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A Cu/ZnO Nanowire/Cu Resistive Switching Device

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Abstract: A new device has been realized using flip-chip joining two printed circuit boards (PCBs) on which zinc oxide (ZnO) nanowires were synthesized. Energy dispersive X-ray measurement has been conducted for the ZnO nanowires, confirming that Cu elements have been diffused into the nanowires during the chemical growth process. From $I-V$ measurements, this Cu/ZnO nanowire/Cu structure exhibits a resistive tuning behaviour, which varies greatly with the frequency of the applied sinusoidal source.
Keywords: Cu/ZnO; Nanowires; Flip-chip; Resistive switching; Device

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The resistive switching devices have proved to be very important in the recent decade because they could revolutionarily promote the development of random access memory, sensors and neural systems. The concept was first postulated by Chua in 1971 [1], and followed by the first prototype by Williams *et al.*, [2] in 2008 by using a sandwiched Pt/TiO_2/Pt structure. Since then, tremendous publications have reported the development on this type including a flexible memristor with aluminium/titanium dioxide/aluminium (Al/TiO_2/Al) layers [3], memristive devices made of silver/amorphous-Si/p-type silicon (Ag/a-Si/p-Si) sandwiched layers [4], and a memristor made by a single layered vanadium dioxide (VO_2) thin film [5] and ZnO nano/microwires [6]. All the prior arts so far have enabled the memristive devices to form into very large arrays. However discrete devices based on low cost materials and fabrication processes are equally important and have not been mentioned previously, which can have interesting applications in adaptive analog circuits and sensors [7].

In this letter, we focus on the dynamic $I-V$ characteristics of a novel discrete resistive switching device made of PCBs and ZnO nanowires. In terms of fabrication of the device, first of all, ZnO nanowires were synthesized on a thin copper track of a PCB using a method named localized growth based on joule heating. This method was detailed in one of our previous publications [8]. Two identical PCBs with ZnO nanowires are joined together using epoxy to form the sandwiched device, which is schematically shown in Fig. 1(a). The photograph of a fabricated device is shown in Fig. 1(c). The copper tracks are used for both electrical testing and the possible diffusion source. The effective area (1000 μm × 1000 μm) refers to the place that has abundant nanowires, which was seen on the centre part of the copper track. Figure 1(b) is a scanning electron photograph of the ZnO nanowires using Hitachi S-4800 before the device was assembled, and an energy dispersive X-ray measurement is presented in Fig. 2, which proves that there is certain amount of Cu elements being diffused in the ZnO nanowires. The relative concentrations of Zn, oxygen, and Cu elements are around 74.2%, 17.2%, and 8.5%, respectively. Since the nanowires were grown on a thin seed layer covering the copper track, it is anticipated that the Cu elements are doped

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rather than on surface. The thickness of the seed layer is roughly 1 μm and the length of the ZnO nanowires ranges from 1-2 μm, giving total thickness of 2-3 μm. The X-ray penetration for ZnO nanowires was reported as 3-132 nm [9]. So it is not expected that X-ray will penetrate through to the copper track during the measurement. The conduction mechanism of ZnO thin film resistive switching device is understood that conducting filaments forming and rupturing along nanowire boundaries is the possible cause [10]. The switching mechanism of nanowires device could be due to a combination of filaments effect where the doped Cu elements are additional filaments sources, Schottky effect between nanowire boundaries, and bulk metal-dielectric-metal capacitive effect. It also firstly validates that the cost-effective hydrothermal synthesis process provides both nanowires growth and elements doping simultaneously.

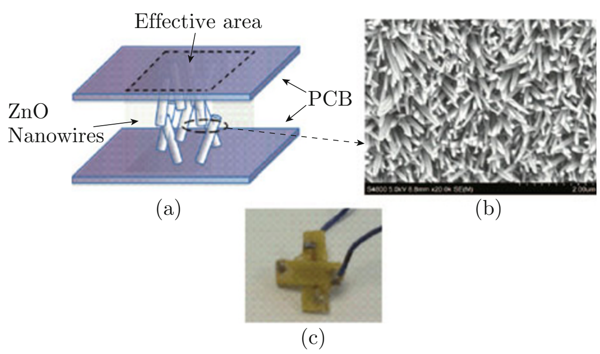

Fig. 1 (a) Schematic graph of the device (effective area is around 1000 μm × 1000 μm); (b) Scanning electron photograph of ZnO nanowires on copper; (c) Photograph of a fabricated device.

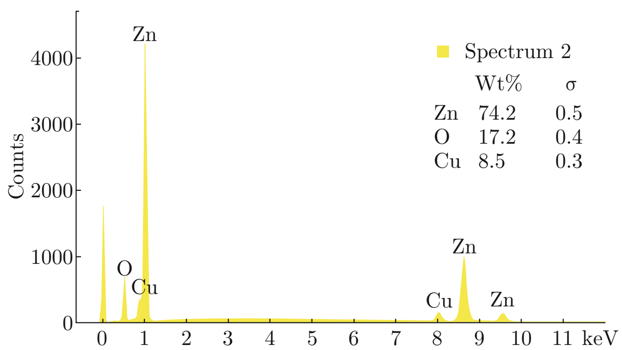

Fig. 2 Energy dispersive X-ray result showing elements distributions in the ZnO nanowires.

$I-V$ measurement on the fabricated device was conducted using an oscilloscope, a signal generator, and a fixed value linear resistor (88 kΩ) according to the circuit diagram shown in Fig. 3. V_1 and V_2 were probed by the two-channel oscilloscope. The electrical current of the circuit I, is calculated by V_2/R, and voltage across the memristor is $V_1 - V_2$. Voltage source is a sinusoidal wave with amplitude of 4 V_{p-p} and varying frequencies. Using sinusoidal signal to test the wave response of the device is viable, which was reported in [11]. It is seen from the first set of measurement in Fig. 4(a) that it behaves as a resistance switching device, similar to the behaviour of an Au/ZnO Schottky diode [12] and a Pt/TiO_2/Ti nanocrosspoint junction [13]. The two limiting value R_1 and R_2 are extracted from the measurement to be 6.25 MΩ and 1.26 MΩ, respectively; hence the resistance ratio is around 5.

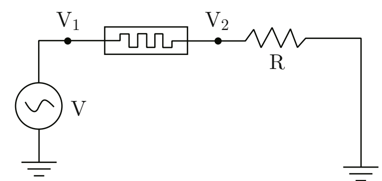

Fig. 3 Circuit diagram shows how $I-V$ curve of the device was characterized.

It is seen from the Figs. 4(b)-4(e) that the $I-V$ curve does not cross the origin, which implies that some energy has been stored in the device at higher frequencies, reflecting combined resistive switching and capacitive behaviours. This could be empirically explained based on charge equilibration processes [14]. When an electrical current flows through the device, charges will be accumulated to one end of the device with consequent depletion on the other end, finally reaching to a stabilization stage of resistive dipoles, which macroscopically appears resistance changes. At low frequencies (30 Hz), the system has enough time to reach the equilibrium state; therefore the $I-V$ curve crossing the origin shows a clear resistive switching behaviour (Fig. 4(a)). As the frequency of the alternating signal increases to 600 Hz, the system stabilization process cannot catch up with the alternating speed of the applied signal; the device therefore shows a hysteresis loop not crossing the origin (Fig. 4(b)). At this point, the device is still displaying resistive switching behaviour; but its resistance (tangent line of the loop) varies dynamically instead of the quasi-binary shape displayed in Fig. 4(a). The delayed response of the charges causes some energy U_M being stored in the system, which can be mathematically written as [15]

$$U_M = \int V(t) \cdot I(t) \cdot dt \tag{1}$$

It is envisaged that the stored energy is proportional to the area enclosed by the hysteresis loop. From the Figs. 4(c) & 4(d), as the frequency further increases to 2 kHz and 8 kHz, more energy has been stored in the system, hysteresis loop is getting more significant, and resistance of the device becomes purely dynamic values. It shows that the switching even is dependent on the frequency of the applied voltage, for example the $I-V$ curve of Fig. 4(b) partially remains the binary

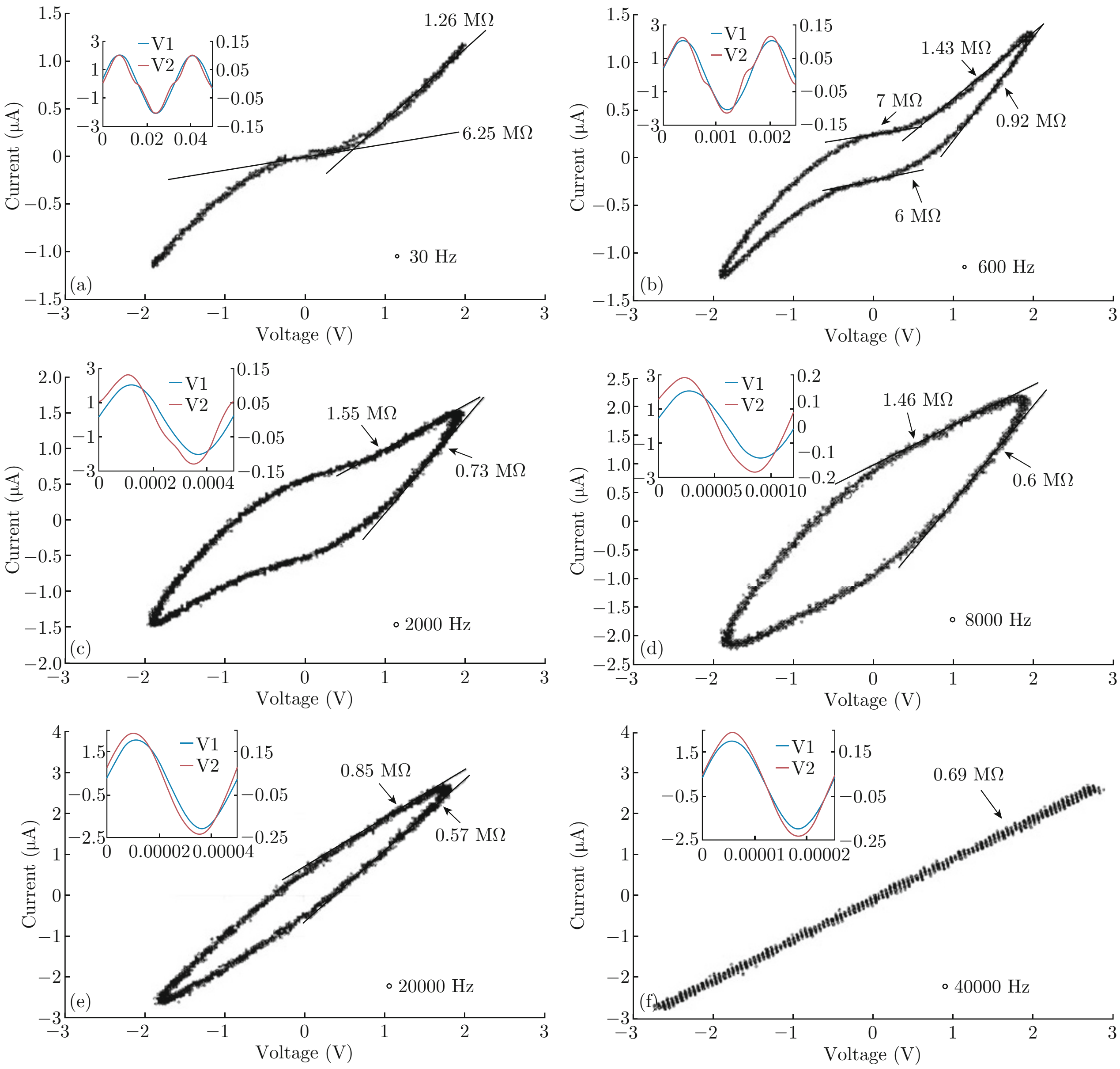

Fig. 4 $I-V$ testing of the device. The frequency of the external source varies from 30 Hz to 40 kHz, giving different $I-V$ characteristics.

switching effect, however at 2 kHz, 8 kHz and 20 kHz, the binary switching effect is hardly seen. Instead capacitive effect becomes more significant. Therefore the device cannot be described by the ideal memristive equation for alternating sources. The equation matching with the practical system reported in this letter could be written in the form of combining a memristive device and a variable capacitor whose value is a function of accumulated charge q, voltage V, and time t.

$$V(t) = M(x_1, I, t)I(t) + C^{-1}(q, t)q(t, V) \quad (2)$$

$$\dot{x}_1 = f(x, I, t) \quad (3)$$

where $V(t)$ and $I(t)$ represent voltage and current across the device, M and C are memristance and capacitance respectively. x denotes a vector representing n internal state variables [14]. It is seen from the equation (2) that the voltage across the device is not only related to electrical current and memristance, but also a function of accumulated charge q. In memristor case, charge mobility plays a key role in charge transport. When the mobility is high enough, the charge transport is faster than the external signal change and the system reach the equilibrium state. Therefore it could mathematically explain the phenomenon in Figs. 4(b)-4(e) where the hysteresis loop does not cross the original point. When the frequency is increased further to 20 kHz, even capacitive behaviour is diminishing. It can be imagined that at such high frequency, the process of forming resistive dipoles cannot respond the applied alternating signal, resulting in a reduced capacitance value. For the highest frequency of 40 kHz that was applied to the device, the device behaves exactly like a linear resistor with resistance value of 0. 69 MΩ (Fig. 4(f)). It is reasonably concluded that at this point the resistive switching process in the device are not responding the applied voltage at all, showing a linear $I-V$ curve. Insert graphs in Figs. 4(a)-4(f) are $Y-T$ measurement of the V_1 and V_2. It is also shown that the resistance at 40 kHz is lower than the low resistance state of the device at 30 Hz, which is possibly due to the electrons hopping among localized oxygen vacancy defects [16]. The resistances labelled in Figs. 4(b)-4(e) were extracted at specific voltage points. If looking at the overall trend, the resistance keeps reducing as frequency increases. That is caused by reducing capacitive impedance as frequency increases, $X_c=1/(\mathrm{j}\omega C)$. It should be noted that the performance degradation happens over time a long time period. Future study is planned in terms of device stability.

In summary, we report a resistive switching device that was realised by sandwiching PCB and ZnO nanowires. The chemical synthesis of nanowires on copper also gives rise to doping of Cu element. The $I-V$ characteristics of the device have been characterised with a range of alternating voltages varying from 30 Hz to 40 kHz. For the first time, it is shown experimentally that the device exhibits both switching resistance and capacitor behaviour. The $I-V$ curve at higher frequencies does not cross the origin, which indicates that some energy is stored in the system. The conduction mechanism of the device has also been discussed.

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