Copper doping effect on the electrical characteristics of TiO₂ based Memristor

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Keywords

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Abstract

Nanostructures as a starting point to solve the scaling problems of the CMOS technologies, have been concerned the attention of numerous researchers. By strong demanding for nonvolatile memory technology, resistive memories based on metal oxide has been common due to several advantages, such as low-power consumption, good scalability and fast switching speed. Even though high-temperature fabrication process has a large area limitation by their material characteristics. Metal oxide thin films are respectable candidate to fabricate at nano scale solid state electronic device. Metal/Metal-Oxide/Metal structure is employed to several devices such as Non-volatile able memories, RRAMs, resistance switching based devices and memristor. The foundation of the primary TiO₂ based memristor served a number of consequences for understanding the conduction mechanisms during the formation of hysteresis loop. Also, the current-voltage characteristics (hysteretic loop) which is formed by mobile anions or oxygen vacancies motion in the set and reset process, is clarified the resistive switching behavior by swapping the resistance of TiO₂ thin film. Here, the effect of Cu doping into TiO₂ based memristor by focused on the hysteresis loop characteristics is considered. Similarities of hysteresis loop form in Cu doped devices are explored. Hysteresis loop is symmetric for structures having pure TiO₂; however, asymmetric character appears after Cu doping. After the formation process hysteresis loop of the Cu doped devices shown higher conductance path on (I-V) characteristic than the initial forming process loop in positive cycle loop as the un-doped TiO₂. Also, in spite of un-doped TiO₂, this (I-V) hysteresis loop character shown lower path conductance than primary forming process in the negative cycle loop. Surface roughness of 30nm thick TiO₂ is increased from 0.3nm to 0.77nm as Cu doping increased from %10 to %30. Unfortunately, XRD results cleared that there is no exchange in crystallinity but optical band gap decreased as Cu doping increased.

1.Introduction

Initially memristor theory is proposed by Leon Chua [1]. Up today, its electrical characteristics have been the focus point of researchers. Memristor as a forth elements of electronics have resistance switching properties which is promising next generation nonvolatile memory due to its artless structure, simple processing, fast switching and high-density fabrication. Charge-based memory devices such as flash memory and dynamic random-access memory (DRAM), have physical and technological confinement when the device sizes have minimized. Therefore, switching mechanism centered on resistance change is an alternative solution to overcome device dimensions shrunk [2-5]. Several semiconductor materials and oxides or insulators have been discovered to reveal resistive switching properties, such as chalcogenides [6,7], organic materials [8,9], amorphous silicon [10,11], perovskite oxides [12,13], binary transition metal oxides (such as NiO [14-16], TiO₂ [17-19], ZnO [19]) and graphene oxide (GO) thin films [20]. Among the various of candidate materials to select, two terminal metal oxide based resistive switching memories due to advantages includes, low-power consumption, scalability down to nano scale, and fast switching speed are promising for future electronics. Pt/TiO₂/Pt as the first structure of the memristor introduced by HP [21]. Recently, a developing computing paradigm, neuromorphic computing which is based on working principles of neural systems in the brain, attracted the most special attention about memristor structures. In the other hand, learning activities in the brain memory are processed by dynamic mass changes and spikes occurrences between the neural networks. This progression is titled

as synaptic plasticity. However, it is not simple which common memristors gradually executed the mimic of the bio synapse function and conduction but the doped oxide based memristor as have reported in literature can indeed emulate [23-26]. As an example, self-assembled Ag nanoclusters in TiO₂ films are employed Ag dopant gradient to boost the memristor enhancement. Under the negative and positive pulse trains, memristor is revealed respectively high and low resistance switching, which can completely match with stimulus and blockage spike of the bio synapse [27]. Also, self-doping memristors introduced to emulate the ion dynamics (Ca²⁺) of biological synapses in Ag/Ag: Ta₂O₅/Pt structure [28]. Another work is a penetrate Ag into oxide of Pt/SiO₂N_y-Ag/Pt device. In this study Ag filament formation/captured could emulate Ca²⁺ mimic of bio synapses. There are many studies about synapse functions emulation by emerging devices such as memristor-based synapses, phase change synapses, ferroelectric synapses, 2D material synapses, and metal-oxide-semiconductor (CMOS) based artificial synapses. In neuromorphic engineering, CMOS based artificial synapses circuits have high power consumption due to multipart structure needs. The most attractive candidate among these structures are two terminal memristor which is exactly identical synapses [28]. Low power consumption and also three-dimensional scalability of memristors have advantages over conventional CMOS technology [30-31]. Consequently, the investigation of doping effect on the electrical characteristics of memristors is important agenda which is noticeable for bios naps emulation modeling. Here, it is focused on the Cu doped TiO₂ based memristor. The current-voltage characteristic of (Al/p⁺/Si/Cu+TiO₂ or

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TiO₂/Cu) structure devices are considered by adding Cu. Cu doping effect on electrical parameters of these memristors are investigated.

2. Experimental Setup and Measurements

The Al/p⁺⁺Si/(TiO₂) or (TiO₂+Cu)/Cu structures (as shown in Fig1.a, b. processed on a p⁺⁺Si wafer as a memristor by HiPIMS technique. At the first step inorganic and organic cleaning process called as RCA1 and RCA2 applied to silicon wafers. Thin SiO₂ film is grown at 1000°C for 10min and under the dry oxygen flow. Back ohmic contact is formed after thermal evaporation Al (1200Å) and annealing at 580°C/5min, under the Argon atmosphere. Lithography process through oxide layer is used for windows opening. Lift-Off process used for TiO₂ or TiO₂+Cu growth and top metal deposition, Fig1.a, b. Device size was 100x100µm². Output of homemade pulsed DC source was set to 580V and 650V respectively for Ti and Cu targets, with pulse durations equal to 50ms. On the other hand, the pulse frequency of applied voltage to Ti target was 5 Hz. According to thickness measurements of TiO₂ (500Å) and Cu grown rate ratio on time, the DC pulse frequency which is applied to Cu target in the sputtering chamber choose as 290,435,580,725,870mHz, respectively for 10,15,20,25,30%Cu doping as shown in the Fig1. c. Ar and O₂ flow rates set to 30sccm and 0.4sccm respectively. Initial base pressure was below 5x10⁻⁵ Torr. During the deposition the base pressure was 5.13x10⁻³Torr. Fiber optic coupled Ocean HR4000 spectrometer used for plasma emission monitoring during the film growth and later used for transmission measurements. Time depended (I-V-t) measurements were carried out by a computer controlled Keithley 2400 and 6514 at room temperature. Films grown on SiO₂/p⁺⁺Si were analyzed using Rigaku DMax-2200XRD with a Cu-Kα(λ:1.5405Å) radiation source (at 20–60° scan range). AFM measurements for surface morphology were carried out by using AFM NanoMagnetics Instruments.

Figure 1. Schematics of (a) (Al/p⁺⁺Si/TiO₂/Cu) device, (b) (Al/p⁺⁺Si/(TiO₂+%kCu)/Cu) device, 10%<k<30% (c) DC pulse timing applied to Ti and Cu targets from HiPIMS power supplies.

a. Memristor characteristics (I-V and R-t)

As grown structures of Al(1200Å)/p⁺⁺Si/TiO₂(500Å) and (TiO₂+Cu)/Cu(500Å) devices is shown in Fig.1a. During every I-V-t measurement sweep rate was equal to 0.5V/sec, and compliance current was 20mA during each cycle. Forming process is seen in Fig.2a. The set voltage of forming was approximately 1.5V which increased by repetition loop number. According to measurement results in Fig.2a, after each cycle, the hysteresis loop area is shrunk. In Fig.2a the set/reset of memristor which is known as resistive switching, this mechanism is defined and to be explained by drift of

the oxygen ions or vacancy. Memristor resistance is decreased after each loop, Fig.2a, b, c. Performed R-t measurement is carried out at +2V and -1.5V. Additionally, symmetric I-V) character recognized in the un doped TiO₂ device.

Figure 2. (I-V) characteristics of the (Al/p⁺⁺Si/ TiO₂/Cu) device. (a)The forming process in the sweep rate 0.5V/s. Resistance change under the constant voltage applied as (b) +2V and (c) -1.5V

As shown in the Fig.3, the set voltage pointed in the pure and Cu doped TiO₂ is performed individually and then plotted together. The comparison of set voltages appears during the forming process of doped and un-doped TiO₂ memristor is shown in Fig.3. Addition of Cu into TiO₂ layer the set point is formed at higher voltages. The increase set voltages are completed approximately as a sharp filament formation while loop progressing. Although repeated measurements do not show efficient stability in switching process, but the forming process is acknowledged by accumulative of Cu which is doped to TiO₂ during the film growth.

2.2 Cu Doped Memristor's Characteristics (I-V and R-t)

The (I-V) characteristics of pure and 10,15,25% Cu doped TiO_2 based memristor is shown in Fig. 4a,b,c,d where sweep rate was 0.1V/s and compliance current was 20mA. In spite of the pure TiO_2 based device an asymmetric (I-V) is achieved after Cu doping into TiO_2 , Fig.4. Repeated loops are clarified improvement of resistance in the negative cycle and reducing the resistance in positive cycle of hysteresis. In the other words, by Cu impurity increase, the device is converted to an inverter. To support the recurrence performance of resistance switching behavior of memristor, resistance measurement is done. As shown in the Fig.5a, b resistance increase under the +2V bias and resistance decrease under the -4V supports the observation given in Fig. 4c.

Figure 3. The set voltage comparison in the forming process of Cu doped and un-doped TiO_2 memristors.

Figure 4. (I-V) characteristics of memristor of (a)un doped TiO_2 , (b)10% Cu doped device, (c) 15% Cu doped device and (d) 25% Cu doped device. The result shown the asymmetric I-V relation by addition Cu impurity. Resistance increase during the positive cycle and decrease during the negative cycle property clearly appear after %25 Cu doping.

Figure 6. (I-V-t) characteristics of 30%Cu doped memristor. Current increase during the positive cycle and current decrease during the negative cycle after each loop is characteristic property of memristor.

The XRD results of TiO_2 and Cu doped TiO_2 layers on silicon substrate by R-HiPIMS, are shown in Fig.6. As shown in this figure, the peak labelled as "T" in XRD plots are related to titanium dioxide or Ti_2O_3 at $2\theta=33.21^\circ$, and the other peaks are related to brookite $\text{TiO}_2(\text{B})$, (A, R) Ti_5O_{15} rutile and anatase phases. Peak donated with "C" to be related to compound of Titanium, O and Cu ($\text{Cu}_3\text{Ti}_4\text{O}$ and Cu_3TiO_4). As reported, Cu-doped (1.7-3.2%Cu) TiO_2 nanorods, have ferromagnetic properties. The XPS analyses shows that ferromagnetic property is centered on existence of oxygen vacancies which improvement by Cu doping. In same study, as reported, highly crystalline anatase phase is clarified in the Cu doped nanorods by high-resolution transmission electron microscopy (HRTEM) analyses [32]. Therefore, XRD results given in Fig.6 is supported by literature which, Cu doping has negligible effect on crystallinity of TiO_2 .

Figure 7. XRD results of pure and doped TiO_2 by Cu

2.4 Optical Characterization

Fiber optic coupled Ocean HR4000 spectrometer is used to determine the absorption measurements for estimating the band gap of as grown thin films of memristor devices. Tauc plot is plotted by measuring the absorption coefficient α and using the $(\alpha h\nu)^n = B(h\nu - E_g)$ function [22], where, ν is the frequency, h is the Planck constant, B is the Boltzmann constant and the band gap is E_g . The fitted amount of the band gap for several number of measurements of the absorption coefficient for pure and (10,15,20,25,30%) Cu doped TiO_2 shown in Fig.7 respectively is 3.389,3.154,2.698,2.653,2.547 and 2.458eV. The comparison of the fitted amount of the band gap is plotted in this figure. As shown in Tauc plot the band gap is shifted to lower amount of band gap by growing Cu doping level.

2.5 AFM Measurement Result

During TiO_2 growing process, Cu concentration was changed by adjusting the time duration and trigger signal frequency applied to the power supply of Cu target. Although the measurements related to the exact copper content in the films did not clarified, the effect of copper addition on the surface roughness was investigated by AFM measurements. For comparison all film thickness kept constant at 30nm. Height distributions for $2 \times 2 \mu\text{m}^2$ area scanning is given Fig. 8, indicate at highest Cu content peak height is shifted to higher value and distribution range increases.

The surface roughness for the pure TiO_2 without any additives is 0.30nm. Surface roughness is a measure for the Cu doping effect on TiO_2 film surface morphology. The analysis AFM measurements are given in Fig. 9 roughness increased from 0.41nm to 0.52nm.

Figure 9. Height distributions of pure and Cu doped TiO_2 thin films as calculated from AFM data.

Figure 10. (a, b, c, d, e, f) AFM images showing the surface morphology of 30nm thick TiO_2 and Cu doped films on the silicon substrate.

3.Conclusion

Declaration of Conflict of Interests

The authors declare that there is no conflict of interest.

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