

Stress-strain curves derived from continuous nano-indentation of W-C-N films

Soo In Kim¹, Kyu Young Lee¹, Joo Young Kim¹, Hwan Won Oh¹,
Hyun Woo Kim², and Chang Woo Lee^{1*}

¹Nano & Electronic Physics, Kookmin University, Seoul 136-702, Korea

²Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Korea

* Corresponding author: cwlee@kookmin.ac.kr

Keywords: W-C-N diffusion barrier, indentation, stress-strain curve, stress – depth curve

In semiconductor metallization processes, diffusion barrier is essential for preventing diffusion between metal (Cu: copper) and Si (silicon). However, the Cu has some problems such as easy reaction, poor adhesion, and diffusion into Si. In this study, we suggest tungsten -carbon -nitride (W-C-N) thin films for diffusion barrier that were made by rf magnetron sputtering. Subsequently, heat treatments execute as high temperature up to 800 °C. The films were analyzed continuous stress – strain test according to depth (from surface to Si substrate) by in-situ nano-indenter. The elastic modulus (Er) and hardness (H) of W-C and W-C-N thin films are changed from 152.08 to 168.31 GPa and from 12.05 to 13.2 GPa, respectively. After annealing at 800 °C, the Er and H values are decreased compared with as-deposited state of W-C and W-C-N films from 105.1 to 131.31 GPa and 2.25 to 11.9 GPa, respectively. From the stress – depth graph, the W-C-N thin film was more stable than that of W-C film after annealing up to 800 °C. From these results, the W-C-N thin film is more effective to prevent interdiffusion between Cu and Si.

1. Introduction

Through the rapid development of electronic industry, the machines and electronic appliances need nano-size line width device. The Al (aluminum) interconnects have been primarily used for circuit lines but the specific resistance of Al has a higher value than that of Cu (copper). Therefore, copper has been used to construct circuit lines for devices with narrower line width. However, the Cu has some problems such as reaction with Si easily, poor adhesion, and diffusion into the substrate of Si (silicon). So we suggest tungsten related diffusion barrier added impurities to insert between Cu and Si [1-3]. The barrier has low sheet resistance and not to react with Si and Cu for high temperature annealing process.

In this paper, the W-C-N diffusion barrier was deposited by rf magnetron sputtering method and it needs to be characterized. Recently, we have been measured through spectroscopy equipments such as XRD (X-Ray Diffraction), XPS (X-ray Photoelectron Spectroscopy) and so on. These measurement methods are average value of sample spot about over than micro meter's area in macro scale.

Thus, we study the nano-surface properties of W-C-N diffusion barrier according to the concentration of nitrogen impurities of as-deposited and annealed

state annealing for various annealing temperature (up to 800 °C). Also, the Nano-indentation system was used for analyzing the deformational characteristics of W-C-N thin film such as yield points, hardness, and surface stability.

2. Experimental

There is a way to understand the features of the surface called uniaxial compressing test. In this test, the stress only occurs in one direction; compressive or tensile. During the indentation test, the stress occurs in every direction. However, there is a similarity between compressive or tensile tests when analyzing the results, compressive or tensile methods also need to transform the load - depth graphs to stress - h_c graphs (where h_c is contact depth). In the stress - h_c curves, the stress means the pressure of the indenter and the h_c means the contact depth of indenter [4].

$$\text{Indentation Stress } (\sigma) = \frac{F_{\text{Load}}}{A_c} \quad (1)$$

From the load - depth graph, we can get the value of F_{Load} . The evaluation of the stress requires knowledge of both the applied force F_{Load} and the projected contact area A_c . During the indentation, A_c is computed from the contact depth (h_c). The

contact depth h_c is earned through the equation (2) [3-6].

$$h_c = h - \epsilon \frac{F_{Load}}{S} \quad (2)$$

(ϵ : geometrical constant of the tip, S : stiffness)

Because we used the Berkovich tip, the value of ϵ is about 0.75. Stiffness is defined as the initial slope of the unloading curves like (3) [5-6].

$$\text{Stiffness (S)} = \frac{F_{Load}}{dh} \quad (3)$$

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{s}{\sqrt{A_c}} \quad (4)$$

From the stiffness, one of the important mechanical features, elastic modulus, can be earned through the formula (4). β is a constant related to the geometry of the indenter tips. The value of β is 1 for spherical tips, 1.012 for Vickers tips, and 1.034 for Berkovich tips. To get the area A_c , we did the tip area calibration and through the fitting procedure, the equation (5) is earned [7-9].

$$A_c = 24.5 h_c^2 + \sum_{i=0}^8 C_i h_c^{\frac{1}{2i}} \quad (5)$$

After all the calculation, the final formulas to compute the values of stresses are below.

$$\text{Indentation Stress } (\sigma) = \frac{F_{Load}}{24.5 h_c^2 + \sum_{i=0}^8 C_i h_c^{\frac{1}{2i}}} \quad (6)$$

The W-C and W-C-N thin films were deposited by rf magnetron sputtering. The purity of W-C target is 99.95% and of W target is 99.99%. W-C and W-C-N thin film was used nitrogen gas flow rate of 0 and 2 sccm, respectively and rf power were fixed. The total pressure during the depositions was kept at 3×10^{-3} Torr in room temperature. After deposition, the samples were annealed at 800 °C.

Nanoindentation was performed on the nano-surfaces by the Triboindenter (Hysitron Corp.) by indenting for 5 seconds until the force reaches 3000 μ N, hold still for 5 seconds, and unload for 5 seconds. Berkovich tip was used to indent the

sample. Indentation was executed 16 times per each sample and thus, totally 64 indentations were performed.

3. Result and Discussion

Figure 1 shows the load force - depth graphs that the indentation datas are almost the same in sample 1, 3 (W-C and W-C-N thin films for as-deposited state), and 4 (W-C-N thin film for annealed state). On the other hand, the result of sample 2 (W-C thin film after annealed) is move back and it means that the hardness value of sample 2 is changed less than other samples. From these datas, the elastic modules (E_r) and hardness (H) are calculated, and table 1 shows that the values of E_r and H according to the N_2 gas flow and the annealing temperature at 800 °C, respectively.

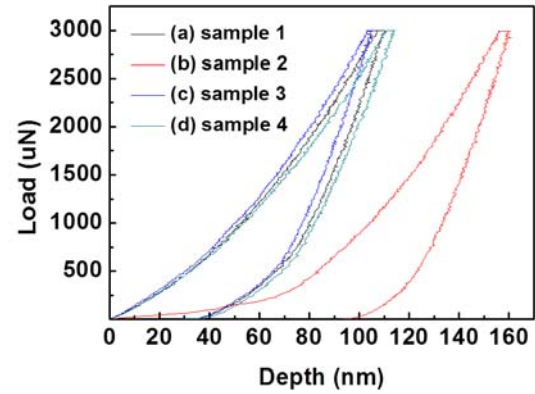


Fig. 1. Load force - depth graph of samples as a function of nitrogen gas flow and post annealing.

	Not – annealed (sample 1 and 3)		Annealed at 800 °C (sample 2 and 4)	
	Er (GPa)	H (GPa)	Er (GPa)	H (GPa)
0 sccm	152.08	12.05	105.1	2.25
2 sccm	168.31	13.2	131.31	11.9

Table 1. Elastic modulus and hardness of W-C and W-C-N thin film as a function of N_2 gas flow and post annealing.

The elastic modules and hardness values of as-deposited W-C and W-C-N thin films are changed from 152.08 to 168.31 GPa and from 12.05 to 13.2 GPa, respectively. After annealed state annealing at 800 °C, the Er and H values are changed from 12.05 to 13.2 GPa and from 2.25 to 11.9 GPa and these values are less than that of as-deposited W-C and W-C-N films, respectively. From these results, nitrogen is effective that the W-C-N thin film included nitrogen makes more flexible and hard.

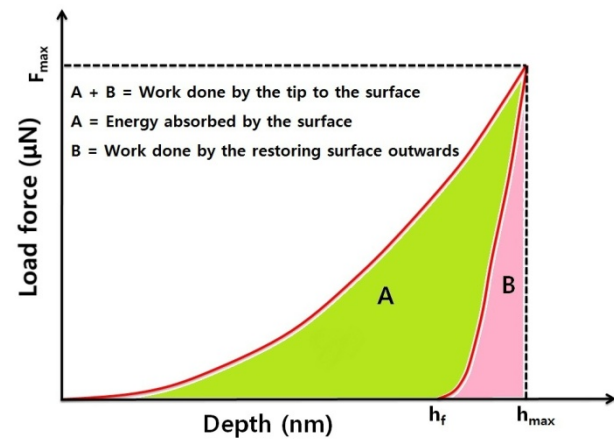


Fig. 2. Schematics of load force - depth graph during sharp indentation of a ductile material and relation of surface energy during indentation.

	Sample 1	Sample 2	Sample 3	Sample 4
Average absorbed energy (10^{-12} J)	61.8	82.6	58.23	63.67
Standard deviation of 16 points	0.38	1.1	0.44	0.37

Table 2. Average absorbed energy and Standard deviation of 16 points at each sample.

Especially, the hardness value of W-C thin films was decreased from 12.05 to 2.25 GPa (81.32 %) after annealing at 800°C. However, the hardness value of W-C-N thin films was a little decreased from 13.2 to 11.9 GPa (9.85 %). From precedent results, it is plausible that the nitrogen is able to protect diffusion effectively so called impurity effect but the W-C film is reacted with Si substrate at 800°C.

Figure 2 shows the schematics of load force - depth graph during sharp indentation and relations of surface energy such as absorbed and restored energy. When the surface is restoring due to the elasticity, then surface is pushing outwards. The work done on nano-surface is equivalent to the area B. Therefore, area A can be interpreted as work (=energy) absorbed by the nano-surface. To analyze the absorbed and the restored energy of W-C and W-C-N thin films for as-deposited and annealed state by in-situ nano-indenter system, these sample properties are shown in Table 2. The result of sample 2 is more dispersed. It means that the surface of W-C thin film after annealed state is not more uniform. The value of standard deviation calculated from 16 points is far bigger than that of other three samples. From these results, Er and H of sample 1, 3 and 4 keep more stable condition than that of sample 2. The higher absorbing energy means that less energy is coming out from the surface during the restoring stage. From these results, W-C-N thin film included N₂ gas flow of 2 sccm has good physical properties and protects interdiffusion even annealing up to 800°C. Thus, W-C-N thin film is more stable than that of W-C thin film for annealing process. The W-C thin film not included N₂ gas flow has damaged to unbearable stress. Furthermore, annealed samples seem to be more absorbing energy than as-deposited samples. The larger absorbing energy means that the less energy was coming out from the thin film surface during the restoring stage. This is related to the elasticity. If thin film has absorbed more energy, then the property of film is less elastic. Therefore, the annealed samples are less elastic than the other two samples. Actually, the elastic modulus of thin film is decreased after the annealing process. On the other hand, the mechanical properties and stabilities of thin film about depth direction have some problems, so we tried to analyze the thin film as a function of depth direction and of annealing temperature in W-C-N thin film. Figure 3 shows the stress distribution according to depth (surface to substrate of W-C and W-C-N thin films). Figure 3 also shows the typical characteristic value of elastic - plastic mechanical property. The first influenced point means the critical stress of thin films and the depth point is about 12 nm. The graph of sample 1, 3 and 4 is quite similar but sample 2 is different. This is means that

the mechanical property of W-C thin film without nitrogen gas flow is changed according to depth profile

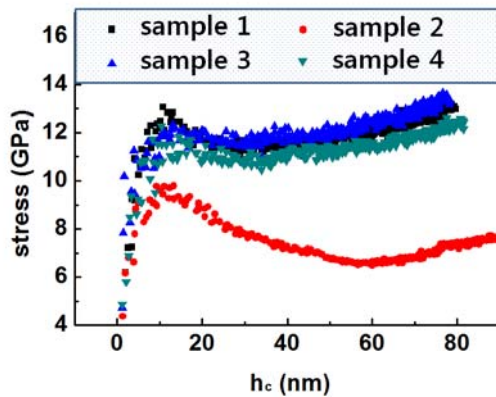


Fig. 3. Stress - h_c graph of W-C and W-C-N thin film as a function of nitrogen gas flow and post annealing.

To compare with the W-C and W-C-N thin films, sample 1, 3, and 4 has maximum stress of 12.5 to 13 GPa at about 12 nm, but the stress value of sample 2 is about 10 GPa at about 12 nm. From previous studies, the W-C thin film has damaged at annealed state and those results were analyzed XRD, XPS, and so on. But these results are averaged by right size and depth transmittance [1]. However, the W-C-N thin films added N_2 gas flow of 2 sccm had kept similar stress at all about depth whether annealing was executed or not. This means that the W-C-N thin film with added nitrogen is thermally more stable than W-C thin film.

4. Conclusion

From the continuous indentation tests performed on 4 kinds of samples, stress - h_c curves are earned. Although, the W-C sample annealed at 800°C (sample 2) shows unstable degeneration, on the other hand, all other samples (sample 1, 3, and 4) revealed their feature of stability. These results show that the nitrogen is added at W-C films, they become more stable during high temperature annealing about 800°C than not added ones. Thus, there is no problem for using W-C-N films when they are used in semiconductor processes because when nitrogen is added, they are resistant to heat. These results

show the candidate of W-C-N film as an alternative diffusion barrier for Si based metal barriers.

Acknowledgment

This work was supported by research program 2011 of Kookmin University in Korea.

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