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Preparation of alumina films from a new sol–gel route

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Abstract

A new sol–gel route was applied to prepare alumina films by using $AlCl_3 \cdot 6H_2O$ as starting material and acetylacetone (AcAc) as additive. Our research results show that AcAc and aluminum form a complex compound in the sol, which makes the sol very stable. Meanwhile, the complex structure prevents the decomposition going on quickly during the sintering process and the obtained films are free of cracks. The as-prepared films were amorphous. When the sintering temperature reached up to 600°C, γ-Al_2O_3 began to form and was transformed to α-Al_2O_3 at temperatures over 1200 °C.

Keywords: Alumina film; Sol–gel method; Acetylacetone

1. Introduction

Films of alumina have numerous electrical, optical and wear-resistant applications. Many techniques are applied to prepare the materials, including physical vapor deposition (PVD) [1,2], chemical vapor deposition (CVD) [3–5] and sol–gel,etc. Among these, the sol–gel method is an emerging route with high promise for very homogeneous films, which can be formed at relatively low temperatures.

Generally, the aluminum alkoxides, such as aluminum sec-butoxide and aluminum iso-propoxide, are chosen to prepare alumina films by the sol–gel method [6–8]. However, these usual precursors are expensive for the fabrication of ceramics films and are harmful to people's health. It seems that the low-cost inorganic salts are not chosen as often as the alkoxides in the sol–gel method [9]. For the obvious advantages of the inorganic precursors over the alkoxide precursors, it is worth pursuing research on this field.

In order to disperse the inorganic salts in solvent to form a stable sol and eliminate the cracks often encountered in the sol–gel process, it is important to select a suitable additive. The acetic acid is the reagent in most common use [9–11]. However, the method requires a two-stage process: the hydroxide is precipitated from the inorganic salts;and the sol is then obtained by peptizing the precipitate. In the present work we select the β-diketone as the stabilizing reagent. By mixing the $AlCl_3 \cdot 6H_2O$ and acetylacetone (AcAc) in a suitable solvent, the stable sol was directly formed and high-quality alumina films were obtained from the sol.

2. Experimental

The starting material used was $AlCl_3 \cdot 6H_2O$. It was dissolved in ethanol. Acetylacetone (AcAc) was added to the solution as the chelating agent. The molar ratios of solvent and AcAc to the $AlCl_3 \cdot 6H_2O$ were 20 and 2, respectively. The mixture was stirred vigorously for several hours at room temperatures and the obtained solution became pale yellow clear sol.

Si(100) wafers were selected as the substrates. Before coating, the Si substrates were cleaned by ultrasonic treatment and dilute HF solutions. The dip-coating method was used for the preparation of the films. After dipping the substrate into the sol for a moment, and then pulling it up at a constant speed (about 4 cm/min), the resulting films were dried at room temperature for 15 min and then heated at 100°C for 30 min to form a dry gel film on the substrate. The same step was repeated several times. The films were sintered at several temperatures for 3 h to form alumina films.

The solution was analyzed by Fourier transform infrared spectroscopy (PE-1600 FTIR). The phase analysis of the thin films was performed using an X-ray diffractometer (Dmax-3B). The morphology and thickness of the films were examined by scanning electron microscopy (SEM)

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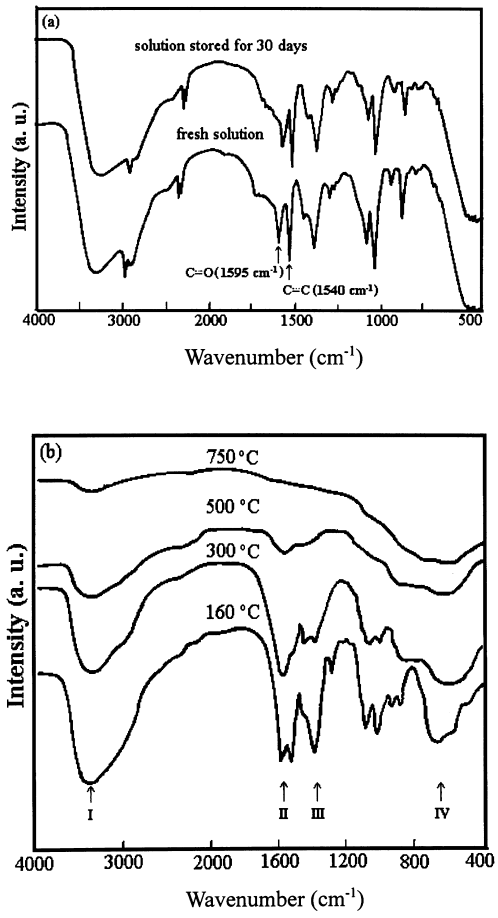


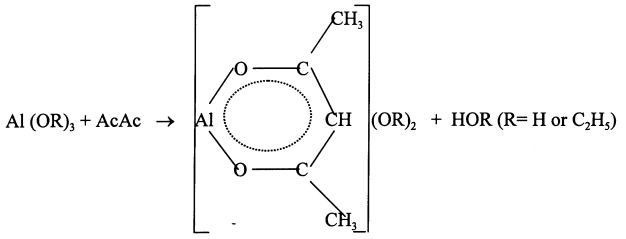
Fig. 1. Infrared spectra of the solutions (a) and the gel treated at various temperatures (b).

(AMAY 1910 FE). The reaction of the gel during the sintering process was studied by IR, DTA and TG.

3. Results and discussion

3.1. Sol solution analysis

The clear and colorless solution was obtained by dissolving $AlCl_3 \cdot 6H_2O$ into ethanol. Then AcAc was added to the solution and the pale yellow clear sol was formed after stirring the solution vigorously for several hours at room temperature. The sol is very stable without any large physical changes including color, viscosity and transparency when stored in atmosphere for several months. The IR spectra of the fresh precursor sol and the sol stored for 30 days are shown in Fig. 1a. There are almost no differences between the two spectra, which suggest that the solution is very stable against any chemical reactions. As we know, the β-diketones have the keto and enol forms and in the IR spectrum there are two characteristic peaks around 1700 cm^{-1} and 1620 cm^{-1} assigned to C═O stretching of keto and enol types. In Fig. 1a the two characteristic peaks corresponding to the AcAc completely disappear, and two new sharp peaks located at 1595 cm^{-1} and 1540 cm^{-1} appear. The peak at 1595 cm^{-1} can be assigned to C–O bonding with Al to form a complex, and the 1540 cm^{-1} peak to C–C bonds of the six-membered ring of the complex [8,12]. It is well known that Al^{3+} is easily hydrolyzed or alcoholyzed. When the $AlCl_3 \cdot 6H_2O$ is dissolved in the ethanol solutions the hydrolysate or alcoholate of aluminum may be formed. As AcAc is added to the solution the chelate complex between Al and AcAc will be formed due to the strong chelating ability of AcAc with aluminum. Accordingly, the following reaction may be inferred as follows:



The above-mentioned high stability of the sol can be attributed to the AcAc chelating effect, which prevents the hydrolysis and condensation of aluminum from forming gel network quickly.

3.2. The reaction of gel during sintering

IR spectra of the bulk gel treated at various temperatures are shown in Fig. 1b. The dry gel at 160°C has four main strong absorption bands at 3400 cm^{-1} (band I), 1595 cm^{-1} and 1540 cm^{-1} (band II), 1394 cm^{-1} (band III) and 620 cm^{-1} (band IV), which correspond to ν(O–H) and ν(C–H), ν(C–O) and ν(C═C), δ(–CH3), and ν(Al–O)[13]. With increasing temperatures the absorption strength of the organic groups (bands I–III) decrease gradually. However, at 500°C the intensity of band III is still very large, which indicates the high stability of the six-member ring of the complex. For the sample calcined at 750°C, complete absence of the peaks was observed except for

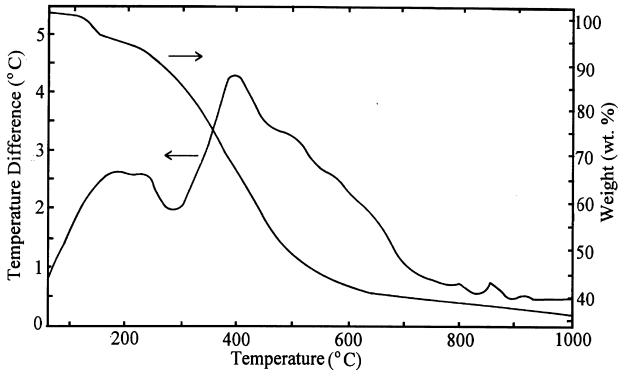


Fig. 2. Thermogravimetry (TG) and differential thermal analysis (DTA) of alumina bulk gels.

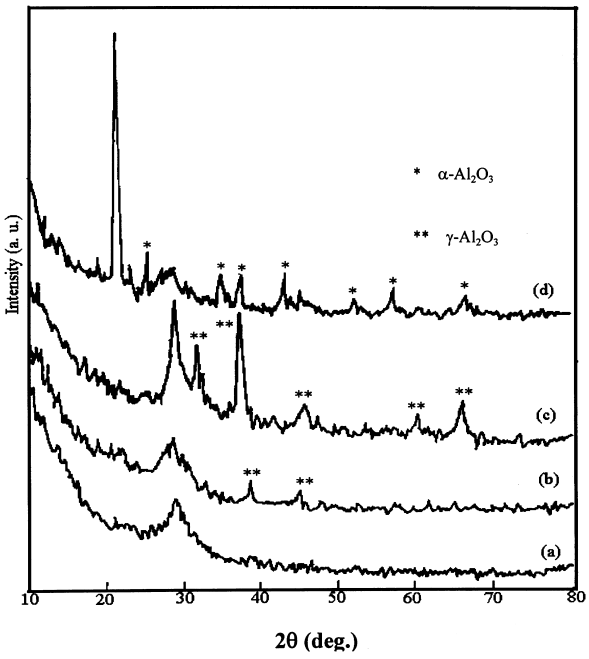


Fig. 3. X-ray diffraction patterns of alumina films sintered at different temperatures: (a) 400°C; (b) 600°C; (c) 800°C; (d) 1200°C.

the broad band around 600 cm^{-1}due to Al–O vibrational modes.

DTA and TG curves for the alumina bulk gel are shown in Fig. 2. There is a small weight loss initiating at 80°C for desorption of the adsorbed moisture and the evaporation of the solvent. Another big consecutive reduction of weight initiating at 150°C is due to the decomposition of organic groups in the gel [6]. An exothermic peak around 400°C in the DTA curve accompanies this weight loss. In fact, this big exothermic peak is made up of a few small peaks. The result suggests that the decomposition of the organic groups may go on progressively, which is conformed by the above IR spectra. Around 800°C there is also a small exothermic peak due to the crystallization process of alumina. The above results imply that during the sintering process the organic groups begin to decompose from 150°C and decompose completely around 700°C.

3.3. The structure and morphology of alumina films

The XRD patterns of the films sintered at different temperatures are shown in Fig. 3. These patterns show that the films are amorphous until the sintering temperature rises to 600°C. At 600°C γ-Al_2O_3 is formed and it is transformed to α-Al_2O_3 above 1200°C [9,10].

The thickness of the alumina films sintered was obtained by the cross-sectional view of the samples by SEM. The film thickness varied from 0.3 to 0.9 μm, corresponding to the different dip-coating times. The surface morphology of the films obtained from the above solution (solution A) sintered at 800°C for 3 h is shown in Fig. 4a. From the photograph we can see that the film is even, smooth and compact. No crystal grains were seen, which indicated that the crystal grains are very small. For comparison the solution without the AcAc additive (solution B) was prepared under the same conditions and the films obtained from the solution were prepared using the same procedure. The morphology of the film is shown in Fig. 4b. A lot of cracks, bumps and holes were observed in the films. From the two different results we can see that the AcAc may play a key role in the experiments. As mentioned above, the complex formed between the AcAc and aluminum was very stable and during the heat treatment the decomposition went on step by step, therefore the film grew fine and close without cracks.

4. Conclusion

By using $AlCl_3 \cdot 6H_2O$ as starting material and AcAc as additive, crack-free and smooth alumina films have been obtained. The XRD results show that the films are amorphous when the sintering temperature is below 400°C. The γ-Al_2O_3 begins to form at 600°C and it is transformed to α-Al_2O_3 above 1200 °C. The coating sol is very stable and the sintered films are free of cracks. The research indicates that AcAc and aluminum can form a complex compound in the sol. The compound with a stable chelating ring structure plays a key role in the sol and gel process, which makes

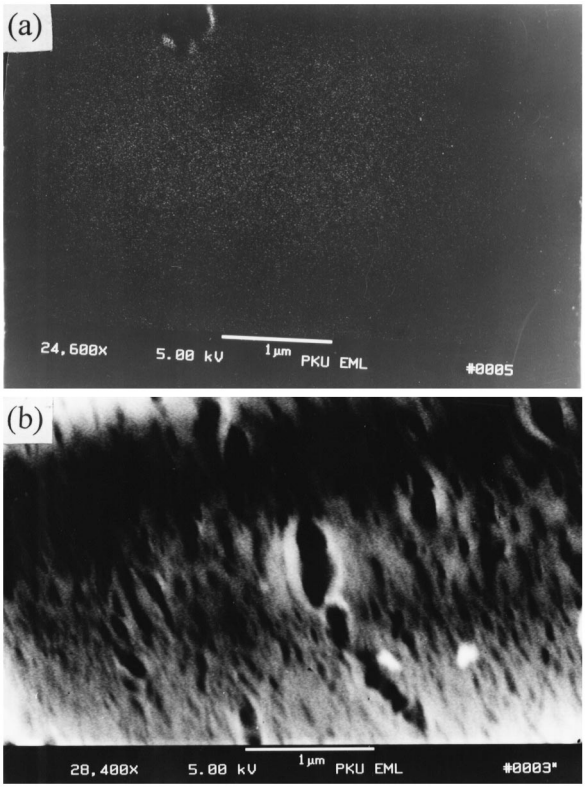


Fig. 4. SEM of alumina films sintered at 800°C for 3 h: (a) prepared from solution A; (b) prepared from solution B.

the sol stable enough and prevents cracks forming in the films during the sintering process.

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