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CHARACTERIZATION OF TiN/B-C-N MULTILAYERS BY TRANSMISSION ELECTRON MICROSCOPY, ION BEAM BACKSCATTERING, AND LOW ANGLE X-RAY DIFFRACTION

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The effects of Ar ion irradiation on the structure and stability of multilayered DC sputtered thin films of TiN/B-C-N have been studied. An increase of the bilayer repeat length to a maximum of 12.8% and departure of nitrogen from the film was observed indicating the interdiffusion between TiN and B-C-N layers. For the highest dose ($5x10^{16}$ ions/cm^2) the multilayered structure partly disappears. The various mechanisms are discussed in terms of stress-driven diffusion and viscous flow of atoms.

1. INTRODUCTION

Thin film multilayers have been the focus of extensive study due to various interesting properties and the broad range of applications from integrated circuits, magnetic storage media, to wear resistance coatings. The incorporation of ion implantation in semiconductor processing poses urgent need to establish a fundamental understanding of ion-induced defects and their impact on the structural integrity of materials. During ion irradiation of materials, significant atomic rearrangement can be achieved leading to changes in composition through mixing, enhanced diffusion, creep or viscous flow [1-3], and changes in mechanical state through, for example, relaxation of stresses [4]. These mechanisms become particularly important in multilayers where the presence of the numerous interfaces may play a significant role in aiding the diffusion process. In this study, a combination of transmission electron microscopy, ion beam backscattering, and low angle X-ray diffraction techniques were utilized to investigate the effect of 300 keV argon ion irradiation on the structure of the TiN/B-C-N multilayers.

2. EXPERIMENTAL

The multilayer structures were prepared by DC magnetron sputter deposition. The base pressure in the chamber was below $2x10^{-8}$ Torr. A 3 mTorr (25%Ar + 75% N_2) working gas pressure was used to sputter the target materials of Ti and B_4C at a power of 500W. The temperature of the substrate during deposition was lower than 100°C. The deposition rates were about 0.1 nm/s for TiN and about 0.2 nm/s for the B-C-N compound. The periodicity of the multilayer was controlled by the time of deposition for each target. The multilayers, consisting of 40 bilayers of 2 nm TiN and 2 nm B-C-N, were deposited on silicon {100} substrates. After deposition, the multilayers were irradiated with 300 keV Ar ions for doses between $5x10^{12}$ ions/cm^2 and $5x10^{16}$ ions/cm^2. According to the TRIM calculations [5], the

range of Ar ions is ~ 250 nm, which is larger than the thickness of the multilayers. Ion backscattering has been used to determine the average composition of the multilayers prior and post the irradiation. Microstructures of the films were studied by high resolution transmission electron microscopy (TEM). The repeat bilayer length and the interdiffusion between layers were analyzed by low angle X-ray diffraction. A detailed description of the data reduction was outlined in [6,7].

3. RESULTS AND DISCUSSION

Figure 1 shows a high resolution cross sectional TEM image of the multilayer after deposition. The first 2 nm thick layer on top of the silicon is SiO_2. It can be seen that TiN (dark contrast layers) is fully crystallized, while B-C-N layers appear to be amorphous. The corresponding electron diffraction pattern of the multilayers confirms that TiN is crystalline and there is a strong <111> texture of the TiN layers. After irradiation at low doses, TEM shows no major modification of the structure, except a small increase of the total thickness of the coating. Electron diffraction patterns taken from the multilayers indicated a small increase of the size of the TiN crystallites, while no significant change in lattice parameter in TiN was detected. After the $5x10^{16}$ ions/cm^2 irradiation, the layered structure was highly damaged and the TiN and B-C-N layers were no longer discernible in the deepest part of the film. Nevertheless, the TiN compound remained crystalline as indicated by electron diffraction and high resolution TEM.

The composition of TiN and B-C-N was determined by ion backscattering on 1µm thick coating deposited in the same conditions of pressure and power. It was found that TiN contains: 52%N, 46%Ti, 2%O and B-C-N contains: 38%B, 14%C, 48%N. The N/Ti ratio in the multilayer was deduced to be equal to 2.31. Table 1 gives the average amount of titanium and nitrogen contained in the films after various irradiation. It is shown that the titanium amount is constant but that there is a decrease of the nitrogen content for irradiation doses higher than $5x10^{14}$ ions/cm^2.

Low angle X ray reflectivity was performed to accurately determine the bilayer repeat length. The experimental low angle X-ray spectra obtained after various ion irradiation are shown in Figure 2. The spectrum obtained after the $5x10^{12}$ ions/cm^2 irradiation is similar to the one from the non-irradiated multilayer. The spectrum obtained after the $5x10^{16}$ ions/cm^2 irradiation (not shown in the figure) did not present any peak in this angle domain. Between these two doses, a shift of the first order Bragg peak towards smaller angle and a decrease of the intensity of this peak are observed. The shift of the peak corresponds to an increase of the bilayer repeat length Λ. The values of the bilayer repeat length calculated by fitting the experimental curves with theoretical ones are reported in Table 2. The largest bilayer length observed after the $5x10^{15}$ ions/cm^2 irradiation corresponds to an increase of 12.8%. The theoretical reflectivity values calculated for a larger repeat length are expected to increase for a constant number of bilayers [8]. Since the multilayer did not present major structural degradation until the highest dose, the observed decrease can be directly related to less compositionally abrupt interfaces between each layer, i.e. interdiffusion between the layers. This decrease in the intensity of the peak is reported in Table 2 as the ratio I/I_0 where I is the intensity of the peak after irradiation and I_0 the intensity before irradiation. The interdiffusion length can be calculated owing to [9]:

$$\bar{x} = \left[\mathrm{Ln}\left(\frac{I_0}{I}\right) \frac{\Lambda^2}{8\pi^2} \right]^{1/2}$$

where Λ is the bilayer repeat length. The values obtained for the different doses are reported in Table 2.

The curvature of the samples was measured before and after irradiation to determine the residual stress in the multilayers. The relative changes in the stress level: $(\sigma_{IRR} - \sigma_{AD}) / |\sigma_{AD}|$ (where σ_{IRR} is the stress after irradiation, and σ_{AD} is the as-deposited stress: -1750 MPa) deduced from these measurements are plotted in Figure 3. It can be seen that the stress is initially highly compressive after deposition, and is less compressive when the irradiation dose increases. The stress becomes tensile for doses above $2.5x10^{15}$ ions/cm^2 and is finally nearly equal to zero for the highest dose.

The results in Table 2 indicate that the interdiffusion length increases with increasing doses very rapidly at first (up to $5x10^{13}$ ions/cm^2). This corresponds to the beginning of the relaxation of the stress as shown in Figure 3. In this regime, the interdiffusivity is very high. As the irradiation dose increases further, the interdiffusivity becomes much lower, while Λ continues to increase but at a slower rate. The fall in the interdiffusivity can be related to the decrease of the stress. Once the stress is nearly equal to zero (above $2.5x10^{15}$ ions/cm^2), the interdiffusion length and the ratio N/Ti are nearly constant, while Λ still increases. As suggested by the TEM results, the increase is not due to an increase of the lattice parameter of TiN. One possibility is that it is resulted from a global displacement of atoms perpendicularly to the surface. This can be explained by a viscous flow of the atoms perpendicular to the stress field in the cascade region of the argon ions [3]. In the vicinity of argon ion tracks, many atoms are ejected from the cascade core. Some of the lighter atoms moves toward the surface, leading to the departure of nitrogen, but mostly moving perpendicularly to the surface because of the stress field are trapped at the interfaces or condense on dislocations whose Burgers vectors are parallel to the stress field [2], leading to the observed increase of the repeat bilayer length. This mechanism allows also a stress relaxation. Finally, when the damages introduced in the layers become too high, the two mechanisms of diffusion and the viscous flow lead to a complete mixture of the layers and the layered structure disappears. This is observed after $5x10^{16}$ ions/cm^2 irradiation at a depth of about 110 nm, corresponding to a dpa of 40.

4. CONCLUSIONS

Study of the stability of sputter deposited TiN/B-C-N multilayers irradiated with 300 keV argon ions has been performed using TEM, ion backscattering and low angle X-ray diffraction. Up to a dose of $5x10^{15}$ ions/cm^2, interdiffusion between layers occurred accompanying by the loss of nitrogen and the bilayer repeat length increased. After a $5x10^{16}$ ions/cm^2 irradiation, the multilayered structure disappeared in the most damaged area of the film, i.e. near the silicon substrate. These modifications are explained by diffusion and viscous flow of atoms perpendicular to the film.

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irradiation	Ti (10^{17} at/cm^2)	N (10^{17} at/cm^2)	N/Ti
as deposited	3.35	7.73	2.31
$5x10^{12}$ ions/cm^2	3.33	7.60	2.28
$5x10^{13}$ ions/cm^2	3.18	7.40	2.32
$5x10^{14}$ ions/cm^2	3.26	7.15	2.19
$5x10^{15}$ ions/cm^2	3.43	6.55	1.91
$5x10^{16}$ ions/cm^2	3.30	6.30	1.91

Table 1: Titanium and nitrogen contents in the multilayers after irradiation.

irradiation	Λ (nm)	I/I_0	x (nm)
$5x10^{12}$ ions/cm^2	4.20	1	0
$2.5x10^{13}$ ions/cm^2	4.23	0.74	0.261
$5x10^{13}$ ions/cm^2	4.30	0.58	0.357
$2.5x10^{14}$ ions/cm^2	4.45	0.36	0.506
$5x10^{14}$ ions/cm^2	4.53	0.33	0.537
$2.5x10^{15}$ ions/cm^2	4.70	0.18	0.693
$5x10^{15}$ ions/cm^2	4.74	0.18	0.698

Table 2: Bilayer repeat length Λ, decrease of the intensity of the first order Bragg peak and interdiffusion length as a function of the irradiation dose

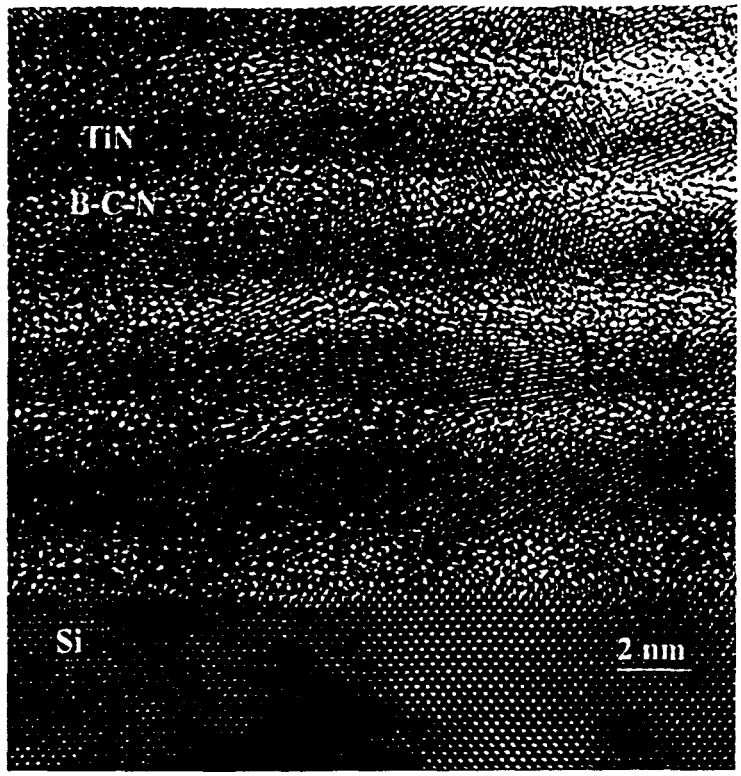

Figure 1 Cross-sectional TEM image of the as-deposited TiN/B-C-N multilayers.

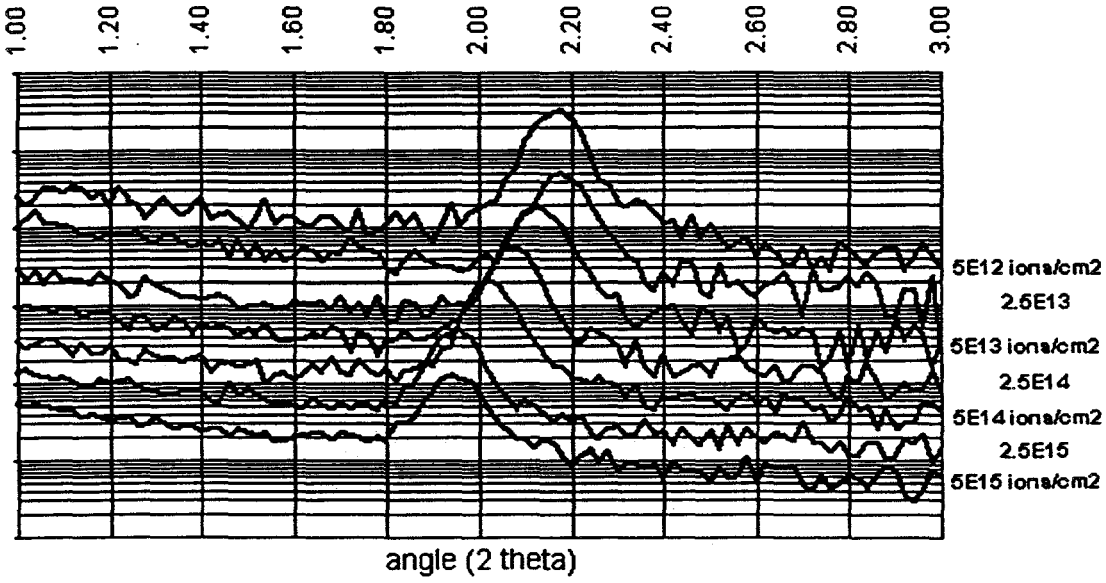

Figure 2 Low angle X-ray diffraction spectra of the multilayers after irradiation with 300 keV argon ion for doses ranging from $5x10^{12}$ to $5x10^{15}$ ions/cm^2

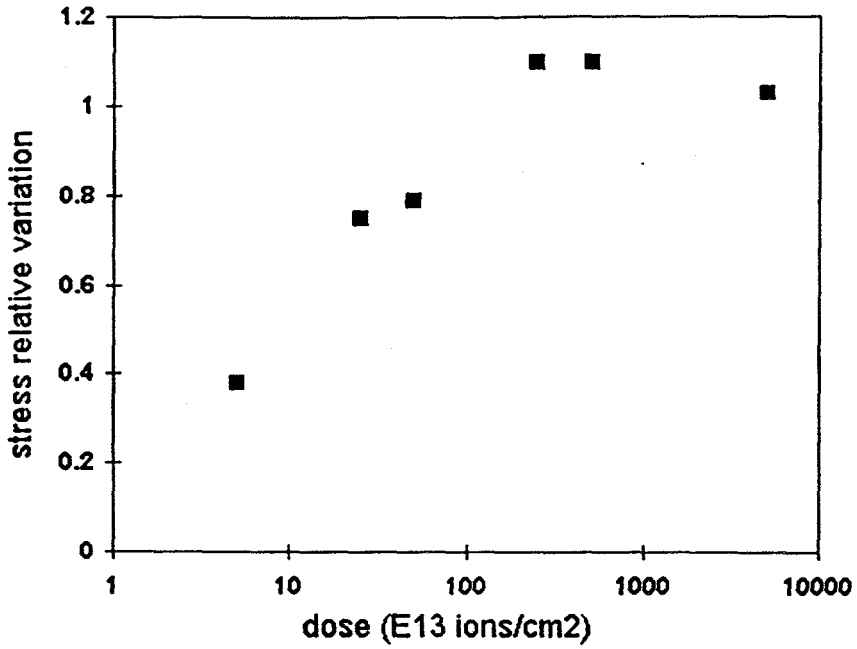

Figure 3 Relative change of stress in the multialyers as a function of the implantation dose