Materials Science in Semiconductor Processing 72 (2017) 122–127

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Influence of annealing temperature on the structural and optical properties of nanocrystalline zirconium oxide

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ARTICLE INFO

Keywords:
Zirconium oxide
Chemical synthesis
Sol-gel preparation
Powder technology
Nanocrystalline materials
Annealing temperature

ABSTRACT

Nanocrystalline zirconium oxide powder was prepared by sol-gel method using zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) and ethylenediaminetetraacitic acid (EDTA) in ammonium hydroxide (NH_4OH) solution. The as-synthesized complex product was annealed at 650 °C, 750 °C and 850 °C for 2 h to get fine ZrO_2 powder. These samples were further analyzed by Scanning electron microscopy (SEM), X- ray diffraction (XRD), Energy-dispersive X- ray spectroscopy (EDX), UV-vis analysis, Fourier transform infrared (FT-IR) spectroscopy, Photoluminescence spectroscopy (PL) and Raman Spectroscopy to study their structural and optical properties. The structural studies revealed that nanocrystalline ZrO_2 powder exhibits monoclinic phase with variation in crystallite size with annealing temperature. The UV–vis absorption band edge of ZrO_2 decreases from 514 nm to 451 nm as annealing temperature rises from 650 °C to 750 °C. It seems that the drastic reduction in band gap energy may be one of the novel unexpected characteristics of ZrO_2. The FTIR analyses further confirmed the formation of nanocrystalline monoclinic ZrO_2. PL analysis revealed the novel emission peaks at 305 and 565 nm. The Raman spectroscopy confirmed the transformation of amorphous zirconium hydroxide to *m*-ZrO_2 with increase in temperature from 650 °C to 850 °C.

1. Introduction

Investigations on zirconium oxide (ZrO_2) have enlightened its large scale applications such as in catalysis [1], passivation and protective coatings [2] and fuel-cell technology [3] in accordance with its unique dielectric, physical, chemical, and optical properties. It has good chemical stability, low electrical conductivity, high melting point and high dielectric constant [4–6].

But literature showed that these mentioned properties of ZrO_2 are highly dependent on synthesis method. The reports available on the methods of synthesis of zirconium oxide gel are based on the use of zirconium alkoxides [7,8], mineral zirconium salts and electrolysis of zirconium chloride salts [9]. As compared to other methods, the sol-gel method is simple and economic and hence commercially important. Liu et al. [10] have prepared ZrO_2 nanocrystals by precipitation method. They have revealed that the phase transformation of ZrO_2 nanopowder occurs from tetragonal phase to monoclinic as calcination temperature increases from 500 °C to 1200 °C. Wang et al. [11] have reported a novel method for the preparation of ZrO_2 precursor through hydrolysis and polymerization. Xie et al. [12] have demonstrated that at room temperature the monoclinic zirconium oxide (*m*-ZrO_2) with high surface areas can be prepared by exposing tetragonal zirconium oxide (*t*-ZrO_2) to water vapor. The Pechini-type sol-gel process was reported by Lin et al. [13] to prepare ZrO_2 nanopowder. The phase transition from tetragonal to monoclinic was observed in the annealing process. Wang et al. [14] have optimized the conditions to prepare pure *t*-ZrO_2 structure. They have further examined the impacts of hydrated surface structure on the stabilization of *t*-ZrO_2. Zheng et al. [15] have synthesized nanocrystalline ZrO_2 by the L-lysine assisted hydrothermal method. They showed the coexistence of monoclinic and tetragonal phases of ZrO_2 on the basis of the selection of the synthesis parameters. Chepurna et al. [16] in 2011 synthesized hydrated zirconium oxide by sol-gel process. Chang et al. [17] have prepared mesoporous spherical ZrO_2 by sol-gel method with $ZrOCl_2{\cdot}8H_2O$ precursor followed by annealing at 500 °C in air. Chintaparty [18] has synthesized ZrO_2 nanoparticles by hydrothermal method at different calcinatation temperatures. Keukeleere et al. [19] have synthesized ZrO_2 nanocrystals by solvothermal reaction of benzyl alcohol. They have shown that crystallographic phase change of ZrO_2 occurs from pure cubic to pure monoclinic by changing the reaction mechanism via different zirconium precursors. Pure cubic zirconium oxide (*c*-ZrO_2) nanocrystals were obtained by using zirconium acetate, ethoxide and propoxide

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http://dx.doi.org/10.1016/j.mssp.2017.09.036
Received 8 June 2017; Received in revised form 27 September 2017; Accepted 28 September 2017

while pure *m*-ZrO_2 nanocrystals were obtained by using zirconyl chloride ($ZrCl_4$). Many methods of synthesis of ZrO_2 are available in the literature. Solvothermal and some sol–gel methods require an additional crystallization step at high temperatures and produce poorly crystalline particles which results into highly agglomerated ZrO_2 nanocrystals. However, other methods require long reaction times, high temperatures and also suffer from the formation of mixed ZrO_2 phases.

The objective of the present work was to synthesize pure monoclinic zirconium oxide by sol-gel technique without using any sophisticated setup and study the influence of annealing on the optical and structural properties of nanocrystalline monoclinic zirconium oxide. The effect of annealing temperature on structural, morphological and optical properties of *m*-ZrO_2 synthesized by sol-gel method is discussed.

2. Experimental section

The chemicals, zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), ethylenediaminetetraacetic acid (EDTA) and ammonium hydroxide (NH_4OH) supplied by SRL, Mumbai were used for synthesis.

2.1. Reaction mechanism

The reaction mechanism of the formation of zirconium oxide precursor has already been explained by Wang et al. [11]. In the present work, we have modified the concentration of reagents by keeping the basic reaction mechanism same to achieve the desired product. The precursor of zirconium oxide was formed through hydrolysis and polymerization by the reaction between zirconyl chloride octahyadrate and EDTA in ammonia solution via sol-gel method. The tetramer $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$ was formed through the hydrolysis of zirconyl chloride octahydrate.

$$4ZrOCl_2 + 24H_2O \rightarrow [Zr_4(OH)_8(OH_2)_{16}]^{8+} + 8ClO_4^- \quad (1)$$

The ionized complexing agent forms when ammonium hydroxide (NH_4OH) reacts with EDTA a complex compound R $(COOH)_n$) i.e.,

$$R(COOH)_n + nNH_4OH \rightarrow R(COO^- + NH_4)_n + nH_2O \rightarrow R(COO^-)_n + nNH_4^+ + nH_2O \quad (2)$$

The ionized complex agent reacts with the tetramer $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$ to produce a large complex compound i.e.,

$$[Zr_4(OH)_8(OH_2)_{16}]^{8+} + R(COO^-)_n \rightarrow [Zr_4(OH)_8(OH_2)_{16-n}(-OOC)_n R]^{8+} + nH_2O \quad (3)$$

Or

$$[Zr_4(OH)_8(OH_2)_{16}]^{8+} + R(COO^-)_n \rightarrow [Zr_4(OH)_{8-n}(OH_2)_{16}(-OOC)_n R]^{8+} + nOH^- \quad (4)$$

The complex product exhibits the characteristics of the solution on polymerization. The zirconium complex particles are formed as

$$2HOZrOCOR(COO^-)_{n-1} \rightarrow HOZrOCOR(COO^-)_{n-2} \quad COOZrOCOR(COO^-)_{n-1} + OH^- \ldots \rightarrow polymer \rightarrow particle \rightarrow sol\text{-}gel \quad (5)$$

Finally, the zirconium complex compound was annealed to obtain the zirconium oxide fine powder.

2.2. Synthesis

To prepare zirconium oxide, 100 ml of 0.1 M zirconyl chloride octahydrate solution was prepared in distilled water and kept at room temperature. Then, 100 ml of 0.125 M EDTA solution was mixed with 20% NH_4OH in 100 ml of distilled water to form an ionized complexing agent. Further, the solution of zirconyl chloride and ionized complexing agent were mixed together to start the reaction. At 60 °C, the solution was further stirred for 4 h. For several times, the obtained product was washed with distilled water. It is then dried in an incubator at 60 °C for 72 h to obtain the end product. The as-synthesized powder sample was then annealed at 650 °C, 750 °C and 850 °C for 2 h to obtain fine zirconium oxide nanopowder at these temperatures.

2.3. Characterization

The powder X- ray diffraction data recorded by X-ray diffractometer (XRD, Rigaku "D/B max-2400", $\lambda = 1.54$ Å) was analyzed to investigate crystal structure of ZrO_2. The morphological and elemental analyses were performed by scanning electron microscopy (SEM, JEOL-JSM 6360-A) and energy-dispersive X-ray spectroscopy (EDX), respectively. The UV- vis absorption spectra of ZrO_2 was measured by UV–vis spectrometer (JascoV-670) in the wavelength range 200–800 nm. The FT-IR spectroscopic studies were performed using FT/IR-6100 type A spectrometer in transmittance mode in the range from 400 to 4000 cm^{-1}. Photoluminescence (PL) spectra were recorded at room temperature by using a fluorescence spectrophotometer (SPEX Fluorolog-2). Raman spectra were recorded using a Jobin Yvon Horibra LAB RAM-HR spectrometer equipped with a He-Ne laser. The excitation wavelength is 632.8 nm and output powder is 50 mW. The resolution of the spectrometer is 1 cm^{-1}.

3. Results and discussion

3.1. X- ray diffraction analyses

Fig. 1 shows the X-ray diffraction patterns of as-synthesized and annealed ZrO_2 nanopowder. The spectrum of as-synthesized ZrO_2 powder shows broad peaks centered around $2\theta = 30.24°$ and 53.12° which confirms its amorphous nature. However, the annealed ZrO_2 nanopowder showed crystalline nature with lattice parameters $a = 5.312$ Å, $b = 5.212$ Å, $c = 5.147$ Å, and $\beta = 99.218°$. The observed XRD data is in good agreement with the standard data (JCPDS 37-1484) [20,21] (Table 1). The spectrum of annealed ZrO_2 powders showed that the powder crystallinity increases with annealing [22]. After annealing at 650 °C, 750 °C and 850 °C for 2 h the powder samples were totally decomposed to ZrO_2 showing (−111), (111), (200) and (022) peaks due to its monoclinic phase [10,12]. Here, no phase transformation was observed with annealing which generally occurs at higher annealing temperature [12,13,17,19]. The major peaks due to monoclinic ZrO_2 appeared at $2\theta = 28.298°$, 31.614°, 34.207° and 50.247° for the sample annealed at 650 °C, $2\theta = 28.471°$, 31.767°, 34.416° and 50.312° for 750 °C and $2\theta = 28.478°$, 31.674°, 34.388° and 50.368° for 850 °C [13,23,24]. However, many published reports have shown that the surface energy theory fails to explain the evolution of

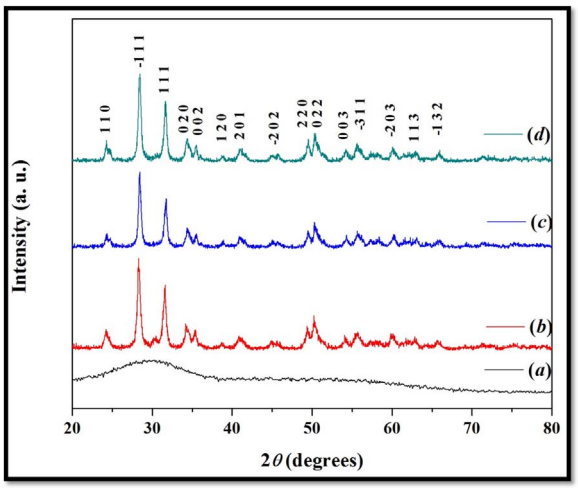

Fig. 1. XRD pattern of ZrO_2: (*a*) as- synthesized, (*b*) annealed at 650 °C, (*c*) annealed at 750 °C and (*d*) annealed at 850 °C.