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Influences of preparation methods on bipolar switching properties in copper nitride films

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ABSTRACT

Copper nitride (Cu_xN) films were prepared by plasma immersion ion implantation (PIII) as well as by reactive magnetron sputtering (RMS). Based on X-ray diffraction (XRD) analysis, a semiconductive phase Cu_3N could be found in the films prepared by both methods. On the other hand, a copper-rich conductive phase Cu_4N was observed only in the film prepared by PIII, in which gradually distributed nitrogen could be identified by secondary ion mass spectroscopy (SIMS) analysis. The resistive switching properties have been studied after depositing Ni as the top electrode. The Ni/Cu_xN/Cu memory devices prepared by PIII method showed a forming-free characteristic with a low operation voltage of ± 0.2 V, excellent DC and AC endurance performances at least longer than 600 times and 10^5 times with resistance window of 50 and 12 respectively. On the contrary, the resistive switching behavior for the device prepared by RMS needed a forming process and was unstable. The excellent performances in PIII prepared films were attributed to the coexistence of metallic Cu_4N phase and gradually decreased nitrogen concentration. It was supposed that the Cu atoms bridge the small gaps between the bottom and top electrodes and form the conducting filaments.

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1. Introduction

Resistive random access memory (RRAM) is considered as one of the most promising candidates for the next generation nonvolatile data memory (NVM) because of low power consumption, short operating time and great theoretical endurance [1,2]. In recent years, copper based compounds, such as copper oxide (Cu_xO) [3,4], copper sulfide (Cu_2S) [5] and copper organics (CuTCNQ) [6] have been integrated into RRAM devices since its compatibility with Cu interconnection process in complementary metal oxide semiconductor (CMOS) technology.

As one of the important copper based compounds, copper nitride (Cu_xN) with anti-ReO_3 type structure has received attention as a promising optical storage material [7]. Nowadays, many methods have been applied to grow Cu_xN films, such as rf-magnetron sputtering [8], pulse laser deposition [9] and reactive direct current sputtering [10] etc. The structure, electrical properties, and composition of Cu_xN have been widely studied. Gallardo-Vega et al. have explored the electrical resistance of Cu_xN film as a function of the lattice constant [9]. It was reported that both Cu_3N and Cu_4N phases belong to the cubic system. The former has a lattice constant of 3.82 Å, slightly smaller than that of Cu_4N, and shows a semiconducting character while Cu_4N is metallic. This phenomenon had been predicted in Moreno-Armenta's work in 2004 [11]. According to their conclusion, ideal Cu_3N with anti-ReO_3 type structure is a semiconductor with a small indirect band-gap of 0.25 eV when the lattice constant is 3.82 Å, however Cu_4N would be an ideal conductor when an extra Cu atom is inserted into the center of the unit cell, which results in an expansion of the lattice constant to 3.88 Å. Thus the stoichiometry and the copper content would play an important role for the electrical properties of the film.

Plasma immersion ion implantation (PIII) technology was designed by Conrad et al for high-flux implantation in 1987 [12], and now is widely used in surface modification of metal [13], alloy [14] and polymer [15] for its simple system design, low cost and high implantation efficiency on the non-planar surfaces. Most recently, Lu et al. [16] firstly reported that the copper nitride films prepared by PIII with implantation voltage gradually up to 15 kV could show reversible resistance variance character. However, this Cu_xN based RRAM device only provided an endurance of about 50 with an acceptable resistance window of about 10 times. Thus, it was believed that the electrical properties of Cu_xN based RRAM devices could be further optimized and improved.

In this work, both PIII and conventional RMS technologies were employed to synthesis Cu_xN thin films. The Cu_xN based RRAM devices are subsequently fabricated after depositing Ni as top electrode. The different composition and bipolar resistive switching behaviors of these two kinds of films are investigated and discussed.

2. Experimental

A copper layer with a thickness of about 1 μm was deposited by a standard electrochemical plating (ECP) method on TaN/SiO_2/Si substrate

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to form a $Cu/TaN/SiO_2/Si$ multilayer structure. Copper nitride film was formed by implanting N + ion into the top copper layer by a PIII system (PIII-Cu_xN film) at a room temperature with progressively increased negative high voltage from 2 to 10 kV at nitrogen working pressure of 0.8 Pa and radio frequency power of 70 W, so as to control the total nitrogen concentration accurately and to form a gradually increasing nitrogen concentration from the bottom to the top in the Cu_xN film. The total implant dose was estimated about 4.1×10^{16} cm^{-2} and the implantation depth was theoretically simulated to be about 45 nm. The film made by RMS (RMS-Cu_xN film) was grown on the $Cu/TaN/SiO_2/Si$ substrate by using a copper target with a purity of 99.9% at a room temperature. The working gas was a mixture of 99.999% pure nitrogen at 89 SCCM (standard cubic centimeter per minute) and 99.999% pure argon at 22 SCCM. The CuN_x film thickness was about 50 nm determined by a stylus profilometer (Kosaka Laboratory ET3000). Subsequently Ni was deposited as the top electrode with a diameter of 100 μm and a thickness of 100 nm by physical vapor deposition (PVD) method, while the copper layer was used as the bottom electrode for both PIII-Cu_xN and RMS-Cu_xN films.

X-ray diffraction (XRD, CuKα, BRUKER-D8 system), secondary ion mass spectrometry (SIMS, CAMECA IMS-6F) and X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System) were employed to characterize the structure and composition of the Cu_xN films. The electrical, properties of these $Ni/Cu_xN/Cu$ memory devices were measured by Keithley 4200-SCS semiconductor parameter analyzer.

3. Results and discussions

XRD patterns from the films are shown in Fig. 1. Three peaks of $2\theta = 39.0°$, $2\theta = 35.9°$ and $2\theta = 41.4°$ marked by vertical dash lines are observed in both films, and they are attributed to Si (001), TaN (111) and TaN (200) from the substrates respectively. The strongest peak in both films at $2\theta = 43.2°$ is attributed to Cu (111). However, for the PIII-Cu_xN film, the diffraction peak from the (110) of the Cu_3N phase is presented, while for the RMS-Cu_xN film, the peaks from the (110) and (111) planes of Cu_3N are observed. It is clear that the PIII-Cu_xN film shows a different preferred orientation from the RMS-Cu_xN film. It was well known that the Cu_3N (111) plane has a more closely packing structure than the Cu_3N (110) plane. The different orientation could be attributed to the different crystal growth mechanism for these two methods, which leads to different mobility of Cu and N atoms during the film growth process and forms different preferred grain orientations [17].

The chemical states of Cu and N atoms in the Cu_xN films are characterized by XPS using C 1s at 284.6 eV as the internal reference as shown in Fig. 2. For Cu 2p peaks in Fig. 2a, there are no obvious

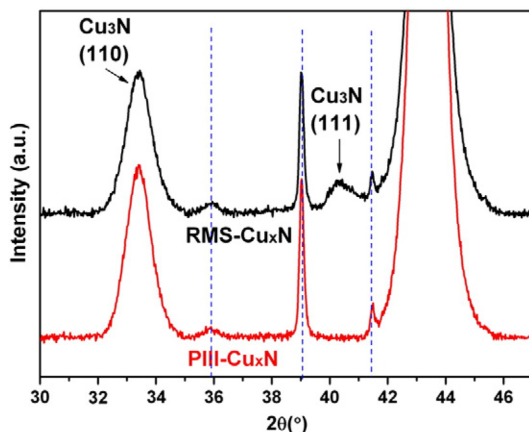

Fig. 1. XRD patterns for PIII prepared and RMS prepared Cu_xN films.

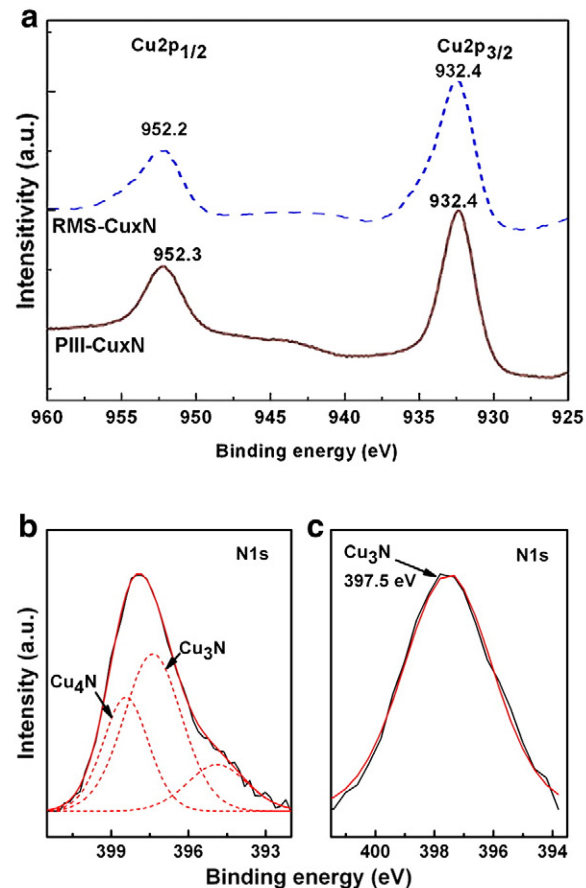

Fig. 2. Chemical states of a) Cu 2p for both Cu_xN samples, N 1s for b) PIII prepared and c) RMS prepared Cu_xN films including the N 1s peak fitting for both of the films.

position or shape differences between two kinds of samples, however, both of the Cu 2p peaks in two samples have a slight shift to higher energy compared to the pure Cu 2p peaks (951.9 eV and 932.2 eV) which could be attributed to the Cu–N bonding [16,18]. To further clarify this, N 1s peaks are shown in Fig. 2b and c. For the PIII-Cu_xN film as shown in Fig. 2b, the asymmetrical N 1s-peak could be separated into three components: a strong peak at 397.4 eV attributed to the Cu–N bonding in Cu_3N [19], a relatively weak peak at 398.4 eV attributed to the Cu–N bonding in the Cu_4N phase [20] by Depla et al., and a weak shoulder at 394.8 eV, whose source remains unknown since this bonding energy is even smaller than the lowest N 1s-bonding energy (396.9 eV) in the Cu_xN films, as reported by Cristina et al. [19]. For the RMS-Cu_xN film as shown in Fig. 2c, on the other hand, the N 1s-peak located at 397.5 eV is quite symmetrical, and can be simply attributed to the Cu–N bonding in Cu_3N [19]. In addition, the ratio of Cu and N atoms in two kinds of copper nitride films obtained by XPS analyses are both near 3:1 which indicate that there could be some N-rich areas at surface of the PIII-Cu_xN film.

Fig. 3 shows the distribution profiles of nitrogen and copper in the PIII-Cu_xN film measured by SIMS. The N concentration in the film was decreased gradually. This phenomenon is easy to understand as the N-ions were accelerated and implanted into the copper film at gradually increased negative voltages by PIII system. The multi-energetic implantation results in the transition of N-rich phase to Cu-rich phase from the surface to the bottom of the film within an effective depth of 50 nm. This SIMS result met with the simulation result mentioned above rather well.

The RRAM devices made by these two kinds of Cu_xN films were studied by direct current sweeping measurements. The positive bias

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