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Dependence of precursor composition on patterning and morphology of sol–gel soft lithography based zinc zirconium oxide thin films

Susanta Bera, Moumita Pal, Saswati Sarkar, Sunirmal Jana*

Sol–Gel Division, CSIR-Central Glass and Ceramic Research Institute, 196 Raja S.C. Mullick Road, P.O. Jadavpur University, Kolkata 700 032, India

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ABSTRACT

Array-like surface patterned zinc zirconium oxide thin films (135–163 nm thickness) on soda lime silica glass substrate were prepared by sol–gel soft lithography from the precursor solutions (8 wt% equivalent metal oxides) having zinc acetate dihydrate (ZA) and zirconium oxychloride octahydrate (ZOO = 0–100 mol% w.r.t. ZA) in ethanol-2-butanol medium with acetylacetone. The ZOO concentration in solutions strongly influenced the pattern formation, crystallinity, morphology and optical property of the films. The films were crystalline in nature and enriched with only h-ZnO or a mixture of h-ZnO and c-ZrO_2 below 55 mol% of ZOO content. On increasing ZOO concentration, a systematic change in morphology of h-ZnO nano/micro crystals from spherical to rod-shaped to sunflower-like particles was evident from electron microscopes (FESEM and TEM). Below 30 and above 65 mol% of ZOO, light surface patterns formed. However, the films from 30 to 65 mol% ZOO containing solutions evident distinct surface patterns with average periodicity, 1.5 μm and peak height, 20–70 nm by AFM measurements. The films were also characterized by UV–vis and FTIR spectral studies. Water and chloride contents from ZOO in the precursor solutions found to play a key role for generation of the film characteristics.

1. Introduction

Zinc zirconium oxide (ZZO) thin films are attractive to the materials researchers owning to their important properties and applications (e.g. sensing, ferromagnetic, transparent conducting, good UV shielding, etc.) [1–3]. The material can be used [4] for hot corrosion resistance and thermal barrier protection. It has high visible transmission, large band gaps, excellent surface adherence and hardness on several substrates. The applications of ZZO films could be extended for the surface patterned [5–8] thin films. However, the study on zinc zirconium oxide thin films are scanty [3,4,9]. Hayashi et al. [3] studied sol–gel based ZnO–ZrO_2 films from zinc acetate dihydrate and zirconium n-propoxide as ZnO and ZrO_2 sources respectively in presence of monoethanolamine as complexing agent by a single step coating process and showed the effects of ZrO_2 addition (Zn/Zr = 0–40 molar ratio) on the microstructure (spherical clusters), crystallization and optical properties (like ultraviolet ray shielding, visible transmission). Zr doped (0–3 at% w.r.t. Zn) transparent conducting ZZO thin films [9] consisted of polycrystalline hexagonal ZnO with change in the orientation from ⟨1 0 0⟩ to ⟨1 0 1⟩ to ⟨0 0 2⟩ plane on increasing Zr content. They showed the film morphology, band gap and electrical resistivity depends on Zr content. However, pulse laser deposited [1] ZZO films having 40–90 wt% of ZrO_2 consisted of cubic zirconia and were insulating at room temperature but semiconducting above 677 °C.

In sol–gel ZnO thin films, surface morphology which could inevitably change the film properties [10–12] mainly depends on the starting materials [13], composition and chemistry of sol/solution [14], depositions variables such as deposition speed, curing temperature and atmosphere [15]. The study in this respect can help us to reveal some new type of surface features which could be useful to explain the experimental results vis-à-vis their applications in advanced electronic and opto-electronic devices [16]. Moreover, additive in the precursor solution plays an important role in tailoring film surface morphology. For example, addition of low amount of zirconium oxide to ZnO results in improvement of film surface microstructure [4] but high amount might form different morphologies.

Now-a-days, a cost effective soft lithography (e.g. capillary force lithography) is well known for fabrication of order structure on the thin film surface for various applications such as photovoltaics, super capacitors, biological sensors and electrodes, and various other electronic and optical devices [17]. Inorganic oxide thin film system would be patterned [18] from a suitable precursor solution by soft lithography. However, in multi oxides film system many difficulties [19] are to be faced in comparison to bulk to have specific morphology and other characteristics, favourable for obtaining defect free, high fidelity and structurally stable patterned films

* Corresponding author. Tel.: +91 33 23223405, fax: +91 33 2473 0957.
E-mail addresses: sjana@cgcri.res.in, janasunirmal@hotmail.com (S. Jana).

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which would require for device fabrication. Although, the patterned films on single oxide systems (e.g. SnO_2, ZnO, ITO, TiO_2) are known [20,21] but a few reports are available [18,20,21] on multi oxides film. Any how, to the best of our knowledge, no systematic study is available on patterning of zinc zirconium oxide, a multi oxides film system.

In the present work, we report the effect of zirconium oxychloride octahydrate (ZOO) content in precursor solution upon surface patterning and morphology of zinc zirconium oxide thin films (ZZO) on soda lime silica glass by soft lithography. The crystallinity and optical property of the films were also characterized. The precursor solutions for ZZO film formation were prepared from zinc acetate dihydrate (ZA) and ZOO (0–100 mol% w.r.t. ZA) at a fixed equivalent oxides content (8 wt%) in ethanol-2-butanol medium using acetylacetone as stabilizer.

2. Experimental

2.1. Preparation of precursor solution

All reagents were used as received. The precursor solutions for zinc zirconium oxide (ZZO) thin film on soda lime silica glass were made by using zinc acetate dihydrate (ZA, Sigma–Aldrich, ACS reagent ≥99%) or zinc chloride (ZC, Sigma–Aldrich, ≥98%) and zirconium oxychloride octahydrate (ZOO, Indian Rare Earths Ltd., >99%) or zirconium propoxide (ZIP, Fluka, ∼70% in propanol) as the sources of ZnO and ZrO_2, respectively varying ZOO content from 0 to 100 mol% w.r.t ZA in ethanol (Merck, Purity≥99.5%) – 2-butanol (Merck, assay ≥99%) medium (ethanol: 2-butanol = 1.15, vol. ratio). Initially, requisite amount of ZA/ZC and ZOO/ZIP were dissolved in ethanol by stirring followed by drop-wise addition of acetylacetone (acac, Merck, assay ≥98%) as a solution stabilizer (acac: ZA = 1.5, mol ratio). Finally, adequate amount of 2-butanol was added to the aliquot which resulted a homogeneous solution after continuous starring for 4 h. The solutions were designated as SZZR00, SZZR05, SZZR10,. . ., SZZR100 according to the content of ZOO from 0, 5, 10,. . ., 100 mol% (within 5 mol% interval) respectively. The solutions (equivalent to SZZR25) were also prepared from zinc chloride (ZC) and zirconium (IV) propoxide (ZIP). These were designated as SZZR25S′ and SZZR25S″ respectively. The equivalent metal oxides weight percentage (wt%) of all the solutions was kept fixed at 8.0.

2.2. Deposition of films

As-prepared solutions did not produce homogeneous films on to soda lime silica glass substrate (microscopic glass slide, Riviera, India, dimensions: 76.2 mm × 25.4 mm × ∼1.0 mm); however, after aging for 48 h, these generated homogeneous films on cleaned [13] glass substrate. The film deposition was made by dip coating (Dip Master 200, Chemat Technology Inc., USA) technique (withdrawal speed, 18 cm/min). As-deposited films were immediately used for fabrication of array-like surface patterns.

2.3. Fabrication of array-like surface patterns

Initially, PDMS (polydimethylsiloxane) stamp containing the negative replica of a commercially available compact disc (CD) as master was prepared [22]. The stamp was used to transfer the pattern (array-like) of the master onto the as-deposited film by pressure less/low pressure capillary force soft lithography technique. The chemical inertness of PDMS stamp towards the precursors for the film formation allowed for sub-micron (periodicity ∼1.5 μm and ∼120 nm height) pattern replication. The details of patterning scheme are given in our previous report [22]. Finally, the zinc zirconium oxide patterned films were resulted after curing the patterned gel films at 450 °C for 1 h (rate of heating, 1.5 °C/min) in air. The non-patterned films were also prepared from the precursor solutions maintaining the same film deposition and curing conditions. The coated cured patterned films were designated as ZZR00, ZZR05, ZZR10,. . ., ZZR100 from SZZR00, SZZR05, SZZR10,. . ., SZZR100 precursor solutions respectively whereas the films derived from SZZR25S′ and SZZR25S″ were designated as ZZR25S′ and ZZR25S″ respectively.

The above preparations were made in 10,000+ clean room with a relative humidity, 45–50% at 25 ± 2 °C.

2.4. Characterizations

Physical thickness (T) and refractive index (RI) of ZZO films were measured using a spectroscopic Ellipsometer (J. A. Woollam) at wavelength, 632.8 nm. The T and RI were found to increase with ZOO concentration in the precursor solutions. These were 135–163 nm (T) and 1.69 to 1.88 (RI) for ZZR00 to ZZR80 films respectively. The film surface morphology (surface feature including shape and size of particles as well as the presence of array-like patterns) and tentative metal contents (Zn and Zr) were analyzed by FESEM and FESEM–EDS (ZEISS, SUPRA^{TM} 35VP) respectively. Atomic force microscope (Nanonics, Israel NSOM AFM) was used to find out the average peak height of the patterns from their respective line scan profiles. TEM/HRTEM and TEM–EDS measurements were made by Tecnai G^2 30ST (FEI) electron microscope operating at 300 kV from the scratched off film onto 300 mesh carbon coated cupper grid for determination of shape and size of particles, crystal phase, content of metals etc. X-ray diffraction (XRD) study of the films was done by Rigaku SmartLab using Cu Kα radiation (1.5406 Å) operating at 9 kW in the diffraction angle (2θ), 25–70°. The crystallite size [13] was also calculated using Scherrer's equation. UV-Vis-NIR spectrophotometer (Shimadzu UV-PC-3100; photometric accuracy: transmission ±0.3%, wavelength resolution, 0.10 nm) was used to measure UV–vis transmission spectra of the films. Substrate corrected FTIR vibration spectra of the films were recorded using a FTIR instrument (Nicloet 5700, USA, wavenumber accuracy: ±4 cm^{-1}). The pH of solution at room temperature (∼30 °C) was checked with the help of Systronics, India make pH meter (model 361).

3. Results and discussion

3.1. Phase structure of films

The XRD reflections (Fig. 1a) of zinc zirconium oxide patterned thin films derived from the precursor solutions containing up to 25 mol% of ZOO revealed only hexagonal ZnO (h-ZnO) (JCPDS card 36-1451) whereas metastable cubic-ZrO_2 (c-ZrO_2) [23] along with h-ZnO appeared from ∼30 to 50 mol% of ZOO. However, the films derived from ≥55 mol% ZOO containing solutions were found to be XRD amorphous. We measured the size of h-ZnO and c-ZrO_2 crystallite at 2θ values corresponding to ⟨1 0 0⟩ and ⟨1 1 1⟩ planes respectively using Scherrer's equation [13]. The crystallite size (Fig. 1b) of h-ZnO found increased from 5.4 to 11.6 ± 0.5 nm when ZOO concentration enhanced from 0 to ∼35 mol% and then decreased. Whereas the crystallite size of c-ZrO_2 remained within 6–8 nm in the XRD crystalline films. This could be explained [24] on the basis of increasing water and chloride concentrations from ZOO (discussed later) used in the precursor solutions. It was important to mention that although the ionic size of Zr(IV) (0.84 Å) is larger than Zn(II) (0.74 Å) still an adequate amount of Zr(IV) could be expected to substitute [2] Zn(II) in ZnO lattice which would result a greater lattice distortion (enhancement of 'c' in h-ZnO) and more the substitution more would be the distortion. In this study, the value of 'c' measured from the respective XRD peaks along ⟨0 0 2⟩ plane found