Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials, Tokyo, 1986, pp. 727-728

Deposition Mechanisms of $Si_xN_yH_z$ Films in Synchrotron Radiation-Excited CVD and Measurements of Hydrogen Content

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INTRODUCTION In a usual photo chemical vapor deposition (CVD), $Si_xN_yH_z$ films are produced from a SiH_4+NH_3 gas system. On the other hand, in the synchrotron radiation (SR)-excited CVD, $Si_xN_yH_z$ films can be deposited from a SiH_4+N_2 gas system, which is the ideal starting material for the fabrication of ultra clean $Si_xN_yH_z$ films. This gas system is also attractive from the view point of lowering the hydrogen content, which severely affects the film properties. In the present work, the deposition mechanisms of $Si_xN_yH_z$ films in SR-excited CVD and the dependence of hydrogen content on deposition conditions were investigated.

EXPERIMENTS Experiments were conducted in the beam line BL-1C at the KEK Photon Factory (1). Source gases were 100% SiH_4 and N_2. The storage ring current during the experiments was 90∿230 mA. Substrate temperature (T_s) was 190±15°C. The positive d.c. voltage was applied to the electrode, which was set parallel to the grounded substrate. Two types of substrate configurations, i.e. perpendicular and parallel to the SR beam, were tested.

RESULTS and DISCUSSION The deposition rate in the parallel configuration was about 0.1 nm/min for 100 mA ring current. The deposition rate in the perpendicular configuration was about four to six times larger than that in the parallel configuration, and increased with bias application.

Figure 1 shows the edge profile of the film deposited at the no bias state by the SR beam passing through a 1 mm diameter orifice in the perpendicular configuration. It is clear that the observed edge profile is close to the edge profile (CALC.(SURF.)) of the beam intensity distribution calculated from the Fresnel diffraction equation rather than the edge profile (CALC.(GAS)) of the deposition pattern calculated from arriving probability of active species to the surface (2). The temperature rise due to SR beam irradiation was negligible. These results indicate that, in the perpendicular configuration, the surface phase decomposition induced by SR irradiation is a main process in the deposition at the no bias state.

Hydrogen content of the deposited films were evaluated by the the infrared absorption spectroscopy. No absorption peak corresponding to N-H bonds was observed in any of the samples. From the observed absorption band areas of Si-H stretching vibration and its reported value of the absorption cross section, the total amount of bonded hydrogen contained in the film were calculated (3) and shown in Table 1. The hydrogen content in the present film formed at the no bias state (Sample no.1) is somewhat smaller than the reported value (∿1.6×10^{22} cm^{-3} for the film of N/Si=1.1) of the plasma-CVD film produced from the SiH_4+N_2 gas mixture at T_s=200°C (4).

Furthermore, it was found that there exists a certain relationship between amounts of Si-H bonds and the film composition (N/Si) determined by Auger electron spectroscopy, as shown in Fig 2. The hydrogen content decreases with increase of the N/Si.

Dependence of the hydrogen content and the N/Si on applied bias was measured within a low bias range of 0 to 30 V. It was found that bias application has little effect on the N/Si, but increases the hydrogen content as shown in Fig. 3. It was confirmed by quadrupole mass filter measurements that a large amount of hydrogen ions were generated in gas phase. Incorporation of these hydrogen ions into the films might be enhanced by bias application.

In conclusion, it was shown that surface phase decomposition induced by SR irradiation is a main process in the deposition of $Si_xN_yH_z$ films at the no bias state in the perpendicular configuration. The hydrogen content in the films decreases as the N/Si increases. Low bias application increases the hydrogen content with little change of the N/Si.

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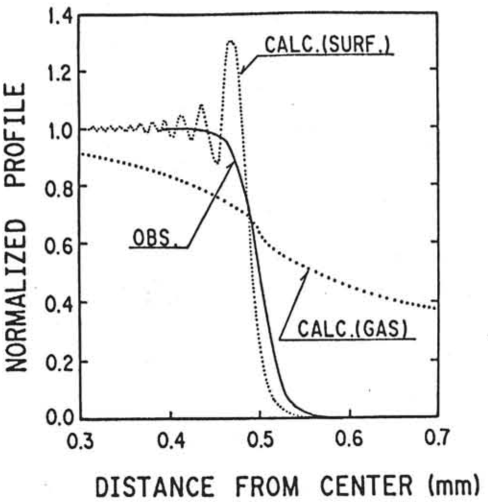

Fig.1 Comparison of observed edge profile with calculations.

Table 1. Deposition conditions.

Sample no.	V_a (V)	P_{SiH_4} (Pa)	P_{N_2} (Pa)	Si-H bonds (cm^{-3})	N/Si
1	0	2.7	40	4.1×10^{21}	1.1
2	0	2.7	13.3	6.7×10^{21}	0.44
3	0	4	8	15.3×10^{21}	0.16
4	10	2.7	13.3	7.9×10^{21}	0.43
5	10	4	20	18.9×10^{21}	0.38
6	10	4	16	44.3×10^{21}	0.31
7	10	4	8	30.2×10^{21}	0.17

All samples were formed in a perpendicular configuration.

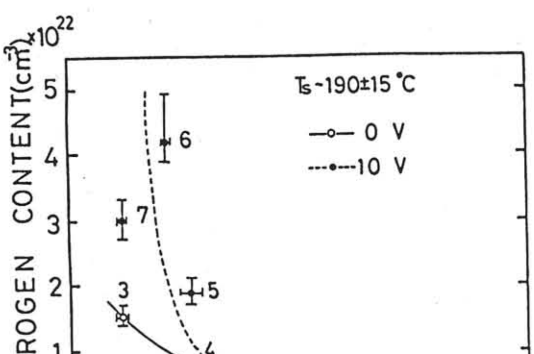

Fig.2 Relationship between hydrogen content and film composition. Numbers correspond to sample no. in Table 1.

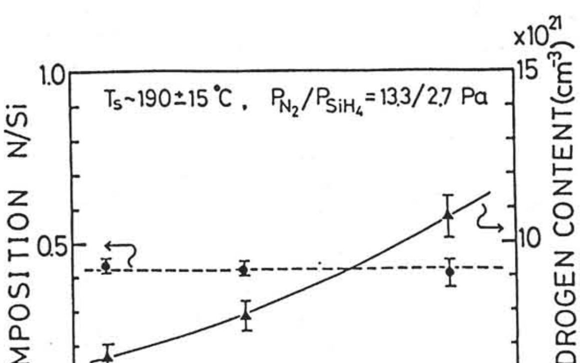

Fig.3 Dependence of hydrogen content and film composition on applied bias.