Preparation of B_2O_3–P_2O_5–SiO_2 coating films by the sol–gel method

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The $xB_2O_3 \cdot (20-x) P_2O_5 \cdot 80SiO_2$ (in mol %) glass films with $x = 0$, 10 and 20 have been prepared from metal alkoxides by carrying out the coating in a dry atmosphere. These coating films have shown a larger value of load at scratch and a smaller shrinkage during heat-treatment by replacing P_2O_5 in the films with B_2O_3. It has been found that B_2O_3 more effectively reduces the glass transition temperature of SiO_2 glass than P_2O_5. The concentrations of sodium ions, which migrated from soda-lime–silica glass substrates during the film formation, were higher in phosphosilicate and borophosphosilicate films than in borosilicate and pure silica films. This finding should be ascribed to the gettering effects of phosphorus for sodium ions.

1. Introduction

Glass films in the binary systems B_2O_3–SiO_2 and P_2O_5–SiO_2 and the ternary system B_2O_3–P_2O_5–SiO_2 are very important in silicon semiconductor devices as an intermetallic dielectric layer and a surface passivation layer [1, 2]. The glass films in these systems have several advantages over pure SiO_2 glass films: the reflow temperature of glasses can be greatly reduced by the incorporation of B_2O_3 and P_2O_5 into SiO_2 and thus densified glass films are obtainable at much lower temperatures than in pure SiO_2. Furthermore, phosphorus provides trapping sites for alkali ions and suppresses the migration of the alkali impurities in the silicon semiconductor devices [1, 2].

The intermetallic dielectric layers and the surface passivation layers are usually prepared by the melting of glass powders [3, 4] and chemical vapour deposition (CVD) [5–8]. The sol-gel method is also a promising technique for the preparation of these glass layers since metal alkoxides which are starting materials in this method can be easily purified by distillation and thus they are converted into homogeneous glasses with high purity at relatively low temperatures. Moreover sol-gel coatings smooth out the surface roughness in the silicon semiconductor devices and relieve problems of step coverage on deposition of metal electrodes.

As far as the ternary system B_2O_3–P_2O_5–SiO_2 is concerned, several papers have been reported on the preparation of monoliths by the sol-gel method [9, 10]. On the other hand, there are few reports on the sol-gel derived films containing B_2O_3 and/or P_2O_5 more than 20 mol %. It is probably due to the

fact that these films are easily attacked by water vapour in the coating atmosphere, and readily lose their homogeneity. In our previous papers, it was shown that alkali-free borosilicate glass films in the binary, B_2O_3–SiO_2 [11, 12], and the ternary, MO–B_2O_3–SiO_2 ($M = Zn$, Mg) [13, 14], systems were prepared by the sol-gel method when the coating was carried out in a dry atmosphere. In the present work, sol-gel derived $xB_2O_3 \cdot (20-x) P_2O_5 \cdot 80SiO_2$ (in mol %) glass films with $x = 0$, 10 and 20 have been prepared by carrying out the coating in a dry atmosphere. The structure, hardness, thermal and optical properties and alkali passivation behaviour of the films have been studied as a function of both heat-treatment temperature and composition of the films.

2. Experimental procedure
2.1. Preparation of coating films

Silicon tetraethoxide, $Si(OEt)_4$, tri-ethyl-phosphate, $PO(OEt)_3$, and boron tri-iso-propoxide, $B(O\text{-}iPr)_3$, were used as starting materials for SiO_2, P_2O_5 and B_2O_3, respectively. The chemical compositions of the coating films examined in this work were $20P_2O_5 \cdot 80SiO_2$, $10B_2O_3 \cdot 10P_2O_5 \cdot 80SiO_2$ and $20B_2O_3 \cdot 80SiO_2$ (in mol %), which were hereafter designated as 20P80S, 10B10P80S and 20B80S, respectively.

Fig. 1 shows the preparation procedure of B_2O_3–P_2O_5–SiO_2 coating films in the present work. In the preparation of all the coating solutions, $Si(OEt)_4$ was mixed with ethanol, EtOH, adjusting the molar ratio of $EtOH/Si(OEt)_4$ to 5, then 6 wt %
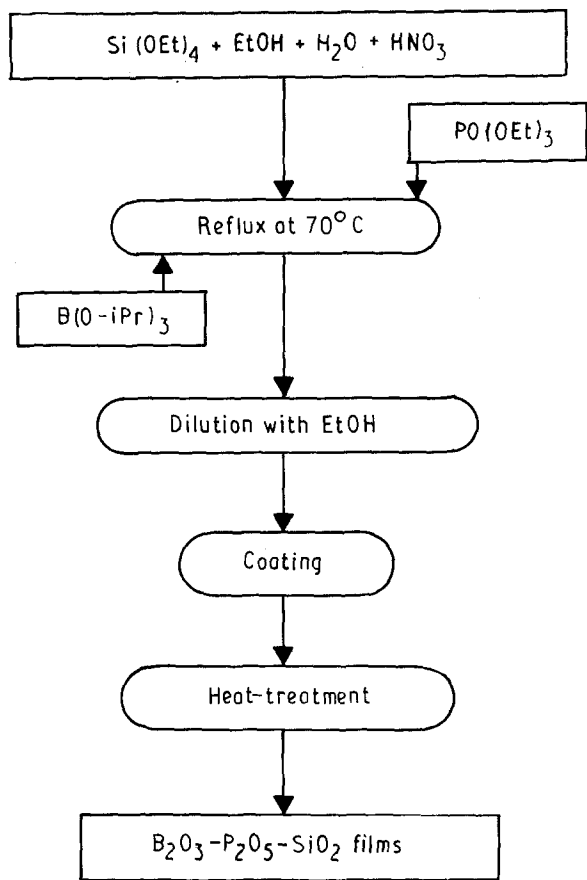
2.2. Measurements of film properties

The i.r. spectra for the coating films on stainless steel plates were obtained using an infrared spectrophotometer (260-50, Hitachi, Japan) in a reflection mode. For the evaluation of hardness of the coating films, the load at scratch, L_{sc}, of the films on Corning 7059® glass plates was measured using a hand-made apparatus in the same way as described in a previous paper [11]. Thicknesses of the films on optically flat BK-7® glass discs were measured using a surface profilometer (SE-30C, Kosaka Laboratory, Japan). Thermal analyses for bulk gels in the $B_2O_3-P_2O_5-SiO_2$ system were performed on differential thermal analysis (DTA) and thermogravimetry (TG) (Thermoflex, Rigaku, Japan). Optical transmission spectra of the soda-lime-silica glass plates coated with the films were measured using a spectrophotometer (UV-240, Shimadzu, Japan). Depth profiles of sodium ions in the coating films on soda-lime-silica glass plates were obtained using electron spectroscopy for chemical analysis (ESCA-750, Shimadzu, Japan).

3. Results and discussion

3.1. Changes in structure and hardness of films during heat-treatment

Fig. 2 shows the infrared absorption spectra of the 20P80S coating films as a function of heat-treatment temperature. The films were kept at a given temper-
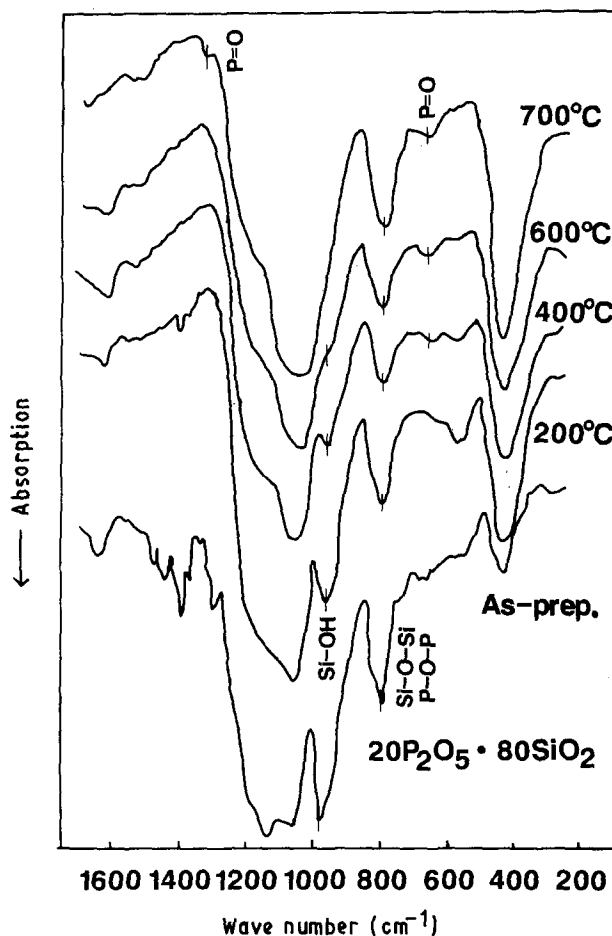

Figure 1 Preparation procedure of the $xB_2O_3 \cdot (20-x)$ $P_2O_5 \cdot 80SiO_2$ $(x = 0, 10$.and 20 mol %) glass films.

HNO_3 was added to the solution, so that the molar ratio of $H_2O/Si(OEt)_4$ became 6. In the case of the preparation of 20P80S coating solution, the above mixed solution was refluxed at 70 °C for 3 h for the partial hydrolysis of $Si(OEt)_4$ and then $PO(OEt)_3$ was added to the solution, followed by reflux at the same temperature for an additional 3 h. In the case of 10B10P80S, the first reflux for the partial hydrolysis of $Si(OEt)_4$ was carried out for 2 h, the second reflux was continued for 2 h after the addition of $PO(OEt)_3$ and the final reflux was continued for 2 h after the addition of $B(O-iPr)_3$. In the case of 20B80S, the first reflux was carried out for 4 h and the second reflux was continued for 4 h after the addition of $B(O-iPr)_3$ in the same way as reported in previous papers [11, 12]. All the solutions obtained in these ways were further diluted with EtOH to control the film thickness.

The coating process was performed in a dipping-withdrawing manner in a humidity-controlled glovebox; the withdrawing speed was kept at 3.6 mms^{-1}.

Soda-lime-silica glass plates and Corning 7059® glass plates were mainly used as substrates for coating. Stainless steel plates and optically flat BK-7® glass discs (Schott Glaswerke) were also used for the measurements of infrared spectra and film thickness, respectively. The substrates coated with films were kept for a while in the glovebox to let the solvents evaporate and then heat-treated in air using an electric furnace. The temperature of the heat-treatment was raised stepwise at intervals of 100 °C for 10 min.

Figure 2 Infrared absorption spectra of $20P_2O_5 \cdot 80SiO_2$ coating films as a function of heat-treatment temperature.

ature for 10 min. The strongest absorption peak is seen at around 1100 cm^{-1}, which is assigned to the stretching mode of Si–O bonds [15]. This peak was found to shift to lower wave numbers with increasing heat-treatment temperature up to 700 °C. The absorption peak at 950 cm^{-1}, which is assigned to Si–OH groups [16], decreases in intensity with increasing heat-treatment temperature and almost disappears over 600 °C. The peak associated with the bending mode of Si–O–Si bonds is also observed at 430 cm^{-1} [15]. The intensity of this peak at 430 cm^{-1} increases with increasing heat-treatment temperature. The weak absorption peak at 550 cm^{-1} is assigned to the four-membered Si–O ring structure [17]. There exist some sharp absorption peaks at around 1400 cm^{-1}. These peaks originate from organic groups in PO(OEt)$_3$, which is the starting material for P$_2$O$_5$. These organic groups in PO(OEt)$_3$ remain in the gel films up to 200 °C. Weak absorption peaks appear at 1310 cm^{-1} over 700 °C and at 650 cm^{-1} over 400 °C, which can, respectively, be assigned to a stretching mode and bending mode of P=O bonds [18]. The absorption peak at around 800 cm^{-1} is considered to be a result of the overlapping of the bands due to Si–O–Si bonds and P–O–P bonds [15, 18].

Fig. 3 shows the infrared absorption spectra of the 10P10B80S coating films as a function of heat-treatment temperature. As the heat-treatment temperature
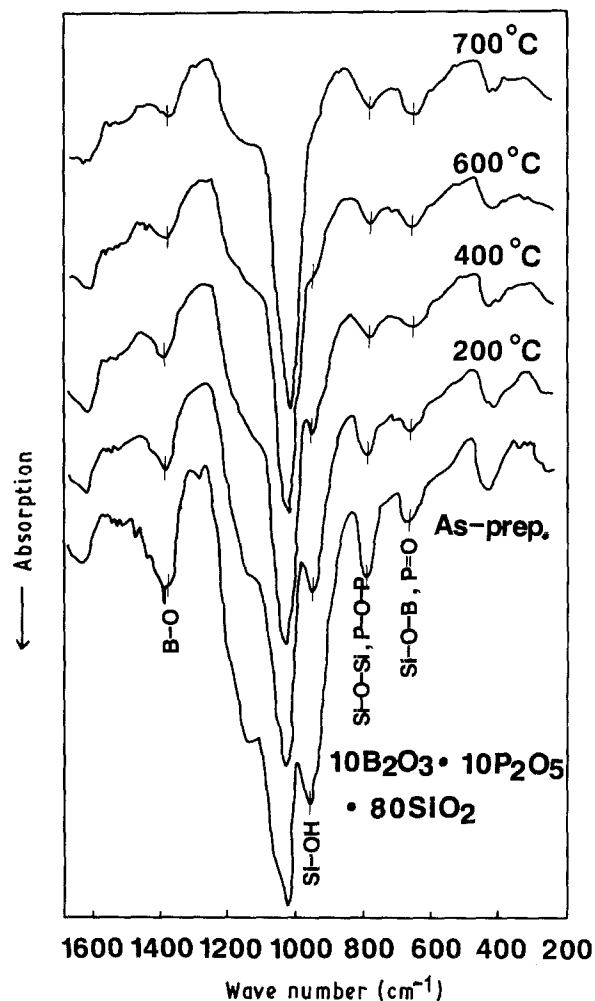
is increased, the absorption peak at around 1100 cm^{-1} due to Si–O bonds shifts to lower wave numbers and the peak at 950 cm^{-1} due to Si–OH bonds decreases and almost disappears over 600 °C. These changes during heat-treatment are similar to those observed in the 20P80S coating films (Fig. 2). An additional peak related to B$_2$O$_3$ component is seen at around 1400 cm^{-1}, which is assigned to B–O bonds [19]. The absorption peak at around 650 cm^{-1} in 10B10P80S films is considered to be a result of the overlapping of the bands due to P=O bonds [18] and Si–O–B bonds [19].

Fig. 4 shows the infrared absorption spectra of 20B80S coating films as a function of heat-treatment temperature. A shift of the absorption peak at 1100 cm^{-1} to lower wave numbers and a decrease in intensity of the absorption peak at 950 cm^{-1} during the heat-treatment are observable as in the 20P80S (Fig. 2) and 10P10B80S (Fig. 3) coating films. Another peak related to Si–O–B bonds becomes appreciable at 920 cm^{-1} [19] over 600 °C accompanied by a decrease in the intensity of the absorption peak at 950 cm^{-1} due to the Si–OH group.

Small differences in structural development of the coating films during the heat-treatment are observed among the 20P80S, 10P10B80S and 20B80S films. The intensity of the peak at 430 cm^{-1} due to Si–O–Si bonds in the 20P80S films (Fig. 2) and the 20B80S films (Fig. 4) increases with increasing heat-treatment temperature, whereas in the 10B10P80S films only slight changes are observed (Fig. 3). In addition, the weak absorption peak at 550 cm^{-1}, which is assigned to the four-membered Si–O ring structure [17], is seen
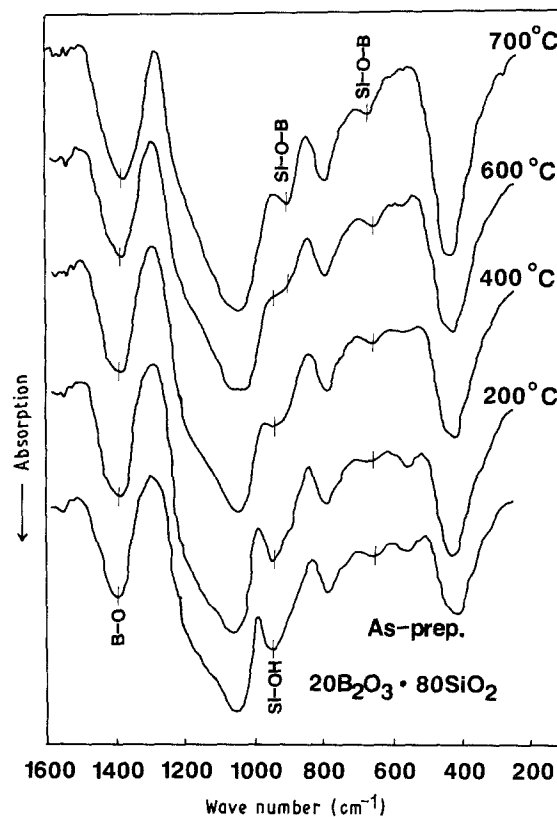

Figure 3 Infrared absorption spectra of $10B_2O_3 \cdot 10P_2O_5 \cdot 80SiO_2$ coating films as a function of heat-treatment temperature.

Figure 4 Infrared absorption spectra of $20B_2O_3 \cdot 80SiO_2$ coating films as a function of heat-treatment temperature.

to decrease with an increase in the heat-treatment temperature in the 20P80S (Fig. 2) and the 20B80S films (Fig. 4), while such a change in infrared spectra is not clearly observed in the 10B10P80S films (Fig. 3). From these results, it is considered that the structural evolution in the 10B10P80S films during heat-treatment is somewhat different from those in the 20B80S and the 20P80S films.

The structural development of the coating films with increasing heat-treatment temperature is further discussed on the basis of the load at scratch, L_{sc}, and shrinkage of the films. L_{sc} of a film was defined as the minimum weight loaded on a stylus to make detectable scratches under an optical microscope [11]. Fig. 5 shows changes in L_{sc} of the coating films as a function of heat-treatment temperature. All the coating films were heat-treated for 10 min at a given temperature. As the temperature is increased, L_{sc} of all the coating films increases. The incorporation of P_2O_5 component lowers L_{sc}. The 20B80S films show the highest value of L_{sc} at a given temperature and almost a constant value over 600 °C. On the other hand, L_{sc} of the 20P80S films is very low even after the heat-treatment at 600 °C. Organic groups in $PO(OEt)_3$ tend to remain in the gel films at relatively high temperatures as shown in Figs 2 and 3; it is thus considered that the organic groups prevent the development of a glass network structure below 200 °C and their decomposition increases the porosity in the films and thereby decreases L_{sc} of the films.

The shrinkage of the film thickness during the heat-treatment is shown in Fig. 6 for the 20P80S, 10B10P80S and 20B80S films coated on BK-7® glass discs. After the heat-treatment at 500 °C, the shrinkage of the films decreases by replacing P_2O_5 with B_2O_3 and the shrinkage of the 20B80S films in the range 400–500 °C is small, compared with those of the 10B10P80S films and the 20P80S films. These findings correspond to the changes in L_{sc} of the films with increasing heat-treatment temperature, i.e. organic groups originated from $PO(OEt)_3$ in the as-prepared films cause a large shrinkage of the films during the heat-treatment.
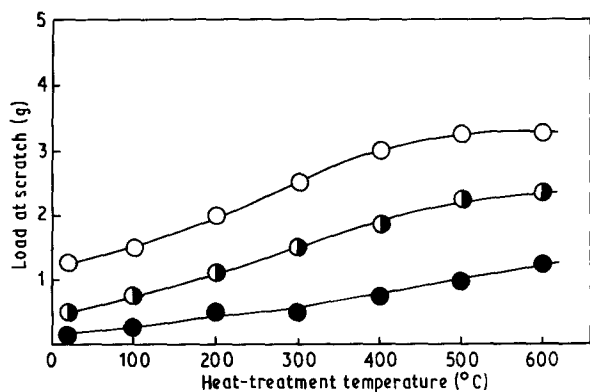
3.2. Thermal analysis

Fig. 7 shows DTA curves for the powders of 20P80S, 10B10P80S and 20B80S bulk gels; the bulk gels were obtained by keeping the coating solution before the dilution at 50 °C and dried for about 2 months at the same temperature. The endothermic peaks below 200 °C are ascribed to the removal of residual solvents and water in the bulk gels. Two such endothermic peaks are observed in 20P80S and in 10B10P80S gels, whereas only one endothermic peak is seen in 20B80S gels, suggesting that there exist two different sites for adsorption of the solvents and/or water in the gels containing P_2O_5. Several exothermic peaks due to burning of organic groups are observed in the range 250–500 °C. It can be seen that the gels containing P_2O_5 show a large exothermic peak in the range
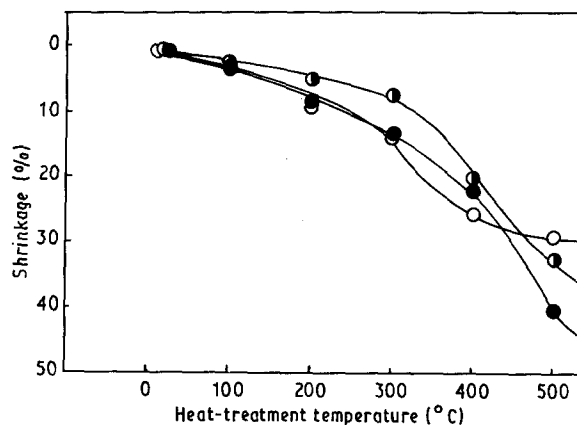

Figure 6 Shrinkage of the $xB_2O_3 \cdot (20-x)P_2O_5 \cdot 80SiO_2$ ($x = 0$, 10 and 20 mol %) coating films with increasing heat-treatment temperature: (○) 20B80S; (◑) 10B10P80S and (●) 20P80S.

Figure 5 Changes in load at scratch of the $xB_2O_3 \cdot (20-x)$ $P_2O_5 \cdot 80SiO_2$ ($x = 0$, 10 and 20 mol%) coating films with increasing heat-treatment temperature: (○) 20B80S; (◑) 10B10P80S and (●) 20P80S.
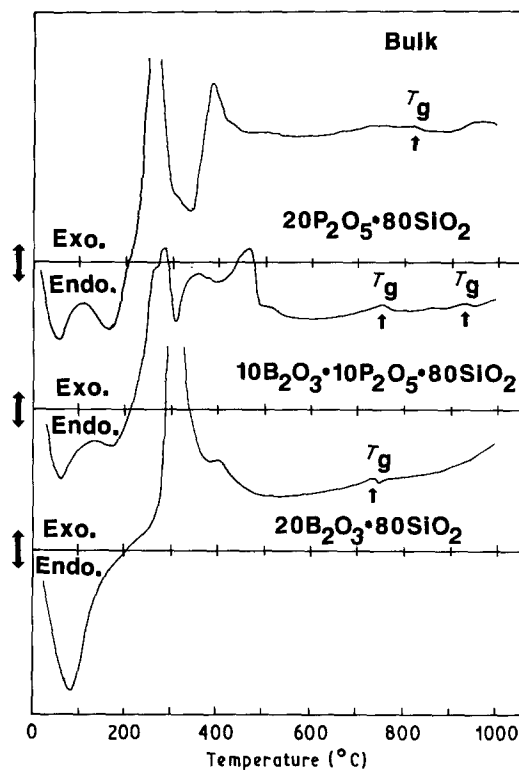

Figure 7 Differential thermal analysis curves for the $xB_2O_3 \cdot (20-x)P_2O_5 \cdot 80SiO_2$ ($x = 0$, 10 and 20 mol %) bulk gels; heating rate = 10 °C min⁻¹.

400–450 °C. This fact is in good agreement with the results that the larger amounts of organic groups remain in the films containing P_2O_5 as shown in the infrared absorption spectra, the lower L_{sc} and the larger shrinkages for these films.

The glass transition temperature, T_g, is observed in each gel. The 20B80S gel shows the lowest T_g (= 720 °C) among the gels examined. In other words, B_2O_3 reduces T_g more effectively than P_2O_5. These results are consistent with the fact that 20B80S coating films are densified at the lowest temperature among the coating films examined. The 10B10P80S gel shows two T_g at 750 and 938 °C, indicating that phase-separation might occur in a glass of this composition. The bulk gels containing larger amounts of P_2O_5 showed the larger weight loss in the TG curves due to the removal of solvents and/or water and due to burning of organic groups.

All the bulk gels were amorphous in their X-ray diffraction patterns after heating up to 1000 °C. Woignier et al. reported that the crystallization of BPO_4 was observed in B_2O_3-P_2O_5-SiO_2 bulk gels prepared by the sol-gel process [9]. In our investigation, however, no BPO_4 crystallite was observed even after the heat-treatment at 1000 °C. It should be ascribed to the lower reactivity of tri-ethyl-phosphate, $PO(OEt)_3$, rather than that of tri-methyl-phosphite, $P(OMe)_3$, which was used in Reference 9 as a starting material for P_2O_5.

3.3. Optical transmission

Transparent coating films containing B_2O_3 were obtained only by carrying out the coating in a dry atmosphere. Fig. 8 shows the optical transmission spectra in the visible range for the soda-lime-silica glass plates coated with 10B10P80S films; sample (a) was coated in a dry atmosphere (18 °C and 20% R.H.) and sample (b) in an ambient atmosphere (18 °C and 60% R.H.). Both samples were heat-treated at 500 °C for 10 min, the film thicknesses of which were about 100 nm. The transmittance of sample (a) is higher than 90% in the visible range, indicating that the transparent 10B10P80S coating films with the lower refractive index than that (1.51) of the substrates are formed. On the other hand the transmittance of sample (b) is much lower than those of sample (a) and the glass plate itself. Such a low transmittance of sample (b) was found to result from the deposition of crystalline H_3BO_4 and small cracks by the attack of water vapour in the atmosphere during the coating process.

3.4. Alkali passivation effects

Fig. 9 shows the depth profiles of sodium ions which migrated from the soda-lime-silica glass plates into the 20P80S, 10B10P80S and 20B80S films; the profile in sol-gel derived pure SiO_2 film is also shown for comparison. These profiles were obtained by electron spectroscopy for chemical analyses (ESCA). All the films were heat-treated at 500 °C for 20 min in air. The concentration of sodium ions in the glass plates was
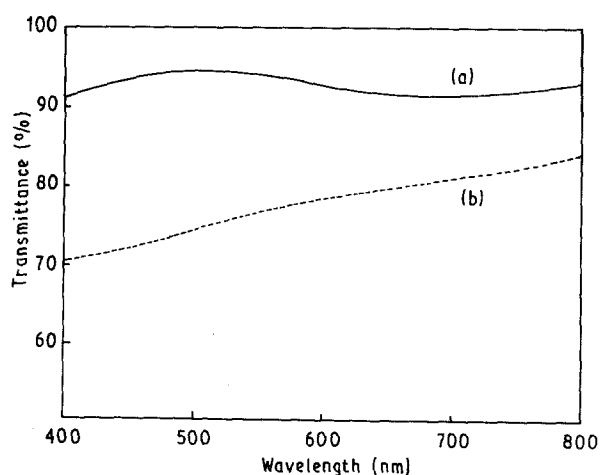

Figure 8 Optical transmission spectra of soda-lime-silica glass substrates coated with the $10B_2O_3 \cdot 10P_2O_5 \cdot 80SiO_2$ films; coated in: (a) dry atmosphere and (b) ambient atmosphere.
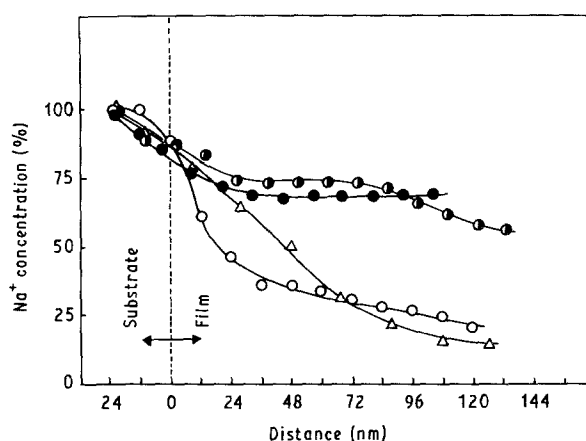

Figure 9 Concentration profiles of sodium ions which diffused from soda-lime-silica glass substrates into the $xB_2O_3 \cdot (20-x)P_2O_5 \cdot 80SiO_2$ ($x = 0$, 10 and 20 mol %) coating films. All the films were heat-treated at 500 °C for 20 min: ($\triangle$) SiO_2; ($\bigcirc$) $20B_2O_3 \cdot 80SiO_2$; ($\bullet$) $10B_2O_3 \cdot 10P_2O_5 \cdot 80SiO_2$ and ($\bullet$) $20P_2O_5 \cdot 80SiO_2$.

taken to be 100% as reference. It is worth noting that the sodium concentrations in the 20P80S and 10B10P80S films are higher than those in the 20B80S and pure SiO_2 films. Among the coating films examined, the concentration of sodium ions is the lowest in the 20B80S film. These results indicate that phosphorus effectively acts as a getter for alkali ions.

4. Conclusion

Sol-gel derived $xB_2O_3 \cdot (20-x)P_2O_5 \cdot 80SiO_2$ (in mol %) glass films with $x = 0$, 10 and 20 have been prepared by carrying out the coating in a dry atmosphere. The organic groups in $PO(OEt)_3$ used as a starting material for P_2O_5 tended to remain up to relatively high temperatures. Coating films containing larger amounts of P_2O_5 showed a lower value of load at scratch and a larger shrinkage during the heat treatment than the coating films containing smaller amounts of P_2O_5. The 20B80S coating films showed

the highest value of load at scratch at a given temperature and almost a constant value over 600 °C. Glass transition temperatures, T_g, were observed in all the bulk gels. It was found that B_2O_3 effectively reduced T_g more than P_2O_5. The 10B10P80S bulk gel showed two T_g, indicating that the phase-separation might occur in a glass of this composition. All the bulk gels were amorphous after the heating up to 1000 °C. The low humidity in the atmosphere during coating was very important to form transparent B_2O_3-P_2O_5-SiO_2 glass films which have neither crystalline H_3BO_3 nor small cracks. The concentrations of sodium ions, which migrated from soda-lime–silica glass substrates during the film formation, were higher in 20P80S and 10B10P80S films than in 20B80S and pure SiO_2 films. It should result from the gettering effects of phosphorus. Among the coating films examined, the concentration of sodium ions was the lowest in the 20B80S film.

Acknowledgement

References

1. A. TAKAMATSU and T. YOSHIMI, *Gekkan Semiconductor World* **8** (1989) 78.
2. A. C. SHARP and J. PATEL, *Vacuum* **35** (1985) 441.
3. Y. MISATO, H. HACHINO, S. HARA and M. HANAZONO, *J. Electrochem. Soc.* **131** (1984) 359.
4. Y. MISATO, *ibid.* **131** (1984) 2619.
5. A. J. LEARN and B. BAERG, *Thin Solid Films* **130** (1985) 103.
6. T. FOSTER, G. HOEYE and J. GOLDMAN, *J. Electrochem. Soc.* **132** (1985) 505.
7. R. A. LEVY, P. K. GALLAGHER and F. SCHREY, *ibid.* **134** (1987) 430.
8. F. S. BECKER and S. ROHL, *ibid.* **134** (1987) 2923.
9. J. WOIGNIER, J. PHALIPPOU and J. ZARZYCKI, *J. Non-Cryst. Solids* **63** (1984) 117.
10. K. CHOU, *ibid.* **110** (1989) 122.
11. N. TOHGE, A. MATSUDA and T. MINAMI, *J. Amer. Ceram. Soc.* **70** (1987) C-13.
12. *Idem, J. Ceram. Soc. Jpn.* **95** (1987) 182.
13. N. TOHGE and T. MINAMI, *Chem. Express* **3** (1988) 455.
14. *Idem, J. Non-Cryst. Solids* **112** (1989) 432.
15. R. HANNA, *J. Amer. Ceram. Soc.* **48** (1965) 595.
16. K. KAMIYA, S. SAKKA and M. MIZUTANI, *J. Ceram. Soc. Jpn.* **86** (1978) 552.
17. K. KAMIYA, T. YOKO, K. TANAKA, Y. IWAMOTO and H. SUZUKI, *Rep. Asahi Glass Found. Ind. Technol.* **50** (1987) 149.
18. J. WONG, *J. Non-Cryst. Solids* **20** (1976) 83.
19. A. S. TENNEY and J. WONG, *J. Chem. Phys.* **56** (1972) 5516.