Control of thermoelectric properties of ZnO using electric double-layer transistor structure

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We have successfully controlled the thermoelectric properties of ZnO by changing the carrier concentration using an electric double-layer transistor (EDLT), which is a field-effect transistor gated by electrolyte solution. The resistivity and thermopower decreased abruptly by applying a gate voltage \( V_G \) larger than a threshold voltage \( \sim 2 \text{ V} \), indicating an increase in carrier concentration on the ZnO surface. The temperature dependence of the resistivity became metallic, which is characterized by the weak temperature dependence of the resistivity, when the gate voltage exceeded \( 2 \text{ V} \). Corresponding to the resistivity, the temperature dependence of the thermopower changed markedly. The thickness of the induced metallic layer was estimated to be about \( 10 \text{ nm} \) and the power factor at \( 2 \text{ V} \) was calculated to \( \sim 8 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2} \), which is six or seven orders of magnitude larger than that of the bulk ZnO \( (V_G = 0 \text{ V}) \). Thus, the EDLT is considered to be a useful way to optimize thermoelectric properties by tuning the carrier concentration. \( \text{© 2014 The Japan Society of Applied Physics} \)

1. Introduction

Thermoelectric materials are of increasing interest for applications such as power generators and heat pumps. Thermoelectric efficiency is characterized by the figure of merit \( Z = S^2/\rho \kappa \), where \( S, \rho, \) and \( \kappa \) are the thermopower, resistivity, and thermal conductivity, respectively. The key to realizing an efficient thermoelectric device lies in finding materials with a large power factor \( S^2/\rho \) and low thermal conductivity \( \kappa \). It is, however, difficult to control these physical quantities independently since \( S, \rho, \) and \( \kappa \) are functions of the carrier concentration. According to thermoelectric transport theories, \( ZT \) at the optimum carrier concentration is a function of the parameter \( m^*\mu/k_1 \), where \( \mu \) is the carrier mobility, \( m^* \) is the effective mass, and \( k_1 \) is the lattice thermal conductivity. Thus, a large \( m^* \) (which increases \( S \)), large \( \mu \) (which decreases \( \rho \)), and small \( k_1 \) are required to improve \( ZT \).

On the other hand, low dimensional systems such as thin-film superlattices are known as another way to improve thermoelectric properties. A theoretical prediction indicates that the enhancement of \( Z \) arises from an increase in the density of states near the edge of the conduction band when electrons are confined in a quantum-well structure.\textsuperscript{13} Such an enhancement of \( Z \) has been confirmed experimentally in a PbTe/Pb\textsubscript{0.927}Eu\textsubscript{0.073}Te superlattice.\textsuperscript{21} In the case of transition-metal oxides, the improvement of thermoelectric properties have been reported in a SrTiO\textsubscript{3}/SrTi\textsubscript{0.3}Nb\textsubscript{0.7}O\textsubscript{3} superlattice\textsuperscript{3} and in a water-electrolyte-gated field-effect transistor (FET) of SrTiO\textsubscript{3}.\textsuperscript{30} Recently, it was found that a two-dimensional electron gas (2DEG) in a MgZnO/ZnO heterointerface, where the mismatch in the spontaneous polarization of the two piezoelectric compounds is compensated by the charge accumulation at the interface, shows a very large mobility of over \( 300,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \).\textsuperscript{5,6} Therefore, the 2DEG on ZnO is considered to be promising for thermoelectric applications. Moreover, bulk ZnO is an n-type thermoelectric material with a large power factor of \( \sim 2 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2} \), and there have already been a number of studies on optimizing its thermoelectric properties by chemical doping.\textsuperscript{7–9} Here, we controlled the carrier concentration by using an electric double-layer transistor (EDLT) on a ZnO surface and measured its thermoelectric properties. An EDLT is a FET whose insulating layer is replaced with a polymer electrolyte or ionic liquid. When a gate voltage \( (V_G) \) is applied between the gate electrode and the sample, ions in the liquid are aligned along the surface of the sample, forming a charged double layer that act as a nanoscale capacitor. This technique has the advantage of accumulating carriers up to a density of \( \sim 10^{13} \text{ cm}^{-2} \) on the interface of the sample, which is one or two orders of magnitude larger than that in conventional FETs. The capability of accumulating a large number of carriers has given rise to new findings such as a metal–insulator phase transition (MIT) in ZnO\textsuperscript{10,11} and electric-field-induced superconductivity in SrTiO\textsubscript{3}\textsuperscript{12} and ZnCl\textsubscript{2}\textsuperscript{13} KTaO\textsubscript{3}\textsuperscript{14} and MoS\textsubscript{2}\textsuperscript{15} In this paper, we report the first achievement of controlling the thermoelectric properties of ZnO by using an EDLT.

2. Experiment

ZnO polycrystalline samples were synthesized by a conventional solid-state reaction. A commercial ZnO powder (4N) was pressed into a pellet and sintered at 1000 \( ^\circ \text{C} \) for 15 h in air. The sintered sample was cut into a rectangular shape (about \( 3 \times 1 \times 0.3 \text{ mm}^3 \)) and polished with an abrasive of 1 \( \mu \text{m} \) aluminum oxide (3M Lapping Film) to make the surface flat. A commercial single crystal was also used for an EDLT in order to determine the effects of the surface condition on the EDLT operation. Schematic pictures of the EDLT are shown in Fig. 1. The source and drain electrodes were made of Au paste and covered with silicon adhesive sealant to avoid a chemical reaction between the electrolyte and Au electrodes. The gate electrode was made of Pt foil in order to avoid chemical reactions. As seen in Figs. 1(a) and 1(b), the resistivity and thermopower were measured simultaneously with the same configuration. When a positive \( V_G \) was applied between the gate and source electrodes, cations in the electrolyte were aligned along the ZnO surface and a negative image charge was induced on the surface of the ZnO sample. We chose the electrolyte of KClO\textsubscript{4}, which was solvated by poly(ethylene glycol) (PEG), \((\text{K}^+ : \text{ClO}_4^-) \) in PEG \( = 1 : 20 \). The melting point of PEG (molecular weight \( 1,000 \)) is 310 \( ^\circ \text{C} \), and the ions \((\text{K}^+ \text{ and ClO}_4^-) \) in gelatinous PEG can move above 260 \( ^\circ \text{C} \). In this measurement, \( V_G \) was always changed at 300 \( ^\circ \text{K} \) since an electrochemical reaction occurs between the ZnO surface and the electrolyte at a high temperature. As shown in Fig. 1(a), the resistivity \( \rho \) was measured by a two-probe method, where the drain current...
was monitored while applying a drain voltage ($V_D$) of 0.1 V. Figure 1(b) shows the setup for the measurement of thermopower. A temperature gradient was applied using a heater attached near the source electrode (the hot side of the sample) and the temperature difference $\Delta T$ was monitored by using a copper-constantan differential thermocouple. Since the leakage current between the Pt gate and the sample induces a voltage drop $V_G$ ($R_G = I_D/V_D$), an offset voltage $V_0$ was added into the measured $V_T$. However, when $V_0$ was carefully subtracted from $V_T$, the actual thermal electromotive force ($V_0$) was proportional to $V_G$. At temperatures below 260 K, the leakage current was significantly small because the PEG was completely frozen. In this temperature range, no offset voltage was observed and the measured $V_T$ was a perfectly linear function of $V_G$. Hence we can accurately determine the value of $S$ from the slope of the thermal electromotive force. Here, $S$ between the source and drain electrodes was measured at two different $T$ of approximately 1 and 2 K, and the thermopower was determined by $S = (\Delta V_2 - \Delta V_1)/ (\Delta T_2 - \Delta T_1)$. To measure the Hall coefficient, Hall electrodes were attached perpendicular to the drain current direction. The Hall voltage ($V_H$) was measured by the constant current method ($I_D = 1 \mu A$) while sweeping the magnetic field between $\pm 5$ T. All measurements were carried out under an atmosphere of helium gas so as to prevent the electrolyte from absorbing water, which induces the leakage current ($I_G$) between the Pt gate and the sample. We have confirmed that the thermal conductivity of PEG was about two orders of magnitude lower than that of polycrystalline ZnO. Thus, it is considered that the EDLT device structure hardly affects the thermal properties of the sample.

3. Results and discussion

Figure 2(a) shows the temperature dependence of the resistivity for polycrystalline ZnO annealed in various atmospheres and single crystal. (b) Transfer curve (drain current $I_D$ versus gate voltage $V_G$) of polycrystalline samples and single crystal.
and a temperature of 300 K. The measurement of \( I_D \) was carried out while changing \( V_G \) from 0 to 4 V, and back to 0 V. The sweep rate was as slow as 0.05 V/min, which prevents hysteresis caused by the slow response of the electrolyte to the applied electric field. It has been confirmed that \( I_D \) reproduces the initial values after gate sweeping. Therefore, the carriers were induced reversibly and no electrochemical reactions occurred on the surface of the sample. \( I_D \) increased abruptly upon applying \( V_G \) larger than a threshold voltage (about 2 V) and leveled off above \( V_G = 3 \) V. Thus, these EDLT devices exhibited typical transistor behavior although the surface of the polycrystalline ZnO was not atomically flat. We could not evaluate the surface condition because a scanning electron microscope or atomic force microscope was not available in our laboratory. The roughness of the surface of the polycrystalline samples is thought to be more than 1 \( \mu \)m. It is considered that an atomically flat surface is required for the EDLT operation because the ions in the liquid form a nanoscale capacitor on the surface. However, as seen in the figure, the EDLT operation is not sensitive to the surface and was observed in both the single crystal and the polycrystalline samples. Rather, the on–off ratio of the device in each polycrystalline sample was larger than that of the device in the single crystal. Since the off-state current is determined by the range of bulk resistivity, the polycrystalline sample annealed in oxygen showed the largest on–off ratio. Hereafter, we discuss the polycrystalline sample annealed in air since it shows not only a large on–off ratio but also large conductivity in the on state.

The gate voltage dependences of \( I_D, I_G, \) and \( S \) at room temperature are shown in Fig. 3. As seen in Fig. 3(b), the leakage current of this device was quite low and was comparable in magnitude to that reported in ZnO single crystals.\(^{10}\) In Fig. 3(c), a sharp decrease in \( S \) was observed at the same threshold, implying that the surface of ZnO becomes metallic upon carrier doping. In the FET configuration, the metallic surface and insulating bulk substrate are considered to form a parallel circuit. Therefore, the observed total sheet conductivity \( (\sigma_{\text{total}}) \) and thermopower \( (S_{\text{total}}) \) are given by

\[
\sigma_{\text{total}} = \sigma_{\text{sur}} + \sigma_{\text{bulk}},
\]

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

where \( \sigma_{\text{sur}} \) and \( S_{\text{sur}} \) are the thermopower and sheet conductivity of the metallic surface, and \( \sigma_{\text{bulk}} \) and \( S_{\text{bulk}} \) are those of the insulating bulk substrate, respectively. As discussed later, since the thickness of the surface metallic layer is five orders of magnitude smaller than that of the bulk substrate, we considered \( \sigma_{\text{bulk}} \) as the conductivity at \( V_G = 0 \) V. Figure 4(a) shows \( \sigma_{\text{total}} \) and \( S_{\text{total}} \) as a function of \( V_G \). Using \( \sigma_{\text{sur}} \) and \( S_{\text{sur}} \) (the thermopower at \( V_G = 0 \) V), \( \sigma_{\text{sur}} \) was calculated and is shown in Fig. 4(b). As seen in Fig. 4, \( \sigma_{\text{total}} \) and \( S_{\text{total}} \) are dominated by those of the metallic surface at large \( V_G \). Thus, these results prove that we can measure the transport properties of the metallic surface layer above \( V_G = 2 \) V.

In the case of a SrTiO\(_3\)/SrTi\(_{0.58}\)Nb\(_{0.42}\)O\(_3\) superlattice, a marked increase in \( S \) at room temperature \( (S_{\text{room}}) \) is observed when the thickness of the SrTi\(_{0.58}\)Nb\(_{0.42}\)O\(_3\) layer becomes less than 1.56 nm (corresponding to a four-unit-cell layer thickness).\(^{3}\) The \( S_{\text{room}} \) value for the one-unit-cell layer thickness of the SrTi\(_{0.58}\)Nb\(_{0.42}\)O\(_3\) reached 480 \( \mu \)V/K, which is 4.4 times larger than that of the three-dimensional bulk SrTi\(_{0.58}\)Nb\(_{0.42}\)O\(_3\). On the other hand, in the case of the EDLT of SrTiO\(_3\),\(^{12}\) it is reported that an increase in \( V_G \) reduces the thickness of the accumulation layer on SrTiO\(_3\) because an increase in \( V_G \) reduces the dielectric constant of SrTiO\(_3\) owing to its incipient ferroelectricity. Therefore, a marked increase in \( S \) is expected when \( V_G \) is increased to shrink the accumulation layer. However, as seen in Fig. 3(c), the enhancement of \( S \)

![Fig. 3. (Color online) Gate voltage \( (V_G) \) dependence of \( I_D, I_G, \) and \( S \) at room temperature.](image-url)

![Fig. 4. (Color online) \( \sigma_{\text{total}} \) and \( S_{\text{total}} \) plotted as a function of \( V_G \). Here, we considered \( \sigma_{\text{bulk}} \) as the conductivity at \( V_G = 0 \) V. (b) \( S_{\text{total}} \) and \( S_{\text{sur}} \) versus \( V_G \). \( S_{\text{sur}} \) was calculated by using \( \sigma_{\text{sur}} \) and \( \sigma_{\text{bulk}} \) (thermopower at \( V_G = 0 \) V).](image-url)
was not observed at large $V_G$, but the thermopower and resistivity decrease simultaneously similarly to the behavior induced by the conventional doping effect.

To investigate whether the thermoelectric properties of the accumulation layer are two-dimensional or not, the Jonker plot, in which $S$ is plotted with respect to the sheet conductivity ($\sigma_s$), is shown in Fig. 5. The relation between $S$ and $\sigma$ is theoretically given\(^{3,16}\) by

$$S = -a \log \sigma + b.$$  

When the system has a 3D energy band with a parabolic density of states near the Fermi surface, the parameter $a$, which is the slope of the $S$–log $\sigma$ line, is given by

$$a = \frac{k}{e} \ln 10 = 198 \mu V/K.$$  

As seen in Fig. 5, the value of $S$ decreases with increasing $\sigma_s$, and the slope of $S$ is in good agreement with the theoretical prediction for the 3D system ($-198 \mu V/K$), which is shown by the triangle as guide to the eye in Fig. 5. These results indicate that the thickness of the surface metallic layer is not as thin as STO superlattice, as discussed later.

Figure 6(a) shows the temperature dependence of the sheet resistivity ($\rho_s$) at various $V_G$. $\rho_s$ at low $V_G$ (below 1 V) showed semiconducting behavior, in which the resistivity increased abruptly at low temperature. In contrast, at high $V_G$ (above 2 V), the temperature dependence of $\rho_s$ was weak and the absolute value of $\rho_s$ was significantly small, particularly at low temperatures, indicating that a large number of electrons accumulated on the surface and that a metallic state was realized. The temperature dependence of $S$ at various $V_G$ is shown in Fig. 6(b). Corresponding to the resistivity, the temperature dependence of $S$ changed markedly. Below the threshold voltage, the resistivity was too high to measure the thermopower at low temperatures. At high $V_G$, the absolute value of $S$ decreased with decreasing temperature and was nearly constant below 200 K. These behaviors of $S$ are considered to be due to the metallic state of the surface.

In order to estimate the carrier concentration ($n$), Hall effect measurement was carried out. Here, we used a different sample from that used for the measurement of resistivity and thermopower. Although the thickness of the surface metallic layer ($d$), and hence $n$, cannot be directly obtained, we can roughly estimate $d$ by using the sheet carrier concentration $n_s$ (evaluated from the Hall coefficient) and the critical carrier concentration ($n_c$) at the metal–insulator transition (MIT) in ZnO. In general, a metallic state emerges when the mean distance between donors $r$, which is deduced from the donor density (carrier concentration) $n = 4/(\pi D^2)$, becomes much smaller than the effective Bohr radius ($a_B$), which is 1.7 nm for ZnO. Therefore, $n_c$ is calculated as $n_c = 3/4\pi a_B^2 \approx 4.9 \times 10^{19}$ cm$^{-3}$.\(^{17}\) Figure 6(c) shows $n_s$ obtained by Hall effect measurement. The temperature dependence of resistivity showed metallic behavior when $n_s$ exceeded $5 \times 10^{13}$ cm$^{-2}$ [shown as a dotted line in Fig. 4(c)]. At the critical point of the MIT, the formula $n_c = n_s/d = 5 \times 10^{13}/d$ should be applicable. Thus, $d$ was estimated to be approximately 10 nm. The quantum confinement of electrons is thought to occur when $d$ becomes less than the thermal de Broglie wavelength, which is generally expressed by $\lambda_D = h/(2\pi m^* k_B T)$, where $h$ and $k_B$ are Planck’s constant and the Boltzmann constant, respectively. By using the $m^*$ value of 0.3$m_0$ in ZnO, $\lambda_D$ is estimated to be $\approx$8 nm. The reason why the enhancement of $S$ was not observed in this system is probably because the thickness of the 2DEG in our system ($\approx$10 nm) is slightly larger than that at which quantum confinement of electrons starts to occur ($\approx$8 nm).

![Figure 5](image5.png)

**Fig. 5.** (Color online) Absolute value of $S$ as a function of sheet conductivity (Jonker plot).

![Figure 6](image6.png)

**Fig. 6.** (Color online) Temperature dependence of (a) sheet resistivity, (b) thermopower, and (c) sheet carrier concentration at various $V_G$. 111101-4 © 2014 The Japan Society of Applied Physics
Using the obtained $d$, the power factor of this EDLT device with the application of $V_G = 4 \text{ V}$ is estimated to be $8 \times 10^{-5}$ W m$^{-1}$ K$^{-2}$ at 300 K. This value is six or seven orders of magnitude larger than that of the bulk state ($V_G = 0 \text{ V}$). Although the power factor is not as large as that reported for ZnO ceramics under the optimum doping condition ($\sim 2 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$), the EDLT is considered to be a useful way to optimize thermoelectric properties by tuning the carrier concentration.

4. Conclusions

We have successfully controlled the thermoelectric properties of ZnO by using an EDLT configuration. The resistivity and thermopower decreased markedly upon applying a gate voltage larger than a threshold voltage, indicating the increase in carrier concentration at the surface. We have confirmed the reproducibility of the gate–voltage dependence of the resistivity and thermopower. This suggests that the carriers are induced reversibly and that no electrochemical reactions occurred on the surface. Contrary to one’s expectation, these observations appeared both in single-crystal and powder samples, implying that the EDLT function is not robust to the surface condition although the carriers are induced in the vicinity of the surface. Three-dimensional behavior was observed in the Jonker plot (slope of the $S$–log$\sigma$ plot), which is consistent with the result that the estimated thickness of the metallic surface layer ($\sim 10 \text{ nm}$) was too large compared with the thermal de Broglie wavelength in ZnO ($\sim 8 \text{ nm}$). The power factor was estimated as $8 \times 10^{-5}$ W m$^{-1}$ K$^{-2}$ at 300 K, which is six or seven orders of magnitude larger than that of the bulk ZnO ($V_G = 0 \text{ V}$). Thus, we consider that the thermoelectric properties are improved by controlling the carrier concentration by using the EDLT configuration in ZnO.