Optical and mechanical performance of nanostructured cerium oxides for applications in optical devices

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Abstract. Nanostructured CeO$_{2-x}$ films have been grown by electron beam evaporation (EBE) and ion beam assisted deposition (IBAD). The CeO$_{2-x}$ consists of grains with size 9-28 nm and nanoscale voids enhancing the surface and quantum-size effects. We investigate the size-dependent electronic properties of nanostructured CeO$_{2-x}$ films and we establish relations between them and the film structure, composition and morphology. We investigate how the structure and morphology variations affect the absolute values of the dielectric function at the UV-Vis and IR spectral regions. The nature of the fundamental gap $E_g$ of CeO$_{2-x}$ is also considered. In addition we study in detail the light absorption mechanisms in the UV spectral regions and we correlate them with the reported band structures of the pure CeO$_2$ and Ce$_2$O$_3$. We also employ nanoindentation testing to compare the mechanical response of CeO$_{2-x}$ films grown by EBE and IBAD. Correlations between the mechanical properties of the films and the growth parameters have been made providing the possibility of tailoring films with good mechanical performance for optical device applications.

1. Introduction
Ceria (CeO$_2$) is a rare-earth oxide that is optically transparent in the visible and near IR spectral region. Nanostructured films of Ceria (CeO$_{2-x}$, x<0.2) exhibit unique physical properties, such as fluorite structure with lattice constant ($a=0.541$ nm) similar to that of Si, high refractive index $n$ and UV-absorption and dc-dielectric constant. Therefore, nanostructured CeO$_{2-x}$ films are suitable for applications in optical [1,2], electro-optical [3,4], microelectronic [5] and opto-electronic [6] devices. Several deposition techniques have been used to grow Ceria films; among them is electron beam evaporation (EBE) and Ion Beam Assisted Deposition (IBAD) [1,7,8,9]. In this work, the optical properties of the deposited films were measured

2. Experiment
The CeO$_{2-x}$ films were deposited on commercial Czochralski-grown Si(100) and Si(111) single-crystal wafers (with a 2 nm native oxide layer) in an ultra-high vacuum chamber (base pressure <1x10$^{-9}$ Torr). The first set consisted of CeO$_{2-x}$ samples, 0.12-0.5 µm thick, grown by EBE at different substrate temperature $T_s$ (RT-950°C). The second set consisted of CeO$_{3}$ films, about 0.5 µm thick, grown by IBAD at RT. IBAD growth was realized by evaporation of CeO$_2$ and subsequent bombardment with a focused Ar$^+$ ion beam generated at a Kauffman broad-beam ion source with Ar$^+$ ion energy 0.75 or 1.25 keV. The optical properties of the deposited films were measured ex-situ at RT using a phase-
modulated spectroscopic ellipsometer (Uvisel by Jobin-Yvon), in the energy range 1.5-6.5 eV with a step of 10 meV at 70° angle of incidence.

The mechanical properties of the films were measured using a Nano Indenter XP system (MTS Systems Corp.), placed in a vibration-free isolated cabinet. The hardness (H) and elastic modulus (E) of the films were measured with a Berkovich, three-sided pyramidal diamond indenter [10].

3. Results and Discussion
XRD was used to study the microstructure of the CeO$_{2-x}$ films. XRD revealed the nanostructured character of the films, showing broad diffraction peaks, which are typical for nanocrystalline materials. The mean grain size range was between 9-28 nm. All the grains are in the cubic fluorite structure of CeO$_2$.

The XRD peaks have been fitted by pseudo-Voigt curves in order to determine their angular position, broadening and intensity. The different growth techniques and conditions affect the broadening and the relative intensity of the various XRD peaks due the variations of grain size and orientation, respectively. No sign of crystalline Ce$_2$O$_3$ has been detected by XRD. However, XPS has detected a considerable portion of Ce$^{3+}$, suggesting that the Ce$_2$O$_3$ phase is amorphous and it is located at the grain boundaries [7]. The films grown by IBAD are in-plane compressed, while the EBE-grown films are stress-free. The mean grain size G of CeO$_{2-x}$ was determined from the broadening of the XRD peaks through Scherrer’s formula [11]. The calculated grain sizes for the IBAD- and EBE-grown films are presented in reference 12. The grain size is a very important parameter and determines the porosity of the film [12] and the extent of grain boundaries [7], which in turn affect the optical and mechanical properties of CeO$_{2-x}$.

The optical properties of the CeO$_{2-x}$ films have been investigated by SE in the Vis-UV spectral region (1.5-5.5 eV). The determination of the complex dielectric function enables the investigation of the material’s electronic structure [2] is directly related to the joined density of states (JDOS) for interband absorption]. The material’s electronic structure [and consequently the determined ε(ω)] is very sensitive to the materials’ microstructure. In the case of transparent films (as CeO$_{2-x}$) the measured quantity is the pseudo-dielectric function $<\varepsilon(ω)>$, which takes into account contributions from the substrate and the film’s thickness due to the multiple reflections originating from the film-substrate interface. The $<\varepsilon(ω)>$ spectra were analyzed using two Tauc-Lorentz (TL) oscillators [13,20] to simulate the O$_{2p}$→Ce$^{4f}$ and O$_{2p}$→Ce$^{5d}$ interband transitions [7].

Following the procedure described in Ref. 7, we extracted the dielectric function of CeO$_{2-x}$ itself. Figure 1 shows the dielectric functions of representative CeO$_{2-x}$ films grown by IBAD and EBE. We also indicate by vertical lines the spectral regions of visible, UV-A, UV-B and UV-C radiation; it is worth to note that the maximum optical absorption (max $\varepsilon_2$) is located in the UV-A and UV-B spectral regions, making the CeO$_{2-x}$ films appropriate for UV-filters. The dielectric function spectra, as determined by the TL fits, are characterized by three major parameters: the fundamental gap $E_g$ and the energies $E_{01}$ and $E_{02}$ of the maximum absorption of the O$_{2p}$→Ce$^{4f}$ and O$_{2p}$→Ce$^{5d}$ interband transitions, respectively, as shown in figure 2. $E_g$ increases with $T_s$ due to the elimination of defects and grain boundaries [7]. $E_{02}$ degrades with $T_s$ due to the variations of Ce$_2$O$_3$ content, because $E_{02}$ averages the contributions of CeO$_2$ and Ce$_2$O$_3$ phases [7,12,16].

Increasing Ce$_2$O$_3$ content, which is associated with the grain boundaries [7], causes strong redshift of $E_{02}$ [7] and in good agreement with the band-structure calculations [16]. However, we should mention that the variations (6.5-8 eV) of the second TL oscillator with Ce$_2$O$_3$ content are comparable with the error of the $E_{02}$ values calculated by the TL-fit (~1.5 eV). On the other hand, $E_{01}$ remains almost constant (ranging within 160 meV close to 4 eV) for all films because it originates exclusively from pure CeO$_2$ grains [7,15]. The main disadvantage of the TL analysis is the underestimation of the fundamental gap [13,22] and the inability to identify the nature (direct or indirect) of the gap, since the TL model describes only amorphous materials [15]. In order to determine accurately the fundamental gap and to identify its nature, we followed the Tauc formulation [16]. For energies $E$ close to $E_g$ the
The absorption coefficient $\alpha = \frac{4\pi k}{\lambda}$, where $k$ is the extinction coefficient, and $\lambda$ the photon wavelength, follows the formula: $\alpha \cdot E \propto (E - E_g)^m$, where $m=1/2$ or 2 for direct and indirect interband transitions. Therefore, the direct and the indirect gap can be determined by linear fits close to the absorption edge of the quantities $(\alpha E)^{1/2}$ and $(\alpha E)^2$ for indirect and direct transitions, respectively, as shown in figure 2. Using this procedure we identified the indirect gap as the fundamental gap of CeO$_{2-x}$ since it is located at least ~0.3 eV below the direct gap for all films.

**Figure 1.** Dielectric function spectra of representative IBAD- and EBE-grown CeO$_{2-x}$ films; the vertical lines indicate the visible, UV-A, UV-B and UV-C spectral regions.

**Figure 2.** Tauc plots for the determination of the indirect (left axis) and direct (right axis) gap of a representative EBE-grown CeO$_{2-x}$ film, showing that the fundamental gap is the indirect one, which is located about 0.3 eV below.

In addition to the optical characterization, mechanical testing of the CeO$_{2-x}$ has been also carried out. Figure 3 shows two representatives load-unload curves from conventional indentation test, performed to the CeO$_{2-x}$ films grown with EBE and IBAD deposition techniques for maximum load of 0.4 mN. The values of $H$ and $E$ of the CeO$_{2-x}$ films are shown in Table 1. In figure 3, the $H$ and $E$ as a function of the CeO$_{2-x}$ film’s density (determined by XRR in reference [8]) are presented. The CeO$_{2-x}$ films of higher density exhibit higher values of $H$ and $E$. Hardness represents a complex combination of the deformation characteristics of thin films. The hardness values of the CeO$_{2-x}$ films range from 3.5 to 10.3 GPa depending on the growth technique. The CeO$_{2-x}$ hardness increases with increasing growth temperature from $T_s=RT$ to $T_s=950^\circ C$, for the EBE-grown films, as a consequence of the density increase for higher growth temperatures. Although the phenomenological correlation between $H$ and the film density has been established, we found that the actual dominant factor, which determines the film hardness is the mean grain size [12]. The dependence of $H$ on grain size of EBE-grown films follows well with the Hall–Petch equation [12,17]. Elastic modulus is a measure of the stiffness of a material. From figure 4, the elastic modulus of the CeO$_{2-x}$ films decreases slowly with increasing growth temperature from 175 GPa at $T_s=RT$ to 120 GPa at $T_s=950^\circ C$. There are conflicting results in the literature regarding the variation of elastic modulus (E) with grain size in nanocrystalline materials. Some experimental results indicate a reduction in E when grain size is reduced to nanoscale, while others show almost no grain size effect [18]. However, according to our results the elastic
modulus is less dependent on grain size than hardness. Elastic modulus is anisotropic in nature, and thus it may be also sample orientation dependent.

Table 1. Experimental results of H and E for the CeO$_2$-x films grown with different deposition techniques (EBE and IBAD) for a maximum load of 0.4 mN.

| Samples | H (GPa) | E (GPa) | H/E$^2$ (GPa) |
|---------|---------|---------|---------------|
| EBE     | 10.3    | 175     | 0.0357        |
| IBAD    | 2.98    | 69.75   | 0.0054        |

Figure 3. Hardness and elastic modulus as a function of the CeO$_2$ film’s density and $n^2$ (at $\lambda=12400$ nm).

4. Conclusions
In this work the microstructure, optical and mechanical properties of nanostructured CeO$_2$-x films, grown by EBE and IBAD, were studied. We found strong variations of films’ mean grain size, density and orientation with the growth temperature and the energy of ionized species. The optical properties are strongly affected by the film structure; the direct and indirect gap of the O$_2p$→Ce$_{4f}$ transition is correlated with the concentration of trivalent [Ce$^{3+}$] and indirectly with the grain size, which determines [Ce$^{3+}$]. On the other hand, the grain size is the dominant factor, which determines the hardness of the films. The hardness was found to be well correlated with the mean grain size following the Hall-Petch equation.

5. References
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