Properties of Nano Thin Film Composed of Nan Crystalline Zro_2 Prepared by (SOL - GEL) Method

Kassim Mohammed Sahan
Ministry of Science and Technology, Renewable Energies Directorate, Hydrogen and Biofuel Department/Baghdad
Email: sahansahan68@gmail.com

Aqel Mashot Jafar
Ministry of Science and Technology, Renewable Energies Directorate, Hydrogen and Biofuel Department/Baghdad

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ABSTRACT

Nano-crystalline ZrO_2 was prepared by sol-gel method and deposited on glass substrate by dip-coating technique method in the room temperature. $ZrOCl_2$ was dissolved in a solvent mixture composed of H_2O_2 and ammonia. The dissolving reaction produced a colorless, transparent peroxozirconium complex solution. The mean nanocrystalline size was about 7.55 nm. The zirconium film thus obtained was transparent 90% with 5.03 eV band gap. Atomic force microscopy (AFM), X-ray diffraction and (UV-Vis) used to determine the properties of the thin film. The as-deposited thin film was of high purity of ZrO_2 and good adhesion to the substrate. The annealing was caused crystallization of tetragonal and monoclinic phase present in the zirconia at 550°C in air. The film showed very flat surfaces consisting of nanoparticles with particle size of ranging (2-10 nm).

Keywords: ZrO_2 nanoparticles; Sol-Gel processing; Crystallization; Nano-thin film; AFM; XRD; Energy gap.

خواص غشاء رقيق نانوي مكون من مادة اوكسيد الزركونيوم البلورية النانوية المحضرة بطريقة (السول – جيل)

الخلاصة

لقد تم تحضير مادة اوكسيد الزركونيوم البلورية النانوية بطريقة الهلام (السول- جيل) ورسبت على ركيزة زجاجية بطريقة الطلاء بالتغطيس في درجة حرارة الغرفة. مادة كلوريد الزركونيوم $ZrOCl_2$ ذوبت في مذيب مركب من مادة بيروكسيد الهيدروجين مع الامونيا. ناتج التفاعل محلول معقد من مادة بيروكسيد الزركونيوم عديمة اللون والشفافة. متوسط حجم البلورات النانوية لاوكسيد الزركونيوم حوالي (7,55) نانومتر. غشاء الزركونيوم الذي تم الحصول علية ذو شفافية 90% ويمتلك فجوة طاقة بحدود 5,03 إلكترون فولت. خصائص الغشاء فحصت باستخدام مجهر القوة الذرية AFM وجهاز حيود الأشعة

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

السينية XRD والمطياف UV-Vis. الغشاء المرسب يمتلك نقاوة عالية من المادة ZrO_2 والتصاقية جيدة مع الركيزة. الغشاء المرسب تم تلدينه الى درجة حرارة 550 م^0 في الهواء وعملية التلدين سبب حالة بلورية لمادة الغشاء ZrO_2 في الطور البلوري الرباعي والأحادي. يظهر فحص الغشاء سطح مستوي جدا يتألف من جزيئات نانوية بإبعاد تتراوح (2-10) نانومتر .

INTRODUCTION

Practical synthesis methods are still under development in order to obtain zirconium with controlled particle size and general properties. A common synthesis route consists of the calcinations of the hydrous zirconia obtained from hydrolysis of zirconium salts in various media. It was found that the properties of zirconia obtained by hydrolysis depend on several chemical parameters [1]. Ultra thin films of ZrO_2 were synthesized on soda lime glass and SnO_2 coated glass, using $ZrCl_4$ and H_2O precursors by atomic layer deposition (ALD), a sequential CVD technique allowing the formation of dense and homogeneous films [2]. Polycrystalline zirconia thin films were obtained on silica substrates by the spray pyrolysis technique using a water/isopropanol solution of a precursor containing zirconium in the form of an anionic oxalate complex. The as-deposited products were amorphous. Crystallization with formation of homogeneous dense nanostructured cubic zirconia thin films occurred after heat-treatment in air at temperatures T= (500-700)$^\circ$C [3]. Zirconia thin films are of importance due to their thermal, mechanical, and chemical stability, and have attracted much attention for applications such as optical coatings, buffer layers for growing superconductors, thermal-shield or corrosion-resistant coatings, ionic conductors, and oxygen sensors[4]. By spin-coating sol solutions, which contained $ZrCl_4$ in anhydrous isopropanol, on substrates, the morphology and thickness of thin films were easily controlled by changing the concentrations of $ZrCl_4$ in sol solutions. A highly porous film with large specific surface area (180 m^2/g) was obtained at 150g $ZrCl_4$/l without the addition of templates [5]. Many different methods of producing nanosize powders such as sol-gel processing, hydrothermal processing, and ion exchange resin manufacture methods [6]. Preparation of ZrO_2 by conventional precipitation from aqueous solutions of the zirconyl salts leads usually to a mixture of the stable monoclinic m-ZrO_2 and metastable tetragonal t-ZrO_2 forms [7]. Multi-layered zirconia ZrO_2 thin film on the Pt/Ti/SiO_2/Si substrate has been prepared as humidity sensing material by sol–gel method. Annealing temperature was 450°C. A TiO_2 thin film was added in between ZrO_2 film and the substrate for improving the adhesion [8]. The ZrO_2thin films deposited on Si (100) were successfully synthesized by sol-gel process and deposited by using spin-coating technique [9]. Zirconium dioxide thin films were prepared by e-beam evaporation method to study the effect of substrate temperature on the structural, surface morphology, compositional, and optical properties [10].

THE AIM OF THE PROJECT

Is the preparation of ZrO_2 nano-crystalline and nano-thin film in the field of advance ceramic and glass applications?

EXPERIMENTAL SECTION

Nan sized zirconia powders were prepared by a sol-gel process, and to investigate the effects of the processing conditions on the formation, morphology, and phase of the powders. Preparation of precursor solution and deposition of Thin Films by dip-coating method. The experimental flowchart is shown in Figure (1). Zirconium ox chloride ($ZrOCl_2$.$8H_2O$, 99.0%, BDH), was selected as the Zr source. A mixture of hydrogen peroxide (H_2O_2, 30%, Aldrich) and ammonia (NH_3 H_2O, 28%, Aldrich) in appropriate quantities was used as the solvent. Specifically, 0.25 g of ($ZrOCl_2$. $8H_2O$) was added to (7.5 ml) of ammonia and stirred for 30 min, then (25 ml) H_2O_2 3% was added, accord to the following equations:

$$ZrOCl_2 + 2NH_4OH \leftrightarrow ZrO(OH)_2 + 2NH_4Cl$$

$$4ZrO(OH)_2 + 2H_2O_2 + 8NH4^+ + 8H_2O \leftrightarrow [Zr_4(O_2)_2(OH)_4(OH2)_{16}]^{8+} + 8NH_3$$

$$[Zr_4(O_2)_2(OH)_4(OH_2)_{16}]^{8+} + 8OH^- \leftrightarrow 4ZrO_{1.4}(OH)_{1.2} + 19.6H_2O + O_2$$

After the mixture was stirred for (6 -7) hr, the zirconium oxychloride completely dissolved, and a homogeneous colorless and transparent solution was obtained. Typically, the pH of the as-prepared transparent solution was about 10, which decreased to about 9 when the solution recovered to be transparent after reaction for 48 hr. The as-prepared peroxozirconium solution can maintain transparency for at least one week at room temperatures 25°C, where as it is unstable and became turbid after being stored at room temperature for longer than (3 -5) hr. ZrO_2 was obtained after dehydration and release of hydroxyl groups by annealing, accord to the following equation:

$$ZrO_{1.4}(OH)_{1.2} \leftrightarrow ZrO_2 \text{ (amorphous)} + 0.6H_2O$$

The crystallization temperature 550°C, suggesting the formation of an amorphous ZrO_2. Last, the structure rearrangement based on thermodynamics promotes the polymorphic transformation accord to the following equations:

$$ZrO \text{ (amorphous)} \leftrightarrow t\text{-}ZrO \leftrightarrow m\text{-}ZrO$$

The precipitated zirconia precursors were washed by respected cycles of centrifugation and re-dispersion in water. Washing was performed for a minimum of five times in ethanol. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 100 mL ethylene glycol under vigorous stirring. The substrate of (2.5 x 2.5) cm^2 microscopy glass was cleaned ultrasonically in acetone, ethanol, and deionized water. After the substrate was dried at 60°C, it was further irradiated by UV light (80 mW/cm^2) for 5 min. The cleaned substrate was then floated on the surface of the produced solution at room temperature 25°C to deposit a thin film. After soaking for 6 hr, the substrate was carefully rinsed with deionized water before drying at 60 °C for 12 hr. After drying at 60°C for 12 hr was annealed at temperature 550°C.

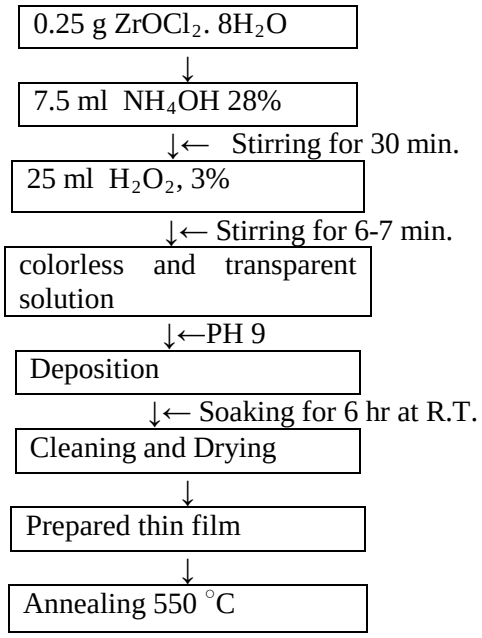


Figure (1) Schematic flowchart for the solution preparation and film deposition.

CHARACTERIZATION

Composition and crystal structure study by X-ray diffraction (XRD-Shimadzu 6000, Cu-Kα) for dip-coating technique. The thickness of film was measured by means of a thin film (Stellar Net Inc.) and AFM. The transmittance of film coated was measured in the wavelength range of (190-1200) nm using a (SPECTRO UV/VIS Double Beam (UVD-3500) Labomed, Inc.). A blank sample of substrate was used as a reference in the measurement of optical transmittance and thickness. AFM investigation of the surface morphology of sample was investigated by contact mode atomic force microscopy (AA 3000 Scanning probe microscope, Angstron Advanced Inc.). Photomicroscope meter (leit3-Metallax).

RESULTS AND DISCUSSION

Zirconium oxide can be prepared by the sol-gel technique using inorganic precursors, like $ZrOCl_2$, as zirconium alkoxides. The XRD pattern of the prepared sample is shown in Figure (2). The amount of tetragonal and monoclinic phase present in the zirconia was estimated by comparing the areas under the characteristic peaks of the monoclinic phase (2θ= 28.5° and 31.6° for the ($11\bar{1}$) and (111) reflexes respectively) and the tetragonal phase (2θ= 30.4° for the (101) reflex). The mean crystalline size was about (7.55 nm) calculated from the full-width at half-maximum (FWHM) of XRD lines by using the Debye-Scherrer formula [11]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where *D* is the grain size of the crystallite, λ (1.54059 Å) is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction. Figure (2) indicated that the ZrO_2 nanoparticles prepared by sol-gel method were mixture of the tetragonal and monoclinic phases [8]. Figure (3) shows the transmission curve as a function of wavelength in the UV-Vis range for deposited at room temperature. It is observed an 90% trasmission in the visible for thin film. In case the film resulted transparent in the visible energy range. Figure (4) shows the UV–Vis absorption spectrum of the ZrO_2 film, showing an absorption (λ_{max} = 240 nm) edge corresponding to an average value for optical band gap of 5.03 eV. The direct energy gap of the thin film ZrO_2 is calculated (Eg = 5.03 eV) as shown as in Figure (5).The absorption coefficient was increased at the range (Eg = 5 - 6 eV) as shown in Figure (5).

$$(ah\nu)^2 = C\left(h\nu - E_g\right)$$

Where C is a constant, Eg the optical band, α is the optical absorption coefficient, hν is the photon energy gap, h the Plank's constant. The absorption increased steeply when the wavelength was below 240 nm which corresponded to a band gap of 5.17 eV [12][13]. The thickness of the film closed to (11.13 nm), as shown in Figure (6) and Figure (3), this value was agreement with the thickness of film determined by means of a thin film (Stellar Net Inc.) through used a blank sample of substrate as a reference in the measurement of thickness. AFM images Figure (6) clearly shows the particulate characteristics of the as-deposited thin film, the upper peak of thin film was (11.13 nm) also the Root-Mean-Square (RMS), representing surface roughness, is about (1.07 nm) for the measured areas of (500 x 500) nm^2. The high transparency indicates fairly smooth surfaces and relatively good film homogeneity, which is consistent with the AFM observations as shown as in Figure (6) and photo macroscopic observations as shown as in image (1), the images shown then particle shape were spherical crystals. The film was annealed at 550°C in air, was caused crystallization of tetragonal and monoclinic phase.

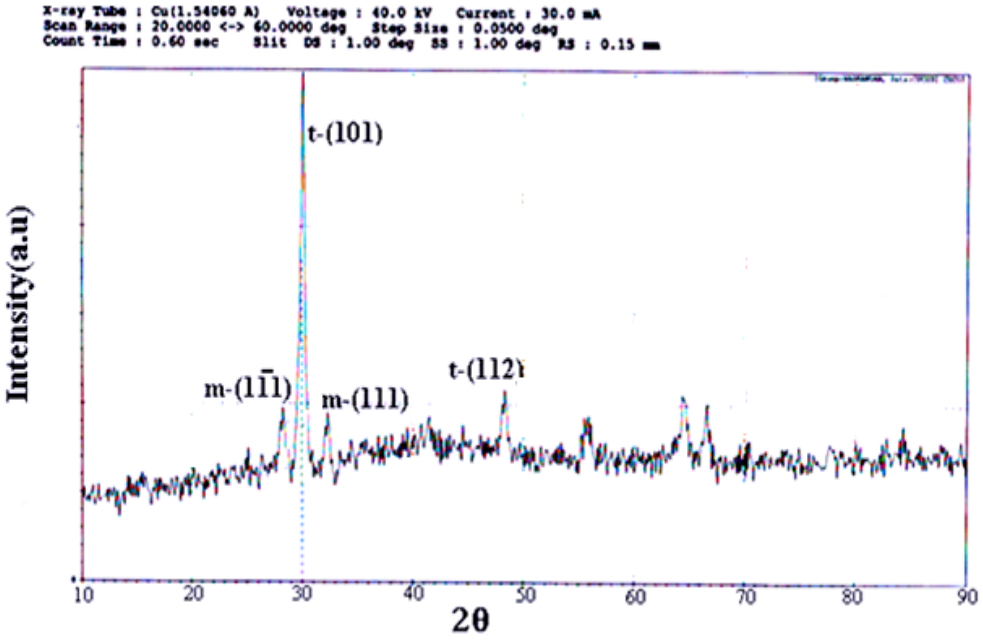


Figure (2) XRD profiles for the as-deposited thin film and the films after annealing at temperatures 550°C for 30 min in air. The JCPDS file numbers for tetragonal and monoclinic phases are 42-1164 and 37-1484, respectively.

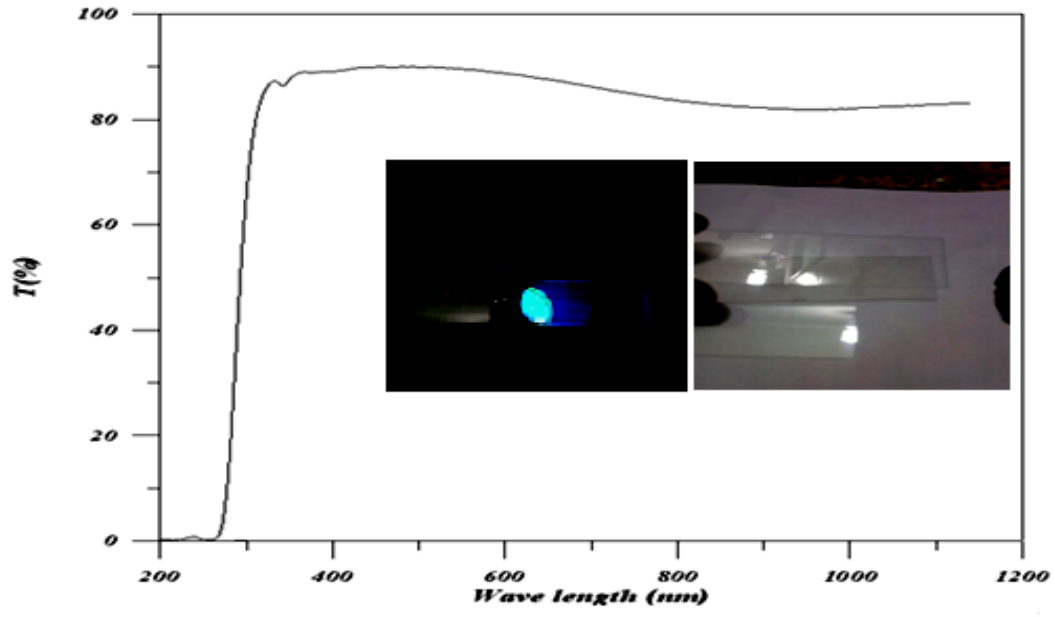


Figure (3) The UV–Vis trasmission spectrum of the ZrO_2 thin film.

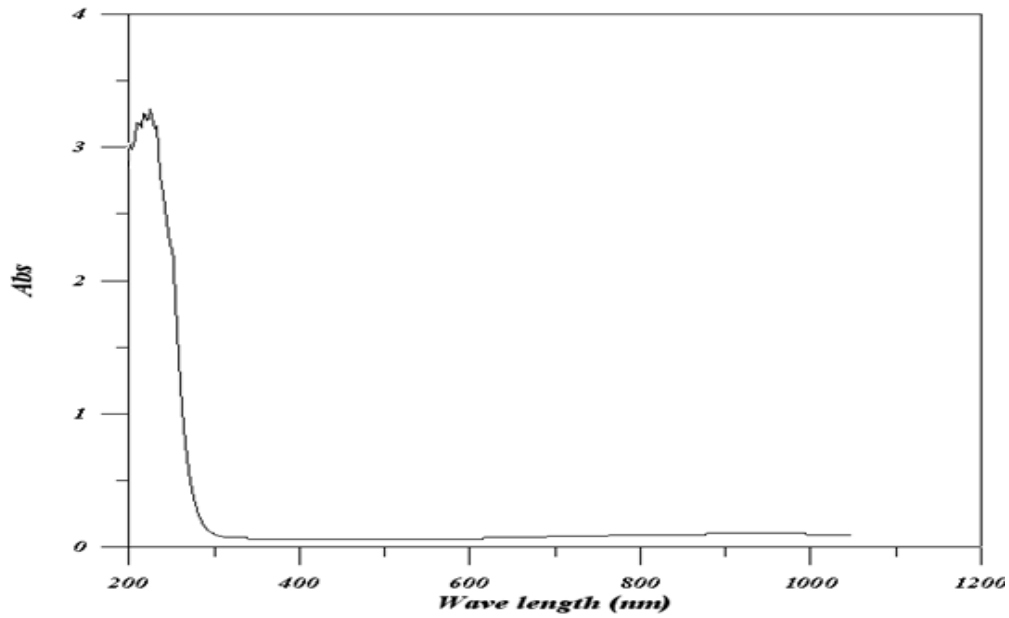


Figure (4) The UV–Vis absorption spectrum of the ZrO_2 thin film.

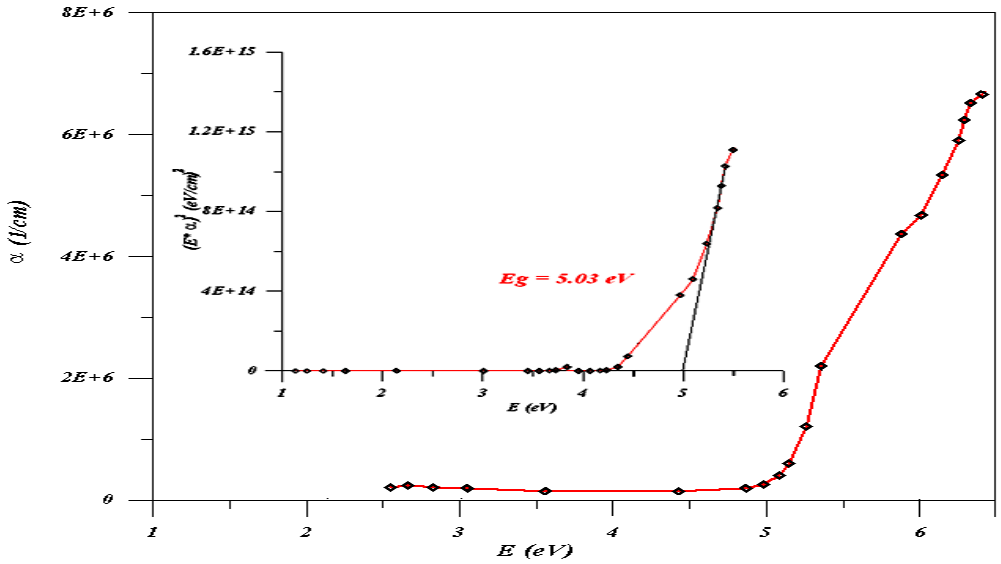
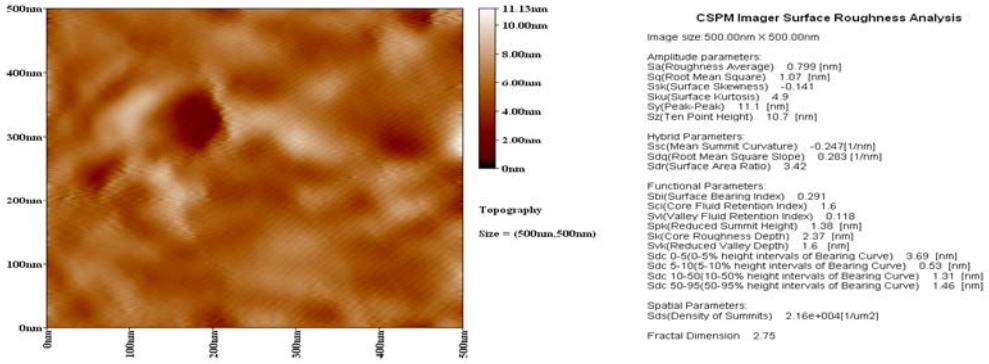


Figure (5) shows the energy band gap and absorption coefficient as afunction of energy.



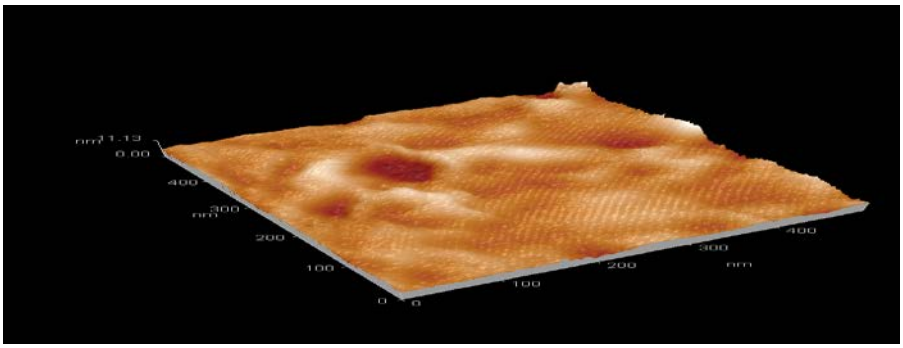


Figure (6) AFM images for the as-deposited thin film deposition at 25°C and annealing at 550°C for 30 min in air.

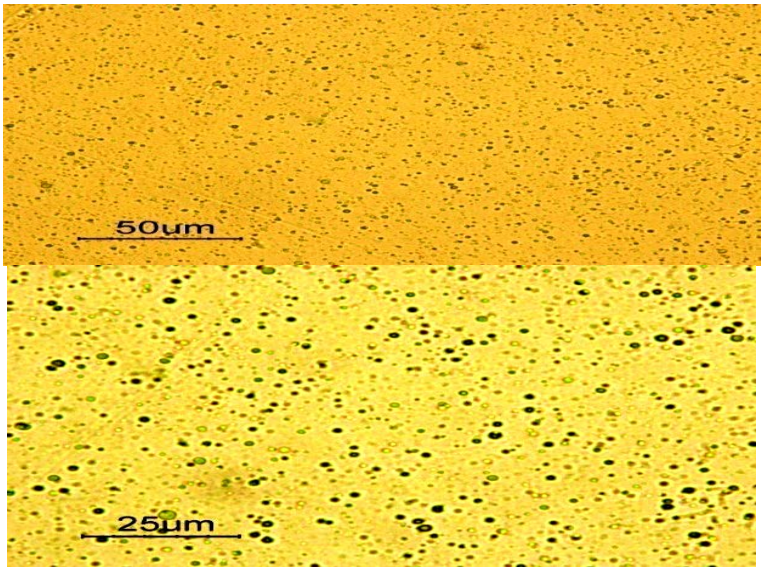


Image (1) Photomicroscope images show spherical crystals for ZrO_2.

CONCLUSIONS

The as-deposited thin film could transform to tetragonal and monoclinic ZrO_2 after annealing at 550 °C temperatures. The as-deposited film was composed of closely packed homogeneous nanoparticles of 7.55 nm diameters, and showed a very flat surface with a RMS roughness of 1.07 nm for a measured area of (500 x 500) nm^2. Heating resulted in dehydration and release of hydroxyl groups and produced stoichiometric ZrO_2 thin film, either amorphous or crystalline. Both the as-deposited thin film and those after annealing were highly transparent. The optical band gap for the crystalline ZrO_2 thin films was 5.03 eV regardless of their phase structures, which is comparable with those reported for bulk or film-form ZrO_2. The sol.gel method is an effective method for preparing the nano ZrO_2 powders. According to the obtained results, the surfactant prevents the aggregation between the primary particles and leads to obtain nano zirconia. The nano particles also affect the crystallite phase composition and lead to stabilization of tetragonal phase at room temperature.

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