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Laser desorption/ionization from nanostructured surfaces: nanowires, nanoparticle films and black silicon

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Laser desorption/ionization is a key method in the analysis of large biomolecules. The goal in these experiments is to efficiently produce ions from the molecules deposited on the surface of a substrate with minimal or controlled amount of fragmentation. It is also essential, that the composition of the produced ions reflect the composition of the sample on the surface. In recent years, various methods of soft laser desorption/ionization (SLDI) have been developed to achieve this goal. The most successful version of the method, matrix-assisted laser desorption/ionization (MALDI) was demonstrated for different laser wavelengths (UV and IR) and various laser pulse lengths (ns, ps and fs pulses) [1,2]. Combined with mass spectrometry MALDI is capable of identifying biomolecules of moderate to large size (i.e., m/z 1,000 to 100,000). The presence of matrix in this method, hoever, creates an obstacle in the analysis of small molecules, essential in a large number of applications (e.g., pharmaceutical). An alternative approach to optimizing the characteristics of the laser pulse is to adjust the properties of the desorption surface. By providing a nanoporous environment, desorption/ionization on amorphous silicon (DIOS) was the first method to offer interference free analysis in the low mass range [3]. In this contribution we report on experiments with new desorption surfaces including silicon nanowires [4], nanoparticle films and black silicon. Due to their optical and chemical properties, thin films formed of nanoparticles are potential new platforms for SLDI mass spectrometry. Thin films of gold nanoparticles (with 12±1 nm particle size) were prepared by evaporation-driven vertical colloidal deposition and used to analyze a series of directly deposited polypeptide samples. In this new SLDI method, the required laser fluence for ion detection was equal or less than what is needed for MALDI but the resulting spectra were free of matrix interferences. A black silicon-based substrate was also developed as a matrix-free laser desorption ionization surface. When low-resistivity wafers were processed with a mode-locked Nd-YAG laser in air, SF_6 gas, or water environment, regularly arranged conical microspikes formed on the silicon surface. The radii of the spike tips varied with the processing environment, ranging from about 500 nm in water, to 2 µm in SF_6 gas, and to 5 µm in air. Mass spectra induced by a nitrogen laser showed the formation of protonated ions of angiotensin I (1296 Da), substance P (1347.6 Da), and insulin (5733.5 Da) from the processed Si surfaces but not from the unprocessed areas. Threshold fluences for desorption/ionization were comparable to those used in MALDI. Internal energy measurements of the ions desorbed from the newly developed nanostructured surfaces indicated reduced energy transfer compared to surfaces without nanostructures.

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