

## Diffusion Barrier Properties of W-C-N Thin Film between $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and Si

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**Tungsten carbon nitride (W-C-N) thin films were produced by reactive radio frequency (RF) magnetron sputtering of tungsten in Ar-N<sub>2</sub> gas mixture. The effects of the variation of nitrogen partial pressure on the composition, and structural properties of these films as well as the influence of post-deposition annealing have been studied. When  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  was coated on the W-C-N/Si substrate, coercivity ( $H_c$ ) and magnetization at room temperature shows 58.73 Oe, and 29.4 emu/cc, respectively. In order to improve the diffusion barrier characteristics, we have studied the impurity behaviors to control the ratios of nitrogen and carbon concentrations.**

**Key words :** tungsten carbon nitride thin film

### I. Introduction

Tungsten has been studied as a low resistive refractory metallization material in ultra large scale intergrated (ULSI) circuit metallization schemes. Particularly, thermally stable metallization technique is one of the important submicron processes because miniaturization cause serious problems such as an increase in contact resistance due to the silicidation and degradation of shallow junction by the interdiffusion of metal and Si during heat treatment [1]. So we suggest tungsten carbon nitride ternary compound diffusion barrier as an effective thermal stability and describe the effects of the N and C concentration on phase transition, as well as the metallurgical and barrier properties of W-C-N thin films. In addition, These days the doped perovskite manganites  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  (where A is a divalent alkaline-earth ion) have received much attention because of the colossal magnetoresistance (CMR) effect observed in the optimally doped sample ( $x \sim 0.3$ ). Particularly, epitaxial thin films possess their potential in technological applications such as magnetoresistive sensors and magnetic random access memory [2]. That's why we have studied magnetic properties of LSMO on tungsten carbon nitride (W-C-N) ternary compound thin film such as roughness and magnetoresistance, and so on.

### II. Experimental Details

Tungsten carbon nitride (W-C-N) thin films were deposited

on Si substrates by using a magnetron sputtering system. Substrates were p-doped (100) oriented Si wafers with resistivities of 5~6  $\Omega$ -cm. Prior to the sputtering, substrates were cleaned, spun-dried, and loaded into the reactor. The sputtering targets were a tungsten (W) disk with a purity of 99.99% and a tungsten carbide (WC) disk with a purity of 99.95%. Before the deposition, Ar pre-sputtering was performed to remove the native oxide layer on the target. The deposition temperature was maintained at room temperature during the sputtering process. The flow rates of N<sub>2</sub> and Ar gases were separately controlled with mass flow controllers. The total pressure of (N<sub>2</sub>+Ar) in the sputtering reactor was kept at a constant value of 7 mTorr while the N<sub>2</sub> gas flow ratio, N<sub>2</sub>/(N<sub>2</sub>+Ar), were varied from 0 to 2.5%. The co-sputtering condition was that the RF power density of the W target was varied from 4 to 7 W/cm<sup>2</sup> and that of the WC target fixed at 0.25 W/cm<sup>2</sup>, respectively and the thickness of W-C-N film was varied from 500 to 1,000 Å. The resistivity and the crystalline structure of the as-deposited W-C-N thin films were determined by using four point probe method and X-ray diffraction (XRD), respectively. After thermal treatment at various temperatures for 30 minutes in N<sub>2</sub> ambient environment, the phase transformation of the W-C-N thin film and interfacial reaction of the W-C-N/Si thin film were investigated by using the XRD, respectively. Also water-based coating sol for LSMO thin film was prepared using the mixture of acid, distilled water, and ethanol as solution.  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  sample were coated on W-C-N/Si substrate by using spin coating method. Then it is annealed at 800 °C for 180 minutes in O<sub>2</sub> ambient, increase

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and decrease temperature is 5 per minutes gradually.

### III. Results and Discussion

Figure 1 shows the resistivities of W-C-N/Si films as a function of N<sub>2</sub> partial pressure ratio (N<sub>2</sub> PPR). When N<sub>2</sub> PPR is increased gradually, the resistivities are also increased up to N<sub>2</sub> PPR=3.0%, and then the resistivity value is increased drastically from N<sub>2</sub> PPR of 5% to 7.5%. The resistivity of the deposited W-C thin film is 170 μΩ-cm. In the case of N<sub>2</sub> included nitrogen samples,

the resistivity of the W-C-N thin film increases as N<sub>2</sub> partial pressure ratio increases.

Figure 2 shows the XRD patterns of W-C-N thin films as a function of N<sub>2</sub> partial pressure ratio from 0 to 2.5%. Figure 3(a) shows that (110) oriented α-W peaks at 40.4°, and (200), (211), (320), (321) oriented β-W peaks at 35.4°, 44.1°, 66.7°, 69.8° are observed. Figure 3(b) and 3(c) show that (100) oriented a δ-WN peak at 35.6°, (110), (211) oriented α-W peaks at 40.4°, 73.4°, (200) oriented a β-W<sub>2</sub>N peak at 43.9°, and (320), (321) oriented β-W peaks at 66.8°, 70.2° are observed. These peaks are a little

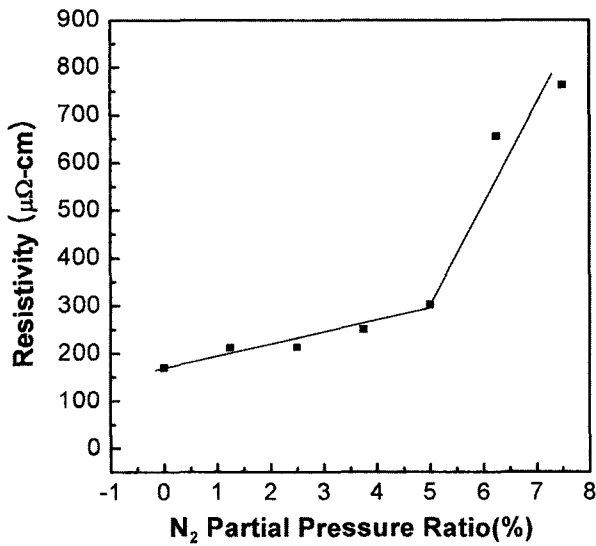


Fig. 1. Resistivity of W-C-N thin films of pressure at 7 mTorr as a function of N<sub>2</sub> PPR.

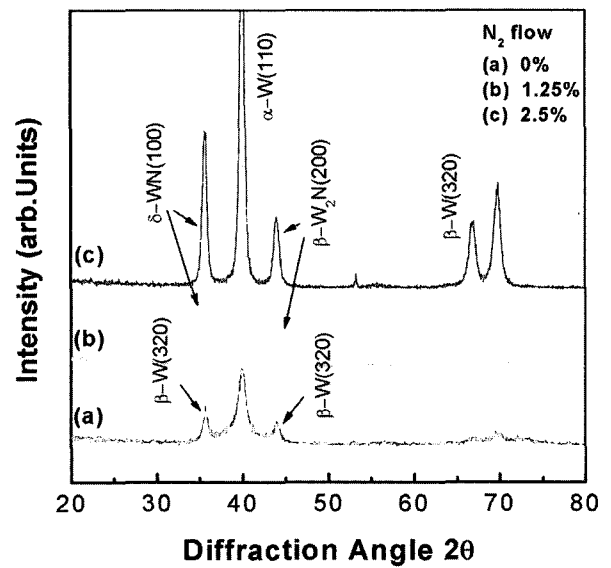


Fig. 3. XRD patterns of W-C-N thin films as a function N<sub>2</sub> PPR of (a) 0%, (b) 1.25%, (c) 2.5%, respectively.

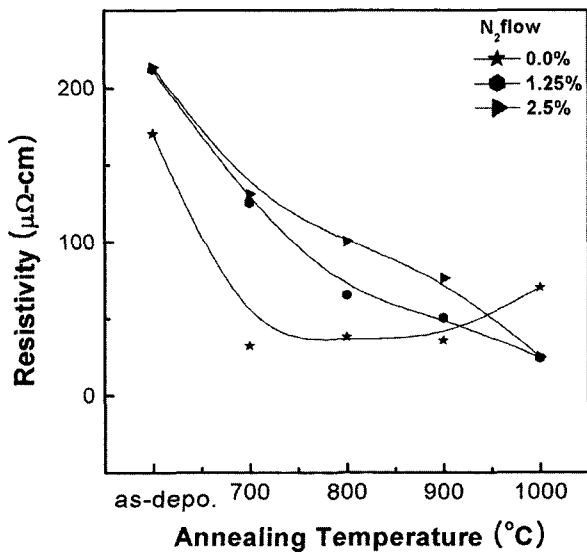


Fig. 2. Resistivity of W-C-N thin films as a function of vacuum furnace annealing temperature.

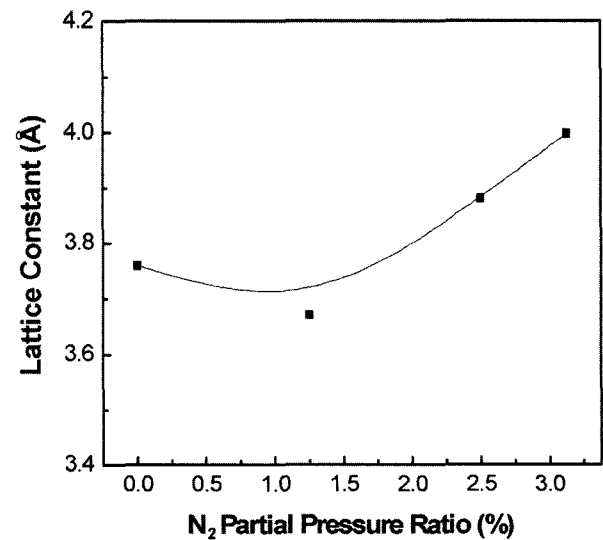
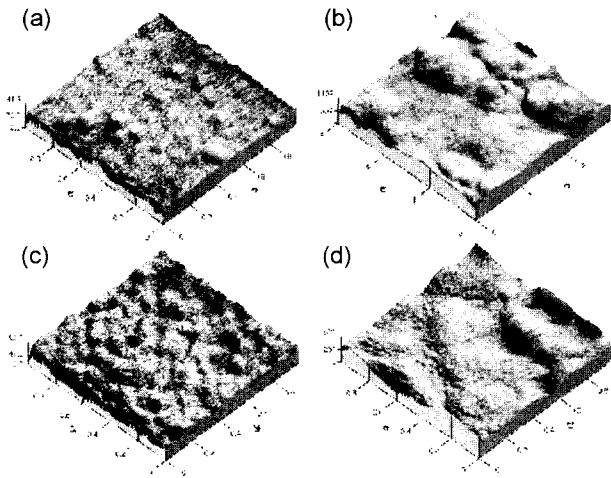
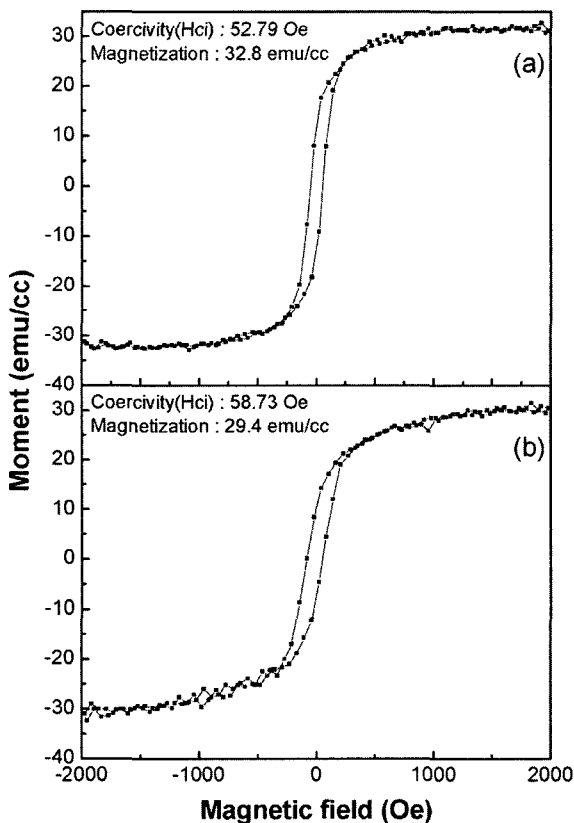


Fig. 4. Lattice constant of W-C-N thin films as a function of N<sub>2</sub> PPR from 0 to 3.13%.



**Fig. 5.** Atomic force microscopy (AFM) images of (a) W-C-N/Si and (b) LSMO/W-C-N/Si thin films at N<sub>2</sub> PPR of 0%, (c) W-C-N/Si and (d) LSMO/W-C-N/Si thin films at N<sub>2</sub> PPR of 1.25% as a function of pressure at 7 mTorr.



**Fig. 6.** Magnetization hysteresis loop of LSMO/W-C-N/Si thin film at N<sub>2</sub> PPR of (a) 0 and (b) 1.25% at pressure of 7 mTorr with field in-plane direction up to 0.2 T at room temperature.

bit shifted thus, one can infer dominance of the nitrogen concentrations over the carbon concentration. These results mean that the increase of nitrogen concentration affects

the structure of W-C-N thin film.

Figure 4 shows lattice constant of W-C-N thin films as a function of N<sub>2</sub> partial pressure ratios from 0 to 3.13%. The lattice constant of sample without nitrogen is 3.7601 Å. When N<sub>2</sub> PPR is 1.25%, the lattice constant value is decreased as a value of 3.76 Å up to 3.67 Å after then the lattice constant is increased from 3.88 Å to 3.99 Å. In this result, we may confer that carbon and nitrogen compete in making reaction with tungsten.

Figure 5 shows the atomic force microscopy (AFM) images of W-C-N/Si and LSMO/W-C-N/Si thin films. The LSMO/W-C-N/Si rms roughness of 7 mTorr is higher than W-C-N/Si thin films. The rms roughness value of (a) and (c) W-C-N/Si and (b) and (d) LSMO/W-C-N/Si thin films are 7.12 and 4.135 Å, and 65.524 and 63.483 Å, respectively.

Figure 6 shows magnetization hysteresis loop of (a) LSMO/W-C/Si and (b) LSMO/W-C-N/Si thin film at room temperature with field in-plane direction up to 0.2 T. It is generally believed that the in-plane and out-plane thin films are indifferent strain states because of the lattice mismatch in heterostructure [4]. The saturation moment ( $M_s$ ) is (a) 32.8 emu/cc and (b) 29.4 emu/cc. The coercivity ( $H_c$ ) of these films are (a) 52.79 Oe and (b) 58.73 Oe.

#### IV. Conclusions

The effects of the composition and structural properties of W-C-N/Si thin films for various nitrogen partial pressure ratios, as well as the influence of post-annealing behavior have been studied. When La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> was coated on the W-C-N/Si substrate, coercivity ( $H_c$ ) and magnetization at room temperature showed 58.73 Oe, 29.4 emu/cc, respectively. In order to improve the diffusion barrier characteristics, we have studied the impurity behaviors to control the ratios of nitrogen and carbon concentrations.

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