PREPARATION OF BORON NITRIDE THIN FILMS BY SPUTTERING USING R.F. INDUCTIVELY COUPLED PLASMA

Yu Kasori ,Shigeru Ito and Kazuo Akashi

Department of Industrial and Engineering Chemistry,Faculty of Science and Technology,Science University of Tokyo,2641,Yamazaki,Noda,278,Japan

abstract

Boron nitride thin films were deposited by sputtering of hexagonal BN (h-BN) target using R.F. inductively coupled plasma. In this new process, higher plasma density than that in usual capacitive coupled plasma sputtering can be obtained, so high rate deposition of BN films can be expected. Moreover the formation of cubic boron nitride (c-BN) film might be possible under certain circumstances. In this process,the potential of the substrate was independently controlled by an R.F. power supply,regardless of power input to the plasma, to assist the formation of c-BN phase. We first tried to prepare uniform BN thin films,and then intended to find the condition to prepare c-BN phase.

1.Introduction

Sp^3-bonded c-BN, which is stable under high pressure, is characterized by its excellent thermal conductivity and very high hardness which is next to that of diamond. Moreover,c-BN is non-reactive with iron and different from diamond in this property.Thus, various kinds of plasma assisted physical vapor deposition (PVD) [1-3] and chemical vapor deposition (CVD) [4-7] processes to prepare c-BN thin film are being actively investigated. But, finely crystallized c-BN thin film has never been prepared yet in both PVD and CVD processes.

In our study, boron nitride thin films were deposited by sputtering of h-BN target using an R.F. inductively coupled plasma. In this new process, higher plasma density than that in usual capacitive coupled plasma sputtering can be obtained, so it can be expected to attain high rate deposition of h-BN and obtain c-BN film under certain circumstances.

We first tried to prepare uniform h-BN film by sputtering of h-BN cylindrical target inserted into the torch,using N_2 and Ar gases.Then other gas such as H_2 or He was added in the system.Moreover an R.F. power was independently supplied to control the potential of the substrate to assist the formation of c-BN phase.

2.Experimental

Schematic diagram of the experimental apparatus of sputtering using R.F. inductively coupled plasma is shown in Fig. 1. Plasma was inductively generated in a quartz tube (the inner diameter :44mm) with R.F. power supply (frequency :4MHz ,plate input :3.3kW) through a three turned Cu coil wound outside the tube. N_2(99.9999 % in purity)and Ar (99.9995 %) gases were introduced into the plasma torch with desired flow rates. H_2(99.99999 %) or He(99.9999 %) gas was also added in the system with a desired flow rate, in some cases. These gases sputtered a h-BN tube (the inner diameter :35mm) inserted into the quartz tube. A Si substrate (the size :12.5 × 12.5mm ,0.5mm in thickness) with a polished mirror-like (100) surface was placed horizontally on a Si sheet fixed on the top of the substrate holder. The

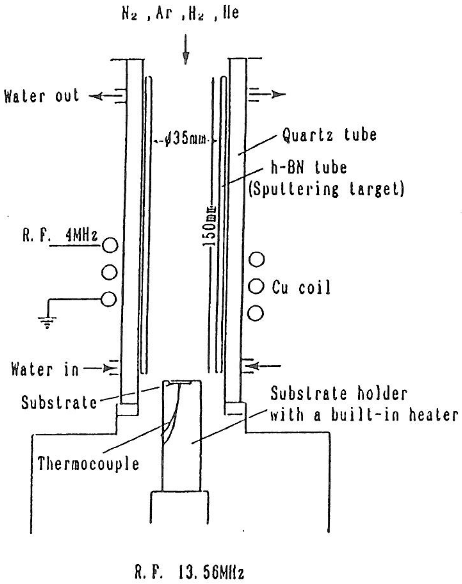


Fig.1 Schematic diagram of the experimental apparatus.

substrate holder included a nichrome wire heater and a Cu electrode. The temperature of the Si sheet in contact with the substrate backside was measured by a thermocouple (C.A.) and kept at a desired constant value during the deposition.The substrate potential was negatively biased by applying R.F. power (frequency :13.56 MHz) between the Cu electrode and a movable pedestal (the ground) in order to control the energy of ion bombardment. The biased substrate potential was measured as the value from the ground potential by a Vdc meter.

Prior to the deposition, hydrogen plasma was generated and maintained to remove residual contaminants and oxygen in the apparatus for 20 minutes. Then,the substrate holder was raised to an established position using a movable pedestal and the film deposition was carried out for desired times. After the deposition,the substrate was cooled to room temperature in hydrogen flow.

Infrared transmission spectra measured for the deposited film are significant to distinguish sp^2 and sp^3 B-N bonding.In the spectra for sp^2-BN, a strong absorption peak at 1380-1400 cm^{-1},weak ones at 780-800 cm^{-1} due to B-N in plain stretching and B-N-B out of plain bending,are confirmed respectively.On the other hand,the absorption at 1050-1100 cm^{-1} can be attributed to transverse optics mode of c-BN. In this study,FTIR spectra were measured,to confirm the existence of c-BN phase in the film.

The crystallinity of the film was investigated by XRD and TED. The chemical composition of the film was estimated by XPS. The thickness of the film was measured with a stylus instrument.

3.Results and discussion

3.1 Effect of hydrogen in the system

The film prepared at 800℃ and 40Pa under Ar and N_2 plasma,was white, powder-like,and nonuniform. Then we expected hydrogen might increase the uniformity of the film,and tried to introduce hydrogen in plasma. Fig.2 shows FTIR spectra of the films prepared at different H_2/Ar flow ratios, 800℃,and 40 Pa. When H_2/Ar was 1/5,absorption peak at 1380cm^{-1} in FTIR spectra became strong drastically. Fig. 3 shows SEM images of the films prepared at same conditions. SEM images of those films showed that grain size of film prepared in H_2/Ar=1/5 plasma was smaller than that in H_2/Ar=0/1 plasma. Furthermore some difference occurred in color of these films. Color of the film prepared in H_2/Ar=0/

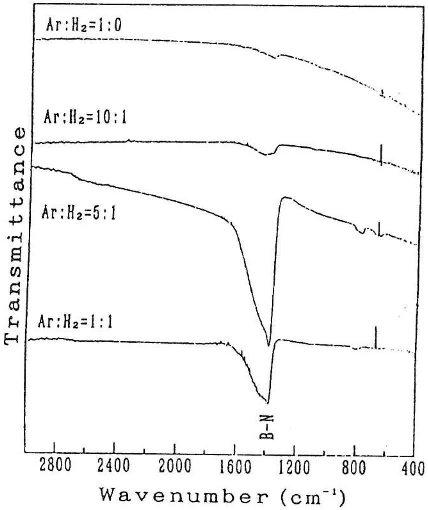
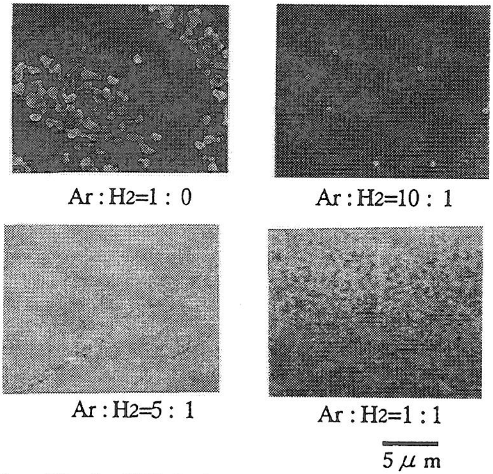


Fig.2 FTIR spectra of the films prepared at different Ar/H2 flow ratios, 4.0kW, 40Pa, 800℃.


Ar : H2=1 : 0

Ar : H2=10 : 1

Ar : H2=5 : 1

Ar : H2=1 : 1

Fig.3 SEM photographs of the films prepared at different Ar/H2 flow ratios, 4.0kW, 40Pa, 800℃.

1 was white and cloudy,otherwise that of film prepared in H2/Ar=1/5 was white and semitransparent and that of film prepared in H2/Ar=1/1 was colorless and transparent. From this fact,we can estimate hydrogen reacts with sputtered particle and forms a stable intermediate,which prevents condensation of each sputtered particle before its arrival to the substrate. However,as hydrogen flow rate increased,crystallinity of the film grew worse,as estimated from the full-width-half-maximum(FWHM) of XRD pattern. We suppose hydrogen intruded into the prepared film and destroyed crystal structure of the film. Fig. 4 shows FTIR spectra of the films at different substrate potentials and 800℃ under H2/Ar=1/1 or H2/Ar=0/1 plasma.The absorption peak assigned to c-BN didn't appear,regardless of the control of substrate potential by R.F. power supply.In FTIR spectra of the films under H2/Ar=0/1 plasma at same conditions, same results were obtained.

3.2 Effect of pressure

Pressure in the system was decreased by the control of diffusion pumping capacity to improve uniformity of the prepared film without using hydrogen. Fig. 5 shows FTIR spectra of the films at different pressure levels under Ar plasma.As the pressure decreased,thickness of the prepared film decreased ,and that absorption peaks at 1380-1400cm^{-1} and 780-800

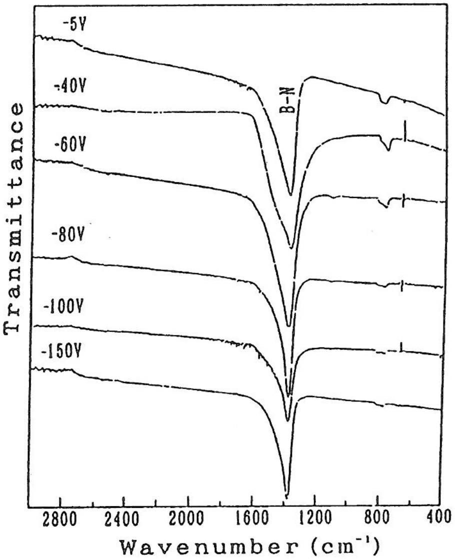


Fig.4 FTIR spectra of the films prepared at different substrate potentials, 40Pa, 4.0kW, and 800℃, under Ar/H2 = 1/1 plasma.

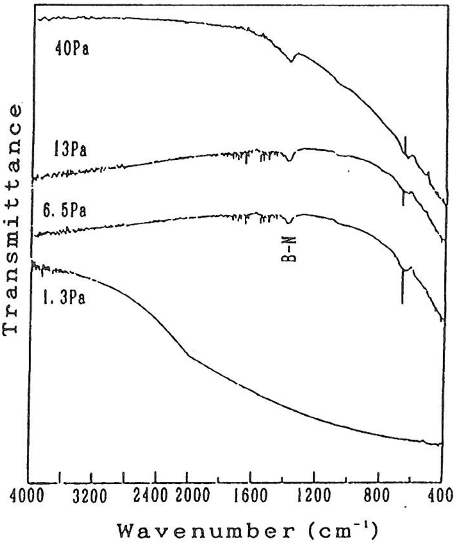


Fig.5 FTIR spectra of the films prepared at different total pressures , 4.0kW, and 800℃, under Ar plasma.

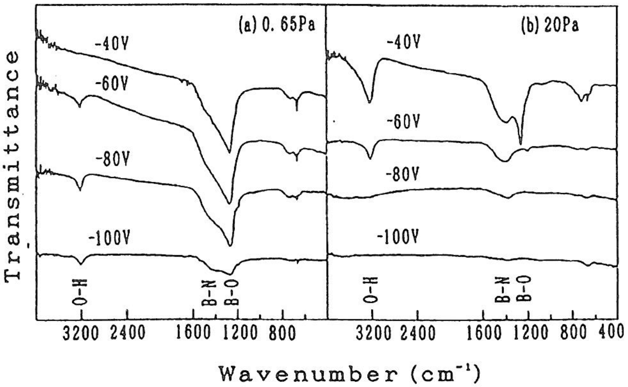


Fig.6 The changes of FTIR spectra of deposited films with the change of total pressure (3.5kW, 300℃, under Ar plasma) .

cm^{-1} due to B-N stretching , and B-N-B bending , respectively, in the film prepared at 1.3 Pa were disappeared,but the distribution of the film thickness became uniform. The absorption peak assigned to c-BN didn't appear, regardless of the control of substrate potential by R.F. power supply(Fig. 6). In Fig. 6, absorption peaks due to O-H stretching and B-O in plain stretching at 3200cm^{-1} and 1200cm^{-1} ,respectively,appeared, which suggests the existence of oxygen in the film.This result also suggests sputtering of the quartz tube under reduced pressure.Then we tried to introduce N_2,H_2, and He in the system,and examined the degree of sputtering of quartz tube.

3.3 Effect of added gases

We tried to introduce N_2,H_2, and He in the system,respectively with a gas flow ratio (Ar/(added gas)=1/1). When H_2 and He gases were added, FTIR spectra showed the existence of oxygen. But when N_2 was introduced, the absorption peak corresponding to the existence of oxygen didn't appear. XPS spectra also show the decrease of oxygen content in the film. However the absorption peak assigned to c-BN didn't appear,regardless of the control of substrate potential by R.F. power supply.

4 Conclusion

In our experiments for formation of BN film by sputtering, we have not found the condition for the formation of c-BN phase.It means suitable plasma condition for c-BN formation have not been attained. So we would like to try to introduce other gas such as Xe in plasma,and control plasma condition. Such gas seems to be effective for increasing the plasma excitation.

References

[1] Mieno M and Yoshida T J.J.Appl.Phys. 29 L1175 (1990)
[2] Murakawa M and Watanabe S Surf.Coat.Tech. 43/44 128 (1990)
[3] Ikeda T,Satoh T and Satoh H Surf.Coat.Tech. 50 33 (1991)
[4] Okamoto M,Utsumi Y and Osaka Y J.J.Appl.Phys. 29 L1004 (1990)
[5] Ichiki T and Yoshida T Proc.11th Int.Sym.on Plasma Chem. 1022 (1993)
[6] Weber A,Bringmann U,Nikulski R and Klages C Dia.Rel.Mat. 2 201 (1993)
[7] Karim M Z,Cameron D C,Murphy M J and Hashmi M S J Surf.Coat.Tech.49 416 (1991)