Raman spectroscopy as a tool for characterizing the structural order of carbon materials

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Raman spectra of carbon and graphite materials are known to reflect their structures sensitively because Raman spectra are very sensitive to the changes that break the translational symmetry of graphite crystal, such as lattice defects, finite size of crystallites, edges of graphite layers. The Raman spectrum of graphite crystal has a strong active mode at about 1580 cm^{-1}, which is called G band. The introduction of lattice disorder or the reduction in crystallite size gives rise to the disorder-induced Raman lines in the first-order Raman spectrum, at about 1360 and 1620 cm^{-1} under an Ar ion laser of 514.5 nm, which are designated as D and D' bands, respectively.

A variety of carbon materials have been characterized mainly by using the G and D bands [1-5]. The values of the intensity of D band I_D relative to that of G band I_G, I_D/I_G, the full width at the half maximum intensity of G band, G-FWHM, and the position (Raman frequency shift) of the G band, G-RF, are used for the characterization [1-5]. However, the relation between these parameters and the structures has not been investigated precisely.

We have carried out systematic measurements of Raman spectrum and X-ray diffraction (XRD) for different types of carbon and graphite materials with homogeneous texture, and the relation between Raman and XRD parameters was examined extensively [6-8]. The incident beam with wave length of 514.5 nm of 1 μm in diameter was used for the Raman measurements, and the power on the sample surface was about 2mW. The X-ray measurements were conducted using Cu-Kα rediation and the diffraction patterns were corrected by the Gakushin method. It should be noted that the laser probe sampling depth of carbon and graphte materials is about 50 nm at 515.4 nm, while the XRD data are obtained from whole sample thickness, 0.2 mm of poweder method and about 20 μm of film sample in our experiments.

The value of I_D/I_G has been used to estimate the mean crystallite size L_a value and it has been used to study graphitization of carbon materials [1, 2]. It has been known, however, that I_D/I_G shows texture dependence because the intensity of the D band depends on the texture of the carbon materials strongly, though I_D/I_G shows a smooth relation against heat treatment temperature with a constant heat treatment time in a carbon material of a definite texture [3-5]. Fig. 1 shows the relationship between I_D/I_G and L_a for Kapton-derived carbon film (KAP) heat treated at verious temperatures and the data from literatures. The I_D/I_G values are plotted as a function of mean interlayer spacing d_{002} obtained from XRD for the KAP and vapor-grown carbon fiber (VGCF) samples in Fig. 2. There are no common relationship between I_D/I_G and L_a and also I_D/I_G and d_{002}. It is known that G-FWHM is a parameter for graphitization, though it is qualitative evidence [3-5]. In Fig. 3, the values of G-FWHM are plotted as a function of d_{002} for the KAP, VGCF and pyrolytic carbon (PC) samples. We prefer d_{002} as a parameter of the degree of the structural order of carbon materials rather than L_a because the L_a values larger than 100 nm and smaller than 2 nm evaluated from XRD are ambiguous. Figure 3 revieals that G-FWHM also shows texture dependence. G-RF increases slightly with the decrease of structural order, and accurate measurements of Raman shift are required. In order to correct the Raman shift, the 1458.52 cm^{-1} line from Ne lamp was used. Figure 4 shows the plots of G-RF as a function of d_{002} for KAP, VGCF and other samples. G-RF decreases with increasing d_{002} for the graphitized carbon samples ($d_{002} < 0.34$ nm), and it increases with increasing d_{002} for the samples with turbostratic structure ($d_{002} > 0.34$ nm).

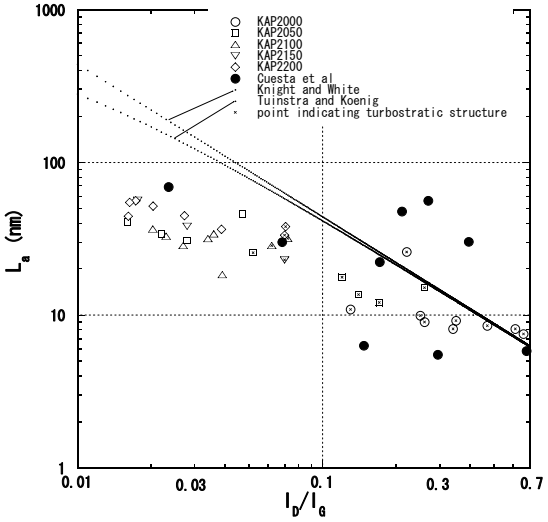

Fig. 1. Plots of L_a against I_D/I_G.

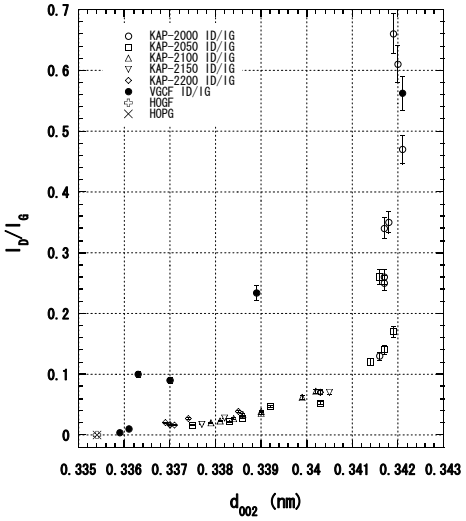

Fig. 2. Plots of I_D/I_G against d_{002}.

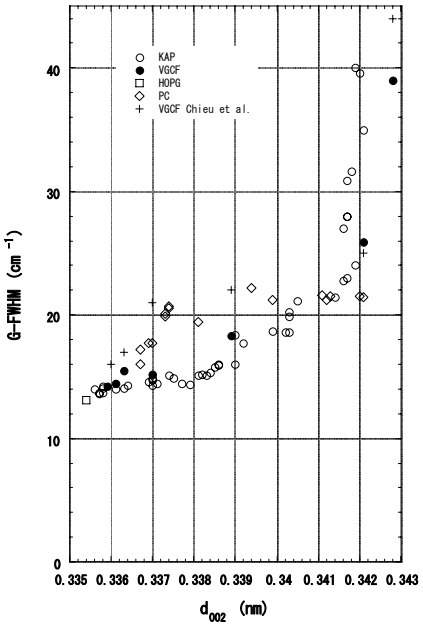

Fig. 3. Plots of G-FWHM against d_{002}.

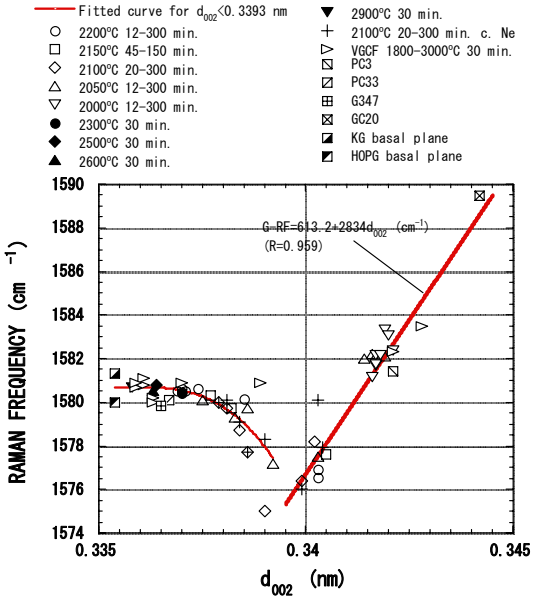

Fig. 4. Plots of G-RF against d_{002}.

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