**INTRODUCTION**

- Mid-IR spectroscopy provides access to the information rich fingerprint region of the electromagnetic spectrum enabling identification and quantification of organic contaminants.
- Strong background absorption of water in the mid-IR region limits sensitivity.
- Sensitivity towards organic contaminants can be increased by coating highly attenuated total reflectance (ATR) crystals with polymer coatings.
- Analytes are reversibly absorbed and thereby concentrated in the coatings in the region probed by the evanescent wave, while excluding spectral interferences of water.
- Limits of detection (LOD) for chlorinated and aromatic hydrocarbons in the mid-low ppb region have been obtained.
- Polymer coatings used in literature rely on long enrichment paths, e.g. as thick porous a-SiO2 films or long porous enrichment materials.
- Diffusion can be enhanced by porous enrichment materials.
- Soft templating of sol-gel materials provides access to mesoporous films that can be easily organically modified.

**DESIGN OF ENRICHMENT LAYER**

Ordered periodic mesoporous materials with controlled pore size are synthesized by using surfactants as sacrificial template. e.g. soft templates such as surfactants or amphiphilic block copolymers.

**SYNTHESIS & CHARACTERISATION**

Mesoporous silica coatings were synthesized by acidic condensation of tetraethylorthosilicate in ethanol with cetyltrimethyl ammonium bromide as co-condensation agent. The silica films were obtained by spin-coating on polished silicon wafers and subsequent calcination at 400 °C or dissolution in acetone.

**OPTICAL SETUP**

ATR-Setup:
- Silicon wafer (20 x 10 mm pieces) with 45° (20 µm) connected to a peristalic pump.
- Transferable into Bruker Vertex 80v with UK-cooled MCT detector.
- Noise (RMS) 1.5 * 10^-1 A.U. (2200 – 1800 cm^-1, 128 scans, 16 s, water on coated Si ATR).

**MID-IR SPECTROSCOPY**

**TRANSLATION OF A.U. TO ABS. CONCENTRATIONS**

The path length d applies to transmission measurements and corresponds to the effective path length d_e in ATR spectroscopy and is defined as:

\[
d_e = d \times \frac{n_{silica} \times n_{air}}{n_{silica} + n_{air}}
\]

where:
- \( n_{silica} \) and \( n_{air} \) are the refractive indices of the silica film and air, respectively.

**ENRICHMENT FROM GAS PHASE**

- Hydrophobic film repels water, which is largely alleviated from the probed region (compare water absorption bands for coated and uncoated silicon wafer).
- Limit of detection for benzonitrile : 1 ppm
- Response and regeneration time: < 5 s
- Enrichment factor for benzonitrile : 200

**SYNTHESIS**

Mesoporous silica coatings were synthesized by acidic condensation of tetraethylorthosilicate in ethanol with cetyltrimethyl ammonium bromide as co-condensation agent. The silica films were obtained by spin-coating on polished silicon wafers and subsequent calcination at 400 °C or dissolution in acetone.

**CHARACTERISATION**

Coatings are IR transparent in the information rich region at >3300 cm^-1. FTIR-KBr spectrum of functionalized films shows absorption bands of Si-O-Si stretching modes around 1070 cm^-1. Bands at 1260 cm^-1 can be assigned to C-O deformation modes. X-ray diffraction patterns of two films are shown below and are in good agreement with literature. Transmission electron micrographs clearly show highly ordered pore structures throughout the film.

**TRANSLATION OF A.U. TO ABS. CONCENTRATIONS**

- Transmission measurements:
  \[
  K = \frac{1}{n_{silica} \times n_{air}} \times \frac{n_{silica} \times n_{air}}{n_{silica} + n_{air}}
  \]

**ENRICHMENT FROM AQUEOUS PHASE**

- Hydrophobic film repels water, which is largely alleviated from the probed region (compare water absorption bands for coated and uncoated silicon wafer).
- Limit of detection for benzonitrile : 1 ppm
- Response and regeneration time: < 5 s
- Enrichment factor for benzonitrile : 200

**REFERENCE**


**CONTACT**

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