Co-sputtering of Lu$_2$O$_3$, Eu$_2$O$_3$ and Ga$_2$O$_3$ for optoelectronics applications

Pramod Mandal$^1$, Uday P Singh$^2$ and Sudesna Roy$^1$

$^1$School of Mechanical Engineering, Campus 8, KIIT University, Patia, Bhubaneswar – 751 024
$^2$School of Electronics Engineering, KIIT University, Patia, Bhubaneswar - 751024

E-mail : Sudesna.royfme@kiit.ac.in

Abstract: In this paper oxides of lutetium, gallium and europium were co-sputtered on to soda lime glass substrates to produce mixed rare earth oxides by physical vapour deposition (RF magnetron sputtering). Post deposition, the films were characterized by FESEM, XRD, ED-XRF and UV-Vis spectroscopy. The combinatorial oxides were successfully deposited on soda lime glass substrate with an aggregate thickness of 433 nm with uniform nanocrystalline microstructure and a transparent surface, with no visible cracks and defects. The optical properties show that the optical transmittance in the visible region (300 to 800 nm) is around 83%. The Tauc plot calculates that the band gap to be 3.96 eV indicating its good light absorbing capability. This shows that co-sputtering is an effective method to produce mixed rare earth oxides with wide band gap which can increase the operating temperatures and switching speeds for opto-electronic devices (like LED and radar).

Keywords: PVD RF-co-sputtering method, Lutetium oxide, Europium oxide, Gallium oxide.

1. INTRODUCTION

Co-sputtering typically utilises more than one cathode for sputtering of multi-component thin films, either sequentially or at the same time in the vacuum chamber. This results in formation of mixtures of elements or compounds that in nature is difficult to form. This is particularly useful for developing mixed oxides by partially substituting the atoms of one type of oxide by the other, keeping in mind that that the crystal structure, valency and electronegativity of the parent and substituted atoms are similar. It is an useful tool over chemical methods where stoichiometry can be easily varied by varying the plasma power used for the target materials.

Lutetium, gallium and europium are oxides of rare earth materials (belonging to the actinide series) that have cubic structure and similar valency. Lutetium (III) oxide is a highly sought out rare earth material that has many uses in medical and electronic. This is due to the outstanding scintillation properties, high chemical stability, with high density of 9.5 g/cm$^3$. Moreover, it has a wide band gap of 5.5 eV which makes it highly useful material in designing semiconductors [1-4]. However, due to its very high melting point (2500 ºC) and inability to form crystals, lutetium oxide is commonly used to make single crystals but rather used as thin films. Gallium oxide, on the other hand, is also a rare earth oxide (of the actinide series) that also has a cubic structure and has band gap of 4.8 eV. Recently gallium oxide has attracted much interest, since its increases the band gap over gallium nitride and silicon nitride (~1.1 eV) [5-7]. Therefore it is of interest in this paper that we combine to form mixed oxides of gallium and lutetium oxides using europium as the activator. Europium oxide is red phosphors material used for imaging purposes and has strong bonding capability with other oxide
materials [8-9]. For this co-sputtering via physical vapour deposition, is a versatile tool that can be employed to fabricate thin films of mixed oxides of varying stoichiometry by changing the plasma power. Moreover, the parameters can be manipulated to alter thickness and hence composition [1, 2]. Therefore in this work we have co-sputtered a combination of lutetium oxide (Lu$_2$O$_3$), europium oxide (Eu$_2$O$_3$), and gallium oxide (Ga$_2$O$_3$) on soda lime glass substrate and tested for its performance in optical and electronics application [3].

2. MATERIALS AND METHOD

The sputtering target material used were lutetium oxide (99.9% purity), europium oxide (99.9% purity) and gallium oxide (99.9% purity), purchased from Ultra Nano Tech Pvt. Ltd. Co-sputtering was done in a three cathode RF magnetron sputtering with plasma purchased from .These oxides were deposited at an Argon pressure of 35 sccm and base pressure of 7x10$^{-6}$ mbar. Sputtering was done for 3 hrs. Soda lime glass was used as substrate (75 mm x 20 mm x 1 mm) and kept at a distance of 8 cm from the target material [10-11]. The substrate was cleaned with propanol and DI water prior to the set-up. A schematic of the sputtering system is shown in Figure 1[1, 4, 11].

![Figure 1. Schematic diagram of RF co-sputtering set-up](image)

Characterization of the coating was done through field emission scanning electron microscope (Carl-Zeiss Merlin-II FE-SEM), energy dispersive spectroscopy by Oxford Instruments, x-ray diffraction (Cu-Kα radiation XRD-6100), ED-XRF (Shimadzu 7000) and UV-Vis spectrophotometer (Shimadzu 2450).

3. RESULTS AND DISCUSSION

3.1. Appearance

Figures 2 (a) and (b) show the as deposited soda lime glass substrate before and after deposition. The deposited coating is a transparent layer which is clearly visible when the adhered tape is removed. This was then sent for further characterization.
Figure 2. Photograph of (a) uncoated substrate, and (b) coated substrate

3.2. Thickness
The thickness of the coating was measured by ED-XRF. The aggregate film thickness obtained was 433 nm. The composition of the coating identified by their individual metallic components was 12 at% Lu, 70 at% Eu and 18 at% Ga.

3.3. Microstructure
Figures 3 (a) and (b) show the FESEM micrograph of the coating at low and high magnifications range. The average grain size was identified to be 100 nm by the line intercept method.

Figure 3. FESEM micrographs of the deposited coated (a) low and (b) higher magnifications

Figure 4 shows the EDS line spectrum of the coating. The elemental composition as determined by the EDS was (by weight %) C-17.30, O-58.06, Si-4.29, Ca-0.97, Ga-16.07, Eu-2.25, and Lu-1.07. It is to note that the carbon shown in the spectrum comes entirely from the conducting carbon layer added to improve conduction of the oxide during FESEM and EDX.
3.4 Phase Analysis

Figure 5 shows the intensity vs. 2 theta plot of the sample analysed by x-ray diffraction (Cu K $\alpha$ radiation). It shows a broad peak, indicating that the structure obtained was nano-crystalline which often shows up as an amorphous peak [12]. This is also corroborated by the microstructure of the coating, as shown in Figure 3(b) which shows an average grain size of ~100 nm.

3.5 Optical Property

The optical property of the coating was calculated by a UV-Vis spectrophotometer. Figure 6 shows the transmittance (%) of the coating against the wavelength (nm). The maximum transmittance from the plot is about 83 % in the visible wavelength (300 to 800 nm) where the transmittance for the soda-lime glass substrate along is at least 90% in the visible spectrum. The optical band gap for the coating material is calculated from the Tauc plot.

Figure 7 shows the Tauc plot calculated for the coating using the transmittance data obtained in Figure 6. The calculated energy band gap is 3.96 eV.
3.6. Discussion

The co-sputtered coating, with a thickness of 433 nm, is transparent with a darkish tint visible against the transparent soda lime glass substrate. The microstructure indicates that the coating is indeed nanocrystalline, with average grain size about 100 nm. The surface was smooth with no visible cracks or defects even at high magnifications. Compositional analysis shows that, although the target materials were sputtered at same parameters, the amount of material sputtered was maximum for europium, followed by gallium and least for lutetium. The resultant coating has a Eu$_{1.4}$Ga$_{3.6}$Lu$_{0.24}$O$_3$ non-stoichiometric structure.

The coating is highly translucent with a maximum transmittance of ~83% in the visible spectrum. The optical properties can be further improved by increasing the crystallinity of the microstructure. This can be done by post fabrication heat treatment methods, which allow atomic diffusion and relieve stress by annealing. The band gap, however, calculated using the Tauc plot is found to be 3.96 eV for this material. This is wide band gap (WBG) material that has numerous applications in both optical as well as electronics industry, since it allows devices to operate at higher temperatures and faster switching [1-9]. The band gap is certainly closer to that of gallium oxide and is a good contender for WBG opto-electronic devices.
4. CONCLUSION

Mixed oxides of lutetium, gallium and europium were successfully deposited on soda lime glass substrate using co-sputtering RF magnetron equipped with plasma. The resultant coating, with a thickness of 433 nm, was slightly darkish and translucent with the maximum transmittance in the visible spectrum to be around 83%. The microstructure was nanocrystalline in nature with an average grain size of ~100 nm. However, the xrd plot shows that the material is highly amorphous, probably due to the high energy plasma ions that may have embedded in them. This may also be contributing to the decrease in transmittance of the coating. The optical properties can be further improved by annealing the coating to allow diffusion and remove excess stress associated with the deposition process.

The band gap calculated by the Tauc plot is 3.96 eV, which shows that the material is a wide band gap material. This is beneficial for potential application in LED and radar devices, as it increases its operating temperatures and switching speeds.

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