JOURNAL OF MATERIALS SCIENCE **33** (1998) 5607–5611

Preparation and characterization of ZrF_4-BaF_2-EuF_3 planar glass films by electron cyclotron resonance plasma-enhanced chemical vapor deposition

Y. KAWAMOTO*, R. KANNO, A. KONISHI
Photonics Materials Laboratory, Division of Science of Materials, Graduate School of Science and Technology, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan
E-mail: kawamoto@kobe-u.ac.jp

An electron cyclotron resonance plasma-enhanced chemical vapor deposition apparatus, which is suitable for producing planar fluoride glass films, was developed. A ZrF_4-BaF_2-EuF_3 planar glass film was synthesized by using β-diketonates of Zr, Ba and Eu as starting materials and NF_3 as a fluorinating gas. A CaF_2 single crystal plate and a fused quartz glass plate were employed as substrates. The planar glass film obtained was colorless and transparent. As an attempt a planar waveguide which has a ZrF_4-BaF_2/ZrF_4-BaF_2-EuF_3/ZrF_4-BaF_2 sandwich structure was also formed on a CaF_2 substrate. The planar glass film and the planar waveguide were characterized by using techniques such as XPS, X-ray diffraction, DTA, ellipsometry, IR absorption, Mössbauer spectroscopy and SEM.

1. Introduction

Since fluorozirconate glasses were discovered by Poulain *et al.* in 1975 [1], heavy metal fluoride glasses have attracted considerable attention because of the potential of application to photonics materials. Recently much attention has been paid to rare earth-containing fluoride glasses because of their potential for active photonics devices such as low transmission-loss optical fibres (*e.g.* [2]), fibre lasers (*e.g.* [3]), fibre amplifiers (*e.g.* [4]), light upconvertors (*e.g.* [5]), *etc*. This potentiality is because of the low phonon energies of fluoride glasses which decrease the non-radiative emission probabilities.

In recent years, planar waveguide technology has been developed in order to fabricate more compact optical devices. For developing such devices, preparation of planar glass films holds the key to the solution of the attainment of planar waveguides.

Usually fluoride glasses are prepared by the following melt-quenching procedure: Raw materials of high purity fluorides are weighed and put into Pt crucibles with small amounts of $NH_4F \cdot HF$. The batches are melted at appropriate temperatures in an Ar atmosphere. Then the melts are quenched by pouring them into brass molds. Unfortunately, such a procedure is unsuitable for preparing planar waveguides.

Therefore, several techniques of preparing planar films of fluoride glasses have been attempted. For example, there are physical vapour deposition (PVD) [6], a multistep process of sol-gel and fluorination (*e.g.* [7]) and chemical vapour deposition [8]. Rare earth-doped PbF_2-ZnF_2-GaF_3 thin films were synthesized using the PVD technique. However, this technique can not be applied to the glass systems in which the vapour pressures of the respective glass components are very different. On the other hand, the combined processing of sol-gel and fluorination is in a preliminary stage [9]. At the present stage, chemical vapour deposition seems to be a promising technique for producing planar films of fluoride glasses.

The first attempt to prepare fluoride glasses by organometallic chemical vapour deposition was done on BeF_2 and BeF_2-AlF_3 glasses in 1987 [8]. Subsequently Fujiura *et al*. succeeded in the preparation of ZrF_4-BaF_2 glass films by a plasma-enhanced organometallic chemical vapour deposition technique [10]. Although filmy ZrF_4-BaF_2 glasses have been synthesized by a plasma-enhanced organometallic chemical vapour deposition technique, the glasses were contaminated with appreciable amounts of oxygen because of the use of fluorinating gases of SF_6 and O_2. Thus, oxygen-free fluorozirconate glass films have not been synthesized yet.

More recently the present authors developed the apparatus of electron cyclotron resonance plasma-enhanced chemical vapour deposition and attempted the synthesis of ZrF_4-BaF_2-LnF_3 planar glass films (Ln = rare earth elements). This letter reports the result

* Author to whom all correspondence should be addressed.

on the preparation and characterization of ZrF_4-BaF_2-EuF_3 planar glass films.

2. Experimental procedure

2.1. Sample preparation

Fig. 1 shows the schematic diagram of apparatus developed in the present study. Microwave radiation at 2.45 GHz was introduced into the microwave cavity resonator, the size of which was 15 cm diameter and 22 cm long. The plasma chamber, a fused quartz vessel of 6 cm diameter and 22 cm long, was placed at the center of the resonator. Magnet coils for electron cyclotron resonance plasma excitation were arranged around the periphery of the resonator. An NF_3 gas was employed as a fluorinating reagent. The NF_3 gas was introduced into the plasma chamber and effectively absorbed the microwave energy to generate plasma. The plasma flowed out from the plasma extraction window toward a substrate. The flow rate of the NF_3 gas was 60 sccm and the microwave power introduced was 30 W.

It is necessary that starting materials for chemical vapour deposition volatilize at comparatively low temperatures and are thermally stable. In the present work, β-diketonates of Zr, Ba and Eu were used as starting materials, taking into account their volatility and their thermal stability; tetrakis (1,1,1,5,5,5-hexafluoroheptane-2,4-dionato) 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 (2,2,6,6-tetramethyl-3,5-heptanedionato) europium, $Eu(dpm)_3$.

The $Zr(hfa)_4$, $Ba(hfa)_2$ (tg) and $Eu(dpm)_3$ starting materials were individually heated and vapourized at 85, 165 and 190 °C, respectively. These temperatures were determined by thermal analyses of these metal β-deketonates. The flow rates of Ar carrier gas for the $Zr(hfa)_4$, $Ba(hfa)_2(tg)$ and $Eu(dpm)_3$ starting materials were 1, 1 and 0.3 sccm, respectively. These gases were mixed and introduced into the reaction chamber to react with NF_3 plasma. The reaction chamber was evacuated to 2×10^{-3} Torr. The products of the vapour phase reaction were deposited on substrates heated at 300 °C. A CaF_2 single crystal plate and a fused quartz glass plate were employed as substrates. The deposition rate was around 1 μm/h. Planar films of about 3 μm in thickness and about 1 cm^2 in area were prepared. The choice of a CaF_2 substrate is due to the thermal expansion coefficient which is close to those of fluorozirconate glasses. A fused quartz glass was used due to the ease of taking the products off.

As an attempt a planar waveguide which has a ZrF_4-BaF_2 (about 1.5 μm thick)/ZrF_4-BaF_2-EuF_3 (about 1.5 μm thick)/ZrF_4-BaF_2 (about 1.5 μm thick) sandwich structure was also prepared on a CaF_2 substrate.

2.2. Characterization

X-ray photo-electron spectroscopy (XPS) measurements were made with an ULVAC-PHI ESCA5400, using Mg-Kα radiation as a photo-electron excitation source.

X-ray diffraction (XRD) measurements were made with a Rigaku RINT 2000 X-ray diffractometer by a thin film technique with a glancing angle of 2° using Cu-Kα radiation.

Differential thermal analysis (DTA) measurements were carried out under an Ar gas flow at a heating rate of 10 K/min with a Rigaku TAS 100 differential thermal analyzer.

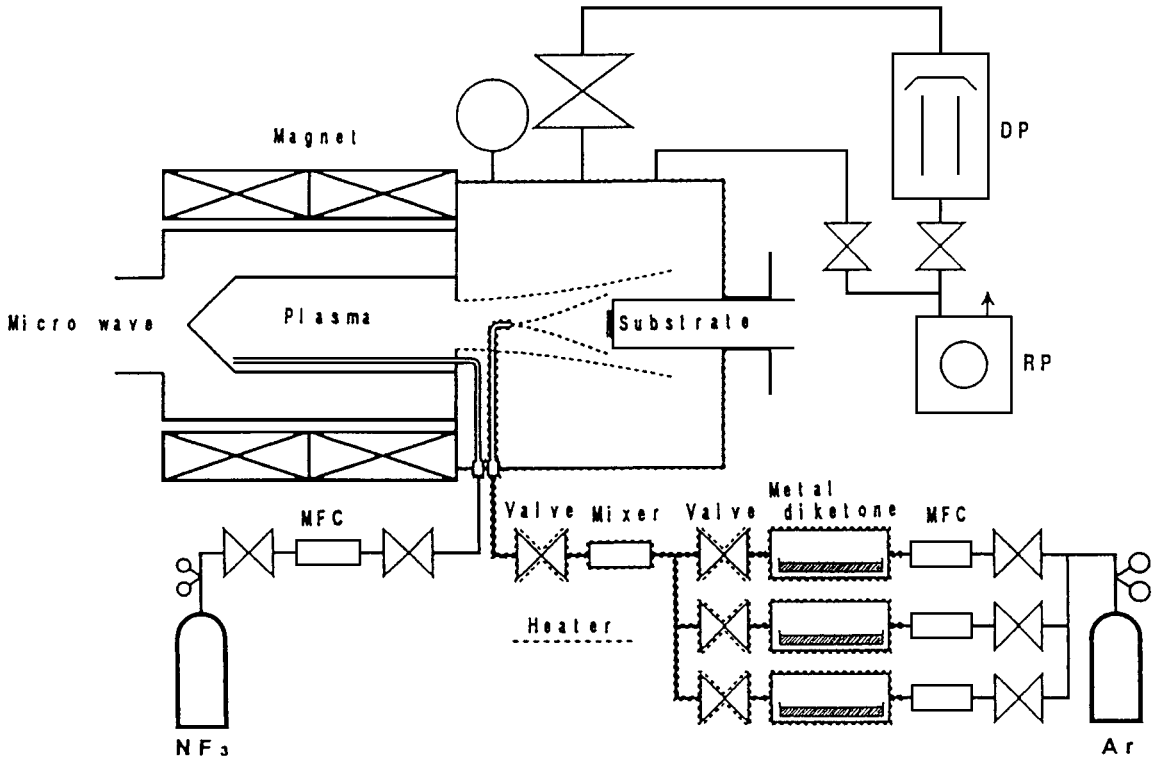


Figure 1 Schematic diagram of electron cyclotron resonance plasma-enhanced chemical vapour deposition apparatus.

Film thickness was measured by using a Kosaka Laboratory Surfcorder SE-2300S apparatus.

Refractive index was measured with a Mizojiri DHA-XA2Y ellipsometer using He-Ne laser (632.8 nm).

Infrared absorption spectra were measured with a Perkin-Elmer PARAGON 1000 PC FTIR spectrophotometer by using a KBr pellet technique.

Mössbauer spectra were measured according to the procedure described elsewhere [11].

Scanning electron microscope (SEM) observation and line analyses of Zr, Ba and Eu elements were made with a JEOL-JSM-5800LVC scanning electron microscope with JED-2100X. The spot size of an electron beam was about 1 μm diameter.

3. Results and discussion

The composition of the prepared ZrF_4-BaF_2-EuF_3 film was determined by XPS measurements. A $60ZrF_4 \cdot 30BaF_2 \cdot 10EuF_3$ glass, which was prepared by a conventional melt-quenching method, was used as a reference specimen. Fig. 2 shows the XPS spectra of the prepared film and the reference glass. The composition was evaluated from the peak areas of Zr3d, Ba3d5 and Eu4d lines. The composition of the film was estimated to be about $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$. Moreover, the XPS analysis revealed that the film has no oxygen contamination.

Fig. 3 shows the X-ray diffraction pattern of the prepared planar film, together with that of the conventionally prepared $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ glass. It can be seen that both halo patterns are in good agreement. It is concluded that the $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ planar film is an amorphous film.

Fig. 4 shows the DTA curve of the $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ planar film. The fact that the planar film exhibits a small endothermic shoulder due to glass transition indicates that the $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ planar film is in a vitreous state.

The ellipsometric analysis revealed that refractive index of this planar film is 1.523, being almost the same as that (1.530) of the conventionally prepared $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ glass.

Fig. 5 shows the infrared absorption spectra of the $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ planar glass film and the $72ZrF_4 \cdot 15BaF_2 \cdot 13EuF_3$ glass prepared by a conventional melt-quenching method. In the figure a band at about 500 cm^{-1} is assigned to the antisymmetric

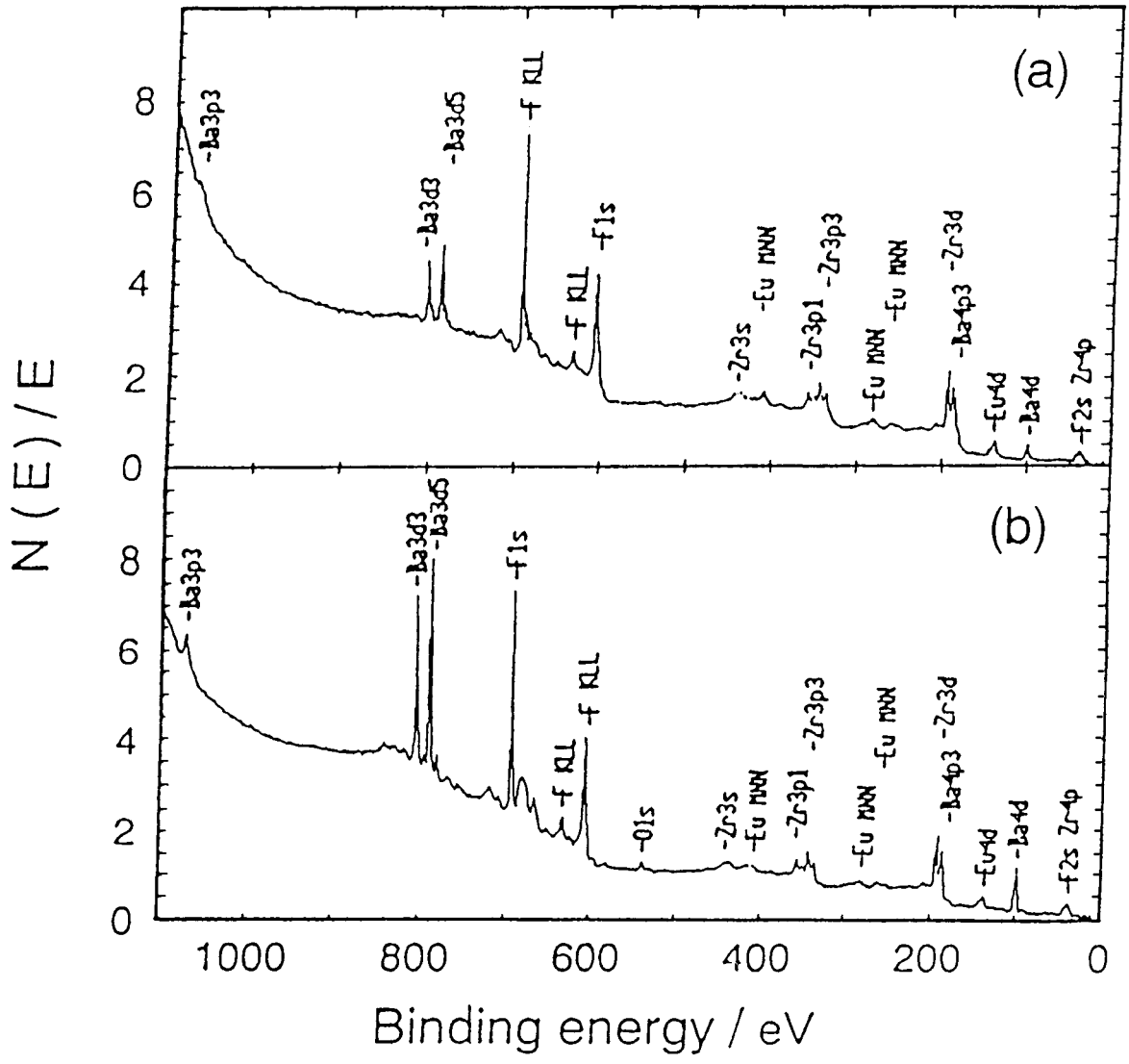


Figure 2 Wide scan XPS spectra of (a) ZrF_4-BaF_2-EuF_3 planar film and (b) $60ZrF_4 \cdot 30BaF_2 \cdot 10EuF_3$ glass prepared by conventional melt-quenching procedure.

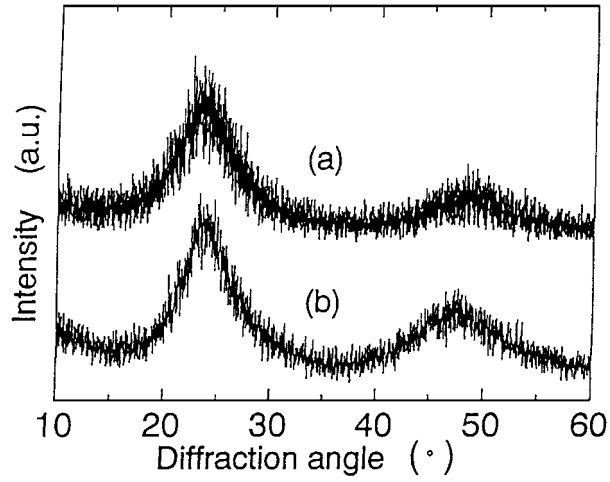


Figure 3 XRD patterns of (a) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ planar film and (a) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ glass prepared by conventional melt-quenching procedure.

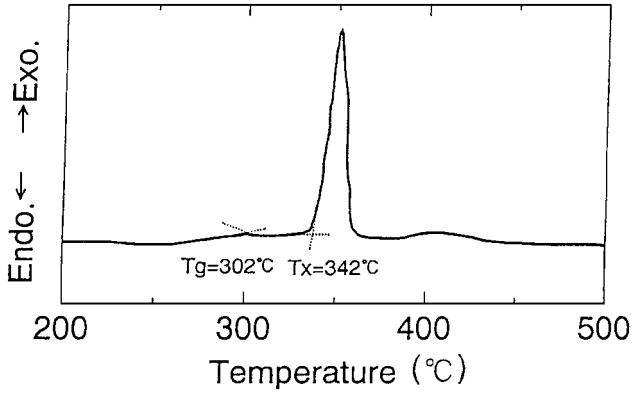


Figure 4 DTA curve of $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ planar film.

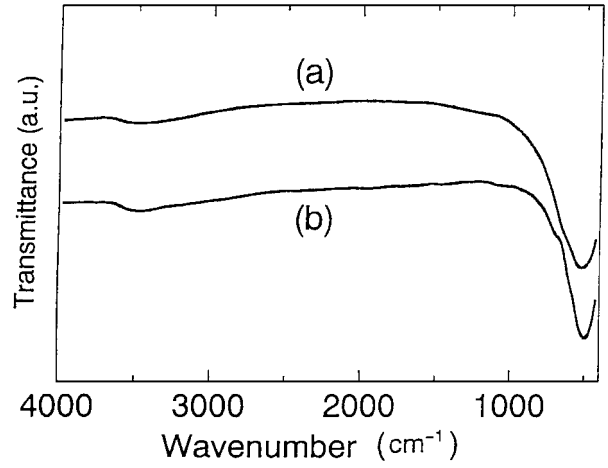


Figure 5 Infrared absorption spectra of (a) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ planar glass film and (b) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ glass prepared by conventional melt-quenching procedure.

stretching vibration of ZrF_n polyhedra [12]. Almost complete agreement can be seen between both spectra, indicating that the F coordination environment around Zr in the planar glass film is the same as that in the conventional glass.

Fig. 6 shows the ^{151}Eu Mössbauer spectra of the $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ planar glass film and the conventionally prepared $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ glass,

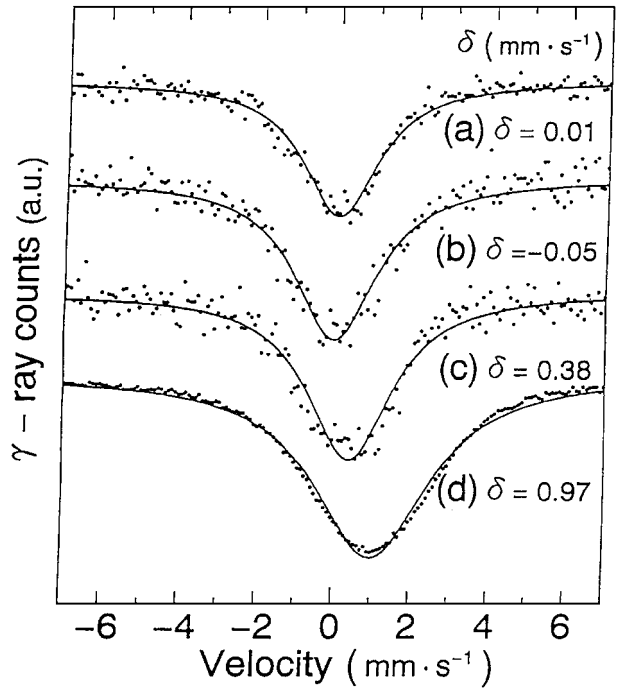
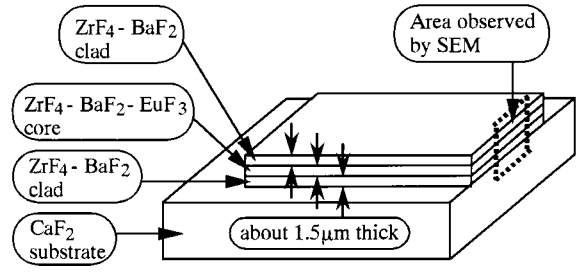
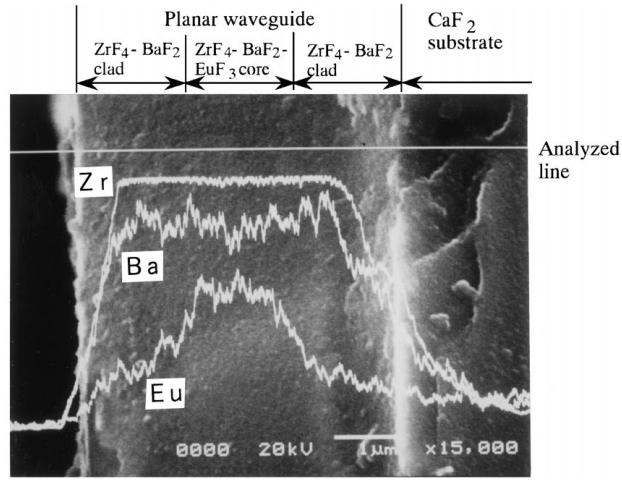


Figure 6 ^{151}Eu Mössbauer spectra of (a) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ planar glass film, (b) $72ZrF_4{\cdot}15BaF_2{\cdot}13EuF_3$ glass prepared by conventional melt-quenching procedure, (c) $Eu(dpm)_3$ complex and (d) Eu_2O_3 crystal.



(a)



(b)

Figure 7 (a) Planar waveguide with ZrF_4-BaF_2 (about 1.5 μm thick)/ ZrF_4-BaF_2-EuF_3 (about 1.5 μm thick)/$Zr\,F_4$-BaF_2 (about 1.5 μm thick) sandwich structure. (b) SEM image of a square region of (a) and line analyses of Zr, Ba and Eu elements.

together with those of $Eu(dpm)_3$ complex and Eu_2O_3 crystal. The isomer shift, δ, is a measure of the electron density at the nucleus, which is affected by the valence, electronic state and coordination environment. As can

be seen, the present planar glass film exhibits almost the same δ value as the conventionally prepared glass. This indicates that the local environments around Eu ions in the planar glass film are the same as those in the conventional glass.

In the present work a planar waveguide depicted in Fig. 7(a) was prepared on crystalline CaF_2 substrate as an attempt. In order to examine element distribution in the cross section, line analyses of the Zr, Ba and Eu elements were performed by using SEM. Fig. 7(b) shows the SEM image and the Zr, Ba and Eu line analyses of the ZrF_4-BaF_2/ZrF_4-BaF_2-EuF_3/ZrF_4-BaF_2 sandwich planar waveguide. Since the spot size of the electron beam in the line analyses was about 1 μm in diameter, no sharp drops were observed in element concentration. The present SEM result indicates that a planar waveguide is successfully produced by the present electron cyclotron resonance plasma-enhanced chemical vapour deposition technique.

4. Conclusion

The synthesis of a ZrF_4-BaF_2-EuF_3 planar glass thin film was attempted by electron cyclotron resonance plasma-enhanced chemical vapour deposition, using β-diketonates of Zr, Ba and Eu, and NF_3 as sources. The metal β-diketonates were thoroughly fluorinated and the planar film synthesized was oxygen-free, transparent and colorless. A planar waveguide with the ZrF_4-BaF_2/ZrF_4-BaF_2-EuF_3/ZrF_4-BaF_2 sandwich structure could be also synthesized. It is concluded that the present synthesis technique can be applicable to the production of planar waveguides of rare earth-doped fluoride glasses.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (No. 0955591).

References

1. M. POULAIN, M. POULAIN and J. LUCAS, *Mater. Res. Bull.* **10** (1975) 243.
2. S. MITACHI, S. SHIBATA and T. MANABE, *Electron. Lett.* **17** (1981) 128.
3. M. C. BRIERLEY and P. W. FRANCE, *ibid.* **23** (1987) 815.
4. Y. OHISHI, T. KANAMORI, T. KITAGAWA, S. TAKAHASHI, E. SNITZER and G. H. SIGEL Jr., *Optics Lett.* **16** (1991) 1747.
5. R. S. QUIMBY, M. G. DREXHAGE and M. J. SUSCAVAGE, *ibid.* **23** (1987) 32.
6. M. F. JOUBERT, A. REMILLIEUX, B. JACQUIER, B. BOULARD, O. PERROT and C. JACOBONI, in "Extended Abstracts of the 9th International Symposium on Non-Oxide Glasses," Hangzhou, China, May 1994, p. 641.
7. A. KONISHI, R. KANNO and Y. KAWAMOTO, *Mater. Res. Bull.* **30** (1995) 193.
8. A. SARHANGI and D. A. THOMPSON, in "Extended Abstracts of the 4th International Symposium on Halide Glasses," Monterey, USA, January 1987, p. 274.
9. A. KONISHI, R. KANNO and Y. KAWAMOTO, *J. Alloys and Compounds* **232** (1996) 53.
10. K. FUJIURA, Y. NISHIDA, K. KOBAYASHI and S. TAKAHASHI, *Jpn. J. Appl. Phys.* **30** (1991). L1498.
11. M. TAKAHASHI, R. KANNO and Y. KAWAMOTO, *J. Phys. Chem.* **100** (1996) 11193.
12. R. M. ALMEIDA, in "Handbook on the physics and chemistry of rare earths Vol. 15, Chapter 10: Fluoride glasses," Elsevier Science Publishers, Amsterdam 1991, p. 330.

Received 21 September 1997
and accepted 15 July 1998