni: O atomic ratio equal 1:1:3 is observed only for the first thirty minutes of sputtering. For deeper parts of the film it is closer rather to 2:1:4. The two regions in the figure are roughly separated by the red dashed line. It may indicate that EuNiO3 is followed by a layer of compound similar to Eu2NiO4 before reaching the substrate. From optical measurements of EuNiO3/Si film one can conclude that the Eu2NiO4 layer thickness is few hundred nm. The SiO2 layer starts to be fully visible after about 400 minutes of sputtering. In the measurement we did not reach the pure silicon substrate however some of the silicon substrate was present at every depth of the sample.
**Figure 5.** Depth profile of EuNiO$_3$/Si (60 nm). 2keV Ar$^+$ ions were used for sputtering.

In the oxygen depth profile first two lines relate to the surface oxygen with noticeable high ratio of contaminants over the perovskite oxygen (figure 6). The perovskite oxygen is present in the film up to 400th minute of measurement where the intensity of 529 eV line diminishes to zero and a state at about 534-544 eV from SiO$_2$ occurs and at this depth can be partly charged.

**Figure 6.** O1s depth profile of EuNiO$_3$/Si (60 nm). Surface of the sample is clearly dominated by adsorbed contaminant oxygen (line at around 532 eV) whereas deeper in the sample perovskite oxygen is the main component.

Nickel 2p depth profile has been displayed in figure 7. This profile confirms the thesis of existence of Eu$_2$NiO$_4$ layer between silica and EuNiO$_3$. The trivalent state at around 855-856eV disappears slowly after fifth cycle (50 minutes of sputtering) leaving only the divalent state around 854 eV. This state can be also partly induced by reduction due to sputtering. Such effect is known for transition
element oxides. A shift of lines visible in the region close to SiO$_2$ layer is probably caused by variation of the neutralization conditions necessary because of charging effect.

![Figure 7](image1.png)

**Figure 7.** Profile of Ni2p of EuNiO$_3$/Si (60 nm). Ni chemical state is at least partly reduced due to sputtering. At region close to the SiO$_2$ surface there is probably some charging shifting the lines. The layer of EuNiO$_3$ can be discontinuous (islands on insulating SiO$_2$) and this is the reason for charging.

In valence band no large changes are visible for various depths of the film (figure 8). The part connected with the film valence band structure includes a peak at around 2eV which corresponds to Eu4f induced 2$^+$ valence state. The structure slightly changes at the film-silica border and a clear shift to the higher binding energies is visible giving rise to a higher energy gap.

![Figure 8](image2.png)

**Figure 8.** Valence band profile of EuNiO$_3$/Si (60 nm). The peak at about 2eV comes from the induced Eu4f states with valence 2$^+$. 
In figure 9 spectra of Ni2p band for EuNiO$_3$ on various substrates are given. The first peak at around 855.4eV can be attributed to the nickel oxidation states Ni$^{2+}$. The second peak at around 856.7eV corresponds to trivalent Ni. Analysis of the Ni multiplets is based on the fitting results and has to take into account other result obtained for the similar systems [8]. All spectra have characteristic satellites at around 860eV and 878eV. The intensity of these satellites in relation to the main peak of the spin – orbit doublet is known to depend on the valence state of Ni. It is very pronounced for NiO [8]. Each sample shows presence of Ni divalent and trivalent states. However in the case of EuNiO$_3$/SrTiO$_3$ the trivalent state is almost negligible.

![Figure 9. Ni2p spectrum in room temperature for thin films on various substrates.](image)

The O1s spectra consist of at least two lines (figure 10). Mizokowa et al. [9] studied polycrystalline sample PrNiO$_3$ by XPS. They obtained a peak in O1s region at around 528.3eV. They found also a characteristic feature at around 531eV which was ascribed to the surface contamination. Our spectrum

![Figure 10. O1s spectrum in room temperature for thin films on various substrates.](image)
shows also line at around 529-530 eV. Such low energy line seems to be characteristic for nickelates with perovskite structure. Second line detected at 531 eV (for EuNiO$_3$ on SrTiO$_3$ and NdGaO$_3$) or at 532.5 eV (for EuNiO$_3$/Si) come from surface contamination. These conclusions were drawn on the basis of Galicka’s thesis [8]. The highest level of contamination is present in EuNiO$_3$/Si and the lowest in EuNiO$_3$/SrTiO$_3$.

4. Conclusions

EuNiO$_3$ thin films were obtained by radio frequency sputtering. During the process a nickel deficiency was found and it was necessary to insert additional nickel pellets to the target so that the atomic ratio Eu/Ni would be close to 1. In order to obtained the right oxygen stoichiometry the films were annealed at approximately 800°C and oxygen pressure of around 170 bar.

After sputtering process and before oxygen annealing, the X-ray diffraction showed three important points. Films were still a mixture of Eu$_2$NiO$_4$ and NiO, they were poorly crystallized (for example for the film on NdGaO$_3$(110) with 210 nm lines related to NiO are very large) and strongly oriented. It is evident since the intensity of the (200) and (101) peaks are strong in comparison with the XRD pattern of the target for example.

After annealing some films were still highly textured. A careful examination of the films after annealing shows the evolution of expected EuNiO$_3$ phase. Film on SrTiO$_3$(100) with 120 nm thickness shows a line around 23° which is displaced towards higher angles after annealing. This is related to a decrease of the unit cell of perovskite subcell, from 99.06 nm to 93.27 nm. This line can be indexed as the (110) of the EuNiO$_3$ structure. We also observed that some of the films show unidentified lines probably due to reaction with substrate during annealing.

XPS measurements revealed that the films can be inhomogeneous in their bulk. Depth profiling of one of the samples confirmed that the film deposited on the Si consists not only of EuNiO$_3$ layer but also of a much thicker Eu$_2$NiO$_4$ layer present just above SiO$_2$. It indicates that annealing is a very surface sensitive process and does not allow to obtain desired composition in whole film.

Analysis of Ni2p photoemission line indicates that spin-orbit doublet of Ni$^{2+}$ and Ni$^{3+}$ consists of mixed-valence states of 2+ and 3+ valence. A careful examination of those spectra through phase transitions will be reported in future works.

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