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Study of Samarium Doped Cerium Oxide Thin Films Formed by E-beam Technique

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Samarium doped cerium oxide (SDC) thin films were deposited onto optical quartz (SiO_2) and Alloy 600 (Fe-Ni-Cr) substrates by e-beam evaporation of $Sm_{0.15}Ce_{0.85}O_{1.95}$ nanopowder. The influence of electron gun power and temperature of substrate on film thickness, porosity, refractive index and crystallite size was studied. Properties of the deposited films were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmittance spectroscopy in a visible light wavelength region. Thickness, porosity, and refractive index of films on optical quartz were calculated from the transmittance spectra data by using Swanepoel method. It was determined that electron gun power (in range from 0.12 kW to 0.78 kW) has influence on film thickness (increased from 0.7 μm to 4.8 μm) and crystallite size (increased from 5 nm to 19.2 nm) which increase as the gun power increases. Decrease of porosity (from 34.8 % to 7.1 %) and increase of refractive index (from 1.63 to 1.9), indicating the increase of film density, were observed while increasing the temperature of substrate (from 100 °C to 600 °C) during evaporation.

Keywords: electron beam deposition, samarium doped ceria oxide (SDC), solid oxide fuel cells (SOFC), refractive index, film porosity, film density.

1. INTRODUCTION

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 creates oxygen vacancies within its crystal structure. 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 ant to be extracted from it in a low oxygen environment [1, 2]. A lot of new type of technologies such as catalysts, chemical sensors and gas purification membranes make use of these properties [3 – 6]. The main focus is to use this material as an electrolyte in solid oxide fuel cells (SOFC) [7 – 12].

Extensive research shows that CeO_2 doped with Sm or Gd have the highest ionic conductivities from all of the doped cerium oxide family of materials and one of the highest ionic conductivities from all of the ion conducting materials. This is especially noticeable in a 600 °C to 800 °C temperature range where ion conductivity of samarium doped ceria oxide (SDC) can be three times higher then YSZ at 800 °C which is most commonly used as an electrolyte in SOFC technology [7 – 10].

Electrolyte is one of the smallest but also one of the most important components of SOFC. Many parameters such as thickness, density, grain size, grain boundary surface area, impurities and others can influence ion conduction through the electrolyte and the overall performance of a fuel cell as well. Thus the choice of the material for electrolyte is as much important as the quality of the electrolyte itself. Thinner, fully dense and optimum grain size electrolytes are needed to reduce the resistance to ionic transport [13 – 16]. Therefore the goal of this work was to deposit SDC thin films on optical quartz (SiO_2) and Alloy 600 (Fe-Ni-Cr) substrates by e-beam deposition technique and to determine how the e-beam gun power and temperature of the substrate influence the parameters mentioned above.

2. EXPERIMENTAL

SDC thin films (up to 5 μm of thickness) were deposited on optical quartz (SiO_2) and Alloy 600 (Fe-Ni-Cr) by e-beam deposition technique (EB-PVD). Prior to deposition substrates were cleaned in an ultrasonic bath (in pure acetone) for 15 minutes and their surface was treated in plasma for 7 minutes (Ar gas). 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 kW 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. The experiments were performed for 30 minutes and temperature range from 100 °C to 600 °C was chosen due to the limits of experimental setup. Cubic phase samarium doped ceria ceramic nanopowder $(Ce_{0.85}Sm_{0.15})O_{1.925}$ (99.9 % purity based on trace metal analysis, 5 nm – 10 nm particles of powder) was used as evaporation material. Before deposition SDC powder was pressed into pallets. The residual gas pressure in the vacuum chamber during deposition was 2×10^{-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 thickness was calculated from transmittance spectra using Swanepoel method [17]. Transmittance spectra data was used to calculate refractive index and porosity of SDC thin films deposited on optical quartz, also. Transmittance measurements were performed with Spectruma 300 spectrometer in 370 nm – 750 nm wavelength range. Film structure was analyzed by X-ray

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diffraction (XRD) (DRON-UM1) with standard Bragg-Brentan focusing geometry (with an error of 0.01°) in a $10° - 70°$ range using Cu K_α ($\lambda = 0.154059$ nm) radiation. Crystallite size of thin films was estimated using Scherrer's equation:

$$D = 0.9 \frac{\lambda}{B \cos \theta}, \quad (1)$$

where D, λ, θ and B are: the crystallite size, X-ray wavelength of 0.154059 nm, Bragg diffraction angle, and full width at half maximum of the diffraction peak, respectively [18]. Some estimations of the crystallite size were done using XFIT program with a Voigt function modeling, also. The calculations showed that the strain in the formed SDC thin films is small and could be neglected.

3. RESULTS AND DISCUSSIONS

X-ray diffraction patterns of the films (~2 μm thick) deposited on optical quartz substrate are presented in Fig. 1. Similar patterns are also observed when films are deposited on Alloy 600 substrate. Comparison of those patterns with the pattern of a powdered SDC material reveals the same crystalline phase, which is cubic (according to Crystallographica Search-Match, Version 2).

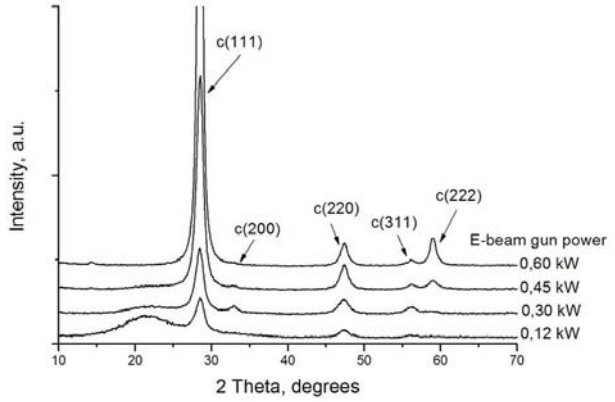

Fig. 1. XRD patterns of SDC thin films deposited on optical quartz (SiO_2) substrate at different e-beam gun powers

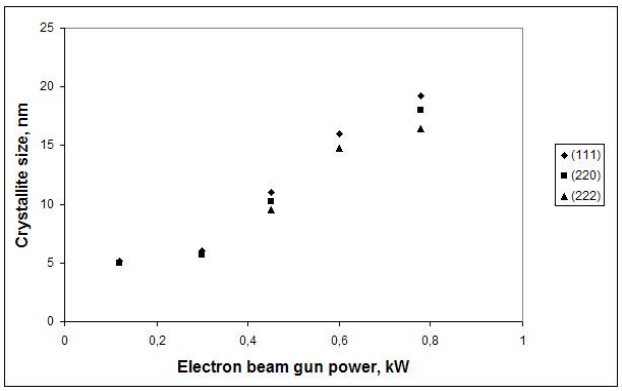

Fig. 2. Crystallite size dependence on e-beam gun power of SDC thin films deposited on Alloy 600 (Fe-Ni-Cr) substrate (calculated using Scherrer's equation)

Also all the patterns show five peaks, which correspond to five crystallographic planes (111), (200), (220), (311) and (222) with the peak (111) having the highest intensity. It is clearly visible that the intensity and spread of individual peaks vary and it depends on e-beam gun power (Fig. 1). X-ray diffraction data was used to calculate crystallite size and texture coefficient. Crystallite size as a function of e-beam gun power is shown in Fig. 2. An increase in crystallite size (from 5 nm to 19.2 nm) is observed when higher e-beam gun power is applied.

As the e-beam gun power rises so does the temperature in the crucible which gives more energy to evaporating particles. Such particles have higher mobility and longer surface diffusion length on the surface of substrate. This enables them to form fewer but larger clusters and islands of a newly growing film, which later become the base of crystallites that the film consists of. The higher temperature can also cause evaporation of large clusters rather then individual particles. These clusters form larger islands of SDC material on substrate and cause growth of larger crystallites. Difference in the crystallite size of different crystallographic orientations is relatively small, but difference in texture coefficient is very noticeable. Texture coefficient used in this work is the ratio between intensity of one peak (for example (111)) with the sum intensity of all peaks. Calculations show that crystallographic orientation (111) is dominant at all e-beam gun powers and becomes more preferred as the e-beam gun power increases.

E-beam gun power can also be useful to control thickness and porosity of SDC films. SEM images (Figs. 3, 4) show films, which cover the whole surface of a substrate and have dense columnar structure. Such columnar growth was observed also by I. Porqueras [19] forming CeO_2 thin films. But it is impossible to etermine actual density or

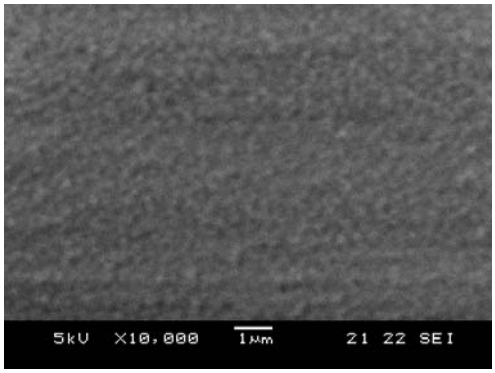

Fig. 3. SEM picture of the surface of SDC thin film deposited on Alloy 600 (Fe-Ni-Cr) substrate at e-beam gun power of 0.6 kW

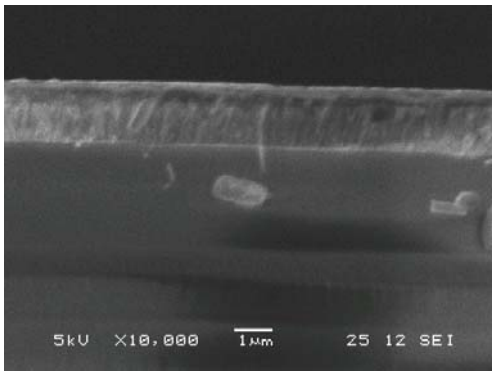

Fig. 4. SEM picture of a cross section of SDC thin film deposited on optical quartz (SiO_2) substrate at 500 °C substrate temperature (e-beam gun power 0.3 kW)

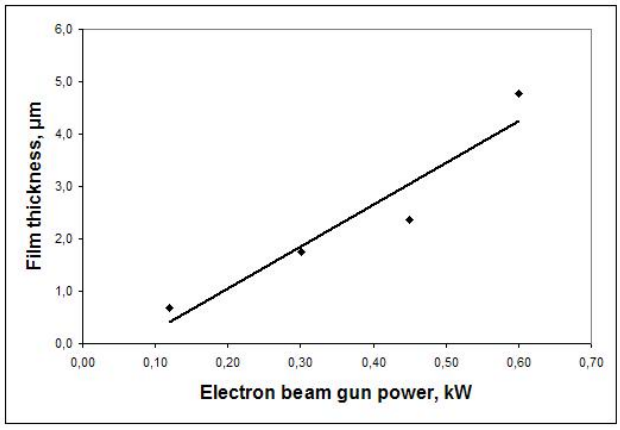

Fig. 5. Thickness dependence on e-beam gun power of SDC thin films deposited (deposition time 30 min.) on optical quartz (SiO_2) substrates

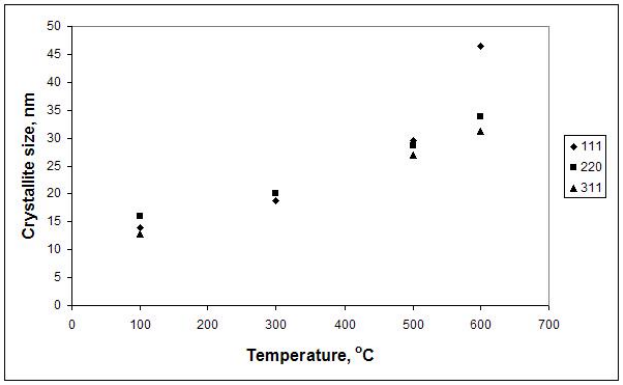

Fig. 6. Crystallite size (calculated using Scherrer's equation) dependence on substrate temperature of SDC thin films deposited on Alloy 600 (Fe-Ni-Cr) substrates

porosity of films from SEM images. Transmittance measurements were performed with films deposited on optical quartz to evaluate thickness, refractive index and porosity of films. The film thickness measurements (Fig. 5) correspond well with the measurements made from SEM images of cross sections of the deposited films. Taken into account this and previous experiments [20, 21] it could be assumed that correlation between e-beam gun power and film thickness is linear in the tested power range. This gives a good reference for practical applications of SDC thin film production by EB-PVD method. It was also observed that e-beam gun power has not effect on film porosity and refractive index in the tested power range – the refractive index and porosity did not change. It is evident that e-beam gun power, substrate temperature and crystallite growth from 5 nm to 19.2 nm is not sufficient to reduce pores inside the structure of a film. Further testing is required to determine if porosity of 26 % is too big for SOFC applications. Film density is very important to prevent gas leakages through the electrolyte. Also such stable porosity and refractive index for a variable film thickness could be useful in some optical applications.

Some experiments were performed to determine the influence of the initial substrate temperature on formed SDC thin film density. Based on previous experiments, a constant power of a 0.3 kW was chosen to produce SDC thin films less than 2 µm thickness. All films were deposited for 30 minutes. Initial substrate temperatures were

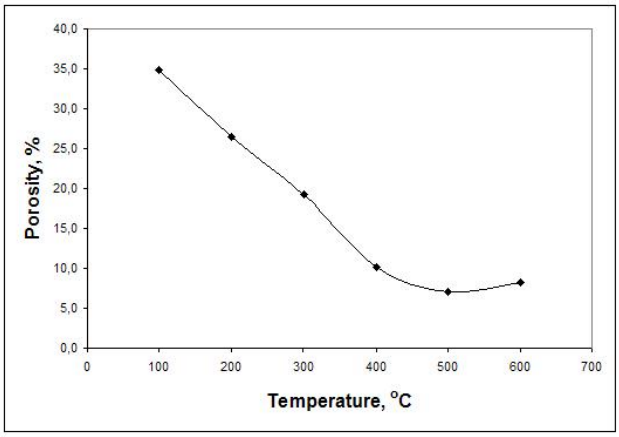

Fig. 7. Porosity dependence on substrate temperature of SDC thin films deposited on optical quartz (SiO_2) substrates

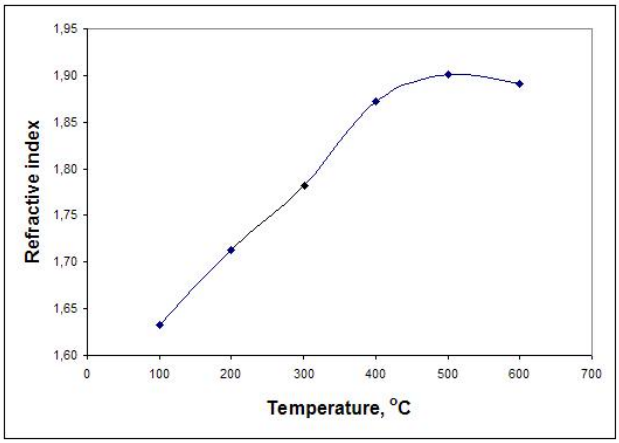

Fig. 8. Refractive index dependence on substrate temperature of SDC thin films deposited on optical quartz (SiO_2) substrates

raised from 100 °C to 600 °C with a 100 °C increase. X-ray diffraction patterns showed highly crystalline structure with the same peaks. Crystallite size calculations show an increase in size although this time crystallites grow larger up to 47 nm (Fig. 6). The similar substrate temperature influence on the crystallite size was obtained by forming CeO_2 thin films by e-beam deposition [22]. This increase can be explained similarly as in the previous experiments except this time energy transfer to particles is from the substrate (due to higher substrate temperature). It could be seen a dramatic decrease in film porosity if we look at Fig. 7. As the film becomes denser, refractive index increases (Fig. 8) and approaches the value of the bulk material. Decrease of porosity from 34.8 % to 7.1 % shows that porosity can be controlled by controlling initial substrate temperature. Looking at Thornton structure zone diagram [23] we can say that as the temperature increases structure of film changes from porous structure characteristic to Zone 1 to structures characteristic to Zone T or Zone 2 where structure consists of densely packed fibrous or columnar grains. It is observed that porosity reaches its lowest level at 500 °C and later starts to rise. Further testing is required to see if this effect is consistent. Higher temperatures could be employed to lower porosity even more but experimental setup does not allow such possibility.

4. CONCLUSIONS

Samarium doped ceria oxide (SDC) thin films could be deposited by EB-PVD technique. E-beam gun power and substrate temperature has influence on various properties of formed SDC thin films. Crystallite size increases from 5 nm to 19.2 nm, porosity and refractive index stayed almost the same (26 % and 1.72 % respectively) when e-beam gun powers from 0.12 kW to 0.78 kW were applied. Higher initial substrate temperatures were applied for further densification of thin films. Crystallite size grew from 12 nm to 47 nm, porosity decreased from 34.8 % to 7.1 % and refractive index increased from 1.63 to 1.9 as initial substrate temperature increased from 100 °C to 600 °C was applied while at constant e-beam gun power of 0.3 kW. The properties of SDC thin films exhibit high dependence on e-beam gun power and substrate temperature which can be manipulated to achieve the desired result.

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