# STRUCTURAL CHARACTERIZATION OF BORON-DOPED SUBMICRON VGCFs

*K. Nishimura, Y. A. Kim, T. Matushita, T. Hayashi and M. Endo*
*Faculty of Engineering, Shinshu University,*
*500 Wakasato, Nagano 380-8553, Japan*

## Introduction

Submicron VGCFs with diameter of around 0.1μm obtained by the decomposition of benzene at around 1100°C, using floating catalyst method are very promising for applications to composite material as the filler as well as anode materials in lithium-ion battery due to high surface-to-volume ratio and highly graphitic structure. To monitor the structural deviations of the fibers due to boron-doping, in the present study Raman technique is mainly used. Since boron-doping process takes place at near surface of carbon materials, Raman technique provides a sensitive tool for monitoring the boron-doping process, especially focusing on boron-induced disorder in the host material.

## Experimental

The manufacturing process for submicron VGCFs has been reported elsewhere [1]. Boron-doping for the fibers was performed using boron carbide as the dopant, which has average diameter of 26μm. 3 weight percent of boron carbide and fibers were mixed using electric mixer for 20 seconds, and this mixture was carbonized, and graphitized at specific temperature for 10minute. Raman technique with different geometries, such as parallel and vertical directions, was mainly used accompanying with XRD and FE-SEM.

## Results and Discussion

Undoped fiber show relatively low slope of interlayer spacing for this range, and larger interlayer spacing for sample at 3000°C (Fig. 1) as compared that of normal VGCFs with diameter of ~20μm, possibly due to the size effect reported previously. On the other hand, variations of interlayer spacing for boron-doped fibers are distinctively distinguished into three regions. Generally, lower value is attributed to substitutional boron atoms in the host material as the graphitization catalyst. Abrupt decrease for the range from 1800 to 2000°C means that substantial diffusing process would occurred in this region. And for the range from 2000 to 2600°C, gradual decrease tendency is observed following the solubility of boron for carbon material. The minimum value is observed for sample at 2600°C, and with increasing temperature, interlayer spacing increased due to diffused out process from the substitutional to the interstitial. Finally, lower value for sample at 3000°C is ascribed to the structural restoration such as annealing out of vacancy and disorder caused by diffused out process.

Fig. 2 shows the variation of the relative intensity $(I_D/I_G)$ for boron doped sample. For the range from 1800 to 3000°C, the value is a little varied within the range from 0.75 to 0.5. On the other hand, undoped sample show gradual decreased tendency with increasing temperature, especially the slope from 200 to 2600°C is very higher (Fig. 3). Since the relative intensity $(I_D/I_G)$ is deeply related with the crystallite size, it is sure that the structural disordering would be induced by boron doping process. In terms of the variation of crystallite size, it is better to mention the depolarized ratio $(I_V/I_P)$ for both samples (Fig. 4). The depolarized ratio of the G peak for HOPG is unique whereas that of polycrystalline is about 3/4. Undoped samples show relatively linear development of crystallite as a function of temperature. But, boron doped samples show same tendency for sample at 2300°C, and deviate as compared that of undoped sample from 2500 °C approaching to minimum value for the sample at 2700°C, and finally increase with increasing temperature. This kinds of behavior would be explained by the doping process of boron into the host material, diffused out process and structural restoration. Fig. 5 shows the variation of Raman frequency of G peak as a function of temperature. Undoped sample show decreased tendency with increasing temperature, and finally approaching the value of HOPG. But boron doped sample show upshifted tendency, and critical step is observed for sample at 2700°C, which is well consistent with the results of the depolarized ratio. The explanation for the upshifted G peak for boron doped sample is not clear, but the most possible explanation is strong coupling between graphene layers due to decreased interlayer spacing.

## Conclusions

The effect of boron atoms for submicron VGCFs was analyzed by using XRD and Raman scattering. Whereas substitutional boron atom in the host materials is the graphitization catalyst for the c direction, the effect of boron for a-direction is decreased in the crystallite size. Therefore, the upshifted Raman frequency of G peaks and

relatively low relative intensity ratio as well as the depolarized ratio would be combination effects; (1) strong coupling between graphene layers, (2) dislocation centering on boron atoms of the substitutional in the host material.

## References

1. Speck JS, Endo M, Dresselhaus MS. Structure and intercalation of thin benzene derived carbon fibers. J Crys Grow 1989;94:834-848
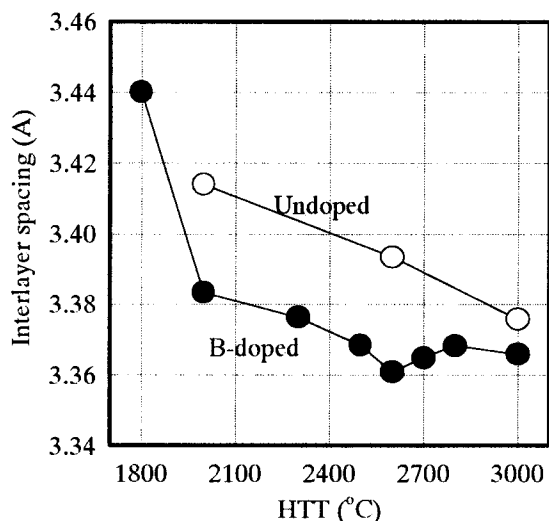
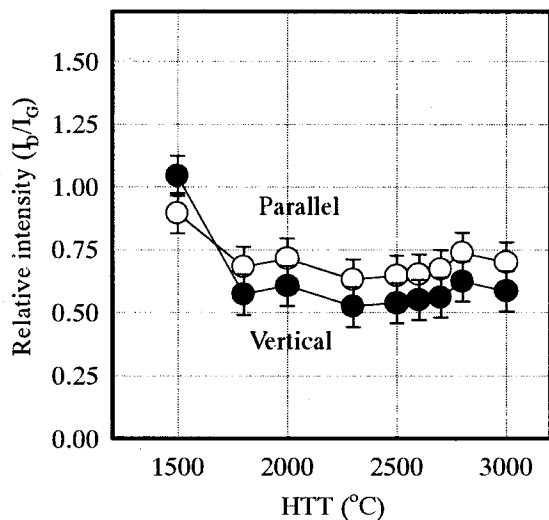**Figure 1.** The Variations of interlayer spacing as a function of temperature.



**Figure 2.** The variations of the relative intensities ($I_D/I_G$) for boron doped submicron VGCFs
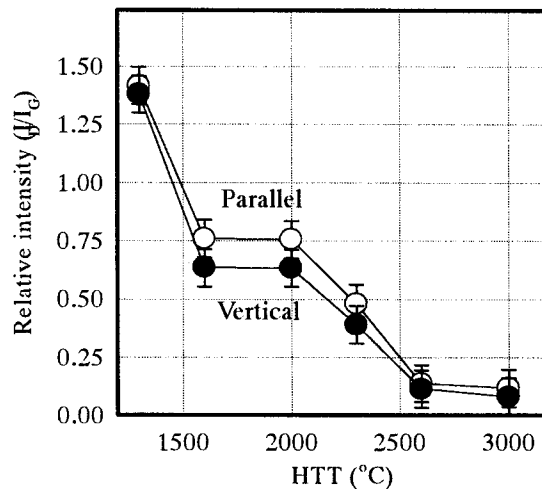


**Figure 3.** The variations of the relative intensities ($I_D/I_G$) for undoped submicron VGCFs
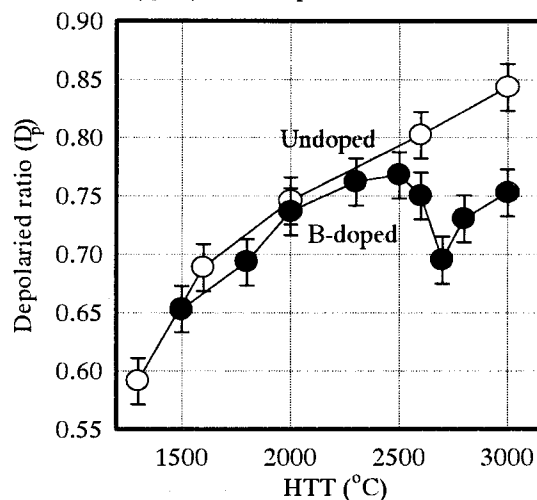


**Figure 4.** The variation of the depolarized ratio ($I_V/I_P$) of G peaks as a function of temperature.
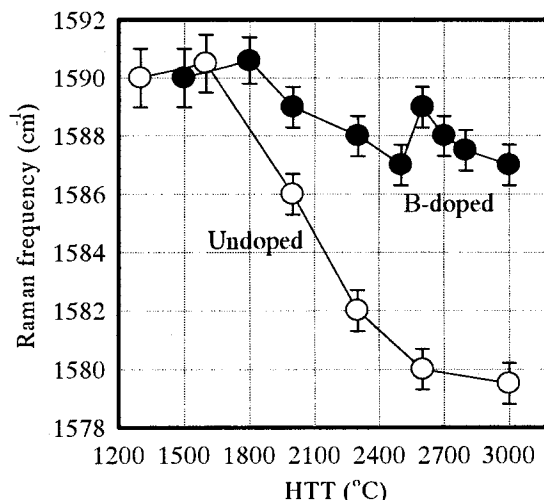


**Figure 5.** The variations of Raman frequency of G peak as a function of temperature.