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ENHANCED IONIC CONDUCTION AT THE FILM/SUBSTRATE INTERFACE IN LiI THIN FILMS GROWN ON SAPPHIRE(0001)

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ABSTRACT

The ionic conductivity of LiI thin films grown on sapphire(0001) substrates has been studied *in-situ* during deposition as a function of film thickness and deposition conditions. LiI films were produced at room temperature by sublimation in an ultra-high-vacuum system. The conductivity of the LiI parallel to the film/substrate interface was determined from frequency-dependent impedance measurements as a function of film thickness using Au interdigital electrodes deposited on the sapphire surface. The measurements show a conduction of ~ 5 times the bulk value at the interface which gradually decreases as the film thickness is increased beyond 100 nm. This interfacial enhancement is not stable but anneals out with a characteristic log of time dependence. Fully annealed films have an activation energy for conduction (σT) of $\sim 0.47 \pm .03$ eV, consistent with bulk measurements. The observed annealing behavior can be fit with a model based on dislocation motion which implies that the increase in conduction near the interface is not due to the formation of a space-charge layer as previously reported but to defects generated during the growth process. This explanation is consistent with the behavior exhibited by CaF_2 films grown under similar conditions.

INTRODUCTION

Materials with large ionic conductivities have applications in devices such as sensors, fuel cells and solid-state batteries. One method of achieving increased ionic conduction in certain materials is the addition of a non-conducting second phase.¹ Since the first report 20 years ago², this has been shown to increase the conductivities of many different materials by several orders of magnitude.¹⁻¹⁰ The largest class of materials for which this phenomenon has been observed is the alkali- and alkali-earth halides such as LiI^{1,6} and CaF_2 .¹⁰

Several ideas have been put forth to explain the observed enhancement, but there is still debate in the literature concerning the mechanism. The most popular explanation is the space-charge layer model based on the work of Kliever and Kohler¹¹ and applied extensively by Maier¹² and others. According to this explanation, a difference in formation enthalpies of cation and anion vacancies creates an excess charge, localized at a surface or interface, that is offset by excess vacancies. These vacancies, located near the interface in the so-called "Debye layer", are charge carriers and lead to enhanced conduction within the layer. A second explanation, proposed by Dudney¹³, is based on crystalline defects. In this model dislocations and/or grain boundaries produced due to the misfit of the second-phase particles are presumed to provide excess carriers and/or an easy path for diffusion and hence lead to large conductivity values.

Recently, we have shown that the conductivity enhancement in CaF_2 at the interface with sapphire(0001) and in $\text{CaF}_2:\text{Al}_2\text{O}_3$ composites is caused by dislocations which originate at the $\text{CaF}_2:\text{Al}_2\text{O}_3$ interface.¹⁰ The strongest evidence for this was the observation of a dependence of the conductivity of pure CaF_2 films grown on sapphire(0001) substrates on annealing time and temperature. At a given temperature, the conductivity was observed to decrease with the log of time which could be modeled with the decrease in dislocation density due to climb and annihilation

during annealing.

In this paper we report the ionic conductivities of LiI deposited on sapphire(0001) substrates. *In-situ* frequency-dependent measurements *during* growth show that the conduction is enhanced at the film-substrate interface by approximately a factor of 5 relative to the bulk film at 27 °C. During annealing at or above the growth temperature, the conductivity decreases with a characteristic $\log(\text{time})$ dependence consistent with a dislocation mechanism. The temperature dependence of the conductivity showed that unannealed films had an activation energy for conduction of $\sim 0.51 \pm 0.3$ eV while fully annealed films had an activation energy of $\sim 0.47 \pm 0.3$ eV, consistent with bulk measurements.

EXPERIMENTAL PROCEDURE

All experiments were performed in a UHV deposition system that has been described in detail elsewhere.¹⁰ Briefly, the system consisted of a stainless steel chamber equipped with a Varian model HV-8 cryopump and a 450 l/sec turbopump backed by a two stage mechanical pump. LiI (Aesar, 99.95% pure) was sublimated at temperatures of $\sim 325 - 360$ °C from a BN crucible placed inside an effusion cell. All experiments were carried out at a pressure $< 10^{-9}$ Torr. The substrate was fixed to a Nb block which could be radiatively heated to temperatures in excess of 500 °C. The substrate temperature was monitored by a Chromel-Alumel thermocouple embedded in the block, which was used during T-dependent conductivity measurements as feedback for a control circuit to achieve a constant temperature ramp.

The substrates used were sapphire(0001) wafers polished on one side obtained from Kappler Crystal Optics, Inc. Interdigital Cr:Au electrodes were deposited onto the substrates using standard photolithographic techniques. The symmetric electrodes consisted of 20×0.2 mm fingers with a electrode spacing of 0.2 mm leading to a geometric factor l/w of 2.53×10^3 . The electrodes were connected via Ta clips to Cu wires attached to a Ni-wire feedthrough on the vacuum jacket.

A Hewlett-Packard model 4192A LCR meter was used for the impedance measurements. A 0.1 V signal was applied across the electrodes and the resulting current was amplified by a current-mode preamplifier (PAR model 184) set to a gain of $10^5 - 10^7$ which was attached to the vacuum feedthrough. The signal from the preamplifier was input to the LCR meter which measured the gain and phase of the current with respect to the input signal. These values were used to compute the real and imaginary parts of the impedance. During deposition, gain and phase were determined for 7 frequencies at half-decade intervals between 10 Hz and 10 kHz every 20 seconds. Post-deposition measurements which could be performed over longer times spanned the frequency range of 5 Hz to 20 kHz with 20 points per decade of frequency evenly spaced on a log frequency scale.

RESULTS

The conductivity measured as a function of thickness is shown in Figure 1. The solid lines represent conductance values calculated from the measured impedance assuming a parallel RC circuit. The calculated conductance curves have similar slopes for thicknesses greater than ~ 100 nm although the value of the conductance differs by a factor of 3 to 5.

In order to establish the true value of conductance an impedance plane analysis¹⁵ was performed for each thickness. In this analysis, the real and imaginary parts of the impedance are plotted in the complex plane. Circuits which can be modelled by lumped R and C parameters lead to semicircular arcs centered on the real axis whose real-axis intercepts and maxima are determined by the R and C values. Distributed and other non-ideal elements lead to depressed arcs and other shapes which cannot be described by any simple model. In *all* the frequency-dependent impedance

measurements for LiI we found that for low impedance values (i.e. at high frequencies) the complex-plane plots were well-described by a parallel RC circuit with lumped parameters. The arcs passed very near to the origin and showed no discernible depression (i.e., < 5 degrees for these data) when fit to a semicircle. The conductance values obtained from this type of analysis are plotted as the square data points in Figure 1.

After deposition, the conductance of the films was measured as a function of time. A typical plot of the annealing behavior is shown in Figure 2 for a 280-nm-thick LiI film. For $t \geq 100$ minutes, the conductance decreases with a characteristic $\log(\text{time})$ dependence. This dependence was present in all the LiI films we grew and is similar to the behavior seen in CaF_2 films grown on sapphire as well.¹⁰ At some point the conductance should approach a limiting "bulk" value, although this was not observed during these experiments because of the long annealing times which would be required at this temperature.

After growth, the conductance of the films was measured as a function of temperature. Figure 3 shows the conductance determined from several different analyses of a 250 nm LiI film grown at 27 °C. After growth, the film temperature was varied between 25 and 100 °C at a rate of 0.3 degrees per minute for two heating and two cooling ramps over a period of about 16 hours. During this temperature cycling, the conductance at 25 Hz was continuously monitored. The frequency dependence of the conductance was then measured at four discreet temperatures between 25 and 100 °C, after which dc measurements were performed over a period of several days to determine whether an electronic component contributed to the conductivity (no electronic conduction was detected). After this the conductance measured at 25 Hz was again monitored for a second temperature cycle, this time between 25 and 200 °C. During a third cycle, also between 25 and 200 °C, the conductance measured at 3 kHz was monitored. Finally, the 3 kHz conductance was monitored as the entire chamber was heated to 160 °C using the system bakeout tapes in order to check the accuracy of monitoring the temperature of the sample block. Data from the first and final temperature cycles and from the cooling ramp of the second cycle are plotted in the figure. Lower conductivity values were obtained for single-frequency measurements at low frequencies compared to both high- and multiple-frequency measurements. However, the slopes, which

Figure 2. Conductivity of a LiI film as a function of thickness. The solid lines represent values calculated from single-frequency measurements assuming a parallel RC circuit. The data plotted as square points were obtained from an impedance-plane (Cole-Cole) analysis.

Figure 1. Conductance measured at 25 Hz for a 280 nm LiI film grown at 27 °C and annealed at room temperature. The fitted curve was obtained from equation 2.

Figure 3. Arrhenius plot of the conductance as a function of reciprocal temperature. The same activation energies are obtained independent of the type of analysis.

determine the activation energy, were, within error, the same for all the methods used.

DISCUSSION

Measurements on single-crystal LiI have shown that conduction occurs by Li vacancies whose formation and migration enthalpies are 1.06 and 0.43 eV, respectively.¹⁶ Similar results have been obtained for polycrystalline material in the extrinsic region^{17,18} although some discrepancies in the measured formation enthalpies have been noted. Room temperature conductivities for nominally pure material (10 - 100 ppm of divalent impurities such as Mg, Fe and Ca) have been reported to be between 2×10^{-8} and 3×10^{-7} S-cm⁻¹. [Ref. 16-18]

After an initial incubation period, the conductance of our films increases rapidly before leveling off at a thickness of approximately 100 nm. The conductivity of the films, obtained from the slope of the data in Figure 1, is $\sim 1 \times 10^{-5}$ S-cm⁻¹ in the near-interface region and $\sim 2 \times 10^{-6}$ S-cm⁻¹ in the bulk film. The latter value is a factor of 7 to 100 higher than reported for bulk cubic LiI crystals, and reasons for this disparity are discussed below.

According to the space-charge-layer theory, enhanced conduction occurs in a layer whose thickness is given by 2λ , where λ is the Debye length.¹⁹ For a planar configuration, we have¹⁹

$$\lambda = (\epsilon\epsilon_0 kT/2e^2 N_v)^{1/2} \quad (1)$$

Inserting $\epsilon = 8.5^{20}$ and calculating N_v from the measured mobility¹⁷ of 4×10^{-7} cm²·V⁻¹·s⁻¹ and bulk conductivity of 2×10^{-7} S-cm⁻¹ yields $\lambda = 1.4$ nm, which implies an enhanced-conduction layer thickness of 2.8 nm. This is almost a factor of 50 too small for our observations, and if we use the larger conductivity measured far from the interface for the bulk value this thickness is even less.

The annealing experiments provide further evidence that the space-charge explanation is inadequate to explain our results, as nothing in the Debye-layer theory predicts a decrease in

conductivity over time. On the other hand, the annealing behavior can be fit extremely well to a model, based on the work of Johnston²¹, which assumes that conduction is enhanced in the overlapping strain fields of piled-up dislocations. An expression for the conductivity as a function of time may be written as¹⁰

$$G = G_0(n/n_0) = G_0\{1 - m\log[1 + (t - t_0)/\tau]\} \quad (2),$$

where

$$m = kT/n_0 \gamma S b^3 \quad (3),$$

and

$$\tau = (kT/\nu \gamma S b^3) \exp(W_0/kT - 1/m) \quad (4).$$

Here ν is an attempt frequency, W_0 an activation energy for free dislocation climb, S is the yield stress, b is the dislocations' Burgers vector, γ is a constant of order unity, n_0 is the initial number of dislocations in a pileup, t is the time and T the absolute temperature. Although the yield stress for LiI has not been reported, we can estimate it from equation (3) and the fitted value of m if we assume that n_0 is given by the interface-to-bulk enhancement ratio (between 5 and 50). Taking $\gamma = 1$ and $b = 4.24 \text{ \AA}$ (the Li-Li spacing in the cubic structure) gives $2 \times 10^7 < S < 2 \times 10^8 \text{ dynes-cm}^{-2}$. Using the former value for S and assuming $\nu \sim 10^{13}$, we can use equation (4) to show that $W_0 = 0.93 \text{ eV}$. These values are both reasonable (the yield stress¹⁰ for CaF_2 is $1.5 \times 10^8 \text{ dynes-cm}^{-2}$ and the activation energy for intrinsic conduction in LiI is 0.96 eV ¹⁶).

Several explanations are possible for the high "bulk" conductivity values we obtain in the region of film far from the interface. On the one hand, the film itself is annealing as it is being grown. It is likely that even the film deposited far from the interface contains lattice defects that lead to an enhanced conduction. The measured film conductance is then actually a convolution of the actual as-deposited conductance (which leads to an increase) and annealing (which leads to a decrease). For CaF_2 films grown on sapphire where the enhancement ratio was much greater the conductivity was actually seen to decrease with thickness at high growth rates as the annealing rate of the near-interface region outpaced the increased conductance due to additional material being deposited. The best way to obtain the true "bulk" conductance for the film is to measure the conductivity perpendicular to the surface. This is difficult because of the highly reactive nature of LiI.

A second possible explanation is that the film is a phase other than cubic LiI. Wassermann and coworkers^{22,23} reported that LiI produced by evaporation onto a variety of substrates crystallizes in a metastable wurtzite phase when deposited near room temperature. This phase has a conductivity at room temperature about 20 times higher than cubic LiI of comparable purity and is characterized by an activation energy for conduction of $\sim 0.5 \text{ eV}$ compared with the $0.4^{22} - 0.43^{16-18}$ reported for LiI.

The data plotted in Figure 3 show that the film conductivity is greatly reduced during the first heating cycle to 100°C . Although the sharp feature near 85°C attributed to the phase transition is not evident in this plot, it was observed in some films grown under apparently identical conditions when heated at a faster rate ($0.5 \text{ deg.-min}^{-1}$ vs. $0.3 \text{ deg.-min}^{-1}$). In addition, the activation energy measured during repeated cycling between 25 and 100°C was $0.51 \pm 0.03 \text{ eV}$, consistent with data for the wurtzite phase. After heating to 200°C , on the other hand, the activation energy decreases to $0.47 \pm 0.3 \text{ eV}$, consistent with cubic LiI.

The possible presence of a second phase complicates the interpretation of the data, but several points should be noted. First, the growth and annealing were both carried out at temperatures well

below the reported wurtzite-to-cubic phase-transition temperature and therefore the reduction in conductivity enhancement took place with only a single phase present. It should also be noted that even after annealing to well above the reported transition temperature and after a bulk activation energy for conduction in cubic LiI is achieved, the film still undergoes annealing (note the difference between the second and fourth temperature cycles). Therefore, a conduction enhancement due to lattice imperfections is also present in the cubic phase. Finally, we note that the enhancement factor we observe for a single interface, between 5 and 50 depending on the "bulk" value used, is significantly lower than that found in LiI:Al₂O₃ composite material produced by bulk processing.^{1,6,13} This may be explained by a dislocation mechanism since large numbers of dislocations may be produced and stabilized by the presence of ultrafine inclusions.

CONCLUSIONS

LiI films grown on sapphire(0001) exhibit enhanced conduction at the film/substrate interface. The enhancement is not stable but rather decays as the film anneals with a characteristic log of time dependence. This type of annealing behavior is characteristic of dislocation motion and annihilation and indicates that the enhancement is due to defects in the material rather than a space-charge layer.

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