# Evaluation of pore size distribution for Nano-Clustering Silica thin films based on the Grazing Incidence Small Angle X-ray Scattering

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For the recent high performance CMOS devices, low-k materials with a dielectric constants, k<2.3, and high elastic modulus, E=10GPa, are requested for the interlayer dielectrics of the Cu interconnects to reduce a signal delay due to the wiring capacitances. To reduce a dielectric constant, materials with nanometer pores in the films are developed. Nano-Clustering Silica (NCS) is one of these materials. In such materials, as the average pore size and the size distribution closely relate to their mechanical rigidity and the dielectric constants, the evaluation of these parameters become important.

The x-ray small angle scattering is a powerful technique to determine the average pore size and the size distributions. To apply the technique for thin films on the substrate, a transparent configuration can not be used. In this study, we developed a grazing incidence small angle x-ray scattering technique with a Imaging Plate (IP) detector, where the global structure of small angle scattering including interference effect between pores/particles can be measured simultaneously. At BL19B2, we selected a x-ray with the wavelength of 0.14 nm. The incident angle of x-ray was set at 0.2 degrees which is between the critical angle of x-ray total reflection for the NCS films and Si substrate. To reduce the background signal originated at the slit and by the air, we used a x-ray collimator and a He pass in addition to the He dome as shown in figure 1.

Figure 2 shows the intensity of scattered x-ray measured by IP for Pt nanoparticle as a standard sample and the two kind of NCS samples with 170nm thick. For Pt sample, we see the strong interference effect emerged like wings. For NCS samples, difference of radial spread indicates that the pore size of sample-1 is smaller than that of sample-2.

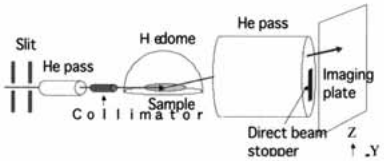


Fig.1 GISAXS configuration with IP.

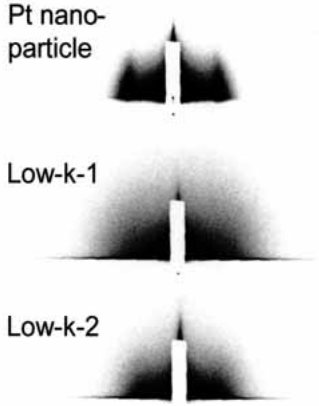


Fig.2 Intensity map of scattered x-ray.



# X-ray diffraction study on a new nano-carbon material

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New nano-carbon material, carbon nanohorns (CNHs), attract much attention as a promising nano-scaled material used in various application fields, for examples, the catalyst support in the fuel cell electrodes, gas storages, and a carrier in the drug delivery systems. Each nanohorn is composed of horn-shaped single-walled graphene sheets, like carbon nanotubes, and it forms dahlia-flower-like aggregates as shown in Fig. 1. This sharp-pointed surface structure with large surface area has great advantages in supporting very fine catalyst particles, and in storing large amount of gases. Besides, the interior space of nanohorns allows us to put various atoms or molecules, even drugs in it.

To improve the performances of above applications, we need further structural information, such as defect structures as well as macroscopic structure of the aggregates. Thus, in this study, we have investigated nano- and macro-structures of CNHs aggregates by using x-ray diffraction (XRD).

As-prepared CNHs include a few percent of amorphous carbon (a-C) and giant graphite balls (GGB, graphite particle with the diameter of ca. 100nm~1μm) as byproducts. Since the combustion temperatures of these products are different, we can separate these by appropriate thermal treatments. We have prepared the following three samples: (1) as-prepared (CNHs, a-C and GGB). (2)550 ℃ treated (CNHs and GGB). (3) 690℃ treated (GGB). Powder XRD measurements were made on a beamline BL19B2 at SPring-8.

By comparing XRD profiles for these three samples, we obtained the XRD contribution that comes from CNH aggregates. Figure 2 shows XRD profiles for these three samples. After subtracting the background, the intensity was normalized at the (002) peak. The difference between XRD for 550℃ treated and 690℃ treated samples gives the XRD contribution from CNHs, and there are three major differences between them. First, the peak intensity for (10) and (11) peaks, that comes from in-plane graphite network, are much larger for CNHs. Since the side wall of CNHs also has the graphite network, this comes from XRD in the side wall of CNHs. The sever boarding indicates that there are many structural defects in the nanohorns. Second, there is a broad peak around (002) peak. This may be attributed to the diffraction from neighboring nanohorns or that from disordered graphite like structures in the interior part. Finally, large small angle scattering was observed for CNHs. This would give information on the particle size of CNHs. The detailed structural analyses are now in progress.

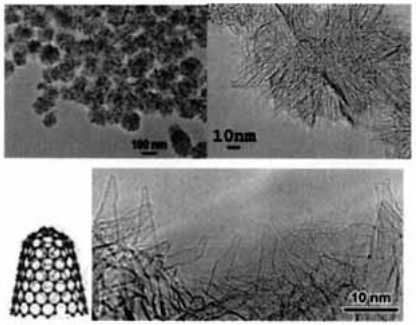


**Fig. 1 The TEM images for carbon nanohorn aggregates.**

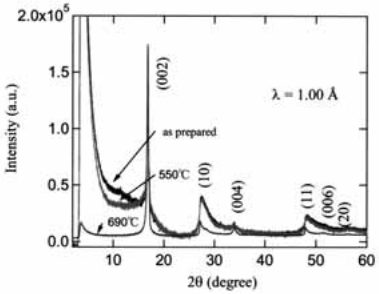


**Fig. 2 Powder x-ray diffraction profiles for three carbon nanohorn samples.**