Impurity Control and functionalization of Polymorphic Phase of Boron Nitride Polycrystals and Single crystals obtained under High Pressure

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1.Introduction

Hexagonal boron nitride BN (hBN) and cubic BN (cBN) are known as the representative crystal structures of BN. The former is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant materials. The latter, which is a high-density phase, is an ultra-hard material second only to diamond. In addition to those, wruztite BN (wBN) is also known as other polymorphic phase. As crystal growth technique is not, however, applicable for wBN due to its thermodynamically metastable nature, fundamental properties of wBN with bulk crystalline form is not well studied so far.

Among those BN crystals, some progresses in the synthesis of high purity BN crystals were achieved by using Ba-BN as a growth solvent material at high pressure (HP) of 5.5GPa[1]. Band-edge natures (cBN Eg=6.2eV and hBN Eg=6.4eV) were characterized by their optical properties. The key issue to obtain high purity crystals is to reduce oxygen and carbon contamination in the HP growth circumstances. Then an attractive potential of hBN as a deep ultraviolet (DUV) light emitter [2] and also superior properties as substrate of graphene devices [3] were realized. By using high purity hBN crystal as a starting material, high purity cBN sintered body and also highly oriented wBN crystalline form were obtained by high pressure phase transformation process [4].

In this paper, recent studies on BN polymorphic phases obtained at high pressure with respect to impurity / isotope controls and their functionalizations will be reported.

2.Experiment

hBN crystals were obtained with Ba-N base solvent by using belt-type high pressure(HP) apprataus at 4GPa and 1600°C. Recovered hBN crystals were cleaned by acid treatment and were studied their optical nature of band edge emission by using Cathodluminecense(CL). For the impurity charactrization, SIMS studies were carried out. Well facetd grown hBN crystals were used as a starting material for obrtaining wBN crystals to realize its mechanical properties. Further more, heat treatement of hBN crystals with graphite furnance were carried out for the preparation of carbon doped hBN crystals. Then variety of hBN crystals with differenet carbon impurity levels were prepared as the starting materials for the synthesis of binderless cBN sintered body at 10GPa and 1700°C. Mecahnical properties of those wBN and cBN sintered body were studied by their hardness measurement.

3.Results and Discussion

Fig.1 shows SIMS depth profile of typical hBN crystals showing less Carbon and Oxygen impurity levels. Fig.2 shows hBN's band edge CL spectra. Inset 215nm CL images show impurity locaization in the dark central portion suggesting different residual impuirty levels of the two crystals. It shoud be noted that intensity of band edge emission seems to correlate to the residual impurity. Since SIMS detection limit is around few ppm level of those impurities, further technical advancement for addressing residual impurity is important.

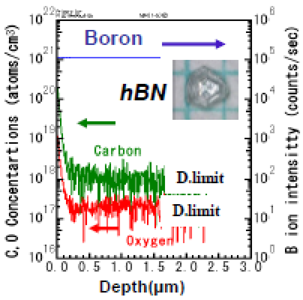

Fig.1 SIMS profile of hBN crystals.

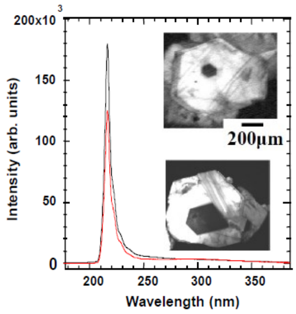

Fig.2 CL spectra of hBN crystals. Inset: 215nm CL image

By using hBN crystal as a starting material, wBN crystals can be obtained by a direct phase transforation at 10GPa and 800°C. Fig.3 shows typical optical images of hBN starting material and resultant wBN crystal. Accoring to XRD study, hBN crystal of single crystalline nature inculidng a few stacking falut changed to wBN with highly oriented crystalline nature but no more single crystalline feature. Precise HRTEM stsudy revealed lotss of staking fault probably due to its phase tarnsformation nature[5]. While hexagonal diamond is known to be back transofrmed to graphite via pressure release process, wBN can be quenched at ambient condition. This tyical difference could be explained by the isight for the stacking fault

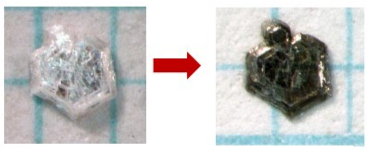

Fig.3 Optical view of hBN and wBN crystals.

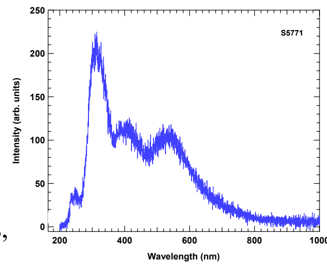

Fig.4 CL spectrum of wBN crystal.

nature with wBN of binary compound system. Drastic change of the color of wBN from hBN as shown in Fig.3 is attributed to the microstrucre of wBN crystal. CL profile of wBN may give trace of band edge nature but is dominated by some deep level emissions with defects as shown in Fig.4. Hardness measuerment were carried out for wBN, cBN and cBN sintered body by using Nano-indentation technique. We got conclusion that Hardness and Young moduls of wBN seems near 90% of those of cBN[6].

It is know that carbon atom can diffuse hBN crystal at high temprature. High temprature anneal of hBN by using graphite furnace at 2000°C was carried out. Then we could prepare some variation of hBN crystals with different carbon content. High pruity hBN crystals exibit carbon impurity levels of less than 10ppm(~ $2x10^{18}/cm^3$) region which is closed to SIMS detection limit, as shown in Fig.1.Commercialy available hBN crystals exhibit typically ten times larger i.e. several 100ppm range. After heat treatment at 2000°C using graphite furnace, C-doped hBN crystals with $10^{21}/cm^3$ of C imourity level were obtained.

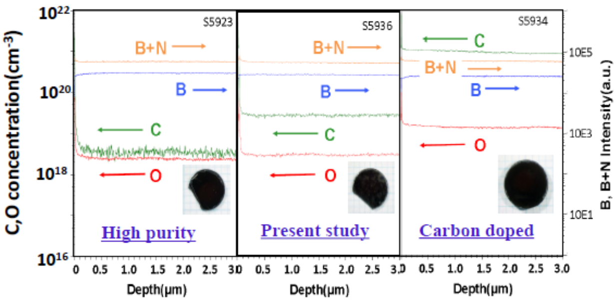

Fig.5 SIMS depth profiles of cBN sintered bodies with different Carbon content.

By using those hBN crystals as a starting materials, binderless cBN sintered bodies were obtained by direct phase transforation at 10GPa and 1700°C [7]. Fig.5 shows SIMS depth profiles of cBN sintered bodies with variety of Carbon impurity levels. It is clearly seen that content of carbon in each cBN sintered boried is well coorelated with starting materials of hBN as decsribed above.

Preliminary study of Knoop hardness test were carried out as shown in Fig.6. Carbon enriched crystals exhibit brittle nature in the indentation load near 50N.Further evaluation of the mechanical properties including wear resistant properties as cutting tools is important for the next study.

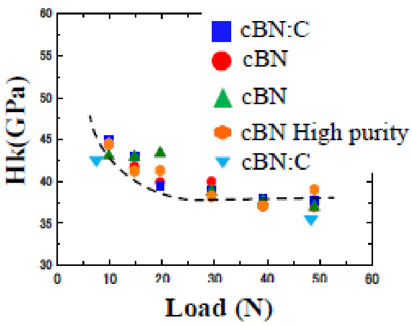

Fig.6 Knoop hardness of binderless cBN sintered boies with diffrenet carbon content.

4.Future Perspectives.

While the current subject is to realize how the major impurities such as carbon and oxygen affect the properties of hBN and cBN, some progerss for the realizationcould be achived by peparation of high pruity hBN crystals. Recentky, hBN takes attnetionas for the application of 2D's materials such as graphene substrates and photonic materials. The properties could be figured out in those studied may gave us valuable insight for the quality of hBN crystals. In view of impurity, not only carbon and oxygen of elemental ones but for isotope componet of BN system is also interesting issue. Now we could achieve to control of boron and nitrogen isotope ratio (^{10}B,^{11}B and ^{15}N) in hBN and cBN crystals by metatheses reaction under HPHT. Ultimate study of impurity control of BN system may gave us new insight for the science of BN materials and their new functionalizations. and ingight

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