

Evolution of sp^2 networks with substrate temperature in amorphous carbon films: Theory and experiment

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1. Introduction

Atomic structure in amorphous carbon (a-C) films: evolution of clustering of sp^2 coordinated atoms with substrate temperature.

Theoretical investigations

- a-C films were generated by realistic molecular-dynamics simulations of ion-beam deposition. An analytic hydrocarbon potential of Brenner was adopted, but with an increased C-C interaction cutoff value (for details, see PRB 68 (2003) 024201).
- Deposition parameters:
 - C⁺ ion energy $E_{ion} = 40$ eV.
 - Substrate temperatures $T_s = -173 - 600$ °C.
- All networks of consecutive sp^2 atoms (sp^2 clusters) were identified in the films. The rings existing inside these clusters were counted using the shortest path criterion of Franzblau (PRB 44 (1991) 4925).

Experimental

- a-C films grown by filtered cathodic vacuum arc (FCVA)
- Substrate temperatures between 50 - 400 °C
- Substrate pulsed bias of -50 V
- Characterization: Raman, x-ray absorption (XANES) and spectroscopic ellipsometry
- NOTE: Combination of the most powerful non-destructive techniques to sample the bonding structure of a-C films

2. Theoretical results

Table 1: sp^2 cluster size distributions (blue - sp^2 -rich films, black - sp^2 -rich films)

T_s (°C)	Ion impacts	Depos. atoms	sp^2 cont. (%)	sp^2 cluster size								Larger clusters (and location) ^b		
				1	2	3	4	5	6	7	8		9	
-173 (run I)	1200	1176	87.3	10	58	-	1	2	1	-	-	-	-	52 (tr), 160 (sr)
-173 (run II)	1200	1175	90.3	11	53	-	1	2	1	-	-	-	-	199 (sr)
-173 (run III)	1200	1180	85.8	14	72	11	-	-	-	-	-	-	-	158 (sr)
20 (run I)	5000	4915	56.8	32	176	5	1	3	2	1	1	-	-	28,30, 1836 (wf)
20 (run II)	5000	4916	55.5	46	191	5	4	3	1	2	-	-	-	14,23,24,34, 1541 (wf)
80	3200	3147	62.3	10	127	2	3	1	1	-	-	-	-	273 (tr), 782 (sir)
130	3200	3156	18.2	6	54	1	1	2	-	-	-	-	-	27, 2157 (wf)
200	5000	4886	15.5	3	49	-	-	-	-	-	-	-	-	3790 (wf)
400	1200	1178	6.3	3	13	-	-	-	-	-	-	-	-	988 (wf)
600	1200	1183	3.3	1	8	-	-	-	-	-	-	-	-	1133 (wf)

^a of inner film region.

^b given only for clusters >50. In these clusters many rings exist. The meaning of the abbreviations used is as follows: tr - transition region near substrate, sr - surface region, wh - through the whole film, itr - from inner film region to transition region, sir - from surface to inner film region.

- In case of small cluster, pairs of sp^2 hybrids are preferred.
- sp^2 networks throughout the whole film begin to occur for sp^2 fractions smaller than 60-70%.

Fig. 1: sp^2 ring size distributions (for the films with sp^2 networks throughout the whole film).

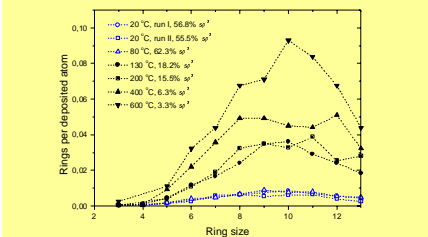
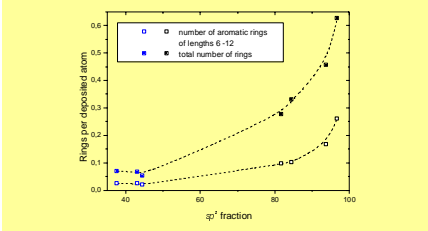


Fig. 2: Increase of total ring numbers in the graphite-like films (especially for sp^2 fractions > 80%).



3. Experimental results and discussion

Raman spectroscopy

Micro-Raman spectra were collected with a Renishaw Ramascope 2000 microspectrometer at an excitation wavelength of 514.5 nm.

Fig. 3: Visible Raman spectra of a-C films grown by FCVA at different substrate temperatures.

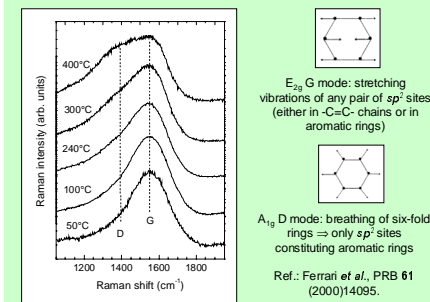
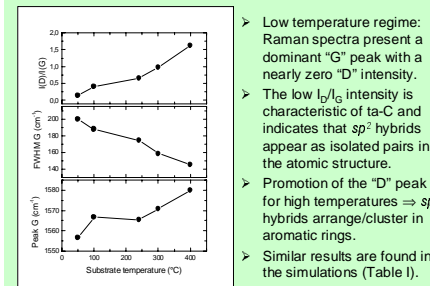


Fig. 4: Fitting analysis of the Raman spectra of Fig. 3.

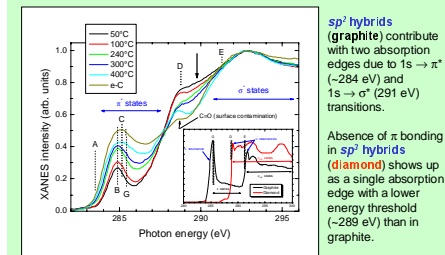


- Low temperature regime: Raman spectra present a dominant "G" peak with a nearly zero "D" intensity.
- The low I_D/I_G intensity is characteristic of ta-C and indicates that sp^2 hybrids appear as isolated pairs in the atomic structure.
- Promotion of the "D" peak for high temperatures $\rightarrow sp^2$ hybrids arrange/cluster in aromatic rings.
- Similar results are found in the simulations (Table I).

X-ray absorption near edge spectroscopy (XANES)

XANES measurements were performed at the beamline SA72 of the SuperAco synchrotron at LURE (Orsay, France). The data were acquired in the total electron yield (TEY) mode.

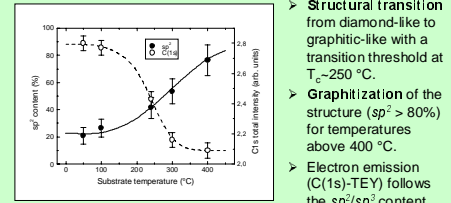
Fig. 5: XANES spectra of a-C films deposited by FCVA at different substrate temperatures together with an amorphous graphite-like (e-C) carbon sample (~100% sp^2 disordered material).



- The increase in the sp^2 content with substrate temperature is revealed by the shift of the σ^* edge onset (from D to E) and the increase in the intensity in the π^* region.
- A weak shoulder (feature A) below the π^* resonance is observed for the samples with the highest sp^2 contents.
- π^* resonance for ta-C (B) and e-C (C) appears at -284.9 eV and 285.2 eV (B), below the position corresponding to -C=C-graphitic environments at 285.4 eV (G).
- Similar trends have been observed by EELS:
 - Lower π^* resonance position: presence of isolated sp^2 pairs (Raman), and defects (e-C) in the graphitic network.
 - The nature of feature A is still unclear but it has been attributed to dangling bonds or core-level excitons.

Computation of the sp^2 content by XANES: relative intensity of π^* to σ^* states [Cuomo et al., APL 58 (1991) 466].
Standard/reference material: e-C (sp^2 content of 95±5 %) (see Fig. 5) (amorphous character similar to the a-C samples studied here).

Fig. 6: Calculated sp^2 content from the XANES spectra (●) and total intensity of the C(1s) edge (○).

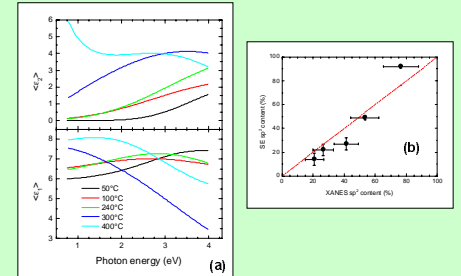


- Structural transition from diamond-like to graphitic-like with a transition threshold at $T_s \sim 250$ °C.
- Graphitization of the structure ($sp^2 > 80\%$) for temperatures above 400 °C.
- Electron emission (C(1s)-TEY) follows the sp^2/sp^3 content
- XANES feature at 284.9 eV (B) dominates up to temperatures above 300 °C $\rightarrow sp^2$ arrangement in small olefinic clusters (chain-like) for sp^2 contents up to 60% (lost of diamond-like character).
- The increase of the π^* intensity around the 285.2 eV (feature C) corresponds to the promotion of graphite-like environments (aromatic rings) and occurs for temperatures above 400 °C.
- Graphitic-like environments dominate over chain configurations only for sp^2 fraction >80% (Fig. 6) (no direct correlation with sp^2 content).
- The simulations predict also a pronounced increase of ring numbers for sp^2 fraction >80% (Fig. 2).

Spectroscopic ellipsometry (SE)

VASE spectroscopic ellipsometer (J.A. Woolam Co., Inc., USA) in the autoretarder mode.
WVASE® software for acquisition and data processing.

Fig. 7: (a) Pseudo-dielectric function obtained from the SE data for the samples considered in this work. (b) sp^2 content calculated by SE vs. XANES data.



- Promotion of the $\pi \rightarrow \pi^*$ transition (~3.8 eV) with substrate temperature \rightarrow increase in the sp^2 content.
- The diamond/graphite effective medium approximation (EMA) provides good values (although under and overestimate the sp^2 fraction for low and high sp^2 contents, respectively).
- The structural rearrangement of sp^2 hybrids with the promotion of graphite-like environments for temperatures above 400 °C (Fig. 5) reflects also in the optical properties.
- Allowance of optical transitions for photon energies below 1 eV suggests the presence of free electrons (graphitic clusters)

4. Conclusions

- The experimental results show a transition from diamond-like to graphitic-like structures with a temperature threshold of $T_s \sim 250$ °C.
- The sp^2 arrangements are dominated by olefinic (chain-like) structures up to ~300 °C, even when the diamond-like character is not dominant.
- Graphitic-like environments are only evident for temperatures above 400 °C.
- The simulations provide the same trends, but the calculated absolute temperature values are too low ($T_s \sim 100$ °C).
- The structural changes at overcritical substrate temperatures $T_s > T_c$ might be explained by the evolution of a medium-range order and the rearrangement of the local-order bonding.

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