Chemical Behaviour of Zirconium Oxychloride Octahydrate and Acetic Acid in Precursor Solution for Zirconia Film Formation on Glass

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Abstract. Precursor solutions for zirconia films on soda lime silica glass substrate were prepared from zirconium oxychloride octahydrate (ZOO) and acetic acid (HOAC) maintaining the mol ratios, [HOAC]/[ZOO] = 2, 4, 6, 8 and 10. A characteristic UV absorption band at ~280 nm in the ~120 h aged precursor solutions was identified for acetate group of the zirconium acetato complexed species. The presence of acetate ligand coordinated with either ZrOOH⁺ or [Zr₄(OH)₈]⁸⁺ or with both was predicted by the studies of UV spectra of aged solutions and FTIR spectra of unbaked films on silicon wafer. Dipping technique was followed for film formation. Thicknesses and refractive indices of the baked (450 ± 5°C) films were in the ranges 1818 ± 20 Å and 1.702-1.762 respectively. The positive SIMS experiment on two typical films baked at 450 ± 5°C derived from the precursors with [HOAC]/[ZOO] = 2 and 6, detected the ionic species, Zr⁺, ZrO⁺, ZrO₂⁺, Na⁺, Ca⁺, Fe⁺, H⁺ while the negative SIMS detected O⁻ and Cl⁻. The relative contents of the ionic species with respect to Zr⁺ were dependent on the acid content of the precursors. Reflection (%) of the baked films in the UV region was also dependent on the acid content of the precursors. Electron diffraction pattern of the typical baked film derived from the precursor with [HOAC]/[ZOO] = 2 exhibited meta-stable cubic phase of zirconia and the grains were found to be elongated (aspect ratio, 2.00-2.33).

Keywords: zirconium oxychloride octahydrate, zirconia film, FTIR spectroscopy, precursor chemistry, SIMS, TEM

1. Introduction

Various starting materials have been used for preparation of zirconia thin film in different coating techniques. Optical properties of the zirconia film were different in most cases [1-5] because of a number of factors such as starting material, substrate, processing temperature etc. which are not usually same. The predominant factor is the chemical behaviour of starting material which controls the property of the developed film. As for example, zirconium oxychloride octahydrate was used as starting material for zirconia film formation in a few cases [4-6]. Chemical behaviour of the starting material in the precursor solutions was not studied although optical properties of the films were found to be different. However, little work [7] has been done on the preparation, properties and structure of complexed species in aqueous solution. In actual practice, precursor solution contains alcoholic solvents in addition to water for maintaining proper viscosity and wettability [5, 8] for film formation. Usually one zirconyl ion co-ordinates to 1-2 moles of acetate ion [7, 9] in aqueous medium while in non-aqueous medium it may co-ordinate to even four acetate ion [9]. Hence, if a mixed solvent system of water-alcohol be used, the chemical behaviour of acetate ion with the zirconium species, [Zr₄(OH)₈]⁸⁺ and ZrOOH⁺ will probably differ and this study with the help of UV spectral analysis of the precursors seems not reported earlier. Effect of the precursor on the properties of zirconia film was also not studied in detail [5, 6]. This work deals with UV and FTIR spectral studies of the precursor solutions to understand the interaction of acetic acid (as a complexing agent) with zirconium oxychloride.
octahydrate. This paper also presents the characterization of the films developed from the precursors by UV-visible and FTIR spectral, SIMS and TEM studies.

2. Experimental

2.1. Preparation of Precursor Solution

Recrystallized zirconium oxychloride octahydrate [ZOO] (Indian Rare Earths Ltd., India), distilled ethyl alcohol (Bengal Chemical, India, dehydrated), distilled 2-butanol (E. Merck India Ltd., for synthesis), nitric acid (Ranbaxy Laboratories Ltd., India, AR), glacial acetic acid [HOAC] (E. Merck India Ltd., GR) and deionized water were mixed in requisite quantities to prepare solutions (series A) of varying [HOAC]/[ZOO] mol ratios as shown in Table 1. The wt% equivalent ZrO₂ in the solutions was 2.0 in all cases. The solutions were aged for about 120 h in order to make ready for homogeneous coating.

2.2. Preparation of Zirconia Films

Soda lime silica glass (Microscopic slide, Blue Star, pic-2, dimensions: 70 mm × 20 mm × 1.5 mm) substrate was thoroughly cleaned [10] and used for coating by the dipping technique with a lifting speed of 18 cm/min in all the cases. Transparent oxide films were formed on both sides of substrate when the gel films were heated to 450 ± 5°C with a soaking period of 30 min. The rate of heating was 5°C/min. The films on soda lime silica glass substrate derived from the ~120 h aged precursor solutions A₁, A₂, A₃, A₄ and A₅ (Table 1) were designated as SLS₁, SLS₂, SLS₃, SLS₄ and SLS₅ respectively. Films SW₁, SW₂ and SW₃ were also prepared on cleaned silicon wafer at same speed using the aged solutions A₁, A₃ and A₅ respectively and baked in similar conditions, and the baked films were designated as SW₄, SW₅ and SW₆ respectively.

2.3. Characterization of Solutions

To characterize the characteristic UV absorption bands of solvent mixture-nitric acid (additives) in the precursors, systematic solution spectra of the additives in dehydrated ethyl alcohol taken as reference medium were recorded with a UV-visible spectrophotometer (Hitachi, U 3210, instrument resolution: wavelength accuracy = ±0.3 nm, photometric accuracy = ±0.004 Abs., ±0.3%T). The concentration of the additives in the reference medium was kept in the range 10⁻³-10⁻⁴ M. UV spectra of the freshly prepared and ~120 h aged solution were also recorded. Concentration of ZOO in the solution was 10⁻² M. Viscosity of the aged solution was measured with a Brookfield digital viscometer (LVTDV-II) using UL adaptor. Viscosity range in the solutions (A₁ to A₅) was found to be almost constant (2.47–2.67 cps).

2.4. Characterization of Films

FTIR spectra of the unbaked films and heat treated (at 450 ± 5°C) films on silicon wafer were recorded using a FTIR (Nicolet, 5PC) spectrometer in the wavenumber range 2000–650 cm⁻¹. Specular reflection (5° angle of incidence) spectra of the films were measured with a UV-visible spectrophotometer. Surface profile of the films was measured with a surface profile analyzer of FLM module (Dektak, Sloan). X-ray diffractograms of the films were obtained by a Philips PW1730 X-ray diffraction unit employed with nickel filtered CuKα radiation. The films were found to be X-ray amorphous. Microstructure of a typical film (SLS₁) was also studied by transmission microscopy (TEM) (JEOL, JEM-200C X). Film thicknesses and refractive indices of the baked films (SLS₁ to SLS₅) were measured with an auto-gain ellipsometer (L116B) equipped with a helium-neon laser having a beam wavelength of 6328 Å and 70° angle of incidence, and in conjunction with Hewlett Packard computer (HP 85B). The SIMS experiment were performed on SLS₁ and SLS₃ films, in the VG Micro Lab, using Ar⁺ primary ion beam with an impact energy of 5.0 keV. The