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Investigation of Sprayed Lu_2O_3 Thin Films Using XPS

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Abstract

Spray pyrolysis method was used to deposit Lutetium Oxide (Lu_2O_3) thin films using lutetium (III) chloride as source material and water as oxidizer. Annealing was carried out in argon atmosphere at 450˚C for 60 minutes of the films. To investigate the composition and stoichiometry of sprayed as-deposited and annealed Lu_2O_3 thin films, depth profile studies using X-ray photoelectron spectroscopy (XPS) was done. Nearly stoichiometric was observed for both annealed and as-deposited films in inner and surface layers.

Keywords

Lu_2O_3, Depth Profiling, X-Ray Photoelectron Spectroscopy, Thin Films

1. Introduction

Lutetium oxide (Lu_2O_3), a rare earth metal oxide, is a promising material in microelectronics field due to its wide bandgap about 5.5 eV [1] [2] [3] [4], good thermal stability [5], high k dielectric constant (k = 11 - 13) [6] [7] [8] and highest lattice energy (−13,871 kJ/mol) [9]. Eu^{3+} doped Lu_2O_3 was investigated as a promising scintillator material because of its high density of about 9.4 g·cm^{-3} and high absorption coefficient in X-ray detectors [10] [11]. Amorphous Lu_2O_3 also possesses promising unipolar resistive switching (RS) behavior [12]. Lutetium oxides superior switching characteristics make it a possible material for flexible electronics.

Lu_2O_3 thin films were deposited by different methods like pulsed laser deposition [13], atomic layer deposition [14] [15], electron beam deposition [16] [17] [18], physical and chemical vapor deposition (PVD–CVD) [19] [20] and sol–gel method [21]. These methods need complex experimental procedure, high vacuum and high temperature.

In this work Lu_2O_3 thin films were fabricated by spray pyrolysis method using lutetium (III) chloride as source material of lutetium. Spray pyrolysis is a low-cost non-vacuum technique to fabricate thin films over large areas and easy to implement. The deposited films can be used as scintillators and in laser applications. Due to immense effect on device performance it is necessary to determine stoichiometry of bulk and surface of Lu_2O_3 films. In the present work, X-ray photoelectron spectroscopy (XPS) depth profiling was used to analyze Lu_2O_3 thin films to determine its stoichiometry.

2. Experimental Details

All the glassware in our experiment has been cleaned by first washing and scrubbing with Alconox, followed by a 20 min. sonication in acetone, methanol, and then washed by isopropanol and DI water. Afterwards, the glassware was dried using N_2 gas. An aqueous solution of (Conc.) 0.050 M Lutetium (III) Chloride ($LuCI_3{\cdot}6H_2O$) has been used for precursor solution spray deposition. The precursor solution was added in 100 mL of deionized water. Substrate temperature was controlled by a hot plate with which a thermocouple was attached within ±5˚C of 350˚C.

Spraying was accomplished using Iwata CM-C precision atomizing spray nozzle and compressed air at 40 PSI was used as the carrier gas. After film deposition, to avoid any thermal stress the substrates were cooled down slowly to room temperature. Substrates were annealed at 450˚C for 60 min. in argon atmosphere. A change in morphology was observed of the Lu_2O_3 thin films after the annealing process.

Composition of the Lu_2O_3 thin film was studied using XPS. The XPS spectra were obtained by using monochromatic Al Kα radiation (1486.6 eV) through a Kratos AXIS Ultra DLD XPS system at a base pressure of 5×10^{-10} Torr, equipped with an electronic neutralization gun to eliminate the charge effect on the sample surface. All binding energy values were calibrated by using contaminant carbon (C 1s 284.6 eV) as a reference. The sample was then ion sputtered with Ar^+ at 4000 eV and 15 mA for 10 minute.

XPSPeak software version 4.1 was used to obtain all the spectra. A mixture of Lorentzian-Gaussian type peaks was used to deconvulate the spectra.

3. Results and Discussion

The composition and chemical purity of as-deposited Lu_2O_3 thin films were analyzed by XPS analysis. The typical XPS survey spectrum of as-deposited Lu_2O_3 is showed in **Figure 1(a)**. The peaks arising from Lu 4d, 4f, 4p, 5p, C 1s and O 1s are clearly seen in the spectrum. No foreign impurities are identified in the spectrum. It is impossible to eliminate carbon contamination in almost all the preparations. The Lu 4d intensity is very large compared to the other Lu peak intensity, and that is why we have reported just Lu 4d spectra of Lu compounds. High resolution spectra of Lu 4d and O 1s core level are shown in the

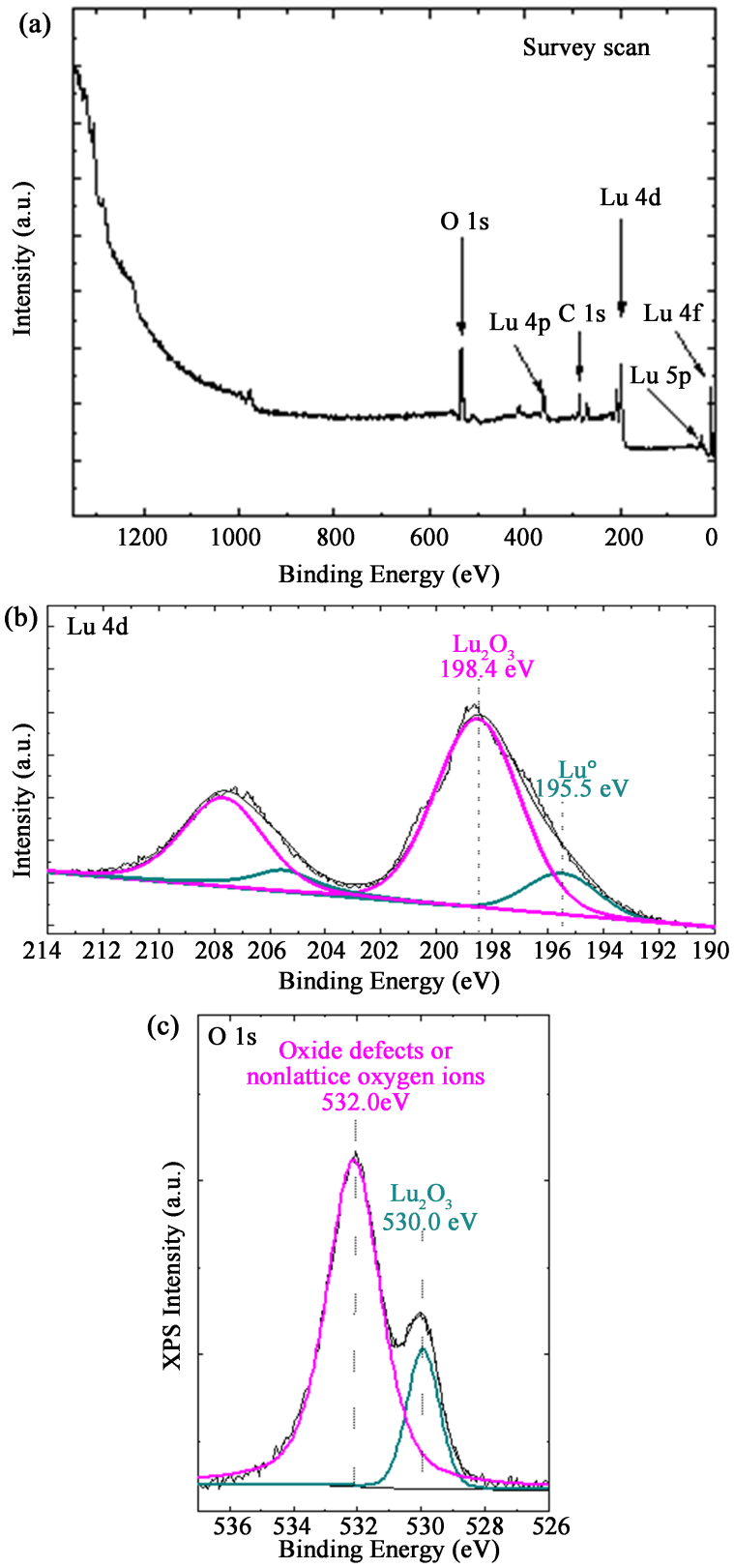

Figure 1. (a) XPS survey spectrum of as-deposited Lu_2O_3 film; (b) High resolution XPS spectra of the Lu 4d core level of as-deposited Lu_2O_3 film; (c) High resolution XPS spectra of the O 1s core level of as-deposited Lu_2O_3 film.

Figure 1(b) and Figure 1(c) respectively. The lower binding energy value 195.5 eV of Lu 4d is characteristic of Lu ions in the oxide thin film. The higher binding energy value 198.4 eV of Lu 4d is for Lu_2O_3 [22]. The presence of Lu ionic peak in Lu 4d core level can be due to the existence of chemical defects, most probably the oxygen vacancies. The lower binding energy value 530 eV of O 1s is for Lu_2O_3. The higher binding energy value 532 eV of O 1s is due to nonlattice oxygen ions or oxide defects [22] [23].

The XPS survey spectrum of as-deposited Lu_2O_3 thin film after 10 min. Ar^+ ion sputtering is showed in Figure 2(a). The peaks arising from Lu 4d, 4f, 4p,5p, C 1s and O 1s are clearly seen in the spectrum. Carbon contaminations were reduced to a low level after 10 min. Ar^+ ion sputtering. High resolution spectra of Lu 4d and O 1s core level are shown in the Figure 2(b) and Figure 2(c) respectively. No chemical shift was observed in Lu 4d for Lu ionic peak and O 1s for Lu_2O_3. A shift of 0.1 eV in O 1s core level for oxide defects and 0.2 eV in Lu 4d for Lu_2O_3 were observed after 10 min. of Ar^+ ion sputtering.

The XPS survey spectrum of annealed Lu_2O_3 thin film is showed in Figure 3(a). The peaks arising from Lu 4d, 4f, 4p, 5p, C 1s and O 1s are clearly seen in the spectrum. High resolution spectra of Lu 4d and O 1s core level are shown in the Figure 3(b) and Figure 3(c) respectively. The lower binding energy value 195.5 eV of Lu 4d is characteristic of Lu ions in the oxide thin film. The higher binding energy value 197.9 eV of Lu 4d is for Lu_2O_3 [22]. The presence of Lu ionic peak in Lu 4d core level can be due to the existence of chemical defects, most probably the oxygen vacancies. The lower binding energy value 529.5 eV of O 1s is for Lu_2O_3.The higher binding energy value 531.7 eV of O 1s is due to nonlattice oxygen ions or oxide defects [22] [23]. No chemical shift was observed in Lu 4d for Lu ionic peak. A shift of 0.3 eV in O 1s core level for oxide defects, 0.5 eV in O 1s core level for Lu_2O_3 and 0.5 eV in Lu 4d for Lu_2O_3 were observed in annealed Lu_2O_3 thin film as compared to as deposited Lu_2O_3 thin film.

The XPS survey spectrum of annealed Lu_2O_3 thin film after 10 min. Ar^+ ion sputtering is showed in Figure 4(a). The peaks arising from Lu 4d, 4f, 4p, 5p, C 1s and O 1s are clearly seen in the spectrum. Carbon contaminations were reduced to a low level after 10 min. Ar^+ ion sputtering. High resolution spectra of Lu 4d and O 1s core level are shown in the Figure 4(b) and Figure 4(c) respectively. No chemical shift was observed in Lu 4d for Lu ionic peak. A shift of 0.6 eV in O 1s core level for oxide defects, 0.5 eV in O 1s core level for Lu_2O_3 and 0.3 eV in Lu 4d for Lu_2O_3 were observed in annealed Lu_2O_3 thin film after 10 min. of Ar^+ ion sputtering as compared to annealed Lu_2O_3 thin film.

4. Conclusion

XPS study in this work presents that composition of surface layers and the inner layers of Lu_2O_3 thin films is almost stoichiometric. The XPS analysis reveals that as-deposited and annealed film contains the elements Lutetium, oxygen, and carbon. After 10 min. Ar^+ ion sputtering the amount of carbon was reduced to a

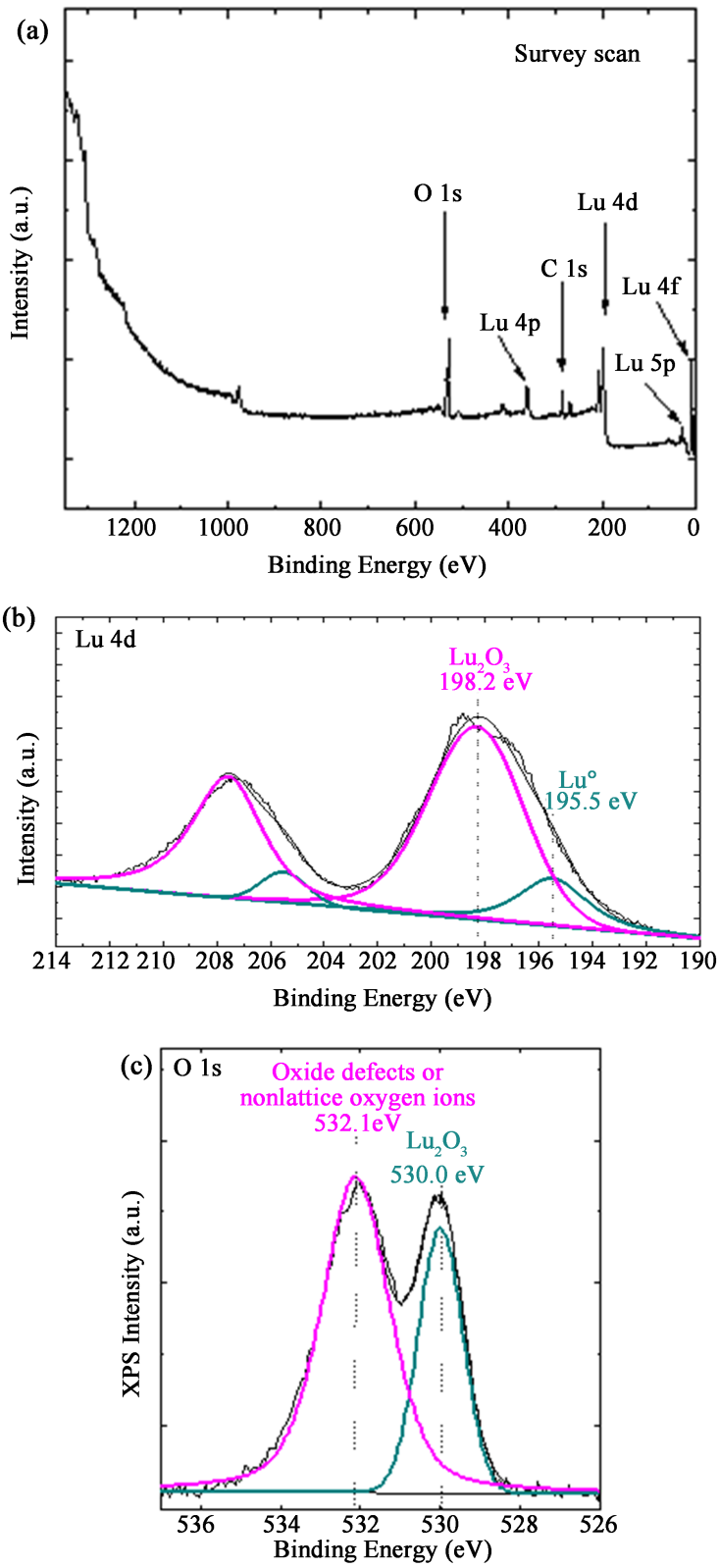

Figure 2. (a) XPS survey spectrum of as-deposited Lu_2O_3 film after 10 min. Ar^+ ion sputtering; (b) High resolution XPS spectra of the Lu 4d core level of as-deposited Lu_2O_3 film after 10 min. Ar^+ ion sputtering; (c) High resolution XPS spectra of the O1s core level of as-deposited Lu_2O_3 film after 10 min. Ar^+ ion sputtering.

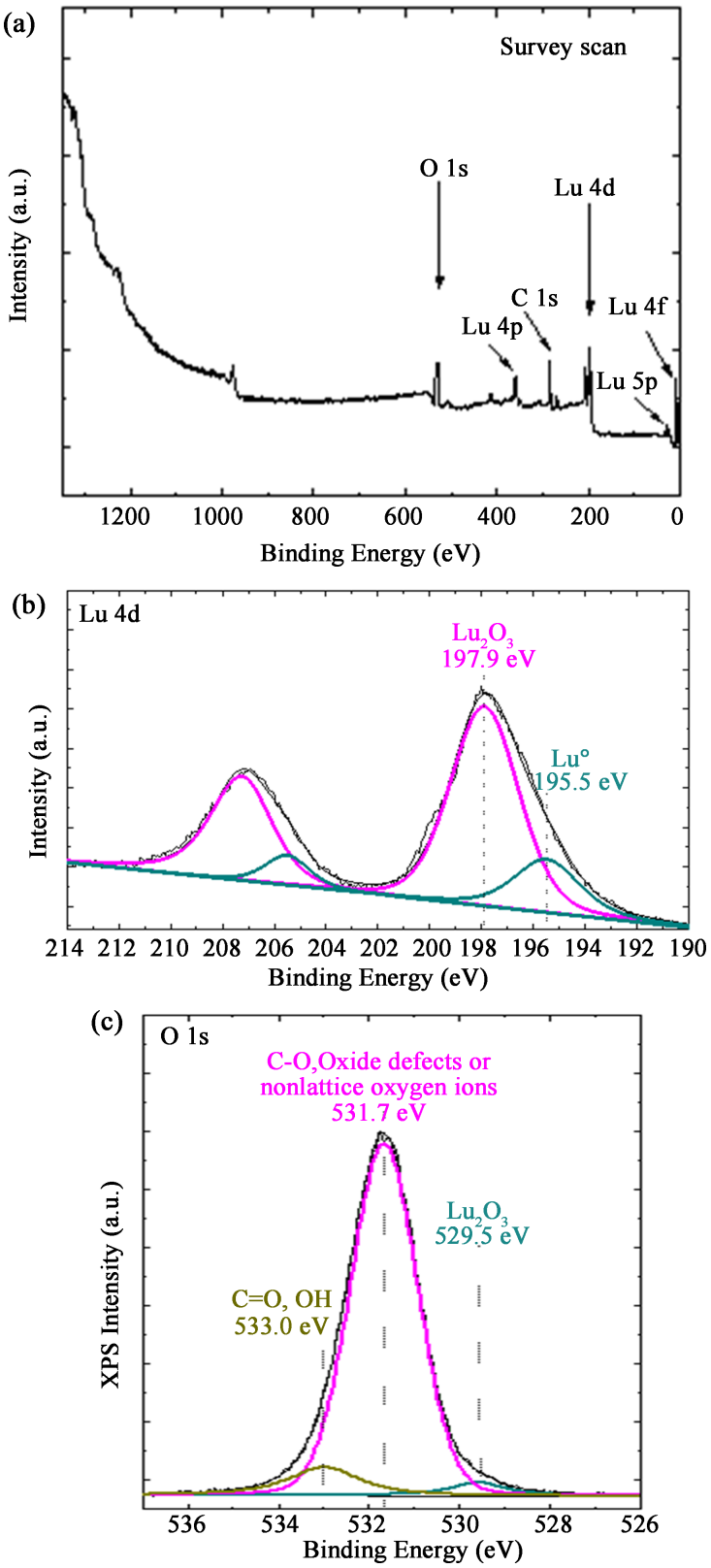

Figure 3. (a) XPS survey spectrum of annealed Lu_2O_3 film; (b) High resolution XPS spectra of the Lu 4d core level of annealed Lu_2O_3 film; (c) High resolution XPS spectra of the O1s core level of annealed Lu_2O_3 film.

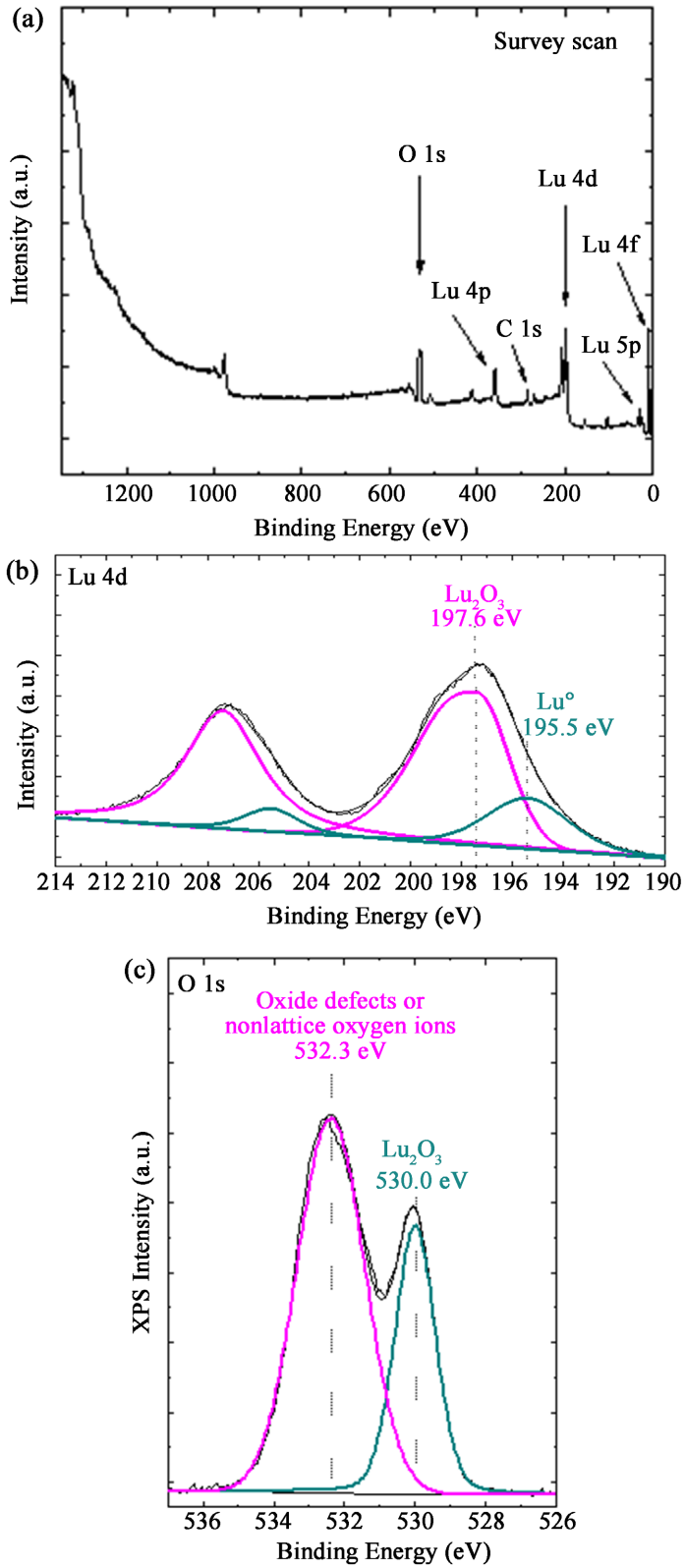

Figure 4. (a) XPS survey spectrum of annealed Lu_2O_3 film after 10 min. Ar^+ ion sputtering; (b) High resolution XPS spectra of the Lu 4d core level of annealed Lu_2O_3 film after 10 min. Ar^+ ion sputtering; (c) High resolution XPS spectra of the O 1s core level of annealed Lu_2O_3 film after 10 min. Ar^+ ion sputtering.

small value. A small chemical shift in Lu 4d for Lu_2O_3 was observed in both as-deposited and annealed Lu_2O_3 thin film after 10 min. of Ar^+ ion sputtering. XPS studies show presence of oxide defects in surface layers and the inner layers of Lu_2O_3 thin films. Hence it is concluded that there is no evidence of the formation of any other Lu-related compounds other than Lu_2O_3 on the surface and in the bulk. So Lu_2O_3 thin films fabricated by low cost spray pyrolysis technique can be applied to fabricate devices that can be used for high temperature environment.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Ordin, S.V. and Shelykh, A.I. (2010) Optical and Dielectric Characteristics of the Rare-Earth Metal Oxide Lu_2O_3. *Semiconductors*, **44**, 558-563. https://doi.org/10.1134/S1063782610050027

[2] Afanas'ev, V.V., Shamuilia, S., Badylevich, M., Stesmans, A., Edge, L.F., Tian, W., Schlom, D.G., Lopez, J.M.J., Roeckerath, M. and Schubert, J. (2007) Electronic Structure of Silicon Interfaces with Amorphous and Epitaxial Insulating Oxides: Sc_2O_3, Lu_2O_3, $LaLuO_3$. *Microelectronic Engineering*, **84**, 2278-2281. https://doi.org/10.1016/j.mee.2007.04.113

[3] Wiktorczyk, T. (2001) Optical Properties of Electron Beam Deposited Lutetium Oxide Thin Films. *Optica Applicata*, **31**, 83-92.

[4] Adachi, G. and Imanaka, N. (1998) The Binary Rare Earth Oxides. *Chemical Reviews*, **98**, 1479-1514. https://doi.org/10.1021/cr940055h

[5] Fanciulli, M. and Scarel, G. (2007) Rare Earth Oxide Thin Films: Growth, Characterization, and Applications. Topics in Applied Physics, Vol. 106, Springer, Berlin, 427. https://doi.org/10.1007/b137342

[6] Bonera, E., Scarel, G., Fanciulli, M., Delugas, P. and Fiorentini, V. (2005) Dielectric Properties of High-κ Oxides: Theory and Experiment for Lu_2O_3. *Physical Review Letters*, **94**, Article ID: 027602. https://doi.org/10.1103/PhysRevLett.94.027602

[7] Scarel, G., Bonera, E., Wiemer, C., Tallarida, G., Spiga, S., Fanciulli, M., Fedushkin, I.L., Schumann, H., Lebiedinskii, Y. and Zenkevich, A. (2004) Atomic-Layer Deposition of Lu_2O_3. *Applied Physics Letters*, **85**, 630-632. https://doi.org/10.1063/1.1773360

[8] Ohmi, S., Takeda, M., Ishiwara, H. and Iwai, H. (2004) Electrical Characteristics for Lu_2O_3 Thin Films Fabricated by E-Beam Deposition Method. *Journal of the Electrochemical Society*, **151**, G279-G283. https://doi.org/10.1149/1.1667523

[9] Iwai, H., Ohmi, S., Akama, S., Ohshima, C., Kikuchi, A., Kashiwagi, I., Taguchi, J., Yamamoto, H., Tonotani, J., Kim, Y., Ueda, I., Kuriyama, A. and Yoshihara, Y.

(2002) Advanced Gate Dielectric Materials for Sub-100 nm CMOS. *Technical Digest-International Electron Devices Meeting*, San Francisco, 8-11 December 2002, 625-628. https://doi.org/10.1109/IEDM.2002.1175917

[10] Zych, E., Karbowiak, M., Domagala, K. and Hubert, S. (2002) Analysis of Eu^{3+} Emission from Different Sites in Lu_2O_3. *Journal of Alloys and Compounds*, **341**, 381-384. https://doi.org/10.1016/S0925-8388(02)00042-7

[11] Zych, E., Hreniak, D. and Strek, W. (2002) Spectroscopy of Eu-Doped Lu_2O_3-Based X-Ray Phosphor. *Journal of Alloys and Compounds*, **341**, 385-390. https://doi.org/10.1016/S0925-8388(02)00043-9

[12] Gao, X., Xia, Y., Xu, B., Kong, J., Guo, H., Li, K., Li, H., Xu, H., Chen, K., Yin, J. and Liu, Z. (2010) Unipolar Resistive Switching Behaviors in Amorphous Lutetium Oxide Films. *Journal of Applied Physics*, **108**, Article ID: 074506. https://doi.org/10.1063/1.3490758

[13] Darmawan, P., Lee, P.S., Setiawan, Y., Ma, J. and Osipowicz, T. (2007) Effect of Low Fluence Laser Annealing on Ultrathin Lu_2O_3 High-K Dielectric. *Applied Physics Letters*, **91**, Article ID: 092903. https://doi.org/10.1063/1.2771065

[14] Zenkevich, A., Lebedinskii, Y., Spiga, S., Wiemer, C., Scarel, G. and Fanciulli, M. (2007) Effects of Thermal Treatments on Chemical Composition and Electrical Properties of Ultra-Thin Lu Oxide Layers on Si. *Microelectronic Engineering*, **84**, 2263-2266. https://doi.org/10.1016/j.mee.2007.04.126

[15] Perego, M., Seguini, G., Scarel, G. and Fanciulli, M. (2006) X-Ray Photoelectron Spectroscopy Study of Energy-Band Alignments of Lu_2O_3 on Ge. *Surface and Interface Analysis*, **38**, 494-497. https://doi.org/10.1002/sia.2268

[16] Malvestuto, M., Pedio, M., Nannarone, S., Pavia, G., Scarel, G., Fanciulli, M. and Boscherini, F. (2007) A Study of the Growth of Lu_2O_3 on Si(001) by Synchrotron Radiation Photoemission and Transmission Electron Microscopy. *Journal of Applied Physics*, **101**, Article ID: 074104. https://doi.org/10.1063/1.2717128

[17] Wiktorczyk, T. (2007) Dielectric Relaxation of Al/Lu_2O_3/Al Thin Film Structures from 10 μHz to 10 MHz. *Journal of Non-Crystalline Solids*, **353**, 4400-4404. https://doi.org/10.1016/j.jnoncrysol.2007.01.096

[18] Wiktorczyk, T. (2005) A Study of Thermally Stimulated Dielectric Relaxation Currents in Al/Lu_2O_3/Al Thin-Film Sandwiches. *Journal of Non-Crystalline Solids*, **351**, 2853-2857. https://doi.org/10.1016/j.jnoncrysol.2005.04.075

[19] Andreeva, A.F. and Gil'man, I.Y. (1978) Some Optical Properties of Films of Rare Earth Metal Oxides. *Journal of Applied Spectroscopy*, **28**, 610-614. https://doi.org/10.1007/BF00619678

[20] Topping, S.G. and Sarin, V.K. (2009) CVD Lu_2O_3:Eu Coatings for Advanced Scintillators. *International Journal of Refractory Metals and Hard Materials*, **27**, 498-501. https://doi.org/10.1016/j.ijrmhm.2008.08.005

[21] Murillo, A.G., Romo, F.C., Luyer, C.L., Ramirez, A.M., Hernández, M.G. and Palmerin, J.M. (2009) Sol-Gel Elaboration and Structural Investigations of Lu_2O_3:Eu^{3+} Planar Waveguides. *Journal of Sol-Gel Science and Technology*, **50**, 359-367. https://doi.org/10.1007/s10971-009-1929-y

[22] Nefedov, V.I., Gatin, D., Dzhurinskij, B.F., Sergushin, N.P. and Salyn, Y.V. (1975) X-Ray Electron Investigations of Some Element Oxides. *Zhurnal Neorganicheskoj Khimii*, **20**, 2307-2314.

[23] Mondal, S., Chen, H.Y., Her, J.L., Ko, F.H. and Pan, T.M. (2012) Effect of Ti Doping Concentration on Resistive Switching Behaviors of Yb_2O_3 Memory Cell. *Applied Physics Letters*, **101**, Article ID: 083506. https://doi.org/10.1063/1.4747695