Preparation of Amorphous Films in the Systems $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ by Rf-Sputtering and Their Ionic Conductivity

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高周波スパッタリングによる $\text{Li}_2\text{O}-\text{SiO}_2$ 系および $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ 系非晶質薄膜の 作製とイオン導電率

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Amorphous thin films in the systems $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ are prepared by rf-magnetron sputtering, and their electrical properties are investigated in order to develop solid electrolytes for thin film solid state ionic devices. These films exhibit high electrical conductivities ranging from 10^{-4} to 10^{-7} Sm^{-1} at room temperature.

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For several years many investigations have been made in the field of lithium ion solid electrolytes for their utilization in battery systems, in electrochromic devices, and so on. Some of these solid electrolytes, such as $\text{Li}_3\text{N}^{(1)}$ and $\text{LiI}-\text{Li}_2\text{S}-\text{B}_2\text{S}_3$ glasses⁽²⁾, have high lithium conductivities in the order of 10^{-1} Sm^{-1} at room temperature, but they are unstable in air. Other solid electrolytes like LISICON⁽³⁾ and oxide glasses⁽⁴⁾, which are stable in air, have lower conductivities in the range of 10^{-3} – 10^{-7} Sm^{-1} . In the use of solid electrolytes, the film forms have practical advantages, because their apparent resistance can be reduced. The low internal resistance is especially important in the field of solid state cells for high power and long-life operation^{(5)–(7)}.

In previous papers^{(8),(9)} we reported that Li_4SiO_4 – Li_3BO_3 glasses could be prepared by rapid quenching and these glasses have relatively high ionic conductivities (10^{-3} – 10^{-5} Sm^{-1} at room temperature). The purpose of the present study is to prepare amorphous thin films in the systems $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ by rf-magnetron sputtering and to measure their ionic conductivities as the extension of the previous investigations^{(8),(9)}.

Film depositions were made by a planner-magnetron type rf-sputtering apparatus (ULVAC, SBR-1104 E) under 1.2×10^{-2} Torr of 50% oxygen–50% argon gas mixture and rf power of 0.6 Wcm^{-2} . Pyrex glass plates (Corning, No. 7740) were used as a substrate. In order to avoid temperature rise of the substrate, the copper substrate-holder was attached and cooled by the flow of ethanol-dry ice coolant. Thus the substrate temperature was kept constant at about 70°C . A powder of Li_4SiO_4 was used as the sputtering target (80 mm in diameter) for the preparation of the $\text{Li}_2\text{O}-\text{SiO}_2$ films. The films in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ were prepared by use of the target of powder mixtures consisting of 40% Li_4SiO_4 and 60% Li_3BO_3 (mol%). Some Li_2O pellets were put on these targets in order to supply additional lithium and to change the composition in the sputtered films. All the sputtered films were amorphous in X-ray diffraction measurements. The chemical composition of the films was analyzed by an atomic absorption spectrophotometer (Hitachi, 170-30) after they were dissolved in HCl solution.

AC conductivities of the films were measured in a dry nitrogen atmosphere by use of a G-C bridge (Ando Denki, TR-1 C) in the temperature range

350–540 K. Figure 1 shows the schematic diagrams of cells for electrical measurements: a sandwich-type cell (A) and a co-planner-type cell (B), the electrodes of which are both evaporated gold. The temperature dependence of the conductivities measured for a 44 $\text{Li}_2\text{O} \cdot 32 \text{SiO}_2 \cdot 24 \text{B}_2\text{O}_3$ film by use of both types of cells are also shown in the figure. The plots lie on one straight line and fit the Arrhenius type equation, $\sigma T = A \exp(-E/kT)$, indicating that the conductivities of films can correctly be determined by either type of cells, (A) or (B) above. In the following results and discussion, the co-planner-type cells are mostly used. This figure also shows that the conductivity of amorphous films is isotropic, since the conductivity is independent of the electrode geometry.

Figure 2 shows complex impedance plots for 68.7 $\text{Li}_2\text{O} \cdot 31.3 \text{SiO}_2$ (mol%) film as an example at various temperatures. The film impedance is attributed to the semicircle which was observed at each temperature, and thus the bulk resistance is identified as the intersecting point of the semicircle with the real axis, denoted by an arrow in the figure. Similar results were obtained for other films in the systems $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$.

Figure 3 shows the temperature dependence of

Fig. 1. Schematic diagram of the sandwich-type and co-planner-type cells for electrical conductivity measurements and temperature dependence of conductivity of a film 44 $\text{Li}_2\text{O} \cdot 32 \text{SiO}_2 \cdot 24 \text{B}_2\text{O}_3$ measured by use of a sandwich-type cell ($\blacktriangle$) and the co-planner-type cell ($\circ$).

conductivity of the films in the system $\text{Li}_2\text{O}-\text{SiO}_2$; as a reference, the temperature dependence of conductivity reported for the rapidly quenched glass of the composition Li_4SiO_4 ⁹⁾ is also shown in the figure. These conductivity data

Fig. 2. Complex impedance plots for the 68.7 $\text{Li}_2\text{O} \cdot 31.3 \text{SiO}_2$ film (mol%) at various temperatures; arrows indicate bulk resistance at each temperature.

Fig. 3. Temperature dependences of conductivity of the films in the system $\text{Li}_2\text{O}-\text{SiO}_2$. The value for the rapidly quenched glass Li_4SiO_4 is also shown for comparison.

of films fit the Arrhenius equation, $\sigma T = A \exp(-E/kT)$. It has been indicated in Fig. 3 that the conductivity of films is increased with the lithium oxide contents but is not so high as that of the rapidly quenched glass.

The relation between the conductivity at 500 K, σ_{500} , and the lithium concentration of the sputtered films in the system $\text{Li}_2\text{O}-\text{SiO}_2$ is shown in Fig. 4. The atomic ratio of lithium to the total cations, $\text{Li}/(\text{Li}+\text{Si})$, is plotted as abscissa in the figure. The conductivity of films increases linearly with increasing lithium concentration in a range of smaller lithium contents, and the conductivity of the rapidly quenched glass Li_4SiO_4 , shown by an open circle, lies on the extrapolated line of the plots for films. In contrast, the conductivity of films tends to decrease in the higher atomic ratio of $\text{Li}/(\text{Li}+\text{Si})$ and it was difficult to obtain a films which had the high conductivity as that of the rapidly quenched glass.

Figure 5 shows the conductivities at 500 K, σ_{500} , of the films in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ as a function of $\text{Li}/(\text{Li}+\text{B}+\text{Si})$ atomic ratio. The conductivity increases with increasing lithium contents but decreases again in higher lithium contents. The extrapolation in the lower lithium content range goes through the value for the rapidly quenched glass of the composition

Fig. 4. Conductivities at 500 K, σ_{500} , of the films in the system $\text{Li}_2\text{O}-\text{SiO}_2$ as a function of atomic ratio $\text{Li}/(\text{Li}+\text{Si})$. The value for the rapidly quenched glass Li_4SiO_4 is also shown for comparison by an open circle.

Fig. 5. Conductivities at 500 K, σ_{500} , of the films in the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ as a function of atomic ratio $\text{Li}/(\text{Li}+\text{B}+\text{Si})$. The value for the rapidly quenched glass $40\text{Li}_4\text{SiO}_4 \cdot 60\text{Li}_3\text{BO}_3$ (mol%) is also shown for comparison by an open square.

$40\text{Li}_4\text{SiO}_4 \cdot 60\text{Li}_3\text{BO}_3$ (mol%), shown by an open square in the figure.

The decrease in conductivity of the films with large lithium contents in both systems is probably caused by the absorption of CO_2 or H_2O in air. In fact, Li_2CO_3 was observed by Raman scattering in some films with high lithium contents.

The films with low Li_2O contents, which show lower conductivities, were stable in air. The apparent resistance even in the films with lower conductivities was several tens of ohms at room temperature across the films with $2000\text{ \AA}$ in thickness and 1 cm^2 in electrode area. Such a resistance is a sufficient value for utilization of the films in lithium cells.

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