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Synthesis and optical properties of BC_xN_y films deposited from N-triethylborazine and hydrogen mixture

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ABSTRACT

BC_xN_y films were obtained by plasma enhanced chemical vapor deposition method using a single-source precursor N-triethylborazine and hydrogen as plasma activating gas. The effect of synthesis temperature on the chemical composition and properties of the BC_xN_y films was investigated. The BC_xN_y films were examined by scanning electron microscopy, Fourier transform infrared and Raman spectroscopy, X-ray energy dispersive spectroscopy, X-ray photoelectron spectroscopy, and ellipsometry and spectrophotometry techniques. These experimental results indicated that the BC_xN_y films produced at low temperatures ($T_{dep} \leq 673$ K) are the polymer-like hydrogenated films with high transparency up to 93% in the visible part of the spectrum. BC_xN_y films produced at high temperatures (>673 K) contain additional phase of disordered carbon which has dramatically reduce transparency. The band gap of the films varied from 0.6 to 4.5 eV, with variation in deposition temperature.

1. Introduction

Boron carbonitride films are gaining importance due to possible applications in different areas. There are atomic bonding similarities among boron nitride and carbon that allow the formation of ternary compounds with a wide compositional range. BC_xN_y compounds have been expected to combine the properties of B–C–N system compounds, with their adjustable properties, depending on composition and structure. At the moment much effort is given to explore the functional characteristics of BC_xN_y films. Researchers have reported on BC_xN_y films with hardness up to 40 GPa (1–4), low dielectric constant (5–7), and good transparency (8–10). Authors (8) have noted the possibility of using boron carbonitride as promising material in electronic, optoelectronic and luminescent devices. According to Ref. (11) BN films have a wide band gap (E_g) 6 eV, incorporation of carbon into the BN film leads to a decrease of E_g for BC_xN_y films. The control of band gap by atomic composition and structure makes them good candidates for the application in electronic and photonic devices. However, there is no corresponding systematic study on the optical properties of the BC_xN_y films depending on their growth conditions. The synthesis of BC_xN_y films by different physical and chemical methods was reported (12). Chemical vapor deposition (CVD) processes can be divided into three groups: 1) by using boron trichloride, 2) using boron hydride, and 3) using complex organoboron compounds as precursors for the boron carbonitride based films. Organoboron compounds have attracted a great deal of attention by researchers as B–C–N–forming the single-source precursors that greatly facilitate growth process.

We have developed CVD processes with two different types of boron containing precursors: alkylamine boranes $R_3N \cdot BH_3$ and borazine derivatives $R_3N_3B_3H_3$, where $R = CH_3$, C_2H_5, to study the effect of molecule design and B:C:N atomic ratios in the precursors on properties of BC_xN_y films. The use of methyl or ethyl radicals allowed changing the amount of carbon in the deposited films. This work continues and supplements our previous studies concerning the preparation of BC_xN_y films by plasma enhanced CVD (PECVD) from trimethylamine borane and its mixtures with He, H_2, NH_3, by low pressure CVD from triethylamine borane and its mixtures with N_2, NH_3, and by PECVD from N-trimethylborazine (TMB) with N_2, H_2, NH_3, and N-triethylborazine (TEB) with He, NH_3 (Table 1). Theoretical prediction of BCN compound formation proposes the composition BC_2N (B:C:N = 1:2:1) (18) due to its stability (19). TEB has the same atomic ratio B:C:N = 1:2:1. We have previously shown for TMB (15) that the addition of hydrogen to gas phase improves the transmittance of the obtained layers in the more wide range of wavelengths.

In this investigation, we report the PECVD synthesis of BC_xN_y films using mixture of TEB and hydrogen. Growth rate, surface morphology, types of chemical bonds and optical properties of these films were studied with respect to the substrate temperature.

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Table 1
Precursors for BC_xN_y film synthesis.

Precursor	Formula	Atomic ratio B:C:N	Additional gas	Reference
N-trimethylborazine	$(CH_3)_3N_3B_3H_3$	1:1:1	N_2, H_2, NH_3	13–15
N-triethylborazine	$(C_2H_5)_3N_3B_3H_3$	1:2:1	He, NH_3	16
Trimethylamine borane	$(CH_3)_3N{\cdot}BH_3$	1:3:1	He, H_2, NH_3	17
Triethylamine borane	$(C_2H_5)_3N{\cdot}BH_3$	1:6:1	N_2, NH_3	3

2. Experimental details

2.1. PECVD synthesis

BC_xN_y films were grown by plasma enhanced chemical vapor deposition (PECVD) using mixture of N-triethylborazine and hydrogen. The experimental setup was described elsewhere (15). The deposition temperature ranged from 373 to 973 K. Residual pressure in the system was fixed at 0.67 Pa, the vapor pressure of the precursor at $P_{TEB} = 1.20$ Pa, and the pressure of the hydrogen at $P_{H2} = 0.60$ Pa, e.g. P_{H2}:P_{TEB} = 1:2 in all experiments. Polished, chemically cleaned silicon Si(100) and fused silica plates were used as substrates.

2.2. Characterization techniques

The surface microstructure and the elemental composition of the films were observed by scanning electron microscope (SEM) JEOL JSM 6700 F equipped with an EX-23000BU analyzer for element composition determination by X-ray energy dispersive spectroscopy (EDX). During EDX the field emission electron gun (W) was operated at an energy of 3 keV (radius of the excitation volume ~0.1 μm) and at a current of 1 nA according to our previous study (20). The X-ray detector EX 64165JNH is characterized by a resolution of 133 eV at the Mn K_α line (5.9 keV) at a count rate of 2000 cps (measuring time 200 s) yielding a dead time loss of about 18%. The spectra were evaluated by means of the program “Analysis Station 3.30.06” of the JEOL Engineering Co., Ltd. using ZAF correction (Z — atomic number, A — absorption, F — fluorescence). Fourier transform infrared (FTIR) spectra of the films were recorded using a SCIMITAR FTS 2000 spectrometer in the range of 300–4000 cm^{-1}. Thirty-two scans and the aperture equal to 4 at achievable resolution of 2 cm^{-1} were used during the measurements. In each case the spectrum of a substrate was subtracted from that of a sample. All FTIR spectra were normalized to thickness of the appropriate film. Raman spectra were recorded on a Spex 1877 triple spectrometer excited by an argon laser at the wavelength of 488 nm. The X-ray photoelectron spectra (XPS) were obtained by a MAC-2 (RIBER) analyzer using non-monochromatic Al Kα radiation at 1486.6 eV, power 300 W, and X-ray beam diameter of about 5 mm. The energy resolution of the instrument was chosen to be 0.7 eV to have sufficiently small broadening of natural core level lines at a reasonable signal–noise ratio. Under these conditions the observed full width at half maximum of the Au $4f_{7/2}$ line was 1.31 eV. The binding energy scale was calibrated in reference to the Cu $3p_{3/2}$ (75.1 eV), Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.7 eV) lines for providing the accuracy of ±0.1 eV in any peak energy position determination. The Au and Cu samples for calibration were mounted on the sample holder near the tested films. BC_xN_y samples were placed in the analysis chamber by transfer through the laboratory atmosphere so the hydrocarbon and oxygen contamination are present on the film surface. Since BC_xN_y are dielectric films, the photoelectron energy drift, due to charging effects, was taken into account in reference to the position of C1s (284.6 eV) line generated by adventitious carbon. The component of adventitious carbon was derived from complex carbon peak structure by means of deconvolution. To decompose the overlapped XPS peaks, we used mixed Gaussian and Lorentzian line shape functions with the parameters of the peaks measured on standard sample h-BN and B_4C as was shown earlier in Ref. (21). The thickness and refractive index of BC_xN_y films were determined by ellipsometry (LEF-3M ellipsometer) at the wavelength of 632.8 nm. The measurements were carried out at seven angles. Optical transmittance of the deposited films was measured using spectrophotometry data (scanning spectrophotometer UV-3101PC Shimadzu) in the range of 190–3200 nm (resolution 2 nm).

3. Results and discussion

Experimental results show that deposition temperature has a great effect on the deposition rate, morphology, bonding types and optical properties of the BC_xN_y films. The BC_xN_y film thickness was 100–300 nm. Growth rate decreased from 26 to 3 nm/min with increasing temperature of synthesis from 373 to 973 K (Fig. 1), that is typical for plasma-chemical processes. Most likely the film growth rate at low temperatures is high due to the formation process of polymer-like film.

3.1. Surface morphology

In Fig. 2 the different surface morphologies of the BC_xN_y films deposited on Si substrates are displayed. The film synthesized at high temperature (973 K) contains particles with size up to 30 nm on the surface (Fig. 2a). With decreasing deposition temperature the particle size is gradually reduced and the surface becomes more smooth and featureless (Fig. 2b).

3.2. FTIR analysis

The bond types in the as-grown films at various deposition temperatures were identified using FTIR-spectroscopy (Fig. 3). IR absorption of investigated BC_xN_y films varies dramatically with the synthesis temperature. The spectra of low temperature films contain main peak at 1435 cm^{-1} and shoulder at 1380 cm^{-1}, corresponding to vibration of B–N bond in cyclic borazine compounds (22), in-plane B–N bond vibrations (23). There are a set of weak peaks at 2490, 2965 and 3425 cm^{-1}, corresponding to hydrogen-containing B–H, C–H, and N–H bond vibrations (24). Therefore they are polymer-like hydrogenated films described by the empirical formula BC_xN_y:H, and hence they have smoother surface as was observed by SEM measurements. At deposition temperature ≥523 K the spectra contain the out-of-plane B–N–B (780 cm^{-1}) vibrations (23) and shift of main peak to lower wave numbers (1380 cm^{-1}), that correspond to in-plane B–N bond vibrations, occurs. At high deposition temperature the main peak contain, probably, shoulders at 1100 and 1600 cm^{-1} corresponding to B–C (25) and C═N (26) bond vibrations.

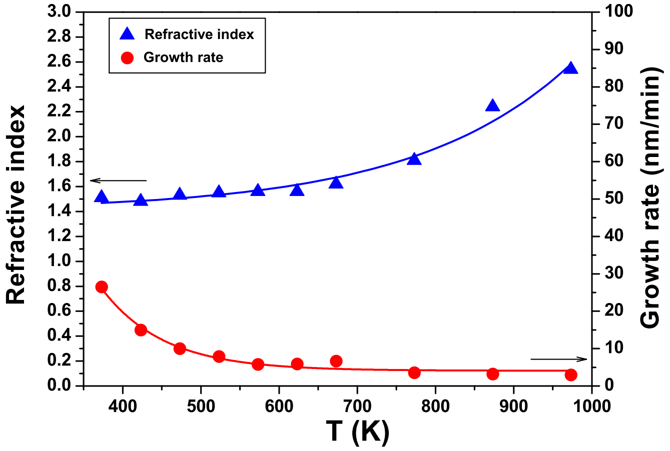

Fig. 1. Temperature dependence of refractive index and growth rate of BC_xN_y films synthesized from TEB + H_2 mixture.