RAPID COMMUNICATION

Preliminary studies on luminescent terbium-doped ZrO$_2$ thin films prepared by the sol–gel process

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Abstract. ZrO$_2$:Tb thin films have been successfully produced from dichloride ethoxide of zirconium, ZrCl$_2$(OEt)$_2 \cdot$ EtOH and TbCl$_3$ by the sol–gel process. These films show luminescent properties when they are excited with UV light (270 nm). The luminescence spectra present typical transitions from the ^{5}D$_4$ level belonging to the trivalent terbium ion. The processes used for film deposition were dipping and spinning on glass microscope slides. The films obtained exhibit an average visible transmission between 85 and 95%. The surface profiles show that these films are fairly smooth. The results of x-ray diffraction show that the zirconia coatings present a metastable tetragonal phase. It is observed that such films have excellent properties and are therefore of high technological interest.

Zirconia coatings, due to their chemical stability, high coefficient of thermal expansion, low thermal conductivity and high thermomechanical resistance [1] have been used to improve the resistance of metals to high-temperature oxidation and electrochemical corrosion [2]. Zirconia has been prepared in bulky, powdered and thin film forms. Thin films of this material have been prepared by using a variety of deposition techniques [3–7]. The sol–gel technique offers many advantages over other methods such as precise control of doping level, simplicity and low-temperature processing. A considerable amount of information has been accumulated regarding the mechanical and other physical properties of zirconia, in contrast to the relatively sparse research done in the area of luminescent properties. The growing interest in this area arises from the potential usefulness of luminescent techniques in the characterization of zirconia-toughened ceramics, from the possibility of using zirconia single crystals as laser hosts [8–11] and the promising applications of rare earth doped zirconia coatings as optically active layers in photoluminescence, cathodoluminescence and electroluminescent devices and in full colour flat panel display technology. For example, some electroluminescent devices consist of homogeneous transparent films, arranged in a MISIM (metal–insulator–semiconductor–insulator–metal) stack. For this application it is necessary to prepare transparent, smooth films. If rough films are used, we have abrupt interfaces in the multilayered devices which produce localized dielectric breakdown at weak spots, especially when the layers are very thin. When the films are not transparent, there is absorption and scattering of the emitted light by the luminescent centres. Because of this, the devices do not have good resolution, contrast or efficiency. The purpose of our research is to prepare zirconium oxide thin films having high transparency in the visible region of the electromagnetic spectrum, low values of surface roughness and emission of visible light when doped with trivalent terbium ions. To our knowledge there has been no report on thin luminescent films of zirconia doped with rare earth ions.

The dichloride ethoxide of zirconium, ZrCl$_2$(OEt)$_2 \cdot$ EtOH, has been obtained and used for this research. It has been proved that this organometallic compound is superior to other alkoxides with regard to its enhanced stability in storage and feasibility of controlling the hydrolysis reaction. This compound was prepared by using the method described by Bradley *et al* [12]. The system and all reagents were carefully dried first. The following reaction is presumed to take place:

$$ZrCl_4 + 3EtOH + 2NH_3 \rightarrow ZrCl_2(OEt)_2 \cdot EtOH + 2NH_4Cl.$$

The dichloride ethoxide of zirconium is a white solid and very soluble in ethyl alcohol. The solutions for coatings were prepared from ZrCl$_2$(OEt)$_2 \cdot$EtOH and a mixture of water:ethyl alcohol (3:7 volume ratio) (0.106 g ml^{-1} equivalent ZrO$_2$, viscosity 1.17 cP). Attempts
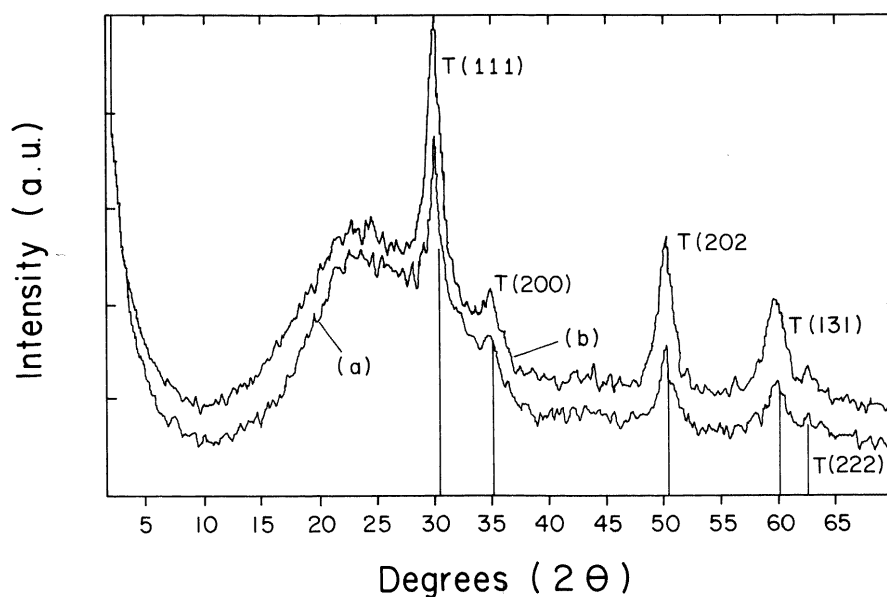
Figure 1. X-ray diffraction pattern of dip-coated ZrO_2:Tb (5 mol%) thin films: (a) sample dried at 100 °C for 5 min and (b) sample dried at 100 °C for 5 min and then baked at 500 °C for 10 min (T = tetragonal zirconia).

to prepare coatings from more concentrated solutions frequently generated a hazy to opaque film, probably due to uncontrolled hydrolysis and precipitation of the hydrated oxide [13]. Doping with terbium was achieved by adding $TbCl_3$ to the previous solution in the range of 1 to 10 mol% in relation to the Zr content in this solution. Thin films were deposited by both dipping and spinning procedures. The dip coating consists of three steps: dipping, withdrawing and heating. A Pyrex glass substrate was vertically dipped into the solution and removed at rates of 150, 200 and 250 mm min^{-1} by a motor-driven puller. This was followed by drying at 100 °C for 5 min and then heating for 10 min at 500 °C for densification. The solution temperatures used for deposition were between 25 °C and 55 °C. All films were obtained by a one-coating run. The same solutions were used for the spin coatings; these samples were prepared at spinning speeds of 1500 to 3000 revolutions per minute (rpm) for 5 s. The spinner used was a Headway Research Inc. ECIOID model. The films were prepared in one layer, then dried and baked in similar conditions to those used for dip coatings.

The spectral transmittance in the wavelength range from 190 to 900 nm was obtained with a Shimadzu UV-260 double-beam spectrophotometer. These measurements were carried out with reference to a Pyrex glass slide similar to those used as the substrate. X-ray diffraction spectra of the films were obtained with a Siemens D-5000 diffractometer with radiation of wavelength 1.5406 Å (Cu Kα) in all cases studied. The photoluminescent measurements were obtained at room temperature by using an automated Spex-FluoroMax spectrofluorometer. All the emission spectra presented here were acquired using the optimal excitation wavelength (270 nm) which was determined by acquiring the excitation spectrum using the emission maximum located at 542 nm. The thickness of the films deposited and the surface roughness were determined

by a Sloan Dektak IIA profilometer. The surface roughness R_a values were evaluated by using the formula

$$R_a = \frac{1}{L} \int_0^L y \, dy$$

where L is the length of a measuring interval and y is the amplitude of the particular roughness value on the length dx. The value of L in all cases was 3 mm.

It has been found that the transparency of the coating films depends upon the temperature and concentration of the solution. The films deposited by the solution prepared at 55 °C were uniform, with good adherence, and were transparent to the eye, whereas the films which were deposited at approximately 25 °C were completely opaque and presented some cracks. From 30 °C to 50 °C, translucent and inhomogeneous films were developed.

X-ray diffraction measurements of synthesized ZrO_2:Tb films showed some peaks corresponding to a metastable tetragonal phase. Figure 1 indicates differences in the intensity of peaks with a sample dried at 100 °C for 5 min (curve a) and then heated at 500 °C for 10 min (curve b). It is clear that by increasing temperature there is an increase in the intensity of peaks which indicates better crystallinity. This pattern shows reflections near 30.2°, 35.2°, 50°, 60° and 62° which are assigned to the (111), (200), (202), (131), (222) lines respectively of the metastable tetragonal phase of the zirconia. In this case, the (111) reflection is more intense than the others, indicating a preferential orientation of the film growth in this direction, perpendicular to the substrate surface. Probably, with longer heating times and/or at higher temperatures, it would be possible to obtain sharper and better defined peaks. It is also possible to observe an amorphous phase. But it is not clear that this amorphous phase is associated with the terbium-doped zirconia film or is due to the influence of the amorphous Pyrex glass substrate.
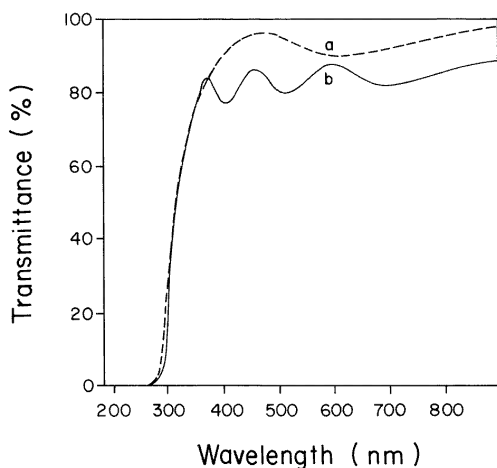
Figure 2. Optical transmission (%) of ZrO_2:Tb (5 mol%) thin films prepared by (a) spinning and (b) dipping (both sides coated) processes.

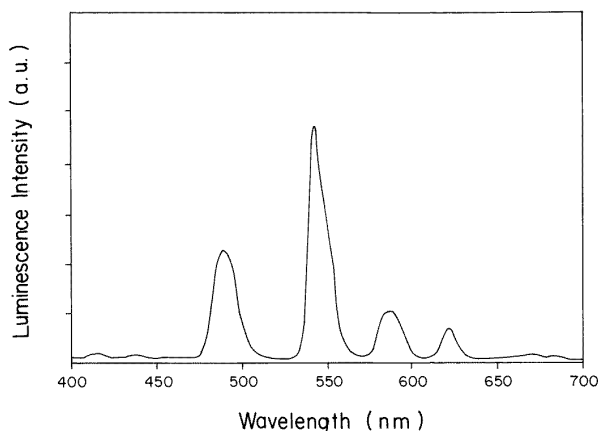**Figure 3.** Room-temperature emission spectra of ZrO_2:Tb (5 mol%) thin film prepared by dipping process, at a lifting speed of 250 mm min^{-1} and 2800 Å thickness.
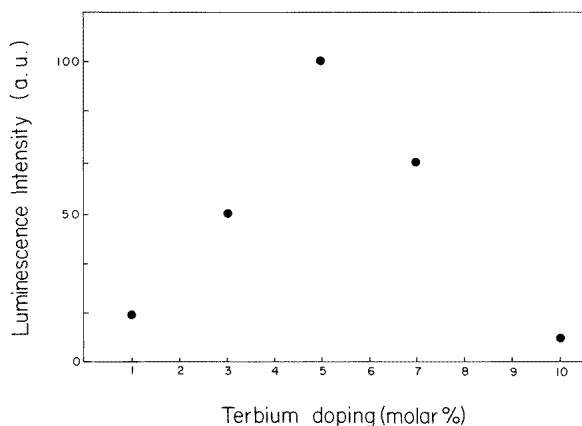

Figure 4. Dependence of relative emission intensity on Tb concentration (mol%) measured by the peak height of wavelength at 542 nm, for ZrO_2:Tb thin films with the same thickness ($\approx$ 2800 Å) synthesized by the dipping procedure.

The lifting speeds play an important role in the thickness of ZrO_2:Tb coatings made by the dipping procedure. The thicknesses obtained were 1600, 2300 and 2800 Å for the samples prepared at 150, 200 and 250 mm min^{-1} respectively. On the other hand, thicknesses of 800, 1500 and 2000 Å were obtained for spin rates of 3000, 2000 and 1500 rpm respectively. Increasing the spinning speed leads to thinner films due to the tight packing of species. In both cases the films were deposited from the solution prepared at 55 °C.

Results of surface roughness R_a measurements (by the dipping process) were in the range 35–55 Å and they seem to be correlated with the film preparation conditions. The smoothest surface was obtained for thinner films (1600 Å) and high surface roughness was observed in thicker films (2800 Å). The situation was similar for spin coated films, but the R_a values were higher, 50–80 Å.

The average transmittance is rather high in the visible region, ranging between 85 and 95% for a 2800 Å (dipping) and 2000 Å (spinning) thicknesses respectively. Figure 2 shows the spectral transmittance of the ZrO_2:Tb films for the samples prepared at a spinning rate of 1500 rpm and 2000 Å thickness (curve a) and at a lifting speed of 250 mm min^{-1} and 2800 Å thickness (curve b). In curve (b), the material was deposited on both sides of the substrate. The transmission in the visible region is limited by several factors: (i) reflection losses which include both specular and scattered (diffuse) components, this backward scattering being mainly due to surface roughness and increases with growing thickness; (ii) absorption in the film, which is primarily due to free carriers; (iii) variations in transmittance may occur due to interference phenomena, which depend upon the thickness. The transmitted part of the incident energy also has specular and scattered (diffuse) components. This forward scattering is due to inhomogeneities in the films in the form of unreacted or partly reacted chemical species generated during the deposition process, trapped gases, segregated impurity atoms or other oxide phases [14]. High average values of visible transmitted light have been achieved in the films that could indicate homogeneity and chemical purity by considering the low values of the surface roughness obtained.

The luminescent characteristics of the films prepared by the dipping process were similar to those prepared by the spinning procedure. Figure 3 shows a representative emission spectrum of ZrO_2:Tb thin film after exciting it by ultraviolet radiation (270 nm). This shows four main emission peaks corresponding to the four most significant transitions arising from the (4f) electron configuration of a Tb^{3+} ion, namely the $^5D_4 \rightarrow {}^7F_6$ transition at $\approx$ 488 nm, the $^5D_4 \rightarrow {}^7F_5$ transition at $\approx$ 542 nm, the $^5D_4 \rightarrow {}^7F_4$ transition at $\approx$ 588 nm and the $^5D_4 \rightarrow {}^7F_3$ transition at $\approx$ 620 nm. Figure 4 shows the dependence of relative emission intensity on Tb concentration as measured by the green peak height centred at 542 nm, for samples prepared by the dipping process. The emission intensity reaches a maximum value at a Tb concentration of 5 mol%, and then decreases with increasing Tb concentration, thus indicating concentration quenching. It is observed that with the increase of Tb ions, a higher efficiency is anticipated;

however, the emission intensity tends to decrease because of non-radiative interaction between ions as the resonant energy transfer becomes stronger. As the concentration is increased, the terbium ions are packed closer and closer together, which favours the transfer of energy from one terbium ion to the next by a resonance process; the energy eventually reaches a sink from which it is dissipated by non-radiative processes rather than by the emission of visible light [15–17].

In summary, luminescent terbium-doped zirconia thin films have been prepared by the sol–gel technique. It was observed that the thickness of the films depended on the lifting speed for dip-coated samples and the spinning rate for those prepared by the spinning process. Lower values of surface roughness were obtained for the thinner films. The optical transmission measured for these films was rather high, and was a function of temperature and concentration of the initial solution. Samples prepared at less than 55 °C were hazy to opaque, and the same effect was observed for the samples prepared from concentrations higher than 0.106 g ml^{-1} equivalent ZrO_2. The obtained films had a metastable tetragonal phase crystalline structure. Strong green photoluminescence emission was observed at room temperature from sol–gel deposited ZrO_2 thin films doped with Tb. The luminescence spectra show the four main peaks centred at 488, 542, 588 and 620 nm, characteristic of the trivalent terbium ion. Also, a quenching of the luminescence is observed for concentrations of Tb higher than 5 mol% in the initial solution. These high-quality films obtained by the sol–gel technique are particularly suitable for electroluminescent devices. Red emission light has also been observed from ZrO_2:Eu^{3+} films prepared by the same technique. These results will be published later.

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