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The Study of the Boron Nitride Thin Layer Structure

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Abstract. The structure of thin layers of boron nitride obtained by low temperature plasma enhanced chemical vapour deposition of borazine as precursor has been investigated by X-ray diffraction method. The diffraction pattern consists of the superposition of the three patterns: from non-crystalline turbostrate am-BN, from polycrystalline h-BN and c-BN. The sizes of intermolecular (nucleus surrounded by "fringe"), 14.8 Å, and intramolecular (nucleus), 7.6 Å, formations are evaluated from the reflection positions in non-crystalline state and confirmed by calculation. Polycrystalline reflections from h-BN and c-BN are in accordance with known ones for these modifications.

1. INTRODUCTION

Boron nitride (BN) is one of the most interesting materials of the III-V compounds, from both a practical and a fundamental scientific view point due to its low density, high thermal conductivity, chemical inertness, very high hardness and high resistivity. There are a wide variety of techniques for preparation of BN thin films. Recently the remote plasma enhanced chemical vapour deposition (RPECVD) became one of the most important technique of thin layers growth. A potentially interesting precursor for BN film production is the borazine ($B_3N_3H_6$) which contains the exact ratio of B:N=1:1 and hydrogen as the only foreign atom.

Synthesis of thin layers of BN by RPECVD using borazine allowed to produce films at temperatures considerably below than in convenient CVD. Considerable recent attention has been focussed on the structure investigations of boron nitride thin films because the physical and chemical properties of these layers strong depend on structure type[1]. In this paper we investigate the structure of boron nitride layers by X-ray diffraction method.

2. EXPERIMENT

The films were grown from the mixture of borazine and helium by RPECVD method [2] on Si (100) single crystal substrates. The synthesized films were characterized by different techniques. The thickness (150-170 nm) and refractive index (1.6-1.7) of the films were determined from ellipsometric measurements at $\lambda = 632.8$ nm. IR spectroscopy was used for a control of chemical composition of these layers.

The experimental diffraction patterns as $I_{exp}(2\theta)$ from the sample surface were recorded on X ray diffractometer DRON 4 [3] with the automated one circle (detector) and the rotation of the sampled studied relative to the incident radiation. The complete intensity curve was recorded three times with set of 10^5 counts for 7-12 minutes in each point of diffraction space. The position of the diffraction peaks were determined by scanning in narrow range of angles with $2\theta = 0.1^\circ$ steps. Systematic error in the intensity measurements dependent on the value of the diffraction angle was eliminated by matching the vertical slit widths during shaping incident radiation, as an example, when the slit width will be doubled the intensity measured in each point of the diffraction space will also be doubled.

Figure 1: Diffraction pattern of BN film obtained under automatic operation. The value R_1 is determined from the location k_1 of the main reflection in the intermolecular scattering (dashed line, calculated using eq.1). The value R_2 is determined from the location k_2 of the main reflection in the intramolecular scattering (dashed-and-dotted line, calculated using eq.2). The dotted line gives the main peak intensity of the intramolecular scattering vanishing when the sample rotating relative to the incident radiation (texture). The reflections from c-BN correspond to those of a supercell with the parameter of $a^* = 4a$ (a is the parameter of cell of c-BN). The reflections from h-BN and c-BN correspond to known in [4,5].

The experimental pattern consisted of three patterns: one from am-BN and two from polycrystalline hexagonal h-BN and cubic c-BN. The h-BN and c-BN reflections have been identified by us according to reported in Refs. [4,5]. Appropriate corrections dependent on the properties of radiation and material [6] were introduced into experimental diffraction patterns. In the case of amorphous boron nitride (am-BN) a procedure of the intensity normalization (obtaining $I_{exp}^{norm}(k)$) involved matching two modified (by k^2 , $k = (4\pi/\lambda)\sin\theta$, $\text{\AA}^{-1}$; $\lambda = 1.5418 \text{ \AA}$, θ being half the Bragg scattering angle) scatterings, namely, experimental $I_{exp}(k)$ and gaseous $I_{gas}(k) = \sum_{i=1}^N n_i f_i^2(k)$, where N and n_i are the numbers of atom kinds and atoms of each kind, respectively, in the formula unit of BN substance; $f(k)$ is the tabulated atomic factor of scattering [7]. The reability of this procedure was confirmed by that the normalization coefficient was practically unchanged with

increase of $k_{\max}$ defining the cut-off of experimental data on the high angle side. The total (t) pattern from am-BN can be represented as the sum of intermolecular (int) and intramolecular (in) scattering [8]:

$$S_t(k) = S_{in}(k) + F(k) \{ S_{int}(k) - 1 \} \quad (1)$$

where $S(k) = I_{\exp}^{norm}(k) / I_{gas}(k)$ the structure factor and,

$$F(k) = \left[\sum_{i=1}^N f_i(k) (\sin k R_{ci}) / k R_{ci} \right]^2 / \sum_{i=1}^N f_i^2(k)$$

is the orientation factor for completely uncorrelated intramolecular formations, in which R_{ci} is the distance between the i -th atom and the gravity center of this formation and N is the number of atoms. The average size of the inter- and intramolecular formation, $R_1 = 14.8$ and $R_2 = 7.6$ Å, respectively, was estimated according to [9] $R_i = 7.73 / k_i - 0.3$, where k_i ($i = 1, 2$) is the reflection location in the experimental diffraction pattern.

The first reflection at k_1 in $S_{int}(k)$ pattern from am-BN is described by the structure factor $S_{hs}(k)$ of hard spheres [10]:

$$S_{hs}(k) = 1 / \{ 1 - \rho \tilde{c}(k) \},$$

$$c(k) = (4\pi\sigma^3/b) \{ [-2\beta/b^2 + 24\gamma/b^5] + \sin b[-\alpha/b^2 + 2\beta/b^2 + 4\gamma/b^2 - 24\gamma/b^4] + \cos b[-\alpha/b - \beta/b + 2\beta/b^3 - \gamma/b + 12\gamma/b^3 + 24\gamma/b^5] \},$$

where $b = k\sigma$, $\alpha = -(1+2\eta)^2/(1-\eta)^4$, $\beta = 6\eta(1+0.5\eta)^2/(1-\eta)^4$,
 $\gamma = -0.5\eta(1+2\eta)^2/(1-\eta)^4$,

ρ is the density (number of molecular formations / Å³), $\tilde{c}(k)$ is the fourier-image of direct correlation function, $\eta = (\pi/6)\rho\sigma^3$ is the packing density, σ is the diameter of hard sphere (molecular formation). The second reflection k_2 is due to molecular formation [10]:

$$I_{in}(k) = \sum_{i=1}^{N_1} n_i f_i(k) \left[\sum_{j=1}^{N_2} m_{ij} f_j(k) \sin(kr_{ij}) / kr_{ij} + \alpha_i \bar{f}(k) \sin(kr_{i1}) / kr_{i1} - \rho_0 \bar{f}(k) \int_0^{R_1} 4\pi r^2 \sin(kr) / kr dr \right]$$

where $\bar{f}(k)$ is the average nuclear factor of both B and N atoms

, $\rho_0 = d/m_H \sum_{i=1}^N n_i M_i$; d is the pycnometric density, m_H is the weight of hydrogen atom, M is the atomic weight, R_1 is the radius of sphere around the first atom outside which the atomic distribution is continuous, $r_{i1} = R_1$ is the thickness of the shell consistent of α_i atoms of intermediate distribution, from discrete to continuous; $r_{ij} = (r_i - r_j) \leq r_1$ is the distance between i -th and j -th atoms in discrete distribution of atoms, i is the index of summation over N_1 atoms of different n kinds chosen for the central ones around which the atoms the nearest environment in coordination spheres to be considered; j is the summation index over m atoms in N_2 coordination spheres surrounding i atoms.

CONCLUSIONS

In our case c-BN was prepared at low pressures and temperatures. This supported the dependence $P(T)$ known for carbon [12] indicating the favored formation of cubic phase over hexagonal at the lower temperatures the lower the pressure.

Using ρ we evaluated d for am-BN equal to 2.66 g/cm^3 that appears to be higher than known (2.29 g/cm^3) density for h-BN and less than that (3.45 g/cm^3) for c-BN. The valuation is performed on the basis of description of intermolecular scattering by a hard-sphere model (turbostrate, $R1 \text{ \AA}$). Intermolecular scattering was extracted from the total one, $I_{\text{exp}}^{\text{norm}}(k)$, after that theoretical calculation of intramolecular scattering was carried out using the model structure of turbostrate as nucleus and "fringe" surrounding it [13]. The nucleus is an averaging over nuclei having both h-BN and c-BN structures, surrounded by the "fringe" consistent of incomplete hexagonal rings B_6N_4 and tetrahedral B_4N and BN_4 , respectively, with account of the stoichiometry of BN. Notice that discrete reflections from polycrystalline phases are easily extracted from the diffraction patterns of am-BN.

The am-BN layers obtained by above mentioned method have mainly turbostrate structure which is intermediate between the structures of non-crystalline and crystalline states. In addition, in these layers h-BN and c-BN are revealed in polycrystalline states. Taking into account the low values of the pressure and temperature the formation of c-BN under these conditions could not be explained by the structural transition of h-BN into c-BN in layers. We assume that c-BN was formed as a condensate before the deposition on the substrate. Such a condensate appears to be skeleton fractal with framework constructed by dendrite type which, in its turn, is surrounded by "fringe".

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