P10A

Max-Planck-Institut für Plasmaphysik, EURATOM Association

Characterization of temperature-induced changes in amorphous hydrogenated carbon thin films

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Motivation

Redeposition of eroded carbon along with codeposition of hydrogen in fusion experiments operating with carbon as a first wall material results in the build-up of hydrogenated carbon films in deposition-dominated areas. Heating of these films during plasma operation can modify them and, especially, drive out hydrogen, thus decreasing the hydrogen isotope retention associated with the formation of these films.

In this work, hard a-C:H films were heated in vacuum to different temperatures and held at these for about 30 minutes. Afterwards, the cooled-down samples were analyzed by various techniques. Fairly strict and reproducible correlations are found between all the determined parameters and the heating temperature.

Sample preparation and annealing

Samples: a-C:H (a-C:D) films with H/(H+C) ≈ 0.3 and a thickness of ≈ 200 nm plasma-deposited on a Si wafer at a substrate bias of ≈ –300 V.

"TESS samples" ▲▼

Film deposition: CH_4 plasma, capacitively coupled rf plasma (CCP) at 13.56 MHz

Initial refractive index: ≈ 2.1

Annealing:
Inside a UHV quartz tube in a tube furnace
Quick ramp to target temperature (< 5 min)
Held at target temperature for 30 min followed by cool down
Temperature range: RT to 1300 K

Pros/Cons:
+ Good temperature calibration with a thermocouple glued to a sample.
+ Heating under UHV conditions.
+ Several small samples can be heated simultaneously
- Transfer to annealing device in air

"PlaQ samples" ▽

Film deposition: CH_4 plasma, ECR plasma (2.54 GHz) with substrate bias via capacitively coupled rf (13.56 MHz)

Initial refractive index: ≈ 2.1

Annealing:
On the resistively heated sample holder of the deposition device
Quick ramp to target temperature (< 15 min)
Held at target temperature for 30–60 min
Temperature range: RT to 870 K

Pros/Cons:
+ Deposition and heating in same device without sample transfer
+ In situ ellipsometry available
- Less reliable temperature measurement

"Erosion samples" ○

Film deposition: CH_4 plasma, CCP (13.56 MHz)

Initial refractive index: ≈ 2.15

Annealing:
During partial erosion of the films by thermal atomic hydrogen.
Quick ramp to target temperature (< 15 min)
Held at target temperature for 30–60 min
Temperature range: RT to 1000 K

Pros/Cons:
- Least reliable temperature measurement/temperature control

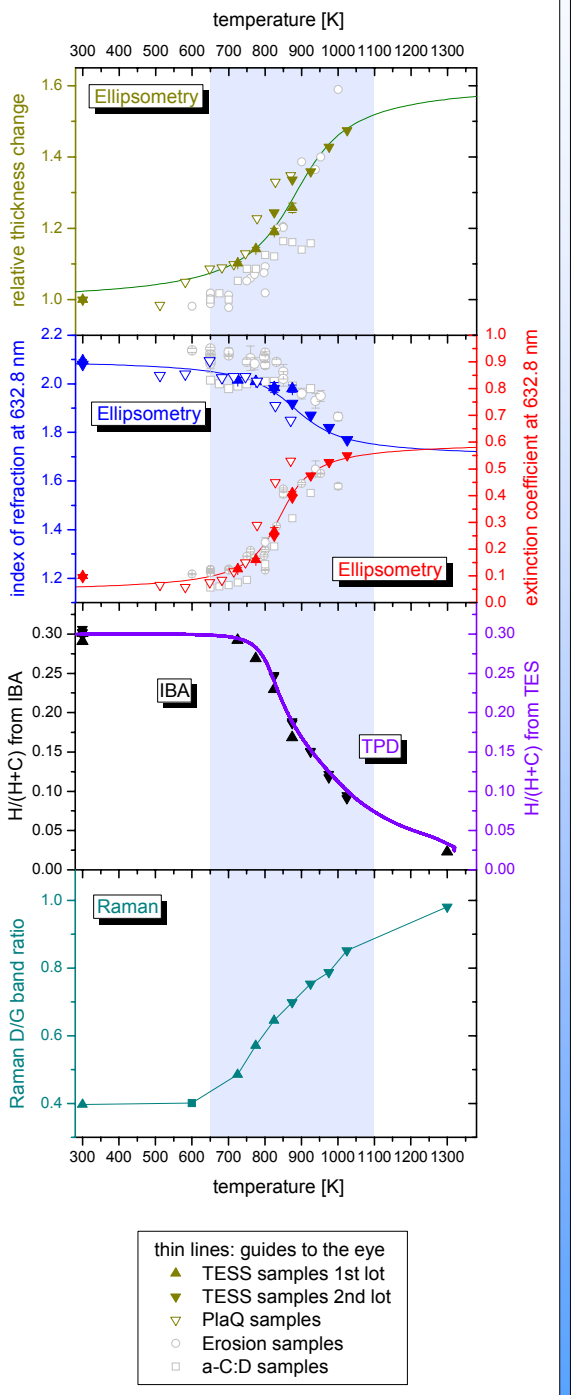
"a-C:D samples" □

Film deposition: CD4 plasma, CCP (13.56 MHz)

Initial refractive index: ≈ 2.0

Annealing:
Inside a UHV quartz tube in a tube furnace
Held at target temperature for 30 min
Temperature range: RT to 925 K

Characterization results



Characterization techniques

Ellipsometry

Method:

Fixed laser wavelength of 632.8 nm.

Either *in situ* during erosion of the film in a mild (low ion energy) oxygen plasma or *ex situ* scanning over an erosion crater from rim to rim.

Provides:

→ **Film thickness.**

→ **Refractive index (related to film density)**

→ **Extinction coefficient (related to sp2 carbon)**

Ion beam analysis (IBA)

Method:

3 MeV ^{3}He

Elastic recoil detection (ERDA) to detect ^{1}H.

Nuclear reaction analysis (NRA) to detect ^{12}C via the $^{12}C(^3He,p)^{14}N$ reaction.

H/(H+C) ratio determined by fixing it to 0.3 for as deposited films (value known from previous quantitative measurement)

Provides:

→ **H/(H+C) ratio (hydrogen concentration)**

Temperature programmed desorption (TPD)

Method:

Sample heated in a quartz tube inside a tube furnace.

Temperature calibrated with a thermocouple inside the quartz tube during a calibration run.

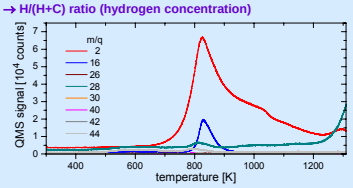
Slow heating ramp of ~ 1 K/min means that the sample is very close to steady state at any given temperature.

Measurement of the released volatile gases by a mass spectrometer in the UHV main chamber.

Remaining H/(H+C) at every teperature determined by assuming 0.3 for the fresh film and 0.023 (IBA at 1300 K) at the end of the measurement and neglecting H loss via desorption of hydrocarbons.

Provides:

→ **H/(H+C) ratio (hydrogen concentration)**



Raman spectroscopy

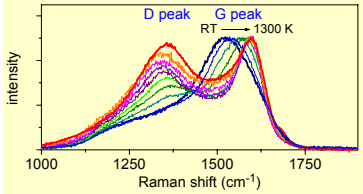
Method:

Raman spectroscopy with μm² spot size and a probed depth between a few tens and a few hundreds of nm

Two interesting peaks in the 1000–1800 cm^{-1} region:
G peak around 1550 cm^{-1}: sp² stretching vibration
D peak around 1350 cm^{-1}: "breathing" mode of aromatic rings.

Provides:

→ **D/G band ratio (linked to size of aromatic domains)**



Conclusions

General Observations

- Temperature-induced changes take place in the temperature range of 650–1300 K
- Quickest change with temperature around 900 K

Observed changes with increasing temperature

- Swelling by up to 50%
- Loss of hydrogen with only about 8% of the initial H remaining at 1300 K (IBA)
- Almost all H released in the form of H_2 as opposed to soft films where a significant fraction is released as hydrocarbons[1]
- Transformation from a-C:H to nano-crystalline graphite-like films[2]
- Decrease of the refractive index
- Increase of the extinction coefficient
- All observed dependences are monotonic. In principle, well defined a-C:H films could serve as low-cost T_{max} thermometers if kept long enough at T_{max}

References:
[1] E. Salançon, T. Dürbeck, T. Schwarz-Selinger, W. Jacob, J. Nucl. Mater. 363–365, 944 (2007)
[2] A. C. Ferrari and J. Robertson, Phys. Rev. B 61, 14095 (2000)