| ESRF | **Experiment title:**<br>Characterization of thermally hydrocarbonized porous silicon modified with grafting of terminal alkenes and alkynes | **Experiment number**:<br>MA-2091 |
|---|---|---|
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**Report:**

The aim of the research was to study the surface chemistry of non-modified and modified thermally hydrocarbonized porous silicon samples. Due to high internal surface area, porous silicon can be used in various applications, such as biosensing and drug carrier matrix applications, and therefore knowlegde regarding the chemical properties of the surface is vitally important. Thermal hydrocarbonization is a convenient method for increasing the chemical stability of porous silicon [1]. Our research group has developed several modifications that enable attachment of specific functional moieties to the hydrocarbonized silicon surface. These moieties can be used in many applications, such as, attachment of cell penetrating peptides to porous silicon nanoparticles [2].

The objective of the current experiment was to study the in-depth homogeneity of different surface modifications with Hard X-ray Photoelectron Spectroscopy (HAXPES). The tuneability of the X-ray beam energy allowed us to compare the core level spectra obtained with photoelectrons originating from increasing depth. The main measurements performed are shown in Table I. Firstly, the untreated hydrocarbonized surface was measured as a reference. The following samples were modified to incorporate different chemical moieties, such as carboxylic acid (sample 2) and azide (sample 5) terminal groups.

The chemical modifications used in samples 2 and 3 have been successfully used in drug delivery and gas sensing applications [2-4]. Samples 4 and 5 were modified using a new approach by including a bromine termination to the hydrocarbonized surface. As bromine can

be substituted using a $S_N2$ reaction, we applied this to include an azide termination to the surface for the first time with porous silicon.

**Table I.** List of the samples with measured core level spectra and respective beam energies.

| | | Measured core levels and beam energies in keV | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Surface termination | Si(1s) | | | C(1s) | | | Br(2s) | | | Br(1s) | | | O(1s) | | | N(1s) | | |
| 1 | Untreated | 9 | 12 | 15 | 9 | 12 | 15 | - | - | - | - | 12 | - | 9 | 12 | 15 | - | - | - |
| 2 | COOH- | 9 | 12 | 15 | 9 | 12 | 15 | - | - | - | - | 12 | - | 9 | 12 | 15 | - | - | - |
| 3 | Alkyne- | 9 | 12 | 15 | 9 | 12 | - | - | - | - | - | 12 | - | 9 | 12 | - | - | - | - |
| 4 | Bromo- | 9 | 12 | 15 | 9 | 12 | 15 | 9 | 12 | 15 | - | - | 15 | 9 | 12 | 15 | 9 | 12 | - |
| 5 | Azide- | 9 | 12 | 15 | 9 | 12 | 15 | 9 | 12 | 15 | - | - | 15 | 9 | 12 | 15 | 9 | 12 | 15 |

Key results of the measurement series are presented in Figure 1. The obtained spectra allowed us to confirm the homogeneity of the surface chemistry when moving from the external surface deeper into the pores, without resorting to ion milling of the surface. The results for the bromine-azide substitution obtained with high beam energies (Figures 1b,c) revealed that while the initial attachment of the bromine termination is successful, the substitution reaction unexpectedly did not completely replace the surface bromines contrary to normal XPS findings. This information allowed us to modify the $S_N2$ reaction conditions appropriately to increase the reaction efficiency.

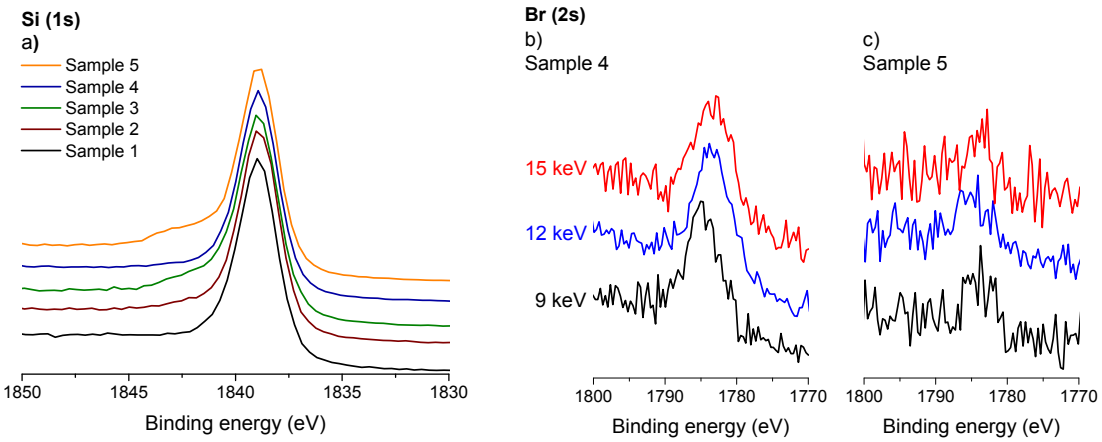


**Figure 1.** a) Si(1s) core level spectra of all samples obtained at 9 keV. Br(2s) core level spectra of samples 4 (b) and 5 (c) with increasing beam energies, showing the partial success of the bromine-azide substitution reaction.

## References:


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