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Preparation and etching processing of planar thin film of Pr^{3+}-doped fluorozirconate glass

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Planar thin-films of a $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ composition were successfully prepared from $Zr(hfa)_4$, $Ba(hfa)_2(tg)$, $Pr(fod)_3$ and NF_3 by an electron cyclotron resonance plasma-enhanced chemical vapor deposition technique. The films obtained were colorless and amorphous. As etching processing of the prepared thin-film, dry etching was performed using Ar, CF_4, SF_6, Cl_2 and Cl_2-BCl_3 gases. The Ar etching in which no reactive ion-etching is anticipated exhibited the fastest etching rate. Wet etching was also performed using a $ZrOCl_2$-HCl etching solution. The etching rate was extremely fast compared with those of dry etching. In this etching, however, undesirable side-etching occurred. At the present stage, therefore, the most preferable etching processing is dry etching by an Ar gas.

1. Introduction

It is well-known that fluorozirconate glasses doped with rare-earth ions have applications to devices with a variety of optical functions [1]. In applications to such optical devices, planar-type thin films of the glasses are often desired, for example, for a production of planar-type optical light-wave circuits. The planar-type optical light-wave circuits have attracted much attention in the field of optical communication technology because these have a valuable advantage in that various functional devices such as splitters, switches, multiplexers, amplifiers and frequency-converters can be integrated in a small area.

Fluorozirconate glasses are usually prepared by melt-quenching procedures under an inactive atmosphere. Unfortunately, the preparation of planar-type thin-films of fluorozirconate glasses by these techniques seems almost hopeless. Therefore, in order to prepare planar and thin fluorozirconate-glass films, other techniques such as vapor-phase reaction [2] and fluorination of oxide gel [3], have been developed. However, these techniques have not been attempted for fluorozirconate glass-systems containing rare-earth ions. One of the present authors, Y. K., and his co-workers have reported that electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR plasma-enhanced CVD) is a technique available for preparing planar thin-films of rare earth-containing fluorozirconate glasses [4]. A key point in deciding whether or not this technique can be utilized to prepare planar thin-films of rare earth-containing fluorozirconate glasses is to determine whether or not rare-earth β-diketonates are suitable for CVD.

The present paper reports a preparation of planar thin-films of Pr^{3+}-containing fluorozirconate glasses by ECR plasma-enhanced CVD. One of the reasons for choosing praseodymium as a rare earth element is that Pr^{3+}-doped fluorozirconate glasses can be used as a 1.31 μm light amplifier, which is not practical in Pr^{3+}-doped SiO_2-system glasses because of their high phonon-energies.

The production of optical light-wave circuits is usually fabricated by etching processing techniques. For example, fabrication of channel waveguides of fluoride glass by mechanical, chemical and photochemical techniques have been attempted on a PbF_2- ZnF_2-GaF_3 system glass by Gao *et al.* [5]. So far, however, such attempts have not been attempted for rare earth-doped fluorozirconate glasses. In the present work, therefore, a preliminary experiment of etching processing for preparing planar-type optical waveguide circuits is also reported.

2. Experimental procedure

2.1. Preparation of planar thin-film of $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ glass

The details of the preparation of planar thin-films of Eu^{3+}-doped fluorozirconate glass using an ECR plasma-enhanced CVD apparatus have been described in a previous paper [2]. In the preparation of Pr^{3+}-doped fluorozirconate glass, β-diketonates of Zr, Ba and Pr were used as starting materials, taking into account their volatility and their thermal stability which were examined by a DTA-TG analysis. The respective β-diketonates are tetrakis (1,1,1,5,5,5-hexafluoroheptane-2,4-dionate) zirconium, $Zr(hfa)_4$, 2,5,8,11,14-pentaoxopentadecane adducts of bis (1,1,1,5,5,5-hexafluoroheptane-2,4-dionato) barium, $Ba(hfa)_2(tg)$, and tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) praseodymium, $Pr(fod)_3$. These metal β-diketonates were individually heated and vaporized at 85, 165 and 190°C, respectively. In order to obtain thin-films of approximately $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ composition, the flow rates of an Ar carrier gas for the $Zr(hfa)_4$, $Ba(hfa)_2(tg)$ and $Pr(fod)_3$ vapors were controlled to 1.9, 1.0 and 0.4 standard $cm^3\ min^{-1}$, respectively. These vapors were mixed and introduced into a reaction chamber evacuated up to 2.66×10^{-1} Pa to react with NF_3 plasma. The products of the vapor phase reaction were deposited on substrates of $CaF_2(111)$ single-crystal plates ($20 \times 20 \times 2$ mm) or CaFK95 glass plates (40 mm in diameter and 5 mm in thickness, Sumita Optical Glass Co.). These substrates were kept at 300°C. The deposition rate was controlled to about 1.7 $\mu m\ h^{-1}$. Planar thin films of 4–7 μm in thickness were obtained.

Samples prepared on the $CaF_2(111)$ single-crystal plates were used for X-ray diffraction (XRD) and refractive index measurements, surface geometry observation and etching processing experiments. Samples prepared on the CaFK95 glass plates were employed for transmission loss measurements.

2.2. Characterization of the prepared thin-films

XRD measurements were made with a Rigaku RINT 2000 X-ray diffraction apparatus by a thin film technique with a glancing angle of 2° using Cu-K_α radiation. Film thickness measurements were made with a Dektak 3030 surface measuring system of Veeco Instruments. Refractive index measurements were made with a METRICON 2010 prism coupler. Transmission losses at wavelengths of 633 and 1550 nm were measured by using a scattering detection technique with a METRICON 2010 prism coupler. Surface geometry observation was carried out with a Dimension 3100 atomic force microscope (AFM) of Digital Instruments.

2.3. Etching processing

Prior to dry-etching or wet-etching processing the surfaces of the prepared $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ planar thin-films on $CaF_2(111)$ plates were spin-coated with a photo-resist and then exposed to UV light through a negative mask. After development, strips separated by 5 μm were obtained.

In dry-etching by Ar, CF_4 or SF_6 gas a SAMCO BP-1 etching apparatus was employed. In dry etching by Cl_2 or Cl_2-BCl_3 gas a SAMCO RIE-10NL loadlock plasma reactive etching apparatus was employed. The experimental conditions of the Ar, CF_4 or SF_6 gas etching and the Cl_2 or Cl_2-BCl_3 gas etching are given in Tables I and II, respectively. In wet etching a 0.4M $ZrOCl_2$ - 1M HCl attack solution was used under weak stirring for 50 s at 25°C. The etching features were observed with a JEOL JSM-5410 scanning electron microscope.

TABLE I Experimental conditions and results of Ar, CF_4 and SF_6 gas etching

Gas	RF power (W)	Gas pressure (Pa)	Etching rate ($nm\ h^{-1}$)
Ar	50	5.3	320
	50	13.3	200
CF_4	50	5.3	300
	50	13.3	120
SF_6	50	5.3	120
	50	13.3	~0

TABLE II Experimental conditions and results of Cl_2 or Cl_2-BCl_3 gas etching

Gas	Flow rate (SCCM)[a]	RF power (W)	Gas pressure (Pa)	Etching time (min)	Etching rate ($nm\ h^{-1}$)
Cl_2	10	100	13.3	20	No evaluation
Cl_2-BCl_3[b]	10	70	13.3	30	100

[a]Standard $cm^3\ min^{-1}$.
[b]Cl_2/BCl_3 ratio = 1 : 1.

3. Results and discussion

The prepared $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ planar thin-films were colorless and transparent from the visible region to the mid-IR region. An XRD pattern of the thin film is shown in Fig. 1, indicating that the thin films are amorphous. The refractive index, $n_{663\ nm}$, of this thin-film was about 1.521. The $n_{663\ nm}$, of a bulk glass of the same composition, which was prepared by a conventional melt-quenching method for comparison, was about 1.530. One of the reasons for a slight difference between both is probably because the composition of the prepared thin-film is not exactly $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$. Transmission losses measured using a 633 nm light were 15.9 dB cm^{-1} in the fundamental mode, 18.8 dB cm^{-1} in the second mode and 18.4 dB cm^{-1} in the third mode, indicating that the present thin films have very

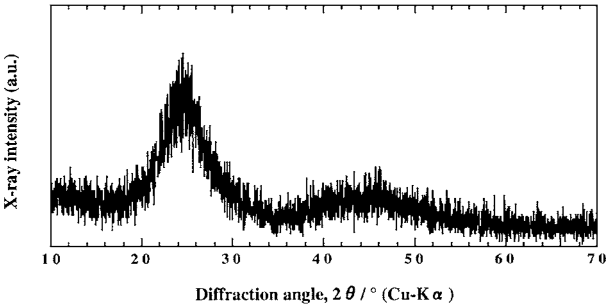

Figure 1 X-ray diffraction pattern of $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ planar thin-film.

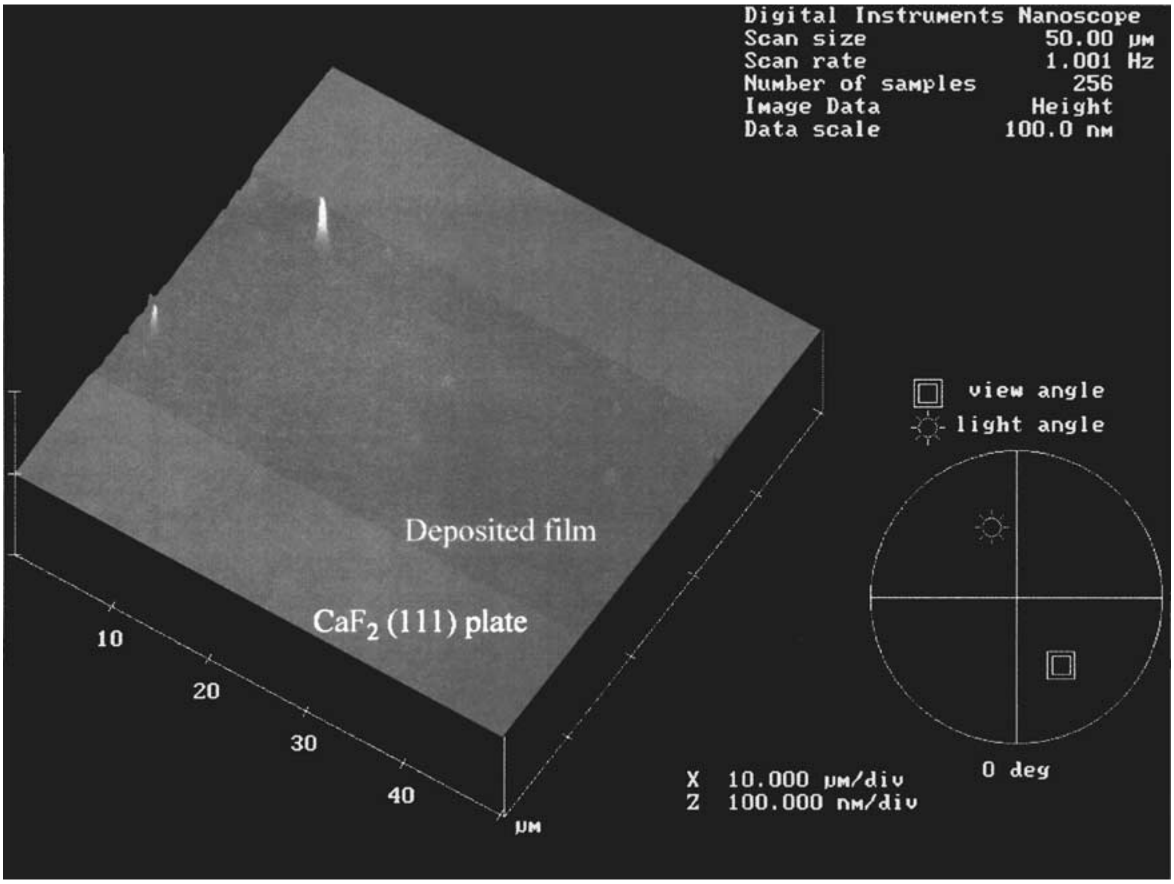

Figure 2 AFM photograph of surface geometry of $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ planar thin-film.

large transmission losses. In general, higher modes are affected by the surface roughness of thin film and/or the interface roughness between thin-films and substrates because of an increase in the number of reflection. In the present specimen, however, differences in loss values between modes are not remarkably large. Therefore, a major origin of the observed transmission loss is probably attributable to a loss in the interior structure of thin film. In fact the surface of thin film is satisfactorily smooth except for a few spots, as can be seen from an AFM photograph of surface geometry in Fig. 2. The transmission losses under a 1550 nm light were 15.9 dB cm^{-1}.

Experimental results of dry-etching processing are discussed. At first, the physical ion-etching effect was examined using an Ar gas. The etching rates obtained under different Ar gas pressures are given in Table I. These etching rates are not fast enough to prepare ridge-type optical waveguides during short etching periods. This result suggests that reactive ion-etching (RIE) processing is advisable. Thus, RIE processing by two kinds of fluoride gases, CF_4 and SF_6, was attempted. The results are given in Table I. From the table, the following facts can be mentioned. CF_4 gave only slightly lower than Ar and SF_6 gave appreciably lower etching rates than Ar, suggesting that no RIE takes place and etching proceeds physically. Moreover, the gas-pressure dependence of etching rate indicates that, in such a physical etching, higher gas-pressures are not necessarily preferable and an optimal gas-pressure seems present. No experiments for optimizing gas-pressure were performed in this work.

In order to ascertain no effectiveness of RIE, dry-etching experiments using a Cl_2 gas or a mixed Cl_2 and BCl_3 gas with a 1 : 1 ratio were performed. If RIE takes place, then faster etching rates than a CF_4 or SF_6 gas should be expected for these gases because the sublimation, melting and boiling temperatures of chlorides are extremely low, compared with fluorides, i.e. sublimation temp. : $ZrCl_4$/300°C and ZrF_4/600°C, melting temp. : $BaCl_2$/962°C and BaF_2/1353°C and boiling temp. : $BaCl_2$/1560°C and BaF_2/2260°C. The experimental results are given in Table II. As can be seen from the table, even a fast etching rate by Cl_2-BCl_3 was about 100 nm h^{-1}, which is similar to the etching rates of CF_4 and SF_6. Therefore, faster dry-etching rates by a choice of gases suitable for RIE are hardly expected. Moreover, in the case of Cl_2 gas the photo-resist was not removed from the glass thin-film surface.

Next, wet-etching processing was examined using a 0.4M $ZrOCl_2$ - 1M HCl solution, which has been already reported to be an appropriate etching solution for PbF_2-ZnF_2-GaF_3 fluoride glasses [5]. The etching rate was very rapid (0.12 $\mu m\ s^{-1}$) and almost the same (0.15 $\mu m\ s^{-1}$) reported on the PbF_2-ZnF_2-GaF_3 system glasses. Unfortunately, however, irregular and also side-etching occurs, as can be seen from a SEM photograph of the etching features in Fig. 3. At the present stage, etching control seems considerably difficult, especially for etching without side-etching.

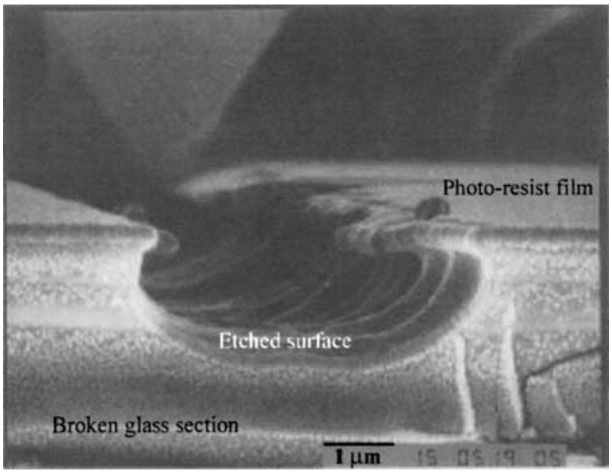

Figure 3 SEM photograph of etching features of $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ planar thin-film etched by 0.4M $ZrOCl_2$ - 1M HCl solution.

4. Conclusion

Planar thin-films of amorphous $60ZrF_4 \cdot 35BaF_2 \cdot 5PrF_3$ were successfully prepared by using β-diketonates of $Zr(hfa)_4$, $Ba(hfa)_2(tg)$ and $Pr(fod)_3$ as starting materials and an NF_3 gas as a fluorinating gas by an ECR plasma-enhanced CVD technique. As a preliminary experiment of etching processing for preparing planar-type optical waveguide circuits, dry-etching of the prepared thin-film was attempted using Ar, CF_4, SF_6, Cl_2 and Cl_2-BCl_3 gases. The physical etching by Ar exhibited the fastest etching rate. Wet-etching of the thin film was also attempted using a $ZrOCl_2$-HCl etching solution. The etching rate was extremely fast, but no satisfactory etching pattern was obtained. At the present stage, therefore, the most favorable etching processing is dry etching by an Ar gas although the etching rate is very slow.

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