

# EFFECTS OF ANNEALING TEMPERATURE ON THE CRYSTALLOGRAPHIC, MORPHOLOGICAL AND ELECTRICAL CHARACTERISTICS OF E-BEAM DEPOSITED AI/Eu<sub>2</sub>O<sub>3</sub>/N-Si (MOS) CAPACITORS

# Ozan Yilmaz<sup>1,2</sup>, Ercan Yilmaz<sup>1,2\*</sup>

<sup>1</sup>Physics Department, Bolu Abant Izzet Baysal University, Bolu, Turkey <sup>2</sup>Nuclear Radiation Detectors Application and Research Center (NÜRDAM), Bolu Abant Izzet Baysal University, Bolu, Turkey

**Abstract.** Rare earth oxides (REOs) play an important role in the semiconductor technology. Europium oxide  $(Eu_2O_3)$  is one of REOs and it has been used in many applications such as optoelectronics, telecommunications, microelectronics and optical devices. However, in this study,  $Eu_2O_3$  MOS capacitors have been fabricated by using the Electron Beam Evaporation (E-Beam) technique and the effects of different annealing temperatures on them have been investigated. Before and after annealing, the crystallographic and morphological properties of the  $Eu_2O_3$  films have been analyzed by X-ray Diffraction and Atomic Force Microscopy. The electrical properties of the devices have been investigated using measuring C-V,  $G/\omega$ -V characteristics. This preliminary study shows that Europium oxide can be suitable for application as a thin film.

Keywords: Europium Oxide, MOS structure, Capacitance-Voltage, Conductance-Voltage

### 1. INTRODUCTION

Metal-oxide-semiconductor (MOS) capacitors have a very important role in microelectronic applications [1]. The SiO<sub>2</sub> layer is conventionally used in MOSbased devices [1], [2]. However, for the last few decades, rare earth oxides (REOs), such as Er<sub>2</sub>O<sub>3</sub>,  $Yb_2O_3,\,Gd_2O_3,\,Dy_2O_3,\,and\,Y_2O_3$  [3]–[8], draw attention in the field of microelectronics. The REOs have lots of properties that can be used as a gate dielectric when their performance compares with SiO<sub>2</sub>. Among those properties are wide bandgap (Eg=4-6 eV), high dielectric constant ( $\epsilon$ =7-20), high recrystallization temperature, thermodynamic stability, high-quality interface with Si with low interfacial state density, and lower leakage conduction than SiO<sub>2</sub> at an equivalent oxide thickness. Europium oxide (Eu2O3) is one of REOs and it has features such as high dielectric constant ( $\epsilon$ =14) [9], large energy band gap (Eg=4.4 eV) [10], [11], high chemical durability and thermal stability [12]. In the account of these properties,  $Eu_2O_3$ has some advantages compared to a silicon dioxide (SiO<sub>2</sub>) as a gate dielectric in many applications such as optoelectronics, telecommunications, microelectronics, and optical devices [9].

In this study,  $Eu_2O_3$  MOS capacitors have been fabricated by using the Electron Beam Evaporation (E-Beam) technique and the effects of different annealing temperatures on them have been investigated. The C–V and G/ $\omega$ –V measurements of the generated  $\mathrm{Eu}_2\mathrm{O}_3$  MOS capacitor were measured at 1 MHz.

## 2. EXPERIMENTAL PROCEDURE

Europium oxide thin film was deposited onto a 500 µm thick n-type silicon (n-Si) wafer with a resistivity of 2-4  $\Omega$  cm by the E-Beam deposition technique. Before the deposition of the oxides, the wafer was cleaned by following the standard radio corporation of America's (RCA) cleaning procedures. The 99.99% pure Eu<sub>2</sub>O<sub>3</sub> granules were used as target material during the film deposition. The base chamber pressure and the substrate temperature were adjusted to below 7.4×10-4 Pa and 150°C, respectively, before the Eu<sub>2</sub>O<sub>3</sub> deposition. The thickness of the europium oxide is approximately determined to be 40 nm with the Spectroscopic Ellipsometer (AngstromSun Technology-Sr100). Then, this wafer was cut into five pieces. One of them was kept as deposited and the others were annealed at 300°C, 500°C, 700°C, and 900°C in a N2 environment for 40 min, respectively. The chemical characteristics of the Eu<sub>2</sub>O<sub>3</sub>/n-Si structure were determined by a Perkin Elmer Spectrum Two FTIR-ATR (Fourier Transform InfraRed – Attenuated Total Reflectance) spectrophotometer. The crystallographic of Eu<sub>2</sub>O<sub>3</sub> thin film was analyzed by a Rigaku Multiflex diffractometer employing CuKa radiation while the morphological change of Eu<sub>2</sub>O<sub>3</sub> thin film depending on annealing temperatures was studied by Atomic Force Microscopy.

<sup>\* &</sup>lt;u>yilmaz@ibu.edu.tr</u>

In order to make the front and back contacts of these devices (Fig.1), the aluminum (Al 99.999%) sputter target was used. The process and sputtering pressures were adjusted below 7.0  $\times$  10–4, and 1 Pa, respectively. The capacitance–voltage and conductance–voltage for the fabricated Al/ Eu<sub>2</sub>O<sub>3</sub>/n-Si MOS capacitors were obtained at 1 MHz at room temperature using Impedance Analyzer (MODEL HIOKI 3532-50 LCR meter).



#### 3. RESULTS AND DISCUSSION

# 3.1. FTIR, XRD, and AFM results

The FTIR spectrum of  $Eu_2O_3$  on Si after annealing at as-deposited and different temperatures can be seen as Figure 2. The peaks (at 2335 cm<sup>-1</sup>, 2100 cm<sup>-1</sup>, 1992 cm<sup>-1</sup>, 1240 cm<sup>-1</sup>, and 1110 cm<sup>-1</sup>) of  $Eu_2O_3$  thin films are getting smaller with increasing of annealing temperature, while it is observed that some small peaks emerge between 840 cm<sup>-1</sup> and 700 cm<sup>-1</sup>. These peaks are related to the Eu-O bending modes[13], [14].



Figure 2. FTIR spectra of  $Eu_2O_3$  /Si thin films at different annealing temperatures.



Figure 3. The XRD pattern of the  $\rm Eu_2O_3/Si$  structure as deposited and annealed at 300 °C, 500 °C, 700 °C, 900 °C.

The diffraction patterns of the annealed thin films (Fig. 3) can be indexed to the cubic phase, which is consistent with the values in the standard card (JSPDS no. 34-0392, quality «\*», a value of 10.86 nm) [15], [16]. The grain size (D) of the film was calculated using Debye-Scherrer formula [17].

$$D = \frac{0.9 * \lambda}{\beta \cos \theta} \tag{1}$$

The values of grain size and crystallinity of the films increase with the increasing annealing temperatures, except for 900°C annealed sample[18], [19] (Table 1).

Table 1. Grain size (nm), Crystallinity (%), and RMS	
Roughness (nm) of deposited Eu2O3/Si depend on annealing	5

Annealing Temp.(°C)	Grain size (nm)	Crystallinity (%)	RMS Roughness (nm)
As-deposited	-	-	0.135
300	23.69	15.70	0.156
500	24.28	15.81	0.200
700	26.45	29.39	0.238
900	12.15	18.01	0.664



Figure 4. The AFM pictures of the Eu<sub>2</sub>O<sub>3</sub>/Si structure a) as- deposited and annealed at b) 300 °C, c) 500 °C, d) 700 °C, e) 900 °C.

The effects of annealing temperature on the surface morphology of the  $Eu_2O_3$  thin films were investigated by AFM measurements (Fig. 5). Although there is no obvious effect of the annealing in the obtained measurements, the slight rises in the root-mean-square (RMS) roughness that have been observed by calculating in the AFM analysis program (Table 1) [12], [20].

#### 3.2. Electrical characteristics results

The electrical properties of  $Eu_2O_3$  MOS capacitor were investigated by capacitance-voltage and conductance-voltage measurements at the 1MHz (Fig. 5, a and b). The graphs of the C-V and G/w-V analyses show an increasing trend with the increasing annealing temperature up to the annealed sample at 900 °C. This phenomenon can appear because of the recovery of stoichiometry that results in the reduction of structural defects [21], [22]. On the other hand, the condition of the sample annealed at 900 °C can be owing to the phase transition depending on the annealing temperature [19], [23].





Figure 5. The electrical (a) C-V and (b)  $G/\omega$ -V characteristics of Al/Eu<sub>2</sub>O<sub>3</sub>/Si/Al MOS capacitors at 1MHz.

# 4. CONCLUSION

In this study, Eu<sub>2</sub>O<sub>3</sub> MOS capacitors have been fabricated by using the Electron Beam Evaporation (E-Beam) technique. The effects of different annealing temperatures on them have also been investigated. The crystallinity of Eu<sub>2</sub>O<sub>3</sub> thin films is sensitive to the annealing, while the grain size of films slightly increases with annealing temperature increase. The results of ATR-FTIR measurements show some changes in the structure of Eu<sub>2</sub>O<sub>3</sub> thin film because of the annealing. The process of annealing was caused by a small increase in the RMS values of Eu<sub>2</sub>O<sub>3</sub> thin films found using AFM analysis. The annealing has been shown to be effective on the electrical properties of the Eu<sub>2</sub>O<sub>3</sub> MOS capacitor. The measurement capacitance and the measurement conductance of Eu2O3 MOS capacitors increase with the annealing temperature increase.

The results show that  $Eu_2O_3$  rare earth materials can be good candidates for microelectronic applications, but more detailed research is required on this rare earth oxide.

Acknowledgements: This work is supported by the Presidency of Turkey, Presidency of Strategy and Budget under Contract Number 2016 K 12-2834.

References

- S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, 3rd ed., Hoboken (NJ), USA: J. Wiley and Sons, 2007. DOI: 10.1002/9780470068328.fmatter
- H. Ono, T. Katsumata, "Interfacial reactions between thin rare-earth-metal oxide films and Si substrates," *Appl. Phys. Lett.*, vol. 78, no. 13, pp. 1832 – 1834, 2001.
   DOI: 10.1063/1.1357445
- [3] S. Kaya, E. Yilmaz, "Modifications of structural, chemical, and electrical characteristics of Er2O3/Si interface under Co-60 gamma irradiation," *Nucl. Instrum. Methods Phys. Res. B*, vol. 418, pp. 74 – 79, Mar. 2018.

DOI: 10.1016/j.nimb.2018.01.010

- [4] A. Kahraman, H. Karacali, E. Yilmaz, "Impact and origin of the oxide-interface traps in Al/Yb2O3/n-Si/Al on the electrical characteristics," J. Alloys Compd., vol. 825, article no. 154171, Jun. 2020. DOI: 10.1016/j.jallcom.2020.154171
- [5] A. Kahraman, "Understanding of post deposition annealing and substrate temperature effects on structural and electrical properties of Gd2O3 MOS capacitor," J. Mater. Sci. Mater. Electron., vol. 29, no. 1, pp. 7993 – 8001, May 2018. DOI: 10.1007/s10854-018-8804-y
- [6] A. Kahraman, S. C. Deevi, E. Yilmaz, "Influence of frequency and gamma irradiation on the electrical characteristics of Er2O3, Gd2O3, Yb2O3, and HfO2 MOS-based devices," *J. Mater. Sci.*, vol. 55, no. 81, pp. 7999 – 8040, Jul. 2020. DOI: 10.1007/s10853-020-04531-8
- [7] U. Gurer, O. Yilmaz, H. Karacali, S. Kaya, E. Yilmaz, "Co-60 gamma radiation influences on the electrochemical, physical and electrical characteristics rare-earth dysprosium oxide (Dy2O3)," *Radiat. Phys. Chem.*, vol. 171, article no. 108684, Jun. 2020.
- DOI: 10.1016/j.radphyschem.2020.108684
  [8] S. Abubakar, S. Kaya, H. Karacali, E. Yilmaz, "The gamma irradiation responses of yttrium oxide capacitors and first assessment usage in radiation sensors," *Sens. Actuator A Phys.*, vol. 258, pp. 44 48, May 2017.
  - DOI: 10.1016/j.sna.2017.02.022
- [9] S. Kumar, R. Prakash, V. Singh, "Synthesis, Characterization, and Applications of Europium Oxide: A Review," *Rev. Adv. Sci. Eng.*, vol. 4, no. 4, pp. 247 – 257, Dec. 2016. DOI: 10.1166/rase.2015.1102
- [10] L. Petit, A. Svane, Z. Szotek, W. M. Temmerman, "First-principles study of rare-earth oxides," *Phys. Rev. B*, vol. 72, no. 20, pp. 1 – 9, Nov. 2005. DOI: 10.1103/PhysRevB.72.205118
- M. P. Singh, S. A. Shivashankar, "Structural and optical properties of polycrystalline thin films of rare earth oxides grown on fused quartz by low pressure MOCVD," *J. Cryst. Growth*, vol. 276, no. 1 2, pp. 148 157, Mar. 2005. DOI: 10.1016/j.jcrysgro.2004.11.325
- S. A. Lourenço et al., "Eu3+ photoluminescence enhancement due to thermal energy transfer in Eu2O3-doped SiO2-B2O3-PbO2 glasses system," J. Lumin., vol. 131, no. 5, pp. 850 – 855, May 2011. DOI: 10.1016/j.jlumin.2010.11.028
- [13] J. G. Kang, Y. Jung, B. K. Min, Y. Sohn, "Full characterization of Eu(OH)3 and Eu2O3 nanorods," *Appl. Surf. Sci.*, vol. 314, pp. 158 – 165, Sep. 2014.

DOI: 10.1016/j.apsusc.2014.06.165

[14] M. Majumder, R. B. Choudhary, A. K. Thakur, U. Kumar, "Augmented gravimetric and volumetric capacitive performance of rare earth metal oxide (Eu2O3) incorporated polypyrrole for supercapacitor applications," *J. Electroanal. Chem.*, vol. 804, pp. 42 – 52, Nov. 2017.

DOI: 10.1016/j.jelechem.2017.09.048

- S. Mukherjee, C. H. Chen, C. C. Chou, H. D. Yang, "Anomalous dielectric behavior in nanoparticle Eu2O3: SiO2 glass composite system," *EPL*, vol. 92, no. 5, article no. 57010, Dec. 2010. DOI: 10.1209/0295-5075/92/57010
- Z. Mo, Y. Zhao, R. Guo, P. Liu, T. Xie, "Preparation and characterization of graphene/europium oxide composites," *Mater. Manuf. Process.*, vol. 27, no. 5, pp. 494 – 498, 2012. DOI: 10.1080/10426914.2011.593241
- B. D. Cullity, Elements of X-ray diffraction, 2nd ed., Boston (MA), USA: Addison-Wesley, 1978. Retrieved from: http://library.lol/main/5F3BD811A44EEDFB22943 BC771EF49F8 Retrieved on: Jan. 24, 2019
- [18] A. A. Dakhel, "Poole-Frenkel electrical conduction in europium oxide films deposited on Si(100)," *Cryst. Res. Technol.*, vol. 38, no. 11, pp. 968 – 973, Nov. 2003. DOI: 10.1002/crat.200310122

- M. P. Singh, K. Shalini, S. A. Shivashankar, G. C. Deepak, N. Bhat, "Structural and electrical properties of low pressure metalorganic chemical vapor deposition grown Eu2O3 films on Si(100)," *Appl. Phys. Lett.*, vol. 89, no. 20, article no. 201901, Nov. 2006.
   DOI: 10.1063/1.2388128
- [20] S. Kumar, R. Prakash, R. J. Choudhary, D. M. Phase, "Structural, morphological and electronic properties of pulsed laser grown Eu2O3 thin films," in *Proc.* 2nd Int. Conf. Condensed Matter And Applied Physics (ICC 2017), Bikaner, India, 2018, pp. 3 – 8. DOI: 10.1063/1.5032948
- H. Nakane, A. Noya, S. Kuriki, G. Matsumoto,
   "Dielectric properties of europium oxide films," *Thin Solid Films*, vol. 59, no. 3, pp. 291 293, May 1979. DOI: 10.1016/0040-6090(79)90438-3
- [22] M. K. Jayaraj, C. P. G. Vallabhan, "Dielectric and optical properties of europium oxide films," *Thin Solid Films*, vol. 177, no. 1 – 2, pp. 59 – 67, Oct. 1989.

DOI: 10.1016/0040-6090(89)90556-7

 P. Zhang et al., "Preparation and Magnetic Properties of Polycrystalline Eu2O3 Microwires," J. Electrochem. Soc., vol. 159, no. 4, pp. D204–D207, Jan. 2012.
 DOI: 10.1149/2.047204jes

10