GROWTH OF HOMOGENEOUS AND GRADIENT BC_xN_y FILMS BY PECVD USING TRIMETHYLAMINO BORANE COMPLEX

M.L.Kosinova[a)*], N.I.Fainer[a)], Yu.M.Rumyantsev[a)], E.A.Maximovski[a)], F.A.Kuznetsov[a)], M.Terauchi[b)], K.Shibata [b)], F.Satoh [b)]

[a)]Institute of Inorganic Chemistry SB RAS
3, Pr. Acad. Lavrentjev, Novosibirsk, 630090, Russia
[b)]IMRAM, Tohoku University
1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan

The ternary B-C-N compounds have a growing interest as materials for light element based coatings. The similar crystalline structure of cubic boron nitride (c-BN) and diamond as well as of hexagonal boron nitride (h-BN) and graphite has led to effort to synthesize hybrids of these materials. Much effort has been devoted to the preparation of both BN and BCN thin films by chemical vapour deposition with use of boron- and nitrogen-containing organic precursors. Molecules of the $R_3N{:}BH_3$ type have attracted a great deal of attention by researchers as B-C-N – forming single-source precursor.

The goal of this work is the fabrication and the study of homogeneous and gradient materials on the base of the BCxNy materials. The major point of the study is focused on the possibility of synthesis of BCxNy thin films by PECVD using trimethylamine borane complex $(CH_3)_3N{:}BH_3$ with/without ammonia and study of refractive index, transmittance, types of chemical bonds, the crystal structure and phase composition of films depending on the growth conditions.

In this study films of the B-C-N system have been synthesized by PECVD using the volatile single-source precursor trimethylamine borane complex $N(CH_3)_3{:}\ BH_3$ (TMAB) with hydrogen, helium or ammonia. Two types of substrates are used, namely Si(100), and fused silica. The thin boron carbonitride films were synthesised at low pressure (7×10^{-3}-4×10^{-2} Torr) and in the temperature region of 473-973 K. The temperature of the TMAB source was constant and equal to 0^oC. The films were characterised by SEM, IR and Raman spectroscopies, XPS, EDS, SAED, and HREM techniques. The structure of the deposited films is investigated using diffraction of synchrotron radiation (SR). The geometrical Bragg-Brentano scheme of registration of diffraction patterns was used.

SEM observation revealed that the surfaces of the all deposited films were smooth and that they were compact and adhered well to the substrates. A value of films' refractive index and deposition rate depend on deposition temperature as well as initial gas composition. The highest transmittance coefficient of BC_xN_y films grown on fused silica at 373÷523 K was 70-90% in the energy range of 2.0÷4.0 eV. The IR spectrum of film synthesized from $TMAB+NH_3$ mixture corresponds to h-BN spectrum. The absorption peaks associated with the B-N bonds are observed at 1380 and 780 cm^{-1}, corresponding to the B-N stretching vibration and the B-N-B bending vibration, respectively. The spectra of films obtained from TMAB and its mixture with hydrogen and helium show the presence of one main broad peak in the region of 1100 - 1500 cm^{-1} centered at around 1290 cm^{-1}. There are superposition of vibration modes of the B-N, C-N and B-C bonds. It is connected with the formation of B-C-N fragments in films. No absorption due to B-H (≈2500 cm^{-1}), C-H (≈2914 cm^{-1}) or N-H groups (≈3400 cm^{-1}) is observed.

The spectrum of low temperature film indicates four absorption bands at 602, 808, 1108 and 1360 cm^{-1}. The two peaks at 808 and 1360 cm^{-1} correspond to h-BN. At approximately 1100 cm^{-1}, a signal can be attributed to boron carbide. In addition, we observe peak at 602 cm^{-1} which is due to Si-Si bonding. From this result obtained it may be concluded that low temperature film consists of a mixture of hexagonal boron nitride and boron carbide. With increasing of deposition temperature up to 973 K, the characteristic main absorption peak is broadened and shifted towards lower wavenumbers (down to 1290 cm^{-1}). The high temperature film might be ascribed to hybrid B-C-N phase. IR spectrum of film synthesized at low concentration of ammonia (2×10^{-3} Torr) is similar to spectrum of ternary BC_xN_y. compound. Increase of ammonia concentration in gas phase leads to h-BN formation.

As for the Raman analysis, the spectra of the BC_xN_y films obtained from TMAB are very similar to that of amorphous carbon, with two broad bands centered at around 1335 and 1518 cm^{-1} (D and G bands of disordered sp^2 carbon). The Raman spectra of the films obtained from $TMAB+NH_3$ have the 1370,7 cm^{-1} peak characteristic of h-BN.

We report on development and characterization of gradient materials on the basis of the boron carbonitride with gradient of chemical composition or grain size.

Investigation of structure and phase composition of boron carbonitride films shows that the variety of gas phase composition leads to change of phase composition of grown films. Increase of the ammonia concentration in initial gas mixture promotes the formation mainly of hexagonal boron nitride. Nanocrystalline component of these films is h-BN phase.

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