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Insulator-to-metal transition in ZnO by electric double layer gating

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The authors report high-density carrier accumulation and a gate-induced insulator-to-metal transition in ZnO single-crystalline thin-film field effect transistors by adopting electric double layers as gate dielectrics. Hall effect measurements showed that a sheet carrier density of 4.2×10^{13} cm^{-2} was achieved. The highest sheet conductance at room temperature was ~1 mS, which was sufficient to maintain the metallic state down to 10 K. These results strongly suggest the versatility of electric double layer gating for various materials. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2772781]

Material interfaces are intriguing playgrounds for controlling their properties and functions. An electric double layer (EDL) formed on a solid/electrolyte interface by applying a voltage provides large electric field.[1] An EDL can be regarded as a nanogap capacitor,[2] and consequently has a huge capacitance. For this large capacitance, EDLs have recently been used as alternative metal-insulator-semiconductor (MIS) structures in field effect transistors (FETs). Such FETs denoted EDLFETs hereafter, have been studied from the viewpoint of sensor applications using aqueous electrolytes,[3] e.g., ion-sensitive FETs.[4] It is believed that EDLFETs can accumulate charges in high density than FETs using SiO_2 and Al_2O_3 gate dielectrics. Motivated by this idea, various EDLFETs have been realized, including conducting polymers,[5,6] carbon nanotubes,[7–9] organic thin films,[10,11] organic single crystals,[12–15] and inorganic semiconductors.[16–18] However, sheet carrier densities (n) in nonaqueous EDLFETs have only been indirectly estimated. Direct measurement of n is thus crucial for further development of EDLFETs. The most reliable determination of n is the Hall effect measurement. The accurate Hall effect measurement requires high mobility to obtain sufficiently large Hall voltage, because only small source-drain voltage V_{DS} can be applied to EDLFET. High mobility is also favorable for inducing insulator-to-metal (I-M) transition by the gate voltage (V_G), because higher conductivity is required for this phenomenon. Therefore, we adopted ZnO, a n-type semiconductor with high mobility.

Although the electron mobility can be as high as 230 cm^2/V s in bulk crystals[19] and 440 cm^2/V s in lightly doped n-type single-crystalline films,[20] the field effect mobilities (μ_{FE}) in polycrystalline FETs have been limited to the order of 10 cm^2/V s.[21] Single-crystalline FETs have shown $\mu_{FE} \sim 70$ cm^2/V s, but it is difficult to make excellent gate structures keeping high mobility.[22] Indeed, a high-mobility two-dimensional electron gas could be accumulated in polarization-mismatched but lattice-matched ZnO/$Mg_xZn_{1-x}O$ interfaces, where the first quantum Hall effect was observed among epitaxial oxide heterostructures.[23] However, tuning of the electron density by an external field has not been demonstrated in this system. Therefore, it is interesting to employ epitaxial ZnO thin films to EDLFETs for the possibility to induce and tune the quantum Hall effect, and to apply to various oxides.

Here, we report EDLFETs with a ZnO single-crystalline thin film showing that $n = 4.2 \times 10^{13}$ cm^{-2} could be accumulated, as determined by the Hall effect measurement. Furthermore, the gate-induced I-M transition was found in ZnO. These results demonstrate that EDLFETs are useful for investigating gate-induced electronic phenomena.

Figure 1 illustrates a schematic diagram of a ZnO EDLFET in a Hall-bar configuration immersed in an electrolyte. Epitaxial ZnO thin films were deposited by pulsed-laser deposition on $ScAlMgO_4$ substrates using a $Mg_{0.15}Zn_{0.85}O$ insulating buffer layer (100 nm). Films of 700 and 25 nm in thickness (1 and 2, respectively) were grown at an intermediate temperature range and had low carrier density, exhibiting insulating temperature dependence of conductivity (details were given in Ref. 20). The films were patterned into a Hall-bar geometry (220×60 μm^2), and Ti/Au electrodes were evaporated on the films.

After wiring the devices, electrodes, Au wires, and Ag paste were passivated with silicone adhesive sealant (TSE397, GE Toshiba Silicones Co., Ltd., Japan). The Hall-bar sample and a Pt coil, used as a counter-(gate) electrode, were installed in a glass container with a diameter of 10 mm, which was filled with electrolyte AClO$_4$/PEO ($M_W = 1000$) [A=Li, K, and Cs, PEO: poly(ethylene oxide)]. The mixing ratios were [O]/[Li]=20/1, [O]/[K]=20/1, and [O]/[Cs] =30/1, where [O]/[A] is the molar ratio of the PEO unit ($-CH_2CH_2O-$) and AClO$_4$.

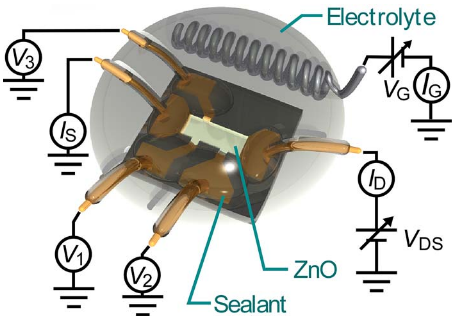

FIG. 1. (Color online) Illustration of the Hall-bar device, which is immersed in electrolyte. A gold pad, Ag paste, and gold wire were covered by adhesive sealant. The gate voltage was applied by a Pt coil (counterelectrode) through the electrolyte.

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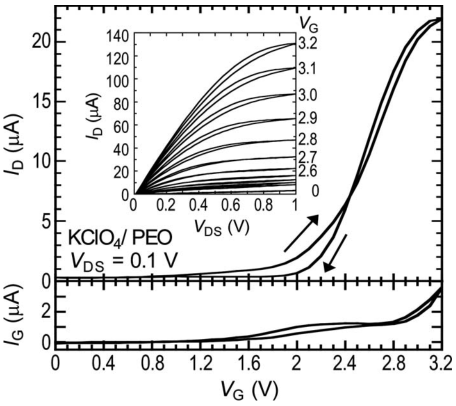

FIG. 2. Top panel shows drain current (I_D) against gate voltage (V_G) for ZnO film 2 with KClO$_4$/PEO electrolyte at 300 K. The arrows indicate the scan direction. The leakage current (I_G) is also shown against V_G at the bottom. Data were taken at the source-drain voltage V_{DS}=0.1 V. The inset shows the relation between I_D and V_{DS} at various V_G for ZnO film 2.

When the positive V_G was applied to the Pt counterelectrode, the electric field moved anions and cations in the electrolyte to the counterelectrode and ZnO single-crystalline film, respectively. Finally, an EDL consisting cations and electrons accumulated on the surface of the ZnO was formed. The carrier density on the surface of the ZnO was thus changed by V_G. The change of the carrier density and consequent modulation of the resistance of ZnO were determined by Hall effect and four-probe measurements applying V_{DS} to the ZnO (see Fig. 1).

The measurements were carried out in a physical property measurement system (Quantum Design) with an Agilent Technology E5270 semiconductor parameter analyzer. The Hall effect measurements were performed under a He atmosphere at 300 K. The Hall voltage $V_H \equiv V_3 - V_1$ (see Fig. 1) was detected by sweeping a magnetic field (B) between 9 and −9 T, and n was calculated from $n = BI_D/eV_H$, where I_D is the drain current and e is the elementary charge. The temperature dependence of the sheet resistance (R) was measured under a He atmosphere, while decreasing the temperature at 1 K/min. V_{DS} was fixed at 0.1 V for measurement of the transfer curves (I_D vs V_G), Hall effect voltages, and temperature dependence of R.

The device characteristics at 300 K are shown in Fig. 2 for a ZnO EDLFET using KClO$_4$/PEO electrolyte. Figure 2 displays a typical transfer curve showing a small hysteresis, indicating negligible deterioration of the ZnO, because I_D of backward scan would have significantly decreased from that of forward scan if the single-crystalline film had deteriorated. The gate leakage current (I_G) shown in the bottom panel of Fig. 2 was small compared to I_D within the V_G region in the present study. The output characteristics (Fig. 2 inset) showed typical saturation behavior, indicating that the device operation was equivalent to that in a normal MISFET.

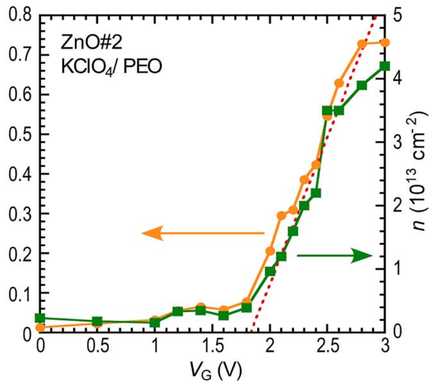

FIG. 3. (Color online) Gate voltage (V_G) dependence of sheet conductance (G, spheres) from the four-terminal experiment and sheet carrier density (n, squares) derived from the Hall voltage, for KClO$_4$/POE electrolyte. The dashed line shows a fit to the n-V_G plot between 2 and 2.5 V, from which we evaluated the capacitance of the EDL.

In the present experiment, we tested two batches of ZnO films (1 and 2, tabulated in Table I) and three kinds of electrolytes, AClO$_4$/PEO (A=Li, K, and Cs). Both ZnO films, irrespective of their film thickness and the initial carrier density, displayed fairly reproducible transfer characteristics, and G reached almost 1 mS. The effects of the difference of the electrolyte on the transistor characteristics were minimal, while the ZnO films of different batches showed differences in transfer curves, involving G in the off-state and the threshold voltages. Immersing the ZnO films in the electrolyte caused a dramatic reduction in G (Table I). G of ZnO 1 and 2 decreased from 8.6 to ~0.01 μS and from 40 to ~10 μS, respectively, simply by placing the films in the electrolyte. The decreases in G are possibly related to the charge transfer between ZnO and the electrolyte.

G and n derived from Hall effect measurements at 300 K on ZnO film 2 are plotted against V_G in Fig. 3 for the KClO$_4$ device. The increase in G by application of V_G shows excellent agreement with the increase in n. The maximum n measured was 4.2×10^{13} cm^{-2}, substantially larger than those achieved with ordinary gate insulators. We note that the initial carrier density was negligible and the high carrier density was purely accumulated by the EDLFET.

The direct determination of n by Hall effect measurements gives the most reliable estimation of the EDL capacitance with a nanoscale thickness. Conventional capacitance measurements using impedance analyzers provided a value of 15 μF/cm^2,[14] but some ambiguity still remains due to additional contributions to the measurement, such as leakage current. The n increases almost linearly above a certain threshold voltage, as shown in the dotted line in Fig. 3. The gate capacitances derived from the slopes of the dotted lines were 7.4 and 7.7 μF/cm^2 for the KClO$_4$/PEO and CsClO$_4$/PEO electrolytes, respectively. These capacitance values tell us details of the EDL in the devices.

TABLE I. Properties of ZnO single-crystalline thin films used in the present study.

Sample	Thickness (nm)	Carrier density n		Hall mobility μ_H (cm^2/V s)	Conductance	
		Sheet (cm^{-2})	Net (cm^{-3})		Sheet (μS)	Net (S/cm)
1	700	5.4×10^{11}	7.7×10^{15}	100	8.6	0.12
2	25	3.0×10^{12}	1.2×10^{18}	90	40	17

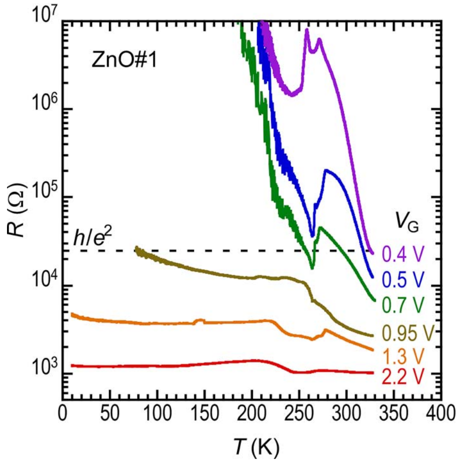

FIG. 4. (Color online) Temperature dependence of the four-terminal sheet resistance (R) at various gate voltages (V_G) for EDLFET of ZnO 1 with $KClO_4$/PEO electrolyte. Data for only cooling scans are displayed for simplicity. Despite large undulations at 220–280 K, which are ascribed to the effect of glass transitions of the PEO used, a gate-induced insulator-to-metal transition was clearly observed.

An EDL consists of three layers, called inner Helmholtz plane (IHP), outer Helmholtz plane (OHP), and diffusion layer. An IHP consists of ions specifically adsorbed on the surface. This contribution was ignored, because the specific adsorbabilities of the cations in the anodic region should be relatively small.[2] An OHP consists of solvated ions whose solvating molecules contact the surface. The capacitor gap of the OHP is, therefore, the diameter of the solvated ions, and is independent of the concentration of ions. On the other hand, the thickness of the diffusion layer decreases as the concentration of ions increases. In the high concentration limit of the present experiment, the contribution of the diffusion layer is also negligible. Hence, the gate capacitance was approximately equal to the capacitance of the OHP in the present experiment. From the capacitance values, the thickness of the EDL can be estimated using a parallel plate capacitor model. Taking into account the relative dielectric constants of the PEO (10) (Ref. 24) and the ZnO (8.5),[25] we can determine the thickness of the EDL capacitor as 0.95–1.2 nm. This value is quite reasonable in terms of the classical treatment of the OHP.

The temperature dependence of R for the ZnO film 1 is plotted in Fig. 4 at various V_G. R at low V_G increased as the temperature was lowered, whereas those at large V_G were almost temperature independent, providing firm evidence that a metallic state was realized by EDL gating. The undulation of the curves between 220 and 280 K in Fig. 4 is attributed to glass transitions of the electrolyte. Nonetheless, it should be emphasized that the observation of gate-induced I-M transition at low temperature in ZnO FETs demonstrates the effectiveness of high-density charge accumulation in the EDLFET structure. It is also interesting to note that the low-temperature metallic state was observed only below the quantum resistance $h/e^2 \sim 25.8$ kΩ, in fair agreement with the expected behavior of the EDLFET device structure, where accumulated charges form a two-dimensional system. The gate-induced I-M transition in oxides has recently been gathering a lot of interest.[18,26] Our EDLFET technique should be extremely useful for this branch of materials research.

In conclusion, n of ZnO single-crystalline thin films were controlled over a wide range by EDLFETs. The maximum in n derived from Hall effect measurements was 4.2×10^{13} cm^{-2}, which is several times larger than that achievable by conventional MISFETs. Furthermore, the Hall effect measurements provide a direct method to estimate the EDL capacitance at semiconductor/electrolyte interfaces. Due to the high-density carrier accumulation, we could observe a gate-induced I-M transition with temperature dependence of resistivity. This result provides an opportunity of gate tuning of the low-temperature properties in oxide semiconductors such as the quantum Hall effect. Also, our results demonstrate that the EDLFET is a very powerful and versatile method to control and investigate electronic properties in a wide variety of semiconductors.

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