ZnO Nanowire Based Photoelectrical Resistive Switches for Flexible Memory

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In this work, a non-volatile resistive optoelectronic memory was demonstrated in a flexible system that plays the dual roles of a reversible photo-reactive element and a signal-collecting element. We attempted to demonstrate the tactile sensor by detecting the rotation angle and bending angle of the wearable information appliance worn by the user. This motion-sensing for certain critical angle and information-storing functionality is enabled by photo-tunable resistive switching behaviors, which result from bending the flexible device in diverse convex angles with respect to the incident light direction. Furthermore, we investigated the basic mechanism of resistive photoelectrical switching behaviors by studying the effects of electrostatic barrier at the Au/ZnO junction, e.g., a Schottky barrier depending on the photonic and electric condition. Moreover, by employing a polymer structure, application in a prototype device provided improved endurance or retention of data.

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Recently, novel approaches are introduced for wearable technologies that communicate with next-generation computing interfaces. Wearable systems that provide continuous measurement of key numerical parameters demonstrate progress in various fields, personal health-monitoring, medical care, sports science, and fashion electronics, etc. 1–3 However, for realization of wearable devices, it is required to develop the ability to store or process information in a memory system having a multifunctional and integrated platform. 4 In this work, a non-volatile resistive optoelectronic memory was demonstrated in a flexible system that plays the dual roles of a reversible photo-reactive element and a signal-collecting element.

In addition, because next generation IT devices can generally operate with diverse functionalities, the introduction of multifunctionality into the existed electronic devices is important in realizing the future IT devices. In this study, we attempt to demonstrate the possible ability to recognize a user gesture by detecting the rotation angle and bending angle of the wearable information appliance worn by the user. This motion-sensing for certain critical angle and information-storing functionality is enabled by photo-tunable resistive switching behaviors, which enable exclusive response only with the appropriate directional motion of the device relative to the fixed light source direction. The output data of the switching ability can also result from bending the flexible device in diverse convex angles with respect to the incident light direction, making it suitable for optical writing under the same lighting conditions, e.g., when the sun is shining.

To realize this motion-controlled memory device, a resistive photo-switching device made of ZnO nanowire was prepared by fabricating electrode contacts on both ends of the ZnO nanowire for which the size of the gap across the opposing electrode to the nanowire is the same lighting conditions, e.g., when the sun is shining.

Experimental

Preparation of electrodes on a polyimide substrate.—The commercially purchased polyimide source was spin–coated onto the flat substrate, i.e., Si wafer or glass. The pre-polymer-deposited substrate was placed onto a hot plate, and the temperature was gradually increased from 50°C to 300°C for 10 hours in air to render the film transparent. The aligned patterns were created by coating the photoresist with a mask. The electrodes were prepared using thermal evaporation of Au/Ti with thicknesses of 40/4 nm. The conventional lift-off method was used to remove the sacrificial photoresist. The polyimide substrate film with Au electrodes was detached from the flat substrate in 70°C DI water.

Fabrication of a zinc-oxide nanowire aligned device.—The ZnO nanowires were prepared according to a method described in the previous chapter. In brief, 0.01 M of Zn(NO₃)₂ × 6H₂O (98%, Aldrich) was dissolved in DI water, and 0.3 M of ammonium hydroxide (29 wt% NH₄ in water, 99.99%, Aldrich) was added. Next, the mixture was reacted for 24 hours at 95°C. Hydrothermally grown ZnO wires were ultrasonic dispersed in ethanol for 1 minute. The dispersed solution was transported onto the polyimide substrate with Au electrodes and dried. The disengaged nanowires have an average diameter of less than 1 μm and a length of 15 μm. The Au wire ultrasonic wedge bonding is applied for the Au electrodes to create a direct contact before this MIM (metal-insulator-metal) structure –Au/ZnO nanowire/Au– is covered with the PDMS (polydimethylsiloxane).

Preparation of the PDMS mold.—PDMS (Sylgard-184, an elastomeric PDMS kit manufactured by Dow Corning) was used. To prepare the PDMS mixture, the elastomer base was mixed with a curing agent at a 10:1 ratio by mass and subsequently stirred. The mixture was poured onto the Si wafer. The pre-polymer-coated Si wafer was placed on a flat area for even spreading and subsequently held in a desiccator for 3 hours to out-diffuse trapped air bubbles. The sample was cured at 70°C for 2 hours. The cured flexible PDMS substrates (0.5 mm thick) were cut to 1 mm × 1 mm for spacers and 2 cm × 8 cm for coverlayers.

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Results and Discussion

Digital images and optical microscope images indicate the device consisting of Au/ZnO nanowires/Au on a polyimide substrate (Figure 1). Several ZnO nanowires are dispersed, and in the enlarged figure of optical microscope image (inset of Figure 1d) shows one of the ZnO nanowire lies across between two Au electrodes with a spacing of 8 μm. A schematic diagram of the device structure and electrical configuration is shown in Figures 1a–1f.

The self-rectifying type of current (I)-voltage (V) behavior is observed in the Au/ZnO/Au nanowire device during voltage sweeps from $-1.5 \text{ V}$ to $1.5 \text{ V}$ (Figure 1g). In this I–V curve, the Au/ZnO junction represents an electrostatic barrier, e.g., a Schottky barrier with alignment of Fermi levels. This junction system exhibits rectification properties with a forward-to-reverse bias ratio (IF/IR) of $\sim 10^3$ at 1.5 V. The diode current $I$ across a Schottky barrier is governed by the general thermionic emission equation in forward bias expressed as

$$ I = I_s \left\{ \exp \left( \frac{eV}{nk_B T} \right) - 1 \right\} $$  \[[1]\]

Where $I_s$ is the reverse saturation current, $e$ is the electric charge, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $n$ is the diode ideality factor.\[14,15\] By fitting the linear region of the semi-log I–V curve into the above equation, the ideality factor is calculated as 2.67. This estimated value, which is higher than the ideal case ($n = 1$), implies that thermionic emission is not the dominant transport mechanism. Other mechanisms such as tunneling, recombination, interfacestate-assisted transport or a rough semiconductor surface are likely present.\[16–18\]

The resistive switching behavior of a single or multiple ZnO nanowire device under dark conditions is shown in Figure 1h. In this paper, the main criteria for bias sweeping direction are originated from the effective diode under dark condition. An unusual I–V curve was observed with deficient hysteresis in the forward bias region, whereas electrical bi-states appear at the reverse bias. This observation can be elucidated by an accumulation and dissipation of (positively charged) oxygen vacancies ($V_{ox}^-$ or $V_{ox}^{++}$). When a negative bias is applied on the Au electrode, the oxygen vacancies in ZnO immediately migrate toward cathode interface through the applied electric field. Because the oxygen vacancies are donors, the Schottky barrier decreases significantly in the oxygen-vacancy accumulated region, i.e., a reduction in the energy barrier occurs at the depletion layer. Thus, the current increases significantly, possibly due to the presence of electron injection and tunneling.\[19\] As a result and as mentioned above, the modified barrier accounts for the notable hysteresis in the negative bias together with two distinguishable resistance states. However, if positive bias is applied on the Au electrode, a slight hysteresis exists due to the increased barrier from the accumulation of oxygen ions. These observed electrical characteristics correspond well to the scenario of migrating oxygen vacancies.

When the previously described Au/ZnO nanowire/Au junction is transferred to a polymer substrate, i.e., polyimide film, a flexible or non-flat photo-detecting memory device can be constructed. By adopting PDMS as a flexible and transparent roof that can control the light direction depending on the incident angle from the light source, bimodal characteristics of resistive switching (RS) can be achieved, i.e., RS with light ON mode and OFF mode.
As a light transmission/reflection guiding polymer, polydimethylsiloxane (PDMS) was selected because of its suitable optical and physical properties (≈1.4 refractive index, over 85% transmittance at a 370-nm wavelength with 5-mm PDMS, 0.44-MPa elastic modulus).\textsuperscript{20–22} An air gap created by PDMS spacers separates the PDMS roof and the bottom ZnO nanowire devices (Figures 2a and 2b). In this structure, a thin film of PDMS was used as the medium of higher refractive index, and the air gap was used as the medium of lower refractive index such that total reflection can be achieved at the interface between the PDMS and air (n = 1) at light incidence angles greater than the critical angle (≈45°). Note that the PDMS-covered optical probe immediately contacts the PDMS roof to prevent light refraction before reaching the roof. The air gap also permits ambient functionalization to the nanowire by keeping it from sticking to PDMS, which has a low gas permeability and air solubility (≈15.4 Vol% of air solubility at STP and 579 Barrer for oxygen gas at 20°C).\textsuperscript{23,24} The highly bendable properties of the Au/ZnO nanowire/Au on the polyimide substrate and the incorporated system with the PDMS roof are shown in Figures 2c and 2d, respectively.

With this conjunction system, the electrical properties were tested with UV irradiation over the PDMS layer. The UV illumination condition was provided by a 500-W Xenon arc lamp (66902 Arc Lamp Housings, Newport, Inc.) with a spectrum that spans the range of 200–2500 nm. A photon with wavelength of ≈370 nm was supplied by the monochromator (77250 Monochromator, Newport, Inc.), and an optical fiber (77564 Fiber Optics, Newport, Inc.) connected via standard couplers. Figure 2e indicates the irradiated UV condition illuminated perpendicularly to the direction of the sample; over 85% of the incident UV reaches the sample after passing through the 5-mm PDMS.

The resistive switching data collected under the illumination condition are presented in Figure 2f, and the gray scaled data are represented by the dark condition, as shown for comparison. Upon illumination, the set voltage (V\textsubscript{set}) decreases from −30 V to −23 V, and in forward bias, a non-rectifying behavior is shown in the purple line of Figure 2f, which is different from the data of the same bias sweeping under dark conditions (light gray line of Figure 2f). From this data, meaningful change would provide a chance to elucidate the underlying mechanism and enable demonstration of novel applications with an aid of photonic stimulus.

Under UV illumination, it is widely known that ZnO promotes the formation of free charge carriers by creating electron–hole pairs (EHP) predominantly through band-to-band transitions adjacent to the surface with photon energies larger than the semiconductor bandgap (E\textsubscript{g}). The photogenerated carriers may migrate to the opposite potential under the built-in electric field.

As a n-type semiconductor with acceptor-type surface states, ZnO has an upward-bent banding type built-in potential (inset of Figure 1g).\textsuperscript{25} This built-in potential drives photogenerated holes toward the interfacial region and photogenerated electrons toward the bulk. This
redistribution of surface charges leads to a reduction of the interfacial band bending, which results in a conductivity increase in the nanowire. In this work, Kelvin probe force microscopy (KPFM) is adopted to measure the change of surface potential upon illumination in a non-contact and nondestructive manner. As shown in Figure 3, the AFM (atomic force microscopy) and KPFM images of a single nanowire on a Pt-coated Si substrate are exhibited at the same point in the dark (Figures 3a–3b) and after illumination (Figures 3e–3f). The scale bars for the respective AFM and KPFM images of the sample before and after UV illumination are similarly displayed for comparison. The darkest area in the KPFM image corresponds to the middle section of the ZnO nanowire. In Figures 3c and 3g, by comparing the measured electrical potential variation along the plot line (yellow dashed line in Figures 3b, 3f), two effects of UV illumination can be observed: (i) an overall increase of 50–150 mV in the average surface potential after illumination of the sample and (ii) greater shift of the surface potential in the Pt region in the vicinity of the interface than in the ZnO center region. The overall increment in surface potential after light illumination indicates the electron accumulation in both the ZnO and Pt regions. The higher contrast of the surface potential after illumination is exhibited for the respective AFM and KPFM images of the sample before and after UV illumination are similarly displayed for comparison. The schematic images and digital images show each bending and rotating state. The measured resistive switching curve is shown in the upper row (Figures 3a and 3e) and result in the upper I–V curve (c). The lower row indicates the device in convex angles lower than the critical angle, which are the ON angles that allow UV travel to reach the NW (Figures 3b and 3f) and result in a lower I–V curve (d). Note that flexible strain is applied in the perpendicular direction to the alignment of the nanowires to minimize the participation of piezoelectric effect, which might be derived from bending pressure and could affect the electrical characteristics. These data also show that the current at the applied negative bias is significantly enhanced.

The surface potential change with UV exposure originates from the transportation and separation processes of the photo-generated charge carriers. As elucidated in the previously reported paper, in the dark, ZnO absorbs oxygen molecules, which are transformed into oxygen ions. The chemisorbed oxygen ions thereby induce surface band bending and create the depletion region (Figure 3d). Upon UV illumination, the photo-generated holes migrate to the surface or the interface due to the built-in potential, and the holes are neutralized by oxygen ions; this process drives the reduction of the depletion layer near the surface (Figure 3b). The remaining unpaired electrons become free carriers, which results in the increasing conductivity of the entire ZnO layer. The steepness of the potential profile of ZnO near the boundary complies with the thinned depletion layer and decreases interface work function. Free electrons can tunnel through the reduced barrier, in accordance with the significant increase of the surface potential of Pt near the interface. Therefore, the change in surface potential upon UV illumination is in accordance with the generation of carriers, which leads to reduction of the interfacial barrier. By taking advantage of the flexibility of the polyimide substrate and PDMS roof, the device represents a differentiated resistive switching behavior with respect to rotating and bending angles (Figure 4). The schematic images and digital images show each bending and rotating state. The measured resistive switching curve is shown in the upper I–V curve (c). The lower row indicates the device in convex angles lower than the critical angle, which are the ON angles that allow UV travel to reach the NW (Figures 4b and 4f) and result in a lower I–V curve (d). Note that flexible strain is applied in the perpendicular direction to the alignment of the nanowires to minimize the participation of piezoelectric effect, which might be derived from bending pressure and could affect the electrical characteristics. These data also show that the current at the applied negative bias is significantly enhanced.

The current ratio under UV illumination with ON angles compared with that at OFF angles (ION/IOFF) is 1×10^2 at 5 V. With ON angle UV-illuminating bending and rotating angles, the current ratio between LRS and HRS in resistive switching performance (ILRS/IRHS. ON angle) is improved vs. that of the OFF angles (ILRS/IRHS. OFF angle). Under illumination with ON angle bending or rotating conditions, the photogenerated carrier and reduced barrier cause a decrease in the set voltage (Vset) and a non-rectifying behavior in forward bias.

To explain more completely, we take into account the effects of an external electric field on a ZnO semiconductor, which can perturb the entire carrier transport in two ways: (i) the modified electric field might influence the separation efficiency of the photogenerated excitons, and (ii) the bias polarity and altered barrier could affect the accumulation and dissipation of oxygen vacancies in the adjacent interface. The first effect is due to the different band bending changes under forward and reverse biases. As the positive external electric field is applied with a direction opposite to the built-in field, the surface barrier is decreased. In contrast, as the negative external electric field is applied, the surface band bending increases in an upward manner because the direction is same as that with the built-in field. The separation efficiency of photogenerated excitons increases due to the strengthened built-in field with negative bias application; however, it decreases with the application of positive bias. The contrasting modified electric field constitutes a reduction in the rectifying property.
under UV illumination. For the second effect, because oxygen vacancies are known to be positively charged mobile carriers, they do not accumulate under the anode but do accumulate under the cathode. In addition, a stronger negative electric field draws additional oxygen vacancies to the interface and aids in thinning the depletion layer, leading to the electron tunneling feature, i.e., the SET process. Bera et al. also reported that tuning the current values from $2 \times 10^{-4}$ A/cm$^2$ to $6 \times 10^{-2}$ A/cm$^2$ in the LRS by altering the applied maximum negative voltages from −5 V to −8 V because higher negative voltages attract more oxygen vacancies.

Additionally, stability tests were carried out (Figures 4g–4i). As illustrated in Figure 4g, no configurational change occurs except for removal of impurity particles before and after the bending (with a bending radius of 5 mm) and blowing test. Therefore, it is expected that the practical bending angle would not damage this device. The cumulative probability distribution data present the uniform current distributions of each state, the bi-level resistance states of the device with $\theta_i$ less than $\theta_c$, and one resistance state with $\theta_i$ larger than $\theta_c$. Because the reading voltage was selected at −5 V in this measurement, the resistance of latter state appears relatively negligible (Figure 4h). The charge retention time is also measured up to 2000 s with good stability (Figure 4i).

Conclusions

In conclusion, an Au/ZnO nanowire/Au junction is used to demonstrate a light tunable resistive switching device. Under illumination, the resistance of ZnO decreases due to inherent photoconductivity, which was supported by KPFM. Subsequently, the potential profile of ZnO near the boundary suddenly increases with respect to the reduced depletion region; as a result, free electron transport increases across the interfacial barrier. The modified effective electrostatic barrier influences the separation efficiency of photo-generated excitons and the accumulation/dissipation of oxygen vacancies in the adjacent interface as well. Therefore, UV-induced resistive switching based on interface states was demonstrated without assistance of another interlayer. In addition, integration of nanostructured Au/ZnO/Au photo-detecting memory and flexible PDMS and polyimide frame structures make it possible to provide a prototype for a wearable system that is capable of detecting, storing and computing data. This unusual device structure allows optical writing at a particular convex bending or rotating angle with respect to the direction of the incident photons, and the memory unit is able to store the obtained data simultaneously.

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References