Amorphous Silicon Carbon Nitride Films Grown by the Pulsed Laser Deposition of a SiC-Si_3N_4 Mixed Target

Nae-Man Park, Sang Hyeob Kim, and Gun Yong Sung

We grew amorphous SiCN films by pulsed laser deposition using mixed targets. The targets were fabricated by compacting a mixture of SiC and Si_3N_4 powders. We controlled the film stoichiometry by varying the mixing ratio of the target and the target-to-substrate distance. The mixing ratio of the target had a dominant effect on the film composition. We consider the structures of the SiCN films deposited using 30 ~ 70 wt.% SiC in the target to be an intermediate phase of SiC and SiN_x. This provides the possibility of growing homogeneous SiCN films with a mixed target at a moderate target-to-substrate distance.

Keywords: PLD, SiCN, mixed target.

Manuscript received May 2, 2003; revised Sept. 24, 2003.

This work was supported by the Ministry of Information and Communication in Korea and authors would like to thank Dr. I.-S. Han and Dr. S.-K. Woo at Korea Institute of Energy Research for fabricating targets.

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I. Introduction

Considerable interest has developed in the amorphous silicon carbon nitride (a-SiCN) thin film, a new type of Si-based film for use in semiconductor industries due to its high thermal conductivity, high hardness, wide band-gap, and excellent resistance to corrosion [1], [2]. As shown in most previous studies, a-SiCN thin films have been generally grown using chemical vapor deposition or a sputtering system [1]-[6]. Pulsed laser deposition (PLD) is now a well-established technique for producing a wide variety of thin films. High quality ceramic films can be processed at much lower temperatures using this method, compared to chemical vapor deposition or sputtering. The interaction of intense laser pulses with a target surface generates particles which show non-equilibrium characteristics during deposition; these excited species with high kinetic energies can lead to the formation and growth of films in metastable states.

In this work, we report on a SiC-Si_3N_4 mixing ratio in a target on a-SiCN films when the mixed target is ablated in a vacuum, resulting in films with a variable composition of SiCN as a function of the mixing ratio in the target. We examined the atomic concentration and bonding configuration in the film using Auger electron spectroscopy (AES) depth profiling and X-ray photoelectron spectroscopy (XPS).

II. Experimental Details

We achieved deposition of the a-SiCN films using a PLD system. The ablation energy source was a KrF excimer laser of

λ=248 nm with a fixed fluence of 1 J/cm^2 which was operated at a repetition rate of 1 Hz. The beam was focused onto the surface of a 25-mm diameter mixed target, a cold isostatic compaction of 99.9 % Si_3N_4 and 99.9 % SiC powders with a mean size of less than 1 μm and pressed at 2×10^4 psi for 5 min. The SiC content of the target varied between 10 to 90 wt. %. To avoid cone formation on the target surface, the target was rotated at 2 rev./min. We pumped the high-vacuum chamber used in the system down and maintained it at a pressure of below 9×10^{-6} Torr by means of a turbo-molecular pump. The interaction of the laser with the target produced a plume normal to the target surface, and the ejected species were deposited onto the substrates, which were facing the target at a variable distance, D, in the range of 30 to 70 mm. We used a p-type (100) silicon wafer and a quartz plate as substrates, each with dimensions of 5×5 mm^2. We turned the laser on and precleaned the target for 1 min. The shutter hiding the substrate surface from the ablation plume was then opened and the deposition initiated. The chemical composition and atomic concentration of the a-SiCN films were determined by XPS and AES depth profiling. We carried the XPS measurements out using a system with an Mg-K*a* monochromatic X-ray source and a hemispherical analyzer after completing a 20-min pre-sputtering period. AES depth profiling permitted us to determine the homogeneity of the composition throughout the depth of the films.

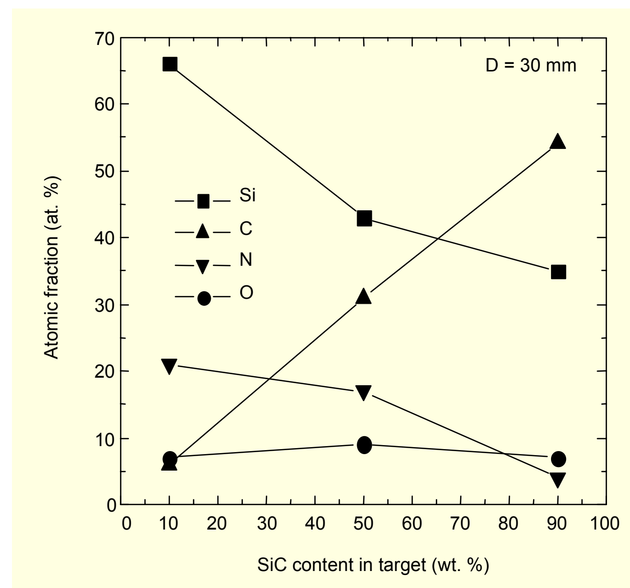

Fig. 1. Atomic concentrations of a-SiCN films as a function of SiC content within the target.

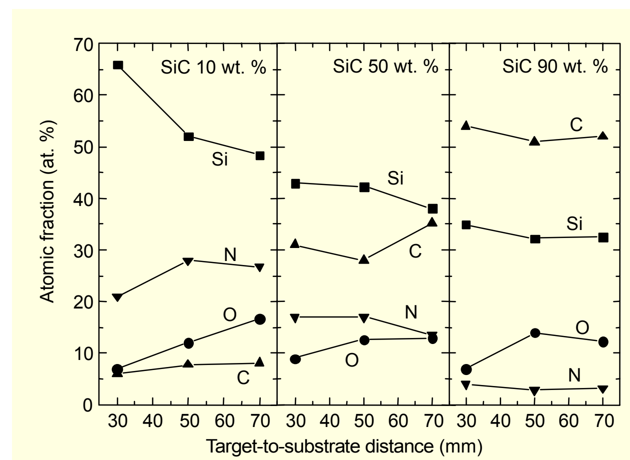

Fig. 2. Atomic concentrations of a-SiCN films as a function of the target-to-substrate distance, D.

III. Results and Discussion

Figure 1 shows the atomic concentrations of a-SiCN film compositions measured by AES as a function of the SiC content in the mixed target. By increasing the SiC content in the target, the Si and C contents increased drastically by approximately 30 and 50 at. %, respectively. The N contents decreased monotonically and the O content did not change significantly. The increase in C content and the decrease in N content parallel the change of the SiC/Si_3N_4 composition in the target. However, although the Si source remained nearly unchanged, the Si content dropped from 66 to 35 at. %. In the laser ablation of sintered Si_3N_4 targets in a vacuum, Si-rich silicon nitride films are normally observed because Si-related species are more abundant than N-related species in the plume [7], [8]. On the other hand, C-rich silicon carbide films can be deposited during conditions of a low laser energy density of 2 J/cm^2 and a low repetition rate of 1 Hz [9]. In our case, it is likely that the same reactions occurred because the mixed target was a compaction of powders and the laser fluence was as low as 1 J/cm^2. Therefore, the proportion of rich composition in the film was larger than in the case of the sintered target. Figure 2 shows the atomic concentrations of a-SiCN films as a function of D. The O content increased up to 2 times when D was increased, resulting from the reaction of particles with oxygen sources in the chamber. This is discussed in detail in the XPS analysis. Si content decreases in most films when D is increased. The trend for N concentration is also consistent with that of the Si content. However, The increase in N content of the films for a target of 10 wt. % SiC cannot be explained exactly at this time. In this case, the C content showed a different behavior and increased when D was increased. A possible reason for this is that the laser fluence of 1 J/cm^2 is sufficiently large to dissociate Si-C bonds, but heavy Si atoms or radicals with a low kinetic energy are not able to travel farther than C atoms in a plume of low density, resulting in the different behaviors with respect to the Si and C content.

To investigate the bonding in the a-SiCN films, we measured

a typical XPS bonding spectra for the samples deposited as functions of the SiC content in a target and target-to-substrate distance, as shown in Figs. 3, 4, and 5. Figure 3 shows that the Si 2p, C 1s, N 1s, and O 1s XPS peaks are dependent on the SiC content in the mixed target used for deposition of the SiCN films at D=30 mm. The Si 2p peaks indicate the presence of Si-N and Si-C bonds, located at approximately 102.6 and 100.9 eV with SiC contents in the range of 10 to 90 wt. %. Two shoulder peaks are also observed at 101.1 and 104.5 eV in the spectrum of a 10 wt. % SiC target, and are assigned to the Si-C bond and thick SiO_2 bond, respectively [10]. As the SiC content in a target is increased, the main peak shifts from the Si-N bond towards Si-C, and a Si-C-N bond appears at 101.7 eV for a film grown using a 50 wt. % SiC target. The C 1s spectrum in Fig. 3 is likely the C-Si located at approximately 283.5 eV. The N 1s core level spectra of the same samples in Fig. 3 indicate the presence of two states. The components are located within the range of 397.7 to 398.6 and at 400 eV. The state corresponding

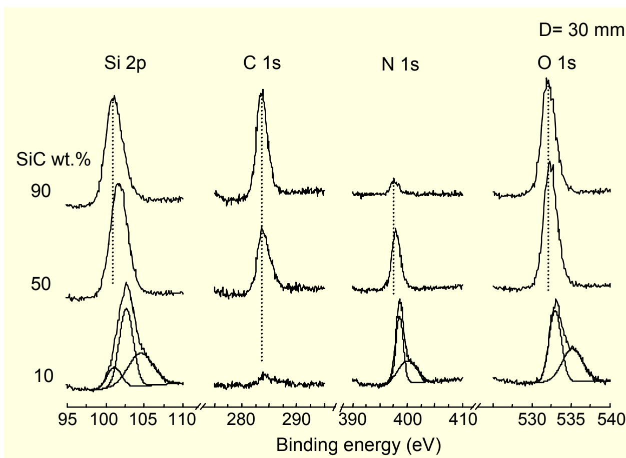

Fig. 3. XPS spectra of a-SiCN films with various SiC contents in a target at a target-to-substrate distance, D, of 30 mm.

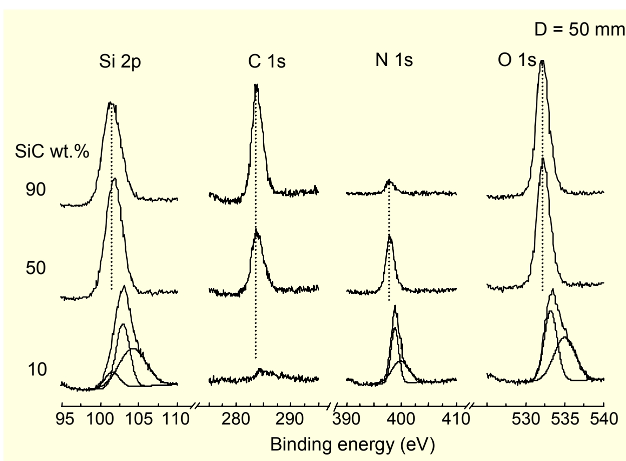

Fig. 4. XPS spectra of a-SiCN films with various SiC contents in a target at a target-to-substrate distance, D, of 50 mm.

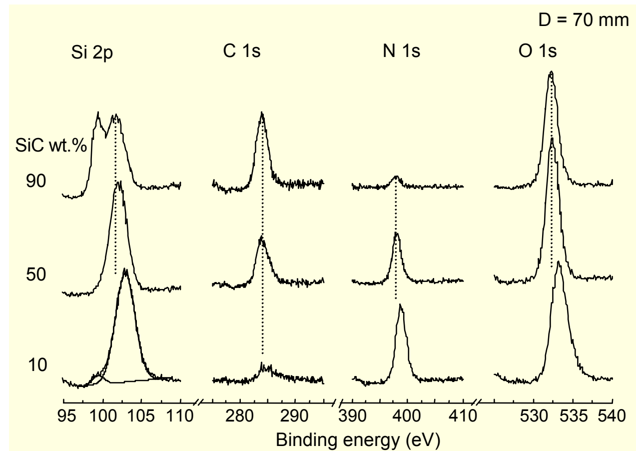

Fig. 5. XPS spectra of a-SiCN films with various SiC contents in a target at a target-to-substrate distance, D, of 70 mm.

to the range of 397.7 to 398.6 eV can be attributed to a N-Si bond, and the peak at 400 eV is consistent with a N-(Si,O) bond. The binding energy of N-Si shifted to a lower energy with an increasing SiC content of the target. We consider this to be a result of a larger charge transfer from the silicon atoms to the nitrogen atoms below the limit of N saturation in the N-deficient film [11]. A peak at around 400 eV is normally assigned to a N-C bond in a SiCN film [5], [12], but no C-N bond in the range of 286 to 288 eV is apparent in the C 1s spectra. As a result, the peak at 400 eV is assigned to N-(Si,O), which is nitrogen bridged to silicon and oxide creating Si_2-N-O where oxygen, with a higher electronegativity than nitrogen, causes a N-O bond formation with a charge transfer from nitrogen to oxygen [13]. In the corresponding O 1s core level spectra, as shown in Fig. 3, three components are observed at 532, 533, and 535.2 eV which are associated with SiC:O, O-Si, and SiO_2, respectively. The O 1s peak at 532 eV corresponds to oxygen in silicon oxicarbide [14] and the peak at 535.2 eV in silicon dioxide [15]. The peaks at 104.5 eV in the Si 2p spectrum and 535.2 eV in the O 1s spectrum can be attributed to silicon and the oxygen in SiO_2. The shift in the main O bonding suggests that the oxygen source is different as the SiC content in a target is increased. In the film deposited with a target composition of 10 wt. % SiC, the origin of the oxygen appears to be the thick oxidized Si_3N_4 powder in the target, while oxygen arises from the oxides in the chamber in film deposited using a 90 wt. % SiC target. This results in different O bonds; one being oxygen in SiO_2 due to the oxidized powder and the other in SiC due to the oxidation of radicals, although the total oxygen content is similar in all films.

As we increase D from 30 to 50 mm, the Si 2p and C 1s peaks shift towards a higher binding energy of about 0.2 to 0.3 eV, but the dependence of film composition on the mixing ratio of the target shows a similar characteristic, as demonstrated in

Fig. 4. However, in the oxygen related peaks of the N 1s and O 1s spectra in the film deposited using a 10 wt. % SiC target, the intensities decrease with an increase in D at the positions of 400 and 535 eV, which is related to the thick oxidized Si_3N_4 powder in the target. A possible explanation for this result is that oxidized SiN molecules are very heavy compared to non-oxidized molecules or radicals and, as a result, their mean free path is very short, resulting in a decrease in their content in the film as D is increased. This is clear in the film deposited at a D of 70 mm, in which no shoulder is evident at positions corresponding to 400 and 535 eV in the N 1s and O 1s spectra, as shown in Fig. 5. However, the total oxygen content increases with an increase in D, probably due to the low base pressure of 8×10^{-6} to 9×10^{-6} Torr. Figure 5 also shows the Si 2p and C 1s peaks for the films deposited at a D of 70 mm, where the Si-rich phase can be clearly observed in the film deposited at a 90 wt. % SiC in the target at approximately 99 eV. This suggests that Si nanophases can be formed using a SiC target at conditions of a low energy density of the laser and a large target-to-substrate distance, but they must be avoided in order to obtain a homogeneous SiCN film. Therefore, a target-to-substrate distance of 50 mm is appropriate for a SiCN film with a uniform composition.

IV. Conclusion

We grew a-SiCN films by PLD with a mixed target of SiC and Si_3N_4 powders. The SiCN film stoichiometry was controlled by the mixing ratio of the target and the target-to-substrate distance. The films deposited at 10 and 90 wt. % SiC in the target are mainly composed of SiN and SiC phases, respectively. However, we consider the structures of the SiCN films deposited using 30 to 70 wt. % SiC in the target to be an intermediate phase of SiC and SiN_x. A large target-to-substrate distance is desirable to suppress the introduction of oxygen from an oxidized target into the film, while still being able to contribute to the formation of a Si phase. At a moderate distance, the PLD technique using a mixed target of Si_3N_4 and SiC powders appears to be a useful method for the deposition of homogeneous SiCN films.

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