

Electrical Conduction in Phosphate-based Glass Containing Tin Oxide Prepared by Sol-Gel Process

Masahiro TAHASHI*, Hideo GOTO* and Toshiyuki IDO*

(Received July 11, 2011)

We prepared phosphate-based glass containing tin oxide by the sol-gel process. The time response of current and the effects of humidity on electrical conduction were investigated. A few kinds of carriers having different mobility were observed in the sample. The mobility of the fast carrier was $1 \times 10^4 \text{ m}^2/\text{Vs}$ regardless of the relative humidity, while that of slow carrier increased linearly with relative humidity, from $3 \times 10^6 \text{ m}^2/\text{Vs}$ at 20% to $1 \times 10^5 \text{ m}^2/\text{Vs}$ at 50%.

Keywords: Phosphate; Tin; Glass; Sol-gel method

1. Introduction

Glass materials are of great importance because of their many structural and compositional varieties, as well as their wide range of applications. Among glass materials, phosphate-based glass has attractive mechanisms of electrical conduction that arise from proton conduction. Consequently, phosphate-based glass has recently received considerable attention as a possible electrolyte for fuel cells. Furthermore, phosphate-based glass is expected to have another mechanism of conduction by electrons not ions. This conduction mechanism can potentially be applied in various electronic devices. A phosphate is a salt of phosphoric acid. Phosphoric acid forms three ions in its dissociated states: H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} . These ions react with additives such as metals, and it is possible to impart various properties to phosphate by using additives. Tin, which is used as additive in this study, is a common non-toxic metallic material with four valence electrons. Tin dioxide, SnO_2 , is an n-type oxide semiconductor with excellent detection characteristics as a sensor for gases including hydrogen¹⁻⁵⁾ and carbon monoxide⁶⁾. Prior to this work, the effects on electrical conduction of adding tin to phosphate-based glass have not been well understood. In this study, we fabricated phosphate-based glass containing tin oxide by the sol-gel process and investigated the electrical properties of

the material as a function of humidity and the time response of current.

2. Experimental

Phosphate-based glass containing tin oxide films were deposited on glass substrates by sol-gel processing. Tin monoxide powder (99.9%, Type 36630, Yoneyama Yakuhin Kogyo Co., Ltd, Japan) and phosphoric acid solution (85.0%, Type 05010, Yoneyama Yakuhin Kogyo Co., Ltd, Japan) were used as starting materials. These materials were mixed in a molar ratio of $\text{P}/\text{Sn} = 0.2$. The mixture was placed under reduced pressure of 55 kPa for 24 h, which afforded the transparent sol solution. The sol solution was coated on a glass substrate and then heated in air at a rate of $5^\circ\text{C}/\text{min}$, and then held at 375°C for 8 h.

At room temperature, a DC bias was applied at various relative humidity (R.H.) levels. Biasing was applied by a pulse train at 5 V, and the induced current was measured by the four-point probe method and the time response of the current was observed with an oscilloscope (DL-1620, Yokogawa Electric Corporation).

3. Results and discussion

The state of the samples was significantly affected by the addition of tin oxide. Phosphate-based glass is

* Department of Electrical Engineering

known to be unstable in a humid atmosphere, but the prepared sample was found to be stabilized by the addition of tin oxide. Figure 1 shows the transient current response at relative humidity of 40% at room temperature, for a time period of 0.1 s. The current increased rapidly and reached a maximum at 0.01 s, regardless of the relative humidity. After reaching a maximum, the current decreased exponentially. We estimated the relaxation time from the slope of logarithmic plots of the current. Figure 2 shows the relative humidity dependence of relaxation time.

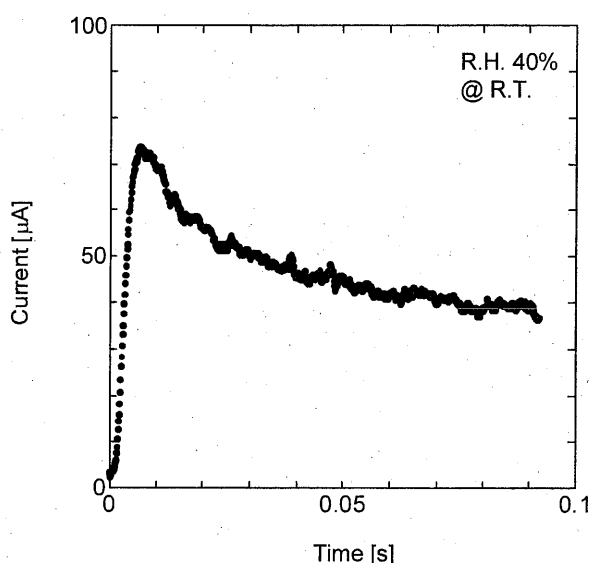


Figure 1 Transient current response at relative humidity of 40% at room temperature for short time period of 0.1 s.

The relaxation time did not depend on the relative humidity and was approximately 0.03 s. The mobility was calculated to be $1 \times 10^{-4} \text{ m}^2/\text{Vs}$. The current tended to continue decreasing over the measurement range. The transient current response for a longer period of 10 s, which was measured under the same conditions described above, is shown in Fig. 3. After the relaxation time shown in Fig. 2, the current continued to decrease and then reached a constant value after a few seconds. We also estimated the relative humidity dependence of the relaxation time and electrical conductivity for the longer time period.

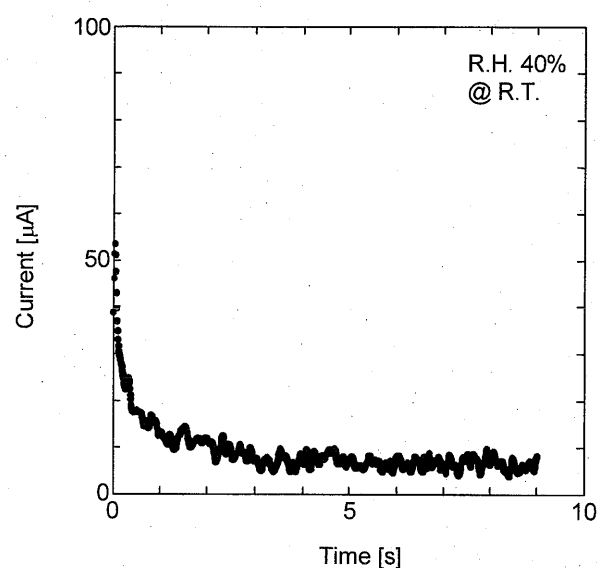


Figure 3 Transient current response at relative humidity of 40% at room temperature for long time period of 10 s.

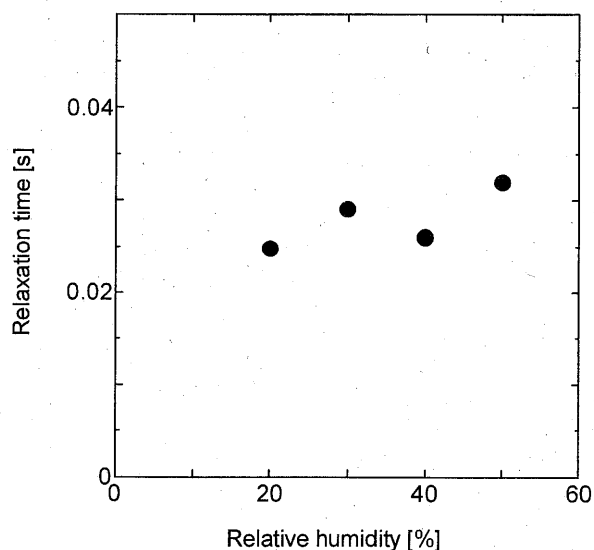


Figure 2 Relative humidity dependence of relaxation time for time period of 0.1 s.

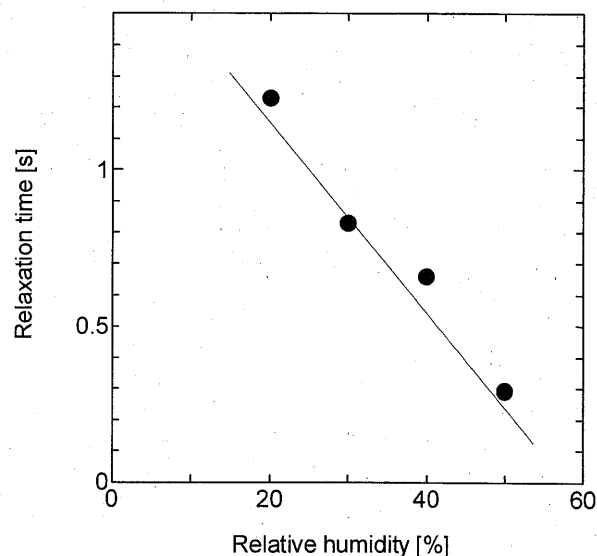


Figure 4 Relationship between relative humidity and relaxation time for long time period.

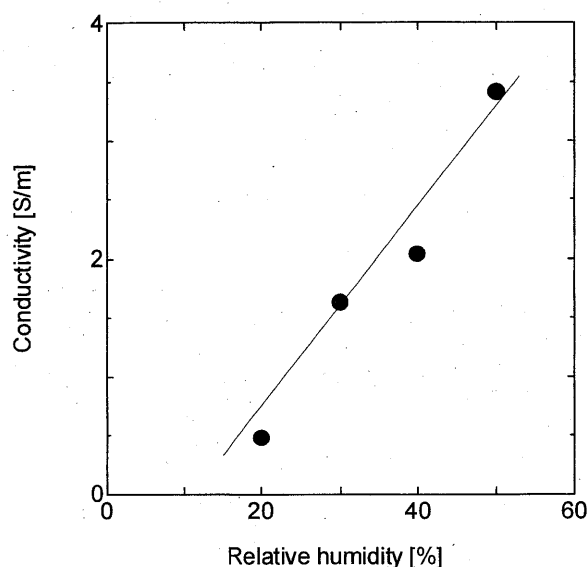


Figure 5 Relative humidity dependence of conductivity calculated from saturated currents.

Figure 4 presents the relationship between relative humidity and the relaxation time for a time period of 10 s. The relaxation time decreased linearly as relative humidity increased. Moreover, the relaxation time was one or two orders of magnitude larger than that measured for the short time period. The mobility values were $3 \times 10^{-6} \text{ m}^2/\text{Vs}$ and $1 \times 10^{-5} \text{ m}^2/\text{Vs}$ at relative humidity of 20% and 50%, respectively. Furthermore, the relative humidity dependence of the conductivity that was calculated from the saturated current is shown in Fig. 5. The conductivity depended on relative humidity and increased linearly with increasing relative humidity.

From the time response of current for both short and long time periods, it can be seen that current increased and reached maximum value at 0.01 s, and then decreased over a relaxation time of 0.03 s. Then, the gradient of response curve changed, and the current decreased more steeply. Finally, the current reached a constant value within a few seconds. These results indicate that a few kinds of carriers are present in the sample. The relaxation time measured for the short time period does not depend on the relative humidity. On the other hand, the relaxation time measured for the long time period depends on relative humidity; thus, the ionic components generated by humidity affect the mechanism of electrical conduction^{7,8)}. In the steady state, the current continues to flow, indicating that electrons contribute to electrical conduction. The ionic components generated by humidity supply the

electrons that act as carriers in the sample, since the conductivity measured from the saturated currents depends on relative humidity as shown in Fig. 5.

4. Summary

Tin-doped phosphate-based glass was prepared by the sol-gel process. We investigated the time response of current and the effects of relative humidity on the electrical conduction mechanism. It was found that a few kinds of carriers were present in the sample: transport of the fast carrier was independent of humidity and transport of the slow carrier was affected by humidity. Therefore, the ionic components generated by humidity have an effect on the mechanism of electrical conduction, and the ionic components supply electrons that act as carriers in the sample, thus leading to continuous current that depends on humidity.

Acknowledgements

This research was partly supported by The Hibi Research Grant and Chubu University Grant (B).

References

- 1) B. N. Pal and D. Chakravorty, *J. Phys. D* 38 (2005) 3537.
- 2) A. Rothschild and Y. Komem, *J. Appl. Phys.* 95 (2004) 6374.
- 3) N. Yamazoe and N. Miura, *Chem. Sens. Technol.* 4 (1992) 19.

- 4) N. Yamazoe, J. Fuchigami, M. Kishikawa, and T. Seiyama, *Surf. Sci.* 86 (1979) 335.
- 5) K. Wada and M. Egashira, *Sens. Actuators B* 62 (2000) 211.
- 6) A. Salehi, *Sens. Actuators B* 96 (2003) 88.
- 7) M. Nogami, R. Nagao, C. Wang, T. Kasuga, and T. Hayakawa, *J. Phys. Chem. B* 103 (1999) 9468.
- 8) C. Wang, Y. Abe, T. Kasuga, and M. Nogami, *J. Ceram. Soc. Japan* 107 (1999) 1037.