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MICRO-RAMAN CHARACTERIZATION OF THIN FILMS AND STUDY OF THE 
TRANSFORMATIONS INDUCED BY A PULSED ELECTRIC-FIELD 

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ABSTRACT 

Micro-Raman spectra of thin films of various carbonaceous compounds are presented. The relative 
Raman scattering cross sections of films of graphite and diamond are revised (a factor of two is found 
instead of 50 as in literature ). Second order and third order Raman spectra of graphite and diamond-
like films are presented and discussed in terms of resonance Raman effect. Study of carbonaceous thin 
films under electric field is in progress. 

INTRODUCTION 

This work is a part of our activity on solid electrolytes, electrodes and materials for microelectronics 
and microelectrochemistry. The micro-Raman allows to characterize thin films without a preparation 
of the sample and we plan to perform an in-situ study of structural changes in the film at the 
interface electrode/ electrolyte of a battery, in other term when an electric field is applied. Note that 
10 V for one micron thick layer corresponds to a field of one megavolt/cm; this is the typical electric 
field that we generate on different samples under a pulsed regime (5 ns to 100 ns of DC electric field 
duration with a repetition rate of 1 to 10 Hz) in order to avoid irreversible phenomena. 

Graphite and carbonaceous compounds are well known as electrode materials. In particular graphite 
and now C60, C70 compounds can intercalate alkaline ions and are then quite attractive for 
electrochemical applications. Moreover diamond films and doped diamond films are also promising in 
microelectronics. For the moment we have not yet obtained significant and reproducible results on 
bulk and thin films of carbonaceous compounds under high electric fields. Thus we present here some 
results which constitute a basis for further investigations of carbonaceous compounds. Although there 
is an abundant literature (1-3) on the subject, we felt the necessity to clear some basic points such as; 
(i) Relative scattering intensities of graphite and diamond, (ii) Resonant Raman scattering of 
graphites and derivatives, (iii) second and third order scattering of graphite and derivatives,(iv) limits 
of detectivity and analysis of structural and optical properties of very thin films (12 Å) compared 
with thick films of the same compound. 

EXPERIMENTAL 

Samples: The graphite was a single crystal of HOPG, it was freshly cleaved before 
Raman studies. No spectral difference was observed for a sample placed in a He filled glass tube and 
for a sample at the room atmosphere. 

The various carbonaceous films presented in figure 1 have been obtained by a plasma torch 
technique by Priem et al (4 ) at CENG. 

The thin films of 12 Å and 2000 Å presented in figure 5 have been obtained by laser 
ablation of graphite under high vacuum by Ferrer et al (5 ) at ESRF. 

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Raman: The spectrometer was the multichannel XY Dilor model equipped with a microscope. The Raman spectra were excited by Argon laser lines at 514.5, 488.0 nm and Kr line at 647.1 nm. The laser power was kept between 1 and 10 mw on the sample. The laser was focused on an area of about 1 micron of diameter. The experimental linewidth was of 3.8 cm for spectra presented here.

RESULTS AND DISCUSSION

1) Various forms of carbon:

Figure 1 presents various carbonaceous compounds which are produced when methane and hydrogen react on to a substrate of Mo as function of temperature. At the exception of diamond the nature and the structure of the other compounds is not yet elucidated, although the same spectral characteristics are met for quite different conditions of elaboration (6). At least nine bands coexisting in variable proportion can be identified.

Figure 2 shows that still more carbonaceous species can be met. Spectra in figures 2b - 2d have been obtained on microcrystals resulting of a mechanical treatment of the graphite crystal. One recognizes in figure 2d a spectrum nearly similar to the one of figure 1a (and identical to the diamond-like spectra of Andre (4)). Spectra of figures 2c and 2b are strongly similar to the C60/C70 mixture spectrum.

As a conclusion, this figure confirms that carbon can exist under numerous states. It remains to elucidate the actual chemical composition and the structure of these states!

Fig. 1: Micro-Raman spectra ($\lambda=488.0$ nm) of various carbonaceous films deposited in a Mo substrate at different temperatures (See text and ref. 4.)
(a) amorphous carbon, (b) pathological film where the diamond line at 1330 cm$^{-1}$ begins to appear, (c) mixture of diamond-like carbon and of diamond, (d) diamond film of poor quality (FWHM $\approx$ 10 cm$^{-1}$, luminescence background), (e) typical diamond film (crystals well faceted).

Fig. 2: Micro-Raman spectra ($\lambda=488.0$ nm) of various carbonaceous compounds
(a) mixture of C60/C70 compounds, (b), (c), (d) small fragments of graphite crystal having been submitted to a severe deformation and cut with a razor blade.
2) Graphite: cross section scattering and resonance Raman effect.

a) The estimation of the relative composition of diamond and of graphite-like compounds in thin films is based on the statement that the scattering cross section of graphite is 50 times larger than that of diamond (3,7) and thus it should be impossible to detect "small quantities" of diamond in carbonaceous films. Our experiments using a microscope objective of X100 and the 488.0 nm exciting line for a 10 mW of laser power and the same slit for studying films of diamond and of pure graphite show that the ratio of cross sections S(graphite)/S(diamond) is actually comprised between 2 and 4 (and not 50!) even when one takes into account the actual thickness of graphite sampled by the laser (50 nm for an intensity reduction of I/Ic of the incident laser beam). Otherwise for two films of one micron thickness, the observed scattering intensity ratio I(graphite)/I(diamond) is reversed and equal to ten! This can be seen in comparing figures 1c and 3b. In other terms for "transparent" or less absorbent carbonaceous compounds such as amorphous carbons (α<5,10⁴ cm⁻¹) the Raman responses will tend to equalize. In these conditions the conclusion reported in (8) on composite samples of diamond and graphite are not surprising.

b) Figure 3 shows that with the 488.0 excitation, the first and higher orders scattering of graphite, although induced in thin surface layer (~50 nm) is quite strong. This is true as well for pure ordered graphite (fig 3b), as for disordered graphite (fig 3c). The second order is nearly as strong as the first order, indicating the resonant character of the scattering. The 2708 cm⁻¹ band (2D band) in fig. 3c is clearly the overtone of the 1349 cm⁻¹ mode (D band), while no evident overtone band of the E₂g in plane mode (G band) is observed, neither in disordered nor in pure graphites. This fact is in favor of the assignment of the D mode to an A₁g mode in the K point at the border of the Brillouin zone, which would be Raman active in finite crystallites (1). Only overtones of totally symmetric modes are expected in Albrecht's theory of resonance Raman scattering (9). Thus in pure graphites the A₁g mode would be at 2730 cm⁻¹ = 1365 cm⁻¹. The 3240 cm⁻¹ (2G') in pure and 3230 cm⁻¹ (2G') in disordered graphites could be due to the same branch as the E₂g mode (enhanced by the B terms of Albrecht's expression). Finally note that the A₁g mode is involved in the 2923 cm⁻¹ (G+D) band and in the 4280 cm⁻¹ (G+2D) band as well for disordered as for pure graphite, confirming that the A₁g character is responsible for the resonant activity of these combination bands.

With the 647.1 nm excitation, the G mode at 1578 cm⁻¹ decreases in intensity by at least a factor of two (taking into account the μth correction, the spectrometer response, and the spectral width). The second order feature at 2680 cm⁻¹ is lowered by a factor of 5, the 2730 cm⁻¹ feature is not observed. At the evidence, the resonant character of the scattering is strongly reduced, the absence of the overtone of the A₁g mode is particularly striking. The 2680 cm⁻¹ feature would come from a border zone mode of low symmetry (B terms).

Fig 3: Micro-Raman spectra of a single crystal of graphite
(a)λ= 647.1 nm,
(b)λ= 488.0 nm,
(c)λ= 488.0 nm, disordered graphite (intercalated with titanium fluoride)

Fig 4: First and second order spectra of amorphous and diamond-like films, prepared by quite different techniques.
(a) plasma torch,
(b) sputtering of graphite with Argon,
(c) laser ablation of graphite.
3) Second order of amorphous carbon: As stated in (10-11) a resonance Raman effect takes place in these graphitic compounds. The second order of fig. 41 can be interpreted on the same basis as graphites. As stated in (10-11) a resonance Raman effect takes place in these graphitic compounds. The second order of fig. 41 can be interpreted on the same basis as graphites. As graphite the overtone (2D) of the D line is the strongest component of bands around 3000 cm⁻¹. The A band which is not present in graphite has its overtone counterpart at about 2800 cm⁻¹. At the difference with pure graphite, the combination band G+D is quite strong. This shows that G and D lines do not belong to independent species such as e.g. sp² and sp³ carbon clusters respectively. Nevertheless the D mode could involve mainly "terminal" bonds involving border sp² carbons of graphitic clusters connected to sp3 carbon atoms (themselves bonded to H or other sp3 carbon atoms). Normal mode calculations have been recently undertaken (12) in order to test such a model. Finally, the above discussion shows that possibility that the Raman bands observed in the 2700-3000 cm⁻¹ range could be due to CH stretching bands is unlikely because of the systematic correspondence between fundamentals and overtones, absence of Raman bands in this range for H free films prepared under high vacuum.

4) Thin film of amorphous carbon

Figure 5 compares the spectra of amorphous carbon films of 2000 Å and 12 Å respectively deposited on a silicon substrate and prepared in the same conditions. The spectrum 5b which has been obtained in 16x30 s illustrates the limits of the detectivity of the instrument. Comparison between the 2000 Å and 12 Å films shows as stated in (13) that the structure of the 12 Å film is different, some fine structure is evidenced in the broad 1500 cm⁻¹ band. In addition, some features characteristic of the interface and not due to SiC can be seen, the broad band near 300 cm⁻¹ could be due to oxidation products of the substrate (SiO near 300 cm⁻¹, SiO₂ near 500 cm⁻¹).

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