Simultaneous control of thermoelectric properties in p- and n-type materials by electric double-layer gating: New design for thermoelectric device

Ryohei Takayanagi¹, Takenori Fujii²*, and Atsushi Asamitsu¹,²

¹Department of Applied Physics, University of Tokyo, Bunkyo, Tokyo 113-8656, Japan
²Cryogenic Research Center, University of Tokyo, Bunkyo, Tokyo 113-0032, Japan
E-mail: fujii@crc.u-tokyo.ac.jp

Received March 9, 2015; accepted March 19, 2015; published online April 8, 2015

We report a novel design of a thermoelectric device that can control the thermoelectric properties of p- and n-type materials simultaneously by electric double-layer gating. Here, p-type Cu₂O and n-type ZnO were used as the positive and negative electrodes of the electric double-layer capacitor structure. When a gate voltage was applied between the two electrodes, holes and electrons accumulated on the surfaces of Cu₂O and ZnO, respectively. The thermopower was measured by applying a thermal gradient along the accumulated layer on the electrodes. We demonstrate here that the accumulated layers worked as a p–n pair of the thermoelectric device. © 2015 The Japan Society of Applied Physics

Since thermoelectric devices can convert waste heat into useful electricity, they are expected to be used as clean energy without discharging CO₂. Moreover, they can be used as refrigerators through the Peltier effect. Thermoelectric devices are made from an array of p- and n-type materials connected electrically in series but thermally in parallel. It is therefore important to explore both p- and n-type materials that have a high efficiency in order to make high-performance devices.

The efficiency of the thermoelectric materials are determined by the figure of merit of the materials, $ZT = S^2T/ρκ$, where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $ρ$ is the resistivity, and $κ$ is the thermal conductivity. Therefore, the thermoelectric materials need to have a large $S$, a small $ρ$, and a small $κ$. Since $ρ$, $S$, and $κ$ are functions of the carrier concentration, it is necessary to control and optimize the carrier concentration in order to enhance the figure of merit. Good thermoelectric materials are typically heavily doped semiconductors with a carrier concentration of $10^{19}$ to $10^{21}$ carriers/cm$^3$.

The most popular way to control the carrier concentration is chemical doping, such as chemical substitution or intercalation. However, it is difficult to synthesize a variety of samples whose doping ratio is precisely controlled. Moreover, the doped elements inherently act as disorder and may lead to an increase in the resistivity. The other way to control the carrier concentration is a method using the electric-field effect, which is completely free from disorder. It is reported for SrTiO$_3$ that the thermopower was modulated by using a field-effect transistor (FET) structure with a gate insulator made of water-infiltrated nanoporous 12CaO·7Al$_2$O$_3$ glass. On the other hand, an electric double-layer transistor (EDLT) is a FET whose insulating layer is replaced with an electrolyte and has the ability to accumulate carriers up to $10^{14}$–$10^{15}$ cm$^{-2}$ on the surface of a sample, which is one or two orders of magnitude larger than that in conventional FETs. This large amount of carrier accumulation lead to various achievements in condensed-matter physics, such as the metal-insulator transition in ZnO, the field-induced superconductivity in SrTiO$_3$, ZnCl$_2$, KTaO$_3$, and MoS$_2$, and the formation of a p–n junction in MoS$_2$. We have previously reported that the thermoelectric properties of ZnO have been controlled by using an EDLT. In that report, the conductivity and thermopower have been modulated by gating; thus, the power factor has been improved. The EDLT is therefore considered to be a powerful method to find new thermoelectric materials by controlling the carrier concentration.

In this paper, we propose a new concept for a thermoelectric device that can control the thermoelectric properties of p- and n-type materials simultaneously by electric double-layer gating. Here, the electric double-layer capacitor (EDLC) structure was applied to the thermoelectric device. The advantage of our technique is the simplification of the design for the thermoelectric devices compared to using an FET structure. We do not need to use gate electrodes for each p- and n-type material. Moreover, EDLCs have already been applied for practical uses such as a rechargeable battery. In order to design a thermoelectric device, we used ZnO, which already controlled the thermoelectric properties by using an EDLT, as a negative electrode. However, there are few materials, which show typical p-type transistor behavior by electric double-layer gating, to date. A NiO single crystal was reported as a p-type material for the EDLT channel with a relatively small on/off ratio of 130. However, we could not reproduce the EDLT device operation, probably because we could not form the electrodes of the interdigitated comb-shaped array that reduce the effective device resistance. Several materials such as MoS$_2$, WSe$_2$, and Bi$_2$Te$_3$ display both p- and n-type conduction by changing the sign of the gate voltage, but this ambipolar operation was confirmed only in a thin film or thin flake sample. In order to configure a thermoelectric device, finding a p-type material with good device performance in a bulk sample as well as high thermoelectric properties is demanded. We investigated a p-type material for the EDLT and found that Cu$_2$O, which was grown by the floating-zone (FZ) method, displayed the typical p-type transistor behavior. Cu$_2$O is well-known as an oxide semiconductor, which has a direct band gap of about 2.1 eV. Cu$_2$O usually shows p-type conductivity since copper vacancies introduce an acceptor level ~0.5 eV above the valence band. By using p-type Cu$_2$O and n-type ZnO as the positive and negative electrodes, we have successfully accumulated holes and electrons simultaneously on their surfaces by applying a gate voltage between the two electrodes.

A single crystal of Cu$_2$O was grown by the FZ method. A commercial Cu$_2$O (99.9%) powder was pressed into a rod and sintered at 1000 °C for 12 h in pure Ar (99.99995%), so as not to be oxidized to CuO. The single-crystal growth was carried out by using an image furnace with two ellipsoidal...
mirrors. The growth velocity was 3.5 mm/h, and the growth atmosphere was air. The powder X-ray diffraction pattern for the crashed sample is in good agreement with Cu$_2$O diffraction pattern. Hence, the grown crystal was confirmed to be Cu$_2$O. ZnO polycrystalline samples were synthesized by sintering a commercial ZnO powder (99.99%) at 1000°C for 15 h in air. The samples were cut into a rectangular shape with a thickness of about 3 × 1 × 0.3 mm$^3$, and the surface was polished with the abrasive of a 1 micron alumina lapping film to obtain a flat surface.

Before performing simultaneous p- and n-type control, we evaluated the thermoelectric performance of each material by using an EDLT configuration. A schematic figure of the EDLT is shown in Fig. 1(a). The source and drain contacts were made by a Au paste, which was covered with a silicone adhesive sealant to avoid a chemical reaction with the electrolyte. Pt foil was used as the gate electrode, and KClO$_4$ in poly(ethylene glycol) (PEG) was chosen as the electrolyte. The number-average molecular weight of PEG was 1,000, and the mixing ratio of KClO$_4$/PEG was [K$^+$] : [O] = 1 : 20. The resistivity was measured by the two-probe method. The absolute value of the drain voltage ($V_D$) was 0.1 V. In order to measure the thermopower, a heater was attached near the source electrode, as shown in Fig. 1(b). The temperature gradient $\Delta T$ (approximately 1–2 K) was measured by a copper-constantan differential thermocouple, and the sample voltage was measured between the source and drain electrodes.

In order to control the thermoelectric properties of the p- and n-type materials simultaneously, we applied the EDLC structure to the thermoelectric device, as shown in Fig. 1(c).$^{23}$ Compared to the EDLT configuration, the Pt-foil gate electrode was replaced with a p-type Cu$_2$O bulk sample. At 300 K, the PEG is gelatinous, and ions can be easily moved by an electric field. When a gate voltage ($V_G$) is applied between the p- and n-type samples at 300 K, ions in the electrolyte are aligned on the surface of the samples, forming a charged double layer called a Helmholtz layer. Therefore, positive and negative image charges are induced on the surfaces of Cu$_2$O and ZnO, respectively. However, the p- and n-type materials must be connected in series for the thermoelectric device, as shown in Fig. 1(d). Since PEG is perfectly frozen and loses ionic conductivity below 260 K, Cu$_2$O and ZnO were connected below 260 K after applying $V_G$ at 300 K. Accordingly, measurements of the properties of the whole device were carried out at 250 K. The device resistivity was measured by the two-probe method by connecting the p- and n-type materials, as shown in Fig. 1(d). The device thermopower was measured by attaching a heater to the connected side of the sample, as shown in Fig. 1(e). Since the absorption of water into the electrolyte causes an electrochemical reaction on the interface of the sample, all measurements were carried out under a He atmosphere.

Figure 2 shows $V_G$ dependencies of the conductance ($\sigma$), gate current ($I_G$), and $S$ of Cu$_2$O at room temperature, which was measured by the EDLT configuration. $V_G$ was swept from 0 to $-4$ V and then back to 0 V with a sweep rate of 0.1 V/min. The drain voltage $V_D$ was kept at 0.1 V during the measurement. No evidence of electrochemical reaction between the electrolyte and the sample were observed; that is, no changes in $\sigma$ and $S$ have been observed after sweeping $V_G$. $\sigma$ increased by applying a negative $V_G$ below $-2$ V and leveled off at $V_G$ < $-3$ V. This result confirms the typical p-type transistor behavior because the negative $V_G$ produces holes on the Cu$_2$O surface. The on–off ratio of the device was a relatively small value of 4, probably because the Cu$_2$O sample used in this measurement had a relatively low resistivity ($7.5$ k$\Omega$ cm).$^{10,16}$ Therefore, the insulator–metal transition was not realized by the electric double-layer gating. The magnitude of the leakage current ($I_L$) was comparable to...
that in a ZnO single crystal$^{9,10}$ and ceramics,$^{16}$ which confirms the device quality. A slight hysteresis was observed in the forward and backward curves of $\sigma$, implying the slow response of ions in the gelatinous electrolyte. As seen in Fig. 2(c), $S$ was clearly changed by using the EDLT configuration from 820 to 720 $\mu V/K$. This is the first result showing that the thermoelectric properties of the p-type material are controlled by an EDLT. Since the depth distribution of the accumulated carriers is not clear, it is difficult to estimate the resistivity and thermopower of the accumulated surface. However, if the accumulated surface and insulating bulk substrate are regarded as a parallel circuit for simplification, the observed total conductance ($\sigma_{\text{total}}$) and thermopower ($S_{\text{total}}$) are given by

$$\sigma_{\text{total}} = \sigma_{\text{sur}} + \sigma_{\text{bulk}},$$

$$S_{\text{total}} = \frac{S_{\text{sur}} + S_{\text{bulk}}}{\sigma_{\text{sur}} + \sigma_{\text{bulk}}},$$

where $S_{\text{sur}}$ and $\sigma_{\text{sur}}$ are the thermopower and conductance of the accumulated surface, respectively, and $S_{\text{bulk}}$ and $\sigma_{\text{bulk}}$ are the thermopower and conductance of the bulk substrate, respectively. As discussed in a previous report, since the thickness of the accumulated layer on the surface is much smaller than that of the bulk substrate, we considered $\sigma_{\text{bulk}}$ as the conductance at $V_G = 0 \text{ V}$.

A large contribution from the bulk substrate exists in the conductance over the whole range of gate voltages. However, only a slight decrease can be seen in the thermopower of the accumulated surface. These behaviors are due to the relatively large conductivity in the bulk substrate and the low on-off ratio.

By using the same Cu$_2$O sample that was used in the measurement of the EDLT configuration, simultaneous control of the thermoelectric properties has been attempted with the EDLC configuration. $V_G$ was applied between the positive Cu$_2$O electrodes and the negative ZnO electrodes in order to accumulate holes on the surface of Cu$_2$O and electrons on the surface of ZnO. First of all, the thermoelectric properties of each material were measured separately; that is, the drain current ($I_D$) or the electromotive force were monitored between the source and drain contacts for each material for changing $V_G$. Figure 3 shows $I_D$ and $S$ of the p-type Cu$_2$O surface and n-type ZnO surface at 300 K. Both materials showed typical FET behavior, which indicates that we have successfully controlled the carrier concentrations of the p- and n-type materials simultaneously. The on-off ratio of the p-type channel was 3.8, which was in good agreement with Fig. 3(a). In contrast, the on-off ratio of the n-type channel was approximately 20, which was slightly smaller than that reported in Ref. 16. Since the bulk thermopower and resistance were smaller than the reported values, the carrier concentration of the sample used here may be slightly larger than that used in the previous report. The on-off ratio tends to decrease with decreasing resistivity because the off-state current is determined by the bulk resistivity. Thus, the on-off ratio of the device is likely to differ from sample to sample. Considering these results, the accumulated carriers on the surfaces of the p- and n-type materials are almost the same as those of the EDLT configuration. As a consequence, the controllability of the carrier concentration is considered to be comparable to conventional EDLTs.

The gate voltage was removed after cooling the device to 250 K, where PEG was perfectly frozen, and the accumulated carriers could not move. Then, the p- and n-type materials
were connected to measure the thermoelectric properties of the whole device. The thermopower and resistance of the whole device \( S_{\text{dev}} \) and \( R_{\text{dev}} \), respectively, at 250 K are shown in Fig. 4. \( S_{\text{dev}} \) and \( R_{\text{dev}} \) obviously decreased by applying \( V_G \). These results indicate that the carriers remain accumulated after cooling the device, although the p- and n-type electrodes were connected. In the case of the thermoelectric device, \( S_{\text{dev}} \) and \( R_{\text{dev}} \) should be the sum of the p- and n-type materials, \( S_{\text{dev}} = S_p + S_n \) and \( R_{\text{dev}} = R_p + R_n \), where \( S_p, S_n, R_p, R_n \) are the thermopowers and resistances of the p- and n-type materials. The calculated \( S_p + S_n \) and \( R_p + R_n \) are also plotted in Fig. 4. As shown in Fig. 4, \( S_{\text{dev}} \) and \( R_{\text{dev}} \) were almost the sum of each material. The increase in \( S_{\text{dev}} \) and \( R_{\text{dev}} \) is considered to be due to the temperature dependencies of each material, which increase with decreasing temperature.

The output power of the device was estimated from \( P = S_{\text{dev}}^2 / R_{\text{dev}} \). The output power increased by applying \( V_G \), where \( P \) at \( V_G = 4 \text{ V} \) was more than 10 times larger than that at \( V_G = 0 \text{ V} \). This indicates that the carrier concentration of the device can be optimized by the electric double-layer gating.

In conclusion, we have successfully controlled the thermoelectric properties of p- and n-type materials simultaneously by electric double-layer gating for the first time. In this study, the EDLC configuration has been applied to a thermoelectric device, and the output power of the device has been increased to more than 10 times that when \( V_G = 4 \text{ V} \) was applied. Moreover, we confirmed that the controllability of the carrier concentration was comparable to that of conventional EDLTs. Since the basic structure of our device is the same as an EDLC, which has already been applied for practical uses such as a rechargeable battery, it has the potential for practical application.

On the other hand, it was found that the Cu2O single crystal shows the typical FET behavior with an on–off ratio of about 4. Since few materials have been reported as a p-type material that shows the typical FET behavior by electric double-layer gating, further investigation of p-type materials will be required to make a high-performance thermoelectric device.

\[ R_{\text{dev}} (250K) \]
\[ S_{\text{dev}} (250K) \]

**Fig. 4.** \( V_G \) dependence of the whole device at 250 K: (a) resistance and (b) thermopower. Red lines show the thermopower and resistance of the whole device. Blue lines show the sum of the p- and n-type materials.

1) G. D. Mahan, Solid State Phys. 51, 81 (1997).
2) M. Ohtaki, T. Tsutaka, K. Eguchi, and H. Arai, J. Appl. Phys. 79, 1816 (1996).
3) L. D. Zhao, D. Berardian, Y. I. Pei, C. Byl, L. Pinsard-Gaudart, and N. Dragoec, Appl. Phys. Lett. 97, 092118 (2010).
4) I. H. Inoue, Semicond. Sci. Technol. 20, S112 (2005).
5) C. H. Ahn, J. M. Triscone, and J. Mannhart, Nature 424, 1015 (2003).
6) R. E. Glover, III and M. D. Sherrill, Phys. Rev. Lett. 5, 248 (1960).
7) H. Ohta, J. Mater. Sci. 48, 2797 (2013).
8) H. Ohta, Y. Sato, T. Kato, S. W. Kim, R. Nomura, Y. Ikahara, and H. Hosono, Nat. Commun. 1, 118 (2010).
9) H. Shimotani, H. Asanuma, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Appl. Phys. Lett. 91, 082106 (2007).
10) H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Adv. Funct. Mater. 19, 1046 (2009).
11) K. Ueno, S. Nakamura, H. Shimotani, A. Ohtomo, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nat. Mater. 7, 855 (2008).
12) J. T. Ye, S. Inoue, K. Kobayashi, Y. Kasahara, H. T. Yuan, H. Shimotani, and Y. Iwasa, Nat. Mater. 9, 125 (2010).
13) K. Ueno, S. Nakamura, H. Shimotani, H. T. Yuan, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nanotechnol. 46, 408 (2011).
14) K. Taniguchi, A. Matsumoto, H. Shimotani, and H. Takagi, Appl. Phys. Lett. 101, 042603 (2012).
15) Y. J. Zhang, J. T. Ye, Y. Yomogida, T. Takenobu, and Y. Iwasa, Nano Lett. 13, 3023 (2013).
16) R. Takayanagi, T. Fujii, and A. Asamitsu, Jpn. J. Appl. Phys. 53, 111101 (2014).
17) H. Shimotani, H. Suzuki, K. Ueno, M. Kawasaki, and Y. Iwasa, Appl. Phys. Lett. 92, 242107 (2008).
18) Y. Zhang, J. T. Ye, Y. Matsuhashi, and Y. Iwasa, Nano Lett. 12, 1136 (2012).
19) H. T. Yuan, M. S. Bahraray, K. Morimoto, S. F. Wu, K. Nomura, B. J. Yang, H. Shimotani, R. Suzuki, M. Toh, C. Koc, X. D. Xiu, R. Arita, N. Nagasoa, and Y. Iwasa, Nat. Phys. 9, 563 (2013).
20) H. T. Yuan, H. W. Liu, H. Shimotani, H. Guo, M. W. Chen, Q. K. Xue, and Y. Iwasa, Nano Lett. 11, 2601 (2011).
21) S. J. Pearton, C. R. Abernathy, M. E. Overberg, G. T. Thaler, D. P. Norton, N. Theodoropoulou, A. F. Hebard, Y. D. Park, F. Ren, J. Kim, and L. A. Boatner, J. Appl. Phys. 93, 1 (2003).
22) T. Ito, H. Yamaguchi, K. Okabe, and T. Masumi, J. Mater. Sci. 33, 3555 (1998).
23) R. Kötz and M. Carlen, Electrochim. Acta 45, 2483 (2000).