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Preparation and characterization of MgF_2 thin film by a trifluoroacetic acid method

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Abstract

The preparation of magnesium fluoride (MgF_2) thin films on silica glass substrates was studied by a trifluoroacetic acid (TFA) method using trifluoroacetic acid as a fluorine source. The coating solution was prepared by adding a mixture of magnesium ethoxide, isopropanol and TFA. MgF_2 thin films were obtained by heat-treatment of the gels-coated films below 500°C in air. Higher optical transmittance of the films was observed as compared to the substrate. Field emission scanning electron microscope (FE-SEM) observation revealed a particle size of less than 50 nm in the films. The formation process of MgF_2 from trifluoroacetate gels was discussed according to the results of the thermal analysis of the gel. © 1997 Elsevier Science S.A.

Keywords: MgF_2; Thin film; Trifluoroacetic acid; Transmittance; Microstructure

1. Introduction

Magnesium fluoride (MgF_2) has been widely applied as optical thin films [1], for example, as anti-reflective coatings on glasses, because of its high transparency, low refractive index and high chemical and mechanical stability. Recent requests to develop new optical devices make MgF_2 thin films of great importance as insulators and/or transparent matrix for functional materials such as ferromagnetic fine particles [2], nanocrystalline semiconductors [3] or organic electroluminescent molecules [4]. Metal/MgF_2 multilayer materials are also extensively studied [5]. The preparation of these composite materials is basically performed by physical methods such as physical vapor deposition, molecular beam epitaxy, reactive evaporation, etc.

The chemical routes, such as the sol–gel method, are commonly used to prepare optical thin films in the field of oxide materials. However, chemical preparation of fluoride thin films has not been adopted so far because of difficulty in handling fluorine sources, usually hazardous HF or F_2 gas. If similar chemical processes for fluoride thin films are developed by using alternative fluorinating reagents without cares, researches in MgF_2-based composite thin films can be much stimulated. As far as we know, only two works deals with the chemical route to MgF_2 thin films. Yoshino et al. [6] reported the solution method for MgF_2 thin films using basic magnesium carbonate as a starting material, trifluoroacetic acid (TFA) as a fluorine source and n-butyl acetate as solvent. Thomas [7] reported the colloidal suspension method to prepare porous fluoride thin films using HF as a fluorine source. To extend research in optical fluoride materials, development of novel chemical processes is of fundamental importance.

We propose here a new process for MgF_2 thin films with a view of applying it to the preparation of composite films with fine particles of metals. In the present report, we prepared MgF_2 thin films by a TFA method using magnesium ethoxide as a starting material, isopropanol as solvent and TFA as a fluorine source, and examined the formation process of MgF_2 from trifluoroacetate gels. The films were characterized by an observation of microstructure by field emission scanning electron microscope (FE-SEM) and a measurement of optical transmittance.

2. Experimental details

0.57 g (0.005 mol) of $Mg(OC_2H_5)_2$ (Wako) was dissolved in 15 ml of isopropanol (i-C_3H_7OH) (Dried). After adding 1 ml (0.0132 mol) of TFA (CF_3COOH) (Wako), the solution was stirred for 4 h at room temperature. The

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concentration of Mg was 0.31 M and the molar ratio of F/Mg was on the order of 8. The resultant solution was spin-coated on silica glass substrates at 2650 rpm. The coated films were heated at 300, 400, 500 or 600°C for 10 min in air immediately after coating.

The phase identification was done with an X-ray diffractometer equipped with a thin film attachment using CuK α radiation. The thickness of the films was measured with a Sloan Dektak II profilometer. The microstructure of the films was observed with an FE-SEM. It should be noted that we needed the samples prepared by repeating the coating procedure 5 times to make these measurements available.

The optical transmittance of the films was measured at wavelengths between 200 and 800 nm with a Hitachi U-3500 UV–visible spectrophotometer. The thermal analysis of gels, which was obtained by drying the coating solution at 80°C for 24 h, was performed with a Seiko TG/DTA30 system. In order to examine composition of the solution, the solvents were evaporated in vacuum and analyzed by a ^{1}H NMR.

3. Results and discussion

3.1. Characterization of MgF_2 thin film

According to the X-ray diffraction (XRD) analysis of the films, no diffraction peak was observed after the first coating procedure. Because this was attributed to the insufficiency of thickness of the films, the coating procedure was repeated 5 times. Fig. 1 shows the XRD patterns of the films after 5 cycles of the heat treatment at 300–600°C. The films start to crystallize at 300°C as shown in the pattern where broad and weak peaks at 27.5, 40.8, 44.0 and 53.8° due to MgF_2 appear. Peak intensity increases and peak width decreases gradually with increasing heat-

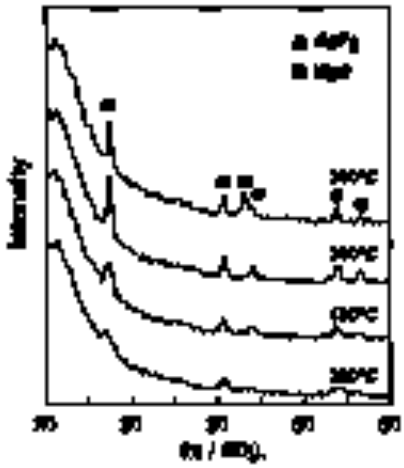

Fig. 1. The XRD patterns of the films after repeating the coating procedure 5 times. The coating temperature is 300, 400, 500 and 600°C.

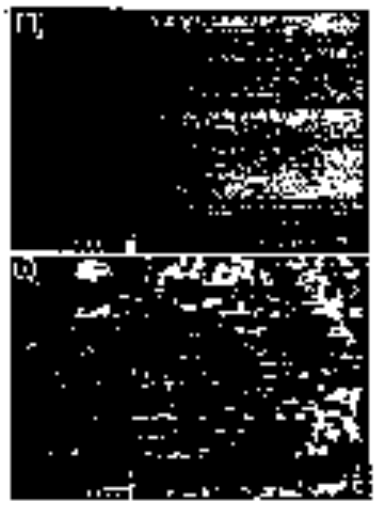

Fig. 2. The FE-SEM photographs of the films coated at (a) 400°C and (b) 500°C.

ing temperature up to 400 and 500°C, implying that the growth of MgF_2 grains proceeds with increasing temperature. At 500°C, peak intensity of MgF_2 decreases and diffraction peaks due to MgO appear, indicating that the formation of MgO competes with that of MgF_2 at this temperature. No MgF_2 was formed when the films were heated at temperatures higher than 700°C.

The FE-SEM photographs of the surface of the films heat-treated at 400 and 500°C (coated 5 times) are shown in Fig. 2. No grains can be observed in the film heated at 400°C. This is probably attributed to a small grain size less than 10 nm and/or dense packing of grains in the film, although a more extensive analysis is needed to determine the precise grain size. The thickness of this film was measured to be 0.36 μm with the profilometer. Grains of 20–30 nm in diameter, on the other hand, are clearly observed in the film heated at 500°C. The aggregation of grains is also observed, so the film is very porous. It can be said that the microstructure of MgF_2 thin films, is greatly dependent on the heating temperature.

The optical transmittance of the films is shown in Fig. 3. Note that these films were coated once. It is seen that the transmittance of the films heated at 500 and 400°C is higher than that of the silica glass substrate. The thickness of these films can be estimated to be less than 0.1 μm. These results demonstrate that the anti-reflection effect can be attained by the thin MgF_2 coating on silica glass due to the present grooves. The reason for the decrease in transmittance at lower wave lengths is not presently clear. For the films heated at 200 and 300°C, the transmittance below 450–500 nm is lower than that of the silica glass substrate. Noting that the film heated at 500°C is very porous as observed in FE-SEM, the decrease in transmittance results from the large degree of scattering of incident light by the presence of pores. In the film heated at 500°C, formation of MgO grains is also responsible to this decrease. From the above results, the heat-treatment below

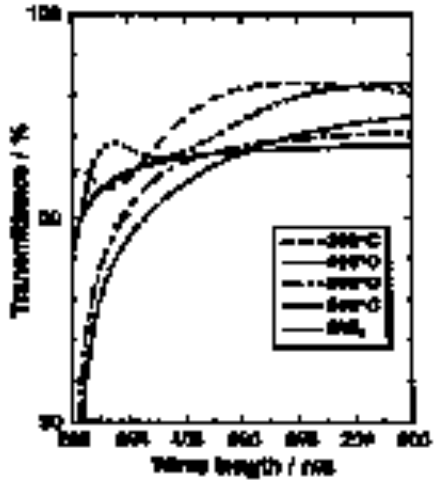

Fig. 3. The spectral transmittance spectra of the films heated at 300, 400, 500 and 700°C. The coating procedure was carried out once. The spectrum of the SiO_2 glass substrate is also shown.

400°C is necessary to obtain good optical property of MgF_2 thin films by the present process.

3.2. Formation process of MgF_2 from gel

In order to examine the thermal process from the gel films to MgF_2 films, thermal analysis was done for the gel obtained by drying the coating solution. Fig. 4 shows the TG/DTA curve of the gel. The exothermic peak is observed at 294°C. The weight loss occurs in two steps; below 270°C and between 270 and 310°C. To consider this result, the gels were heated to 250, 270 and 330°C in air and analyzed by the XRD. At 250°C, no diffraction peaks were observed, implying that the amorphous gel state was preserved. At 270°C, diffraction peaks due to MgF_2 appeared, and peak intensity increased at 330°C. Below 270°C, therefore, the weight loss is considered to be the thermal decomposition of the remainder of organic solvents.

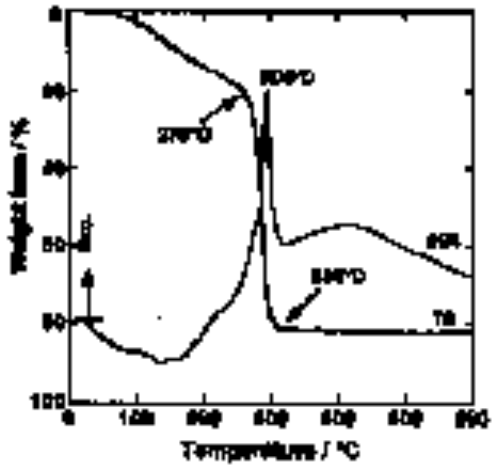

Fig. 4. The TG/DTA curve of the gel obtained by drying the coating solution.

Between 270 and 310°C, crystallization of MgF_2 from trifluoroacetate gels continues.

$Mg(OC_2H_5)_2$ was not dissolved completely in *i*-C_3H_7OH. After TFA was added, the transparent, colorless solution was obtained without any precipitation. According to the ^1H NMR analysis of the evaporated solvent from the solution, C_2H_5OH was detected in addition to *i*-C_3H_7OH. This suggests that the reaction between $Mg(OC_2H_5)_2$ and CF_3COOH or *i*-C_3H_7OH takes place in the coating solution. Noting that MgF_2 is formed at 300°C in spite of much lower boiling point of TFA or 72.4°C, the trifluoroacetate gel in which Mg^{2+} is coordinated by CF_3COO^- ions should be formed in the gel film. Two coordination sites around Mg^{2+} ions forming trifluoroacetate gel are considerable as left models in the following formulas:

$$Mg(OC_2H_5)(OCOCF_3) \rightarrow MgF_2 \quad (1)$$

$$Mg(OCOCF_3)_2 \rightarrow MgF_2. \quad (2)$$

The calculated values of weight loss in Eq. (1) and Eq. (2) are 66 and 75%, respectively. Fig. 4 shows that the weight loss between 270 and 310°C is 74%. This value is comparable to that of 75% in Eq. (2). Therefore, we consider that the trifluoroacetate gel is composed of $Mg(OCOCF_3)_2$ complexes and solvents. By heating the gel, it is assumed that the Mg^{2+} ions react with thermally activated fluorine in CF_3COO^- ions to form MgF_2 crystal. A detailed reaction mechanism is not taken at present.

Further works on the preparation of MgF_2-based composite films are now in progress.

4. Conclusion

MgF_2 thin films on the silica glass substrates were prepared by the TFA method using trifluoroacetic acid as a fluorine source. By heating the trifluoroacetate gel film at 300–500°C, MgF_2 thin films could be obtained. The particle size of MgF_2 increased with increasing heating temperature. The optical transmittance of MgF_2 thin films was higher than that of the silica glass substrate when they were heated at 300 or 400°C. On the formation process of MgF_2, it was considered that the coordination of trifluoroacetate ions to magnesium ions occurred in the solution, leading to the trifluoroacetate gel films after coating. By thermal decomposition of the gel film, MgF_2 thin films could be obtained at relatively low temperatures without formation of MgO.

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