Ionic liquid-gating setup for stable measurements and reduced electronic inhomogeneity at low temperatures

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(Dated: 27 June 2018)

The ionic-liquid gating can be applied to the search for novel physical phenomena at low temperatures because of its wide controllability of the charge carrier density. However, ionic liquid-gated field-effect transistors are often fragile upon cooling because of a large difference in the thermal expansion coefficient between frozen ionic liquid and solid target material. In this paper, we provide a practical technique for setting up ionic liquid-gated field-effect transistors for low-temperature measurements. It allows stable measurements and reduces the electronic inhomogeneity owing to the reduction of the shear strain generated in frozen ionic liquid.

The application of the ionic-liquid gating technique to low temperature physics has attracted considerable attention because of its controllability of the charge carrier density in an extremely wide range.12 This technique uses ionic liquid (organic salt in the liquid phase at room temperature) as a gate dielectric in field-effect transistors in which a target material acts as a channel of charge carriers. In this electric double layer transistor (EDLT), the large capacitive of the electric double layer at the surface of the target material allows to induce charge carriers with a large concentration on the order of $10^{13} - 10^{14}$ cm$^{-2}$. Even when the EDLT is cooled down below the freezing point of the ionic liquid, the electric double layer and the resulting charge carrier density are preserved. Therefore, one can measure the low-temperature electronic properties of the sample with a charge carrier density controlled in a wide range. Electric field-induced superconductivities have been reported in various materials using this technique.13,14

However, there is a practical problem for such low-temperature measurements on EDLTs: frozen ionic liquids often fracture at low temperatures. This induces some detrimental effects on measurements, such as a sudden jump in the resistance-temperature curve (Fig. 1). A large electronic inhomogeneity possibly due to the local detachment of frozen ionic liquid from the sample has also been reported for EDLTs of WS$_2$ and MoS$_2$.15,16 These problems happen presumably due to the shear strain caused by the large difference in the thermal expansion coefficient between the frozen ionic liquid and target sample or its substrate.

In this paper, we introduce an experimental technique which suppresses the shear strain and leads to stable measurements on EDLTs at low temperatures. Our setups for diamond and silicon EDLTs17,18 are shown as examples. This technique will allow stable and efficient low-temperature experiments on EDLTs and studies on high-quality samples with reduced electronic inhomogeneity.

A key feature of our setup is a counter plate placed above the sample/substrate surface (Fig. 2). Ionic liquid is inserted between the counter plate and sample/substrate surface. A similar setup has been used in previous experiments.19,20 We propose here that an adequate spacing between the sample/substrate surface and the counter plate can reduce the shear strain that appears when the device was cooled. Our idea is to compensate for the cooling-induced shrinkage of frozen ionic liquid in a mechanical manner using the shrinkage of the counter plate support. If the shrinkage of the support along z axis is larger than that of the ionic liquid, the ionic liquid is compressed along z axis and expands along the xy plane. If the shrinkage of ionic liquid along the xy plane due to cooling cancels this expansion, there should be no shear strain along the xy plane. The counter plate can be used as a gate electrode if its surface is electrically conductive and a proper wiring is made.

Let us examine the adequate spacing between the sample/substrate surface and the counter plate. We assume that the counter plate and its support are sufficiently thick and rigid so that they are not deformed by external force. We also assume that the thermal expansion coefficient of the sample (or substrate) is small and can be neglected. This is the case when diamond or silicon is used as a substrate or a sample itself, because the thermal expansion coefficients for diamond and silicon are less than $1 \times 10^{-6}$ and $3 \times 10^{-6}$ (K$^{-1}$), respectively, at temperatures below 293 K, which are smaller than those of most of other materials. This assumption is only for the simplification of the calculation shown below. Our scheme can be applied to any material with a straightforward modification.

The length variations of the frozen ionic liquid along the x direction due to the temperature change $\Delta T$ and along the z direction due to the mechanical force are given by

$$\frac{\Delta x_{\text{IL}}}{x_{\text{IL}}} = \alpha_{\text{IL}} \Delta T - \sigma_{\text{IL}} \frac{\Delta z_{\text{IL}}}{z_{\text{IL}}}, \quad (1)$$

$$\Delta z_{\text{IL}} = -z_{\text{IL}} \alpha_{\text{IL}} \Delta T + z_{\text{sup}} \alpha_{\text{sup}} \Delta T. \quad (2)$$

Here, $\alpha_{\text{IL}}$ and $\alpha_{\text{sup}}$ are the thermal expansion coefficients...
FIG. 1. (a) Schematic of a diamond EDLT without a special care to reduce the shear strain. Drain, source, and gate electrodes have been fabricated on the surface of a single crystal diamond. Only the channel of the EDLT on the diamond surface is hydrogen-terminated, which assists the accumulation of holes. The other region is oxygen-terminated. The oxygen termination isolates the channel electrically from the gate. A drop of ionic liquid is applied to cover both the channel and gate electrode. (b) Temperature dependence of the sheet resistance of a diamond EDLT like that shown in (a) at the gate voltage of -1 V. The resistance was measured with a two-point configuration. The resistance suddenly increased (the current decreased to the noise level) at 73 K, which was caused by the fracture of ionic liquid. The source and drain electrodes on the hydrogen-terminated diamond surface were also partially peeled off. (c) The large thermal expansion coefficient of frozen ionic liquid compared to that of diamond leads to the shear strain at the interface.

\[ \Delta x_{\text{IL}} = 0. \]  

Then,  

\[ z_{\text{IL}} = \frac{\sigma_{\text{IL}}}{1 + \sigma_{\text{IL}} \alpha_{\text{IL}}} z_{\text{sup}}. \]  

The value of Poisson’s ratio \( \sigma \) for most materials is 0.3-0.4. We use brass and copper for the support of the counter plate. The thermal expansion coefficient of copper is \( 10 \times 10^{-6} \) and \( 15 \times 10^{-6} \) (K\(^{-1}\)) at 100 and 200 K\(^{-1}\).\(^{22}\) It is difficult to find the data of thermal expansion of frozen ionic liquids at temperatures below their freezing point. We assume that the coefficient for the frozen ionic liquid is close to that of organic charge-transfer salts, which is \((40 - 80) \times 10^{-6}\) at 100 and \((40 - 80) \times 10^{-6}\) (K\(^{-1}\)) at 100 and 200 K\(^{-1}\).\(^{23,24}\) The height \( z_{\text{sup}} \) of the support of the counter plate is 0.45 – 0.5 mm in our experimental setup for diamond EDLTs. If we use these values, the thickness of ionic liquid should be 10 – 40 and 20 – 50 \( \mu \)m for 100 and 200 K to minimize the shear strain. If a softer material with a larger \( \alpha_{\text{sup}} \) is used for the support (for example, polymer), then it is better to increase the ratio \( z_{\text{IL}} / z_{\text{sup}} \). If the sample/substrate is fixed on the sample holder using adhesive tape, its large thermal expansion coefficient should also be taken into consideration.

An optical microscope image of our setup for a diamond EDLT is shown in Fig. 2(c). The diamond is fixed using two copper claws, without the use of adhesive tape. As a counter plate, we used a Ti/Pt or Ti/Au deposited
We were able to measure detailed low temperature transport properties of silicon EDLTs with this setup and could perform stable measurements at low temperatures with this setup. As an example, the temperature dependence of resistance of ten different diamond EDLTs is shown in Fig. 4. The curves vary in a monotonic manner although a few curves cross possibly due to the difference in the surface crystallographic orientation. Furthermore, there is almost no difference between the resistance-temperature curves measured while the sample is cooled down and warmed up. This indicates that the local detachment of ionic liquid is negligible during the thermal process. We observed an electric field-induced insulator-metal transition and Shubnikov de-Haas oscillations of diamond with this setup. An anomalous low-temperature magnetotransport of the electric field-induced charge carriers was also observed in diamond with the (100) surface.

We performed a study of silicon EDLTs as well. Another type of sample holder (Fig. 5) was fabricated for the silicon EDLTs because of the following reasons. The silicon surface of the channel of the EDLTs are hydrogen-terminated to reduce the trap density. This hydrogen termination is crucial for the device operation, but it is easily destroyed by air exposure, in contrast to the diamond surface. Therefore, the electrical wiring between the sample and sample holder could not be performed in air for the silicon EDLTs. The sample holder is designed so that the electrical wiring can be performed using small pieces of indium in an Ar-filled glove box. The sample holder can also be sealed with indium in the glove box.

This sample holder is made of PCTFE (polychlorotrifluoroethylene) and the lid acts as a counter plate. The counter plate support consists of ≈0.40 mm thick PCTFE and 0.1 − 0.15 mm thick indium: $z_{\text{sup}} \approx 0.50 − 0.55 \text{ mm}$. The thermal expansion coefficient of PCTFE is $34 \times 10^{-6}$ and $47 \times 10^{-6}$ at 100 and 200 K. The coefficient $(\alpha_3/3)$ for indium is $27 \times 10^{-6}$ and $28 \times 10^{-6} (\text{K}^{-1})$ at 100 and 200 K using Eq. 4. $\zeta_{\text{IL}}$ for the minimized shear strain is estimated to be $50 − 130$ and $60 − 170 \text{ mm}$ for 100 and 200 K. We set $\zeta_{\text{IL}} \approx 120 − 170 \text{ mm}$ in the actual setup. We were able to measure detailed low temperature transport properties of silicon EDLTs with this setup and the reduction of the contact resistance of electrodes.
the thermal expansion coefficient and Poisson’s ratio of liquid due to residual shear strains. Measurements of or it is caused by local distortion of the frozen ionic date whether this inhomogeneity has an intrinsic origin at low temperatures. The Shubnikov-de Haas oscillations observed in diamond EDLTs suggest a spatially differ. There may still be small remaining strains with a hydrogen-terminated channel, Hall bar electrodes, and a gate electrode is fixed on the main part of the sample holder by a copper claw in an Ar-filled glove box. After a drop of ion liquid is applied, the lid is screwed. This makes the electrical wiring, the seal of the sample holder, and the insertion of the ionic liquid between the silicon and counter plate (lid) at the same time. The dimensions of the silicon chip are approximately 6.0 mm × 6.0 mm × 0.38 mm.

The proposed method minimizes the shear strain in frozen ionic liquid, but the perfect reduction of it in an entire temperature range is difficult. This is because the temperature dependences of αIL and αsup generally differ. There may still be small remaining strains at low temperatures. The Shubnikov-de Haas oscillations observed in diamond EDLTs suggest a spatial inhomogeneity of charge carrier density and mobility at low temperatures. Further work is necessary to elucidate whether this inhomogeneity has an intrinsic origin or it is caused by local distortion of the frozen ionic liquid due to residual shear strains. Measurements of the thermal expansion coefficient and Poisson’s ratio of ionic liquids at different temperatures are also awaited. More elaborate reduction of the shear strain may be possible by setting the spacing so that the integral of \((1/\alpha_{IL})(d\sigma_{IL}/dT)\) (dependent of \(\alpha_{IL}(T), \sigma_{IL}(T), \) and \(\alpha_{sup}(T)\)) between the temperature of interest and the freezing temperature of the ionic liquid would be zero.

In summary, we proposed a practical method to reduce shear strain in frozen ionic liquid for stable measurements of electric double layer transistors at low temperatures. The reduction of shear strain was achieved by compensating for the cooling-induced shrinkage of frozen ionic liquid in a mechanical way using a counter plate and its support. The simple setup will be used for various materials and allow stable and efficient experiments at low temperatures. In particular, it prevents the detachment of frozen ionic liquid from the sample surface and the detrimental breakdown of the device due to cooling. It will also reduce the electronic inhomogeneity caused by the shear strain and thus help to study more intrinsic properties of the target materials.

We appreciate the helpful comments from Y. Ootuka. This study was supported by Grants-in-Aid for Fundamental Research (Grant Nos. 25287093 and 26220903) and the ”Nanotechnology Platform Project” of MEXT, Japan.

1S. Bisri, S. Shimizu, M. Nakano, and Y. Iwasa, Adv. Mater. 29, 1607054 (2017).
2J. Ye, S. Inoue, K. Kobayashi, Y. Kasahara, H. Yuan, H. Shimotani, and Y. Iwasa, Nat. Mater. 9, 125 (2010).
3A. Bollinger, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich, and I. Bozović, Nature 472, 458 (2011).
4K. Ueno, S. Nakamura, H. Shimotani, H. Yuan, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nature Nanotechnol. 6, 408 (2011).
5X. Leng, J. Garcia-Barriocanal, S. Bose, Y. Lee, and A. M. Goldman, Phys. Rev. Lett. 107, 027001 (2011).
6G. Dubuis, A. T. Bollinger, D. Pavuna, and I. Bozović, J. Appl. Phys. 111, 112632 (2012).
7J. Ye, Y. Zhang, R. Akashi, M. Bahramy, R. Arita, and Y. Iwasa, Science 338, 1193 (2012).
8S. Jo, D. Costanzo, H. Berger, and A. Morpurgo, Nano Lett. 15, 1197 (2015).
9W. Shi, J. Ye, Y. Zhang, R. Suzuki, M. Yoshida, J. Miyazaki, N. Inoue, Y. Saito, and Y. Iwasa, Sci. Rep. 5, 12534 (2015).
10Y. Saito, Y. Kasahara, J. Ye, Y. Iwasa, and T. Nojima, Science 350, 409 (2015).
11J. Lu, O. Zheliuk, I. Leermakers, N. Yuan, U. Zeitler, K. Law, and J. Ye, Science 350, 1353 (2015).
12L. Li, E. O’Farrell, K. P. Loh, G. Eda, B. Özyilmaz, and A. C. Neto, Nature 529, 185 (2016).
13D. Costanzo, S. Jo, H. Berger, and A. Morpurgo, Nature Nanotechnol. 11, 339 (2016).
14J. Zeng, E. Liu, Y. Fu, Z. Chen, C. Pan, C. Wang, M. Wang, Y. Wang, K. Xu, S. Cai, X. Yan, Y. Wang, X. Liu, P. Wang, S.-J. Liang, Y. Cui, H. Hwang, H. Yuan, and F. Miao, Nano Lett. 18, 1410 (2018).
15T. Yamaguchi, E. Watanabe, H. Osato, D. Tsuya, K. Deguchi, T. Watanabe, H. Takeya, Y. Takano, S. Kurihara, and H. Kawarada, J. Phys. Soc. Jpn. 82, 074718 (2013).
16Y. Takahide, H. Okazaki, K. Deguchi, S. Uji, H. Takeya, Y. Takano, H. Tsuboi, and H. Kawarada, Phys. Rev. B 89, 235304 (2014).
17T. Takahide, Y. Sasama, M. Tanaka, H. Takeya, Y. Takano, T. Kageura, and H. Kawarada, Phys. Rev. B 94, 161301(R) (2016).
This sample holder was made of brass following Ref. [26]. We noticed that this brass showed a weak superconductivity at temperatures below 7.4 K probably due to its lead impurities. In addition, the TO-5 header for electrical feedthrough is made of a ferromagnetic material. Using a Hall sensor, we confirmed that the influence of these on the magnetic field applied to the sample was negligible at 2-300 K. This is consistent with experiments in Refs. [26,27].

Neoflon PCTFE Molding Powder, Product information, Daikin industries.

J. Smith and V. Schneider, J. Less-common Metals 7, 17 (1964).

G. Dezi, N. Scopigno, S. Caprara, and M. Grilli, ArXiv:1706.01274.