Effects of Nitrogen Partial Pressures during r.f. Magnetron Sputtering on the Crystal Structure and Growth Rate of c-BN Films

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Abstract

The type of atmospheric gases used in sputtering deposition is an important factor in the formation of cubic boron nitride (c-BN) films. All of the c-BN films were deposited on a Si wafer using radio frequency (r.f.) magnetron sputtering with a B₄C target at N₂/Ar+N₂ ratios of 0.2, 0.4, 0.6, 0.8 and 1.0. The characteristics of the c-BN layer were significantly enhanced at a nitrogen partial pressure of 0.6. The highest growth rate of the c-BN layer was measured at 11.6 (nm/min) at a nitrogen partial pressure of 0.6. The lowest surface roughness was obtained at a nitrogen partial pressure of 0.6 when the BCN gradient layer was clearly deposited. Accordingly, the XPS results, the c-BN phase structure improved while the BCN gradient layer was clearly observed. Overall, the growth rate, surface roughness and crystal structure of the c-BN films are significantly affected under certain atmospheric gas conditions such as at a nitrogen partial pressure of 0.6.

Keywords: Cubic boron nitride(c-BN); r.f. magnetron sputtering; Nitrogen partial pressure.

1. Introduction

Cubic boron nitride (c-BN) is a promising material for many potential applications due to its high thermal stability, high abrasive wear resistance and high hardness, which is second only to diamond [1-3]. Because of this great potential, some researchers have studied the thermodynamics of BN synthesis using chemical vapor deposition (CVD). Bohr et al. [4] calculated the Gibbs free energy values of BN and suggested that the c-BN phase is thermodynamically stable than the h-BN phase when the BN phase is synthesized using the CVD method.

The c-BN layer by PVD (physical vapor deposition) method can be effectively controlled by many magnetron sputtering parameters, including the target power, substrate bias, temperature, working gas and pressure. A previous study examined the c-BN films deposited by r.f. magnetron sputtering using a B₄C target in a 100% nitrogen atmosphere [5]. However, many researchers have reported that the nitrogen partial pressure affects the formation of nitrogen compounds, as well as their structures and mechanical and chemical properties [6-8].

In this study, the authors focused on the effects of the c-BN films crystal structure when films were deposited at different nitrogen partial pressures. The films were deposited on Si wafers using r.f. magnetron sputtering with a B₄C target for one hour under nitrogen partial pressures of 0.2, 0.4, 0.6, 0.8 and 1.0.

2. Experimental details

The Si (100) wafers (10 mm × 10 mm) were cleaned ultrasonically in acetone and ethanol. The c-BN films were then deposited using an r.f. (13.56 MHz) magnetron sputtering system with a B₄C target (purity exceeding 99.64%, 4 inch) and an initial chamber pressure of < 1.5 × 10⁻² Pa. The working pressure in the c-BN coating process was 0.28 Pa. A brief ion etching process was used to pre-clean the target and substrate. The B₄C layer was then deposited onto the substrate in an argon atmosphere for 60 min., this atmosphere was then replaced with nitrogen and argon gas for a few minutes. During the c-BN deposition step, the partial pressure of the nitrogen gas (N₂/Ar+N₂) varied according to the following values; 0.2, 0.4, 0.6, 0.8 and 1.0. A negative bias of −180 V DC was applied to increase the ion energy. A substrate temperature of 470 °C was used to crystallize the c-BN. The film thickness was observed using field emission scanning electron microscopy (FE-SEM). The surface roughness for the films was studied using atomic force microscopy (AFM) and the composition and binding energy of the c-BN films were analyzed using X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1 Effect of Nitrogen Partial Pressure

Figure 1 shows the growth rate of a c-BN layer deposited for one hour at a range of nitrogen partial pressures. The growth rate of the c-BN layer changed as the nitrogen partial pressure increased, after a certain nitrogen partial pressure the growth rate declined because nitrogen compounds were formed on the target surface. The highest growth rate of 11.6 nm/min was obtained when the c-BN layer was deposited at a nitrogen partial pressure of 0.6. This result suggests that the nitrogen partial pressure plays an important role in the growth of boron nitride.

Figure 2 shows FE-SEM cross-sectional images of the c-BN films deposited over a range of nitrogen partial pressures. It was found that a thick BCN gradient layer was deposited in nitrogen partial pressures of 0.4, 0.6 and 0.8 but not with the values...
of 0.2 and 1.0. When the gas was changed from Ar to N₂, a BCN gradient layer was formed between the B₄C layer and the c-BN layer. This can be explained by the reaction between the B-C atom bond sputtered from the B₄C target and the N atoms. It has been reported that the BCN gradient layer has an amorphous structure containing not a single complex bond but a multi complex bond such as B-N, C-N and B-C bond with B-C-N hybridization [9]. In addition, the growth of the c-BN layer had a close relationship with the presence of the BCN gradient layer [10].

![Fig. 1. Growth rate of the c-BN layer as a function of the nitrogen partial pressure.](image)

In the conditions with nitrogen partial pressures of 0.2 and 1.0, the BCN gradient layer was not formed. At a low nitrogen partial pressure (0.2), a few B-N, C-N and B-C-N bonds can be formed. Therefore, the BCN gradient layer was rarely deposited due to insufficient N-bond atoms. Moreover, a BCN gradient layer was barely deposited under a nitrogen partial pressure of 1.0 because nitrogen compounds which had formed on the target surface decreased the sputtering efficiency of the target. This implies that the lack of B and C atoms have influenced the formation of the BCN gradient layer.

![Fig. 2. Cross sectional SEM images of the c-BN layers: (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8; (e) 1.0.](image)

Figure 3 shows the mean surface roughness (Ra) from the AFM images of thin c-BN films deposited over a range of nitrogen partial pressures using r.f. magnetron sputtering. It should be noted for a nitrogen partial pressure of 0.6 (the BCN gradient layer was clearly deposited under the c-BN layer) the value of Ra was less than 1.0 nm. Nevertheless, the maximum Ra value (near 3.0 nm) for the c-BN film was attained in a pure nitrogen. This suggests that the nitrogen partial pressure affects the quality of c-BN film deposition.

![Fig. 3. Surface roughness of the c-BN layers obtained over a range of nitrogen partial pressures.](image)

### 3.2 Crystal Structures of c-BN Films

Figure 4 shows the binding energy of the B1s and N1s of the c-BN layer at a range of different N₂/Ar+N₂ ratios, 0.2, 0.4, 0.6, 0.8 and 1.0. Each condition has a different peak binding energy due to the different valence states of the boron and nitrogen atoms. Boron atoms chemically bond with the nitrogen or carbide during the deposition process. A reference value of 284.6 eV was used for the C1s binding energy. The peak for the sp³-BN binding energy was reported to be 190.7 eV and that for the sp³-NB bond being 398.3 eV [11]. Kawashama et al. [12] reported that the B1’s binding energy was dependent upon the nitrogen concentration. Considering the binding peak energy for the B-N bond, the 0.6 and 0.8 nitrogen partial pressures were confirmed to be the best matched bond to the standard energy. In particular, the formation of the c-BN phase at a nitrogen partial pressure of 0.4 and 0.6 corresponded with the N-B bond of the c-BN phase.
4. Conclusions

The characteristics of the c-BN layer were significantly enhanced at a nitrogen partial pressure of 0.6. The highest growth rate of the c-BN layer was measured at 11.6 (nm/min) at a nitrogen partial pressure of 0.6, with a lowest surface roughness of around 1.0 nm at a nitrogen partial pressure of 0.6 when the BCN gradient layer was clearly deposited. According to the XPS results, the c-BN phase structure improved while the BCN gradient layer was clearly observed. Overall, the growth rate, surface roughness and crystal structure of the c-BN films are significantly affected under certain atmospheric gas conditions such as at a nitrogen partial pressure of 0.6.

![Graphs showing high-resolution XPS spectra for the BN film: (a) sp^3-BN and (b) sp^3-NB.](image)

Fig. 4. High-resolution XPS spectra for the BN film: (a) sp^3-BN and (b) sp^3-NB.

References