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Metal-decorated silicon nanowires for laser desorption-ionization mass spectrometry

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Silicon nanowires prepared by wet etching and decorated by metal nanoparticles enable interference-free laser desorption-ionization mass spectrometry of low-molecular-weight analytes.

Laser desorption-ionization mass spectrometry (LDI-MS) using silicon to trap the analyte was introduced by Siuzdak's research group in 1999.[1] This technique enables the detection of analytes at levels down to attomoles without using organic additives or matrices. In the application of matrix-assisted LDI-MS in proteomics and lipidomics, nanostructured inorganic substrates can outperform the more widely used organic matrices when employed to detect low-molecular-weight (LMW) analytes, e.g., ionized species (such as amino acids, sugars, peptides, and lipids) that have a mass-to-charge ratio (*m/z*) below 1000.

The main advantages of nanostructured LDI-MS platforms compared to organic matrices are the reduced spectral background, which is almost interference-free, and better reproducibility of results.[2] Silicon nanowires (SiNWs) represent a very promising building block for several applications. However, they are frequently prepared by a vapor-liquid-solid mechanism,[3] in which a metal catalyst is usually incorporated in the wires, thus negatively affecting their electronic and optical properties.

Metal-assisted wet etching processes are an alternative method for the synthesis of SiNWs.[4] In this process a metal catalyst is usually present in the etching solution as a salt or thin metallic layer. The metal catalyzes the oxidation of silicon by hydrogen peroxide and then silicon dioxide, which is selectively formed where metal and silicon are in contact, is etched by hydrofluoric acid. Important advantages of metal-assisted etching compared to other methods are the ease of doping of the resulting SiNWs and better preservation of their structure and dopant distribution.[5]

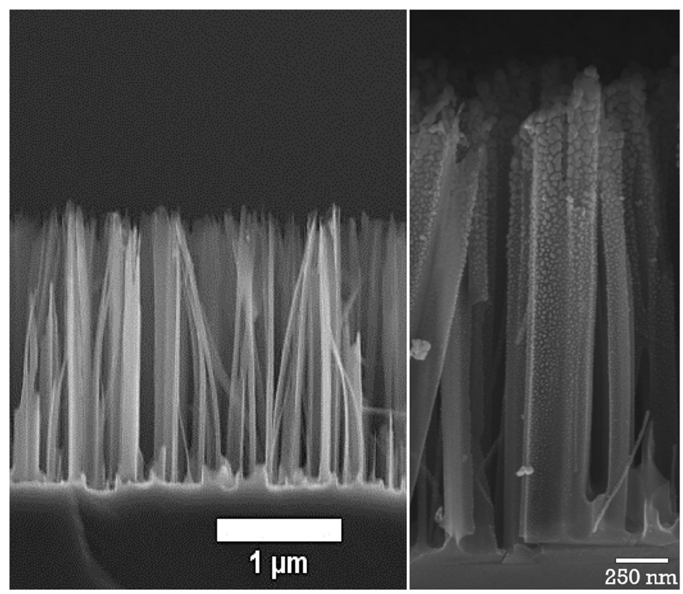

Figure 1. *Cross-section scanning electron microscopy images show 1.8µm silicon nanowires (SiNWs) (left) without and (right) with metal nanoparticles (NPs).*

Moreover, SiNWs can be further decorated by a dense, uniform monolayer of silver or gold nanoparticles (NPs) using an additional pulsed laser deposition stage, thus providing a perfect combination of spherical transition metal nanophases supported by an array of elongated silicon nanostructures.

With the support of two Italian projects, we are presently exploring the potential of metal NP/SiNW systems as a novel platform for LDI-MS applications. We obtained typical SiNWs from p-type (100)-oriented silicon wafers, which we etched with

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hydrofluoric acid to obtain oxide-free silicon surfaces. We then immersed clean substrates in etching solutions comprising, for instance, 40% silver nitrate, 40% water, and 20% hydrofluoric acid to obtain SiNWs with a length of 1.8 or 3.4μm. Next, we used pulsed laser deposition to obtain the complete, dense, and uniform decoration of SiNWs with silver or gold NPs. To fully decorate the surface of the SiNWs from the top to the base, we carried out two deposition cycles: one with 45,000 laser pulses and then another with 60,000 laser pulses. As a result, SiNWs were covered by metal NPs along their entire length. Figure 1 shows cross-section scanning electron microscopy images of 1.8μm SiNWs (left) without and (right) with metal NPs.

The proposed SiNW materials can be used for the direct LDI-MS detection of LMW molecules by depositing a solution of the analyte onto a SiNW platform adhered to an LDI-MS target. Morphological and surface spectroscopic data from mass spectrometry is well correlated as a function of the length, presence of additional metal, and surface composition of the SiNWs. Figure 2 provides an example of the interference-free spectra that we obtained using this approach. We easily detected 500pmol of squalene—a typical molecular marker of high-quality extra-virgin olive oil—as an adduct with silver ions emitted from the NPs of the silver/SiNW platform.

Decoration with metal NPs of SiNWs obtained by metal-assisted wet etching provides an interesting and novel approach

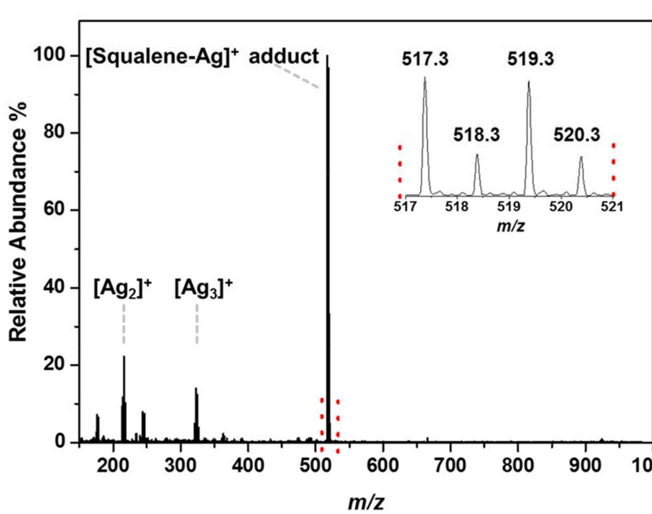

Figure 2. *Laser desorption-ionization mass spectrum of squalene (500pmol) analyzed by 1.8μm SiNWs decorated with silver (Ag) NPs. Inset: Magnification of part of the spectrum outlines the typical isotopic pattern of squalene as an adduct with silver ions. m/z: Mass-to-charge ratio.*

to the production of high-performance nanostructured platforms for the direct mass spectrometric detection of LMW molecules. Bioanalysis, proteomics, lipidomics, and food chemistry are just a few examples of fields where we expect these nanomaterials will be effectively used.

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