

Formation of PbTiO₃ films from multilayered structures of primitive oxides

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Abstract—The possibility of the formation of PbTiO₃ from a multilayer structure of PbO and TiO₂ layers on Pt-coated Si substrates prepared by rapid thermal metal organic chemical vapor deposition (RTMOCVD) followed by an appropriate annealing process was examined. The metal organic precursors of PbO and TiO₂ were Pb(C₂H₅)₄ and Ti(O-i-C₃H₇)₄, respectively. The composition of the PbTiO₃ thin film was adjusted by control of the thickness of each binary oxide layer of PbO and TiO₂. The multilayer structure was converted into crystalline PbTiO₃ by rapid thermal annealing under O₂ ambient at temperature greater than 550 °C. As the annealing temperature was increased from 550 to 750 °C, the peaks related to perovskite PbTiO₃ in the XRD patterns became stronger and sharper. From this study, it was confirmed that the crystalline PbTiO₃ thin films could be prepared from the interdiffusion reaction of multilayer structure composed of primitive binary oxides through the appropriate post annealing process.

Key words: PbTiO₃, Multilayered Structure, Perovskite, MOCVD, Interdiffusion

INTRODUCTION

Ferroelectric PbTiO₃ thin film with applications to piezoelectric, pyroelectric, electro-optic and several electronic devices has recently received a great deal of attention. A variety of methods for ferroelectric PbTiO₃ thin film growth, including metal organic chemical deposition [1,2], plasma enhanced chemical vapor deposition [3], pulsed laser deposition [4], sol-gel [5], RF sputtering [6] and spray pyrolysis [7], have been used. Among these, chemical vapor deposition (CVD) using metal organic precursors is extensively used, as this method offers a high level of controllability of the film crystallinity and electrical properties as well as good step coverage, a high deposition rate and the possibility of commercial-based production.

In the preparation of multi-component ferroelectric oxide thin films, the control of their composition is usually considered as one of the most difficult tasks. Because the composition of ferroelectric material can influence its ferroelectric properties [8], considerable efforts have been made to clear this issue. As binary oxides such as PbO and TiO₂ can be fabricated easily using several deposition techniques, if a multi-component ferroelectric oxide can be fabricated from a multilayer structure composed of binary oxides by a solid state interdiffusion reaction, it would be a very promising method to prepare the ferroelectric oxide films with a suitably well controlled stoichiometry. A similar concept for an interdiffusion reaction technique has been used widely in the preparation of electronic materials such as silicides [9].

However, few works dealing with this technique have been reported in the field of multi-component ferroelectric thin films. In the work of Tochitsky and Romanova [10], PbTiO₃ thin film was prepared by the thermal evaporation of Pb/Ti metals layer by layer on an NaCl substrate followed by annealing in O₂ ambient and oxide formation. Li and Desu [11,12] reported that PbTiO₃ thin films on

Al₂O₃ substrates can be prepared using a metallic Pb/Ti and oxide PbO/TiO₂ multilayer and a subsequent annealing process.

In the present study, perovskite PbTiO₃ thin film is prepared from a multilayer structure of PbO and TiO₂ thin films using an appropriate annealing process. In addition, the morphologies and crystalline structure of the PbTiO₃ thin films are analyzed to confirm the viability of the proposed method in detail.

EXPERIMENTAL

A Pt-coated Si wafer was used as a substrate. The metal organic precursors of PbO and TiO₂ were Pb(C₂H₅)₄ (TEL, 5 N purity) and Ti(O-i-C₃H₇)₄ (TTIP, 5N purity), respectively. A rapid thermal metal organic chemical vapor deposition (RTMOCVD) reactor was equipped with thermal components and a quartz tube with a 65 mm OD. Bubbler containing TEL and TTIP were heated to 23 °C and 36 °C. Each vapor was carried into the reactor by nitrogen. Oxygen was used as an oxidizing gas. The typical growth conditions of PbO and TiO₂ thin film are shown in Table 1; the details of the RTMOCVD process are available in the literature [13]. The multilayer structure of binary oxides was prepared as follows. First, an initial oxide layer

Table 1. Growth conditions of PbO and TiO₂ thin film in a rapid thermal metal organic chemical vapor deposition

Layer	PbO	TiO ₂
Metalorganic source	Pb(C ₂ H ₅) ₄ (TEL)	Ti(O-i-C ₃ H ₇) ₄ (TTIP)
Substrate temperature	380 °C	400 °C
Carrier N ₂ flow rate	40 sccm	20 sccm
Chamber pressure	500 mtorr	400 mtorr
Bubbler temperature	23 °C	36 °C
Reactant O ₂ flow rate	20 sccm	10 sccm
Reactor type	Hot wall	
Substrate	Si wafer and Pt-coated Si wafer	

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of either PbO or TiO₂ was deposited and its thickness was controlled by the process time. Second, all reactant species were eliminated by venting, and the substrate temperature was simultaneously changed to support alternating layers. After a multilayer structure with a designed thickness was prepared, subsequent rapid thermal annealing was done under O₂ ambient at the temperature range of 550–750 °C to convert the structure into a perovskite PbTiO₃ thin film. The composition of the PbTiO₃ thin film could be controlled by the thickness ratio of each binary oxide layer of PbO and TiO₂.

The compositions of the films were analyzed by energy dispersive X-ray spectroscopy (EDX). The crystal structure was evaluated through X-ray diffraction (XRD). Field emission scanning electron micrography (FESEM) was used to observe the cross-sectional view and surface morphology and also to verify the film thickness. Atomic force microscopy (AFM) was used to check the surface roughness of thin films. Ellipsometry and FESEM were used for the thickness measurement of the deposited films in this study.

RESULTS AND DISCUSSION

It was supposed that stoichiometric PbTiO₃ could be obtained simply by alternately pulsing two metal-containing precursors, TEL and TTIP, and an oxygen source, and that the growth rate of the ternary oxide could be predicted by summing the growth rates of the constituent oxides. However, in actuality, both assumptions often fail due to the different reactivities of the precursors [14]. The effects of the surface chemistry usually cause changes in the relative growth rates, which can be determined by comparing the observed film thickness with the theoretical thickness calculated from the growth rates of the binary oxides. This explains why a novel method for the control of the composition is required. In this study, the formation of a multilayer structure of PbO and TiO₂ and the interdiffusion of these two materials are evaluated as a novel method for the fabrication of perovskite PbTiO₃ as shown in Fig. 1.

Theoretically, the thickness ratio of a PbO and TiO₂ layer is required to produce precise stoichiometric PbTiO₃ thin film. As the composition of ferroelectric materials could have a considerable influence on the ferroelectric properties, compositional controllability is very important to obtain some useful properties from multi-component ferroelectric oxides [15]. First, the relationship between the thickness ratio of PbO/TiO₂ deposited by RTMOCVD and the actual atomic ratio of Pb/Ti was evaluated, as shown in Fig. 2. The result indicates that if PbO and TiO₂ have the same thickness, the

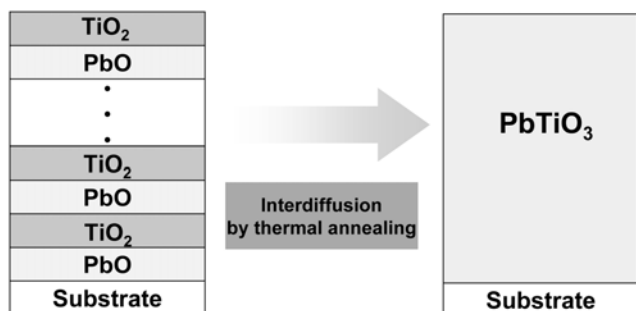


Fig. 1. Schematic of the preparation of PbTiO₃ thin film from the multilayer films composed of PbO and TiO₂.

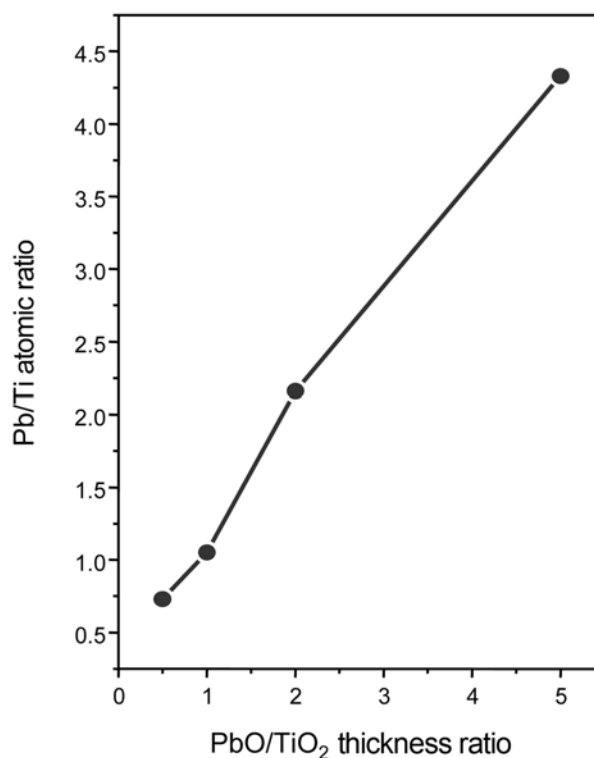


Fig. 2. Correlation between the thickness ratio of PbO/TiO₂ and the related atomic ratio of Pb/Ti.

atomic concentration of Ti would be lower than that of Pb. The atomic ratio of Pb/Ti is 1/0.94.

However, if there is a change in the atomic ratio during a post treatment such as an annealing process, it becomes crucial to obtain or sustain the desired material properties. Therefore, variation of the atomic ratio in PbTiO₃ thin films after an annealing process should be minimized. It was reported [3] that Pb reduction in PbTiO₃ film increases with an increase in the annealing temperature due to the high volatility of the Pb compounds. It appears that structure capping with a TiO₂ layer suitably protects against the evaporation

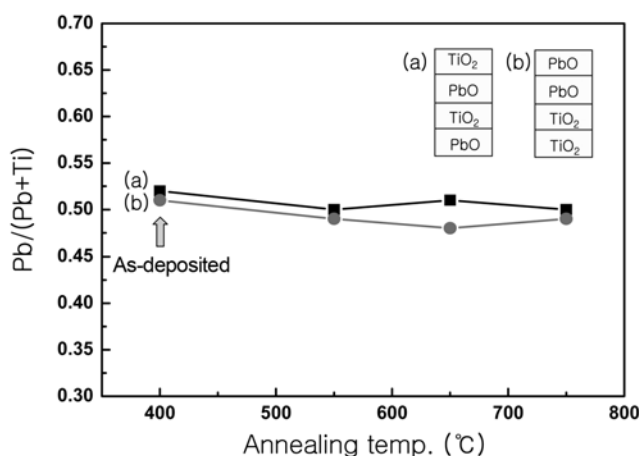


Fig. 3. Effect of annealing temperatures on the atomic ratio of annealed PbTiO₃ thin films from (a) TiO₂ capped and (b) PbO capped.

of the Pb element during the annealing process, whereas with a film topped with a PbO layer, it can be expected that the volatility of the Pb would be accelerated during the annealing step. However, the loss of Pb was not severe, though the annealing temperature ranged from 550 to 750 °C; this compares well with the result of the Ti capped specimen as shown in Fig. 3. The reduction of the total annealing time due to the fundamental capability of a rapid

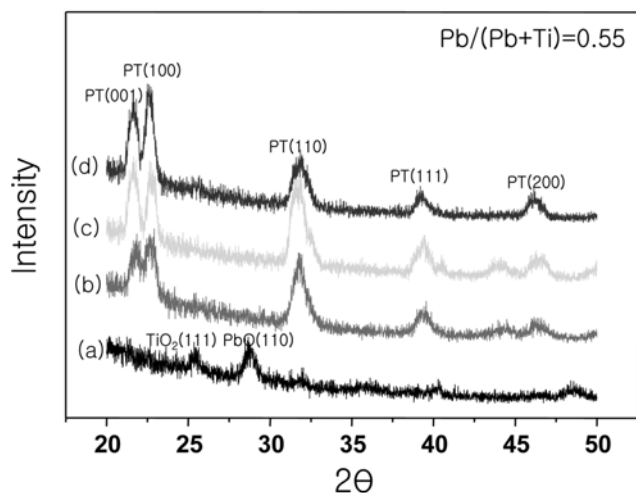


Fig. 4. XRD patterns of the film: (a) as-deposited, (b) annealed at 550 °C, (c) annealed at 650 °C and (d) annealed at 750 °C for 1 hr in oxygen ambient. Atomic ratio of as-deposited film, $\text{Pb}/(\text{Pb}+\text{Ti})$ is 0.55.

thermal annealing process may contribute to the suppression of Pb loss [20].

The crystalline structure of PbTiO_3 films was studied in the films annealed between 550 and 750 °C. Fig. 4 shows the XRD patterns of PbTiO_3 thin films on a Pt-coated silicon substrate as a function of the annealing temperatures. The as-deposited film with an atomic ratio, $\text{Pb}/(\text{Pb}+\text{Ti})$, of 0.55 had the structure of $(\text{PbO}/\text{TiO}_2)_2$ and showed the crystalline peaks of TiO_2 (111) and PbO (110). The indexed peaks refer to the crystalline tetragonal phase of PbTiO_3 according to the JCPDS (6-452) data card. Well-defined crystalline peaks for perovskite PbTiO_3 were observed in all annealed films and the peaks were determined to be at the (001), (100), (101) and (111) orientations. As the annealing temperature was increased from 550 to 750 °C, these peaks in the XRD patterns became stronger and sharper, indicating better crystallization. This result shows that perovskite PbTiO_3 can be prepared successfully by the interdiffusion of multilayer binary oxides after an appropriate post-annealing process.

Fig. 5 shows AFM surface images of as-deposited thin films annealed at 550, 650 and 750 °C for 1 hr. The surface roughness and grain size increased as the annealing temperature increased. The values of R_{rms} were 12.661, 13.698, 14.034 and 15.475 nm for the as-deposited and annealed films at 550, 650 and 750 °C, respectively. The grain size in the ferroelectric thin films has an influence on a number of properties. An increase in the grain size leads to an increase in the coercive field, a decrease in the remnant polarization, a depression in the dielectric constant and a smearing of the ferroelectric transition [16].

It is well known that the crystal structure of PbTiO_3 thin film is

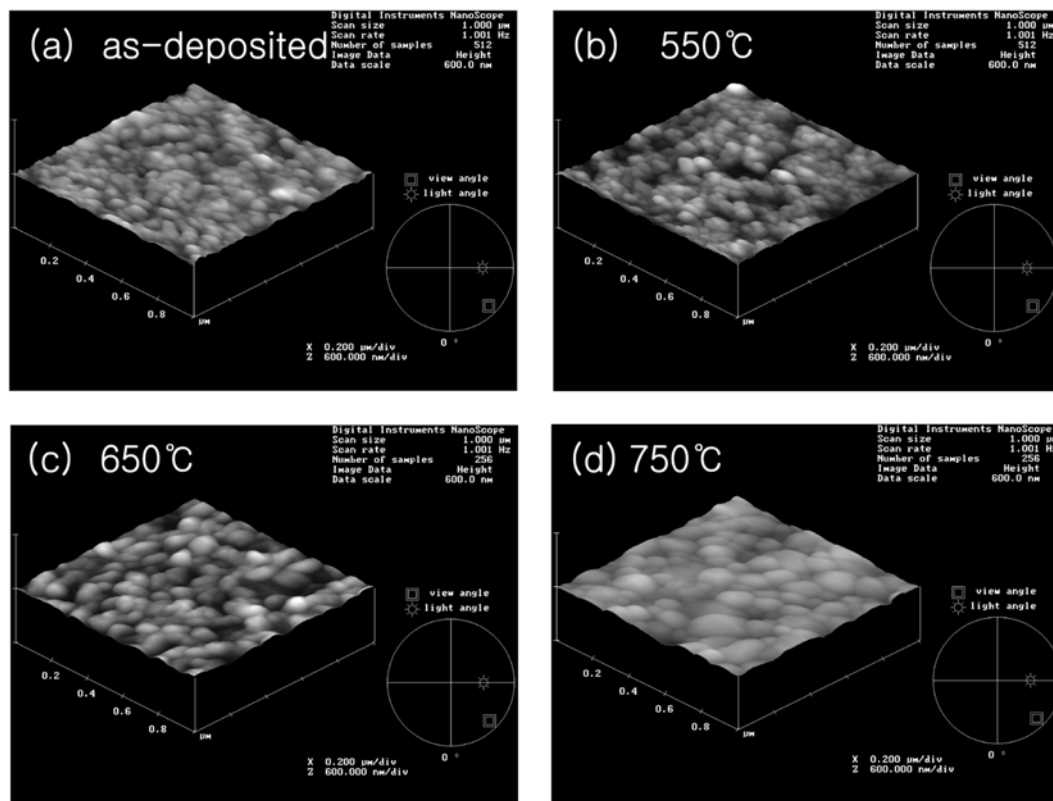


Fig. 5. AFM images of the film: (a) as-deposited, (b) annealed at 550 °C, (c) annealed at 650 °C and (d) annealed at 750 °C for 1 hr in oxygen ambient. Atomic ratio of as-deposited film, $\text{Pb}/(\text{Pb}+\text{Ti})$ is 0.55.

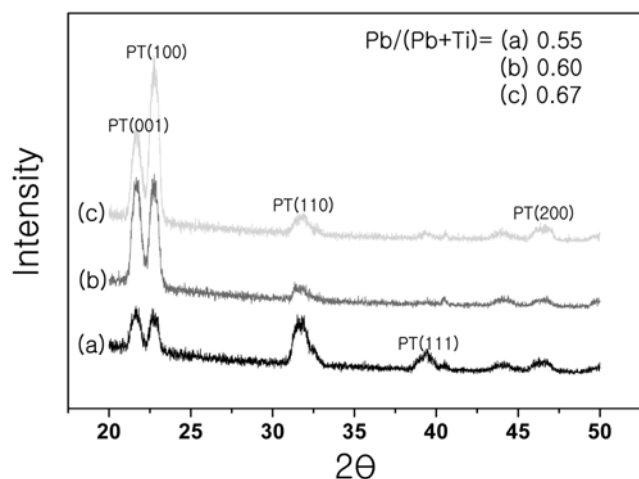


Fig. 6. XRD patterns of the annealed PbTiO_3 thin films at 650°C for 1 hr under oxygen ambient. Atomic ratios, $\text{Pb}/(\text{Pb}+\text{Ti})$, of each film are (a) 0.55, (b) 0.60 and (c) 0.67.

sensitive to the substrate temperature and the Pb/Ti atomic ratios. Fig. 6 shows the diffraction patterns of perovskite PbTiO_3 thin films annealed at 650°C for 1 hr under oxygen ambient, where the $\text{Pb}/(\text{Pb}+\text{Ti})$ atomic ratios of the films were (a) 0.55, (b) 0.60 and (c) 0.67 in the successive images. All of the specimens showed diffraction patterns related to the perovskite structure, where the peak of the strongest intensity had changed from the (001) to the (100) peak and (110) peak. Moreover, the (110) peak was weakened as the Pb content increased. Interestingly, it was reported [3] that when lead-rich films with $\text{Pb}/(\text{Pb}+\text{Ti})$ ratios between 0.55–0.65 were annealed above 600°C , the presence of excess Pb , probably in the form of amorphous lead oxide, somehow promoted the crystallization of the PbTiO_3 phase.

Fig. 7 shows the surface morphologies of annealed PbTiO_3 thin films according to the variation of Pb content in the film. As the Pb content increased from $\text{Pb}/(\text{Pb}+\text{Ti})=0.38$ to 0.60, the grain size was bigger and smoother. The stoichiometric amount of Pb reacts with the Ti element to form perovskite PbTiO_3 during annealing. The excess Pb element exists as a PbO compound of amorphous and/or microcrystalline phase, which fills up the grain boundary and reduces the leakage current path in the grain boundary region [17].

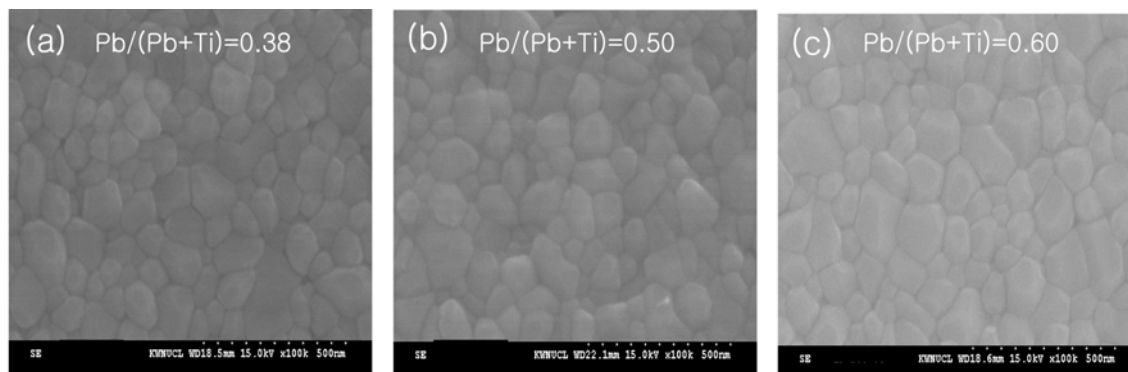


Fig. 7. Surface morphologies of PbTiO_3 films annealed at 750°C under oxygen ambient for 1 hr. Atomic ratios, $\text{Pb}/(\text{Pb}+\text{Ti})$, of each film are (a) 0.38, (b) 0.50 and (c) 0.60.

The formation of PbO networks in PbTiO_3 thin films remarkably decreased the electrical conductivity of the film [18]. In contrast, as the Ti content in films increased, the domains of the TiO_2 crystal with a high leakage current increased; additionally, the leakage current of the films may be predominated by the properties of the crystal-line TiO_2 [19].

CONCLUSION

Perovskite PbTiO_3 thin films on Pt-coated Si wafer were successfully prepared through an interdiffusion process of PbO and TiO_2 multilayer films prepared by rapid thermal metal organic chemical vapor deposition (RTMOCVD). The exact composition of the PbTiO_3 thin film could be controlled by the thickness ratio of each constituent binary oxide layer of PbO and TiO_2 . As the annealing temperature increased, the peaks related to perovskite PbTiO_3 in the XRD patterns became stronger and sharper. The surface roughness and grain size were increased as the annealing temperature increased. From this study, it was confirmed that a well defined perovskite PbTiO_3 thin film could be prepared by the interdiffusion of a multilayer structure of binary oxides PbO and TiO_2 with an appropriate post-annealing process.

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REFERENCES

1. G. R. Bai, H. L. M. Chang, C. M. Foster, Z. Shen and D. J. Lam, *J. Mater. Res.*, **9**, 156 (1994).
2. M. Shimizu, H. Fujisawa and T. Shiosaki, *J. Crystal Growth*, **174**, 464 (1997).
3. W. G. Lee and S. I. Woo, *Intergr. Ferroelectr.*, **5**, 107 (1994).
4. M. A. Khan, T. P. Comyn and A. J. Bell, *J. Eur. Ceram. Soc.*, **28**, 591 (2008).
5. S. J. Milne and S. H. Pyke, *J. Am. Ceram. Soc.*, **74**, 1407 (1991).
6. C. M. Wu, T. J. Hong and T. B. Wu, *J. Mater. Res.*, **12**, 2158 (1997).
7. H. Huang, X. Yao, X. Q. Wu, M. Q. Wang and L. Y. Hang, *Thin Solid Films*, **458**, 71 (2004).

8. B. Jaffe, W. R. Cook and H. Jaffe, *Piezoelectric ceramics*, Academic Press, London (1971).
9. S. P. Murarka, *Silicides for VLSI applications*, Academic Press, New York (1982).
10. E. I. Tochisky and N. I. Romanova, *Thin Solid Films*, **110**, 55 (1983).
11. C. C. Li and S. B. Desu, *Ceramic Transaction*, **25**, 59 (1991).
12. C. C. Li and S. B. Desu, *Mat. Res. Soc. Sympo. Proc.*, **243**, 387 (1992).
13. B. Y. Song, Y. J. Kwon and W. G. Lee, *Korean Chem. Eng. Res.*, **45**, 378 (2007).
14. M. Nieminen, S. Lehto and L. Niinistö, *J. Mater. Chem.*, **11**, 3148 (2001).
15. S. Saha and D. Agrawal, *Am. Ceram. Bull.*, **71**, 1424 (1992).
16. R. E. Newnham, K. R. Udaykumar and S. Trolier-McKinstry, *Chemical processing of advanced materials*, L. L. Hench and J. K. West (Eds.), John Wiley, New York (1982).
17. D. L. Hankey and J. V. Biggers, *J. Am. Ceram. Soc.*, **64**, C172 (1981).
18. M. Kitabatake, T. Mitsuyu and K. Wasa, *J. Non-cryst. Solids*, **53**, 1 (1982).
19. T. Kamata, M. Kitagawa, M. Shibuya and T. Hirao, *Jpn. J. Appl. Phys.*, **3330**, 3594 (1991).
20. H. Tabata, T. Kawai, S. Kawai, O. Murata, J. Fujoka and S. Minakata, *Appl. Phys. Lett.*, **59**, 2354 (1991).