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Effect of irradiation ion species on internal stress in boron thin films

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Abstract

Internal stress has been studied under concurrent ion bombardments during the deposition of boron thin films. Boron thin films prepared by the vacuum evaporation exhibited fairly large compressive stress of about 0.5 GPa even without ion irradiation. Hydrogen ion irradiation with 100-400 eV energy resulted in the large compressive stress of 0.8-1.2 GPa due to the ion peening effect. On the other hand, under the irradiation with 100-400 eV helium ion the stress relief was observed and the compressive stress decreased by a factor of about 2. This may be caused by the large sputtering (5-15%) that will modify film structure in the bulk and surface morphology, resulting in porous, rather dense film.

Keywords: Wall conditioning; Wall coating; Low Z wall material

1. Introduction

Ion bombardment of films during deposition has been observed to strongly modify some of the properties of the thin film [1-3]. Energy and momentum of the incident energetic particles contribute to the physical changes in the film, such as a change in the grain size, film density, number of voids, film stress and electrical resistivity.

Usually all thin films are in a state of stress. The stress has deleterious effects on the performance of the film, such as adhesion failure and substrate deformation. We have investigated the internal stress in the boron thin films by the apparatus based on the measurement of curvature of a substrate for the reliability problem of boronization [4]. Boron films have been prepared by the ion plating, which is a kind of physical vapor deposition (PVD) and a combination of evaporation and glow discharge processing. It was found that the boron thin films produced by the vacuum deposition exhibit fairly large compressive stress of the order of GPa. For the ion plating with a dc glow Ar plasma, increase in intrinsic compressive film stress was generally found with increasing negative bias of the substrate in the range from -100 to -400 V.

Boronization of the first wall is playing an important role in improving plasma performance in the fusion device. In the tokamak experiments, boronizations were usually prepared by a chemical vapor deposition (CVD) using the glow discharge plasma, which were produced by the discharge (0.2-0.4 A, 300-500 V) of the gas mixture (boron compound, H and He) between the anode inserted and the grounded vessel wall as a cathode [5,6]. In the usual glow discharge, the cathode material is bombarded by plasma ions accelerated in the cathode fall, over which most of the voltage drop occurs. Then in boronizations boron thin films are subjected to the ion bombardment with the energy of 300-500 eV. These films may have large internal stress and may result in the peeling phenomena when films have enough thickness with several μm.

This work has been performed to study bombardment effects of the ion species on the internal stress in boron thin films. The results of the internal stress measurements in the ion irradiation experiments will be presented and its enhancement and relief mechanisms for the compressive stress will be discussed.

2. Experimental procedures

The ion plating apparatus and the internal stress measurement system used for these experiments are shown in

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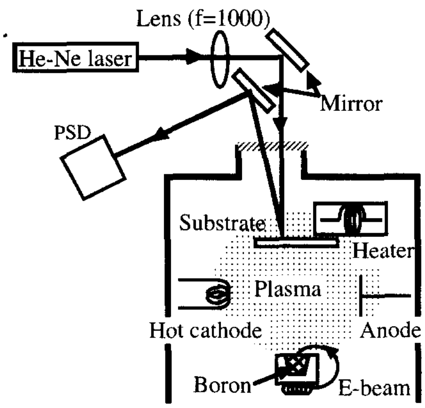

Fig. 1. Schematic of experimental apparatus.

Fig. 1 [4]. Boron thin films were prepared by the ion plating method with hot cathode glow discharge (typically 45 V, 800 mA) with a base pressure of 1.0×10^{-6} Torr. Typical plasma parameters were $T_e = 5.5$–6.8 eV and $n_e = (1.2$–$2.3) \times 10^9$ cm^{-3} for H and He at about 1 mTorr pressure. The vapor source was a conventional 270° deflection type electron beam gun (EB gun). The molybdenum substrates, which were the cantilevers (9.5 × 30 × 0.4 mm) for the internal stress measurements, were mounted at a distance of 23 cm from the EB gun. Deposition rates were attained typically 0.1–0.5 nm/s. These were measured by a quartz-crystal oscillator thickness monitor during deposition and were calibrated by the absolute thickness measurement with a stylus-type instrument after deposition. Ion irradiations were carried out by the application of negative bias voltage (−100, −200 and −400 V) on the substrate.

The internal stress was determined by measuring substrate curvature as shown in Fig. 1 [4,7]. The curvature of the substrate was deduced by the measurement of resulting translation of reflected He–Ne laser beam (0.5 mW), which was focused with the cylindrical lens ($f = 1000$ mm) on the position sensitive detector PSD placed at 98 cm apart from the substrate. The resolution of the total stress measurement was 1.2 N/m, which was determined by the noise from mechanical vibrations.

3. Results

Positive sign corresponds to compressive stress in the following data. The results of the total stress (the product of average stress and film thickness) are plotted against the thickness for the different conditions of the energy of H and He ion bombardments in Fig. 2. The result obtained in the vacuum evaporation is also plotted for comparison. These data were obtained at the substrate temperature of 300°C and the deposition rate of 0.1 nm/s. All films are in a state of compressive stress. The plots are monotonic and

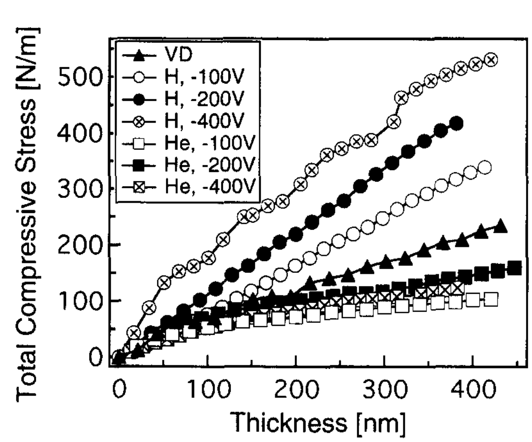

Fig. 2. Total compressive stress versus film thickness for films with concurrent H and He ion bombardments and with no bombardment (vacuum evaporation). All films were prepared at the substrate temperature of 300°C and the deposition rate of 0.1 nm/s.

are roughly approximated by straight lines for H ion bombardments. Thus the compressive stress is uniformly generated through the film. For He ion bombardment experiments the plots, however, are not linear in the early phase of deposition but plots also become almost linear above the thickness of 150 nm. All of the data are less compressive than that of the vacuum evaporation. The dependence of the total stress on the bombardment energy of He ion is not so evident.

The internal stress is deduced from the slope of the total stress plot. In the ion plating films used the H plasma, the film compressive stress increased with increasing the negative bias between −100 and −400 V. Fig. 3 shows the compressive stress of the boron thin films bombarded with H ions as a function of film thickness. The increase in

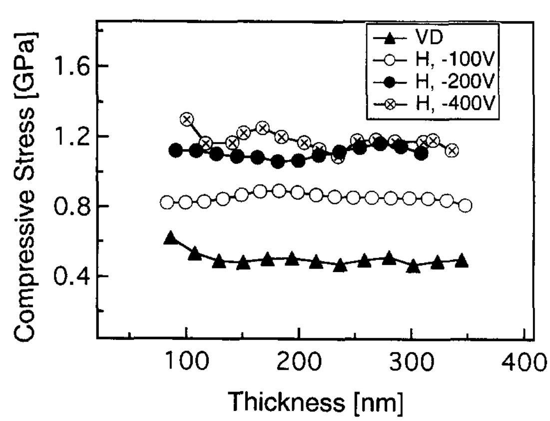

Fig. 3. Compressive stress versus film thickness for films with concurrent H ion bombardment and with no bombardment (vacuum evaporation). These stresses were deduced by the slopes of the total stress plots in Fig. 2.

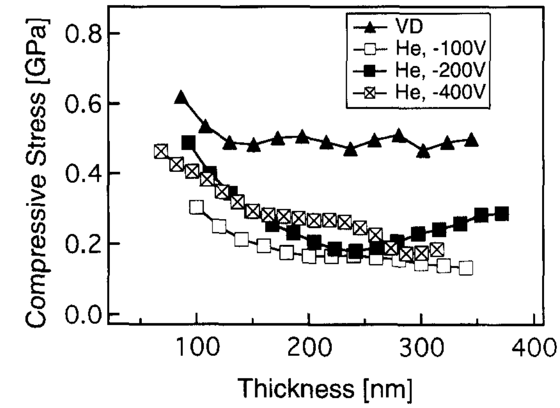

Fig. 4. Compressive stress versus film thickness for films with concurrent He ion bombardment and with no bombardment (vacuum evaporation). These stresses were deduced by the slopes of the total stress plots in Fig. 2.

the compressive stress is evident for −100 and −200 V bias cases. The similar behavior has been observed in the ion plating films with Ar plasmas [4]. In the bias voltage with −200 V, the boron thin film under H irradiation has about 1.1 GPa and film under Ar irradiation has about 1.5 GPa, both showing significant increase in compressive stress. In the −400 V bias case, bombarding effect of H ion, however, shows slight saturation and the stress of the film is almost the same as compared with that for −200 V case.

All stress data under He ion irradiations with the energy between −100 and −400 V showed the stress relief. In Fig. 4, the compressive stress of the boron thin film bombarded with He ions is shown as a function of film thickness. In this case the compressive stress shows fast decay during 0–150 nm and it attains the compressive state with 0.12 to 0.46 GPa, which is about a half of the compressive stress of the film deposited by the vacuum evaporation.

In Fig. 5, the compressive stress at higher substrate temperature with 500°C is shown as a function of thickness. In both films prepared with vacuum evaporation and ion plating with H ion bombardment, increase in the substrate temperature was seen to have an effect on compressive stress enhancement.

4. Discussion

A number of mechanisms have been proposed to explain the compressive stress in films deposited under ion bombardment [3]. The most common mechanism is explained in terms of the ion peening. The ion peening results in interstitial formation that is the origin of the compressive stress and the densification of the film.

Harper et al. have collected many examples of property changes in films induced by the ion bombardment [1,2]. They plotted these changes as a function of the ion-to-atom arrival ratio versus the incident ion energy. By this plot it was suggested that no changes in film properties occurred at energies below 1 eV/atom and the primary changes

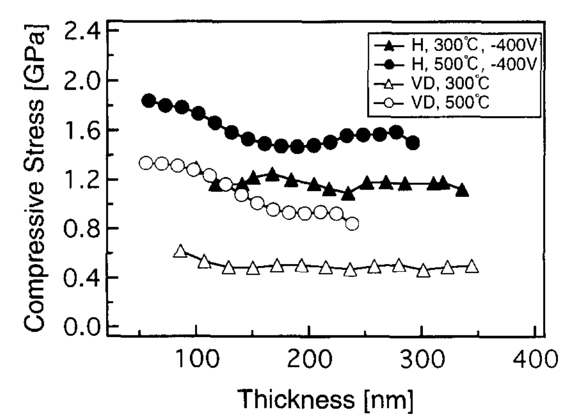

Fig. 5. Compressive stress versus film thickness for films prepared at the substrate temperatures of 500 and 300°C.

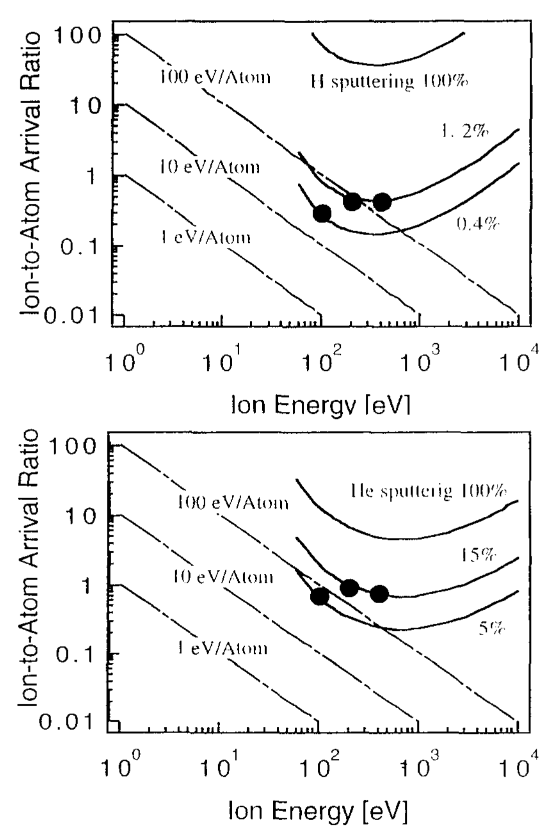

Fig. 6. Harper diagrams for H ion bombardment (top) and for He ion bombardment (bottom).

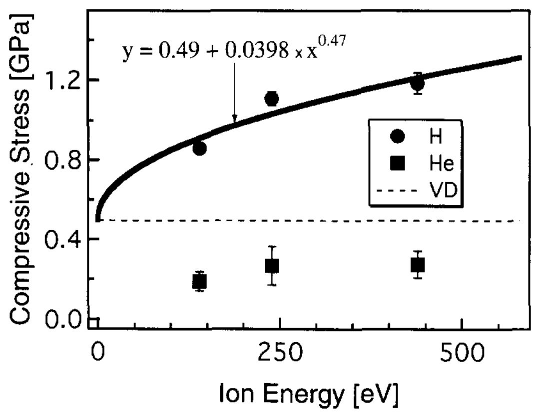

Fig. 7. Compressive stress as a function of the ion bombardment energy. The solid line is the least square fitting curve.

observed in 5–25 eV/atom range. The latter region was termed densification region because of observed changes that was related to density. The energy to get the significant density change was approximately equal to the bond strength or displacement energy. The operation above this region resulted in no density change and this region was termed sputtering region (10–100% sputtering). For our H and He ion bombardment experiments, the plots similar to the Harper diagram are shown in Fig. 6. Incident ion and boron fluxes into the substrate were deduced from the measurements of substrate current (typically 1.2 mA/cm^2), and mass deposition rate (typically 1.6×10^{-8} g/cm^2s), respectively. The dominant incident H-ion was assumed to be H^+ rather than H_2^+ and H_3^+ because in our glow discharge plasma electron temperature was less than 7 eV. In these figures the solid lines are the fractional numbers of sputtered boron times the reciprocal of the sputtering yields of B for H and He ions bombardments. These sputtering yields were obtained by the empirical formula by Matsunami et al. [8]. Displacement energy of B is estimated to be about 23 eV, taking four times of the sublimation energy of 5.77 eV. From Fig. 6, in our experiment H ion bombardment may result in the densification and the stress enhancement. On the other hand, the densification may scarcely occur for He ion bombardment because of the deposition under sputtering dominated region (5–15% sputtering) as shown in Fig. 6. Previous experiments with Ar ion bombardment were carried out under small sputtering rate less than 1% and the stress enhancement was observed.

The compressive stress data, which are obtained by averaging the values from 200 nm to 400 nm in Figs. 3 and 4, are plotted against the ion bombarding energy in Fig. 7. For H ion bombardment, the increase of the compressive stress, which is measured from that of vacuum deposition, changes with ion energy nearly at $E^{0.5}$. This square-root dependence on the incident ion energy suggests that the stress change is momentum rather than energy driven and is explained by the ion peening. The results for He ion bombardment experiments can not be explained by the peening model because of occurrence of stress relief rather than stress enhancement. This stress relief showed the weak dependence on the incident ion energy. It suggests that the densification and its counter effect simultaneously occurred in our He experiments. The possible counter effect is the formation of growing film surface with significant defects and open voids due to large sputtering.

In our experiments, gas and impurity inclusions are not primary mechanisms for compressive stress. This is because the increase in the compressive stress is still observed at higher substrate temperature as shown in Fig. 5 while the H and impurity atoms inclusions may significantly decrease at the higher substrate temperature of 500°C [3,4]. High substrate temperature may be related to densification due to the thermal effects, such as enhanced surface diffusion and atomic rearrangement.

5. Conclusions

We have measured the internal stress of the boron thin films under the concurrent ion bombardment. It was found that H ion bombardment results in the enhancement of the compressive stress due to ion peening effect and He ion bombardment results in the stress relief due to large sputtering effect. In order to achieve the boron thin films with less stress, the use of the He plasma rather than H plasma is desirable if the concurrent ion bombardment with 100–400 eV is involved in the film processing.

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