IR and AFM studies of diamonds for detector applications

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3. NoRDHia workshop
31.08.06
Content

• Experimental setup and what we measure
  – Ultra high vacuum (UHV) chamber
  – Atomic force microscopy (AFM)
  – IR-spectroscopy
  – Drude-model

• The diamond (100) surface
  – surface terminations and related electronic properties
  – Diamond-metal interfaces
  – AFM pictures of E6 diamonds

• First results: Cr on C(100)-(1x1):O

• Outlook
FTIR spectrometer and UHV chamber

(ex-situ)
accessible sample temperatures: 40K to 1300K
surface preparation: heating, sputtering
**Measurement of relative spectra**

<table>
<thead>
<tr>
<th>Wavenumber [cm⁻¹]</th>
<th>Sample</th>
<th>Reference</th>
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**Relative transmission**

\[ \text{wavenumber: } \omega = \lambda^{-1} \]
What we measure

• Mostly transmittance at normal incidence
• For ultrathin metal films \( (d << \lambda / n_{\text{film}}) \)

\[
\frac{T_{\text{film/substrate}}}{T_{\text{substrate}}} \approx 1 - \frac{2 \cdot d \cdot \omega \cdot \text{Im} \epsilon_{\text{ll film}}(\omega)}{c \cdot (1 + n_{\text{substrate}})}
\]

\[
\epsilon_{\text{film}} - \epsilon_{\infty} = \frac{i \sigma(\omega)}{\omega \epsilon_0}
\]

\[
\epsilon_1(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + \omega^2_\tau}
\]

\[
\epsilon_2(\omega) = \frac{\omega_\tau \cdot \omega_p^2}{\omega^3 + \omega \cdot \omega^2_\tau}
\]

\[
\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m_{\text{eff}}}}, \quad \omega_\tau = \frac{1}{\tau}
\]

In-plane conductivity measurement without electrical contacts

\(d \ll \lambda / n_{\text{film}}\)
Thin film corrections

\[ \omega_\tau \rightarrow \omega_\tau(d) = \omega_\tau^{\text{bulk}} + \omega_\tau^{\text{surf}}(d) \]
due to scattering of electrons at the surface, depends strongly on roughness

\[ \omega_p \rightarrow \omega_p(d) = \beta(d) \cdot \omega_p^{\text{bulk}} \]
band bending at interfaces causes change of \( m_{\text{eff}} \) and Schottky effect at metal-semiconductor contacts leads to electron transfer which influences \( n \)

\[ \varepsilon_1(\omega, d) = \varepsilon_\infty - \frac{\omega_p(d)^2}{\omega^2 + \omega_\tau(d)^2} \]
\[ \varepsilon_2(\omega, d) = \frac{\omega_\tau(d) \cdot \omega_p(d)^2}{\omega^3 + \omega \cdot \omega_\tau(d)^2} \]
Example: Fe on MgO(001)

Parameters $\alpha$ (solid circles) and $\beta$ (open circles) for a Fe-film on MgO. $\alpha=0$ and $\beta=1$ correspond to bulk values for the relaxation rate and the plasma frequency, respectively. Below a thickness of $\sim0.8$nm, the film cannot be described by a Drude-type dielectric function.

Fahsold et al., PRB 61, 14108
Thin film growth

Metal thin films can be trapped in many equilibrium conditions, depending on several preparation conditions, e.g.
- evaporation rate
- background pressure
- substrate temperature
- substrate structure
- ...

The diamond (100) surface

Maier et al., PRB 64, 165411 (2001)

Hydrogen terminated diamond exposed to air exhibits a high surface conductivity and is hence inapplicable for detector applications.
Metal-diamond interface

band bending at interface due to constant Fermi energy

barrier height for p-semiconductor (if no Fermi level pinning occurs):

$$\Phi = E_g + \chi - \Phi_M$$
### Electron affinities of diamond surfaces

<table>
<thead>
<tr>
<th>Surface Configuration</th>
<th>$\chi$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(100)-(2x1)</td>
<td>0.5</td>
</tr>
<tr>
<td>C(100)-(1x1):O</td>
<td>1.7</td>
</tr>
<tr>
<td>C(100)-(2x1):H</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Ways to control the barrier height

- evaporating carbide forming metals (Ti, Mo, Cr) and subsequent annealing (~600°C)
- removing oxidation in UHV before metallization

![Diagram showing interfacial band diagrams at the p-diamond/metal interface: (a) as-deposited metal on diamond, (b) conductive graphite layer induced by carbide formation.]

Oxidation of diamond surface

- Wet-chemical treatment with $\text{H}_2\text{SO}_4$ and $\text{KNO}_3$ at 240°C to oxidize the surface and remove conductive graphite phases.
- Alternatively, the surface can be treated by oxygen-plasma.
- Examination of oxidation quality with IR-spectroscopy? (it is known that acid treatment does leave some residual hydrogen on the surface.)

Diffuse reflectance infrared spectroscopy of diamond crystallites stretching mode of a carbonyl group at 1731 cm$^{-1}$

![Graph showing DRIFT spectra of diamond and adamantane](image)

*Figure 1.* DRIFT spectra of (100) diamond oxidized at 700 °C, for 10 min in 150 Torr $\text{O}_2$, and powdered 2-adamantanone — the vibrational spectrum of 2-adamantanone has been assigned$^{33}$ previously.

IR-transmission spectrum

insufficient surface sensitivity in transmission geometry
AFM pictures of an E6 diamond rather smooth, roughness of a few nanometers but in other areas…
Different morphology for different places on the diamond. Influence of wet-chemical treatment?

In order to achieve reliable information about metal film growth, a well defined substrate is needed!
Experimental procedure for Cr-film growth

- oxidizing with $\text{H}_2\text{SO}_4$ and $\text{KNO}_3$ at 240°C
- transferring into UHV and heating to 400°C in order to clean surface
- evaporating Cr with a rate of ~900sec/nm, substrate at room temperature

LEED-pattern of C(100)-(1x1):O
First results: Cr on C(100)-(1x1):O

IR-spectra measured during Cr-evaporation
Development of transmission at different frequencies

crossover

rel. transmittance [%]

\(d\) [nm]

2000cm\(^{-1}\)
3000cm\(^{-1}\)
4000cm\(^{-1}\)
5000cm\(^{-1}\)
6000cm\(^{-1}\)
Effective Drude parameters

- spectra fitted from 3000 to 5000 cm\(^{-1}\), constant \(\omega_p\) and \(\omega_\tau\) for bulk Cr assumed
- from 2.5 nm on, the IR-spectra of the film can be described by a Drude-type dielectric function
AFM measurements

substrate nearby

Cr-Film
Outlook

• influence of diamond morphology on film growth has to be studied
• comparison of wet-chemical and oxygen-plasma oxidation
• investigation of chromium-carbide formation
Thanks

Prof. A. Pucci
PD. Dr. G. Fahsold
F. Meng
O. Skibbe
F. Neubrech
M. Binder
M. Klevenz

E. Berderman
M. Pomorski
M. Nesladek
C. Nebel