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Bulk and surface plasmon excitations in amorphous carbon measured by core-level photoelectron spectroscopy

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ABSTRACT

Bulk and surface plasmon excitations in amorphous carbon (a-C) films have been characterized by core-level loss spectroscopy. Atomically smooth a-C surfaces were used in their as-grown state, after UHV annealing and after covalent immobilization of dense molecular monolayers ($2–4 \times 10^{14}$ cm^{-2}), either perfluorinated or labelled with an ester functionality. X-ray photoelectron spectra reveal a sp^3-rich hybridization of surface C atoms, with a $\sigma + \pi$ plasmon loss distribution centred at 29.5 ± 1 eV, characteristic of a high electron density value. For molecular grafted surfaces, the energy distribution of plasmon losses reveals new contributions in the range 15–25 eV (clearly separated from the energy distribution of the bulk $\sigma + \pi$ plasmon loss of a-C) with an increasing loss probability observed at grazing photoemission angles. A simple parameterization method is presented to derive bulk and surface plasmon loss distributions from angular core level loss spectroscopy (XPS) data, without *a priori* assumptions on the shape of the loss energy distributions.

1. Introduction

Amorphous carbon (a-C) and its alloys are interesting thin film materials due to their outstanding properties, such as high hardness, good tribological properties, chemical inertness and biocompatibility [1–6]. In addition to their applications as protective coatings and solid lubricants, a-C films have emerged as electrodes for analytical electrochemistry due to their large overpotential in aqueous solvent [7] and as injecting electrodes for organic light emitting diodes [8]. Efficient covalent grafting of molecular species to a-C surfaces has been developed to design selective sensors for biomolecular recognition [9,10].

In spite of this technological importance of amorphous carbon surfaces, a clear and comprehensive picture of the relationship between their chemical, physical and electronic properties is still lacking. To this end, non-destructive surface characterizations such as X-ray Photoelectron Spectroscopy (XPS), combined with electron energy loss spectroscopy, are thus highly valuable provided that clear signatures of bulk and surface responses can be identified.

In contrast, the physical and structural properties of bulk a-C films have been extensively studied in relation with thin film deposition and processing conditions. In particular, the density and average hybridization of C atoms, which control hardness and electronic structure properties, can be tailored by adjusting the energy of C$^+$ ions in the so-called subplantation growth mode [1,11,12]. Electron energy loss spectroscopy (EELS) is currently considered as the most reliable technique to determine the density of a-C films. In the field of carbon-based materials, the $\sigma + \pi$ plasmon has been widely used as a useful signature for process control [4,13–21], for a simple calibration of the sp^3 content [15,16,22,23], and for the analysis of complex phase mixtures or interfaces [24–28].

Because of the collective nature of plasmon losses, the low-loss spectrum is best described in terms of the complex dielectric function, $\varepsilon(E)$, of the medium [29–37]. Hence EELS is a powerful tool to obtain the dielectric function over a wide energy range, either in transmission (TEELS [29,38]) or in reflection (REELS [39–42]) geometries. For the same a-C sample, the bulk sensitive TEELS (fast electrons, $E_0 > 10$ keV) and surface sensitive REELS (low energy electrons, $E_0 < 1$ keV) may provide different atom density values because bulk and surface properties of sp^3-rich a-C films can

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be quite different, e.g. a larger surface sp^2 fraction has been evidenced in spatially resolved EELS [43] and confirmed by Monte Carlo simulations [12].

The physics and surface sensitivity of plasmon losses in XPS and REELS are similar in principle, except for the presence of the electron–hole interaction and the lack of collimated beam in XPS. However, very few XPS studies have focused on core-level loss spectroscopy in amorphous carbon films [44–46]. In addition, for amorphous semiconductors, surface plasmon losses are usually too weak to be observed in XPS [44,45,47] or EELS [48] measurements.

In this work, bulk and surface plasmon excitations of amorphous carbon thin films have been observed and investigated as a function of the photoelectron emission angle, using a conventional XPS instrument. Section 2 recalls the physics of bulk and surface plasmon losses and describes the derivation of normalized core level loss distributions from XPS data. Section 3 gives experimental details on the a-C film deposition and surface modifications. Pulsed Lased Deposited (PLD) a-C films, chosen for their high $sp^3/(sp^2 + sp^3)$ hybridization [46] and their very smooth surfaces [49] were characterized either in their as-grown state, or after UHV annealing. In order to obtain a surface chemical label for the separation of bulk vs surface plasmon losses, a densely packed monolayer of organic linear chains has been covalently immobilized on as-deposited a-C surfaces, using thermally assisted grafting of linear alkene molecules, either perfluorinated (CF_2 and CF_3 in C1s spectra) or bearing ester functionalities (O=C–O in C1s spectra).

In Section 4, core-level loss spectroscopy is used to characterize the near-surface electron density derived from the $\sigma + \pi$ plasmon losses, and the structural organization of the sp^2 phase derived from the π plasmon feature, observed in as-deposited and annealed a-C films. Difference spectra are considered to evaluate the effects of the baseline subtraction procedure and possible shifts in the binding energy, e.g. due to band bending. For molecular grafted a-C surfaces, core-level loss spectroscopy shows an increasing total loss probability as the photoelectron emission approaches grazing incidence. The angular dependence of inelastic losses is analyzed in order to separate the contributions of bulk vs surface plasmon losses; the proposed parameterization is validated using monolayer grafting of chemically labelled alkene molecules. Finally, the origin of the strong surface loss probability found in a-C with a dense covalently immobilized molecular layer (as compared to the pristine and annealed a-C) is discussed in Section 5.

2. Core level loss data analysis

2.1. Surface and bulk plasmon excitations

Electrons which pass through a solid interact with the free and bound electrons. Collective excitations run as longitudinal charge density fluctuations through the volume of the solid (volume plasmon) and along its surface (surface plasmon). Their energy, $E = \hbar\omega$, is related to the frequency ω of oscillation; it depends on the density of loosely bound electrons, i.e. those for which $\hbar\omega_P$ (ω_P plasma frequency) is large compared with their binding energy (in semiconductors the electrons in the valence band).

In XPS experiments, due to the small absorption coefficient of X-ray excitation, electron–hole pairs are created homogeneously in the film, over several microns. An electron–hole pair creates an induced charge-density in the medium during photoexcitation (intrinsic loss) and electron transport (extrinsic loss). The origin of the electron energy loss is that the induced electric field in the medium acts on the electron as it moves [29–37].

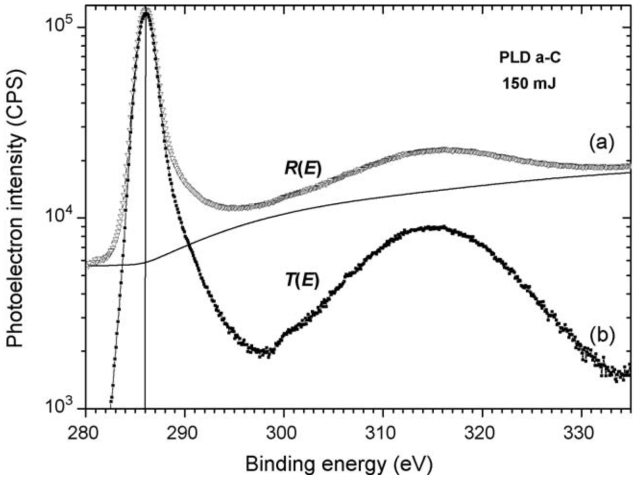

Fig. 1. C1s core level spectrum (log scale) at normal emission angle ($\alpha = 0^\circ$) for a PLD a-C film (150 mJ): (a) raw measurements, $R(E)$; (b) $T(E)$, after subtraction of a Tougaard universal background function [51,52] (continuous line).

In amorphous carbon, the C1s line at a binding energy $E_B \approx 285$ eV is followed by a structured background of electrons extending towards higher binding (lower kinetic) energies (Fig. 1). This broad loss spectrum corresponds to C1s photoelectrons that have suffered energy losses on the way from their point of creation to the sample surface (and across the sample surface) and it is thus characteristic for the sample under investigation. For high-energy primary photoelectrons ($E_0 > 300$ eV), losses in the energy range $\hbar\omega = 5-50$ eV are dominated by the creation of bulk plasmons, and the energy $\hbar\omega_{\max}$ of the maximum in the loss spectrum is commonly identified with the plasmon energy $\hbar\omega_P$ (Fig. 2). The loss spectrum of a-C displays loss features at 5–6 eV and 23–30 eV, respectively attributed to the π and $\sigma + \pi$ plasmon losses [22,23,38,40–42,46].

The usual quantity to describe the energy loss is the product of the inelastic cross-section by the atom density, $K(E_0, \hbar\omega)$, which gives the probability density per unit path length of losing an energy $\hbar\omega$. Because of the collective nature of plasmon losses, the low-loss spectrum is best described in terms of the complex dielectric function, $\varepsilon(\hbar\omega)$, of the solid. For electrons travelling through an *infinite* medium, it is given by [30–36]:

$$K(E_0, \hbar\omega) = (E_0 \pi a_0)^{-1} \int \mathrm{d}k\, k^{-1} \mathrm{Im}\left(\frac{-1}{\varepsilon(\hbar\omega)}\right), \qquad (1)$$

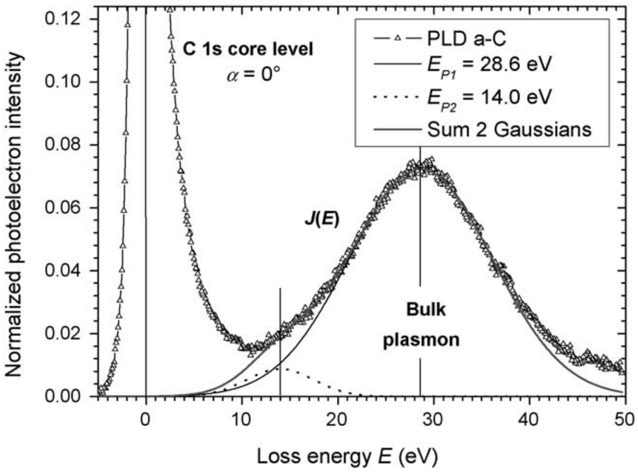

Fig. 2. Normalized loss, $J(E)$, at normal emission angle ($\alpha = 0^\circ$) for a PLD a-C film (180 mJ) and fitting (in the range 13.7–34.7 eV) with a sum of two Gaussians centered at 14.0 and 28.6 eV.