Study on the Film of Ti-Si-C-O Oxides and Its Application in Memristor

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Abstract. The thin films of Ti-Si-C-O oxides are fabricated via direct-current magnetron co-sputtering using a Ti\textsubscript{3}SiC\textsubscript{2} target with oxygen (O\textsubscript{2}). The X-ray photoelectron spectroscopy is used to verified the composition of the Ti-Si-C-O thin films. A memristor is designed as the structure of Pt/TSCO/ITO/glass, and the I-V curves as well as the switching behaviors are studied for the first time. The results indicated that there appear typical pinched hysteresis I-V loops and continuous resistance changes under positive and negative sweeping bias, and that the device conductance can be modulated by consecutive potentiating and depressing programming. The carrier transport mechanism of the device is also investigated and it is found that the Ohmic connection is the leading factor in the linear low electric field region while Schottky emission in the non-linear high electric field region.

1. Introduction
As early in 1971, Prof. Chua at the University of California pointed out from the perspective of symmetry that besides resistors, capacitors and inductors, there is a missing circuit element, namely memristor [1]. In 2008, Strukov etc. at HP Labs published a paper named the missing memristor found in Nature and have realized a memristor predicted by Chua 30 years ago based on the Pt/TiO\textsubscript{2}/Pt structure, and observed the resistance switching behavior in this device, which signalled a new stage in the progress of memristors [2]. With the development of memristors, a variety of materials have been used in these missing devices which show obvious differences in the memristive behaviors like ON/OFF ratio, retention time and endurance characteristics, etc. Depending on the type and characteristics, the materials can be divided into the following categories: binary oxides [3-5], perovskite-type complex oxides [6], solid electrolyte [7], organic chemicals [8], silicon-based semiconductors [9], etc., in which resistance materials have become increasingly popular because of its promise for use in many emerging applications such as neuromorphic devices, photovoltaic device, bioelectronic devices, and memristors[10, 11].

As a ternary layered compound with excellent metallic and ceramic properties, polycrystalline Ti\textsubscript{3}SiC\textsubscript{2} alloy has better thermal, electrical and mechanical properties [12]. However, many researches on Ti\textsubscript{3}SiC\textsubscript{2} are mainly focused on the preparation of bulk or powder materials, and the mechanical or tribological properties as well as comprehensive performance improvements[13, 14]. Up to now, there are few reports that use Ti\textsubscript{3}SiC\textsubscript{2} as memristive materials.

In this paper, we report the fabrication of Ti-Si-C-O (TSCO) oxides films by direct-current (DC) magnetron co-sputtering using a Ti\textsubscript{3}SiC\textsubscript{2} target and verify its composition by using of the X-ray photoelectron spectroscopy. A memristor is designed as Pt/TSCO/ITO/glass structure shown as in Fig. 2(a), and the I-V curves, voltage sweeps and response currents of the memristor are studied to characterize the memristive behavior. The effect of the compliance current $I_{cc}$ on the set voltage $V_{set}$ and the carrier transport mechanism of the device are also studied.

2. Material and methods
As shown in Fig. 2(a), the memristor was designed as Pt/TSCO/ITO/glass structure. The glass substrates (15x15 mm\textsuperscript{2}) with a 110-nm-thin ITO film were cleaned in a sonic bath with acetone and ethylalcohol for 15 minutes respectively, and the ITO film with a resistivity of about 6.5 $\Omega \cdot \square$ was taken as the bottom
A TSCO thin film was fabricated on the above substrates via direct-current (DC) magnetron co-sputtering using a Ti$_3$SiC$_2$ target in an atmosphere of argon (Ar) and oxygen (O$_2$). The chamber was pumped to a base pressure of 7x10$^{-4}$ Pa, and the current was set to 0.3 A. Before sputtering, a flux of O$_2$ and Ar at the ratio of 1:20 was mixed. Argon flow served as working gas was kept at 15 sccm and the mixed gas was kept at 20 sccm to keep the chamber pressure at 0.5 Pa. The TE patterns were made through a photolithography and lift-off technique where the 100-nm thin metal layer was deposited using DC magnetron sputtering under vacuum environment of 8x10$^{-4}$ Pa. The contact area of the individual device was about 200 μm.

All electric measurements were performed based on a Keithley 2636B apparatus and a probe system. During measuring, the voltage was applied on top Pt electrode and the bottom ITO electrode was grounded.

### 3. Results and discussion

The XPS measurement is carried out to verify the composition of the TSCO thin films. In order to eliminate the effect of surface pollutants, all spectra are calibrated with C1s peak at the binding energy of 284.6 eV. Fig. 1(a) shows the full survey spectrum of one TSCO thin film, in which Ti, Si, C and O elements can be observed as we expected, indicating that oxygen has already oxidated with Ti, Si or C in the film during magnetron sputtering. Fig. 1(b), Fig. 1(c), Fig.1(d) and Fig. 1(e) shows the spectrum of Ti2p, Si2p, C1s and O1s, differently. The Ti2p peaks are perceived at the binding energies of 458.31 eV and 464.08 eV (Fig. 1(b)). These two peaks are Ti2p$_{3/2}$ and Ti2p$_{1/2}$, and the aperture between them is 5.77 eV. Compared with the standard XPS spectra, Ti mainly exists in the as-deposited TSCO thin film in the form of +4 valence. The Si2p peaks locate at 101.3 eV and 101.8eV (Fig. 1(c)). The C1s peaks are positioned at 284.1 eV and 288.2eV (Fig. 1(d)), and the O1s peaks are positioned at 529.8eV and 531.3eV (Fig. 1(e)). O mainly exists in the form of Ti-O bonds and Si-O bonds. Si always combines with C or O and generates SiO, SiC and SiO$_2$. The possible chemical components in TSCO thin film are C, TiC, SiC, SiO$_2$ and TiO$_2$.

![Fig. 1 Full XPS survey (a) and Ti2p (b), Si2p (c), C1s (d) and O1s (e) individual XPS spectrum in a TSCO thin film.](image)

As shown in Fig. 2(b), the first current-voltage (I-V) characteristic of the Pt/TSCO/ITO/glass memristor is a pinched hysteresis loop, which is a typical feature of memristor device, exhibiting a characteristic pinched hysteresis loop at the 1st and 3rd quadrant of the I-V plane. The device exhibits standard nonlinear pinched hysteresis, which is consistent with the reported scanning curves of memristors [15]. The sweeping voltage from 0 V to 6 V and 0 V to 6 V is used for the first voltage scan. In addition, consecutive positive and negative DC-sweeps are also used to study the I-V characteristic, as shown in Fig. 2(c) and Fig. 2(d). When the device is loaded first with 5 consecutive positive voltages (0 V to +8 V) sweeps, the amplitude of the current increases gradually (Fig. 2(c)). Also, when 5 consecutive negative voltages (0 V to -8 V) sweeps are loaded to the device next, the current value gradually decreases, and depression occurs (Fig. 4(d)). We take the measured current as an indirect expression of the device conductivity with the scanning voltage. It is shown that the conductivity of the device decreases gradually with the decrease of forward scanning voltage under DC voltage scanning. It is a typical feature for memristor device and also is crucial for emulating biological synapse functions in the electronic synapse.
The resistive behavior of a memristor is mainly reflected in its \( I-V \) curve, and the effect of the compliance current \( I_{cc} \) on the set voltage \( V_{set} \) can be studied by means of \( I-V \) curve as Fig. 3. There are two different modes of resistive switching: bipolar resistive switching (BPS) and unipolar resistive switching (UPS). As in earlier studies, the asymmetric MIM structure always performs as BPS. But in fact, a lot of devices with symmetric MIM structure also show the characteristics of the BPS. Generally, a memristor requires an forming process to establish a subsequent switching behavior. During the process a compliance current is needed to protect the device from being breakdown caused by the high current. As in Fig. 3, the \( I_{cc} \) is set as 1 \( \mu \)A, 2 \( \mu \)A and 4 \( \mu \)A respectively and the sweeping voltage is set from 0 V to 6 V. It can be seen from Fig. 3(a), Fig. 3(b) and Fig. 3(c) that when the \( I_{cc} \) increases from 1 \( \mu \)A to 2 \( \mu \)A, the \( V_{set} \) of the device decreases from 2.6 V to 2 V. While the \( I_{cc} \) increases from 2 \( \mu \)A to 4 \( \mu \)A, the \( V_{set} \) increases from 2 V to 4 V. Under the same scanning voltage, the \( V_{set} \) of the memristor decreases firstly and then increases with the growth of \( I_{cc} \). It can be interpreted that the free electron quantity of the TSCO-based memristor is affected by \( I_{cc} \) under the forward bias. With the increase of \( I_{cc} \), there are enough free electrons which would be generated in the TSCO film to fill the traps, so the \( V_{set} \) of the memristor will decrease gradually at this time. When the \( I_{cc} \) is increased, a higher voltage is required to promote the migration of oxygen vacancy to form the conductive filaments, so the \( V_{set} \) of the memristor will increase.

![Image](image_url)

Fig. 2 The structure of the Pt/TSCO/ITO device (a), typical \( I-V \) curves (b), 5 positive DC-sweeps (0 V to 8 V) (c) and 5 negative DC-sweeps (0 V to -8 V) (d).

In order to identify the carrier transport mechanisms of the TSCO-based memristor, the nonlinear (high electric field) region of the \( I-V \) curve is plotted in log-log scale (Fig. 4(a)), while the low electric field section is fitted linearly which exhibits an Ohmic conduction mechanism (Ohmic slope = 1). The nonlinear region of the \( I-V \) curves is generally categorized by three different carrier transport mechanisms: Schottky emission (SE), Polle-Frenke (P-F) and Space Charge Limited Current (SCLC) [16]. The SE mechanism occurs when electrons obtain sufficient thermal activation energy to pass over the energy barrier at the metal oxide.

![Image](image_url)

Fig. 3 \( I-V \) curves under different compliance current: (a) \( I_{cc} = 1 \mu \)A; (b) \( I_{cc} = 2 \mu \)A and (c) \( I_{cc} = 4 \mu \)A.
interface [17]. SE is the most common carrier transport mechanism in metal oxides [18]. The Polle-Frenkel (P-F) emission is very similar to SE, the thermally activated electrons may jump over from trap level into metal-oxide conduction bands [18-20]. In P-F emission, the barrier height varies with the change of trap levels. The SCLC mechanism can be explained by the trapping and de-trapping process of the charge carriers. The non-linear part for \(I-V^{1/2}\), \((I/V)\rightarrow V^{1/2}\) and \(I-V\) are re-plotted respectively, as the reported before [21] (Fig. 4(b), (c) and (d)). The Linear fitting lines plotted and the fitting equations of each graph are calculated. For SE, P-F and SCLC, the slope of the fitting equation is 16.6, -5 and 0.19, respectively. The highest linearity is SE, followed by P-F and SCLC. Obviously, SE is the dominant carrier transport mechanism in the non-linear high electric field region. The weaker linear dependency of the P-F and the SCLC mechanisms are poorly represented. As a result, the linear region of the \(I-V\) curve points to Ohmic conduction, while the non-linear region of the \(I-V\) curve of the TSCO-based memristor device demonstrates an SE-type conduction mechanism.

![Graphs](image.png)

Fig. 4 \(I-V\) plots of Pt/TSCO/ITO memristor: (a) log \(I\)-log \(V\), (b) log \(I-V^{1/2}\) for SE, (c) log \((I/V)-V^{1/2}\) for P-F and (d) \(I-V\) for SCLC.

4. Summary

In this paper, the TSCO thin films are fabricated by direct-current (DC) magnetron co-sputtering using a TiSiC target in the atmosphere of argon (Ar) and oxygen (O2). The composition of the TSCO thin film is verified by means of X-ray photoelectron spectroscopy (XPS). The TSCO thin film is used as a memristive layer and the TSCO-based memristor is fabricated as Pt/TSCO/ITO/glass structure for the first time. The \(I-V\) curves, voltage sweeps and response currents of the memristors are studied to characterize the switching behavior of the device. The results show that there appear pinched hysteresis \(I-V\) loops in the TSCO-based memristor, and continuous resistance changes could be obtained under positive and negative sweeping bias, indicating that the TSCO-based memristor could be used as an electronic synapse. With the increase of compliance current \(I_{c}\), the set voltage \(V_{set}\) decreases first and then increases. It is found that Ohmic mechanism is the dominant factor in the linear low electric field region while Schottky emission (SE) is the dominant factor in the non-linear high electric field region.

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References

[1] Chua, L.: IEEE. T. Circuits. SYST Vol. 18 (1971), p. 507-519
[2] Strukov, Dmitri B., Snider, Gregory S., Stewart, Duncan R.and Williams, R. Stanley: Nature Vol. 459 (2009), p. 1154-1154
[3] B. Gao, B. Sun, H. Zhang, Lifeng Liu et al: IEEE Electr. Device Lett. Vol. 30 (2009), p. 1326-1328
[4] Y. Wang, Q. Liu, S. Long, et al: Nanotechnology Vol. 21 (2010), p. 045202
[5] Y. Yang, P. Gao, S. Gaba, et al: Nature Commun. Vol. 3 (2012), p. 732
[6] X. G. Chen, X. B. Ma, Y. B. Yang, et al: Appl. Phys. Lett. Vol. 98 (2011), p. 122102-122102-3
[7] Z. Xu, Y. Bando, W. Wang, et al: ACS Nano Vol. 4 (2010) 2010, p. 2515-2522
[8] Y. S. Lai, C. H. Tu, D. L. Kwong, et al: Appl. Phys. Lett. Vol. 87 (2005), p. 5655-5660.
[9] S. H. Jo, W. Lu.: Nano Lett. Vol. 8 (2008), p. 392-397.
[10] Amouzadeh Tabrizi M, Shamsipur M, Saber R, et al: Biosen. Bioelectron. Vol. 98 (2017), p.113-118.
[11] Kawamura K, Tsuchiya T, Takayanagi M, et al: Jpn. J. Appl. Phys. Vol. 56 (2017), p. 06G01
[12] N. Tzenov, M.W. Barsoum, T. El-Raghy.: J. Eur. Ceram. Soc. Vol. 20 (2000), p. 801-806
[13] T. El-Raghy, M.W. Barsoum: J. Am. Ceram. Soc. Vol. 82 (1999), p. 2855-2860
[14] T. El-Raghy, A. Zavaliangos, M. Barsoum, et, al: J. Am. Ceram. Soc. Vol. 80 (1997), p. 513-516
[15] Jo S H, Chang, Ting: Nano Lett. Vol. 10 (2010), p. 1297-1301
[16] Lampert, Murray A.: Phys. Rev. Vol. 103 (1956), p. 1648-1656
[17] Dementjev A P, Ivanova O P, Vasilyev L A, et al: J. Vac. Sci. Technol. A. Vol. 12 (1994), p. 423-427
[18] Lim E W, Ismail R.: Electronics, Vol. 4 (2015), p. 586-613
[19] SZE, Simon M.: Physics Of Semiconductor Devices (Physics of Semiconductor Devices, 2014)
[20] Joshua Yang J, Miao F, Pickett M D, et al: Nanotechnology, Vol. 20 (2009), p. 215201
[21] Gul F, Efeoglu H.: Ceram. Int. Vol. 43 (2017), p. 10770-10775