Structural Modification of Thin Layers of Boron and Silicon Nitrides by Synchrotron Radiation

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Abstract. Modified structures of thin layers (50-200 nm) of c-BN and α-Si_3N_4 obtained by CVD from gaseous phases of proper B-N and Si-N-containing compounds on single crystal surfaces were studied using SEM and X-ray diffraction. Synchrotron radiation (SR) served not only as analyzing tool but as a means of modification and such an application of SR is a novel method to influence on chemical different strength bonding in inorganic materials. SR from 2 to 12A range with expose dose of 120-140 mA cm was used to act on thin layers.

c-BN layer morphology of microcrystals was observed to be SR modified: developed microcrystals (2-3 mkm) of identical rosette-like shape formed homogeneous coating of a surface. SR induced recrystallization of microcrystals at an invariance of crystalline structure due to the existence of strong covalent bonds between boron and nitrogen atoms. For α-Si_3N_4 it was shown that microcrystals in small yards were volatilized because of weak chemical coupling between [SiN_4] pieces and in a bulk of layer traces of the preceding (prior to SR action) shapes of microcrystals and unchanged microcrystals (1 mkm and less) were observed.

1.Introduction

Boron and silicon nitrides have high reagent resistance, hardness, resistance to wear, a wide energy gap, and consequently, they have drawn considerable interest in several fields of science and technology. Thin layers of boron nitride are usable as insulating coatings in devices of microelectronics. This paper deals with the structural and morphological characterization SR-modified thin layers (50 to 200 nm) of c-BN and Si_3N_4 grown by CVD on different thermostated (200-400^{0}C) substrates by plasmochemical decomposition [1] of element-organic precursors. Helium was used as a carrier gas. The helium in plasma at low pressures is capable to form different radicals (He*) which can accumulate energy and activate disintegration of precursor.

Both diffraction measurements and modification of the substrates studied were performed at the storage ring synchrotron facility VEPP-3 at INP SB RAS. SR from 2-12 A range and expose dose 120 to 265 mA min were first used to modify the structure of thin layers. For the purposes of structural analysis X-ray three-crystal diffractometer (θ-2θ) and highly monochromatic SR ($\Delta\lambda/\lambda = 4\bullet10^{-4}$, λ =1.5405A) were used. The structure of matters was established by comparing the diffraction patterns from the computer-simulated structural models for the known modifications of the substances under study with those obtained experimentally. Morphological characterization of grown layers was performed by using a scanning Electron microscope JSM-200.

A special interest in the work reported here was to study the structural changes in the grown thin layers depending on their growth parameters, namely, substrate temperature and the type of substrate materials, and, to consider the possibilities of SR to modify morphology and structure of the deposited layers.

2. BN layers

The c-BN/(100)Si thin layers were synthesized from a mixture of triethylaminobozane (as precursor) with helium (it was used for nonthermal r.f. activation of $BN_3N(C_2H_5)_3$ molecules in gaseous phase) by remote plasma chemical vapor deposition technique. The layers have been deposited at 10^{-2}-10^{-3} Torr and 200-500^{0}C on chemically etched substrates. The thickness (up to 9000 A) of the grown thin coatings was measured by SEM using cleavage surface of a sample.

Diffraction patterns from c-BN/(100)Si displayed the reflection intensity depending on the direction of

incident radiation on a sample surface. The discrete reflections (111), (220), (311), (400) could be indexed as a sphalerite phase with a high unit cell parameter a =4.53 A different from a =3.62 A known for a bulk c-BN. Besides the above peaks, there were observed the reflections (121), (300), (-302), (401) corresponding to the structure in which atoms located in tetrahedral voids of sphalerite lattice were shifted from the original positions by 0.1a of a lattice parameter. Value a =4.5A in BN thin layer on a crystal surface Si(100) corresponded to a distance between silicon atoms located in tetrahedral voids (0.25, 0.25, 0.25) and atoms (0.5, 0.5, 1) in the center of crystalline faces (1, 0, 0).

In SEM micrographs, along with a layer of amorphous am-BN, recognized from the electron diffraction, microcrystals of two morphologies, cube- and rosette-like, spaced on a distance from each other were observed. After energetical SR influence (dose 120-140 mA min) the coating was composed of rosette-like structures of smaller sizes and individual large (5 mkm) cubes and rosettes [2]. Diffraction patterns displayed reflections corresponding to c-BN (a =4.6 A), h-BN (a =2.8, c =4.75A), c-B_4C (a =5.61, c =12.07 A) [2].

The structure of BN layers grown at 100-500^{0}C on (100) substrate using borazine $B_3N_3H_6$ precursor was studied. A layer thickness 5000 A and a refractive index n =1.67-1.85 were measured ellipsometrically. From diffraction patterns follows that the deposited layers of BN consisted of a mixture of am-BN, c-BN (a* =4a, a =3.63 A) and h-BN modifications. The reflection positions in c-BN (a* =4a) pointed to a condensate formation of a fractal-type. Basing on the reflection positions for am-BN intermolecular (nuclei surrounded by a "fringe", R_1=14.8A at k_1) and intramolecular (nuclei R_2 =7.6A at k_2) distances were estimated using mean distance R=7.73/k (interplanar distance d ≈R ≈2π / k, k =(4π/λ)sinθ, A^{-1}). In am-BN the nuclei of this turbostrate structure consist of a mixture of bounded incomplete hexagonal rings of B_6N_4 and tetrahedral B_4N and BN_4 with account of the stoihiometry of BN [3].

3. Si_3N_4 thin layers

The structural study of α-Si_3N_4 layers on single crystal (100)GaAs substrates obtained using hexamethyldisilazane $Si_2NH(CH_3)_6$ precursor showed that they were non-crystalline with crystalline inclusions of α-Si_3N_4. Non-crystalline structure was identified using diffuse reflections in high-speed electron diffraction patterns. A specific cleavage surface suggests also non-crystalline state. The inclusions represented individual shapeless microcrystals and small ring-like yards surrounded by a "necklace" of faceted microcrystals along a perimeter [4] . Inside small yards were or large (5 mkm) microcrystals, or dendrites. An occurrence of dendrites pointed to the conditions of a recrystallization at supercooling.The growth of microcrystals occurred normally to a substrate surface and in a direction of heat removal. The morphology of inclusions in non-crystalline layer depended on the conditions of obtaining coating. Small yards were hemispherical grains of growing microcrystals on substrates. The spherical grains without environment of microcrystals were also observed . The experimental diffraction patterns from thin layers obtained at different substrate temperatures displayed reflections from one and other faces in microcrystals having the same structure α-Si_3N_4. It allowed to draw a conclusion about reproducibility of obtaining α-Si_3N_4 species by this method of synthesis.

Non-crystalline layers with porous areas and inclusions of microcrystals α-Si_3N_4 deposited on (400) GaAs substrates had lattice parameters a =8.3, c =6.2A, γ =120^0 different from those known for a polycrystalline state (a =7.765, c = 5.622A, γ =120^0) [5]. Parameter a =8.3A was consistent with a distance r(Ga-As) between atoms on a crystallographic plane (100) of GaAs. Lattice parameters of microcrystals were found to differ from those known for a polycrystalline state. They were dictated by epitaxial growth conditions in vacuum. The layers obtained at substrate temperature lower 300^{0}C were observed to be non-crystalline with aggregates of shapeless microcrystals. At substrate temperature 300^{0}C and higher inclusions consisted of hemispherical formations arranged as small ring-like yards.

The SEM data indicate that the microcrystals generally grew on defects in substrate- at the points of output of dislocations on a surface of single crystal substrate which were decorated by grown crystallites. While SR irradiated (dose 265 mA min), large (10 mkm) formless microcrystals and dendrites were volatilized and produced caverns of the shape of disappeared species (fig.1). This pointed to weakness of chemical bonding the tetrahedral structural units [SiN_4].

Fig. 1 displays the different parts of the layer before (top) and after irradiation (bottom - traces of shapes of evaporated microcrystals), because experimental procedure of obtaining electron microscopy micrographs excluded the study of the same parts due to specific treatment of samples before each registration.

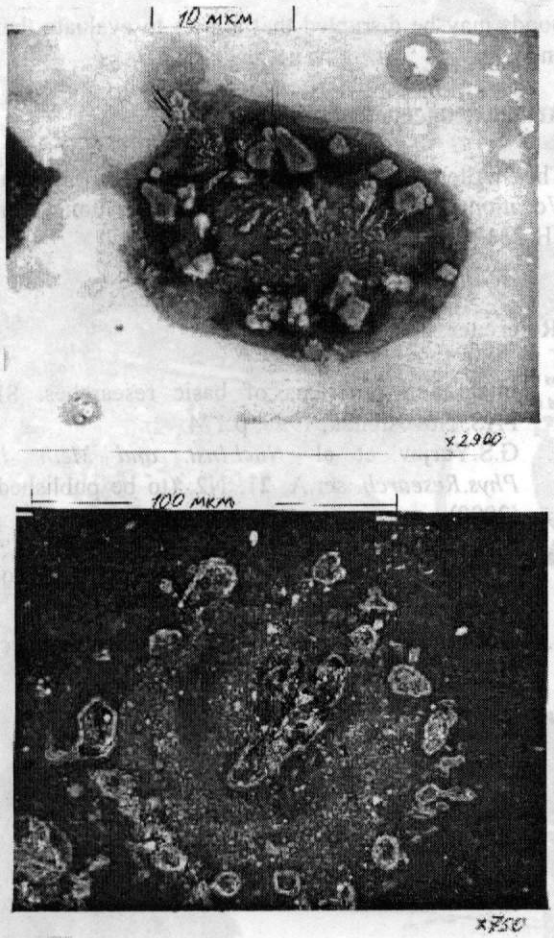

Fig. 1.

The layers of α-Si_3N_4 on single crystal (100)Si substrate. SEM micrographs of layers exhibit inclusions α-Si_3N_4 arranged as aggregates (up to 10 mkm) of shapeless microcrystals and as well faceted individes around small ring-like yards. The latter grown at substrate temperature 250^{0}C were observable as hemispherical individual grains that was confirmed by character of cracks on grains. Microcrystals are arranged about small yards by concentric shells, up to four ones. Small yards have increased in size up to 85 mkm with increasing substrate temperature to 300^{0}C. Further temperature increasing to 400 C resulted in the formation in thin layer of areas of microcrystals (2mkm) giving homogeneous coatings. At substrate temperature 475^{0}C aggregates of shapeless microcrystals and small yards were appeared. Indirect evidence for α-Si_3N_4 structure followed from faceted microcrystals with faces arranged at 120^0 angles in SR irradiated layers.

The structure of thin layers (150 to 300) of α-Si_3N_4 deposited on (100) Si substrates from a mixture of didimethylhydrazinosilan $(CH_3)_2HSiNH(CH_3)_2$ and He* was studied also. In diffraction patterns from the layers obtained at 200, 400, 600^{0}C there were reflections from the crystal faces (h00) of α-Si_3N_4 that indicated a high crystallinity of samples. The reflections (100), (200) were found to be noticeably shifted into small diffraction angle side. This shift, as above, resulted from a lattice deformation of α-Si_3N_4 inducing an increase in parameters by comparison with those known for polycrystalline state. For layers obtained at 500^{0}C the position of a single reflection (100) α-Si_3N_4 was indicative of a similar deformation of lattice.

SEM micrographs of surface of these layers exhibited the areas of microhomogeneity. So, in the layers deposited at 200, 600^{0}C, along with individual microcrystals (1 mkm) there were areas of the faceted microcrystals (3 mkm) concentrated in small ring-like yards (50 mkm). The layers (180 nm) obtained at 400^{0}C consisted of non-faceted individual microcrystals (1 mkm) and areas (up to 10 mkm) (structurally these layers were similar to those obtained with another precursor - tetramethylsilane $(CH_3)_4Si$). Here, there were observable areas spalled off substrate because of thermal expansion mismatch between layer and substrate and inconsistency in structure of their boundary planes. In the layers deposited at 600^{0}C areas of microcrystals achieved 50 mkm.

In the layers (120 nm, 500^{0}C) diverse morphologies were observable: vast (tens of microns) areas of microcrystals (significantly less than 1 mkm), areas (up to 10 mkm) of oval microcrystals (up to 1 mkm), spalled off segments (up to 20 mkm) and separate faceted and non-faceted microcrystals (up to 3 mkm). Spalled off areas both had no voids and had voids (up to 3 mkm).

The diffraction patterns from thin layers (400 nm) α-Si_3N_4 deposited on (111)Si substrate at 400^{0}C using $(CH_3)_6Si_3N_3H_3$ precursor without a gas carrier showed reflections (100) and (201) α-Si_3N_4. Unlike (100) reflection, (201) corresponded with an interplanar distance to reflection from (111) Si substrate indicating that the structure of α-Si_3N_4 layer was formed in accord with a crystal plane of a substrate (111)Si. The position of reflection from α-Si_3N_4 coincides with known for polycrystalline α-Si_3N_4. This indicated lack of deformation in lattice of α-Si_3N_4 layer in a direction [201]. This deformation was absent in layers of 300 and 320 nm thickness obtained, respectively, at 450 and 650^{0}C using $(CH_3)_4SiN_2H_2 + H_2$ precursor. In the first case, (100) α-Si_3N_4 reflection was absent and in latter it was weak and very diffuse suggesting slight evolution (100) plane in comparison with developed (201) face.

The α-Si_3N_4 layers on glassy SiO_2. Microstructure of layers grown on fused quartz surface was composed of aggregates (up to 200 mkm) of microcrystals (up to 10 mkm) both formless and faceted as small yards located in dimples of non-crystalline coating. Diffraction patterns displayed

discrete reflection (100) α-Si_3N_4 on the background of diffuse diffraction halo from substrate.

α-Si_3N_4 layers on (100)Kbr. Morphologies of the layers grown on surface of fresh cleavage of single crystal (100)KBr were studied by transmission electron microscope (including diffraction in transmission version) and represented diverse regions: polycrystalline, needles and monocrystalline.

Conclusions

Structural features of modifications of c-BN and α-Si_3N_4 thin layers deposited by plasma pyrolysis of organic precursors at different temperatures on a set of thermostated substrates were investigated by X ray diffraction.

In the c-BN layers both fractal and deformed crystal structures were shown to be realized depending on a type of precursor. A type of crystallographic plane dictated formation in α-Si_3N_4 distorted and undistorted crystalline structures.

The opportunity of modification of morphological structures in studied substances by SR exposure was shown. In the case of c-BN layers their recrystalization was produced by such an influence. It was shown that at certain energy particle chemical bonds may be disrupted that allows to evaluate their energy.

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