PROOF-OF-CONCEPT EXPERIMENT REPORT

INVESTIGATION ON FAILURE WITH COMMERCIAL CHIPS BASED ANALYSIS

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Proof-of-Concept experiment details

Received sample: 4 chips for electrochemical analysis

Description by customer: the samples consist in commercial chips, one new, 3 already employed in experimental procedures by the company. The chip contains 3 electrodes composed of carbon nanotubes.

Planned analysis:

1st step: SEM imaging of the chips, whit particular attention on the central electrode where the sampling solution is dropped.

2nd step: Raman spectroscopy analysis in order to investigate the contaminations present in the electrodes

Sample preparation: the chips have been provided by the company

Measurement author, dates and place: the SEM and EDS measurement of the sample has been performed by dr. Simone Dal Zilio at Istituto Officina dei Materiali- CNR. The Raman analysis has been performed by dr. Marco Lazzarino at Istituto Officina dei Materiali- CNR.

Main aim of the proposal: the CNT's electrodes don't allow needed reproducibility of the experiments. Possible contamination are investigated as possible reason by the use of available methods and techniques (SEM/EDS, Raman) in the partner labs, in order to verify if these methods are effective in understanding the presence and the sources of contaminations.

SEM and EDS Observation conditions

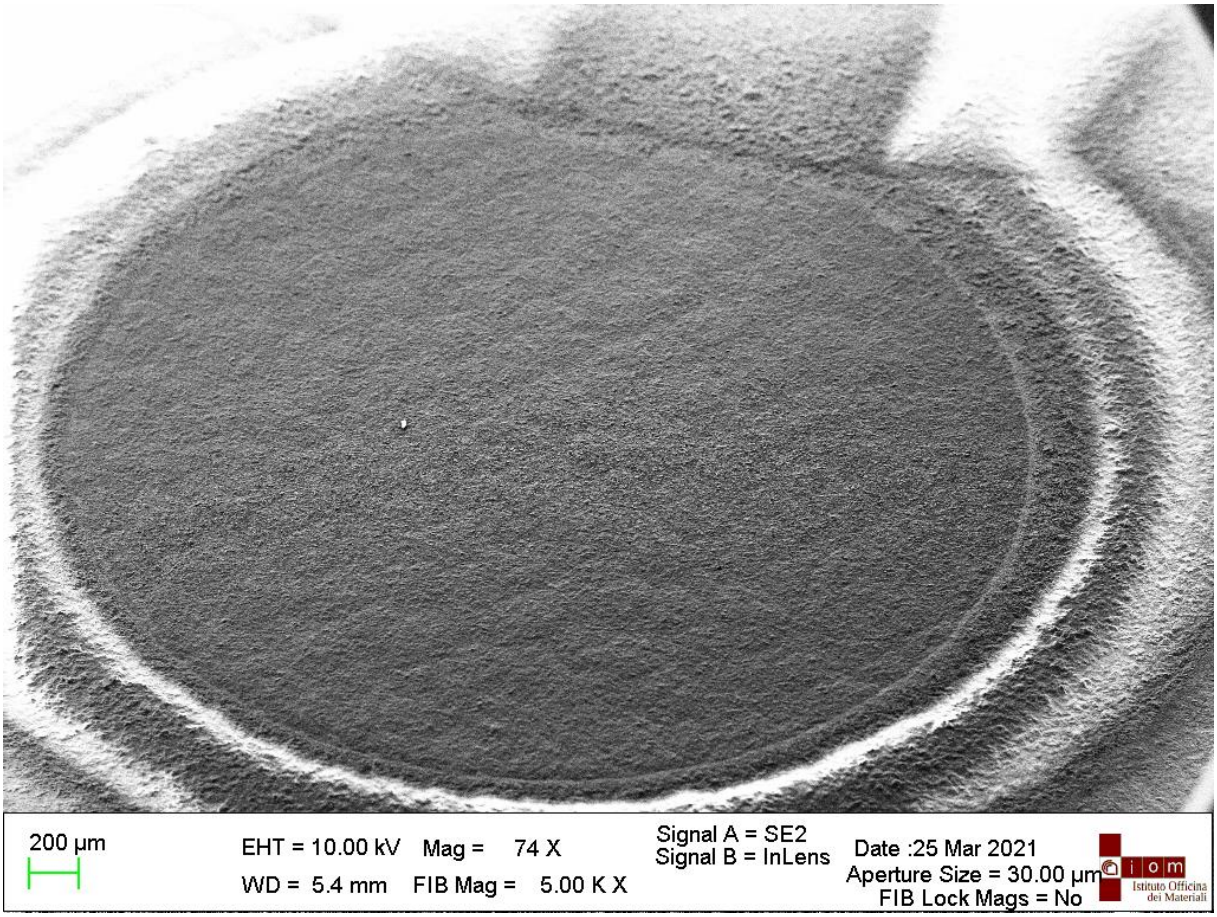
Imaging: beam energy 5-10 KeV; secondary electron detector, inlens detector.

EDX mapping and spectroscopy has been performed with the following parameters:

Beam energy: 15 KeV; Probe current: ~ 350 pA

Morphology

In the next picture is described the details of the CNT's electrodes collect at high magnification. No significant differences can be seen between at this level on the CNT's morphology.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Signal B = InLens
Date :25 Mar 2021
Aperture Size = 30.00 µm
FIB Lock Mags = No
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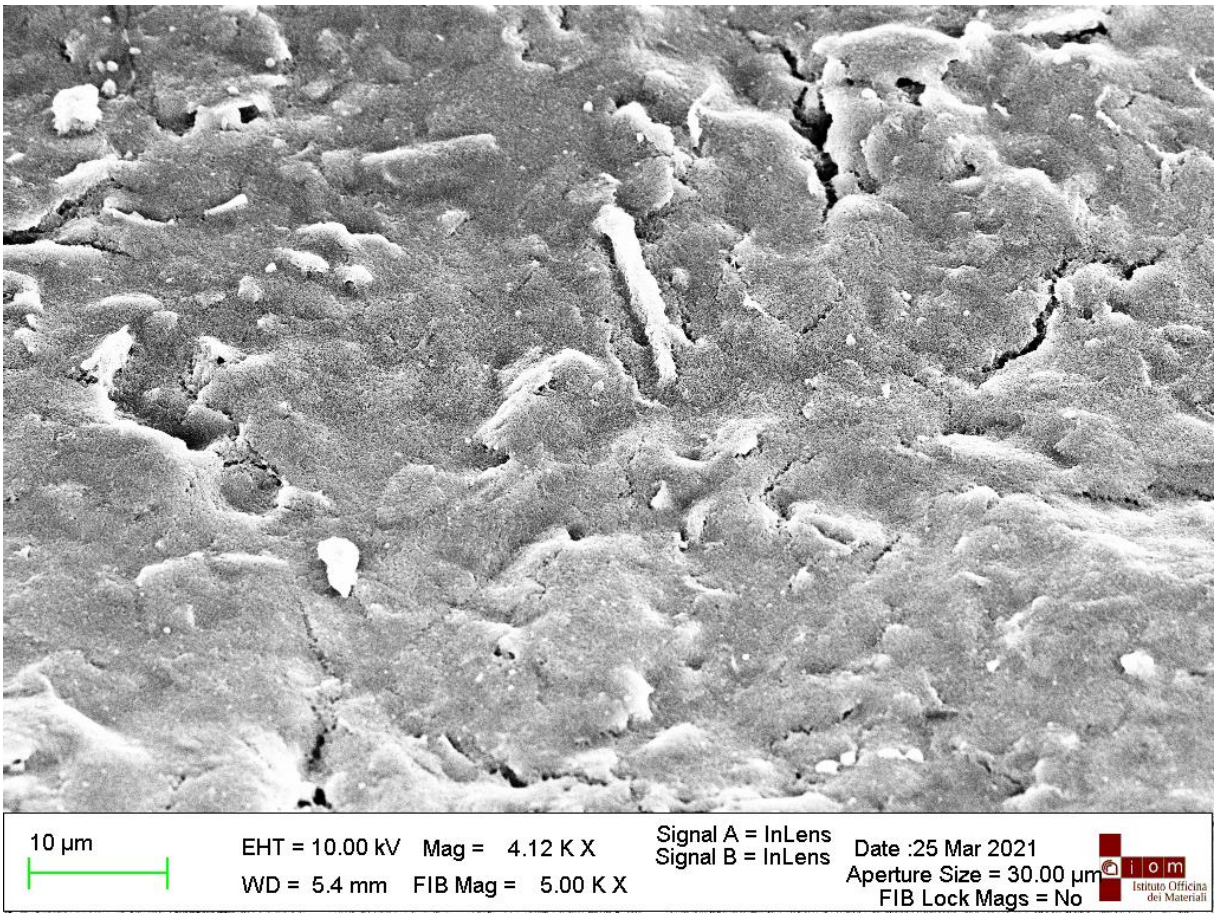
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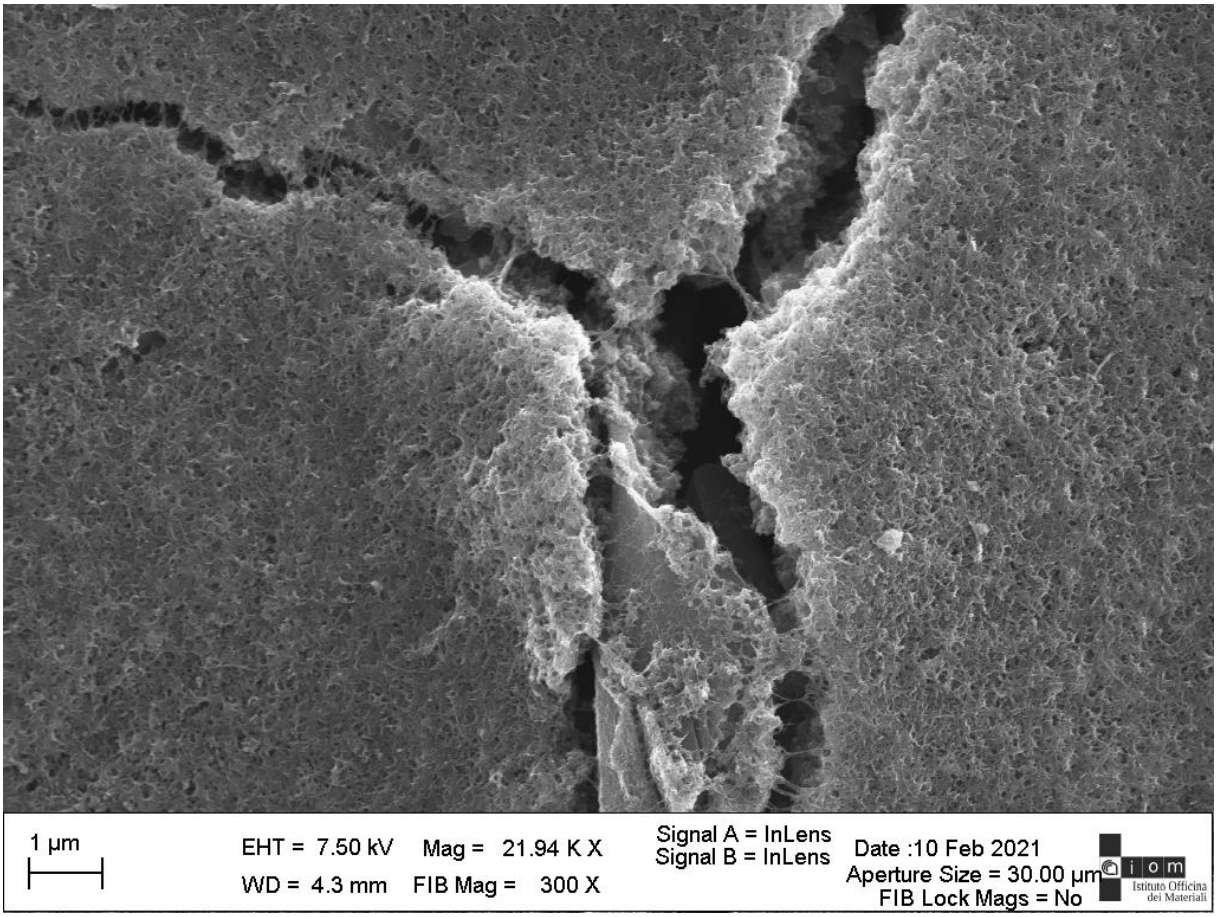
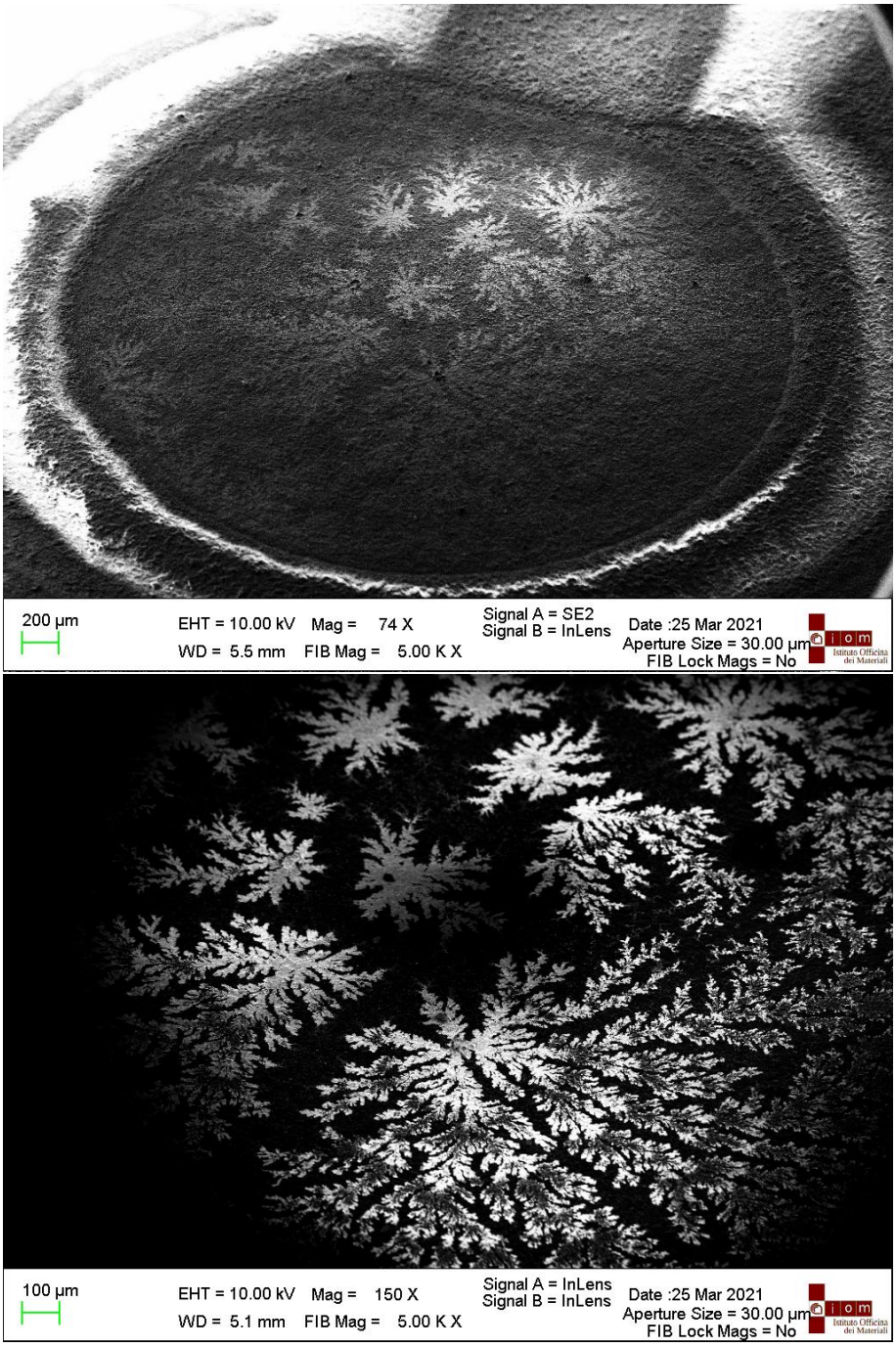


Figure 1Sem images of the central electrode of the clean not used chip.

On the contrary, lower magnification images show more interesting features on the central electrodes, in particular when IL detector is employed. Differently from the clean (unused) chip, the used ones show the evidence of crystal-like growth atop of the CNT's electrodes; the amount and the size are different on each substrate, and the chip n.3 look pretty completely coated by the thin layer of crystal. The thickness of this film is not easy to be estimated because of not uniform coverage, but can by evaluated in few hundred of nanometers.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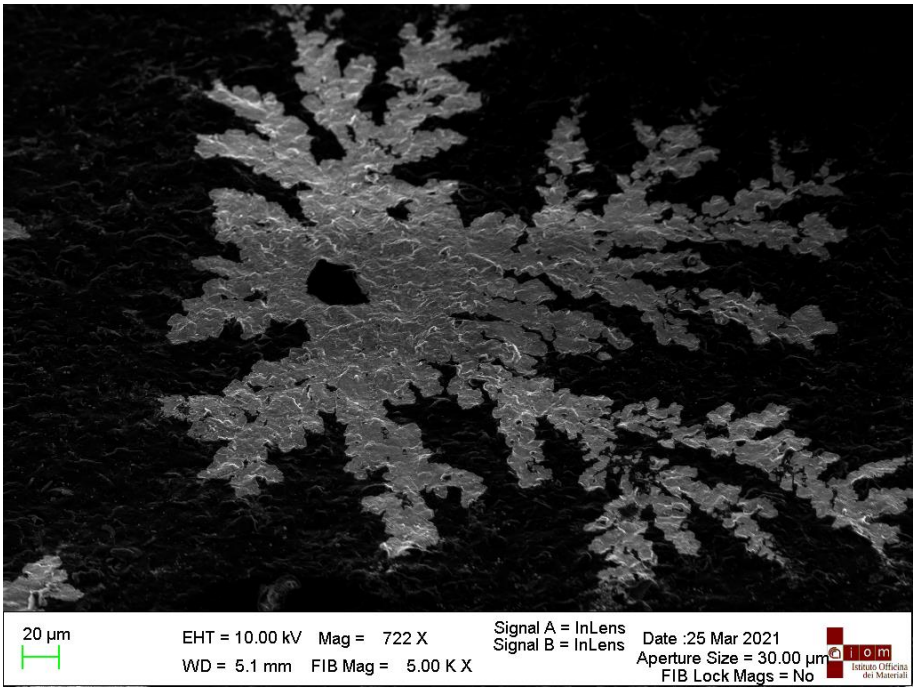

Figure 2 Sem images of the contaminated chips. The crystalline structures are included in the entire surface of the chip.

A second kind of contaminants are also detected on the electrodes, and they look like bright nano particles; they seem to be more concentrated close to the edge of the electrodes, while in the middle region they are not present.

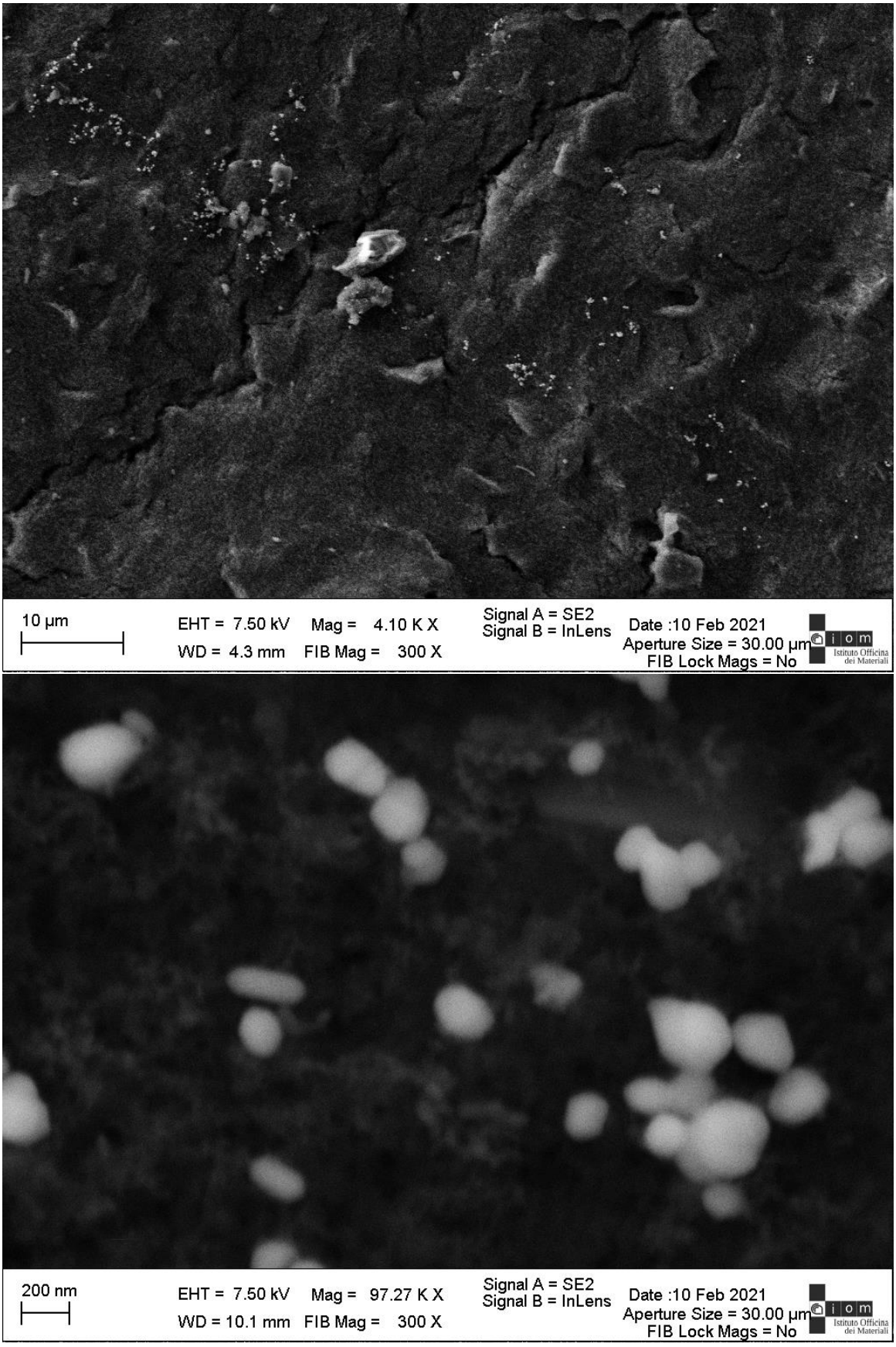

Figure 3 Nanoparticles individuated around the electrode edge.

EDX analysis:

From the EDS analysis, as clearly visible from the maps and the spectra, the material forming the crystal-like structures can be identified in NaCl. We suppose the origin of it can be traced in not suitable or sufficient rinse after the deposition of the sample solution on the chip electrode.

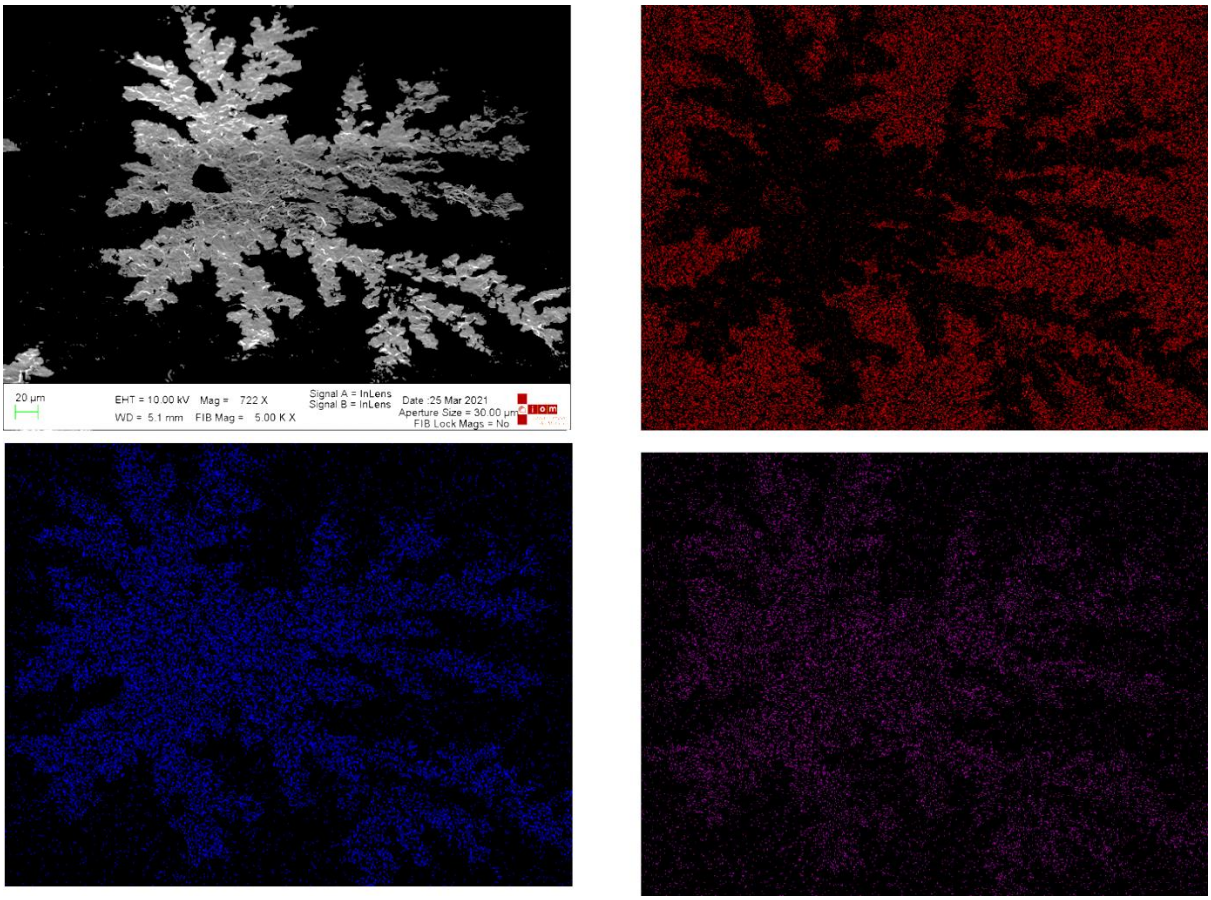

Figure 4 Analysis of the crystalline structures on the central electrode: SEM image, C map, Cl map, Na map.

It was not possible to trace the origin of the other contaminant as the size and concentration of these particles is too low.

Homogeneity and antibody functionalization analysis by Raman Spectroscopy and maps

Report STEP 2 Raman Spectroscopy

The 4 samples have been analysed by Dark Field optical microscopy and Raman spectroscopy.

Raman spectroscopy has been performed using a laser at v532 nm of wavelength of excitation with power at the sample between 2mW and 34mW. Below 2mW the signal was too low to be detected with a reasonable time scale.

The optical imaging allowed the identification of a uniform region covered by CNT and the sparse presence of two kind of defects characterized by different colours: silver and blue. For every sample the measurement where collected in at least 5 different regions selected randomly.

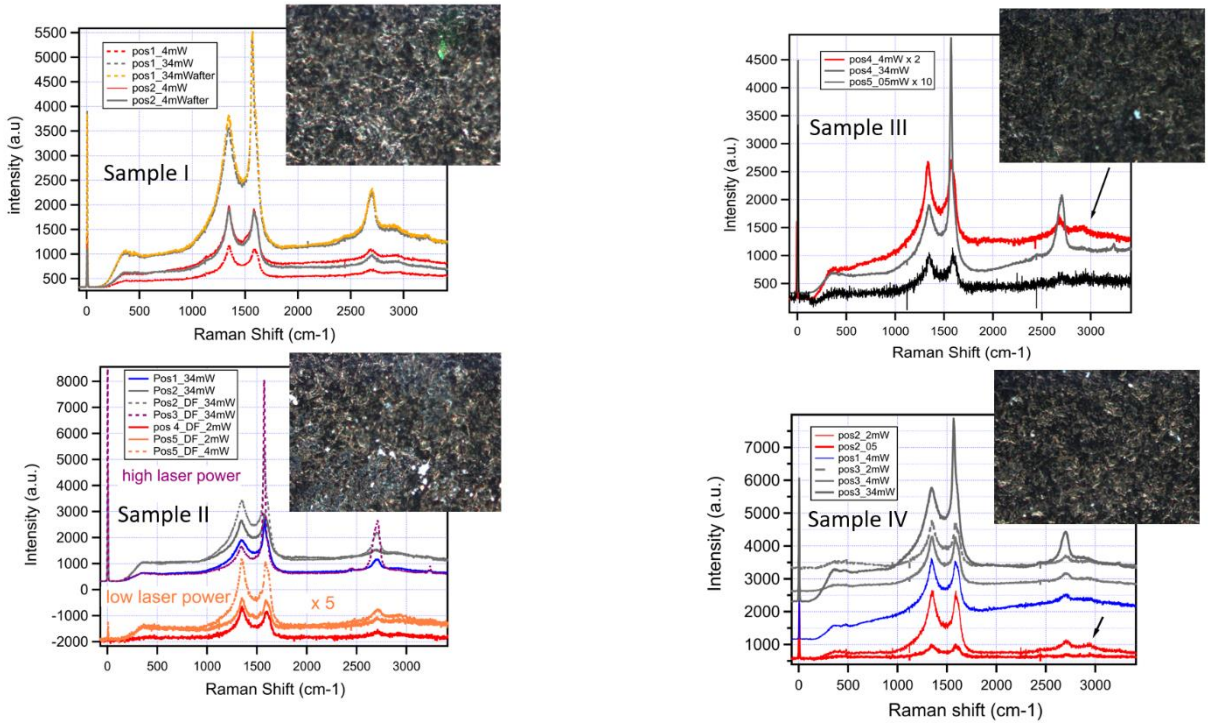

Figure 5

The figure 5 shows the Raman spectra acquired on a CNT covered region. The number of the samples corresponds with the number marked on each sample. Sample I was marked also with an asterisk (*).

The spectra of all the samples appear similar.

The spectra taken at low power show two peaks at 1350cm^{-1} and 1575 cm^{-1} which correspond the D and G bands. Typically, in MW-CNT these two peaks show the same intensity.

A weak peak at 2700 cm^{-1}, known as the 2D peak is also observed, while a weaker shoulder at 2930 cm^{-1} is also observed at low power that corresponds to the D+G peak.

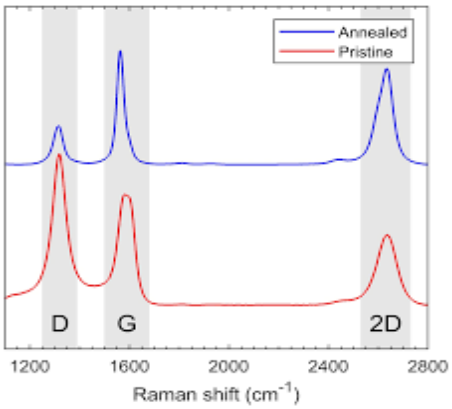

Figure 6

At higher power the spectra change and the G line becomes more intense and thinner, and some measurement, like in sample IV , pos3 34mW the splitting in G- and G+ can also be observed. These spectra are typical of SW-CNT, although the mechanism by which higher energy should trigger the formation of SWCNT was not investigated.

Indeed, in literature this effect was shown for heating of pristine MWCNT up to 3000C. The figure 2 is taken from Hansson et al.- Nanotechnology 31 (2020) 455708. No visual effect was ever observed at the optical microscope after illumination.

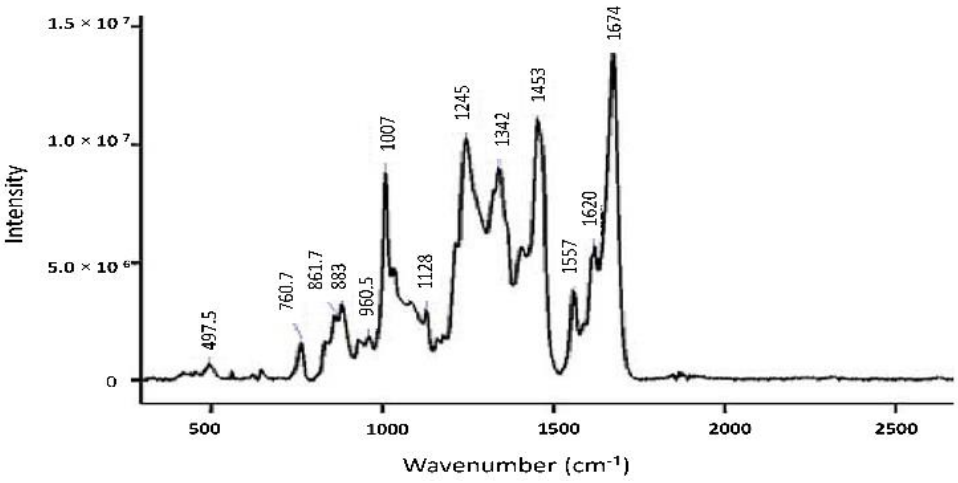

Figure 7 shows a typical Raman spectrum of Antibody.

All the signals are in the range from 700 cm^{-1} to 1670 cm^{-1}. No features associated to Ab have been recognized in the spectra.

We then focused the attention on the small defects scattered on the sample surface:

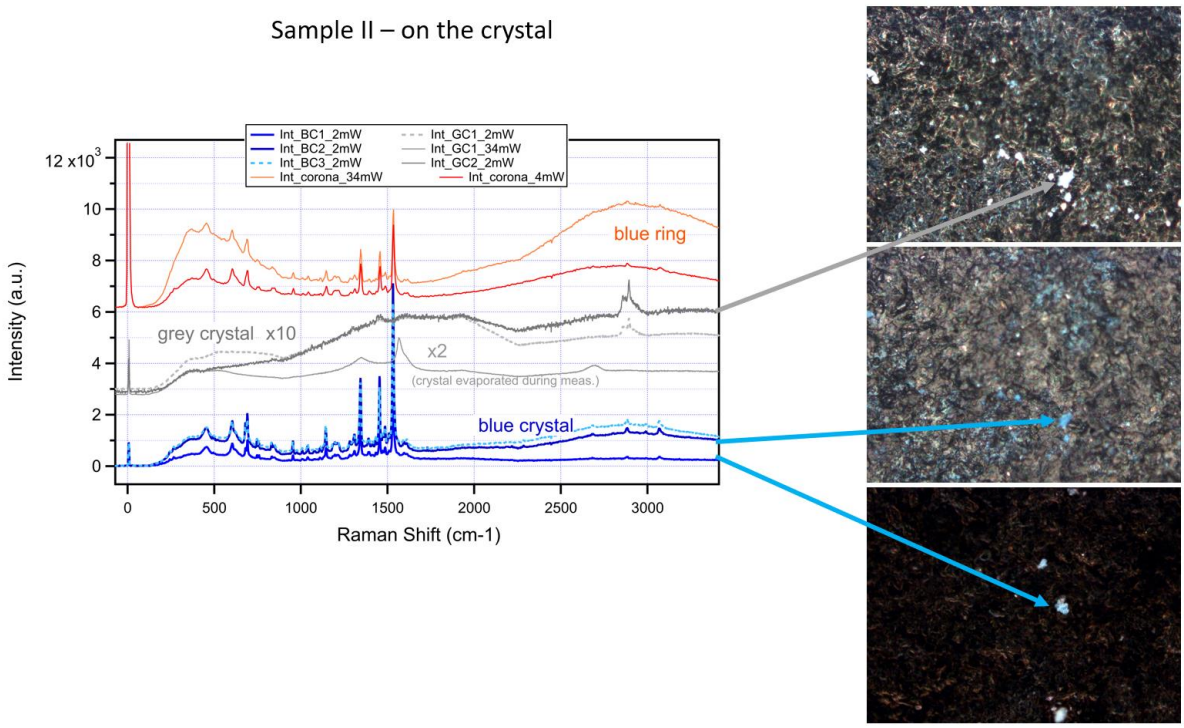

Figure 8

The silver defects show a broad luminescence, quite difficult to interpret without further information, and a typical feature at 2850 cm^{-1} that cannot be related to the CNT (grey spectra in figure 4). This feature disappears after high power illumination and the Raman signature of the CNT below can be observed.

The "blue" defects have a very well-defined Raman signature (blue spectra in figure 4) that can be identified in the Raman spectra of the blue macroscopic ring that defines the active area of the sensor. Therefore, we conclude that these impurities originated during the sensor manufacturing.

In conclusion it was not possible to identify any significant difference between the four samples using Raman spectroscopy.

Conclusions and final remarks

The proposed method allowed to individuate the presence of contamination atop the central electrodes; although the used chips are extremely contaminated, in particular with residuals deposit of huge salt crystals, also the unemployed one contains various contaminants that could affect the electrical properties of the chips, and the functionalisation procedure with antibodies.

The salt contaminants seem to be mostly NaCl residuals, probably included during the functionalisation procedures; accurate rinse may solve the problem.

The rest of contaminants include also paint particles; the company can evaluate an addition procedure for the cleaning of the chips, since we cannot evaluate the effects of these particles on the functionalisation procedure.

This report has been written by Simone Dal Zilio and Marco Lazzarino, 04/11/2021