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Synthesis, conductivity and high-pressure phase transition of amorphous boron carbon nitride

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Abstract

Amorphous BCN was prepared by chemical solid-state reaction between boracic acid (H_3BO_3) and melamine ($C_3N_6H_6$) in mass ratios of H_3BO_3 to $C_3N_6H_6$ of 1:2–1:4 and heat treatment at 1273 K under 10^{-3} Pa. The amorphous B–C–N behave insulating property below 890 K, but semiconductor conductivity above 890 K and show different conductivity–temperature relationships in temperature ranges of 913–963 and 963–1083 K. The conductive activation energy was calculated to be 0.26–0.34 eV at 913–963 K and 1.02–1.10 eV at 963–1083 K, implying that the conduction mechanisms are different in the different temperature ranges. Annealed for 40 min at 1473 K under 4.0 GPa, the amorphous BCN with the chemical composition $B_{0.48}C_{0.29}N_{0.23}$ was prepared in the mass ratio of 1:3 crystallizes into single-phase hexagonal (h-BCN) compound with lattice constants of $a = 0.2506$ nm and $c = 0.6652$ nm. Raman scattering peaks were observed at 1330, 1364,1584 and 1617 cm^{-1} in the Raman spectrum (RS) of h-BCN, of which the peaks located at 1330 and 1617 cm^{-1} are assigned to characteristic peaks of the h-BCN.

1. Introduction

B–C–N compound is a new material, theoretical calculation predicts that B–C–N materials may be a high-temperature semiconductor or new super-hard material with the excellent electrical, optical, and mechanical properties, possessing a full-potential applicable prospect [1,2]. Since Professor Cohen [3] gave the formula of the bulk elastic module (*B*) and bond length (*d*) for covalent crystals based on relationship between the bond energy and molecule volume and predicted that boron carbon nitride

(B–C–N) may become new super-hard materials, synthesis, characterization and properties of B–C–N compounds have been one of important subjects in physical, chemical and material science research field. Many techniques have been used to prepare B–C–N compounds with various compositions and structures. Most of B–C–N compounds reported are of hexagonal or cubic structures [4–6]. An X-ray diffraction (XRD) profile of single phase of B–C–N crystal is even not reported in the literatures. However, since single-phase crystal of B–C–N with large grain size has not been synthesized up to now, the electrical, optical, and mechanical properties of BCN compounds are known little. Therefore, there are many problems to be solved for exploring the applicable methods to prepare the bulk amorphous or crystal BCN as new materials.

In the present work, B–C–N compounds were synthesized by chemical solid-state reaction between boracic acid

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(H_3BO_3) and melamine ($C_3N_6H_6$) and heat treatment under vacuum and high pressure. The structure, phase transition, and conductive properties were investigated.

2. Experimental procedures

Starting materials of H_3BO_3 and $C_3N_6H_6$ with various mass ratios, both are in purity of AR grade, were mixed evenly by rubbing enough firstly, then put into a corundum crucible and annealed isothermally in the muffle stove at the temperatures of 473 K for 1 h and 573 K for 3 h, respectively. The as-prepared samples were called as B–C–N precursors. Rapidly heated to 1273 K under the pressure of 10^{-3} Pa and annealed isothermally for 0.5 h, the precursor transforms into amorphous BCN. High-pressure anneal of the amorphous BCN was performed in a Bridgeman anvil high-pressure apparatus, which was employed to generate quasi-hydrostatic pressure by using pyrophyllite as a pressure-transmitting medium. The phase analysis of the samples was carried out by using XRD with Cu K_α radiation, and the composition, valence bond state, and structure of the sample were detected by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared absorption spectroscopy (FTIR), and Raman scattering spectroscopy (RS). The conductivity of the amorphous B–C–N was measured by using four-point probe method.

3. Results and discussions

3.1. The composition and valence bond of amorphous BCN synthesized by chemical solid state reaction

B–C–N compound was synthesized by chemical solid-state reaction between H_3BO_3 and $C_3N_6H_6$ at temperatures between the melting point of H_3BO_3 (458 K) and the volatile point of $C_3N_6H_6$ (>573 K), and is marked as B–C–N–O–H. The volatilization of H and O from the B–C–N–O–H matrix occurs at a pressure of 10^{-3} Pa and temperature of above 873 K, accompanied by loss of a small amount of C and N. Upon annealing at 1273 K under 10^{-3} Pa, the B–C–N–O–H precursor will lose all of the H and O and transform into B–C–N compound with high purity.

Fig. 1 is typical amorphous XRD, indicating that the amorphous B–C–N compounds were fabricated as the mass ratio of H_3BO_3 to $C_3N_6H_6$ is in the range of 1:2–1:4 and annealing temperature is at 1273 k. The formation of the amorphous BCN may be due to following processes: the chemical bonds of the precursor were broken as it was annealed at a temperature of 1273 K, resulting in that the H and O escape from the precursor and B, C, and N atoms are remained. However, the 1237 K is too low and cannot provide enough thermal energy to drive the B, C, and N atoms to stable thermodynamic equilibrium positions, leading to random packing of the atoms, that is, formation of amorphous BCN. In fact, it was reported that the
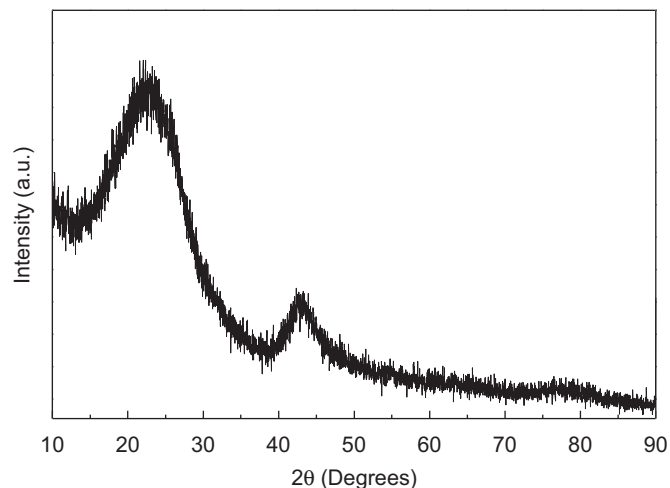

Fig. 1. XRD patterns of amorphous B–C–N prepared by annealing the precursor in the mass ratio of H_3BO_3 to $C_3N_6H_6$ of 1:3.

precursor can transform into crystalline B–C–N phase as annealed at a temperature of 1600 K. [7,8] This B–C–N compound still remains its amorphous state up to 1473 K, exhibiting high thermal stability.

In order to demonstrate that the B–C–N compounds were composed by B, C, and N, XPS measurement was performed for the amorphous BCN prepared at the mass ratio of H_3BO_3 to $C_3N_6H_6$ of 1:3. Fig. 2 shows the B_{1s}, C_{1s}, and N_{1s} XPS spectrum of the amorphous BCN compound. Fig. 2a reveals the XPS spectrum of B_{1s}, which can be fitted well by three sub-spectra using Gaussian profile, with the binding energy (BE) of 189.8, 191.0, and 192.5 eV, respectively. The 191.0 eV is very close to the BE of B_{1s} of B–N bond in hexagonal h-BN, so it is ascribed to B_{1s} electronic radiation of the B–N bond in BCN. The peak at 189.8 eV was assigned to B_{1s} electronic radiation of the C–B–N bond [9]. The 192.5 eV is much close to BE of the B_{1s} of B–O bond in B_2O_3, so it is attributed to B_{1s} electronic radiation of the B–O bond. The B_2O_3 originates from the oxidation of a small amount of B atom at surface of sample. The XPS spectrum of C_{1s} is fitted by three sub-spectra with BE of 283.7, 284.9, and 286.5 eV, respectively, as shown in Fig. 2b. The 284.9 eV is much close to the BE of C_{1s} of 284.5 eV in graphite, so this peak is attributed to electronic radiation of C_{1s} of the C–C bond in the BCN. The peak at 283.7 eV is assigned to C_{1s} electronic radiation of the C–B–N bond in the BCN [9], while the peak at 286.5 eV is due to C_{1s} electronic radiation of the C–N bond, because the BE is close to the BE value of C_{1s} of C–N bond observed in some compounds containing C and N elements [9]. The N_{1s} spectrum shown in Fig. 2c can be fitted with three sub-spectra with the BE of 396.9, 398.2, and 399.5 eV, respectively. Obviously, the peak at 398.2 eV is considered as result of N_{1s} electronic radiation of B–N bond. The peak at 396.9 eV is due to the N_{1s} electronic radiation of C–B–N bond in the B–C–N compound [9], while the peak at 399.5 eV is assigned to be the N_{1s} electronic radiation of C–N bond [10].