

The Studies of Thermally stability of Tungsten Carbon Nitride (W-C-N) Thin Films using Nano-Tribology

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For thin film deposition processes, the physical properties and mechanical properties of materials are more important under high-temperature annealing process because thin film can be easily changed during the heat treatment, such as phase, binding energy, surface stress and so on. In this study, the tungsten carbon and tungsten carbon nitride thin film deposited on silicon substrate were suggested as diffusion barriers using rf magnetron sputter. Then the thin films were annealed up to 800 °C for thermal damage. Nano-indenter was executed 16 points on the nano-surface of thin film to measure the thermal stability. The Weibull statistical distributions verified the uniformity of thin films after annealing. This nanotribology method provides statistically reliable information. From these results, the W-C-N thin film included nitrogen gas flow is more stable for thin film uniformities, mechanical properties, etc.

1. Introduction

From the rapid development of semiconductor integrated circuit, the film thickness of each layer was further reduced. From this reason, it does not overlook the issues of thin layers. So, the deposition process has more complex and diverse. The diffusion barrier was necessary to prevent each interlayer for high temperature annealing process that the thickness of diffusion barrier was tens of nanometer size [1-2]. Thus, the stability and the reliability of thin film surfaces are more important. The tribological performance is affected by physical and mechanical properties of the nano-surface and it is a subject of considerable interest. The nanoindentation method was applied for the characterization of nanomaterials, MEMS, semiconductor and so on [3-5]. Measurement of hardness is possible to approach the structural inhomogeneity of the nano-surface or surfaces inside about boundary, crystal grain, diffusion and so on. The material properties should be maintained during the annealing processes. If the characteristics of material changes, then the mechanical properties of material also be changed. The physical and mechanical properties of different points should be the same at the entire region. But measured properties are not an ideal and have some dispersion. Higher uniformity and low dispersion are important for semiconductor process. In this paper, the W-C-N

thin films were suggested as a diffusion barrier to prevent interdiffusion between Cu and Si substrate [6-7]. To analyze the thermal stability of W-C-N thin film using nano-indenter, we propose the Weibull distribution and this method provides useful and reliable information.

2. Experiment procedure

The W-C-N thin films were deposited by rf magnetron sputter according to the nitrogen gas flow (W-C and W-C-N thin films : nitrogen gas flow of 0 sccm and 2 sccm). The nano-indenter was used to determine the thermal stabilities and the mechanical properties of W-C or W-C-N thin films as-deposited and annealed state annealing for various annealing temperature (up to 800 °C). The hardness measurement of nano-indentation system (Hysitron instruments, Triboindenter) was converted into the compression test system. The nano-indenter was analyzed the film surface using a diamond indenter tip and reaction of indenter tip position (z-axis) and force are in-situ measured. The hardness is able to measure and the continuous indentation curve is able to analyze the change of surface tension. Each sample was measured total number of 16 points.

In general, estimation methods in Weibull distribution have two major ways, such as average rank method and median rank method.

We have calculated using the median-rank method because of the interval data type. We also used an atomic force microscopy (AFM) demonstrated as a powerful tool for probing the mechanical properties of material's nano-surface. AFM (Shimadzu WET-SPM) was use to measure the surface roughness and the surface image.

3. Result and discussion

The specimen processing method can be changed by the processing environment such as measured data, including the load test conditions, microstructure, and heat treatment conditions. Therefore, the statistical characteristics should be evaluated for the physical properties of thin film, as well as quantitative characteristics of the probability distribution. In addition, these datas are very important for reliability of structures, quality control, development and manufacture of nano-devices.

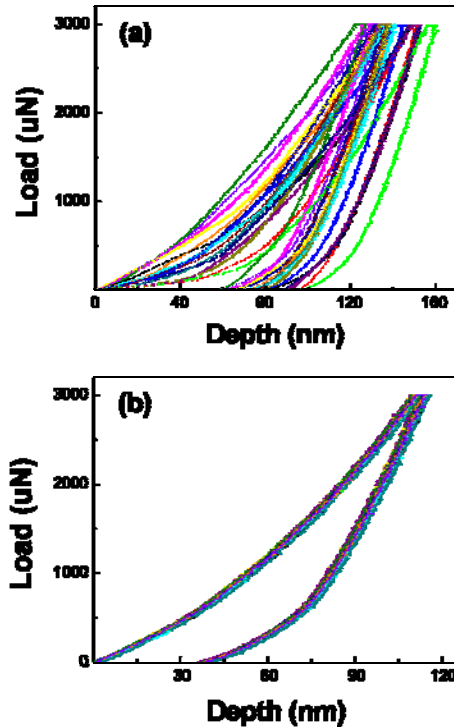


Fig. 1. The load - depth graph of W-C and W-C-N thin film after annealing at 800 °C according to the nitrogen gas flow of (a) 0 sccm and (b) 2 sccm.

Figure 1 shows the load - depth graph of W-C and W-C-N thin films after annealing at 800 °C for 30

min. The loading-unloading lines are repeated 16 times at a fixed loading unloading rate of 300 uN/s for load force of 3000 uN. The dispersion of W-C thin film (N₂ gas flow of 0 sccm) is more wide than that of W-C-N thin film (N₂ gas flow of 2 sccm). From these results, we can calculate the average, the dispersion, and the characteristic value of hardness and these results were shown in table 1. The hardness dispersion of W-C thin film was higher than that of W-C-N thin film (particularly at 800 °C). The increase of dispersion means that the uniformity of film surface was decreased. Film uniformity is critical issue. Acquired data are very reliable to understand the specific properties of nano-surface materials. The dispersion of W-C thin film at 800 °C is more broad than that of W-C-N thin film. Therefore, uniformity can be evaluated the quality of thin film by using Weibull distribution quantitatively. Many groups studied the Weibull statistics that is very useful to analyze the characteristic value of the material to figure out [8-10].

Thin film	Average (Gpa)	Dispersion	Characteristic value (Gpa)
W-C as-depo	12.433	0.1157	12.594
W-C 600 °C	10.817	0.0454	11.651
W-C 800 °C	7.069	1.1241	7.875
W-C-N as-depo	13.173	0.0381	13.270
W-C-N 600 °C	11.957	0.0431	12.848
W-C-N 800 °C	12.005	0.0492	12.106

Table. 1. The average, dispersion, and characteristic value of hardness of W-C and W-C-N thin film after annealing.

From these procedures, Median-rank regression estimates the Weibull distribution data linearly and then it performs simple linear regression on the transformed data in some specific region. Details for these procedures follow. The first step in median-rank determines P of the response variable. N is total number of experiments and i is i^{th} number of experiment.

$$P = (i - 0.5) / N \quad (1)$$

Then x-axis and y-axis data by ascending order were concerned Weibull modulus and characteristic value.

$$Y = \ln(\ln(1/(1 - P))) \quad (2)$$

$$X = \ln(H) \quad (3)$$

Here, H is the experimental data. In Fig. 2, the slope of the graph is Weibull modulus. The larger characteristic value of the Weibull modulus can be interpreted that the physical properties of thin film has good uniformity [11-12]. From the nano-indentation experiment, the hardness of thin films is obtained from the equation derived by I.N. Sneddon [13] and it was acquired from the load - depth (p - h) curves already shown in Fig. 1. Figure 2 also shows that the x value can be determined the characteristic value and interpreted the reliability of samples when y value $\{\ln(\ln(1/(1-p)))\}$ is 0.

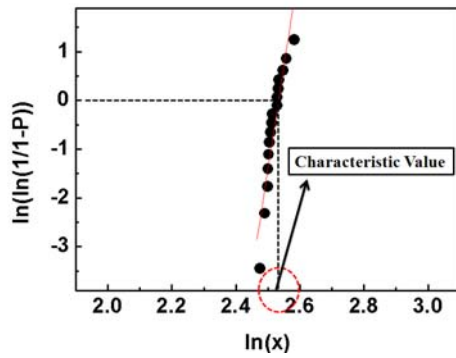


Fig. 2. The schematic diagram of Weibull modulus and characteristic value data.

Figure 3 shows the Weibull modulus value of W-C and W-C-N thin films according to annealing temperature. The Weibull modulus value of W-C-N thin films are changed from 76.883 to 92.507 at before and after annealed state. The value was increased by annealing at 800 °C. On the contrary, the Weibull modulus of W-C thin films are changed from 42.412 to 7.875 as an annealing temperature is changed from as-deposited state to 800 °C, respectively. This extraordinary change indicates that the W-C thin film has inhomogeneity. Hence, the mechanical property of W-C-N thin films has better uniformity than that of W-C film for high temperature annealing process. Therefore, the characteristic value of hardness in W-C film decreased severely according to annealing temperature. When we consider the hardness of thin film, then we go back to table 1. The characteristic value of W-C thin film decreases 12.594 GPa, 11.651 GPa, and 7.875 GPa according to increase annealing temperature. The characteristic value of W-C-N thin film decreases 13.270 GPa, 12.848 GPa and 12.106 GPa but total decrease value rate of W-

C-N thin film is smaller than that of W-C film. It is convinced that the nitrogen impurity provides stuffing effect for preventing the inter diffusion between barrier and Si interface after annealing up to 800 °C. The other mechanical properties of annealed states of the W-C and W-C-N thin film also be discussed later whether nitrogen is included or not.

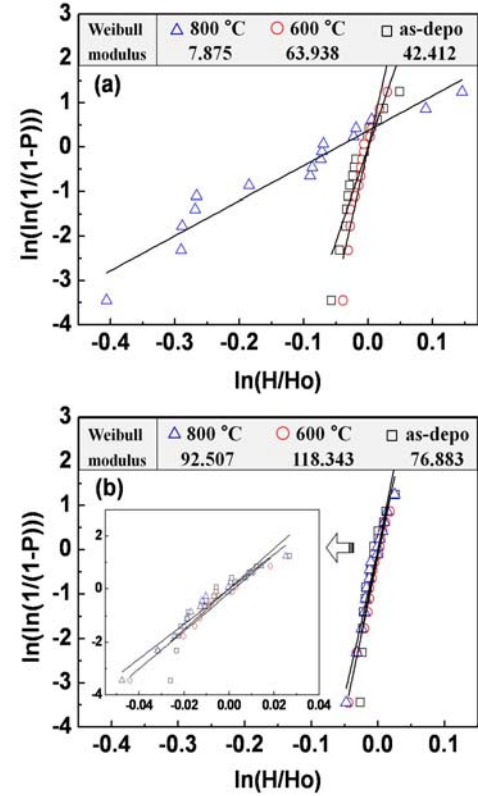


Fig. 3. The Weibull modulus fitting of hardness data for W-C and W-C-N thin film after annealing at 800 °C according to the nitrogen gas flow of (a) 0 sccm and (b) 2 sccm.

From these Weibull modulus results, it is plausible that the W-C thin film has serious damage on the surface. That is presumably caused by high scatter that is related with the surface roughness. To confirm the uniformity, thin films were measured by AFM in order to verify the nano-surface of thin films. Figure 4 shows that the RMS (root mean square) roughness value of W-C-N thin film is 0.427 nm (it's value of as-deposited state has 0.58 nm). But the RMS roughness of W-C thin film has as high value as 15.536 nm (it's value of as-deposited state has 0.68 nm). It has been confirmed that the surface of W-C-N thin film was so smooth because

of added nitrogen. On the contrary, the surface roughness throughout W-C thin film was very rough and uneven. It could be confirmed that the surface of W-C thin film was stressed by heat damage. The surface through thermal damage was changed its mechanical structure seriously. The Weibull modulus measurement was consistent with the result.

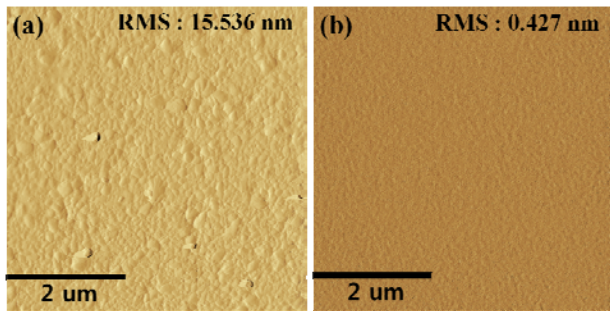


Fig. 4. The AFM image of W-C and W-C-N thin film after annealing at 800 °C according to the nitrogen gas flow of (a) 0 sccm and (b) 2 sccm.

4. Summary and remarks

Physical variation was occurred by stress at high temperature annealing process and physical variation of W-C-N thin film was less than that of W-C thin film because of the nitrogen incorporation. The weibull modulus value of W-C-N thin film was greatly increased due to the crystallization of amorphous state in high temperature environments. On the contrary, the W-C films of not contained nitrogen at high temperatures became inhomogeneity severely. The difference of weibull modulus between W-C and W-C-N films at high temperatures can be compared with the uniformity of thin films certainly. The W-C thin films were stressed by heat treatment and W-C film was transformed seriously.

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