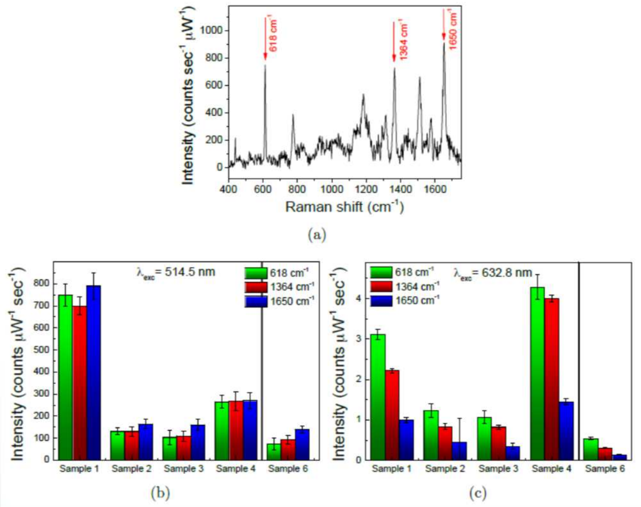

detection power of the decorated substrates characterized by an enhancement factor of the Raman signal higher than 10^8, more than one order of magnitude compared to that one of the Ag NPs deposited with a similar procedure on a flat 2D substrate. Thus, we have been able to effectively detect concentrations as low as 10^{-8} M.

The behavior of different samples under two different exciting wavelengths has been explained through a careful comparison between the morphological and optical characterization. These important results strongly attest the great potentiality of a 3D SERS substrate as powerful sensor with respect to the standard 2D substrate and mark the starting points towards a suitable optimization of the MACEtch and PLD processes in order to continuously improve the material performance as powerful SERS sensor.

Lavoro di Tesi effettuato in collaborazione con:

IMM

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Corso di Laurea Magistrale in Fisica

Giulia Bertino

Silicon Nanowires decorated by Ag Nanoparticles for SERS detection

Tesi di Laurea

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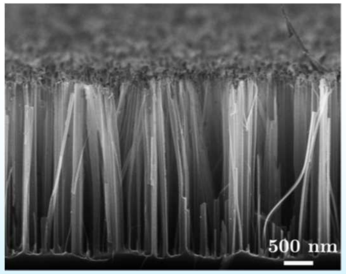
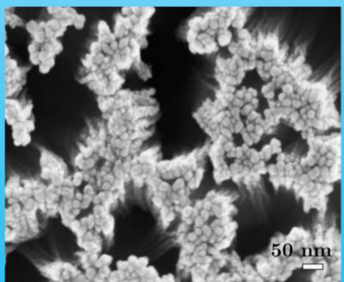
Richard P. Feynman was one of the first and most pioneering dreamer of a new and innovative research in the condensed matter investigation. With his lecture on December 1959, he opened the incoming decades with the `plenty of room at the bottom' vision. And the further decades made real this dream, opening the door to an incredibly wide nanoworld.

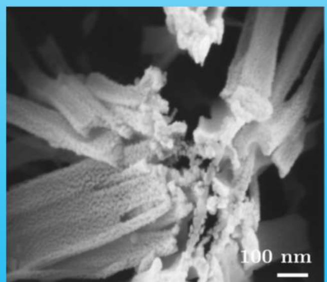
Indeed, today, nanotechnologies are one of the most interesting research objects in the condensed matter field, and they are basic components for a huge range of application fields, like photonics, electronics, photovoltaic and sensing.



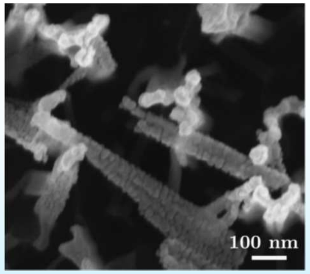
In particular, Silicon Nanowires (Si NWs) strongly attract the worldwide research interests for their unique and advantageous properties. In fact, their shape and geometrical arrangement result in a large surface to volume ratio and in quantum confinement effects, which are useful properties for deep physical principles understanding and innovative applications. Furthermore, their physical properties and dimensions can be easily tuned through a careful choice of the synthesis method adopted.

In general, Si NWs can be fabricated through the well known top -down and bottom-up approaches. The first one collects the lithographic approaches consisting in the use of a mask and an etching beam, like light, electrons or ions. Si NWs synthesized through top-down techniques are ordered and uniformly spaced, yet their dimensions can not get down 10 nm.





With the strong needs for sub-10 nm structures, the bottom-up methods represent a valid solution. Indeed, these techniques are based on the self-assembling and self-organizing properties of the sub-nanometer matter components. For example, the Vapor-Solid-Liquid (VLS) technique overwhelms lithographic limits in terms of Si NWs dimensions. Anyway, it is affected by heavy drawbacks, like the low control on the doping level, which is a strongly detrimental aspect for Si NWs applications, and the catalyst metal presence into the NWs, which limits the performances of the system.

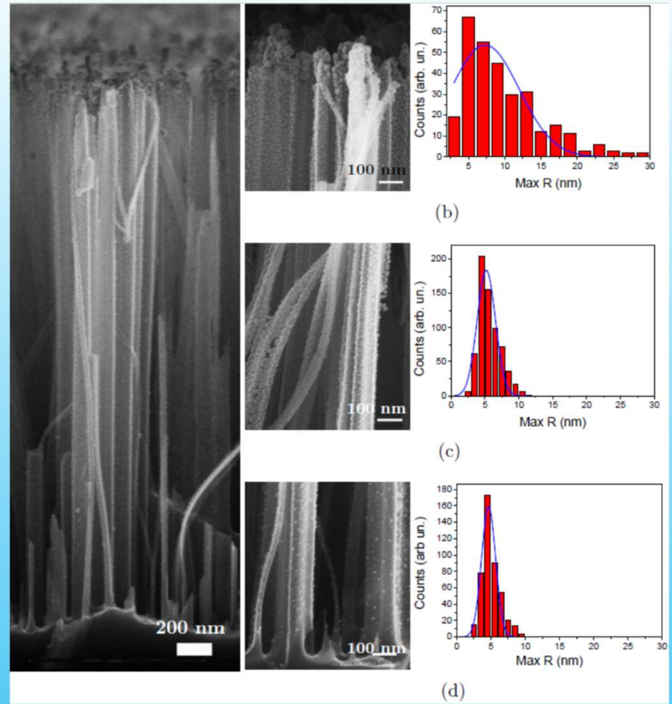


In this thesis work I will show how to effectively solve such synthesis related problems through the innovative Metal-Assisted Chemical Etching (MACEtch) approach. Indeed, MACEtch is a rapid and low cost technique, which allows a uniform and sub-10 nm Si NWs fabrication. In particular, the process can be performed with inexpensive systems and at room temperature. Therefore, the resulting NWs are not affected by metal diffusion and deep impurity levels, which commonly result in undesired radiative phenomena, and the doping is the same of the initial substrate. Thus, the final Si NWs dense forest structure offers a wide range of possibility for further implementations.

In particular, it is possible to decorate the entire array with metal nanoparticles (NPs). Many works are present in literature about deposition of noble metal NPs on Si NWs arrays through chemical methods. Anyway, a complete NWs coverage is very difficult to obtain through the chemical approach.

On the other hand, I demonstrate that it is possible to reach a complete, dense and uniform metal NPs decoration through the physical method of the Pulsed Laser Deposition (PLD). In fact, I am going to show a complete morphological characterization of silver (Ag) NPs decorated Si NWs, revealing few nanometers NPs until the NWs basis. Also, the NPs decoration is uniform and dense on different Si NWs substrates, independently by NWs dimensions and PLD parameters. Moreover, the presented methods is totally implementable with the Si technology, in contrast with chemical methods.

An interesting application for such substrates is the Surface-Enhanced Raman Spectroscopy (SERS) molecular detection. In fact, the small Ag NPs are able to strongly enhance the Raman signal of molecules attached on their surface through a localized plasmon resonance phenomenon. The resonant excitation of the surface plasmons results in a strong amplification of the emitted signal, especially in points among the small NPs, called hot-spots. Therefore, a molecule attached on a hot-spot area experiences a dramatic increase of its Raman signal intensity. As a consequence, very low concentrations of organic molecule can be detected through the SERS approach. Remarkably, Si NWs decorated with Ag NPs are a suitable substrate for SERS applications due to the huge surface of the NWs forest, and, hence, to the high hot-spot density.



In particular, I will highlight the complete SERS characterization of the Ag decorated substrates. We used rhodamine 6G (R6G), an organic dye, as probe molecule and we performed several SERS measurements at different R6G concentrations until 10^{-9} M with two exciting wavelengths.

Our results clearly reveal the detection power of our substrates, underlining their great potential applications in the SERS sensing field. The SERS spectra clearly reveal the