Fabrication and STM Nanostructuring of tetrahedral amorphous Carbon

Teja Roch
STM Nanostructuring of Carbon

Fabrication and STM Nanostructuring of tetrahedral amorphous Carbon (ta-C)

Content:

Who are we?

What are we doing?

Why are we doing Nanostructuring?

→ Results
STM Nanostructuring of Carbon
STM Nanostructuring of Carbon

Working fields

**Aim:**
Customized solutions for the problems of our clients

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<th>Business fields</th>
<th>Core services</th>
<th>Laser materials processing</th>
<th>Plasma coating processes</th>
<th>Materials / Nanotechnology</th>
<th>System technology</th>
<th>Process simulation</th>
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<tr>
<td>Removal / Cutting</td>
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<td>PVD - Vacuum coating</td>
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<td>CVD - Atmospheric coating</td>
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Large, medium and small relevance of the core services for the business fields
STM Nanostructuring of Carbon

Tetrahedral Amorphous Carbon

ta-C = tetrahedral amorphous Carbon

Atomic arrangement: amorphous
Binding: predominantly sp³
Hydrogen content: low (< 1%)
STM Nanostructuring of Carbon

**Diamond**
- tetrahedral $sp^3$ bonds
- three-dimensional network

**Graphite**
- trigonal $sp^2$- bonds
- two-dimensional network

**Amorph**
- $sp^3 + sp^2$ bonds
## Properties of Carbon films

<table>
<thead>
<tr>
<th></th>
<th>Graphite</th>
<th>a-C</th>
<th>ta-C</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³ fraction*</td>
<td>0%</td>
<td>&lt;40%</td>
<td>40-90%</td>
<td>100%</td>
</tr>
<tr>
<td>Density (g/cm³)*</td>
<td>2.3</td>
<td>2-2.3</td>
<td>2.6-3.2</td>
<td>3.52</td>
</tr>
<tr>
<td>Resistivity (Ωcm)*</td>
<td>10⁻²</td>
<td>&lt;1</td>
<td>10⁶-10¹¹</td>
<td>10¹⁶</td>
</tr>
<tr>
<td>Elastic modulus (GPa)*</td>
<td>686/low</td>
<td></td>
<td>400-800</td>
<td>1200</td>
</tr>
<tr>
<td>Thermal stability (°C)*</td>
<td>&gt;700</td>
<td>&gt;200</td>
<td>600 (300)</td>
<td>&gt;700</td>
</tr>
<tr>
<td>Heat capacity (J/kg K)</td>
<td>427***</td>
<td></td>
<td>600****</td>
<td>709 ***</td>
</tr>
<tr>
<td>Heat conductivity @ 25°C (W/m K)**</td>
<td>400 (6)</td>
<td>1-10</td>
<td>900-2000</td>
<td></td>
</tr>
</tbody>
</table>

Properties of Carbon films

Heat stability depends on sp²/sp³ ratio:
→ High sp³ content makes ta-C more stable
R. Kalish et al. APL 74 (1999), 2936

Heat capacity depends on sp²/sp³ ratio:
→ Large optical gap higher heat capacity
(measurement for a-c:H)
W. Hurler et al. Diam and Rel. Mat. 4 (1995) 954
Influence of graphitic top layer

**Film-Volume:**
dominantly: $sp^3$ – carbon bonds

**Film-Surface:**
dominantly: $sp^2$ – carbon bonds
(relaxation of non equilibrium states)

**Film preparation:**
Filtered high current arc

**E-Modul-measurement:**
Laser accustic

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STM Nanostructuring of Carbon

Fraunhofer IWS Dresden
Laser Acoustic measurement

Measurement Opportunities:

- Mechanical properties
- Elastic modulus
- Non-destructive
- Thickness measurements
Filtered Cathodic Arc

**Principle** (Aksenov 1975)

- curved magnetic field
- Manipulation of the electron trajectory to spiral trajectories along streamlines of the magnetic field
- electrostatic attraction Electron-Ion → Movement of the ions along the electron trajectories
- Heavy particles moving linearly → adsorption to the filter
STM Nanostructuring of Carbon

Ultrathin carbon layers on magnetic storage media

lubricant ($\approx$ 1 nm)
carbon top-coat
magnetic layers ($\approx$ 25 nm each)
glass substrate

**service conditions:**
distance $\approx$ 10 nm
velocity $\approx$ 150 km/h

**aim:**
increase of storage density
5 Gb / in$^2$ $\rightarrow$ 100 Gb /in$^2$
by reduction of the thickness of the protecting layer to < 3 nm
**Example: ta-C top layers on magnetic storage media**

**aim:** protection against corrosion and scratching  
**film system:** tetrahedrally bonded amorphous carbon (ta-C)  
**technology:** pulsed high current arc with magnetic filtering (Φ-HCA)

<table>
<thead>
<tr>
<th>demands</th>
<th>ta-C film</th>
</tr>
</thead>
<tbody>
<tr>
<td>low film thickness</td>
<td>dense at $1.6\ nm$</td>
</tr>
<tr>
<td>low roughness</td>
<td>RMS $&lt; 1\ nm$</td>
</tr>
<tr>
<td>particals</td>
<td>$1\ peak &gt; 10\ nm$ on $0.1\ m^2$</td>
</tr>
<tr>
<td>corrosion resistance</td>
<td>achieved at $1.6\ nm$</td>
</tr>
<tr>
<td>scratch resistance</td>
<td>hardness $\geq 30\ GPa$ (at $5\ nm$)</td>
</tr>
<tr>
<td>magnetics</td>
<td>no influence</td>
</tr>
</tbody>
</table>
STM Nanostructuring of Carbon

STM structured ta-C

STM induced local graphitisation of ta-C

STM induced local oxidation of ta-C

Made by T. Mühl
Nano graphitisation of ta-C for data storage

Problem:  
- High speed SPM writing difficult  
- Rewriting of ta-C probably not possible  

→ Long term data storage!

Physikalisch-Technische Bundesanstalt 11.05.2007:  
„there is no optimum system for all long term data storage applications“*

Difficulties:  
- Lifetime of the data storage medium  
- Availability of Hardware  
- Availability of Software  
- …

Application: Libraries, government, bank, …

*http://www.ptb.de/de/org/2/251/251/lebensdauer.pdf
Nano graphitisation of ta-C for data storage

Initial Situation:

- IWS-Standard: PVD-deposition of ta-C
- Phys. effect: Graphitisation of taC:
  \[ \text{sp}^3\text{-bonding} + \text{Energy} \Rightarrow \text{sp}^2\text{-Bonding} \]
  \[ \Rightarrow \text{Change of characteristics:} \]
  - Density ↓ \Rightarrow Volume ↑ \Rightarrow Film thickness ↑ \Rightarrow convexe
  - refractivity ↓
  - electric conductivity ↑
  - thermal conductivity ↓

- IWS-Patent: use of the phys. Effect for data storage
  \[ \Rightarrow \text{feasibility proved} \]
Solution writing: STM or C-AFM?

- **Principle:** A voltage is applied between probe and sample
  \[\Rightarrow\text{Nanostructuring is possible with both methods!}\]

- **Resolution:** < 10 nm \[\Leftrightarrow\text{current flow through one atom (optimum conditions)}\]
- **Probe:** metal filament (e.g. tungsten)

- **Resolution:** ca. 13 nm \[\Leftrightarrow\text{depending on probe diameter}\]
- **Probe:** conductive cantilever (Si) coated or doped
Example of AFM Lithography:

- Nanostructuring with high resolution is possible e.g. line width ~13 nm
- Probe stability is critical!
- AFM Litho needs low moisture (<30%) and tip conditions are critical
Ta-C is isolating is STM possible?

**Scanning Probe Spectroscopy:**
Current to tip movement of Ta-C/Si:n, HOPG and Si:p

**Initial STM parameters:**
- Ta-C/Si:n 4V/70pA
- Si:p 1V/1nA
- HOPG 0,2V/1nA

- Exponential behaviour is expected
- The Ta-C graph is bended, if the tip is moved towards the sample

→ STM tip is close to the ta-C surface
STM Nanostructuring of Carbon

AFM-Roughness of ta-C

- ta-c on Si (Ta-C/si)
  - 20 nm ta-C
  - Silizium
  - RMS = 0,066 nm

- ta-c on Si with Cromium Inter layer (ta-C/Cr/Si)
  - 20 nm ta-C
  - 30 nm Cr
  - Silizium
  - RMS = 0,148 nm

- ta-c on Si with Cromium Inter - and top layer
  - 20 nm ta-C
  - 30 nm Cr
  - 1 nm Cr
  - Silizium
  - RMS = 0,160 nm
STM structuring on different Substrates

**ta-C/Si**

- Topography profile
- Structures on ta-C/si are about 2 nm high

**ta-C/Cr**

- 9 Bits written on 20 nm ta-C
  - Voltage 10 V, current 1 nA
  - Speed 0.5 sec/bit
- High structures at substrate with Chromium inter layer
- Topography profile
- Structures on ta-C/Cr are up to 18 nm high
IV Characteristics

- IV characteristics are averages of the marked areas.
- Conductivity is higher in the structured area
- IV characteristics of structured areas are untypically. Current drops with rising voltage
STM Nanostructuring of Carbon

Structure topography

Topography profile along the blue line

Structuring at 10 V, 1 nA and different writing speed:
Area 1: 0.3 s/bit
Area 2: 0.2 s/bit
Area 3: 0.1 s/bit
Area 4: 0.075 s/bit

Topography profile: lateral bit size ~10 nm
Bit high ~3-10 nm

Positive voltage at the substrate!
Variation of writing speed

- Variation of the STM pulse duration at constant voltage (10 V) and current (1 nA)
- pulse duration was varied between 0.075 s and 0.005 s
- every data point in the graph is an average of 100 bits
- the structuring high shows a logarithmic dependence on the structuring time

Lineares Fitten von Datenhintergrund

Daten: Datenhintergrund_c
Modell: ExpDec1
Gleichung: \[ y = A_1 \exp\left(-\frac{x}{t_1}\right) + y_0 \]
Gewicht: Keine Gewichtung.

\[ y_0 = 4.82427 \pm 0.26819 \]
\[ A_1 = -2.85792 \pm 0.42033 \]
\[ t_1 = 0.01847 \pm 0.0079 \]

\[ \chi^2/\text{DoF} = 0.05933 \]
\[ R^2 = 0.96678 \]
Is ta-C graphitisation thermic or electronic induced?

**Thermic:** depends on power  
**Electronic:** electron energy (voltage)

Mühl et al. revealed that Joule heating due to introduced power can be ruled out.

*T. Mühl APL 85 (2004), 5727*
**Difficulty:**
- If STM-structuring is not performed in UHV but atmosphere
  → etching of carbon can appear
  → Probe heating/sample heating (?!)
- For AFM-structuring it is less difficult
Data Lifetime

Graphite is stable against diamond → a long lifetime could be expected:

To simulate a longer timescale an accelerated aging test was performed
Substrate = periodic structured ta-C

Test period 5 x 24h
- t = 0-2 h, T = 25-70 °C, RH = 85 %
- t = 2-8 h, T = 70 °C, RH = 90-95 %
- t = 8-24 h, T = 70-25 °C, RH = 85 %

SEM pictures where made before and after the life time test

→ No change of the graphitisation could be observed
Conclusion

• Production of particle free ta-C Films is possible
• Ta-C properties can be controlled
• STM Nanostructuring of ta-C with resolution < 10 nm is possible
• No influence of heat (T = 70 °C) and moisture (90 % RH) on graphitisation
• Pulse duration of 5 ms revealed an average structure high of 2.5 nm
• Positive Voltage must be applied to the substrate
• Maximum graphitisation high depends on Voltage and Film thickness
Thank you for your attention!