Fabrication and ionic conduction of ionic conducting thin films

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Abstract

Fabrication technique of a thin film by physical vapor deposition (PVD) was outlined, and the example of some inorganic ionic conductor thin films prepared by pulsed laser deposition (PLD) was described. Typical analysis method of impedance plot by an equivalent circuit and Debye's empirical rule was outlined. Ionic conduction of amorphous lithium lanthanum titanate (LLT) thin film was compared with the polycrystalline LLT, and discussed. Conductivity enhancement of AgI and β-eucryptite thin was discussed in the viewpoint of the forming of high ionic conduction region at the

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boundary between the thin film and insulating substrate, and the theory of the interface ionic conduction was briefly outlined.

1. Introduction

Recently, portable type equipment such as a personal computer and a mobile phone shows remarkable improvement, and these are evolving to smaller and high performance. The advance of the small and high-performance device will be always required in the future. In order to respond to such requirement, as expressed in the word of "nanotechnology", the study about the fabrication and physical property of thin film which thickness is controlled in the nano-meter order are important.

In the field of solid state ionics, the applicant research of a micro battery, micro ion sensors, and a thin film fuel cell, etc. has widely being carried out. For the development of such devices, the study of the fabrication and physical properties of the ionic conductor thin film are necessary to the application for micro-ionic device.

On the other hand, in composite system such as the ionic conductor/insulator system, the phenomenon of the ionic conductivity enhancement has been known. This phenomenon is called as "insulator dispersion effect" or "Liang effect"). Such the insulator dispersion effect has been considered to be useful for the industrial application of the ionic conductors.

The conductivity enhancement has been explained with the forming of the high-ionic conduction region at the boundary between the ionic conductor and the dispersed insulator. It has been considered that the high ionic conduction region would be originated from the space charge at the boundary region. Therefore, in order to clarify the mechanism of the insulator dispersion effect, the study of the high ionic conduction mechanism at the boundary region would be important. However, it is still hardly to say that the mechanism is clarified.

In the case of the composite ionic conductor, to discuss the conductivity enhancement, it would be necessary to treat the system from the viewpoint of the percolation. However, it would be difficult to separate the contribution of boundary region from the effective ionic conductivity of the composite system, because of the complicated system. On the contrary, in ionic conductor thin film has an advantage in the study of the interface ionic conduction and Liang effect, because the interface between thin film and substrate would be realized the interface of the insulator dispersed ionic conductor macroscopically.

Therefore, an ionic conductor thin film is studied by the standpoint not only of the application, but also the academic interest. In this contribution, a fabrication technique of an inorganic ion conductor thin film and the ionic
conduction is mainly described. Especially, as an experimental example, the ionic conduction of an inorganic oxide ionic conductor thin film is described.

Although the various classification of “thin film” is defined, in this contribution, a thin film is classified as follows;

(1) Super-thin film: thin film which thickness is 0.01 µm or less. It is difficult to get the self-supporting film, and prepared on a supporting material such as a substrate. The artificial lattice is also included in this classification.
(2) Thin film: thin film which thickness is about 0.01-10 µm. A thin film with this degree thickness is most widely studied in the field of application.
(3) Thick film: film which thickness is thicker than 10 µm.

In this chapter, super-thin film and thin film are described, and not described about the thick film. The plan of this contribution is the following. The fabrication technique of thin film by physical vapor deposition (PVD) will be briefly outlined in section 2. The typical analysis method of impedance spectra and ionic conductivity is simply described in section 3. In section 4, theory of interface ionic conduction of a thin film, and some example of experimental results and analysis will be briefly outlined.

2. Fabrication techniques of thin film

In this section, some fabrication methods of thin film are described. To prepare the inorganic ionic conductor thin film, various film formation methods is used. Especially, vacuum evaporation, sputtering, pulsed laser deposition which classified into physical vapor deposition (PVD) are used as a cost-effective method to prepare the inorganic thin film. In this section, the outline of the PVD methods is shortly described.

2.1 Vacuum evaporation method

Vacuum evaporation method is a method that a raw material is heated and melted in the vacuum by a heater, the evaporated atom or cluster piles up on the substrate. To melt and evaporate the raw material, not only the resistance heating, but also an electron beam and high frequency is used. Molecular beam epitaxy (MBE) method for the preparation of the artificial lattice is also one kind of the evaporation method in ultra-high vacuum. The merit of the vacuum deposition method is as follows,

(1) The simple and convenient equipment.
(2) The film formation of metal is comparably easy.
(3) It is not dependent on the raw material form such as powder, bulk, and wire.
(4) The film thickness is controlled by the quantity of the raw material, and the control of the film formation rate is difficult.
(5) The adhesion for the substrate of the thin film is comparatively weak.
(6) Deposition of high-melting point materials such as an oxide is difficult.
(7) There is a case in which the component element of the heater is entrapped in a thin film.

As an example of the ionic conductor fabricated by vacuum deposition method, AgI thin film can be prepared on an insulating substrate by applying vacuum deposition method; Ag was deposited on the insulating substrates such as SiO₂ glass by the vacuum deposition method. Afterwards, AgI thin film was formed by the reaction of Ag with I₂. The thickness of prepared AgI film is able to vary by adjusting the quantity of deposited Ag. By X-ray diffraction measurement, the crystal structure of the as-prepared AgI thin films were confirmed to be β-AgI and slightly mixed γ-AgI. Although this method was not deposit AgI directly, it would be also classified into the vacuum deposition.9,10)

2.2 Sputter deposition method

Sputtering method is one of the representative methods of the thin film preparation, because of the convenience of the operation of the equipment.

When an atom or ion with high kinetic energy collide with the solid, it will lose the kinetic energy by the colliding with atoms and molecules that construct the solid. As the result of the momentum transfer from the incident particle, the remove and ejection of particles from the bombarded solid surface is occur. What is called "sputter" is the phenomenon that the atom, which constructs the solid, is removed from the solid surface by bombardment with high-speed ions. The sputtering technique is a method for preparing a thin film with the sedimentation of the removed atom on a substrate. Especially, a radio frequency (RF) sputtering is adapted to a fabrication of insulating thin film. The detail of the mechanism of the sputter is described in the paper of Wehner et al.15,16)

Sputtering technique has the following advantages;

(1) The preparation of a thin film of high-melting point material is comparatively easily.
(2) The thickness of prepared film is comparatively uniform, and the composition is homogeneous.
(3) Accurate control of the film thickness (deposition rate).
(4) It is possible to prepare a crystalline thin film.
(5) Excellent film adhesion for the substrate.
(6) Excellent controllability and responsibility.

On the other hand, the sputtering technique has following demerits;

(1) Its small deposition rate.
(2) There is a case in which the film is damaged by a re-sputtering.
(3) The chemical composition of the target and prepared thin film is often different.
(4) There is a case in which the atmosphere gas is entrapped in a film.

The controlling factor in sputtering technique is as follows;

(1) Introduced gas and the pressure.
(2) The sputtering output.
(3) The distance between targets and substrate.
(4) Quality and configuration of the targets.
(5) Surface state and temperature of the substrates.
(6) The condition of the post annealing after the film formation.

There are many reports about the preparation of an inorganic oxide ionic conductor thin film by the RF-sputtering method. As the examples of ionic conductor thin film fabricated by sputtering method, M.Yamashita and H.Yamanaka prepared Li$_2$S-GeS$_2$-Ga$_2$S$_3$ thin films with a wider composition range by RF sputtering method. They reported that the conductivity of the thin film was almost identical in bulk glasses of similar composition and increased along with increasing Li$_2$S content.\(^{17-18}\).

### 2.3 Pulsed laser deposition (PLD) method

The pulsed laser deposition is one of the physical vapor deposition (PVD) in which raw material is made to evaporate using the laser beam. When a laser beam with the strength over a threshold is emitted to the solid surface, it is converted into electron, thermal and photochemical mechanical. As the result, the explosive evaporation of neutral atoms, molecules, ions of positive and negative, clusters, etc. is generated. Laser ablation method is a method of the film preparation by piling up these emitted particle on the substrate. Especially, it is called as Pulsed Laser Deposition (abbreviated as PLD), when a high-power pulsed laser is used as a laser source. The fabrication of an oxide thin film by the PLD method was already reported in 1970’s. After the high-quality high-temperature superconductor thin film was successfully
prepared at the first time by Wu et al. in 1990, the PLD is used for the preparation and study of various oxides thin film such as high temperature superconductor, ferro-electric material, and magnetic material. 19-25)

For film preparation by PLD, following parameters has to be considered; wavelength and energy density of the laser beam, pulse width and frequency, atmosphere gas and the pressure, substrate temperatures, distances between the targets and the substrates, composition of the target and its filling rates, etc. Advantages of the PLD are as follows.

(1) The deviation of the chemical composition of the prepared film from that of the target material is comparatively little.
(2) Preparation of an artificial lattice is comparable easy.
(3) It is possible to prepare the high-melting point material such as oxides.
(4) It is also possible to prepare a thin film in low vacuum, and reactive deposition in ambient gases. Various atmosphere gas can be used. Film can be also widely formed of the pressure of the atmosphere gas with $1 \times 10^{-10}$ Torr.
(5) By using the high purity target, a high purity thin film can be prepared.
(6) The structure of the vacuum chamber can be simplified, because the laser beam is introduced from the outside the PLD chamber.
(7) It is possible to control the film thickness to the order of nanometers by controlling the number of the laser beam pulses.

On the other hands, following demerit should be also considered in the PLD. In the film preparation by the PLD, there is a case in which the particle with the size of nanometer to micrometer order often piles up. This unexpected particle is called as “debris”. Although the mechanism of the generation of the debris has not been clarified, the debris considered to flie from the target. The generation of the debris should be suppressed, when a uniform and high quarity film is required. There is the correlation between particle size of the debris and filling rate of the target, and there is almost in inverse proportion. Therefore, in order to reduce the debris, it is also one of the effective methods to use the target with high filling rate. Actually, by using the high-filling rate target, effect of decreasing of the debris has been reported.

Although the process of the laser ablation is complicated, and the mechanism is not sufficiently clarified at present, PLD method is useful to prepare the thin film, such as an artificial lattices controlled in atomic level and amorphous thin film, etc.
The experimental setup of the typical PLD film growth system is shown in Fig. 1. An incident laser beam is focused with appropriate energy through a UV-transmitting window on to a rotating polycrystalline target. Typical distance between the substrate and target is 3-10 cm. As a laser source, ArF (wavelength 193nm), KrF (wavelength 248nm) excimer laser or Nd-YAG laser (wavelength 266nm) are mainly used. For the PLD chamber, a rotating mechanism of the target, gas introduction valve for preparing thin film in reactive gas such as the oxygen, pressure gage, and heaters to control the substrate temperature, etc. should be equipped. It is better to equip a RHEED and film thickness meters for observing the epitaxial of a thin film and the thickness. The typical parameters of the laser beam is as follows; (1) irradiation energy: 10-200 mJ/pulse, (2) pulse frequency: 1-10Hz, (3) typical pulse duration: few nano-second to 40ns.

Recently, the detailed technical book on the PLD has been published. 26) As an example, we had prepared amorphous lithium lanthanum titanate (LLT) thin film made on the SiO₂ substrate by the PLD method. The prepared amorphous LLT film is uniform and high quality, and it shows high adhesion (it did not exfoliate, even if it was scratched by a knife). 27)

In last decades, many studies on the preparation of ionic conductor thin film by PLD have been reported. Yugami et. al. reported about the fabrication of SrCeO₃/SrZrO₃ superlattices on MgO single crystal substrate by PLD method using ArF excimer laser, and structural properties of the epitaxial films

![Figure 1. Experimental setup of the typical PLD film growth system.](image-url)
by Raman scattering and 4-axis X-ray diffraction. They revealed that critical periodicity to make strained superlattice is about 15-20 nm for system SrCeO$_3$/SrZrO$_3$ on MgO substrate.\textsuperscript{28}

Kuwata et. al. reported about the fabrication of a solid-state thin-film batteries which consist of an amorphous Li$_2$O-V$_2$O$_5$-SiO$_2$ solid electrolyte (LVSO), crystalline LiCoO$_2$ cathode and amorphous SnO anode by PLD method. The amorphous LVSO thin-film has a smooth and dense surface without any pinhole, whose composition was analyzed to be Li$_{2.2}V_{0.54}Si_{0.46}O_{3.4}$. The ionic conductivity of the LVSO film is estimated by impedance spectroscopy to be $2.5 \times 10^{-7} \ \Omega^{-1}\text{cm}^{-1}$ at room temperature with activation energy of 0.54 eV. Their battery exhibits an open circuit voltage at full charge of about 2.7 V, and a good reversibility on charge-discharge cycling over 100 cycles between 0 and 3.3 V.\textsuperscript{29}

Chiba et. al. reported about the preparation of yttria stabilized zirconia (YSZ) thin films by the laser ablation method. Multi-layer films have been fabricated by the subsequent deposition of two targets with different Y$^{3+}$-concentration (8 and 18 mol%). The structure and ionic conductivity have been examined by XRD and complex impedance methods, respectively. Although, they have observed a slight change of the activation energy of ionic conductivity, the ionic conductivity enhancement cannot be observed.\textsuperscript{30}

Sata et. al. fabricated a proton conducting thin films of SrZrO$_3$ and SrCeO$_3$ by PLD using ArF excimer laser. The fabricated thin films of SrCeO$_3$ and SrZrO$_3$ were grown in the [100] direction on the SrTiO$_3$ (100) substrate and in the [211] direction on the MgO (100) substrate and on the Al$_2$O$_3$ substrate. The Raman scattering spectra show that the thin films grown in the low P$_{O2}$ contain lots of oxygen ion vacancies compared to bulk crystals.\textsuperscript{31}

M. Meunier et. al. reported about the preparation of NASICON and La$_{1-x}$Sr$_x$MnO$_{3+x/2}$ (LSM) ceramic thin films by PLD. NASICON thin films have good ionic conductivity with resistivities between $3 \times 10^3$ and $5 \times 10^4 \ \Omega\text{cm}$ at room temperature, and very smooth and dense LSM thin films are produced by PLD with the perovskite structure after an anneal at 950°C.\textsuperscript{32}

3. Impedance spectrum

From A.C. impedance spectrum of the ionic conductor, one can obtain the important information about the ionic conduction mechanism. In the case of the impedance measurement of the thin film, the impedance spectrum may show an anisotropy. That is to say, the impedance parallel to the film surface will observe the ionic conduction along interface and surface. In the meantime, the impedance perpendicular to the thin film observes the ionic conduction that perpendicularly crosses them. Therefore, to discuss the ionic conduction of the thin film, one have to choose carefully the direction of ionic conduction.
Impedance parallel to the film surface direction can be measured using a comb-type electrode, which is employed on the film by the vacuum deposition or sputtering method. The outline of the typical sample setup is shown in Fig.2. On the other hand, the impedance perpendicular to the film surface, it is required that the ionic conductor thin film should be sandwiched by the electrodes. In order to discuss the ionic conduction around the interface between the ionic conductor and insulator in this configuration, It is necessary to prepare the multi-layer sample such as electrode/insulator/ionic conductor/insulator/electrode.

Impedance spectrum is analyzed using equivalent circuit and some useful empirical formula such as Debeye’s rule. By utilizing these analysis method, one can obtain various information about ionic conduction mechanisms such as ionic conductivity, heterogeneity and electrode interface, etc. In this section, these outlines are simply described.

**Figure 2.** Schematic view of sample setup of a comb-type electrode.

### 3.1 Equivalent circuit of ionic conductor and Cole-Cole plot

The impedance of ionic conductor is often analyzed using the equivalent circuit. As an example of simple case, as shown in Fig.3a, the ionic conductor is treated as a parallel circuit consist with a bulk electric resistance \( R_B \) and capacitance \( C_B \) which is determined by the dielectric constant \( \varepsilon \). In this model, complex impedance \( Z^*(\omega) \) at angular frequency \( \omega \) is given as,

\[
Z^*(\omega) = \frac{R_B}{1 + i\omega C_B R_B}, \tag{1-a}
\]

\[
\text{Re}Z^*(\omega) = Z'(\omega) = \frac{R_B}{1 + (\omega C_B R_B)^2} \tag{1-b}
\]
By eliminating \( \omega \) from eq. (1-b) and eq. (1-c), one can obtain,

\[
\text{Im} Z^\ast (\omega) = Z'' (\omega) = -\frac{\omega C_B R_B^2}{1 + (\omega C_B R_B)^2}.
\]

\hspace{1cm} (1-c)

**Figure 3.** Comparison of equivalent circuit and the impedance plot. a) parallel circuit consist with a bulk electric resistance \( R_B \) and capacitance \( C_B \), b) impedance plot for a single resistance or single capacitance, c) typical equivalent circuit which contain the contribution of ionic conduction at interface region.
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\[
\left\{ Z'(\omega) - \frac{R_B}{2} \right\}^2 + Z''(\omega)^2 = \left\{ \frac{R_B}{2} \right\}^2.
\]

Equation (2) means \(Z'\) vs \(-Z''\) plot would be on a semicircle with radius \(R_B/2\) which center is \((R_B/2, 0)\), and one can estimate the D.C. resistance \(R_B\) from the impedance plot. It should be noted that impedance plot is suitable to estimate \(Z_0\), but it is not able to discuss the frequency dependence, because the frequency information has lost. The angular frequency \(\omega_{max}\) which gives the top of the semicircle is equal to reciprocal of the time constant \(1/(R_B C_B)\). From \(R_B\) and \(\omega_{max}\), it is able to estimate \(C_B\).

In the case of \(R_B<<1/\omega C_B\), eq. (1-a) is approximated as

\[
\tilde{Z}^* \sim R_B,
\]

and it becomes equivalent to a single resistance, and the impedance plot is given Fig.3b (inserted figure). Such curve is observed in high conductivity materials such as semiconductor and metal. On the other hand, in the case of \(1/\omega C_B<<R_B\), eq. (1-a) is approximated as

\[
\tilde{Z}^* \sim -i(1/\omega C_B),
\]

it becomes equivalent to a single capacitance (see Fig.3b inserted figure). Such curve is observed in insulators such as quartz and alumina. For the ionic conductor which ionic conductivity is extremely lowered, the impedance plot close to this curve.

Typical equivalent circuit which contain the contribution of ionic conduction at interface region such as grain boundary is shown in Fig.3c. In this case, the complex impedance \(\tilde{Z}^*(\omega)\) at angular frequency \(\omega\) is given as,

\[
Z^*(\omega) = \frac{R_B}{1 + i\omega C_B R_B} + \frac{R_i}{1 + i\omega C_i R_i}.
\]

Here, \(R_i\) and \(C_i\) is the resistance and capacitance at the interface region, respectively.

The complex impedance plot is shown in Fig. 3c. As shown in Fig. 3c, each component can be separated clearly when time constant \(R_i C_i\) is 2 order larger than \(R_B C_B\). On the other hand, when the time constant \(R_B C_B\) and \(R_i C_i\) is closes, each process can not be separated, and impedance plot traces a distorted circular arc.

Low frequency region of the impedance spectra is also largely affected by
the formation of electric double layer and electrochemical reaction at around the ionic conductor/electrode interface region. Especially, in case of the sample with blocking electrode, the impedance spectrum would be greatly affected by the electric double layer at the electrode.

The equivalent circuit of the blocking electrode is also given by the parallel circuit of resistance $R_i$ and capacitance $C_i$. In this case, $C_i$ and $R_i$ corresponds to an electric double layer and a leak current which can not be ignored, respectively. By the impedance measurement for different sample size or the electrode material dependence or both of them, the contribution of the electrode impedance should be confirmed experimentally.

3.2 Debye’s empirical rule

The frequency dependence of ionic conductivity and impedance of ionic conductor is also analyzed using Debye’s empirical rule which introduce a parameter $\beta$ into the Debye’s relaxation formula,

$$Z^* = Z_\infty + \frac{Z_0 - Z_\infty}{1 + (i\omega\tau)^\beta}$$  \hspace{1cm} (6)

Here, $Z^*$, $Z_0$, $Z_\infty$, $\omega$ an d $\tau$ denotes the complex impedance, DC resistance, impedance at high frequency limit, angular frequency and relaxation time, respectively. DC ionic conductivity $\sigma$ can be estimated from the arc, $\beta$ means the width of the relaxation time distribution. It should be noted that the Debye’s empirical formula also reproduces the dispersion of dielectric constant and electric conductivity well, it is not possible to lead to the mutuality mathematically.33)

From Debye’s empirical rule, the frequency dependence of real part $Z'$ and imaginary part $Z''$ are given as following equations,

$$Z'(\omega) = Z_\infty + \frac{(Z_0 - Z_\infty)[1 + (\omega\tau)^\beta \cos \frac{\pi}{2} \beta]}{[1 + (\omega\tau)^\beta \cos \frac{\pi}{2} \beta]^2 + [(\omega\tau)^\beta \sin \frac{\pi}{2} \beta]^2}$$  \hspace{1cm} (7a)

$$Z''(\omega) = -\frac{(Z_0 - Z_\infty)(\omega\tau)^\beta \sin \frac{\pi}{2} \beta}{[1 + (\omega\tau)^\beta \cos \frac{\pi}{2} \beta]^2 + [(\omega\tau)^\beta \sin \frac{\pi}{2} \beta]^2}$$  \hspace{1cm} (7b)

When $\beta = 1$, the center of the circular arc is on the real axis, and it is equivalent to Debye’s relaxation formula. In the meantime, when $\beta < 1$, the center of
circular arc sinks under the real axis (see Fig.4). This physical meaning is interpreted as the distribution of relaxation time. Actually, for many ionic conductors, it is well known the complex impedance plot is well fitted by equation (6).

As a typical example, the complex impedance plot ($Z'$ versus $-Z''$ plot) of the $\beta$-eucryptite thin film (thickness 1.5$\mu$m) at 800K with Ag ($\circ$: open circles) and Au ($\triangle$: closed triangles) electrode is shown in Fig.5. As shown in Fig. 5, the form of the low frequency region is clearly influenced by the electrode materials, with lower slopes observed with silver. On the other hand, the shape of the circular arcs at high frequency region is not affected by the electrode materials. Therefore, the impedance at high frequency part is considered to be the $\text{Li}^+$ ionic conduction in the thin film.

![Figure 4. Typical impedance plot with a distribution of relaxation time.](image)

![Figure 5. Impedance plot of $\beta$-eucryptite thin film (thickness 1.5$\mu$m) at the 800K. Open circles ($\circ$) and closed triangles ($\triangle$) correspond to Ag and Au electrode, respectively (Ref.38).](image)
4. Ionic conductivity of thin film

4.1 Aging and annealing effect

The physical property of a thin film, which has not been annealed sufficiently, often gradually changes with the passage of time (aging effect). It is considered that it originates from the quench in preparing the thin film; the thin film may be quenched, when the substrate temperature is sufficiently low for the thin film formation. By the quenching, the film formation proceeded with the generating of various defects and strain, etc.

The aging effect is more remarkable for a thinner film, and the degree of the aging effect is different in the material, it is case by case. Some materials may reach the stable state with in several hours, and one other material may need several weeks. Therefore, in order to discuss the physical property of the thin film such as ionic conductivity, it is necessary to confirm whether the sample is in a stable state or unstable state.

As an example, the time dependence of ionic conductivity of as-prepared LLT thin film is shown in Fig.6. In Fig.6, t=0 is a time when the sample is taken out from the PLD chamber. First several hours, ionic conductivity of the amorphous LLT thin film shows rapidly decrease with the passage of time, and after about 300 hours, the decrease rate of ionic conductivity becomes small.

![Figure 6. Aging effect of the d.c. ionic conductivity of amorphous LLT thin film.](image-url)
As in the case of LLT thin film, the aging effect is remarkable at the initial stage after the preparation of the film. Then, in order to stabilize the crystal structure of the thin film, the thin film is often post-annealed at high temperature in several hours.

On the other hand, when the ionic conductivity of an amorphous thin film is measured in wide temperature range, the annealing effect must be also taken into consideration. As an example of the annealing effect, the temperature dependence of the ionic conductivity of the amorphous LLT thin film is strongly affected by an annealing effect; the ionic conductivity decreases with time when the temperature of the sample is kept above room temperature, and especially the ionic conductivity shows a drastic decrease with time above 600K. As shown in this case, the annealing effect is remarkable with temperature increase and irreversible. Thus, in order to avoid the annealing effect, the temperature range for the measurement should be carefully chosen, because the crystal structure may change by the post-annealing. For the reproducibility of the experimental data, the measurement should be carried out for two thermal cycles of heating and cooling. Although the mechanism of the annealing effect has not yet been clarified, it would be originated from the removal of strain or the crystallization of the thin film.

4.3 Ionic conductivity of AgI thin films

It is well known that AgI-insulator dispersed ionic conductor such as AgI-Al2O3, AgI-SiO2, AgI-TiO2, and AgI-BaTiO3 shows the ionic conductivity enhancement. To reveal the mechanism of the conductivity enhancement, it is important to study the ionic conduction at the interface region between AgI and insulating material.

From such standpoint, we reported about the conductivity enhancement of the AgI thin films on tri-glycine sulfate (TGS) single crystal and SiO2 glass substrate. In the measurement of the temperature dependence of D.C. ionic conductivity σ of AgI thin film, a remarkable thermal hysteresis of the ionic conductivity was observed at the 1st heat cycle below 420 K, and at the subsequent cycle, the thermal hysteresis was not observed. This thermal hysteresis is considered due to the annealing effect.

The temperature dependence of dc ionic conductivity of AgI bulk (closed circles) and AgI films for various film thickness are shown in Fig.7a and 7b. The drastically decrease of ionic conductivity around 420 K is due to the α-β structural phase transition of AgI. As shown in Fig.7a and 7b, β-phase AgI films show higher ionic conductivity than that of β-AgI bulk. The conductivity enhancement increases with temperature decreasing. On the other hand, the conductivity enhancement at the α-phase was also observed, however it showed a slightly increase with decrease of film thickness.
Figure 7. Temperature dependence of dc ionic conductivity of AgI thin film. a) AgI thin film on TGS substrate (Ref.9), b) on SiO₂ glass substrate. (△:0.5 mm, □:0.8 mm, ○:1.6 mm) (Ref.10). The conductivity enhancement was observed in AgI films.

Ionic conductivity of AgI thin films on SiO₂ glass substrate for the various temperature is shown in Fig. 8 as a function of the film thickness. Ionic conductivity of AgI thin films increases with decreasing the film thickness in thickness range of from 0.28-2.0 µm, and showed maximum for the film
thickness 0.38 µm. This result suggests that the high ionic conduction region would exist on the boundary region at the insulator substrate and AgI thin film.

It is well known that TGS shows a ferroelectric phase transition at 49 C, and shows the divergence of the dielectric constant. However there is no remarkable change of conductivity around the phase transition temperature of TGS substrate. Therefore, the phase transition of the TGS substrate does not affect remarkably for the ionic conduction in the AgI films.

Furthermore, not only ionic conduction but also the phase transition temperature shows the thickness dependence. Thermal hysteresis of the phase...
transition temperature $T_c$ was observed at around 420 K. In the heating process, $\alpha$-$\beta$ phase transition of all samples were observed at 425 K which is almost agreed with the phase transition temperature of the AgI bulk ($T_c=420$ K). However, in cooling process, the phase transition temperature of AgI thin film shift to the low temperature side with decreasing of film thickness. $T_c$ showed the maximum shift about 401 K for film thickness 0.38 $\mu$m. The report of Tatumisago et al. seems to give the hint of this mechanism. Tatumisago et al. reported that the micro-crystal of $\alpha$-AgI had been stabilized at room temperature in a super ionic glasses by quenching in the system AgI-Ag$_2$O-M$_x$O$_y$ ($M_{x+y}$=B$_2$O$_3$, P$_2$O$_5$, GeO$_2$, MoO$_3$, WO$_3$). They discussed about the lattice strain of frozen $\alpha$-AgI in terms of stress at the interface between the AgI crystals and the surrounding glass material. The result of present paper may be related to their results. That is to say, the shift of phase transition temperature might be originated from the strain of the crystal structure and the defect at the interface.

4.2 LLT amorphous thin films

As mentioned in section 2.3, LLT thin film with the uniform thickness, no cracks and no grain boundaries were prepared by the PLD method. The sample name, color, content ratio and the thickness of the as-prepared thin films are shown in Table 1. The black color of the as prepared thin films is considered to be due to a lack of O$^{2-}$ ions. The content ratio of La and Ti involved in the LLT thin films shows a good agreement with that of the target. Although the Li content in the film deviates about -10% from the target, it would be originated from the higher volatility of Li than other elements, La and Ti.

Complex impedance plots ($Z'$ versus -$Z''$ plot), in the case of the lithium lanthanum titanate LLT thin film at 400K with Au (○: open circles, film thickness 0.59$\mu$m) and Ag (▲:closed triangles, film thickness 0.50$\mu$m) electrode are shown in Fig. 9. There are essentially two parts to each impedance response, a high frequency arc relating to bulk conductivity of the film and a low frequency response indicative of finite length diffusion, as evidence by an inclined spike, $\sim$45°, leading onto a steep spike. It should be noted that although the radius of the circular arcs seem to depend on the electrode material, it is much more likely that this is due to geometry differences, specifically related to the thickness dependence of the ionic conductivity. The high frequency part of the complex impedance plot was well fitted by a Debye-relaxation type arc with $\beta=0.99$. From $Z_0$ and $\tau$ should be able to give the capasitance $C$ and convert about $2 \times 10^{-12}$ F would be bulk.
Table 1. Sample name, Target, and Content ratio of Li, La, and Ti in the LLT thin film. The standard deviation of the values is about ±0.03. Color of the as prepared LLT thin film is black.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Target</th>
<th>Li</th>
<th>La</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLT01</td>
<td>Li&lt;sub&gt;0.1&lt;/sub&gt;La&lt;sub&gt;0.63&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.09</td>
<td>0.66</td>
<td>1.0</td>
</tr>
<tr>
<td>LLT02</td>
<td>Li&lt;sub&gt;0.2&lt;/sub&gt;La&lt;sub&gt;0.6&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.18</td>
<td>0.61</td>
<td>1.0</td>
</tr>
<tr>
<td>LLT03</td>
<td>Li&lt;sub&gt;0.3&lt;/sub&gt;La&lt;sub&gt;0.56&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.28</td>
<td>0.55</td>
<td>1.0</td>
</tr>
<tr>
<td>LLT04</td>
<td>Li&lt;sub&gt;0.4&lt;/sub&gt;La&lt;sub&gt;0.53&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.33</td>
<td>0.53</td>
<td>1.0</td>
</tr>
<tr>
<td>LLT05</td>
<td>Li&lt;sub&gt;0.5&lt;/sub&gt;La&lt;sub&gt;0.5&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.45</td>
<td>0.48</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 9. Impedance plot of Li<sub>x</sub>La<sub>(2-x)/3</sub>TiO<sub>3</sub> (x=0.4, LLT04) thin film (thickness 0.5μm) at the various temperature. Open circles (○) and closed triangles (▲) correspond to Ag and Au electrode, respectively (Ref.27).
Temperature dependence of the ionic conductivity of the amorphous LLT thin films is shown in Fig. 10. Ionic conductivity of polycrystalline LLT is also shown for the comparison. As shown in Fig. 10, the amorphous LLT thin film is a super-ionic conductor above room temperature.

![Graph showing the temperature dependence of ionic conductivity of the amorphous LLT thin films with Au electrode.](image)

**Figure 10.** Temperature dependence of the ionic conductivity of the amorphous LLT thin films with Au electrode. ○: LLT01, □: LLT02, ◇: LLT03, ×: LLT04, +: LLT05, ▲: Li0.1La0.63TiO3 poly crystal (Ref.27).

The values of activation energy inserted in Fig.10 were estimated by using the Nernst-Einstein relationship; temperature dependence of $\sigma$ of thermal activated ionic conduction is well fitted by the Nernst-Einstein relationship which is given by,

$$\sigma = \frac{N(Ze)^2 a^2}{k_BT} \Gamma_0 \exp\left(-\frac{\Delta}{k_BT}\right) f$$

(8)

Here, $N$ is a number density of the carrier, $Ze$ is a charge of the carrier, $a$ is the hopping distance of the ion, $\Gamma_0$ is the attempt frequency, $\Delta$ is the activation energy and $f$ is a correlation factor whose value would be about 1.
Figure 11 shows a comparison of the ionic conductivity of the amorphous LLT thin film and polycrystalline LLT for various Li content at 300 K. The ionic conductivity of the amorphous LLT thin film shows monotonous increase with the increase of the Li content, and it seems to be maximum at around $x=0.4$. On the other hand, as shown in Fig.11, the amorphous LLT thin film shows a higher ionic conductivity than that of the polycrystalline LLT. Especially, the ionic conductivity of LLT01 is about one order higher than that of the polycrystalline one. Such the high ionic conductivity of the amorphous thin film could be originated from,

(1) a structural disorder of the amorphous structure,
(2) an interface enhancement effect,
(3) a stress in the thin film,
(4) due to the absence of grain boundaries.

In order to clarify the mechanism of the ionic conduction in amorphous LLT thin film, a detailed study would be necessary of the components, local structure of the thin film, and the thickness dependence of ionic conductivity.
4.3 β-eucryptite and the amorphous thin films

β-eucryptite thin film is able to prepare by PLD method. Fig. 12a shows an X-ray diffraction pattern of as-prepared thin film. Only a peculiar broad peak of an amorphous structure was observed around 2θ=20-30°. Therefore, the as-prepared thin film would be considered to have an amorphous structure. On the other hand, it was confirmed that the prepared thin film would be crystallized by post-annealing above 800°C in the atmosphere. In particular, the diffraction pattern of the annealed thin film at 1000°C shows good agreement with the diffraction pattern of β-LiAlSiO₄ target (Fig. 12e).³⁸)

Temperature dependence of DC ionic conductivity σ of β-LiAlSiO₄ thin film for various film thickness is shown in Fig. 13. In Fig.13, ○, ◇, △ and ▽ correspond to the data for the film thickness 1.2, 0.075, 0.038 and 0.0075μm, respectively.

![Figure 12](image-url)

**Figure 12.** The X-ray diffraction pattern of a lithium alumina silicate thin film annealed at various temperature for 2 hours in atmosphere. (a) as prepared film, (b) annealing at 600°C, (c) annealing at 800°C, (d) annealing at 1000°C, (e) β-LiAlSiO₄ ceramic (Ref.38).
Figure 13. The temperature dependence of dc ionic conductivity of β-eucryptite thin film. ●: β-eucryptite ceramic. ○: 1.2µm, ◇: 0.075µm, △: 0.038µm, and ▽: 0.0075µm (Ref.38).

As shown in Table 1, the activation energy decreases with a decrease in the film thickness, and the difference of activation energies above and below 700K decreases with a decrease in the film thickness. This thickness dependence of activation energy would be due to the modification of crystal structure around the boundary region of the thin film and the substrate. For example, the crystal structure around the boundary region may be in disorder compared to bulk.

On the other hand, as shown in Fig.13, the ionic conductivity increases with a decrease in the film thickness $d$. Ionic conductivity of β-eucryptite thin film was plotted as a function of the film thickness at various temperatures (see Fig.14). Although there is no remarkable change in the ionic conductivity of the thin film, which is thicker than 0.8 µm, it is higher than the value of β-eucryptite bulk. In particular, as shown in Fig.14, the conductivity enhancement is remarkable for film thickness $d<0.075$ µm. The conductivity enhancement of β-eucryptite thin film would be also considered to be due to the construction of a high-ionic conduction region at a boundary between β-eucryptite and quartz glass substrate.
Figure 14. Thickness dependence of ionic conductivity of $\beta$-eucryptite thin film at various temperatures. Broken curves are fitted curve by eq. (13a). ●: 500K, ■: 600K, ◆: 700K, and ▲: 800K (Ref.38).

Table 2. Sample name, PLD target, thickness, ionic conductivity and activation energy of the amorphous lithium silicate thin films. Color of all samples is transparent.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Target</th>
<th>Thickness [µm]</th>
<th>$\sigma$ [$\Omega^{-1} \text{cm}^{-1}$] (at 500K)</th>
<th>$\Delta$ [eV] (at 500K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSO</td>
<td>Li$_2$SiO$_3$</td>
<td>0.55</td>
<td>$3.0 \times 10^{-5}$</td>
<td>0.70</td>
</tr>
<tr>
<td>LLSO</td>
<td>LiLaSiO$_4$</td>
<td>0.50</td>
<td>$3.9 \times 10^{-4}$</td>
<td>1.09</td>
</tr>
<tr>
<td>LASO</td>
<td>$\beta$-LiAlSiO$_4$</td>
<td>0.70</td>
<td>$4.1 \times 10^{-6}$</td>
<td>0.92</td>
</tr>
</tbody>
</table>

4.4 Amorphous lithium silicate thin films

Amorphous lithium silicate thin film was prepared by PLD method on an optical polished SiO$_2$ glass substrate. Temperature dependence of the ionic conductivity of prepared thin films is shown in Fig. 15. Table 2 shows targets, sample names, the thickness, the ionic conductivity $\sigma$ (at 500K) and the activation energy $\Delta$ (at 500K) of prepared thin films.

As shown in Fig.15 and Table 2, the amorphous structural LSO, LLSO and LASO thin films showed one or two order higher ionic conductivity at 500K than that of polycrystalline Li$_2$SiO$_3$, LiLaSiO$_4$ and $\beta$-LiAlSiO$_4$ target material. Higher ionic conductivity of LSO, LLSO and LASO than that of $\beta$-
LASO would be due to the amorphous structure; a structural disorder of the amorphous thin films increases the conduction of the mobile ion. The results suggest that the amorphous structure is important to obtain high ionic conductible thin film.

On the other hand, ionic conductivity of LSO, LLSO and LASO thin films decrease drastically at around 700-750, 500 and 850-900K, respectively. The drastic decrease of ionic conductivity is due to an anneal effect such as the crystallization of the thin film; high ionic conductivity of amorphous thin film...
would be lost by the annealing effect. Especially, in the case of LLSO thin film, after the decrease of ionic conductivity due to the annealing effect, the temperature dependence of the ionic conductivity is almost same with the polycrystalline LiLaSiO₄.

4.5 Thickness dependence of ionic conductivity

As shown in Fig. 8 and 14, the dc ionic conductivity of AgI and β-eucryptite thin film shows thickness dependence. Such thickness dependence of ionic conductivity is considered to reflect the Liang effect, and it would be possible to discuss by using the ionic conduction theory about the conductivity enhancement of the composite system.

In many theoretical studies have been developing to explain the mechanism of the Liang effect, the studies of Wagner and Maier is major one. Wagner and Maier reported ionic conduction at interface region would strongly depend on the electro-chemical condition at the interface region.

The theoretical study by Wagner et al. would be the first report that treats the conductivity enhancement from the viewpoint of the interface ionic conduction. Jow and Wagner attributed the ionic conductivity enhancement to the space charge region formed at around the interface region between the ionic conductor and second phase such as insulator. Furthermore, Wagner suggest the existence of a third phase between the ionic conductor and the inert second phase (insulator), and they attributed to the formation of the space charge layer is originated from the formation of a thin amorphous phase at the interface region between the ionic conductor and second phase.

J. Maier treated an ionic conduction of ionic conductor/insulator system using the electrochemical model. Especially, the defect chemistry of ionic conductor thin films, and the relation for the parallel ionic conductivity of the thin film with finite thickness was discussed. Maier shows that the conductance data for LiI thin film on sapphire as a function of thickness is able to describe by the electrochemical model.

T. Ishii and J. Kawamura reported about the theoretical study on the ion-hopping conduction of an ionic conductor thin film sandwiched with insulators in terms of the interacting lattice gas model. Using this model, they can successfully explained the results observed in AgI thin film on SiO₂ glass substrate.

Tomoyose et al., and Kobayashi et al., treated a theoretical model about ionic conduction in a layered superionic conductor, which is composed of alternating layers of superionic conductors and ionic crystal, and they discussed a possibility of conductivity enhancement at inter plane.

On the other hand, the thickness dependence of the ionic conductivity can be treated by a classical electro-magnetic theory. As shown in Fig. 16, let
consider that an ionic conductor thin film on the insulator substrate has been composed by two regions; bulk- and high-ionic conduction region. In Fig. 16, $d$ and $A$ are the thickness and the width of the thin film, respectively. $x$ is the distance from the substrate. $\lambda$ is the thickness of the high-ionic conduction region, which is referred as “Debye length” by Maier et al.. $\sigma_\infty$ is the ionic conductivity at bulk-conduction region($\lambda$<$x$<$d$), which corresponds to the ionic conductivity of bulk. $\sigma_\lambda$ ($\sigma_\lambda$ > $\sigma_\infty$) is the average ionic conductivity at the high-ionic conduction region ($0$ < $x$ < $\lambda$).

When the electric field $E(x)$ was applied parallel to the film, current $\Delta I(x)$ which flows the minute cross section $dx \times A$ at $x$ is given as,

$$\Delta I(x) = i(x)A \times dx = \sigma(x)E(x)A \times dx.$$ \hspace{1cm} (9)

Here, $i(x)$, $\sigma(x)$ and $E(x)$ are current density, electric conductivity and magnitude of electric field at $x$, respectively.

In the case of $d$>$\lambda$, considering the boundary relations for electric field at $x=\lambda$, total current $I$ which flow in the film is given by following,

$$I = \int_0^d A i(x)dx = A E(x) \int_0^d \sigma(x)dx = A \left\{ \int_0^{\lambda} \sigma_\lambda dx + \int_{\lambda}^d \sigma_\infty dx \right\} E$$

$$= A [\sigma_\lambda + \sigma_\infty(d - \lambda)] E$$ \hspace{1cm} (10)

On the other hand, in the case of $d$<$\lambda$, $I$ is given by,

\[\text{Figure 16.} \quad \text{A simple model of the ionic conductor thin film with high ionic conduction region at the boundary region.}\]
Figure 17. The conductivity enhancement $\Delta \sigma$ vs $1/d$ plot for various temperature. a) AgI film (Ref.10), b) $\beta$-eucryptite thin film (Ref.38). Broken lines are fitted line with eq. (13a).
Fabrication and ionic conduction of ionic conducting thin films

\[
I = \int_0^\lambda Ai(x)dx = A E(x) \int_0^\lambda \sigma_\lambda dx = A \sigma_\lambda \times \lambda \times E
\]  

(11)

From the measurement, the average (effective) electric conductivity \(\sigma_{\text{eff}}\) is obtained. Therefore, \(I\) is given by,

\[
I = A d \sigma_{\text{eff}} E.
\]  

(12)

From the comparison of equation (9), (10) and (11), one can obtain,

\[
\sigma_{\text{eff}} = \sigma_\infty (1 - \lambda/d) + \sigma_\lambda \lambda/d = \sigma_\infty + (\sigma_\lambda - \sigma_\infty)\lambda/d \quad (d>\lambda),
\]  

(13a)

and

\[
\sigma_{\text{eff}} = \sigma_\lambda \quad (d<\lambda).
\]  

(13b)

The increase of conductivity \(\Delta \sigma\) from the bulk conductivity is given as,

\[
\Delta \sigma = \sigma_{\text{eff}} - \sigma_\infty = (\sigma_\lambda - \sigma_\infty)\lambda/d \quad (d>\lambda),
\]  

(14a)

and

\[
\Delta \sigma = \sigma_\lambda - \sigma_\infty \quad (d<\lambda).
\]  

(14b)

Equation (13a) means, when \(\Delta \sigma\) is plotted against \(1/d\), it should fall on a straight line with slope \((\sigma_\lambda - \sigma_\infty)\lambda\) which passes through the origin.

Furthermore, taken the logarithm of both sides of eq.(13a),

\[
\log \Delta \sigma = \log \{((\sigma_\lambda - \sigma_\infty)\lambda}\} - \log d
\]  

(15)

is obtained. This means that the logarithm plot of \(\Delta \sigma\) as a function of \(\log d\), it should fall on a straight line with slope -1 for the thickness \(d>\lambda\). It should be noted that the above result for \(d>\lambda\) is same with the Mier’s model.\(^{12}\)

On the other hands, in the case of \(0<d<\lambda\), the data should fall on a straight line with slope 0. Therefore, from the crossover of the two straight lines, it would be able to estimate the thickness \(\lambda\) of the high-ionic conduction region approximately. Furthermore, using the estimated \(\lambda\) and the slope of the straight line \((\sigma_\lambda - \sigma_\infty)\lambda\), \(\sigma_\lambda\) would be estimated.

Although the present model is the first approximation, the above model would be effective for the film thickness \(d>\lambda\). In this simple model, \(\sigma_\lambda\) was
treated as a constant value, however it should be treated as a function of $x$; $\sigma_\lambda (x)$. To reveal the function form of $\sigma_\lambda (x)$ and the ionic conduction mechanism at boundary region, more detail study of thickness dependence of ionic conduction for $d<\lambda$ would be required.

Conductivity enhancement $\Delta \sigma$ of AgI and $\beta$-eucryptite thin film on SiO$_2$ glass substrate at various temperature were re-plotted as a function of $1/d$ in Fig.17a and 17b, respectively. As the value of $\sigma_\infty$ in eq.(13a), AgI and $\beta$-eucryptite bulk conductivity at each temperature were used.

For the AgI thin film, the data for film thickness from 0.38-2.0 $\mu$m were well fitted by straight lines with slope $1.27\times10^{-9}$, $8.08\times10^{-9}$ and $5.34\times10^{-8}$ $\Omega^{-1}$, at 300K, 350K and 400K, respectively. In the case of film thickness 0.28 $\mu$m, the experimental result deviated from the straight line. It is considered that the Debye length of a AgI thin film on SiO$_2$ glass substrates would be around 0.28 $\mu$m. Then, by assuming $\lambda=0.28$ $\mu$m, $\sigma_\lambda$ were estimated as $4.65\times10^{-5}$, $2.98\times10^{-4}$ and $2.02\times10^{-3}$ $\Omega^{-1}cm^{-1}$ for, 300, 350 and 400 K respectively.

In the case of $\beta$-eucryptite thin film, $\Delta \sigma$ versus $1/d$ plot for at 500 and 600K was well fitted by eq.(13a) with the parameter $(\sigma_\lambda-\sigma_\infty)\lambda$ 1.05 $\times10^{-11}$ and $1.76\times10^{-10}$ $\Omega^{-1}$ at 500 and 600K, respectively (see Fig. 17b). Values of the parameter $(\sigma_\lambda-\sigma_\infty)\lambda$ and $\sigma_\infty$ obtained for $\beta$-eucryptite thin film are shown in Table 3. By using the parameters in Table 3, thickness dependence of ionic conductivity for various temperatures was calculated. The calculated results seem to reproduce the experimental result well (broken curves in Fig. 14). This result suggests the existence of a high ionic conduction region at the boundary between $\beta$-eucryptite thin film and SiO$_2$ glass substrate, and the thickness of the high-ionic conduction region would be less than 0.038$\mu$m.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [K]</th>
<th>$(\sigma_\lambda-\sigma_\infty)\lambda$ [(\Omega^{-1})]</th>
<th>$\sigma_\infty$ [(\Omega^{-1}cm^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI</td>
<td>300</td>
<td>$1.27\times10^{-9}$</td>
<td>$1.15\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>$8.08\times10^{-9}$</td>
<td>$9.75\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>$5.34\times10^{-8}$</td>
<td>$1.16\times10^{-4}$</td>
</tr>
<tr>
<td>$\beta$-eucryptite</td>
<td>500</td>
<td>$1.05\times10^{-11}$</td>
<td>$2.41\times10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$1.75\times10^{-10}$</td>
<td>$4.82\times10^{-6}$</td>
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<tr>
<td></td>
<td>700</td>
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<td>$5.91\times10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>$5.49\times10^{-9}$</td>
<td>$4.13\times10^{-4}$</td>
</tr>
</tbody>
</table>

Table 3. Parameter $(\sigma_\lambda-\sigma_\infty)\lambda$ and bulk conductivity $\sigma_\infty$ for AgI and $\beta$-eucryptite thin film at various temperature.
5. Conclusions

The origin of the high ionic conduction region would have originated not only because of the increase of the charge carrier density due to a space charge, but also because of other factors such as a decrease in activation energy and modulation of the conduction path originated by a structural disorder at the boundary, etc. In any case the mechanism of the construction of the high ionic conduction region, the fact that the thickness dependence of the conductivity enhancement $\Delta \sigma$ is proportional to the inverse of the film thickness $d$, indicate the existence of high ionic conduction region at the boundary.

To reveal the mechanism of high ionic conduction at interface region between ionic conductor and insulator, it would be important to study the relation between the boundary ionic conduction and physical properties of insulator, such as dielectric property and structural property, phase transition, spontaneous polarization, strain.

References

L1536.


