Sol–Gel Processing of LaF_3 Thin Films

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ゾル–ゲル法を利用した LaF_3 薄膜の作製

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Lanthanum fluoride thin films were prepared on silica glass substrates by a sol–gel method using trifluoroacetic acid (TFA) as a fluorine source. A coating solution was produced from lanthanum acetate and trifluoroacetic acid dissolved in 2-propanol. Trifluoroacetate gel films were formed by spin coating the sol, which were converted to LaF_3 thin films by heat-treatment at 300–500°C for 10 min. The formation of LaF_3 is considered to result from the reaction between lanthanum ions and the fluorine species generated by the decomposition of trifluoroacetate ions at elevated temperatures. The film fired at 300°C had a smooth surface with a grain size of 30 nm. Cracks and voids were only observed in the films fired at 400 and 500°C. The films fired at 300 and 400°C exhibited transmittance of greater than 90% in the visible region.

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1. Introduction

Fluoride thin films have found numerous applications in optics,¹⁾ a well known example of which is the use of MgF_2 in anti-reflective coatings. Recent developments in optical devices have led to fluorides becoming increasingly important materials as immiscible, transparent matrices for functional fine particles or host crystals for luminescent ions.^{2),3)} Lanthanum fluoride is one of the most promising host crystalline materials for luminescent rare-earth ions such as Pr^{3+} , Nd^{3+} or Er^{3+} .⁴⁾ Since optical amplification is possible in such materials, an optical waveguide amplifier based upon rare-earth fluoride thin films has been proposed. Buchal et al.⁵⁾ have studied photoluminescence at 1.5 μm in YF_3 , LuF_3 and LaF_3 thin films doped with Er^{3+} ions and have concluded that LaF_3 is the most suitable as the host crystal. Deposition of fluoride thin films in their work was performed by evaporation of rare-earth fluorides from Knudsen cells in an UHV atmosphere.

The sol–gel coating technique has been utilized to prepare optical thin films of oxides.⁶⁾ The process is based upon the preparation of sols starting from metal alkoxides or carboxylates dissolved in organic solvents. The sols are coated on substrates and organic compounds are evaporated or decomposed by heating, resulting in thin oxide films. If the sols contain fluoro-organic compounds, metal fluorides may be formed by a reaction between metal ions and fluorine species generated by the decomposition of the organic compounds during the heat-treatment. Recently, we reported the sol–gel process through which magnesium fluoride thin films were directly prepared from sols containing trifluoroacetic acid (TFA; CF_3COOH) as a fluorine source.⁷⁾ Since alkaline earth fluorides are thermodynamically stable, their formation from trifluoroacetate sols is understood reasonably well. However, it is interesting to know whether this process can be made applicable to the preparation of rare-earth fluoride thin films. In the present report, we have examined the sol–gel process in preparing LaF_3 thin films.

2. Experimental procedure

1.76 g (equivalent to 0.005 mol) of $\text{La}(\text{CH}_3\text{COO})_3 \cdot n\text{H}_2\text{O}$ was dissolved in 15 ml of 2-propanol. 1 ml (0.0132 mol) of TFA (CF_3COOH) and an equal volume of H_2O were then

added, and the solution was stirred for 2 h at room temperature. The resultant sol was spin-coated on a silica glass substrate at 2650 rpm. The silica glass was then immediately placed in a furnace and fired at a constant temperature between 300–700°C for 10 min in air followed by quenching. This procedure was repeated further two times to obtain thin solid films.

Crystalline phases were identified by X-ray diffraction (XRD) analysis with a diffractometer equipped with a thin film attachment. The film thickness and refractive index were measured by ellipsometry. Chemical analysis of films was performed by X-ray photoelectron spectroscopy (XPS). The surface morphology of films was observed using a field emission scanning electron microscope (FESEM) and microscopic observation of the surface was performed using an atomic force microscope (AFM). The optical transmittance was measured with a Hitachi U–3300 UV-visible spectrophotometer.

3. Results and discussion

Figure 1 represents the XRD patterns for films produced by firing after each of the three coating procedure at one of five constant furnace temperatures. For the film fired at 300°C, weak and broad peaks indicative of LaF_3 are observed. The intensity of the LaF_3 peaks increases with increasing firing temperature to 500°C. From 600°C, the peaks associated with lanthanum oxyfluoride, LaOF , appear in addition to those of LaF_3 . At 700°C, LaF_3 ceased to be observable and an unknown phase, thought to be probably another form of a lanthanum oxyfluoride compound, appears in addition to LaOF . From these results, it is evident that LaF_3 thin films are produced when the gel films are fired at temperatures between 300 and 500°C. Ellipsometry indicates film thickness of 201, 219 and 174 nm in the LaF_3 films where the coating process, which was performed three times, involved firing at 300, 400, and 500°C, respectively.

Since the boiling point of TFA is 72.4°C, TFA ions will be coordinated to La^{3+} ions in the sols and gel films. This state of coordination is sustained until TFA decomposes, after which the generated fluorine species reacts with La^{3+} to form LaF_3 . The formation of LaF_3 was observed at 300°C in the TG/DTA and the XRD analysis of the dried

Fig. 1. XRD patterns of the films fired at 300–700°C for 10 min. The coating procedure was performed 3 times.

trifluoroacetate gel. This formation mechanism is considered to proceed at temperatures below 500°C.

The films were analyzed by XPS to determine oxygen content. Figure 2 shows the XPS spectra in the O1s region for the film fired at 500°C. La_2O_3 (99.99%) and LaF_3 (99.9%) powders were used as references. A weak peak is observed for the LaF_3 powder, supposedly resulting from adsorbed oxygen. A similar peak to this is observed for the film fired at 500°C. We cannot determine from XPS alone whether this peak results from either adsorbed oxygen or impurities. However, since this peak remained after Ar-etching of the film, it probably results from oxyfluoride or oxide impurities. The chemical analysis revealed the ratio of F/La equal to 2.74 and that of O/F equal to 0.46 for the film fired at 500°C. While it is questionable whether the O/F ratio is accurate, it is evident that the amount of oxygen is significant. Increases in film purity will be necessary in future investigations.

The surface morphology of the films was observed by FESEM. As shown in Fig. 3(a), the film fired at 300°C had a smooth surface with a fine microstructure absent of cracks or voids, and a particle size of about 30 nm. An increase in the heating temperature to 400°C, however, results in the formation of cracks as seen in Fig. 3(b). This may be attributable to the quenching after each firing. The

Fig. 2. XPS spectrum of the film fired at 500°C. Those of La_2O_3 and LaF_3 powders are also shown as references.

Fig. 3. FESEM photographs of the films fired at (a) 300°C, (b) 400°C and (c) 500°C. Each film consisted of 3 coats.

film fired at 500°C shows a considerably different morphology as seen in Fig. 3(c), with flake-like grains evident. The grain growth proceeds at this elevated temperature of 500°C, and accordingly many large voids are present in the film. It should be noted that the film heated at 300°C had poor adhesion to the substrates and low scratch resistance. These properties were improved by the firing at 400 and 500°C, but were still unsatisfactory. The improvement of the heating process, therefore, is necessary to obtain high mechanical strength.

The AFM observation was performed to examine the influence of coating time and heating temperature on the deposition process. As shown in Fig. 4(a), the film which involved a single coating process before firing at 300°C has a surface roughness of 20 nm. However, when the coating was repeated twice more under the same conditions, an increase in roughness to 40 nm was observed, as in Fig. 4(b). This is because the coating is being repeated on the already rough surface of the pre-coated LaF_3 film. The kiln temperature of 300°C is the minimum for ensuring the formation of LaF_3 in the present process. Surface smoothing, therefore, may not occur although the grains of LaF_3 are formed at this temperature. As shown in Fig. 4(c), the film coated three times and fired at 400°C has a smoother sur-

Fig. 4. AFM images of the films approximately $1000 \text{ nm} \times 1000 \text{ nm}$; (a) coated once and fired at 300°C , (b) coated 3 times and fired at 300°C , and (c) coated 3 times and fired at 400°C . The full scales of vertical bars are (a) 20 nm, and (b, c) 40 nm.

face compared to the film fired at 300°C . This is considered to reflect a surface transport between grains via surface diffusion or an evaporation-condensation process at the higher temperatures. However, since densification does not proceed in the surface transport process,⁸⁾ the film retains its porosity as can be seen from the figure.

AFM observation results suggest that the microscopic surface roughness is improved by increasing firing temperature. However, this can result in the formation of cracks as observed with the FESEM. Further investigation into the heat-treatment processes will be necessary to obtain a smooth surface without cracking.

The refractive indices at the 633 nm wavelength were measured to be 1.40, 1.39 and 1.34 for the films heated at 300, 400, and 500°C , respectively. These values are lower than the refractive index of LaF_3 , 1.55, previously reported.¹⁾ All the films in the present study, therefore, are very porous, which coincides with results from FESEM and AFM observation.

Figure 5 shows the optical transmittance spectra of the films. The films heated at 300 and 400°C exhibit transmittance of greater than 90–95% in the visible spectrum.

Fig. 5. Optical transmittance spectra of the films fired at 300 – 600°C .

Moreover, the wide range transparency of LaF_3 ⁵⁾ was unaffected in the region 200–900 nm for all the films prepared by the sol-gel process. However, the absorption edge in UV region shifts to longer wavelengths with increasing heating temperature to 500 and 600°C . This behavior is attributed to the conversion of the film from lanthanum fluorides to oxyfluorides and/or oxides at increased firing temperatures.

4. Conclusion

Transparent lanthanum fluoride thin films were prepared on silica glass substrates by a sol-gel process using trifluoroacetic acid as the fluorine source. Spin-coating the sols followed by firing the films at 300 – 500°C resulted in thin LaF_3 films. The films contained oxygen impurities. The surface of the film heated at 300°C was smooth with a grain size of 30 nm. By increasing the temperature, cracks and voids were formed in the films. These results indicate that refinement of the firing process is necessary to obtain smooth LaF_3 films of higher purity.

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