

## Hydrogen and disorder in diamond-like carbon

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### Abstract

Diamond-like carbon is a system of rather high disorder as it has a wide optical absorption tail and a high density of paramagnetic defects. The defect density remains high even in DLCs containing 30–60% hydrogen, so hydrogen does not appear to passivate defects well unlike in a-Si:H. To investigate the role of hydrogen on the disorder in DLCs we have investigated the effect of low concentrations of hydrogen on the disorder in ta-C, by introducing  $10^{-6}$ – $10^{-3}$  mbar hydrogen into the deposition of ta-C by filtered cathodic vacuum arc (FCVA), which corresponds to 0.1–15 at.% hydrogen in the films. Higher pressures of hydrogen reduces the ionisation leading to  $sp^2$  bonding, and ultimately the thermalisation of the plasma leads to nanotubes and fullerenes. The deposited ta-C:H films were investigated by electron energy loss spectroscopy (EELS), Raman spectroscopy, optical measurements, electronic transport and  $^{15}\text{N}$  resonant nuclear reaction analysis. Plasma characterisation with a retarding field analyser showed that the ion current density remains nearly unchanged in the pressure range used to deposit the films. Raman measurements indicate the onset of clustering of  $sp^2$  sites when the hydrogen pressure exceeds  $2 \times 10^{-4}$  mbar. We find that small amounts of hydrogen increase the optical gap up to  $2 \times 10^{-6}$  mbar hydrogen pressure, and then the band gap decreases continuously. The absorption tail sharpens by the addition of hydrogen, as measured by photothermal deflection spectroscopy (PDS) and thus confirms the Raman measurements that suggest that the order in the material increases with increasing hydrogen content. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Diamond-like carbon; Hydrogen; Optical absorption

### 1. Introduction

The use of ta-C as an electronic material is strongly limited by the large number of defect states present. In amorphous silicon hydrogen is introduced into the material to passivate defects. This led to the huge success of a-Si:H. An analogous material to a-Si:H is ta-C:H, which is distinguished from other hydrogenated carbons by its high  $sp^3$  content and a relatively low hydrogen content of  $\approx 30\%$ . ta-C:H is typically deposited by a plasma beam source (PBS) or an electron cyclotron

resonance (ECWR) plasma source [1,2], using acetylene ( $\text{C}_2\text{H}_2$ ) or methane ( $\text{CH}_4$ ) as precursors. Due to the hydrogen to carbon ratio in the precursors of at least 1:1 (in the case of acetylene) the amount of hydrogen in the films cannot be reduced much below 25%. Its defect density decreases to  $2 \times 10^{19} \text{ cm}^{-3}$  after annealing [3] which is lower than the defect density in ta-C ( $10^{20}$ – $10^{21} \text{ cm}^{-3}$ ), but still extremely high in comparison to a-Si:H. This means hydrogen is very ineffective in removing defects in ta-C(:H). The cause for this is so far unknown.

Not much work has been done in the study of highly tetrahedrally bonded carbon films with a hydrogen concentration below this. Davis et al. [4] introduced hydrogen into a FCVA deposition system. They showed that the  $sp^3$  content of the films increases slightly at low

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concentrations of hydrogen (from 82% at system base pressure to 86% at  $2 \times 10^{-6}$  mbar in the deposition system) and thereafter decreases again. The plasmon energy (and hence the density) was also found to initially increase and then decrease again. Not much change occurred in the stress of the films and the optical band gap ( $T_{auc}$ ) was found to increase from 1.9 eV to 2.1 eV [4]. Heterojunctions were reported consisting of a n-Si/ta-C:H/gold sandwich structure. These heterojunctions showed that hydrogen only decreases the amount of defects in a narrow range of a hydrogen flow rate of approximately 0.05 sccm, which corresponds (by a scale given in the same paper) to  $10^{-6}$  mbar hydrogen in the background pressure of the deposition system. Similar work was reported by Cheah et al. [5]. Similar to Davis et al. they report a slight increase in the optical band gap, which decreases again at pressures above 0.8 mtorr and show evidence of C–H bonds in infrared spectroscopy as well as a minimum of the Raman I(D)/I(G) ratio at a hydrogen pressure of 0.01 mtorr.

None of the previous studies could relate the properties of the ta-C:H materials to the hydrogen content. In this work we present experimental data on ta-C:H deposited with a filtered cathodic vacuum arc which can relate structural, optic and electronic properties to the atomic hydrogen content of the samples.

## 2. Experimental details

Films were deposited with a filtered cathodic vacuum arc (FCVA) deposition system as described elsewhere [6]. Hydrogen was introduced as a gas into the deposition chamber near the cathode region. The pressure was controlled by the vacuum gauge sitting next to the samples. The ion energy distribution of the plasma beam was monitored with a retarding field analyser (Faraday cup).

Films were deposited on quartz and silicon substrates at floating potential. Some depositions for electron energy-loss spectroscopy measurements (EELS) were repeated on quartz and at a bias of  $-80$  V. Two films of the original series (at system base pressure and  $10^{-3}$  mbar hydrogen pressure) were, however, investigated from the original series and showed the same  $sp^3$  fraction and a similar plasmon energy to the films deposited at a bias of  $-80$  V. The thickness of the films was measured by profilometer measurements. The hydrogen content was measured by  $^{15}\text{N}$  nuclear reaction analysis (NRA) on films deposited on silicon. The EELS measurements were carried out on a Vacuum Generator HB501 scanning transmission electron microscope with a dedicated parallel EELS spectrometer. The  $sp^3$  fraction is calculated from the spectra using the method of Berger et al. [7]. Raman spectra were

taken using the wavelength of 441.6 nm. The optical bandgap was measured by UV-Vis spectroscopy and photothermal deflection spectroscopy (PDS) for the low-energy region.

## 3. Results

The ion current density of the film forming particle flux remained at the value for a pure carbon plasma ( $0.5 \text{ mA/cm}^2$ ) when the arc was struck in a hydrogen background pressure of  $7 \times 10^{-4}$  mbar. The deposition rate for a film deposited without hydrogen was found to be equal to the deposition rate for a film deposited at a pressure of  $10^{-3}$  mbar hydrogen ( $0.8 \text{ nm/s}$ ).

The results of the hydrogen content of the films against the hydrogen background pressure in the deposition system as measured by  $^{15}\text{N}$  nuclear reaction analysis is shown in Fig. 1. The hydrogen content of the films varies between 0.2 at.% at system base pressure and 15 at.% when the hydrogen background pressure is  $10^{-3}$  mbar. The hydrogen content in the film at  $10^{-3}$  mbar is considerably higher than the nitrogen content at the same pressure (10 at.%) [8].

Fig. 2 shows the carbon K-edges of the samples deposited at different hydrogen pressures in the ta-C system as measured by EELS. The  $\pi^*$  peak at 285 eV can clearly be seen to increase with increasing hydrogen pressure, indicating an decrease in the  $sp^3$  fraction with increasing hydrogen content of the films. The  $sp^3$  fraction is shown in Fig. 3, as well as the plasmon energy of the films. The  $sp^3$  fraction stays constant at 85% up to approximately  $10^{-5}$  mbar hydrogen (1 at.%) in the system and then decreases to 67% at  $10^{-3}$  mbar hydrogen (15 at.%). The plasmon energy decreases continually between 30 eV and 27 eV in the same pressure region, indicating a decrease in density from  $3 \text{ g/cm}^3$  to  $2.1 \text{ g/cm}^3$ , using an effective electron mass of 0.87 [9].

Fig. 4 shows Raman spectra of ta-C:H taken at 441.6

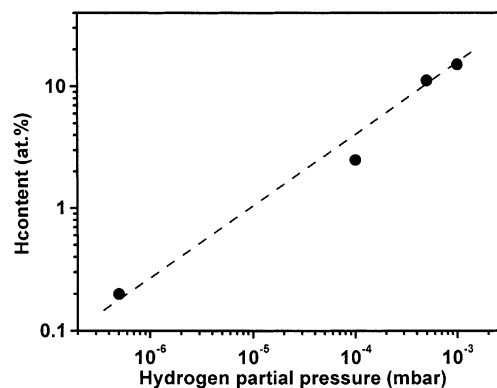


Fig. 1. Hydrogen content of ta-C: H films as a function of hydrogen gas background pressure during deposition.

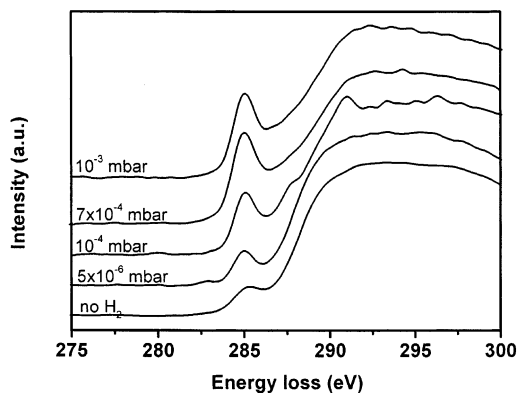


Fig. 2. Electron energy-loss spectra of ta-C:H films, showing an increasing π\* peak at 285 eV with increasing hydrogen background pressure.

nm. An appearance of a D peak can be clearly seen for the spectra of the film deposited at 10<sup>-3</sup> mbar hydrogen pressure. The fitting results of the spectra are shown in Fig. 5. The G peak in all spectra was fitted with a Breit–Wigner–Fano function<sup>1</sup> [10] and the D peak was fitted with a Lorentzian function. The G peak position stays constant at approximately 1590 cm<sup>-1</sup>, but decreases rapidly to 1555 cm<sup>-1</sup> for a film deposited at 10<sup>-3</sup> mbar hydrogen. The value for the full width half-maximum ΔG increases slightly from 266 cm<sup>-1</sup> at system base pressure to approximately 290 cm<sup>-1</sup> at a pressure of 10<sup>-5</sup> mbar. It then decreases again until it reaches approximately 195 cm<sup>-1</sup> at a pressure of 10<sup>-3</sup> mbar. The I(D)/I(G) value was taken as the ratio of the height intensities of the peaks. It is nearly zero for all films, except for the film deposited at a pressure of 10<sup>-3</sup> mbar hydrogen, where the value is 0.14.

Fig. 6 shows the absorption coefficient α as a function of photon energy as determined by UV-VIS spectroscopy and PDS. It can be seen that the slope of

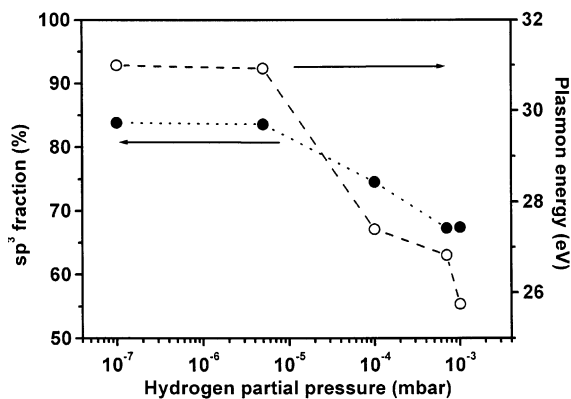


Fig. 3. Plasmon energy and sp<sup>3</sup> fraction of ta-C:H films.

<sup>1</sup>Breit–Wigner–Fano function:  $I(\omega) = I_0(\omega) \frac{1 + 2(\omega - \omega_0)}{q\Gamma^2 + [1 + 2(\omega - \omega_0)/\Gamma]^2}$ .

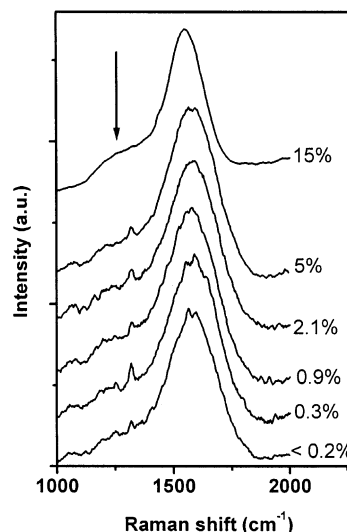


Fig. 4. Raman spectra, taken at 441.6 nm, of ta-C:H films.

alpha against the photon energy becomes steeper with increasing hydrogen pressure. Fig. 7 shows the optical band gap (Tauc) and the Urbach energy determined at α = 10<sup>3</sup> cm<sup>-1</sup> from these measurements. While the optical band gap goes through a maximum at 10<sup>-5</sup> mbar H<sub>2</sub>, the Urbach energy shows a decreasing trend with H<sub>2</sub> pressure.

Fig. 8 shows the room temperature conductivity σ, conductivity activation energy E<sub>A</sub> and prefactor σ<sub>0</sub> as a function of hydrogen pressure. The conductivity initially increases very slightly with hydrogen pressure until it drops rapidly at the sample deposited at a pressure of 10<sup>-3</sup> mbar. The conductivity activation energy was measured by measuring the conductivity between room temperature and 470 K and then fitting

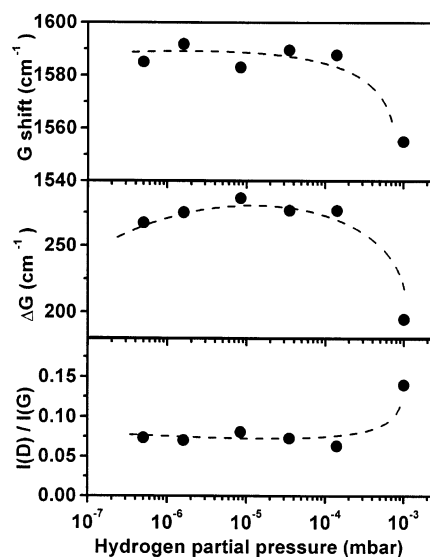


Fig. 5. Fit parameters for Raman spectra: (a) G peak position; (b) full width half maximum of G peak ΔG; and (c) I(D)/I(G).

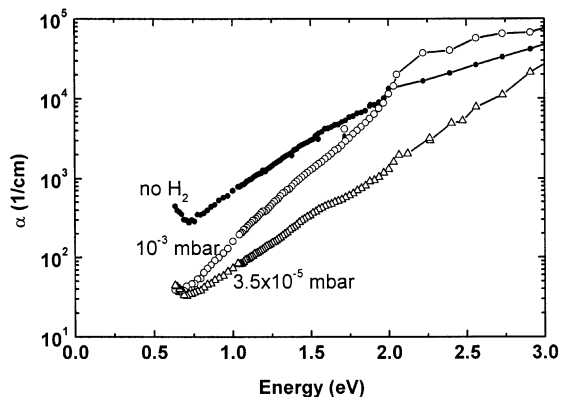


Fig. 6. Absorption coefficient  $\alpha$  as measured by PDS and UV-Vis.

the Arrhenius law of  $\sigma = \sigma_0 \exp[-E_A/(kT)]$ .  $E_A$  initially decreases from 0.4 eV to 0.35 eV and then increases to 0.44 eV for the sample deposited at  $10^{-3}$  mbar. The prefactor  $\sigma_0$  stays constant up to a pressure of  $10^{-6}$  mbar and then decreases steadily down to 0.05 eV at  $10^{-3}$  mbar  $H_2$ .

#### 4. Discussion

No clear connection can be seen between the Raman spectra and the  $sp^3$  fraction or the hydrogen content of the films. While the  $sp^3$  fraction already declines for hydrogen contents above 1% (pressures above  $10^{-5}$  mbar), an obvious change in the Raman spectra can only be seen for the film containing 15% hydrogen (deposited at a pressure of  $10^{-3}$  mbar). At this high hydrogen content, hydrogen induces order into the amorphous carbon matrix, which can be seen from the sharp decrease in  $\Delta G$  as well as the appearance of a D peak, which indicates the formation of aromatic rings. The results of the decrease in  $\Delta G$  and the appearance

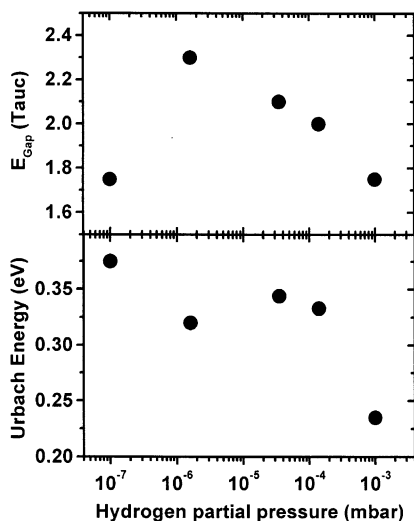


Fig. 7. (a) Optical band gap; and (b) Urbach energy of ta-C:H films.

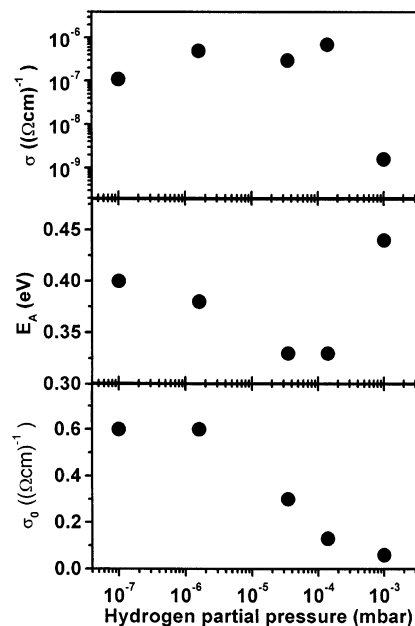


Fig. 8. (a) Conductivity; (b) conductivity activation energy; and (c) prefactor  $\sigma_0$ .

of a D peak at higher hydrogen pressures coincide with the findings of Cheah et al. [5]. High  $sp^3$  ta-C:H samples deposited in a plasma beam source from methane or acetylene as precursors do not necessarily show such a strong D-peak [2]. Hence there is the possibility that the occurring D peak for the sample deposited at  $10^{-3}$  mbar hydrogen might be due to a change in plasma conditions. Ion energy distribution measurements at  $7 \times 10^{-4}$  mbar hydrogen show, however, no sign of a change in the ion current density, and the constant deposition rate over the whole pressure range also indicates that a change of material properties due to a change in plasma conditions is unlikely. The behaviour of hydrogen in the ta-C matrix is opposite from the behaviour of nitrogen. While nitrogen increases  $\Delta G$  and decreases the G position from nitrogen concentrations below 1%, it leaves the  $sp^3$  fraction nearly constant for samples containing up to 9% nitrogen [8]. Even 1% of hydrogen, however, decreases the  $sp^3$  fraction by 10%, while the Raman spectra remains nearly unchanged.

The low Urbach energy, especially for the film deposited at  $10^{-3}$  mbar hydrogen signifies a sharpening of the band edges due to hydrogen. This corresponds well with the decrease of the  $\Delta G$  from the Raman measurements and also the sudden increase in conductivity activation energy for this film is an indication that hydrogen removes states out of the mid-gap. The removal of tail states due to hydrogen can explain the decrease in conductivity by two orders of magnitude for the film deposited at  $10^{-3}$  mbar hydrogen, even though the optical band gap decreases and the  $sp^3$  fraction of this film is only 67%.

Prior to the sudden change happening just before  $10^{-3}$  mbar nitrogen, the conductivity is seen to remain nearly constant while the conductivity activation energy and the prefactor  $\sigma_0$  are decreasing. The results can be explained by a competing effect of the increasing  $sp^2$  fraction, providing conductive paths and leading to a closure of the band gap, and the effect of hydrogen to remove defects out of the band and thus removing states which could have been used for a thermally activated hopping conduction mechanism.

Recently photo-conductivity measurements [11] were used to show that the localisation radius for charge carriers in ta-C is approximately 0.9 nm, while in ta-C:H the value drops to only 0.19 nm/0.3 nm for films deposited with methane/acetylene as a precursor, respectively. This difference in the localisation radius is also reflected in the charge carrier mobilities derived from thin film transistors (TFTs). While the mobility of a ta-C TFT was reported to be in the range of  $10^{-6}$   $\text{cm}^2/(\text{V s})$ , the mobility of ta-C:H TFTs was reported to be only  $10^{-9}$   $\text{cm}^2/(\text{V s})$ .

The effect of hydrogen to remove states out of the band gap and to increase the localisation of charge carrier wavefunctions is thought to be the reason for the decrease in conductivity in the film deposited at  $10^{-3}$  mbar hydrogen, with the optical band gap and the  $sp^3$  fraction decreasing at the same time.

## 5. Conclusions

The presented results can be interpreted by the effect of hydrogen to sharpen the band edges of the material and remove defects out of the band gap. They can also be viewed in the context of a decreasing localisation radius with the introduction of hydrogen and a lower mobility of charge carriers in hydrogenated amorphous carbons. It should be noted that the addition of hydrogen to the deposition plasma for ta-C films increased the  $sp^2$  fraction, rather than etch  $sp^2$  sites

away. It was also found that the addition of hydrogen or nitrogen results in different trends for the behaviour of the  $sp^3$  fraction and clustering of  $sp^2$  sites.

## Acknowledgements

B.K. acknowledges funding from a European Union's Marie Curie Fellowship. S.E.R. acknowledges funding from CONACYT and ORS award scheme. Thanks to Stephan Hofmann from the WSI Munich, Germany, for help and discussions. PDS measurements were performed at the Walther-Schottky Institute, Munich, thanks to Uwe Karrer and R. Janssen for help and discussions.

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