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Structure and optical characterization of photochemically prepared ZrO_2 thin films doped with erbium and europium

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ABSTRACT

Zirconium oxide thin films loaded with 10, 30 and 50 mol% lanthanide ions (Er or Eu) have been successfully prepared by direct UV (254 nm) irradiation of amorphous films of β-diketonate complexes on Si(100) substrates, followed by a post annealing treatment process. The resultant films were characterized by X-ray photoelectron spectroscopy and Atomic Force Microscopy. The results showed that the stoichiometry of the resulting films were in relative agreement with the composition of the precursor films. The effects of annealing as well as the lanthanide ion loading on the photoluminescence (PL) emission intensity were investigated, finding that thermal treatment decreases surface roughness as well as PL emission intensity.

1. Introduction

Photoluminescence properties of many metal oxides such as TiO_2 [1], ZnO [2], WO_3 [3] and In_2O_3 [4] have attracted considerable interest, because they may be used in many fields, such as nanoscopic optical storage elements, or as probes in living systems [5]. However, comparatively few studies have been carried out concerning the photoluminescence (PL) of ZrO_2, especially rare earth doped ZrO_2, such as ZrO_2–Er [6,7], ZrO_2–Eu [8,9] and ZrO_2–Sm [10,11] systems.

However, for developing effective luminescence devices, materials with much lower phonon energy should be selected as hosts because the high phonon energy of the host lattice is responsible for non-radiative relaxation. SiO_2 matrix (phonon energy: $1100\ cm^{-1}$) is widely used as a host due to their high transparency in the visible region. However, the network structure of SiO_2 makes it impossible to introduce high content of dopant without clustering which leads to concentration quenching of emission [12].

ZrO_2 is one of the candidates for the substitution of SiO_2 as host matrix for lanthanide ion due to its chemical and photochemical stability, high refractive index and low phonon energy. The stretching mode of the ZrO_2 is about $470\ cm^{-1}$ which is much lower than that for Al_2O_3 ($870\ cm^{-1}$) or SiO_2 ($1100\ cm^{-1}$) [12].

Various metal ions incorporated into Zirconia materials can achieve special optical properties. Placing f-electron elements in Zirconia-based materials has the potential for solid-state photonic device applications. The ability to stabilize each crystalline phase of Zirconia at ambient temperature provides an opportunity for correlating the optical properties with the structure. In addition, structural modifications may impact the electronic structure of the lattice, and useful chemical and optical properties could emerge. As the main structural difference between these Zirconia phases is due to displacements of the oxygen atoms in the lattice, it is of interest to follow the spectroscopic consequences which accompany the structural modifications [10].

Several preparation techniques have been proposed to fabricate ZrO_2 thin films by dry processes, such as sputtering [13], chemical vapor deposition (CVD) [14] and atomic layer deposition (ALD) [15] and by moist processes such as sol–gel [16] and liquid phase deposition (LPD) [12]. Among these methods, the photochemical deposition technique is a promising and powerful method for fabricating loaded and unloaded ZrO_2 thin films due to its simplicity and low energy consumption.

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In previous articles we have reported a photochemical method for the deposition of a variety of metals and metal oxides [17–19]. In this method, also known as PMOD (photochemical metal organic deposition), thin films of inorganic or organometallic precursors are converted upon irradiation to amorphous films of metals or oxides, depending on the reactions conditions. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin coating onto a suitable substrate and the photolysis of these films results in the photoextrusion of the ligands leaving the inorganic products on the surface as shown in Eq. (1).

$$\mathrm{M(acac)}_{n(\text{thin film})} \xrightarrow{h\nu} \mathrm{M}^0 + n\mathrm{Hacac} \xrightarrow{\mathrm{O}_2} \mathrm{M}_x\mathrm{O}_y(\text{thin film}) + \text{sub-products} \quad (1)$$

where: M = Zr, Eu or Er; acac = acetylacetonate ligand.

In the present work, we report the preliminary results on the characterization of zirconium oxide thin films loaded with lanthanide elements (Er^{3+} or Eu^{3+}) prepared by photochemical deposition.

2. Experimental

2.1. General procedure

Fourier Transform Infrared spectra (FT-IR) were obtained with 4 cm^{-1} resolution in a Perkin Elmer Model 1605 FT-IR spectrophotometer.

UV spectra were obtained with 1 nm resolution in a Perkin Elmer Model Lambda 25 UV–Vis spectrophotometer.

X-ray photoelectron spectra (XPS) were recorded on an XPS-Auger Perkin Elmer electron spectrometer Model PHI 1257 which included an ultra high vacuum chamber, a hemispherical electron energy analyzer and an X–ray source providing unfiltered Kα radiation from its Al anode ($h\nu$ = 1486.6 eV). The pressure of the main spectrometer chamber during data acquisition was maintained at ca 10^{-7} Pa. The binding energy (BE) scale was calibrated by using the peak of adventitious carbon, setting it to 284.6 eV. The accuracy of the BE scale was ±0.1 eV. High resolution spectra were always fitted using Gaussian–Lorentzian curves in order to more accurately determine the BE of the different element core levels. Prior to curve fitting, a background was subtracted by the method devised by Shirley [20]. The approximate composition of the surface was determined by dividing the individual peak area, after appropriate background subtraction, by their respective atomic sensitivity factor (ASF).

X-ray diffraction patterns were obtained using a D5000 X-ray diffractometer. The X-ray source was Cu Kα (λ = 1.5405 Å) and measurements were taken in the 2θ range 0–90°.

Atomic Force Microscopy (AFM) was performed in a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in contact mode. Film thickness was determined using a Leica DMLB optical microscope with a Michelson interference attachment.

The solid state photolysis was carried out at room temperature under a low-pressure Hg lamp (λ = 254 nm) equipped with two 6 W tubes, in an air atmosphere. Progress of the reactions was monitored by determining the FT-IR spectra at different time intervals, following the decrease in IR absorption of the complexes.

The substrates for deposition of films were Indium Tin oxide (ITO) covered glass (1 × 2 cm) and n-type silicon(100) wafers (1 × 1 cm) obtained from Wafer World Inc, Florida.

Fluorescence emission spectra measurements were carry out in a multifrequency phase fluorometer (K2, ISS Inc., Urbana, Champaign, IL, USA) with a L type setup. Excitation was performed with a 400 W UV Xe arc lamp. Excitation monochromator was set at 465 nm for ZrO_2–Eu films and at 488 nm for ZrO_2–Er films, were taken at room temperature.

2.2. Preparation of amorphous thin films

The precursors Zr(IV) acetylacetonate, and lanthanides complexes Er(III) and Eu(III) acetylacetonate were purchased from Aldrich Chemical Company and thin films were prepared by the following procedure: A silicon chip was placed on a spin coater and rotated at a speed of 1500 RPM. A portion (0.1 ml) of a solution of the precursor complex in CH_2Cl_2 was dispensed onto the silicon chip and allowed to spread. The motor was stopped after 30 s and a thin film of the complex remained on the chip. The quality of the films was examined by optical microscopy (1000× magnification).

2.3. Photolysis of complexes as films on Si(100) surfaces

All photolysis experiments were done following the same procedure. Here is the description of a typical experiment. A film of the complex was deposited on n-type Si(100) by spin-coating from a CH_2Cl_2 solution. This resulted in the formation of a smooth, uniform coating on the chip. The quality of the precursor films (uniformity, defects, etc.) was determined by optical microscopy (1000×), while the thickness was monitored by interferometry. The FT-IR spectrum of the starting film was first obtained. The irradiation of the films was carried out at room temperature in air atmosphere, until the FT-IR spectrum showed no evidence of the starting material. Prior to analysis the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface. In order to obtain films of a specific thickness, successive layers of the precursors were deposited by spin-coating and irradiated as above. This process was repeated several times until the desired thickness was achieved.

Normally, the deposition of five successive layers were needed to obtain films of 300–450 nm thickness. Post-annealing was carried out under a continuous flow of synthetic air at 500 °C for 2 h. in a programmable Lindberg tube furnace.

3. Results and discussion

In a previous paper we reported that films of the $Zr(acac)_4$ complex deposited on Si(100) by spin-coating and irradiated under air atmosphere with a 254 nm UV source gives rise to thin films of ZrO_2 [21]. In order to evaluate the photoreactivity of the Er and Eu complexes, thin films of the acetylacetonate complexes were irradiated and the photolysis monitored by FT-IR spectroscopy. It was observed that the band at 1518 cm^{-1} (associated with the carbonyl group of the ligand) decreases in intensity, and after 36 h of irradiation only a minimal absorption remains. These results suggest that the diketonate groups on the precursor material are photodissociated on the surface, forming volatile products which are partially desorbed.

3.1. Characterization of ZrO_2–Ln photodeposited thin films (where Ln = Er or Eu)

For the deposition of ZrO_2–Ln thin films, solutions of $Zr(acac)_4$ with different proportions of the $Ln(acac)_3$ complexes (10, 30 and 50 mol%) were spin-coated on the appropriate substrate and the films irradiated until no IR absorptions due to the precursors were observed.

3.1.1. XPS and XRD analysis

Chemical compositions of the ZrO_2–Ln thin films, both as-deposited and annealed at 500 °C were characterized by XPS (see Fig. 1 and 2). For the as-deposited thin films, spectra show that O, Zr and C were present. The C1 s peak appearing near 284.9 eV