Demonstration of Electric Double Layer Gating under High Pressure by the Development of Field-Effect Diamond Anvil Cell

Shintaro Adachi\textsuperscript{1,a}, Ryo Matsumoto\textsuperscript{1,2}, Sayaka Yamamoto\textsuperscript{1,2}, Takafumi D. Yamamoto\textsuperscript{1}, Kensei Terashima\textsuperscript{1}, Yoshito Saito\textsuperscript{1,2}, Miren Esparza Echevarria\textsuperscript{1}, Pedro Baptista de Castro\textsuperscript{1,2}, Peng Song\textsuperscript{1,2}, Suguru Iwasaki\textsuperscript{1}, Hiroyuki Takeya\textsuperscript{1}, and Yoshihiko Takano\textsuperscript{1,2}

\textsuperscript{1}MANA, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
\textsuperscript{2}Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan

\textsuperscript{a}Corresponding author: ADACHI.Shintaro@nims.go.jp

We have developed an EDLT-DAC that enables us to control the carrier density in the various materials even under high pressure by a novel combination of an electric double layer transistor (EDLT) and a diamond anvil cell (DAC). In this study, this novel EDLT-DAC was applied to a Bi thin film, and here we report the first field-effect under high pressure in the material to our knowledge. Our EDLT-DAC is a promising device for exploring new physical phenomena such as high transition-temperature superconductivity.

Strategic engineering the band structure and as well as the position of the Fermi level plays a crucial role for the exploration of novel phenomena, such as high transition-temperature ($T_c$) superconductivity (HTS). Applying pressure and/or tuning the carrier density is known to be effective for controlling the electronic structure. Recent evolution of the pressure generator and the field-effect device provided alternative route for controlling the electronic structure of a material other than chemical doping. Such devices have allowed us to reach even intrinsically unstable phases in a materials.
Recently, a lot of surprising phenomena have been discovered by the induction of carriers into materials using an electric double-layer transistor (EDLT) structure\textsuperscript{1-7}. This structure consists of an electrolyte which is sandwiched between a gate electrode and a sample surface. When a voltage is applied between the gate and the source electrode of the sample, an electric double layer (EDL) is oriented at a very short distance at the interface between the electrolyte and the sample. This electric double layer works like a dielectric in a capacitor. In the case of EDL gating, since the thickness of the ionic layer is in nanoscale, a large amount of charges can be induced near the sample surface. The following are some of representative examples of field-induced superconductor using the EDLT structure: SrTiO\textsubscript{3} with a low carrier concentration\textsuperscript{8,9}, an atomically flat ZrNCl film from cleaved single crystal\textsuperscript{10,11}, and many other two dimensional systems\textsuperscript{12-16}.

On the other hand, the application of high pressure enables us to reach unknown phenomena such as HTS which is unaccessible at ambient pressure. The recent discoveries of HTS in hydrides using diamond anvil cell (DAC)\textsuperscript{17-20} are a typical example of new material search under high pressure. It is worthy to stress that this occurrence of pressure-induced high-$T_c$ superconductivity has been predicted by theoretical calculations\textsuperscript{21-25} before the experimental discovery of high-$T_c$ hydrides\textsuperscript{17-20}, based on the BCS theory. Such a theory-guided search is becoming a steady approach for the exploration of new superconducting phase. We also have discovered new pressure-induced superconductors by using our original DAC\textsuperscript{26,27} coupled with a data-driven approach\textsuperscript{28-30}.

As discussed above, each of the EDLT structure and the DAC has been recognized as predominant tools for tuning the physical properties in materials. If the combination of high-pressure generation by DAC and electrical field-effect by EDLT is achieved, it will provide us a vast area of the search space for new physical phenomena, that might have been remained only for theoretical studies. In this paper, we report development device which combines an EDLT structure into a DAC (Hereafter, we call this device the EDLT-DAC) for this task. We found that our previously fabricated DAC\textsuperscript{26,27} with the micro-scale boron-doped diamond electrodes and the insulating un-doped diamond is suitable as the base of pressure generator with electric field-effect function. As a first sample to apply the field-effect and pressure, we chose a bismuth (Bi) film since it is well known
that there are extremely few electrons and holes in Bi compared to conventional metals\textsuperscript{33-35} and therefore it is expected to exhibit prominent response upon the electric field, for verifying the characteristics of the fabricated EDLT-DAC.

**FIG. 1.** (color online). Schematic image of a cross-section of (a) the conventional DAC and (b) the EDLT-DAC. In the case of the EDLT-DAC, the pressure medium is an ionic liquid (DEME-TFSI). The gasket (Pt-Ir alloy) also works as a gate electrode. A boron-doped diamond was used as the electrodes, and the un-doped diamond was used as an insulating layer\textsuperscript{26,27}. (c) A cross-sectional image of a sample space of an EDLT-DAC in which EDL gating is performed.

**FIG. 2.** (color online). (a) Optical microscope image of a Bi film on the bottom diamond. (b) Typical EDLT-DAC setup of a sample space with the ionic liquid, ruby crystalline powders, and Pt(80\%)\textendash Ir(20\%) gasket. The diameter of the inner hole in the gasket was about 300 μm.
Schematic drawing of conventional DAC\textsuperscript{31,32} and the EDLT-DAC are shown in Figure 1(a) and 1(b). In a conventional DAC, high pressure is generated in a sample space when pressing two opposing diamond anvils with a polished flat tip (culet). In our EDLT-DAC a similar anvil was used as the upper anvil and our original diamond anvil was used as the lower anvil\textsuperscript{26,27}. The diameter of a culet of the top anvil was 600 μm. Metals are usually used as the sealing material (gasket) around the upper and lower anvils. In previous studies, we used an austenitic stainless steel SUS 316L gasket to generate a pressure of 100 GPa or more\textsuperscript{27}. However, the gasket of an EDLT-DAC is required to be electrochemically stable to work as a gate electrode. So we employed Pt(80\%)\textendash Ir(20\%) alloy because it has an electrochemical stability and enough hardness as a gasket. This alloy has almost the same Vickers hardness, HV (= 240)\textsuperscript{36} as a SUS 316L\textsuperscript{37,38}. A Pt(80\%)\textendash Ir(20\%) sheet with a thickness of 200 μm was used as not only a gasket in the DAC but also a gate electrode in the EDLT structure. By injecting the ionic liquid DEME-TFSI into the sample space after placing the sample and gasket on the lower anvil, the EDLT-DAC was completed. Figure 1(c) is a schematic image of a cross-section of the EDLT-DAC sample space. With this setup, when a positive voltage is applied to the Pt-Ir alloy gate and the source electrode, anions are attracted to the gate electrode and cations are attracted to the sample surface. In this case, electrons should be induced on the sample surface. The vicinity of the sample surface corresponds to the channel region of the conventional FET.

Figure 2(a) shows an optical microscope image of a Bi film on the lower diamond anvil. The thin film of Bi on a lower anvil was prepared by vapor deposition. The film thickness was evaluated to be about 60 – 70 nm by atomic force microscopy. Figure 2(b) shows a typical set-up of the sample space in the EDLT-DAC. Electrical resistance of the Bi film was measured using a standard four-probe method. Applied pressure was evaluated by using Piermarini's equation\textsuperscript{39} as a function of a peak position of the $R_1$ ruby fluorescence line.
FIG. 3. (color online). (a) The time dependence of the resistance in a Bi film at RT from ambient pressure up to 1.92 GPa. The black arrows indicate the point that pressure estimation was performed. Pressure estimation with EDL gating was carried out by a function of a peak position of the $R_1$ ruby fluorescence. Estimated pressures as of this time are described behind the black arrows.

FIG. 4. (color online). (a-e) The time dependence of the normalized resistance in a Bi film at room temperature and that of the gate voltage (see the second axis). Measurement results from ambient pressure (AP) to 1.95 GPa from left to right. $R_0$ is the resistance value when $t = 0$. 
Figure 3(a) shows the time dependence of the resistance in a Bi film at room temperature, where the right axis represents the gate voltage. The applied gate voltage $V_G$ was set either to 0 V or 1 V. The value of the resistance at ambient pressure decreases rapidly from about 510 $\Omega$ and saturates to about 100 $\Omega$ for 40 minutes. This behavior indicates that carriers are induced in the channel of the Bi film by EDL gating. Namely, this result was first observation of the field-effect under pressure. After the saturation, the pressure was applied while keeping the gate voltage 1 V, where the time at which pressure was applied is indicated by the arrows with the corresponding pressure value. The resistance slightly increases after each compressing. This may be due to the pressure-effect on the Bi film or sample deformation. The most surprising fact is that the resistance takes a constant value even after releasing the gate voltage. Stabilization of sample resistance after releasing the gate voltage and applied pressure were similar to the results in the previous works where the EDL is stabilized by cooling (less than 190K). That is, the compression of the ionic liquid may also stabilize EDL.

For quantitative comparison of the time dependence of the resistance with EDL gating under various pressures, we show in Figure 4(a)-(e) the normalized resistance $R_N = (R(t)/R_0)$, where $R_0$ indicates the initial resistance, the range of the left axis has been scaled from 0.6 to 1.1, and the right axis is the value of the gate voltage. In the measurement at ambient pressure of Figure 4(a), after setting the gating voltage to 1 V, the $R_N$ decreased rapidly from 1 with time. After that, the $R_N$ was almost saturated around 0.72 and this resistance was kept for 2 hours. This result is in good correspondence to Figure 3 at ambient pressure ($t < 184$ min). In the next operation when $V_G$ was switched from 1 V to 0 V, the $R_N$ decreased at the moment. A few minutes after the gate voltage was reduced to zero, the $R_N$ increased slowly and non-linearly. This behavior was different from the result (that is, constant resistance even when $V_G$ was changed zero) in Figure 3 with compressing ($t \geq 184$ min). Therefore, it is suggested that this difference in the results is due to the difference in the condition of whether the applied pressure is at ambient pressure or 1.92 GPa.

Figure 4(b)-(e) show the relationship between the $R_N$ and the $V_G$ changes under applying pressure on the sample, we also demonstrated the same procedure as that of ambient pressure after compressing respectively. Figure 4(b) shows the time dependence
of the resistance under 0.22 GPa. In the measurement of Figure 4(b), $R_N$ decreased from 1 with time after setting the $V_G$ from 0 to 1 V. For about 5 hours, the decreasing rate of resistance was suppressed with time. In addition, after setting $V_G$ from 1 V to 0 V, the resistance increased slower than the case of ambient pressure (see Figure 4a). By comparing Figure 4a and 4b, we have found that two effects interfere with the field-effect by applying pressure. The first effect is that when 0.22 GPa was applied, the resistance reduction rate due to the electric field effect was suppressed. The second effect is that by applying 0.22 GPa, the resistance recovery rate when the gate voltage is changed from 1 to 0 V is suppressed. These two suppress-effects showed significantly more when the pressure rise to 0.93 GPa and 1.54 GPa (see fig. 4c and 4d). Finally, at 1.95 GPa, the $R_N$ of the sample did not change even when the gating voltage was of 1 V for 24 h.

We demonstrated that the drop rate of the sample resistance by EDL gating ($V_G = 1$ V in this study) clearly decreased with increasing pressure. We also revealed that after the gate voltage was released (from 1 to 0 V), the recovery of the $R_N$ was suppressed with higher pressure. These behaviors are the features of the field-effect under pressure. The property of the EDL under pressure have many mysteries, but as a suggestive example, the stabilization of an EDL at low temperature cannot be ignored. As an important characteristics of the ionic liquid, Yuan et al. reported that the ionic conductivity is decreased when the ionic liquid is cooled\textsuperscript{4}. Such an interesting nature of ionic liquid has drawn our attention, as it can be highly suitable for saving EDL also under pressure. Namely, if pressure increased the viscosity of an ionic liquid DEME-TFSI, the EDL might be preserved. In general, it is known that the viscosity of a Newtonian fluid increases with increasing pressure: as it has been observed commonly for an organic liquid\textsuperscript{40}, and an ionic liquid trihexyl(tetradecyl)phosphonium dicyanamide\textsuperscript{41}, and also the glass forming liquid\textsuperscript{42}. The possibility of maintaining the charge density of the EDL formed by the field-effect even after the electric field was removed by compression can be an interesting research topic in applied physics. More details of the stabilization of the electric double layer and also the applicability of the EDLT-DAC at higher pressure, lower temperature, and higher gate voltage, are need to be investigated in future research.
In summary, we successfully developed a field-effect diamond anvil cell (called the EDLT-DAC) for tuning the properties of the materials, and applied it to a thin film of Bi. To our knowledge, this is the first observation of the electrical field-effect under high pressure in condensed matter. In addition, we also found that the EDL was stabilized by pressure. The stabilization-effect of the EDL under pressure may contribute to the development of novel devices such as transistors in a field of applied physics. We have demonstrated that our EDLT-DAC is capable of tuning the carrier density of the materials under high pressure, hence our developed device will certainly accelerate the exploration of new physical phenomena that have not been accessible so far.

Acknowledgment

We are grateful to M. Fujioka, M. Tanaka, M. Nagao, H. Hara, S. Harada, T. Ishiyama, and T. Nojima for all the help. This work was supported by JSPS KAKENHI Grant No. JP17J05926, JP19H02177, JST-Mirai Program Grant No. JPMJMI17A2, and JST CREST Grant No. JPMJCR20Q4.

REFERENCES

1. H. Shimotani, H. Asanuma, J. Takeya, and Y. Iwasa, Appl. Phys. Lett. 89, 203501 (2006). DOI: https://doi.org/10.1063/1.2387884

2. M. Weisheit, S. Fahler, A. Marty, Y. Souche, C. Poisignon, and D. Givord, Science 315, 349 (2007). DOI: https://doi.org/10.1126/science.1136629

3. H. Shimotani, H. Asanuma, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Appl. Phys. Lett. 91, 082106 (2007). DOI: https://doi.org/10.1063/1.2772781

4. H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Adv. Funct. Mater. 19, 1046 (2009). DOI: https://doi.org/10.1002/adfm.200801633

5. K. Ueno, H. Shimotani, H. Yuan, J. Ye, M. Kawasaki, and Y. Iwasa, J. Phys. Soc. Jpn. 83, 032001 (2014). DOI: http://dx.doi.org/10.7566/JPSJ.83.032001
S. Z. Bisri, S. Shimizu, M. Nakano, and Y. Iwasa, Adv. Mater. 29, 1607054 (2017). DOI: http://dx.doi.org/10.1002/adma.201607054

C. Navarro-Senent, A. Quintana, E. Menendez, E. Pellicer, and J. Sort, APL Mater. 7, 030701 (2019). DOI: https://doi.org/10.1063/1.5080284

K. Ueno, S. Nakamura, H. Shimotani, A. Ohtomo, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nat. Mater. 7, 855 (2008). DOI: https://doi.org/10.1038/nmat2298

K. Ueno, H. Shimotani, Y. Iwasa, and M. Kawasaki, Appl. Phys. Lett. 96, 252107 (2010). DOI: https://doi.org/10.1063/1.3457785

J. T. Ye, S. Inoue, K. Kobayashi, Y. Kasahara, H. T. Yuan, H. Shimotani, and Y. Iwasa, Nat. Mater. 9, 126 (2010). DOI: https://doi.org/10.1038/NMAT2587

Y. Saito, Y. Kasahara, J. Ye, Y. Iwasa, T. Nojima, Science 350, 409 (2015). DOI: https://doi.org/10.1126/science.1259440

J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, Science 338, 1193 (2012). DOI: https://science.sciencemag.org/content/338/6111/1193

H. Yuan, M. S. Bahramy, K. Morimoto, S. Wu, K. Nomura, B.-J. Yang, H. Shimotani, R. Suzuki, M. Toh, C. Kloc, X. Xu, R. Arita, N. Nagaosa, and Y. Iwasa, Nat. Phys. 9, 563 (2013). DOI: https://doi.org/10.1038/NPHYS2691

S. Jo, D. Costanzo, H. Berger, and A. F. Morpurgo, Nano Lett. 15, 1197 (2015). DOI: https://doi.org/10.1021/nn504314c

E. Uesugi, S. Nishiyama, H. Goto, H. Ota, and Y. Kubozono, Appl. Phys. Lett. 109, 252601 (2016). DOI: https://doi.org/10.1063/1.4972400

E. Uesugi, T. Uchiyama, H. Goto, H. Ota, T. Ueno, H. Fujiwara, K. Terashima, T. Yokoya, F. Matsui, J. Akimitsu, K. Kobayashi, and Y. Kubozono, Sci. Rep. 9, 5376 (2019). DOI: https://doi.org/10.1038/s41598-019-41906-7

A. P. Drozdov, M. I. Eremets, I. A. Trojan, V. Ksenofontov, and S. I. Shylin, Nature 525, 73 (2015). DOI: https://doi.org/10.1038/nature14964

A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, and M. I. Eremets, Nature 569, 528 (2019). DOI: https://doi.org/10.1038/s41586-019-1201-8
19 M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin, and R. J. Hemley, Phys. Rev. Lett. 122, 027001 (2019). DOI: https://doi.org/10.1103/PhysRevLett.122.027001

20 D. V. Semenok, A. G. Kvashnin, A. G. Ivanova, V. Svitlyk, V. Y. Fominski, A. V. Sadakov, O. A. Sobolevskiy, V. M. Pudalov, I. A. Troyan, and A. R. Oganov, Mater. Today (2019). DOI: https://doi.org/10.1016/j.mattod.2019.10.005

21 N. W. Ashcroft, Phys. Rev. Lett. 21, 1748 (1968). DOI: https://doi.org/10.1103/PhysRevLett.21.1748

22 N. W. Ashcroft, Phys. Rev. Lett. 92, 187002 (2004). DOI: https://doi.org/10.1103/PhysRevLett.92.187002

23 D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, Sci. Rep. 4, 6968 (2014). DOI: https://doi.org/10.1038/srep06968

24 F. Peng, Y. Sun, C. J. Pickard, R. J. Needs, Q. Wu, and Y. Ma, Phys. Rev. Lett., 119, 107001 (2017). DOI: https://doi.org/10.1103/PhysRevLett.119.107001

25 H. Liu, I. I. Naumov, R. Hoffmann, N. W. Ashcroft, and R. J. Hemley, Proc. Natl. Acad. Sci., 114, 6990 (2017). DOI: https://doi.org/10.1073/pnas.1704505114

26 R. Matsumoto, Y. Sasama, M. Fujioka, T. Irifune, M. Tanaka, T. Yamaguchi, H. Takeya, and Y. Takano, Rev. Sci. Instrum. 87, 076103 (2016). DOI: https://doi.org/10.1063/1.4959154

27 R. Matsumoto, H. Hara, H. Tanaka, K. Nakamura, N. Kataoka, S. Yamamoto, A. Yamashita, S. Adachi, T. Irifune, H. Takeya, and Y. Takano, J. Phys. Soc. Jpn. 87, 124706 (2018). DOI: https://doi.org/10.7566/JPSJ.87.124706

28 R. Matsumoto, Z. Hou, H. Hara, S. Adachi, H. Takeya, T. Irifune, K. Terakura, and Yoshihiko Takano, Appl. Phys. Express 11, 093101 (2018). DOI: https://doi.org/10.7567/APEX.11.093101

29 R. Matsumoto, Z. Hou, M. Nagao, S. Adachi, H. Hara, H. Tanaka, K. Nakamura, R. Murakami, S. Yamamoto, H. Takeya, T. Irifune, K. Terakura, and Y. Takano, Sci. Technol. Adv. Mater. 19, 910 (2018). DOI: https://doi.org/10.1080/14686996.2018.1548885

30 R. Matsumoto, H. Hara, Z. Hou, S. Adachi, H. Tanaka, S. Yamamoto, Y. Saito, H. Takeya, T. Irifune, K. Terakura, and Y. Takano, Inorg. Chem. 59, 325 (2020).
31 A. Jayaraman, Rev. Mod. Phys. 55, 65 (1983).
   DOI: https://doi.org/10.1103/RevModPhys.55.65

32 K. Shimizu, K. Amaya, and N. Suzuki, J. Phys. Soc. Jpn. 74, 1345 (2005).
   DOI: https://doi.org/10.1143/JPSJ.74.1345

33 A. L. Jain, Phys. Rev. 114, 6 (1959). DOI: https://doi.org/10.1103/PhysRev.114.1518

34 R. A. Hoffman and D. R. Frankl, Phys. Rev. B 3, 6 (1971).
   DOI: https://doi.org/10.1103/PhysRevB.3.1825

35 Y-S. Way and Y-h. Kao, Phys. Rev. B 5, 6 (1972).
   DOI: https://doi.org/10.1103/PhysRevB.5.2039

36 G. Rakhtsaum, Platinum Metals Rev. 57, 202 (2013).
   DOI: http://dx.doi.org/10.1595/147106713X668596

37 O. Takakuwa, Y. Kawaragi, and H. Soyama, J. Surf. Eng. Mater. Adv. Technol., 3, 262 (2013). DOI: http://dx.doi.org/10.4236/jsemat.2013.34035

38 S. M. Yusuf, Y. Chen, R. Boardman, S. Yang, N. Gao, Metals 7, 64 (2017).
   DOI: http://dx.doi.org/10.3390/met7020064

39 G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. 46, 2774 (1975). DOI: https://doi.org/10.1063/1.321957

40 J. H. Dymond, N. F. Glen, J. D. Isdale, and M. Pyda, Int. J. Thermophys. 16, 877 (1995).
   DOI: https://doi.org/10.1007/BF02093470

41 J. C. F. Diogo, F. J. P. Caetano, J. M. N. A. Fareleira, and W. A. Wakeham, J. Chem. Eng. Data 57, 1015 (2012). DOI: https://doi.org/10.1021/je200830j

42 I. Avramov, J. Non-Cryst. Solids, 262, 258 (2000).
   DOI: https://doi.org/10.1016/S0022-3093(99)00712-7