

## FORMATION OF SAMARIUM DOPED CERIA THIN FILMS\*

G. Laukaitis<sup>a</sup>, J. Dudonis<sup>a</sup>, D. Virbukas<sup>a</sup>, and D. Milčius<sup>a,b</sup>

<sup>a</sup> *Physics Department, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania*  
E-mail: gielauk@ktu.lt

<sup>b</sup> *Center for Hydrogen Energy Technologies, Lithuania Energy Institute, Breslaujos 3, LT-44403 Kaunas, Lithuania*  
E-mail: milcius@mail.lei.lt

Received 22 September 2008; revised 2 February 2009; accepted 19 March 2009

Samarium doped ceria (SDC) thin films were deposited by e-beam evaporation of  $\text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.95}$  nanopowder. The influence of electron gun power and temperature of substrate (optical quartz and Alloy Fe–Ni–Cr) on film crystallite size and texture were studied. The formed SDC thin films were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was determined that electron gun power (in range from 0.12 to 0.78 kW) has influence on crystallite size (increased from 5 to 19.2 nm) which increases as the gun power increases. The crystallite size increases from 12 to 47 nm by increasing substrate temperature from 100 to 600 °C. The texture of formed SDC thin films is not influenced by e-beam gun power and substrate temperature. The thermal treatment shows that deposited SDC thin films are stable and the crystallite size and texture are not changing during the heating and cooling.

**Keywords:** electron beam deposition, samarium doped ceria (SDC), solid oxide fuel cells (SOFCs), thermal treatment

**PACS:** 81.15.Jj, 66.30.Dn, 82.47.Ed, 73.61.-r

### 1. Introduction

The widespread commercialization of the solid oxide fuel cells (SOFCs) will depend greatly on lowering material costs and achieving even greater gains in efficiency [1–3]. SOFCs differ in many respects from the other fuel cell technologies: they are composed of all-solid-state materials. Electrolyte has the biggest influence for the SOFC performance. Different types of electrolyte materials could be used, such as lanthanum gallate ceramic including lanthanum strontium gallium magnesium, bismuth yttrium oxide, barium cerate, strontium cerate, zirconium oxide or cerium oxide stabilized by rare earth oxides, etc. [1–6]. In recent years doped ceria, as a potential substitute for stabilized zirconia electrolyte, has increasingly attracted more interest for its higher conductivity in the field of intermediate temperature solid oxide fuel cells (IT-SOFCs) [7].

$\text{CeO}_2$  is a ceramic material that has a fluorite structure and exhibits very high stability up to its melting point. Doping of this material with divalent or trivalent cations (such as  $\text{CaO}$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,

$\text{La}_2\text{O}_3$ ) creates oxygen vacancies within its crystal structure and increases the concentration of oxygen vacancies compared to the pure cerium oxide material. Oxygen vacancies are essential for oxygen ion conduction through the material. Presence of vacancies also allows oxygen ions to be inserted in the lattice of the material in oxygen rich environment and to be extracted from it in a low oxygen environment [8]. Due to their unique properties in electrochemistry, catalysis, and optics, ceria and doped ceria have wide applications in fields such as catalytic support or promoter for automotive exhaust-gas conversion reaction, glass polishing material, gas sensors, UV absorbents, abrasives of the chemical mechanical polishing slurry in semiconductor fabrication, etc. [9–11]. In those applications, nanostructured  $\text{CeO}_2$  materials attracted much attention due to their considerably small sizes and the general improvements in their physical and chemical properties with respect to their bulklike materials. But the main focus is to use this material as an electrolyte in solid oxide fuel cells [11–14].

Extensive research shows that  $\text{CeO}_2$  doped with Sm or Gd have the highest ionic conductivities of the whole doped cerium oxide family of materials and one of the highest ionic conductivities of all the ion conducting materials. This is especially noticeable in a 600 to

\* Results presented at the international conference *Radiation Interaction with Material and Its Use in Technologies 2008*, 24–27 September 2008, Kaunas, Lithuania

800 °C temperature range where ion conductivity of samarium doped ceria (SDC) can be three times higher than in YSZ at 800 °C, which is most commonly used as an electrolyte in SOFC technology [12–14].

Today it is widely accepted that lowering the operating temperature of SOFCs in the range of 600–700 °C is preferable for several reasons: lowering of the operating temperature of SOFC can provide higher thermodynamic efficiency, higher Nernstian voltages, enhanced durability of cell performance, and the usage of cheaper stainless steel interconnects and compliant temperature gaskets [15]. One of the ways for lowering the cost and increasing the performance of SOFC is to use as much as possible thinner electrolyte layers (that is lowering the working temperature of the SOFC and the costs of the other components of fuel cell). Moreover, the electrolyte should be made not porous on the porous substrates [16]. The shortcut between anode and cathode is the second problem. That has the influence on the electrolyte thickness (by now it is within 2–3  $\mu\text{m}$ ).

Many techniques can be employed for thin film preparation, such as traditional wet chemical processing methods (tape casting, tape calendaring, screen printing, transfer printing) or vapour processing methods (chemical vapour deposition, physical vapour deposition, e-beam deposition, sputtering, plasma spray, etc.). Vapour processing methods, despite being more expensive and complex, provide unique possibilities to

make very thin and dense films, to control their thickness, porosity, crystalline structure, grain boundary surface, refractive index, and other qualities [17].

In the present study, SDC electrolyte thin films were deposited using e-beam deposition technique. The formed SDC thin films were thermally annealed at up to 800 °C temperature in the air atmosphere. That was done to find out about the stability of formed SDC thin films and to understand the influence of annealing temperature and technological parameters on SDC thin film texture, crystallite size, and homogeneity.

## 2. Experiment

SDC thin films (up to 5  $\mu\text{m}$  of thickness) were deposited on optical quartz ( $\text{SiO}_2$ ) and Alloy 600 (Fe–Ni–Cr) by e-beam deposition technique (EB-PVD). Prior to deposition the substrates were cleaned in an ultrasonic bath (in pure acetone) for 15 minutes and their surface was treated in Ar ion plasma for 7 minutes. Deposition experiments (where the influence of e-beam gun power on film formation was tested) were performed at room temperature (20 °C) for 30 minutes as the e-beam gun power was increased from 0.12 to 0.78 kW. A constant e-beam gun power of 0.3 kW was chosen to test the influence of substrate temperature on deposited films. Experiments were performed for 30 minutes and temperature range from 100 to 600 °C was chosen due to the limits of experimental set-up.

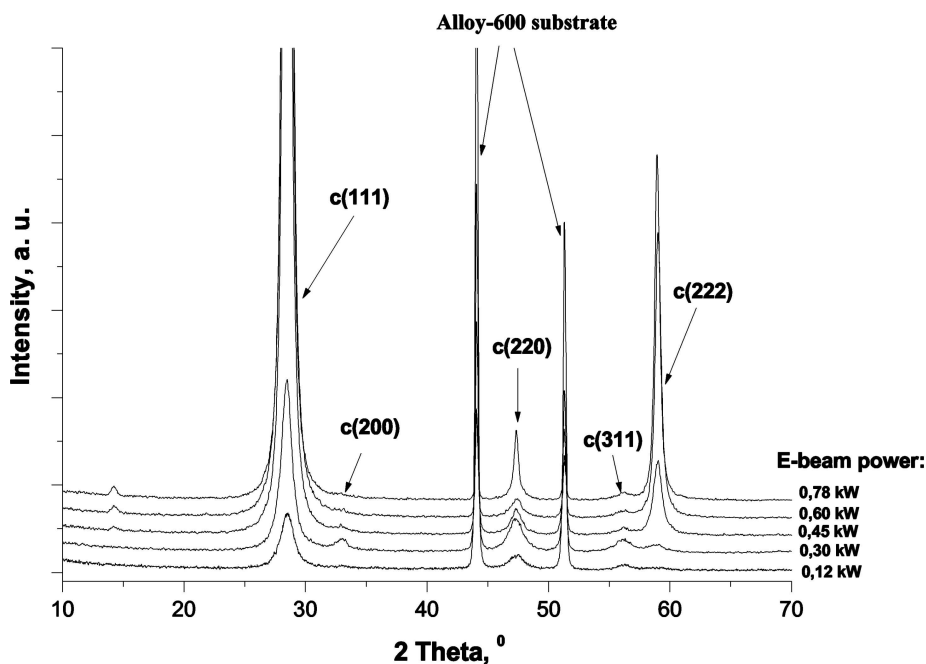


Fig. 1. XRD patterns of SDC thin films deposited on Alloy 600 (Fe–Ni–Cr) substrates at different e-beam gun powers.

Cubic phase samarium doped ceria ceramic nanopowder ( $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$  (99.9% purity based on trace metal analysis, 5–10 nm particles of powder) was used as evaporation material. Before deposition the SDC powder was pressed into pallets. The residual gas pressure in the vacuum chamber during deposition was  $2 \cdot 10^{-3}$  Pa. The distance between the electron gun and the substrate was fixed at 250 mm.

A scanning electron microscope (SEM, JSM5600) was used to investigate the thickness and microstructure of SDC thin films. Film structure was analysed by X-ray diffraction (XRD) (DRON-UM1, BRUKER D8Advance) with standard Bragg–Brentan focusing geometry (with an error of  $0.01^\circ$ ) in a  $10\text{--}70^\circ$  range using  $\text{Cu K}\alpha$  ( $\lambda = 0.154059$  nm) radiation. Crystallite size of thin films was estimated using Scherrer's equation [18].

### 3. Experimental results and discussion

SDC thin films were deposited on optical quartz ( $\text{SiO}_2$ ) and Alloy 600 (Fe–Ni–Cr) substrates. Electron gun power was changed from 0.12 to 0.78 kW to test its influence on film formation and its properties. The XRD diffraction patterns of the formed SDC thin films at different e-beam gun powers shows that the positions of the Bragg peaks are those typical of the cubic ( $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$  SDC (according to Crystallographica Search-Match, Version 2, Fig. 1). XRD peaks of SDC thin films indicate sharp (111) and minor (200), (220), (311), and (222) orientations when cubic phase SDC powder as evaporation material is used. These SDC thin films repeat the crystal structure of the chosen evaporated material at all electron gun powers (Fig. 1). The dominant SDC thin films' orientation remains cubic (111) for both type of substrates. An increase in crystallite size (from 5 to 19.2 nm) is observed when higher e-beam gun power is applied. The crystallographic orientation (111) is dominant at all e-beam gun powers and becomes more preferred as the e-beam gun power rises. SEM images (Figs. 2 and 3) show that SDC thin films are homogeneous and have columnar structure that looks dense.

The substrate temperature during the thin film formation was changed to determine how the initial temperature of a substrate can have an effect on film density. Based on previous experiments, a constant power of 0.3 kW was chosen to produce films of  $\sim 2 \mu\text{m}$  thickness. Initial substrate temperatures were raised from 100 to  $600^\circ\text{C}$  with a  $100^\circ\text{C}$  increment. X-ray diffraction patterns showed highly crystalline structure

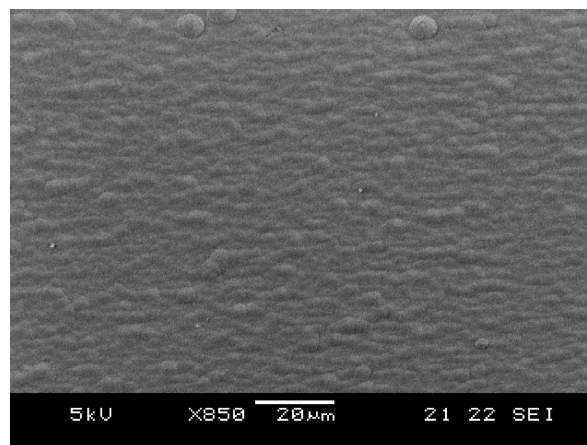


Fig. 2. SEM picture of the surface of SDC thin film deposited on Alloy 600 (Fe–Ni–Cr) substrate at e-beam gun power of 0.6 kW.

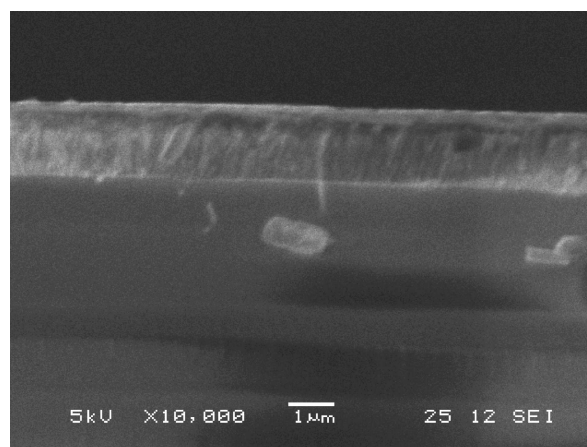


Fig. 3. SEM picture of a cross-section of SDC thin film deposited on optical quartz ( $\text{SiO}_2$ ) substrate at  $500^\circ\text{C}$  substrate temperature (e-beam gun power of 0.3 kW).

with same peaks. Crystallite size calculations show an increase in size although this time crystallites grow larger, up to 47 nm (Fig. 4). This increase is caused by higher mobility and longer surface diffusion times of adsorbed atoms or clusters on the surface of substrate. Decrease of porosity from 34.8 to 7.1% shows that porosity can be controlled by controlling initial substrate temperature [19]. The structure of formed SDC thin films ( $\sim 2 \mu\text{m}$ ) changes from porous structure to the structure which consists of densely packed fibrous or columnar grains as the temperature increases. It is observed that porosity reaches its lowest level at  $500\text{--}600^\circ\text{C}$  substrate temperature.

SDC thin films which had the higher density (substrate temperature  $600^\circ\text{C}$ , e-beam gun power 0.3 kW) were thermally treated in air atmosphere. That was done to find out the influence of annealing temperature to the crystallite size and texture of formed thin films. XRD measurements were done *in situ* during the

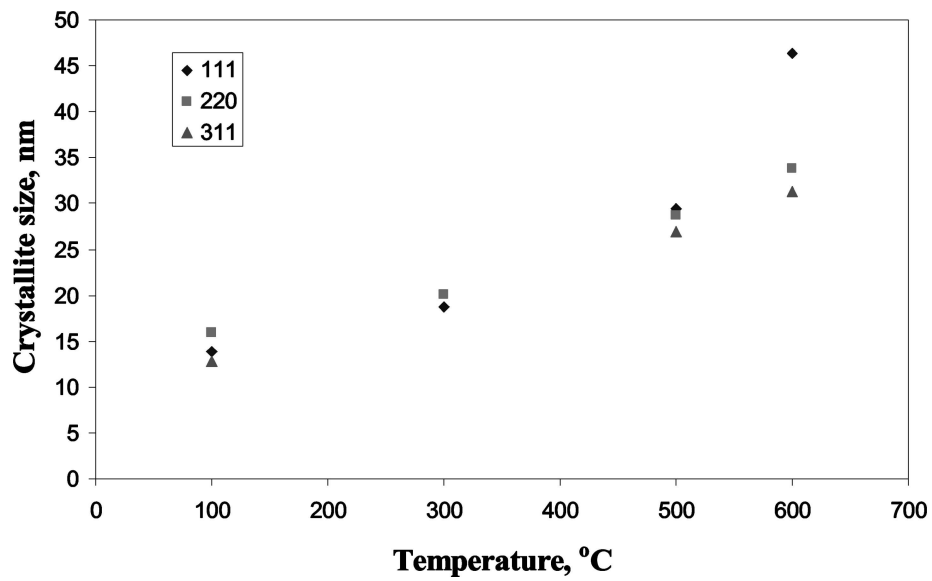


Fig. 4. Crystallite size dependence on substrate temperature of SDC thin films deposited on optical quartz substrate (calculated using Scherrer's equation) at e-beam gun power of 0.3 kW.

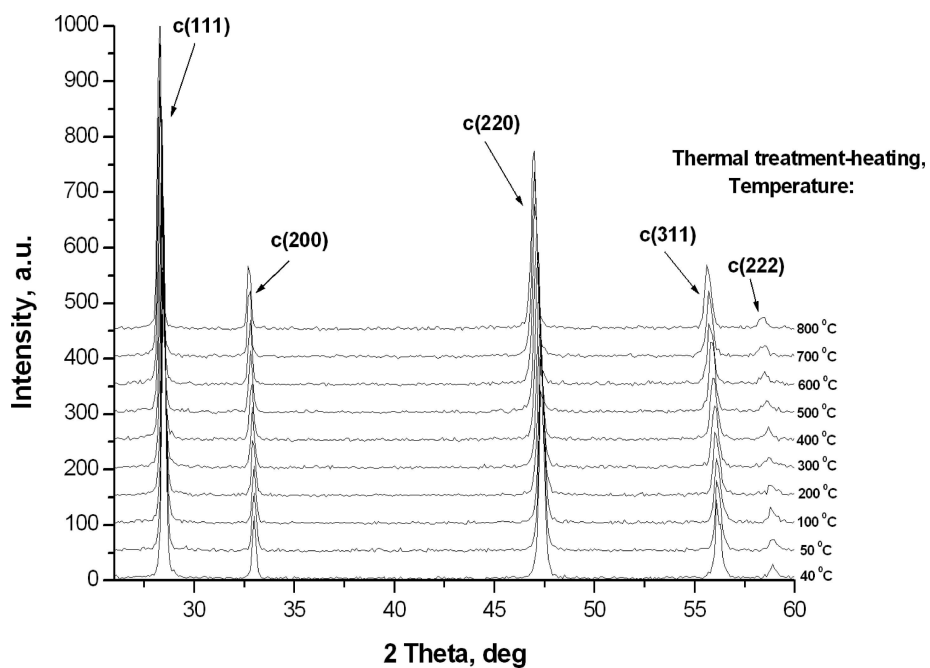


Fig. 5. XRD patterns of thermally treated (heated from room temperature to 800 °C) SDC thin films deposited on optical quartz ( $\text{SiO}_2$ ) substrate at 600 °C substrate temperature (e-beam gun power of 0.3 kW).

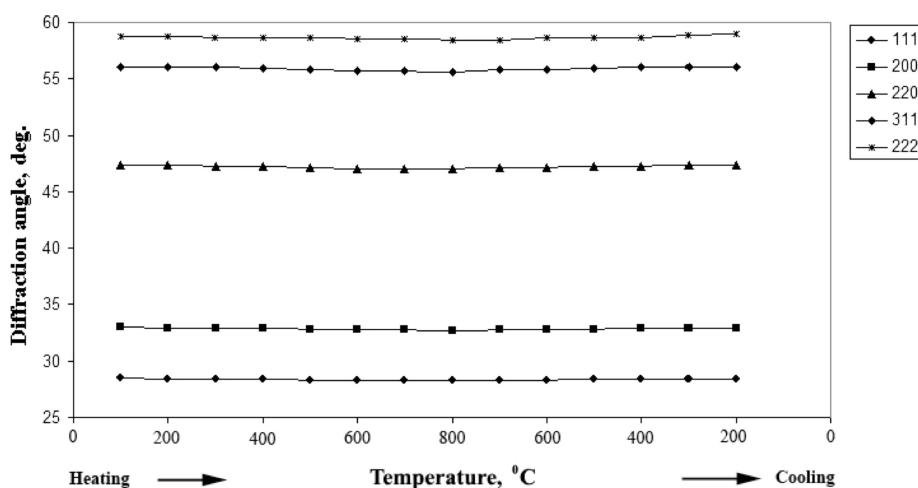


Fig. 6. The positions of XRD diffraction patterns of thermally treated (heated from room temperature to 800 °C and cooled to 200 °C) SDC thin films deposited on optical quartz ( $\text{SiO}_2$ ) substrate at 600 °C substrate temperature (e-beam gun power of 0.3 kW).

heating and cooling of the deposited SDC thin films (Fig. 5). The thermal treatment does not influence the positions of the main diffraction patterns and the crystallite size (Fig. 6) of thin films. They remain constant and correspond to the values before thermal treatment. The texture coefficient does not change either. That shows that the annealing to 800 °C does not change the crystallites' orientation and the SDC thin films formed at 600 °C substrate temperatures are stable.

#### 4. Conclusions

E-beam gun power and substrate temperature has influence on crystallite size and density of samarium doped ceria (SDC) thin films deposited by EB-PVD technique. Crystallite size increased from 5 to 19.2 nm when e-beam gun power was increased from 0.12 to 0.78 kW. Higher initial substrate temperatures influence the density and crystallite size of deposited SDC thin films. Crystallite size grew from 12 to 47 nm, porosity decreased from 34.8 to 7.1% as initial substrate temperature increased from 100 to 600 °C while the constant e-beam gun power (0.3 kW) was kept. The thermal treatment results show that the SDC thin films formed at 600 °C substrate temperature are stable. The crystallites' size and texture do not change and remain constant as the samples are heated from room temperature up to 800 °C and cooled down to 200 °C. That shows that SDC thin films formed by EB-PVD technique could be used in the intermediate temperature SOFC.

#### Acknowledgement

The work was supported by the Lithuanian State Science and Studies Foundation.

#### References

- [1] A. Boudghene Stambouli and E. Traversa, *Renew. Sustain. Ener. Rev.* **6**(5) (2002), 433–455.
- [2] H. Tu and U. Stimming, *J. Power Sourc.*, **127**(1-2) (2004), 284–293.
- [3] F. Tietz, H.-P. Buchkremer, and D. Stöver, *Solid State Ionics* **152–153** (2002), 373–381.
- [4] Masayuki Dokiya, *Solid State Ionics* **152–153** (2002), 383–392.
- [5] Nguyen Q. Minh, *Solid State Ionics* **174**(1–4) (2004), 271–277.
- [6] T.S. Zhang, J. Ma, L.H. Luo, and S.H. Chan, *J. Alloys Compounds* **422**(1–2) (2006), 46–52.
- [7] Bin Lin, Wenping Sun, Kui Xie, Yingchao Dong, Dehua Dong, Xingqin Liu, Jianfeng Gao, and Guangyao Meng, *J. Alloys Compounds* **465**(1–2) (2008), 285–290.
- [8] M.-Y. Cheng, D.-H. Hwang, H.-S. Sheu, and B.-J. Hwang, *J. Power Sourc.* **175**(1) (2008), 137–144.
- [9] K. Muthukumar, P. Kuppusami, R. Srinivasan, K. Ramachandran, E. Mohandas, and S. Selladurai, *Ionics* **13**(1) (2007), 47–50.
- [10] M.J. Godinho, R.F. Gonçalves, L.P.S. Santos, J.A. Varela, E. Longo, and E.R. Leite, *Mater. Lett.* **61**(8–9) (2007), 1904–1907.
- [11] LiNa Gu and GuangYao Meng, *Mater. Res. Bull.* **43**(6) (2008), 1555–1561.
- [12] Min Chen, Bok Hee Kim, Qing Xu, Byeong Kuk Ahn, Woo Jin Kang, and Duan ping Huang, *Ceram. Int.* **35**(4), 1335–1343.

- [13] Z.Q. Yu, Satyanarayana V.N.T. Kuchibhatla, M.H. Engelhard et al., *J. Cryst. Growth* **310** (2008), 2450–2456.
- [14] D. Yang, X. Zhang, S. Nikumb, C. Decès-Petit, R. Hui, R. Maric, and D. Ghosh, *J. Power Sourc.* **164**(1) (2007), 182–188.
- [15] Yeong Yoo, *J. Power Sourc.* **160**(1) (2006), 202–206.
- [16] J. Larminie and A. Dicks, *Fuel Cells Systems Explained* (John Wiley & Sons Ltd., 2003) p. 406.
- [17] L.R. Pederson, P. Singh, and X.-D. Zhou, *Vacuum* **80**(10) (2006), 1066–1083.
- [18] B.B. Patil and S.H. Pawar, *Appl. Surf. Sci.* **253**(11) (2007), 4994–5002.
- [19] M. Jauneika, G. Laukaitis, and J. Dudonis, *Mater. Sci. (Medžiagotyra)* [in press].

## CERIO OKSIDO SU SAMARIO PRIEMAIŠA PLONŲ SLUOKSNIŲ FORMAVIMAS

G. Laukaitis<sup>a</sup>, J. Dudonis<sup>a</sup>, D. Virbukas<sup>a</sup>, D. Milčius<sup>a,b</sup>

<sup>a</sup> *Kauno technologijos universitetas, Kaunas, Lietuva*

<sup>b</sup> *Lietuvos energetikos institutas, Kaunas, Lietuva*

### Santrauka

Dabar ieškoma naujų technologijų bei medžiagų, leidžiančių sumažinti kuro elementų darbo temperatūrą iki 500–600 °C. Viena tokių medžiagų yra cerio oksidas su samario priemaiša (SDC). SDC deguonies jonų laidumas priklauso nuo daugelio veiksnių, t. y. nuo temperatūros, itrio molinės koncentracijos, elektrolito darbo laiko, O<sup>2-</sup> jonų koncentracijos, O<sup>2-</sup> jonų difuzijos koeficiento, elektrolitų storio, kristalitų dydžio bei nuo kristalografinės grūdelių padėties. Šiuos parametrus galima kontroliuoti, naudojant vakuuminis fizikinius dangų formavimo metodus.

Cerio oksido su samario priemaiša ploni sluoksniai buvo formuojami elektroniniu garinimu iš Sm<sub>0,15</sub>Ce<sub>0,85</sub>O<sub>1,95</sub> nano milteilių. Nagrinėta elektronų pluošto galios ir padėklo (optinio kvarco

ir Alloy 600 – Fe–Ni–Cr lydinio) temperatūros įtaka suformuotų plonų SDC sluoksnių mikrostruktūrai, tekstūrai bei kristalitų dydžiui. Suformuoti SDC sluoksniai tirti skenuojančiu elektroniniu mikroskopu (SEM) bei rentgeno spindulių difraktometru (XRD). Nustatyta, kad elektronų pluošto galia (keičiant ją nuo 0,12 iki 0,78 kW) veikia kristalitų dydį – kristalantai didėja nuo 5 iki 19,2 nm, didinant elektronų pluošto galia. Didinant padėklo temperatūrą nuo 100 iki 600 °C, kristalantai padidėja nuo 12 iki 47 nm. Suformuotų SDC sluoksnių tekstūra nėra veikiamą padėklo temperatūros ar elektronų pluošto galios. Atkaitinimas parodė, kad užgarinti SDC sluoksniai yra stabilūs ir kristalitų dydis nei tekstūra nekinta, kaitinant ir aušinant suformuotus sluoksnius.