Available online at www.sciencedirect.com

ScienceDirect

Diamond & Related Materials 16 (2007) 1813 – 1822

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Dispersion relations and optical properties of amorphous carbons

S. Kassavetis [a], P. Patsalas [b,*], S. Logothetidis [a], J. Robertson [c], S. Kennou [d]

[a] Aristotle University of Thessaloniki, Department of Physics, GR-54124 Thessaloniki, Greece
[b] University of Ioannina, Department of Materials Science and Engineering, GR-45110 Ioannina, Greece
[c] University of Cambridge, Department of Engineering, Cambridge CB3 0FA, UK
[d] University of Patras, Department of Chemical Engineering and FORTH-ICEHT, GR-26500 Rion, Greece

Abstract

A dispersion model based on two Tauc–Lorentz oscillators (2-TL), to describe the π–π* and σ–σ* transitions, is applied to a wide variety of amorphous carbons grown by various vapor deposition techniques. The application of identical analysis to the various samples enables the quantitative comparison between various forms of amorphous carbon. The model is applied to spectroscopic ellipsometry data and can describe accurately the optical properties of all amorphous carbons. A validation is performed based on wide-range electron energy-loss spectroscopy spectra. This approach, universal for all carbons, extends the single TL model and can determine accurately the energy position of the π–π* transition and estimate fairly the σ–σ* transitions in addition to the E_g; these parameters as well as the refractive index are correlated to the sp^3 content and density of all amorphous carbons.

Keywords: Amorphous carbon; Optical properties characterization; Optical properties; Electronic states

1. Introduction

Amorphous Carbons, either pure (a-C) or hydrogenated (a-C:H), have been long established as important engineering materials, which can be used as protective overcoats [1–5]. They have also important optical properties [4]. The optical properties of single-layer a-C and a-C:H films have been intensively studied [6–18], in order either to evaluate the potential of such films for optical systems (determination of the refractive index n and the fundamental energy gap E_g) or as an indirect way of evaluating the films' microstructure (e.g. void volume fraction) and bonding (sp^3/sp^2 ratio).

The spectral optical parameters of amorphous carbons are usually acquired by electron energy-loss spectroscopy (EELS) in transmission geometry employing Kramers–Kronig analysis to the valence plasmon [10,19], or by Spectroscopic Ellipsometry (SE) [8,9,13–18]. SE provides the unique combination of non-destructive character, *in-situ* and *real-time* data acquisition and direct determination of the complex dielectric function. The main disadvantage of SE, compared to EELS, is the usually narrow spectral region (usually bounded to 6.5 eV), compared to the large gap of tetrahedral a-C (ta-C), which includes only the low-energy tail of the σ–σ* transition, unless synchrotron radiation SE is used [8]. Many approaches have been employed to analyze the ellipsometric data for a-C, a-C:H, ta-C and tetrahedral a-C:H (ta-C:H); they include effective medium theories (EMT) to determine the sp^3, sp^2 and voids volume fractions [8,9,15], and optical dispersion models to determine E_g, n and the Penn gap [8,14,16,18]. Various optical dispersion models have been used so far, including classical and semiclassical models with symmetric or asymmetric line-shapes to describe individual cases of C-based films [8,14,16,18].

A universal approach for the optical dispersion relations of all amorphous carbon-based films has not been established firmly. This is mainly because of the wide variety of carbon-based films spanning from low-density/high [H] polymeric a-C:H films to ultra-dense ta-C films as well as more complex structures such as carbon-based multilayers [20]. The optical properties of a-C and a-C:H are dominated by the π–π* and σ–σ* interband transitions, which show up as distinct features of the dielectric function [8,10,21], especially in EELS spectra. The π–π* contribution originates exclusively from sp^2 carbon atoms and in particular from the transition of π-bonded electrons (p_z-type orbitals) to π* anti-bonding states. On the other hand, the σ–σ* transition comes from the σ–bonded electrons participating to the

---

* Corresponding author. Tel.: +30 26510 98592; fax: +30 26510 97034.
E-mail address: ppats@cc.uoi.gr (P. Patsalas).

0925-9635/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2007.08.027

covalent bonds of both sp^3 and sp^2 carbon atoms [1,8]. Most of the SE studies in the literature [14,16,18] do not discriminate these two contributions and focus to the analysis of the π–π* transition, which defines the E_g of a-C and a-C:H.

In this work we present a detailed SE study of the optical properties of a-C, ta-C and a-C:H thin and multilayer films grown by various techniques. The SE spectra have been analyzed through the Tauc–Lorentz (TL) model [18,22] for amorphous semiconductors using two TL oscillators, which correspond to the σ–σ* and π–π* interband transitions; this analysis extents the capabilities of the conventional single TL model, which were reported previously [14,16,18]. We validate this dispersion model by applying it to EELS data from the literature [10]. Following this analysis, we determine the fundamental gap (and we note the effect of defects) and the energy positions of the σ–σ* and π–π* transitions with respect to the film bonding and we identify the differences between a-C and a-C:H either in thin-film or multilayer form. We also critically report the calculated quantities of the TL oscillators and identify their accuracy and validity for each category of films. In addition, we correlate the refractive index with the film density for all kinds of films. Additional X-Ray Reflectivity (XRR) and core-level (C1s) XPS measurements have been carried out to determine independently the films' density and hybridization and to correlate them to the optical data.

2. Experimental

Amorphous carbon and ta-C:H films have been deposited on Si[100] single-crystal wafers by rf Magnetron Sputtering (MS) and reactive MS (RMS), respectively. A hot-pressed graphite target (99.999% purity) and Ar carrier gas (99.999% purity) were used in a high vacuum chamber ($P_b < 1 \times 10^{-5}$ Pa). The films were grown either on floating or biased (rf$-V_b = -20$ to -200 V) substrates in order to control the ion irradiation conditions [8]. Particularly, the a-C:H layers were grown in a mixed ambient of reactive (H_2) and carrier (Ar) gases (H_2/Ar=5% vol.). Multilayers consisting of a-C and a-C:H layers of individual density but varying bilayer thickness 10–20 nm (resulting to different average density) were grown and studied. a-C:H films grown by Plasma-Enhanced Chemical Vapor Deposition (PECVD) using a C_2H_2/C_6H_6 gas mixture in a rf parallel plate reactor, and ta-C films grown by Filtered Cathodic Vacuum Arc (FCVA) in a double *s*-bend filtered system and by Pulsed Laser Deposition (PLD), using a focused third harmonic ($\lambda = 355$ nm) beam of a Nd:YAG laser, are also studied. The structural characteristics of all the grown samples for this study are summarized in Table 1.

Dielectric function spectra were acquired (through Δ–ψ spectra) by an *in-situ* phase-modulated ellipsometer (PME), in the spectral range 1.50–5.50 eV (only for the MS-and RMS-grown samples), and by an *ex-situ* PME (Jobin–Yvon) at 70° angle of incidence in the spectral range 1.50–6.50 eV (all samples). Selected samples were also measured by an *ex-situ* variable angle (70°–80°) rotating polarizer ellipsometer (RPE-Sopra) in the spectral range 1.04–5.90 eV, to extent the measured spectra to near-IR region. No significant differences of the Δ–ψ values were observed between *ex-situ* RPE and PME experiments in the overlapping range.

Table 1
The samples grown for this study

Sample	Technique	Material	Structure	Density (g/cm^3)	sp^3 (%at.) by XPS
1	MS	a-C	Monolithic	1.90	25
2	MS	a-C	Monolithic	2.62	44
3	PLD	a-C	Monolithic	2.05	–
4	PLD	ta-C	Monolithic	3.22	–
5	FCVA	ta-C	Monolithic	3.24	83
6	RMS	ta-C:H	Monolithic	1.2	75
7	PECVD	a-C:H	Monolithic	1.3	30
8	PECVD	a-C:H	Monolithic	1.4	32
9	PECVD	a-C:H	Monolithic	1.5	38
10	PECVD	a-C:H	Monolithic	1.7	41
11	MS/RMS	a-C/a-C:H	Multilayer	2.6/1.3	–
12	MS/RMS	a-C/a-C:H	Multilayer	2.6/1.3	–

The film density has been determined by XRR. The XRR measurements were performed in the form of θ–2θ scans for incidence angle 0–3° with 0.0025° step in a Siemens D-5000 diffractometer equipped with parallel beam optics. The surface composition of the films has been studied by *ex-situ* XPS core-level (C1s) spectra, which were acquired in an UHV chamber ($P_b = 4 \times 10^{-8}$ Pa). A hemispherical electron energy analyzer, a twin anode X-ray source (unmonochromatized MgKα line at 1253.6 eV) and a constant pass energy of 97 eV for the analyzer were used, giving a half width at half maximum of 1.6 eV for the reference Ag $3d_{5/2}$ peak.

3. Results and discussion

The films' hybridisation (sp^3/sp^2 ratio) has been determined by XPS C1s core-level spectra as described in more detail in Ref. [9]. XPS was found to slightly underestimate the sp^3 content of highly tetrahedral ta-C films, because it is surface-sensitive and is affected by the existence of the top sp^2-rich surface layer [9,23]. However, this underestimation is very small and is not considered critical for the rest of our analysis and discussion. Although the binding energy separation of the sp^2- and sp^3-bonded atoms is low, XPS of the C1s spectra is the method of choice of many authors for the determination of the sp^3/sp^2 ratio [24–29]. Our criterion for this choice is based upon the fact that the XPS analysis does not incorporate any contribution from the π and σ valence bands and/or the unoccupied π*, σ* states, such as core-level EELS (EELS-CL), which is based on the C1s–σ* transition [10,30–32]. Therefore, XPS can safely discriminate the chemical bonding (sp^3/sp^2 ratio) and the optical properties and can investigate accurately their correlation.

Wide-scan XPS spectra have shown that the a-C and a-C:H surfaces incorporate some O impurities and low concentration of Ar (1.2–2.5% at., only for sputtered films [9]), N, and Si as identified by the O1s, Ar2p, N1s and Si2p XPS peaks, respectively. All of these (except Ar) are removed after sputter etching. The sp^3/sp^2 ratio has been determined by deconvolution of the C1s envelope [9]. Theoretical studies have shown