TRANSPARENT B-C-N THIN FILM FORMED BY PLASMA CVD AND ITS
ETCHING CHARACTERISTICS

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ABSTRACT

B-C-N thin films transparent at wavelengths of 200-1000 nm were deposited by plasma CVD using a capacitively coupled reactor at 13.56 MHz. They were formed from a gas mixture of $B_2H_6$ (5.25 vol. % in $N_2$), methane and argon or nitrogen as carrier gases. The Knoop microhardness was $1825 - 3324$ Kgf/mm$^2$. The films have been characterized by measuring infrared spectra, refractive index, Knoop microhardness, etch rate and composition.

1. INTRODUCTION

Boron compound thin films have a special interest for the technical applications. For example, they may be used as mask substrates for X-ray lithography and low Z layers in a pellet target for laser fusion experiments etc. There are many papers on boron compounds formed by chemical vapour deposition (CVD). Among them are the boron nitrogen compounds which have special interest for their superficial analogies with their organic counterparts[1]. However, there are a few papers about transparent thin films of boron nitrogen compounds formed by plasma CVD [2-4]. All that work was performed with heating the substrate at a temperature of at least 550-620°C [4]. It was noticed that the crystallization of the deposited films was related to the substrate temperature and it decreased with decreasing the temperature. However, no publication has appeared so far concerning the deposition of a hard transparent BN thin film at room temperature and without heating the substrate except ours.

In this paper we describe the formation of a hard transparent B-C-N thin film by plasma CVD at a frequency of 13.56 MHz. The transparent films were deposited at room temperature and without heating the substrate outside the discharge region. The main objective of this work was to investigate the properties of this film as functions of deposition conditions. We have studied the dependence of the transparency, hardness, deposition rate, film composition, etch rate and refractive index on deposition conditions.

2. Experimental

A schematic diagram of the rf apparatus used in our experiments is shown in Fig. 1. A capacitively coupled reactor at 13.56 MHz, which is evacuated from the bottom opening is used. The reactor is evacuated by an oil rotary pump to a pressure of about 6.5 Pa prior to the deposition. This reactor gives a uniform discharge as the electrodes are connected near the carrier
gas inlet. This would lead to deposition of uniform films. Two kinds of carrier gases, namely argon and nitrogen at a flow rate of 800-2000 ml (STP) min \(^{-1}\) are used alternatively. The carrier gas is first discharged at a discharge power level of 20-40 W. Then the reactant gases, which are diborane diluted in nitrogen at 5.25 vol. \(\%\) and methane are introduced in front of the carrier gas glow discharge at a flow rate of (100-500) and (10-135) ml (STP) min \(^{-1}\), respectively. Two types of substrates are used, namely glass (Corning 7059) and polished Si(111). The substrates are placed on a table further downstream out of the discharge region.

A spectrophotometry at a wavelength of 1000-200 nm is used to measure the transparency of the films deposited on the glass substrate. The molecular structure of the deposited films on Si substrates is investigated by IR absorption spectroscopy. Both film thickness and refractive index are determined by an ellipsometer at a wavelength of 632.5 nm by an HeNe laser source \([6]\). A quantitative analysis of film composition is measured by an ESCA MK II (VG Scientific). The microhardness of the films is measured by an E. LEITZ Wetzlar Micro Vickers hardness tester.

3. DEPOSITION

The films were formed at room temperature without heating the substrate. Most of the films deposited in our investigations were found to be stable and adherent to the substrates in room ambient. The films containing boron at atomic percentages of more than 10 \(\%\) were attacked by atmospheric changes after 6 weeks and lost the transparency gradually. For such films, the atomic percentages of oxygen increased proportionally. The most stable films were those containing carbon at atomic percentages of more than 45 \(\%\) and nitrogen at around 25 \(\%\). Deposition at a pressure less than 52 Pa gave transparent films with a moderate deposition rate of 8-12 nm min \(^{-1}\). The films deposited at higher pressures over 52 Pa were increasingly whitely fogged. The transparency of the films on glass substrates was investigated by spectrophotometry at wavelengths of 1000-200 nm. It was noticed that the films obtained at a lower pressure (less than 52 Pa) showed a very high degree of transparency without any noticeable absorption. The deposition rates and thicknesses were as high as 15 nm min \(^{-1}\) and 700 nm respectively \([7]\). The deposition rate was apparently dependent on the reactant gases ratios \([7]\).

The hardness of the films was measured by a microhardness tester. The Knoop microhardness was in the range of 1825-3324 Kg/mm\(^2\).

Most of the films showed very high degree of reproduction.

4. FILM PROPERTIES

4.1. INFRARED

It is very difficult to determine the molecular structure of such complex film only from IR spectra. This spectrum is dependent on both reactant gases ratios, and carrier gas type and flow rate \([7]\). This film is supposed to contain mainly the groups B-N, C-N, B-O and B-CH\(_3\) with relatively strong absorption peaks in the range of the biggest absorption 1250-1400 cm\(^{-1}\). As boron compounds are generally hydrophobic, we can expect 0-H stretching modes at 3400 cm\(^{-1}\). The peak at 3200 cm\(^{-1}\) may be assigned to N-H.

4.2. REFRACTIVE INDEX

The refractive index of the film is 1.3-1.6. In case of using diluted diborane only as the reactant gas, the refractive index is 1.67-2.7. We may expect that this value can be controlled by changing the carbon content in the film. It is noticed that the refractive index depends on both carrier
gas flow rate and the total pressure inside the reactor.

4. 3. COMPOSITION

According to the quantitative analysis of the film and IR spectra, it contains boron, carbon, nitrogen, hydrogen and oxygen. Oxygen was not mixed with the reactant gases but it maybe due to either some leak into the reactor because of the high activity of boron through the rotary pump, or the high reactivity of boron in the discharge region that may react with the glass reactor tube. The last reason sounds to be reasonable because very small amount of silicon appeared in some samples. Despite of the oxygen content in the films, they are stable and adherent to the substrates. Quantitative analysis of the hydrogen content are not available. It is noticed that the atomic content depends on discharge power, total pressure and $B_2H_6:CH_4$ ratios. Figure 2 represents the atomic ratios C/B, N/B and O/B as a function of the discharge power. It is clear that they increase with the discharge power up to a maximum value at a power level of 30 W and then they all decrease. These ratios decrease with increasing the total pressure in the reactor.

4. 4. MICROHARDNESS

The Wetzlar Micro Vickers hardness tester gives the Knoop microhardness values in Kg/mm². Figure 3 displays the dependence of the microhardness on the total pressure inside the reactor. This figure can be divided into two parts in case of argon gas as a carrier gas, one for $B_2H_6:CH_4$ ratios of about 0.6 and the other for ratios of about 0.15. It is clear that the microhardness increases linearly with the total pressure. The microhardness rate for the higher ratios is higher than that for the lower ratios. It must be mentioned here that very high values of microhardness can be obtained but on the account of transparency. Some values of microhardness for nitrogen deposition are also presented. It is clear that these values are lower than those for argon deposition.

Figure 4 shows the dependence of the microhardness on $B_2H_6:CH_4$ ratios with nitrogen. It can be noticed that there is a maximum value at a ratio of about 1.5.

The microhardness depends on C/B, N/B and O/B atomic ratios. A transparent thin film with microhardness value of 3324 Kg/mm² was obtained at C/B, N/B and O/B atomic ratios of 7.6, 2.85 and 2.7 respectively.

4. 5. ETCH RATE

Low pressure plasma etching of 0.53 Pa at a discharge power level of 50 W is performed by using different gases, namely CF₄, O₂ and H₂. The etch rate for each is 125, 55 and 28 mm/min respectively. In case of plasma etching with O₂, the etch depth increases with etch duration up to a value of about 500 nm and then saturates regardless of the etch duration. This means that the etch rate is equal to the deposition rate of B-0.

5. CONCLUSION

A transparent thin film formed mainly from boron, carbon, nitrogen and hydrogen with some oxygen content could be deposited by plasma CVD using a gas mixture of diborane(5.25 vol. % in N₂), methane, and argon or nitrogen as carrier gases. The films are prepared at a discharge power level of 10-40 W, discharge frequency of 13.56 MHz and a low pressure of 12-52 Pa. The deposition was performed at room temperature without heating the substrate.
The substrates were located out of the discharge region. This would keep the deposited films away from the electron bombardment that always occurs in the discharge region.

The films showed very high degree of transparency without any noticeable absorption at wavelengths of 200-1000 nm. Most of the films had very high degree of reproduction. Also, they were stable and adherent to the substrates at room ambient. The stability of the films was noticed to be dependant on both boron and carbon atomic percentages. The Knoop microhardness was 1825-3324 Kg/mm². The deposition rates and thicknesses were as high as 15 mm min⁻¹ and 700 nm respectively. The refractive index was 1.3-1.6. This value is expected to be a function of the carbon content in the film.

The atomic content of the films depended on discharge power, total pressure in the reactor and B₂H₆:CH₄ ratios. The microhardness was a function of the total pressure, B₂H₆:CH₄ ratios and the film composition.

The dry etch rates with CF₄, O₂ and H₂ was 125, 55 and 28 nm min⁻¹ respectively.

REFERENCES


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Fig. 1. Schematic diagram of the experimental apparatus.

Fig. 2. The atomic ratios vs. discharge power.
Fig. 3. Knoop microhardness vs. total pressure
- B$_2$H$_6$: CH$_4$ $\neq$ 0.15 and ▲ B$_2$H$_6$: CH$_4$ $\neq$ 0.6 with argon discharge. △ B$_2$H$_6$: CH$_4$ $\neq$ 0.6 with nitrogen discharge.

Fig. 4. Knoop microhardness vs. B$_2$H$_6$: CH$_4$ ratio.