Study on Resistive Switching Property of Ti Doped Novel NiO Thin Films

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Abstract. Ti doped nickel oxide thin films have been fabricated by sol-gel dip-coating process using nickel acetate and tetrabutyl titanate as source materials. The effect of the amount of Ti dopant on the surface roughness, optical, chemical state and electrical properties of NiO: Ti thin films was observed by atomic force microscopy (AFM), Uv-vis spectroscopy, X-ray photoelectron spectroscopy (XPS) and I-V measurement, respectively. Results show that the Ti doping is an effective ways to improve the resistive switching behaviors and it is a convenient way to understand the mechanism of the resistive switching behaviors.

1. Introduction
Recently, metal oxides based on resistive switching random access memory (RAM) has attracted great interest as the next generation nonvolatile memory materials.[1-3] Nickel oxides are P type and wide band gap semiconductor as resistive switching materials due to excellent durability, electrochemical stability. [4-6] One of the effective ways is doping of different dopant, which can improve the resistive switching properties.[7, 8] Additionally doping is a very convenient ways for semiconductors processing combined with sol-gel process. Point defects in oxide films are known to play a critical role in resistive switching mechanism. These defects may be formed in metal oxides by doping. Doping materials is with bonding valence different from that of the constituting elements of the metal oxide with different oxide formation energy. Recent studies show that the electric conductivity of NiO thin film increases by lithium (Li) and copper (Cu) dopants. In our research, we produced a sol-gel process of tetra valence (Ti) atom dopant. [7-8]

2. Experimental
Please The substrate is self-made transparent and conductive SnO2: Sb (ATO) thin film on Si substrate.[9] The ATO substrates were clean by propanol and acetone step by step. Nickelous acetate (Ni(CH3COO)2 • 4H2O) and ethylene glycol monomethyl ether (CH3OCH2CH2OH) were used as starting materials and Tetrabutyl Titanate was used as a dopant. With ethylene glycol monomethyl
ether as solvent, components were mixed in terms of the molar ratio Ni(CH3COO)2 • 4H2O / Ti =1/0.02, 1/0.04, 1/0.06, 1/0.08 were stirred for 8 hours. Then a dip-coating method was used to make a gel film on the ATO substrate. After anneal the gel films for 20 minutes at 500°C, NiO:Ti thin films were obtained. Then the NiO:Ti thin film was covered by a mask and Pt (99.99%) was evaporated by high vacuum thermal evaporation at 2.0×10-4 Pa for 5 minutes at a speed of 10 nm / min. Finally, the unit Pt/ NiO:Ti /ATO was fabricated.

The Ti-doping NiO films were prepared by dip-coating on quartz and ATO substrates respectively. The optical properties of Ti-doping NiO films were examined by UV-vis spectrum and current-voltage characteristics were examined by Keithley 2400c source meter unit. XPS (X-ray photoelectron spectroscopy) and AFM (Atomic force microscopy) were also used for chemical and physical properties’ research.

3. Results and Discussion

3.1. Morphological characterization

AFM was used to examine the morphology of the surface of NiO:Ti thin films. To evaluate the surface roughness as well as the grain size in films, a scanned area of 1um* 1um was scanned in a tapping mode. The two dimensional AFM images were shown in Fig.1. The result shows that all the samples are uniformed and the room meant square (RMS) value is 1.65nm, 1.86nm, 2.23nm and 3.14nm, respectively. The surface roughness increases as a result of Ti dopant concentration increase. This is because the diameter of Ti atom (0.20nm) is bigger than that of Ni atom (0.16nm). When the amount of Ti dopant is increased, the NiO grains are enlarged. This leads to an increase in the grain size and an increase in surface roughness.

![AFM images of NiO:Ti thin films with different Ti molar ratio concentration. (a) 0.02. (b) 0.04. (c) 0.06. (d) 0.08.](image-url)
3.2. Optical analysis of Ti doped NiO films

Transmittance spectra, reflectance spectra of Ti doped NiO thin films are shown in Fig.2 (a) and (b). The transmittance spectra show that the front edges of the curves represent the intrinsic absorption of nickel oxide. It shows that the films exhibit high transparencies in the visible spectral regions. The highest average transparency is 94.5% when the Ti molar ratio is 0.02. The transmittance of the NiO thin films in the visible region is decreased with the increases of Ti concentration. The optical band gap of Ti doped NiO thin films was calculated using the data of the transmittance and the reflectance versus hν plot. The absorption coefficient (α) is calculated and showed in Fig. 2(c) by the following Eq.(1) and Eq.(2) :[10,11]

\[
\alpha = \frac{(1/d) \times \ln[(1-R)/T]}{(1)\\
\alpha h\nu = C(h\nu - E_g)^{1/2}}^{(2)}
\]

where T is the transmittance, R is the reflectance and d is the film thickness. The band gap of Ti doped NiO thin films is determined by plotting (α hν)² vs hν. The calculated optical band gap energy (E_g) decrease from 3.72ev to 3.64ev as increase of Ti dopant concentration which is shown in Table 1.

| Ti concentration (%) | Optical band gap (ev) | RMS roughness (nm) | Valence band gap edge (ev) | O1s (1) concentration (%) |
|----------------------|-----------------------|--------------------|---------------------------|--------------------------|
| 2.0                  | 3.58                  | 0.81               | 3.72                      | 40.2                     |
| 4.0                  | 3.65                  | 2.33               | 3.69                      | 42.3                     |
| 6.0                  | 3.68                  | 2.58               | 3.66                      | 51.5                     |
| 8.0                  | 3.72                  | 3.27               | 3.64                      | 58.7                     |
3.3. Characterization of chemical bonding states

The chemical states of the elements in NiO:Ti thin films were measured by XPS. XPS spectra were obtained with monochromatic Al Kα (1486.71eV) line at a power of 150 W (10mA, 15kV). The charge neutralizer was applied to compensate for surface charge effects, and binding energies were calibrated using the C1s hydrocarbon peak at 284.8eV. Fig. 3 shows the spectra of Ni3d, Ti2p and O1s.
core level positions for Ti doped NiO thin films. For Ni3d spectra, two peaks which are labeled at 855.04eV and 856.65eV are represented NiO and Ni2O3, respectively. The basic mechanism leading to the appearance of shake-up satellites are sampling the unoccupied discrete orbital which is also shown in Ni3d spectra. In Fig. 3(b), it is shown Ti2p spectra, which is attributed to bond Ti-O. In Fig. 3(c), two peaks located around 533.61eV (O1s(1)) and 532.04eV (O1s(2)) are attributed to bond Ti-O and Ni-O, respectively.[12] From the results, Ti-O bond component increases obviously with increasing the amount of Ti dopant.

For further research, we found out that the chemical nature differences between Ti and Ni elements played an important role since the Gibbs standard free energy of oxide formation for Ti to form TiO2 is much lower than that for Ni to form NiO. Therefore, it is easier for Ti to bond with oxygen in NiO:Ti thin films and the oxygen vacancy appears easily around the Ti atoms. The oxygen vacancies are associated with the statistically homogeneously distributed Ti ions and the conductive filament consisting of oxygen vacancies occur.[13]

3.4. Electrical measurement

Fig.4 shows I-V curves of Pt/ NiO:Ti /ATO unit cells with different Ti doping concentrations from 20 switching cycles for each unit. It shows that all the units are bipolar except Fig.4 (c). For the switching curves at the beginning of I-V test, a forming process is required. The current compliance (CC) is applied to 10 mA. In Fig. 4 (a) when the voltage goes to 6.0 V, the current increases rapidly and this show the OFF state switches to the ON state. During the second I-V sweep at the negative side, when the voltage goes to -6.0 V, the current decreases rapidly which shows the ON state switches to the OFF state. In Fig. 4 (b) when the voltage goes to 10.0 V, the current increases rapidly and this show the OFF state switches to the ON state. During the second I-V sweep at the negative side, when the voltage goes to -2.0 V, the current decreases rapidly which shows the ON state switches to the OFF state. In Fig. 4 (c) when the voltage goes to 20.0 V, the current increases rapidly and this show the OFF state switches to the ON state. During the second I-V sweep at the negative side, the ON state are not hold any more. These are typical switching behavior of the classical filament type conduction. It shows that the Ti doping can effectively increase the carrier concentration and reduce the resistivity of NiO thin films. It has been proven by Fig. (a) and (b). The low resistive state (LRS) resistance in Fig. (b) is less than that in Fig. (a). However, with increasing the Ti concentration, the LRS resistance is increased when the Ti molar ratio concentration is increased to 0.06 and that means the Ti doping is saturated. In Fig. 4 (d), it is a typical semiconductor I-V curve.

4. Summary

Sol-gel process is a convenient ways for doping. The surface roughness (RMS) is influenced by doping when the Ti dopant concentration is increased while the RMS value is also increased. The Eg is decreased when the amount of Ti dopant is increased. The chemical state of Ti dopant is studied by XPS. It shows that Ti exits in Ti-O bond. O1s (1) in Ti-O bond is increased when the amount of Ti dopant is increased. On the other hand, O1s (2) in Ni-O bond is decreased when the amount of Ti dopant is increased. When the concentrations of Ti come to 0.06, Ti doping is saturated. I-V curves shapes are bipolar except when the concentration of Ti is 0.08.

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6. References

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