**Thin Films of Gadolinia Doped Ceria prepared by Pulsed Laser Deposition**

**EXECUTIVE SUMMARY**

Microstructural properties of nano-ionic thin films of gadolinia doped ceria (GDC) prepared by pulsed laser ablation from sintered targets of gadolinia (5-20 mol%) doped ceria are investigated. X-ray diffraction and transmission electron microscopy reveal nanocrystalline grains with textured growth along <111> orientation in these films at low substrate temperature and at lower oxygen partial pressure. TEM study shows a uniform distribution of nanocrystal of 8-10 nm for energies 200 mJ/pulse, nanocrystals embedded in a large crystalline matrix of doped ceria for energies in the range 400-600 mJ/pulse and high density of defect. The study also reveals that the substrate temperature and oxygen partial pressure could influence preferred orientation, while the laser energy could significantly influence defect concentration in these films.

**OUTLINE**

Ceria-based electrolytes have been of interest because of their high ionic conductivity. Replacing Ce$^{4+}$ with divalent or trivalent cations results in the creation of oxygen vacancies and predominantly oxygen ion conductivity over an extended temperature and oxygen partial pressure range in comparison with yttria stabilized zirconia (YSZ). Gd-doped ceria (GDC) has significantly higher ionic conductivity and is a candidate for use in solid oxide fuel cells (SOFC) at temperatures less than 873 K, where the electronic contribution in reducing conditions is small. The lower temperature operation can lead to reduced costs and better long-term performance by reducing effects of interface reactions.

Many studies have been made on the physical properties of GDC and of its applications in SOFCs and sensors. The oxygen gas sensors based on cerium oxide films indicated that the response time of the sensors using films with particle size of 200 nm has been approximately one order of magnitude smaller than that for corresponding sensors using films of particle size of 2 μm. Therefore, it is expected that the nanocrystalline films prepared by pulsed laser ablation (PLD) could offer shorter response time. In the present work, the influence of process variables such as substrate temperature, oxygen partial pressure and laser energy on the microstructural properties is investigated. The deposition of films (111) oriented Si from a sintered GDC target was carried out using a KrF excimer laser of 248 nm wavelength (Compex 205 from Lambda Physik) and a turbopumped deposition system with typical laser repetition rate of 10 Hz using laser energy in the range 200-600 mJ/pulse. In this experiment, the excimer laser was focused onto the GDC target at an angle of incidence of 45°.

It is evident from the XRD patterns that the films are polycrystalline in the temperature range of deposition. The crystallinity of the films is found to increase with increasing substrate temperature. The particle size increases from -15 nm to ~20 nm as the substrate temperature is increased from 473 to 873 K owing to increased mobility of adatoms with increasing substrate temperature. XRD results shown in Fig. 1 indicate a significant influence of the oxygen partial pressure on the growth characteristics of the films. At 5 x 10⁻⁵ mbar base pressure, the films are weakly crystalline and have (111) orientation. With increasing oxygen partial pressure from 0.01 to 0.2 mbar, the films are (200) oriented. At 0.3 mbar of oxygen partial pressure, there is tendency for the increased growth of polycrystalline films.

Lattice images were recorded from nanocrystalline as well as from the large crystalline regions for the films deposited in the energy range 400-600 mJ/pulse. The nanocrystalline regions exhibit crystals of about 7-10 nm size and the interfaces are clean and do not contain any amorphous or secondary phases (Fig. 2(a)). On the other hand, the large crystalline area contains extended defects (Fig. 2(b)), ledges (Fig. 2(c)) and lattice bending in the films. The ledges shown are growth related defects which were mostly seen in grains containing (111) planes with the lattice spacing of about 0.35 nm. Fig. 3(a) illustrates the Raman spectra of GDC films obtained at 873 K as a function of laser energy. These films were deposited in the base pressure of 3 x 10⁻⁵ mbar. Like the effect of substrate temperature, laser energy also shows a significant shift in the Raman line and FWHM when it is increased from 200 mJ/pulse to 600 mJ/pulse (Fig. 3(b)). When Gd replaces Ce at some lattice sites, the Raman line exhibits redshift due to heavier mass of Gd. This redshift depends on the fraction of the substitution. As the laser energy increases, the fraction of Gd incorporated in the film seems to be increasing as suggested by the Raman redshift shown in Fig. 3(b). In contrast, FWHM increases with laser energy and saturates beyond 300 mJ/pulse indicating that there is a rapid increase in the defect concentration initially and it does not increase significantly at higher laser energies.

![Fig. 1: XRD patterns of 10 mol% gadolinia doped ceria films at 873 K, at different oxygen partial pressures](image)

![Fig. 2: (a) HREM image of uniformly distributed nanocrystallites in the GDC films, (b) dislocations, and (c) growth ledges.](image)
One of the most important applications of the laser with condensed material is pulsed laser deposition (PLD) because the process is capable of reproducing the composition of the target material to be evaporated. PLD is basically a growth technique in which photonic energy is coupled to the target material to be deposited via electronic processes. Here an intense laser pulse passes through an optical window of a vacuum chamber and is focused onto a solid (the target), where it is partially absorbed. Above a certain power density, significant material removal occurs in the form of an ejected luminous plume. The threshold power density needed to produce such a plume depends on the target material, its morphology, and the laser wavelength. Material from the plume is then allowed to recondense on a substrate, where film growth occurs. The growth process may be supplemented by a passive or reactive gas or ion source, which may affect the ablation plume species in the gas phase or surface reaction, in which case one talks of PLD. The dominant mechanisms in the formation of plume or ablation plasma from the irradiated surface were found to depend sensitively on laser parameters such as energy density (fluence), pulse duration, wavelength, laser repetition rate as well as the material being irradiated. A general feature of ablation plasmas is their high ion and electron temperatures of the order of several thousand Kelvin and their high degree of ionization. The advantages of the PLD process are flexibility, fast response, energetic evaporation and congruent evaporation. With appropriate choice of ablation wavelength and absorbing target material, high energy densities are absorbed by a small volume of material, resulting in vaporization that is not dependent on the vapor pressures of the constituent cations and sub-oxides. This leads to an excellent composition control in the ablated films. The development of PLD process has got considerable impetus because of its application in the synthesis of high quality single crystalline and multi-layer materials of technological significance. One can also visualize PLD as a technique capable of forming new materials, simply by varying the energy of the atoms on the surface by controlling the kinetic energy of the vapor, substrate temperature and the time between the laser pulses. The pulsed laser ablation can also be used in a controlled way to obtain three dimensional islands of uniform size in a self-assembling process. In the present work, the application of PLD to synthesize nano-ionic thin films of gadolinia doped ceria as a function of process parameters is illustrated.

Fig. 3: (a) Raman spectra of the films prepared at different laser energy at a substrate temperature of 873 K, and (b) Raman shift and FWHM versus laser energy.

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