EFFECTS OF ANNEALING TEMPERATURE ON THE PHOTOLUMINESCENCE PROPERTIES OF ZRO_2 THIN FILMS

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ABSTRACT

This work aims to describe the photoluminescence (PL) of zirconium oxide (ZrO_2) thin films synthesized using anodization method. ZrO_2 thin film are annealed at different temperatures (200,400, and 600 ^oC). PL excitation and emission spectra were also recorded and investigated. When the material was excited by different wavelengths, several emission bands were observed in the range of 300-500nm. The increase of PL intensity with elevation of annealing temperature is related to reduction of OH groups, increase in the crystallinity and reduction in the non-radiative related defects. The luminescence dependence on defects in the film makes it suitable for luminescent.

Keywords: Photoluminescence, Zirconium, Thin film, Annealing

1. INTRODUCTION

Zirconia is a polymorphic ceramic material which may exist in three well-known structural forms: monoclinic, tetragonal, and cubic. Zirconium oxides are characterized by high thermal and chemical stability, good mechanical strength and wear resistance, excellent dielectric properties and good ion exchange properties. Therefore, they find application in many fields, for example as industrial catalysts [1], and catalyst supports, as oxygen sensors [2], and solid electrolytes in fuel cells [3], as gate dielectric materials in metal-oxide semiconductor devices , as protective coatings for optical mirrors and filters and as ceramic materials . Furthermore, oxidesformed on zirconium (and zirconium alloys) are some of the most radiation-resistant ceramics currently known and play a key-role in the

nuclear industry because of their good mechanical properties and corrosion resistance. Optical properties of zirconia and its photoluminescence properties are rarely reported. In addition, thin films of ZrO_2 have attracted special interest owing to their advantageous properties of being highly homogeneous, transparent and their application in optical storage elements, scintillators and luminescent oxygen sensors. Thin films fabrication by anodization method has gained much interest because of its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, chemically homogenous films over large areas that can provide integration with other circuit elements.

Thermal annealing is widely used method to improve crystal quality and to study structural defects in materials. Due to annealing, the structure and the stoichiometric ratio of the material changes. Such phenomena can have major effectson the optical properties, particularly the photoluminescence properties [4,5].

Typical ZrO_2 contains some percentage of HF atoms as impurity and it's very difficult to separate hafnium from zirconium. These impurities may create some shallow levels and other levels in the energy gap. Many experiments have been done in order to obtain more correct conclusions about PL properties. In the experimental studies, a comparative study of PL properties of ZrO_2 has been carried out at different temperatures. The obtained time-resolved spectra and the excitation photon-energy dependence clarify the defect effects, especially, deep and shallow energy level structures in the forbidden gap.

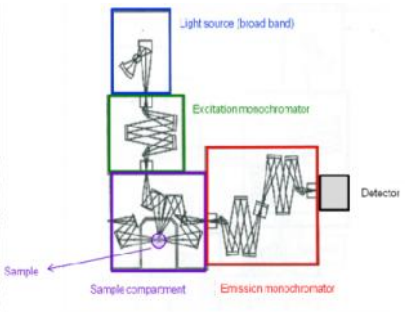
2. EXPERIMENT

Zirconium foils(99.6% purity) of 0.2 mm in thickness and high purity were used. Before anodization, the zirconium sheets (10 mm × 20 mm) were degreased in an ultrasonic bath in acetone, anhydrous ethanol and DI water successively, followed by rinsing with DI ((Distillated))water and drying in the air.

The electrochemical anodization of the zirconium sheet was carried out using a direct current (DC) voltage source. Anodic films of ZrO_2 were grown from the surface of the zirconium sheet by potentiostatic anodization using a platinum sheet as a counter electrode. The electrolytes were 0.5 wt% NaF and 0.2M of Na_2SO_4 in a mixed solution containing volumetric ratio of glycerol and DI water was 1:1 (v/v). The anodization experiments were performed under stirring condition and at room temperature for 3 hours. After anodization, the samples were rinsed with DI water and dried afterwards.

Annealing treatment of oxide thin films samples was performed in the atmospheric conditions for 2 hours at various temperatures (200,400, and 600 ^{o}C).

PL spectral measurements were taken on a Horiba Jobin Yvon(Fluorolog FL3-22) spectrofluorometer with a (Xe) lamp as the excitation light source at room temperature. The obtained spectra were corrected for the measuring system’s spectral response.



FL3-22 spectrofluorometer **Fluorlog layout**

Horiba FluoroLog Spectrophotometer

The Fluorolog-3-22 (JY Horiba Inc.) is a spectrofluorometer consisting of a 450 W xenon arc lamp, a double excitation monochromator, a sample compartment with a cuvette holder, a double emission monochromator, and a photomultiplier tube (PMT). A fiber-optic probe can be coupled to the sample compartment such that spectroscopic measurements can be made remotely. Although the spectrofluorometer has been designed for fluorescence spectroscopy, fluorescence (as either an excitation or emission spectrum) as well as reflectance spectra (in synchronous scan mode) can be measured. The adjustable variables are excitation wavelength(s) and emission wavelength(s), excitation and emission slit widths, sampling increment, integration time, and collection geometry (front face versus right angle collection).

Technical details:

-excitation source: 450 W Xe lamp

-monochromators (excitation emission): f/3.6 Czeny-Turner, double grating, all reflective optics

-diffraction gratings: classically ruled, 1200 tr/mm; blaze 330nm (MEx) and 500nm (MEm)

-emission signal detector: at room tempe-rature-R928P side-on photomultiplier tube (180-850nm);

-software package: FluorEssence 2.0 (powered by Origin 7.5)

Performances:

-excitation range: 240-600nm

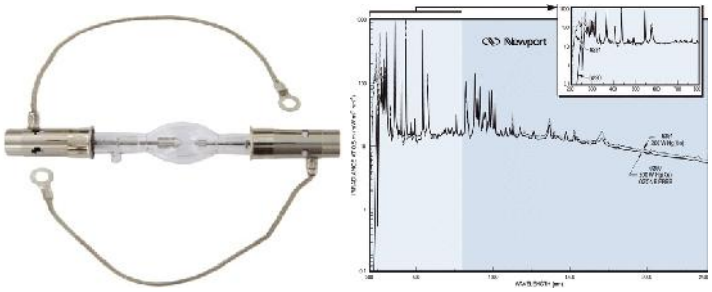
-emission range: 290-850 nm

-photomultiplier response linearity: 2x106 cps (in photon counting mode)

-reference detector: stabilized Si photodiode (200-980nm)

-dispersion (double grating monochromatore): 2.1 nm/mm

-slit settings (bandpass): 0-15 nm



450 W Xe lamp

3. RESULTS AND DISCUSSION

Photoluminescence of thin oxide films

PL emission and corresponding excitation spectra of zirconia thin oxide films are shown in Fig. 1. Wide PL bands are present in the range from 320

to 550 nm. The PL intensity and peak positions of emission and excitation spectra change with excitation and emission wavelength, respectively.

Fig. 1a in emission PL spectra we observed six peaks centered at about 435 nm, 442 nm, 450 nm, 465 nm, 485 nm, and495 nm. For excitation spectra (Fig. 1b), one spectral peak is at constant wavelength at about 285 nm and the other shifts to longer wavelengths while increasing emission wavelength. These results suggest that PL emission band with peak position at 495 nm originates from the first excitation peak (285 nm), while the second PL emission band changes with excitation wavelength.

It is well established that defects and vacancies can lead to the formation of localized states near the conduction band edge. The perturbations due to defects and impurities are characterized by discrete energy levels that lie within the band gap [6]. When the concentrations of such (structural or composition) defects become sufficiently large, they may either segregate to form cavities or distribute in the atom network. Intrinsic (delocalized) states may then be affected by the resulting distortion of the lattice. The principal intrinsic defect in nano crystalline zirconia is anion vacancies.

Two different mechanisms have been proposed to explain ZrO_2 luminescence, an impurity luminescence center model and a structure defect model - electron trapping by the anion vacancies (F+ singly ionized oxygen vacancies). The anodization process leads to the existence of large amounts of surface defects (oxygen-vacancy) in ZrO_2 nano thin films due to their large surface area [7,8].

Currently, the structure defect model mechanism is generallyaccepted.

The 495 nm zirconia emission peak can be due to the capture of electrons by oxygen vacancies from the conduction band [9].

In zirconia thin film prepared by anodization method, the groups coordinated on the surfaces of the films such as Zr(OH) could form electronic states different from those of bulk component. They can form dangling Zr bond during the condensation and dehydration process.

Owing to these surface states, dangling bonds and other factors (such as the influence of O_2 in the atmosphere), there are many Zr^{4+} defect sites. The existence of such defect Zr^{4+} sites (more likely at irregular near-face sites) may photo generate Zr^{3+} centers by electron capture.

The excitation band corresponds to the spectral range of the extrinsic absorption of ZrO_2 caused by preexisting defects [10]. The energy gap of tetragonal ZrO_2 phase is greater than 5eV [11]. The excitation band at 285 nm (5.12 eV) corresponds to energy near the energy gap of ZrO_2 tetragonal phase.

Fig. 2a and b show the PL emission spectra of ZrO2 thin films annealed at different temperatures.

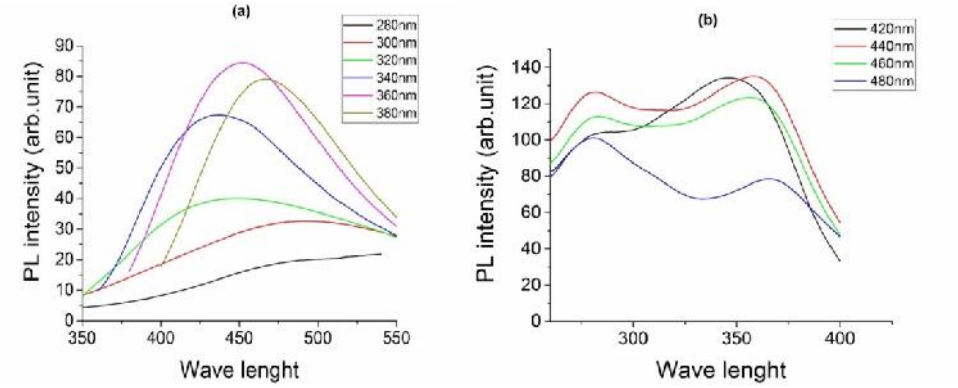


Fig. 1. PL spectra of thin oxide film: (a) emission spectra, (b) excitation spectra.

(a) (b)

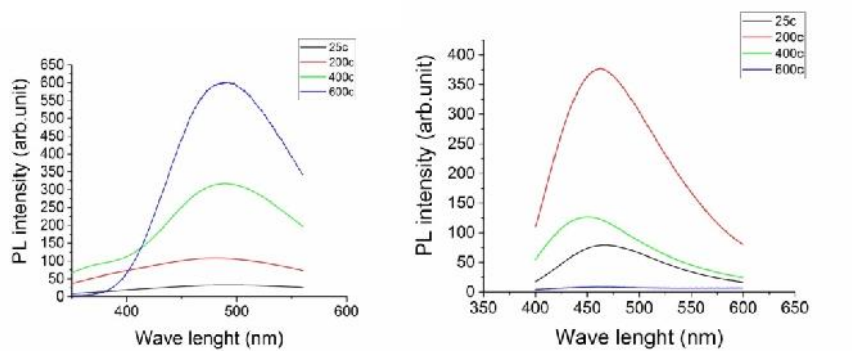


Fig.2.(a) Influence of annealing on emission PL spectra excited at 300 nm, (b) Influence of annealing on emission PL spectra excited at 380 nm.

Fig.2a At low excitation wave lengths, it was observed that with the increase of temperature, the luminescent peak intensity increases. The variation in the PL intensity with temperature is affected by the crystallinity of the films [12], and the quenching mechanism by OH groups [13]. This clearly indicates the reduction of OH groups and increase in Zr–O–Zr, by increasing the treatment temperature.In addition, at low temperature the oxygen sub-lattice may contain many defects, both inside the film and at the

surface [14]. Such defects would be expected to produce various non-radiative centers and hence reduce light emission. After annealing at high temperature, these non-radiative related defects could be reduced and re-structured with a consequent increase in PL.

Fig.2b At high excitation wave lengths, it was seen that with the increase of temperature, the luminescent peak intensity decreases, and at high temperature the luminescent peak intensity is significantly low. During the annealing, oxygen in zirconia films and oxygen diffusing from air into the zirconia films react with the remaining zirconium in zirconia films forming a new zirconium oxide. In this newly formed zirconium oxide many oxygen vacancies are present and the PL intensity increases with increasing annealing temperature. With further increase of annealing temperature the PL intensity becomes weaker because the annihilation rate of oxygen vacancies becomes faster than the formation rate [15].

4. CONCLUSION

Photoluminescence (PL) measurements for zirconia films produced by anodization method, show that well resolved PL bands occur in the range from 320 nm to 550 nm at room temperature. Six peaks centered at about 435 nm, 442 nm, 450 nm, 465 nm, 485 nm, and 495 nm can be observed in emission spectra, while for excitation spectra the dominant peak is found at 285 nm, and the other at about 345 nm to 365nm. At low excitation wave length, increasing of annealing temperature, the PL intensity increases due to the formation of oxygen vacancy defects in zirconia films, which are

responsible for PL. At high excitation wave length the PL intensity decrease by increasing of annealing temperature.

REFERENCES

[1] A.I. Ahmed, S.A. El-Hakam, S.E. Samra, A.A. EL-Khouly, A.S. Khder, Colloid Surf. A – Physicochem. Eng. Asp. 317 (2008) 62–70.
[2] E. Ivers-Tiffe, K.H. Hardtl, W. Menesklou, R. Riegel, Electrochim. Acta 47 (2001) 807–814.
[3] T. Omata, Y. Goto, S. Otsuka-Yao-Matsuo, Adv. Mater. 8 (2007) 524– 530.
[4] G.R. Karagedov, N.Z. Lyakhov, Nanostruct. Mater. 11 (1999) 559.
[5] R.C. Patil, S. Radhakrishnan, Sushama Pethkar, K. Vijaymohanan, J.Mater. Res. 16 (2001) 7.
[6] A.S. Foster, V.B. Sulimov, F. Lopez Gejo, A.L. Schluger, R.M.Nieminen, Phys. Rev. B 64 (2001) 224108.
[7] J. Liopis, Phys. Status Solidi A 119 (1990) 661.
[8] P.A. Arsenev, Kh.S. Bagdasarov, A. Niklas, A.D. Rhyazantsev, Phys. Status Solidi A 62 (1980) 395.
[9] A.S. Foster, V.B. Sulimov, F. Lopez Gejo, A.L. Schluger, R.M. Nieminen, Phys. Rev. B 64 (2001) 224108.
[10] A.V. Emeline, G.V. Kataeva, A.S. Litke, A.V. Rudokova, V.K. Ryabchuk, N. Serpone, Lanmuir 14 (1998) 5011.
[11] R.H. French, S.J. Glass, F.S. Ohuchi, Y.N. Xu, W.Y. Ching, Phys. Rev. B 49 (1994) 5133–5142.
[12] T. Hirata, E. Assari, M. Kitajima, J. Solid State Chem. 110 (1994) 201.
[13] Y. Yan, A.J. Faber, H. de Waal, J Non-cryst. Solids 181 (1995) 283.
[14] R.J. Hong, J.B. Huang, H.B. He, Z.X. Fan, J.D. Shao, Appl. Surf. Sci. 242 (2005) 346–352.
[15] Y. Du, W.L. Cai, C.M. Mo, J. Chen, L.D. Zhang, X.G. Zhu, Appl. Phys. Lett. 74 (1999) 2951.