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硼碳氮薄膜之介電常數與電子特性研究

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硼碳氮薄膜之介電常數與電子特性研究

計畫類別：■ 個別型計畫　　□ 整合型計畫

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台灣大學材料科學與工程學系　陳俊維

1. 中文摘要

本計劃主要是探硼碳氮薄膜之光學及電子傳導特性。主要是探討隨著碳成份之改變，硼碳氮薄膜之光學及電學性質之變化。我們發現藉由調整碳之含量，我們可以成功的調整硼碳氮薄由絕緣性質之特性變成導電之特性。此研究成果目前正在準備投稿中。

2. 英文摘要

Synthesis of boron carbon nitride thin film was attempted by the dual gun magnetron sputtering deposition method using graphite and B_4C as the reactive targets, and nitrogen as the source gas. The bonding configurations, optical and electrical properties of the BCN films were characterized by x-ray photoelectron spectroscopy (XPS), refractive index and the current-voltage (I-V) measurements respectively. It was found that with increasing carbon atomic fraction in the films, the relative fraction of C=C increased at the expense of B-N and B-C, while the total fraction of C=N and C≡N maintained a pretty steady value. The increase in the relative fraction of C=C bond was effective in increasing the optical absorption coefficient and electrical conductivity of the BCN films.

Introduction

Thin films of boron nitride and carbon nitride were devoted to the applications of surface inert and hard coatings [1], because of their superior hardness and chemical inertness [2]. Other applications such as high temperature metallurgy [3], dielectrical thin film coating [4-6], and field emission [7] are other interesting issues for these materials. Moreover, these materials are the promising materials for applications in the electronic and optical fields, such as optical detector and field emitter. Accordingly, composites or solutions of these two materials possess the potential of having properties not achieved by these two materials and need future study.

Amorphous boron carbon nitride compounds are of increased interests in recent years, which are believed to be promising technical materials with many favorable properties for optical [8-10] and electrical applications [11-15]. Many synthesis methods were reported, including chemical vapor deposition (CVD) [13], plasma assistance chemical vapor deposition (PACVD) [16-17], ion-beam deposition [18] and magnetron sputtering [19-21]. Lei et.al. showed that the refractive index and optical band gap of the BCN films prepared by rf magnetron sputtering lay between 2.1 and 2.4, and 1.8 eV and 2.1 eV, respectively. [22] I. Caretti et.al. used ion-beam deposition to grow BCN films [23]. By adjusting the atomic ratios of elements and, consequently, the bonding state in the thin films, the optical and electrical properties of the amorphous BCN (a-BCN) films could be altered substantially.

In this study, a-BCN thin films were synthesized by dual gun magnetron sputtering, in which the graphite target power was varied to study the effect of carbon atomic fraction on the bonding state, and, consequently, the electrical and optical properties of thin films.

Results and Discussion

The various films grown under the conditions shown in Table 1 were amorphous films, as their X-ray diffraction patterns (Figure 1) did not show any characteristic peak of lattice plane. The variation of the compositions of these a-BCN thin films, determined by XPS analysis, with graphite target powder is shown in Figure 2. It can be observed that the power of graphite target substantially affected the composition of the thin films. With the increase of the target power from 0 watt to 80 watt, the concentration of carbon in the films increases almost linearly to a level of about 40 at% and then levels off, while that of boron decreases substantially. These observations indicated that carbon primarily substituted for boron for the films having high concentrations of carbon.

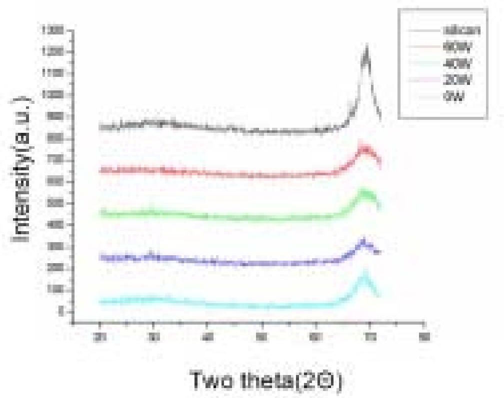
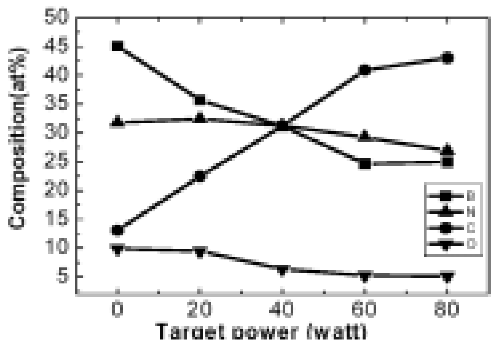


Fig.1

The characteristic C(1s), N(1s), and B(1s) peaks of the a-BCN were recorded using XPS scanning, in order to examine the bonding state of these films. Figure 3, 4, and 5 respectively show that the C(1s), N(1S), and B(1S) peaks of the XPS spectra shifted as the the graphite target power changed from 0 to 60 W. For C(1s) spectra, the binding energies of 282.4 eV, 284.4 eV, 285.6 eV, 287.0 eV peaks were attributed to the B-C, C=C, C=N, and C≡N bonds, respectively.[24-27]



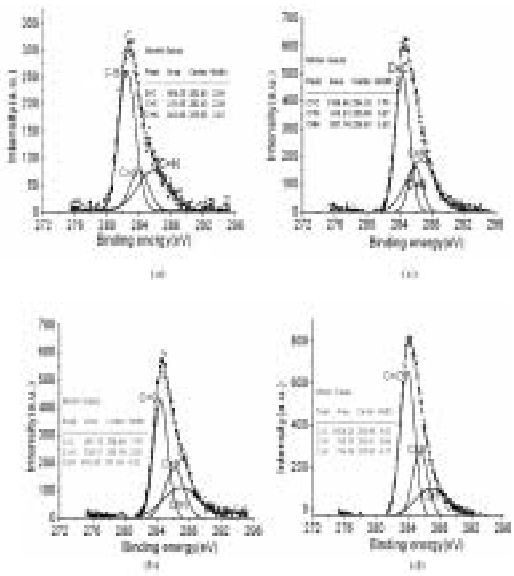


Fig.3

On the other hand, the binding energies of 398.1 eV, 399.5 eV, 399.0 eV in the N(1S) spectra were attributed to the N-B , N≡C and N=C bonds, respectively, while those of 190.3 eV and 188.9 eV were attributed to the B-N bond and B-C, respectively. The relative percentages of bonds determined by the characteristic C(1S), N(1S), and B(1S) peaks are Table 2, which clearly illustrates the transition of bonds with the increase in the graphite target power. With the increase in the graphite target power, the relative intensity of C=C increased at the expense of B-C, while the total percentage of C≡N and C=N remained pretty steady. It is noted that the variation of B-N bond was contrary in the analyses using N(1S) and B(1S).

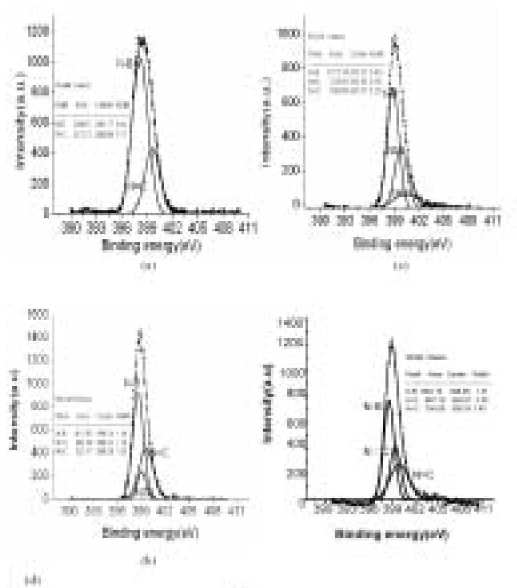


Fig 4

Such a phenomenon could arise from the low concentrations of N and B in the films high graphite target powers. Accordingly, it is believed that the relative percentage of B-N bond was not altered substantially. Based on this observation, it is clear that most of the carbon atoms added to the films, as a result of increased graphite target power, substituted for boron atoms, a result the same as that shown in Figure 2. With such a substitution mode, the relative percentage of C=C bond increased significantly.

In comparison, a prior study also showed that the bonding state and composition of a-BCN films were determined by the graphite target power [20]. However, as the power increased, the relative concentration of carbon increased while those of boron and nitrogen decreased, but the relative percentage of C-C, C-N, and C-B bonds increased. The trend of increased percentages of C-N and C-B bonds with decreased concentrations of boron and nitrogen was very unlikely as the probability of having boron-based and nitrogen-based bonds would surely decrease with the decrease in the concentrations of boron and nitrogen.

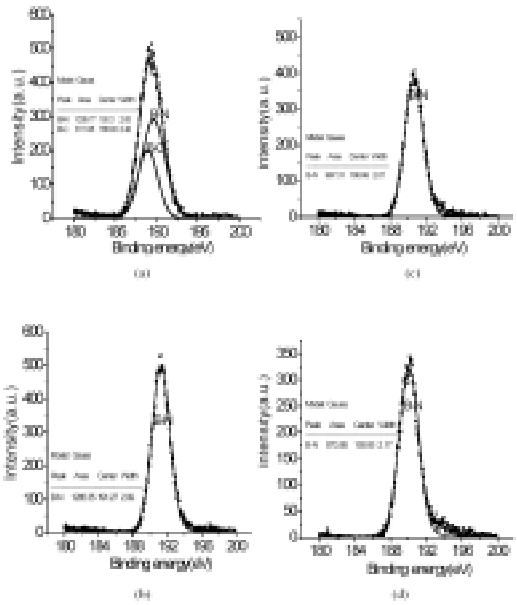
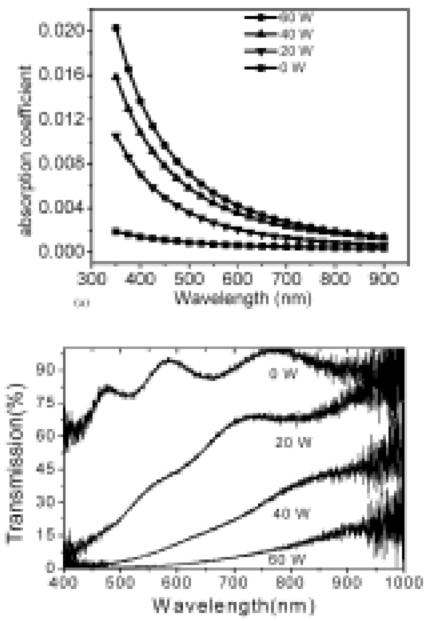


Figure 6 shows that, as the concentration of carbon in the films increased, the absorption coefficient of the films increased from 0.002 to 0.021, while the linear transmission at 730 nm wavelength decreased from 69.6% to 6.3%. Figure 7 illustrates the variations of electrical conductivity and activation energy with graphite target power. It can be clearly observed from this figure that a high concentration of carbon in the films not only increased the films's electrical conductivity but also reduced its activation energy of electrical conductivity. The activation energies were between 8 and 18 meV (are you sure? m means 0.001. The values are different from those shown in the figure. Check it again and let me know your explanation.) for the films deposited on quartz substrates. In comparison, a previous study indicated that BC_2N was a p-type semiconductor, whose acceptor level was between 7.5 and 23 meV for the films deposited on quartz substrate [25].



The above-shown trends in the optical and electrical properties were dictated by the incrase of C=C bonds in the films. With C=C bonds, free π electrons would result in the formation of various energy levels within the forbidden band. Such a developing trend associated with the increased concentration of carbon in the films was also responsible for the effective reduction of the internal stress and increase in friction coefficient [20]

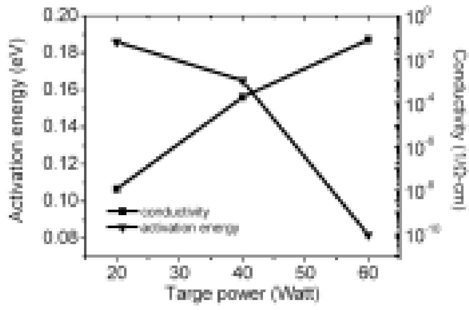


Fig.7

Conclusion

Amorphous BCN films were deposited on (100) p-type Si substrate, using dual gun sputtering system. By varying the graphite target power, the concentration of carbon in the film changed from 17.2 at% to 48.9 at%. Such a transition primarily resulted in the transition of the bonding state of the films from B-C bonds to C=C bonds, which accounted for the increases of the optical absorption coefficient and electrical conductivity of the films.

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本計劃發表之論文:

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