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Magnetic Effects of $La_{0.67}Sr_{0.33}MnO_3$ on W-C-N Diffusion Barrier Thin Films

Moon Kyoo Song, Ji Seop So, In Bo Shim and Chang Woo Lee*

Dept. of Nano & Electronic Physics, Kookmin University, Seoul 136-702, Korea

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In the case of contacts between semiconductor and metal in semiconductor devices, they tend to be unstable because of thermal budget. To prevent these problems we deposited W-C-N diffusion barrier for preventing the interdiffusion between metal and semiconductor. The thickness of the barrier is 1,000 Å and the pressure is 3 mTorr during the deposition. In this work we coated LSMO (CMR material) on W-C-N diffusion barrier and then we studied the interface effects between LSMO layer and W-C-N diffusion barrier. We got results that the magnetic characteristics of LSMO thin film are still maintained after annealing at 800 °C for 3 hr because W-C-N thin diffusion barrier was prevented the diffusion of oxygen between LSMO and Si substrate.

Key words : W-C-N thin film, $La_{0.67}Sr_{0.33}MnO_3$

I. Introduction

The device size and submicron process causes serious problems in conventional metallization due to the solubilities of silicon and metal at the interface, such as an increasing contact resistance in the contact hole and interdiffusion between metal and silicon [1]. Thus, the size of multilevel interconnection of ULSI devices is critical, and it is necessary both to reduce the RC time delay for device speed performance and to enable higher current densities without electromigration [2, 3]. Therefore, to improve the thermal stabilities of interconnection metals, it has been proposed the diffusion barrier to prevent from interaction between metals and semiconductors. Recently, the topic of magnetic semiconductor is very interesting because MRAM is one of candidate of next generation memory devices. Another thing, ferromagnetic materials have been studied for magnetic thin film and sol-gel method has been successfully used for the synthesis of ultrafine metallic and ceramic powder [4]. These thin films have perovskite structure and half-metallic nature [5]. But it can not be used direct on Si substrate because oxygen inside of magnetic thin film penetrates throughout the Si substrate easily. Thus, if ferromagnetic thin films may adopt the Si substrate, it must have diffusion barrier between the magnetic thin film and Si substrate for preventing the diffusion of oxygen and other impurities, In this work, we suggest a tungsten carbon nitride (W-C-N) ternary compound thin film for $La_{0.67}Sr_{0.33}MnO_3$ thin film. We also examine the effects of the nitrogen concentration during the phase transition, as well as the metallurgical and barrier properties of W-C-N thin films.

*Tel: (02) 910-4756, E-mail: cwlee@kookmin.ac.kr

II. Experimental Details

We deposited the tungsten carbon nitride thin films on Si substrate by using RF magnetron sputtering system. The substrate was phosphorus doped (100) oriented Si wafers with resistivities of 5~6 Ω-cm. Prior to the sputtering, the substrates were cleaned, spin-dried, and loaded into the reactor. The sputtering targets were W with a purity of 99.99% and a WC 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 total pressure of (N_2+Ar) in the sputtering reactor was kept at a constant value N_2 of 3 mTorr while the gas flow ratio, $N_2/(N_2+Ar)$, was varied from 0 to 5 %. The cosputtering condition is that the RF power density of W target was fixed at 5 W/cm^2 and that of WC target was varied from 0.4 to 0.7 W/cm^2, respectively, and the thickness of W-C-N film was fixed at 1,000 Å. The impurities of the W-C-N thin films provided a stuffing effect that was very effective for preventing interdiffusion between LSMO thin films and silicon substrate during the subsequent high temperature annealing process. The resistivity and the crystalline structure of the W-C-N thin films were determined by using four point

probe measurement and X-ray diffraction (XRD), respectively. After thermal treatment at various temperatures for 30 minutes in N_2 ambient, 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 XRD. Thermal stability of W-C-N diffusion barrier were determined for various annealing temperature and for various nitrogen concentrations.

LSMO thin film was coated on the W-C-N thin films. Water-based coating sol for LSMO thin film was prepared using the mixture of acid, distilled water and ethanol as solution. The stoichiometry of LSMO thin film is La(0.67)Sr(0.33)Mn(1)O(3). Spin coating of LSMO thin films was applied for spin-coating under 1 atm in air at 4,000 rpm for 30 minutes, the thickness of 1,000 Å was achieved after four times coating. This film was dried on the hot plate for 1 minute at 80 °C. After then it was annealed at 800 °C for 3 hours in atmospheric pressure, During the increasing and decreasing temperature, the ramping rate is 5 °C per minute gradually.

III. Results and Discussion

Figure 1 shows the deposition rate (Å/min) and resistance (Ω/sq) vs N_2 partial pressure ratio (≡N_2 PPR) (%) of W-C-N/Si thin films. The deposition rate is almost gradually decreased from 87 to 80 Å/min as N_2 PPR of 0 to 3.75 %. After then the deposition rate is drastically decreased at 69.3 Å as the N_2 PPR is 5 %. The deposition rate varies from 87 Å/min to 69 Å/min. It has minimum value of about 69 Å/min when N_2 p.p.r. is 5 %. The value is 83 Å/min at N_2 PPR 0%, 82 Å/min at 1.25%, 80 Å/min at 2.5 % and 79 Å/min at 3.75 % respectively. In accordance with the various N_2 PPR, the resistance was increased linearly.

Figure 2 shows the resistitivities of W-C-N thin films as a function of the annealing temperature for N_2 PPR (0 % and 1.25 %) of the W-C-N/Si thin films. The resistivity of the deposited W-C-N thin film (N_2 PPR of 0 %) without

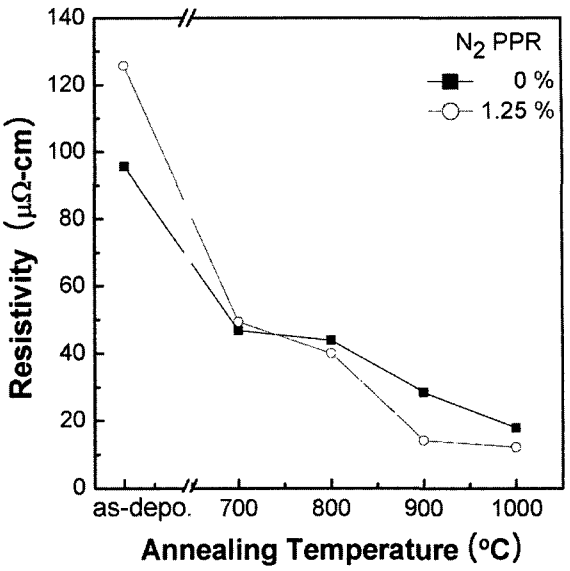

Fig. 2. Resistivities of W-C-N/Si thin films of N_2 PPR of 0 and 1.25 % for as-deposited, and annealed states at 700, 800, 900 and 1,000 °C for 30 min.

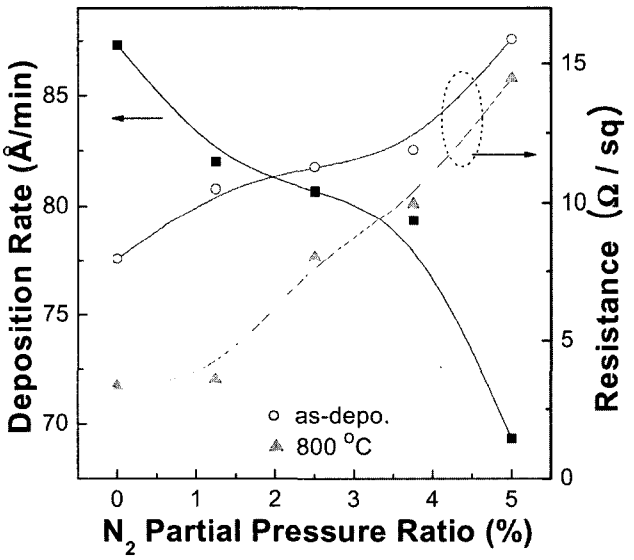

Fig. 1. Deposition rate and resistance of N_2 partial pressure ratio of 0, 1.25, 2.5, 3.75 and 5 % W-C-N/Si thin films for as-deposited and annealing at 800 °C for 30 min.

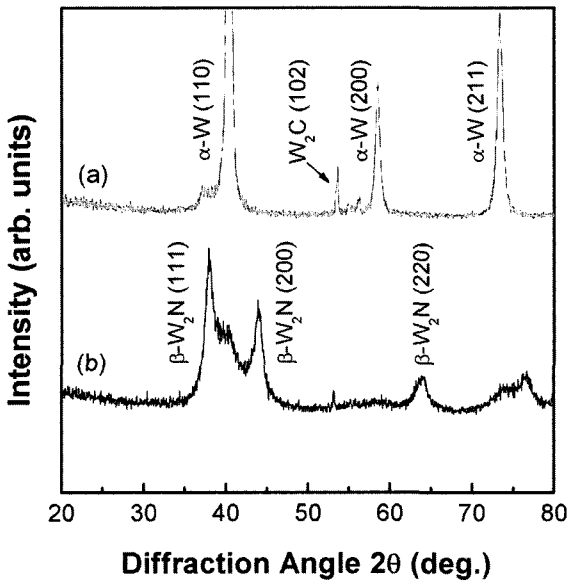

Fig. 3. XRD patterns of W-C-N/Si thin films of N_2 PPR of (a) 0 % and (b) 1.25 % after annealing at 800 °C for 30 min.

thermal treatment is 95 μΩ-cm and the resistivity is decreased as annealing temperature increases up to 1,000 °C. In case of annealed samples, the resistivity of W-C-N thin film is decreased as the annealing temperature increases. After annealing over than 700 °C, the resistivity of W-C-N thin film for N_2 PPR 1.25 % is lower than that of the N_2 PPR of 0 %.

Figure 3 shows the XRD patterns of the W-C-N films with the N_2 PPR of 0 % and 1.25 % after annealing at 800 °C for 30 min. Fig. 3(a) shows that the (110), (200) and (211) oriented α-W peaks are observed at 40.4°, 58.5° and 73.3° and the (102) oriented W_2C peak is observed at 53.5°. Fig. 3(b) shows that the (111), (200), and (220) oriented β-W_2N peaks are observed at 37.9°, 43.8°, 63.8° respectively.

If we incorporate small amount of nitrogen additionally in Fig. 3(b), W-C-N thin diffusion barrier has W_2N structure. This structure is well known and very effective for preventing the impurities from metal or magnetic thin film to Si substrate [6]. That is why we are so interested in the reaction between LSMO thin film and Si substrate.

Figure 4 shows a comparison of XRD peaks of LSMO/W-C-N/Si thin film of N_2 PPR of (a) 0 % and (b) 1.25 % after annealing at 800 °C for 30 min. The (110), (111), (200), (211) and (220) oriented LSMO peaks are observed at 32.9°, 40.5°, 47.1°, 58.4° and 68.8°, respectively. The XRD intensity of LSMO/W-C-N/Si thin film of N_2 PPR of (b) 1.25 % is stronger than that of 0 %. Thus, We can see that the crystallinity of LSMO structure is well formed

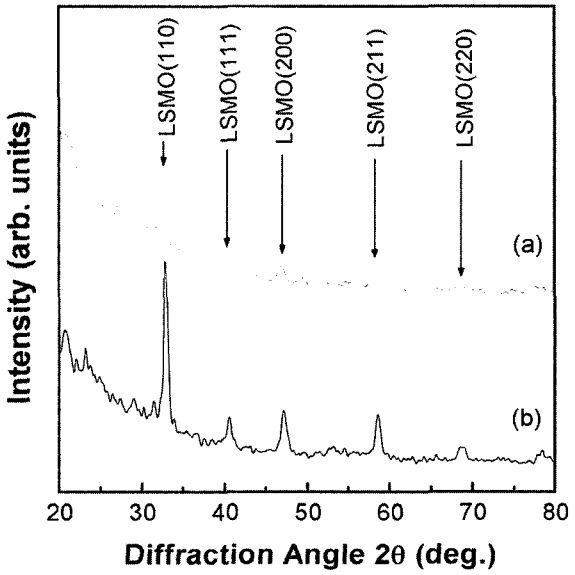

Fig. 4. XRD patterns of LSMO/W-C-N/Si thin films of N_2 PPR of (a) 0 and (b) 1.25 % after annealing at 800 °C for 3 hr in oxygen ambient.

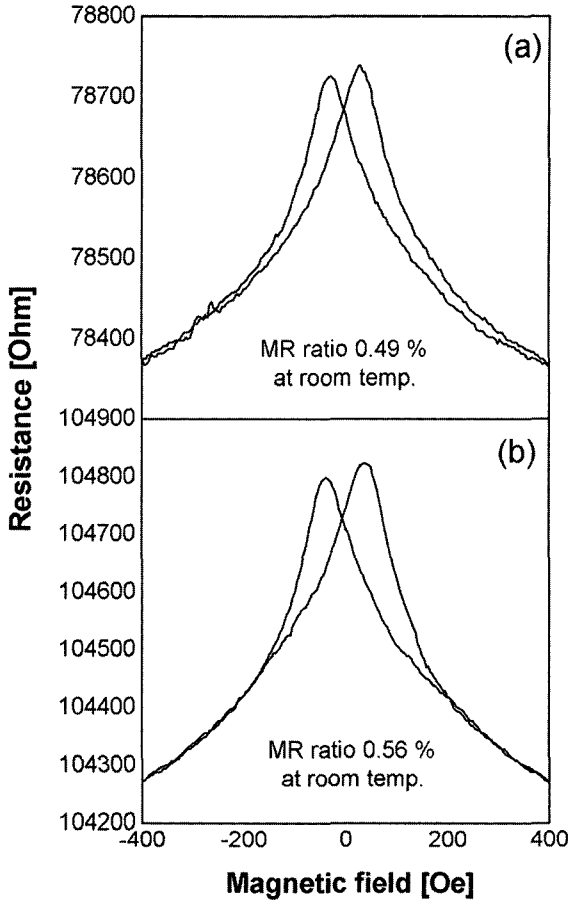

Fig. 5. MR ratio of LSMO/W-C-N/Si thin films of N_2 PPR of (a) 0 and (b) 1.25 % after annealing at 800 °C for 3 hr.

in case of N_2 PPR of 1.25 % in Fig. 4(b). In accordance with these XRD patterns of LSMO/W-C-N/Si, it is plausible that the good crystallinity of LSMO structure is due to the diffusion barrier characteristics of W-C-N thin film (N_2 PPR of 1.25 %) which are preventing the oxygen diffusion much better than that of W-C thin film (N_2 PPR of 0 %).

Figure 5 shows the MR ratio of LSMO/W-C-N/Si thin films after annealing at 800 °C for 3 hr. The MR ratio of the thin film with N_2 PPR of Fig. 5(b) 1.25 % is 0.56 % and this is bigger than that of Fig. 5(a) (N_2 PPR=0 %, MR ratio=0.49 %). From these results, we can infer that the structure of W-C-N thin films of N_2 PPR of 1.25 % has more effective magnetization. Because the crystalline is well structured as we saw at Fig. 3 and Fig. 4.

IV. Conclusions

We already got the results that W-C-N is very interested in barrier metal between metal and Si. In this work, we found that LSMO is also coated on W-C-N thin film and magnetization (MR ratio is 0.56 %) and crystallinity are

well formed. Especially, nitrogen (N_2 p.p.r 1.25 %) makes a thin film better. This means that W-C-N diffusion barrier is better than W-C diffusion barrier. At the same time, magnetic effect of LSMO is formed on W-C-N diffusion barrier. In addition, we can see a good match with LSMO at 800 °C which is a good annealing temperature for LSMO.

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