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Synthesis of boron nitride and other 2D materials with solution growth and their impurity control

Hexagonal boron nitride (hBN) exhibits superior properties as a substrate of 2D opto-electronic devices such as graphene and TMDCs [1]. In order to realize these potential of hBN crystals further, more precise insight for its quality control is important. Another issue is to fabricate fine hBN crystals with high quality via conventional route. Ni or Co-base alloy solvents seem useful to obtain high quality hBN crystals at 1atm of Nitrogen atmosphere, though the yield of the crystals is less than those of high pressure process. Also, controlling of boron and nitrogen isotope ratio (^{10}B,^{11}B and ^{15}N) in hBN and cBN crystals can be now carried out by methatheisis reaction under high pressure and high temperature (HPHT). On the other hands, liquid phase crystal growth process is applicable for other 2D materials such as graphite, black phosphor (BP) and TMDs.

Particularly the present issue to improve their properties of hBN further is to eliminate residual carbon and oxygen impurities. Optical micrograph of recovered hBN crystals obtained at HPHT [2] and 1atm process [3] were shown in Fig1. SIMS depth profiles of those recovered hBN crystals were also shown in Fig.2. In HPHT growth, spatial heterogeneity of carbon impurity level was observed(Fig.2(a) and (b)). In the high purity domains, carbon and oxygen impurity levels were less than detection limits in SIMS study, i.e. $10^{17}/cm^3$ for oxygen and $10^{18}/cm^3$ for carbon, respectively. Recently some strategy for reducing primal carbon impurity level in source of BN materials and additive of Ba compound in grown circumstance seem work well so as to obtain superior crystal with respect to carbon impurity levels. Among the variety of solvent compounds for hBN crystal growth under HP such as Li_3N, Mg_3N_2, Ca_3N_2, only Ba base solvent is effective for obtaining high purity hBN crystals with band edge nature. This fact may be attributed to an effect of affinity of Ba with carbon in the BN's growth circumstance, although insight for the chemistry in this system is not well clarified yet. On the other hands, it is well known that Ni or Co has some solubility of carbon. Because of this nature, diamond crystals were obtained by using Ni or Co solvent via dissolution and precipitation process under HPHT condition. It is therefore expected that Ni or Co base solvent have some benefit to reduce carbon impurity levels in BN's growth circumstances. As shown in Fig.2(c), by using Co-Cr solvent, recovered hBN crystals exhibit similar nature to superior HPHT hBN crystals with respect to carbon and oxygen impurity.

Further study is important for quantitative analysis of residual impurities lower than the present SIMS detection limit. According to optical characterization of those hBN crystals, brightness and also FWHM of band edge emission nature show discernable variation among even superior crystals probably due to a difference of amount of residual carbon impurity.

Also, controlling of boron and nitrogen isotope ratio (^{10}B,^{11}B and ^{15}N) in hBN and cBN crystals can be now carried out by metatheses reaction under HPHT as shown in Fig.3.

In this paper, recent studies for properties of BN single crystals obtained at HP with respect to Carbon impurity and Boron/ Nitrogen isotope control will be reported. Also some attempt for obtaining BP and TMD crystals by melt growth under HP will be also introduced.

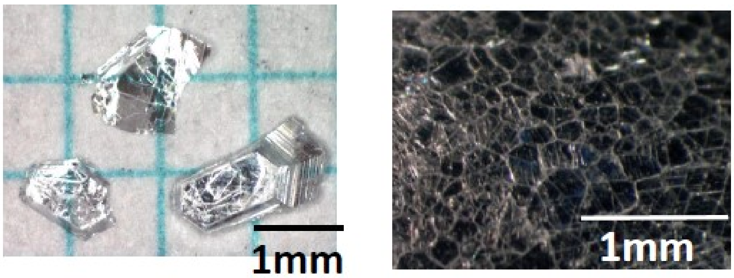

Fig.1 Optical image of hBN crystals obtained. Right:obtained at HPHT
Left: obtained with Co-Cr solvent at 1atm N_2 atmosphere

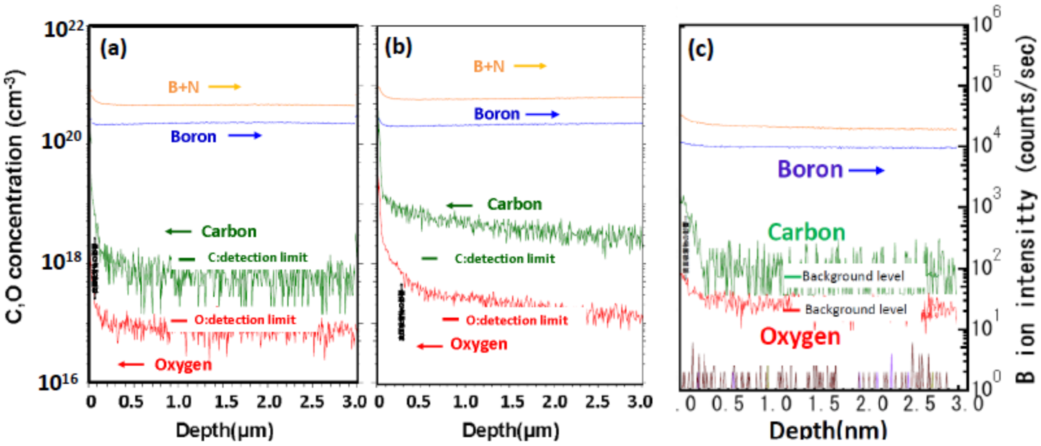

Fig.2 SIMS depth profiles of hBN crystals. (a),(b) obtained at HPHT in two different regions. (c) obtained with Co-Cr solvent at 1atm N_2 atmosphere

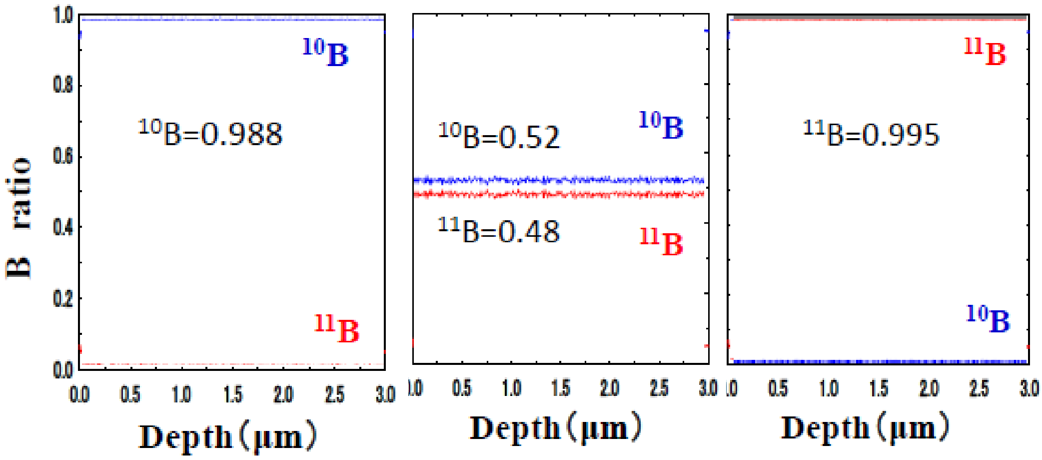

Fig.3 SIMS depth profiles of hBN with controlling Boron isotope ratio.

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