IMPACT

A. Marcelli (Resp. Naz.), S. Macis (Ass.), A. D'Elia (Ass.), S.J. Rezvani (Ass.), S. Lupi (Ass.), and B. Spataro (Ass.)

I. SUMMARY

IMPACT is a project that addresses scientific and technological challenges aimed to advance research frontiers on accelerators. The goal of this project is to enhance the properties of key materials such as copper using advanced coatings technologies. The proposal is based on the experience gained within the framework of NUCLEAR and TERA, two projects funded by the Vth National Scientific Committee. The R&D of IMPACT is oriented to technological advancements useful for future colliders and next generation of accelerators after LHC, the main issue of the European Particle Physics Strategy Form. The main activities of the project performed in 2022 are:

- Coatings of MoO_3 on flat and curved Cu substrates
- Upgrade in the UHV chamber of the evaporation setup to control the evaporation and the annealing temperature
- THz-UV spectroscopy characterization of PVD coatings
- Characterization of the Work Function of the oxide coatings by LEEM spectroscopy
- Setup of the high intensity irradiation optical layout at the TERA laboratory at Sapienza
- New irradiation tests at the ISIS FEL in Osaka
- Physical Laser Deposition of MoO_x on copper

II. ACTIVITY

Thanks to the expertise acquired in the previous projects we are now able to control and deposit transition metal oxides with different degrees of crystallinity on flat and curved surfaces. The evaporation of thin films of transition metals oxides can be used to enhance oxygen free copper properties, for high power RF-cavity, but also to improve the emission properties of photo-anodes, used in state of the art seeded FELs.

III. PHYSICAL LASER DEPOSITION OF MOO_x ON COPPER

In order to adopt a complementary approach to the sample synthesis with respect to Physical Vapour Deposition (PVD), a batch of Mo oxides film deposited on copper and silicon has been produced using the pulsed laser deposition (PLD) technqiue at the Institute of Manufacturing of the Cambridge university. All samples have been synthesized by ablating an MoO_3 target with a laser with wavelength 1030 nm and using a pulse repetition rate of 50.4 MHz. Samples have been deposited with a base pressure in the range $1 - 2.5 \cdot 10^{-5}$ mbar. All Raman spectra showed in this section have been collected using a Jasco Micro-Raman spectrometer with a laser of 532 nm and a laser power of 1 mW.

In Figure 1 we show the optical image of one sample (R26) deposited using the PLD with a nominal thickness of 500 nm. The iridescent puddles in the image suggests that this sample is not crystalline MoO_3 and the regions with different colours point different stoichiometry or the presence of different amounts of defects. The Raman spectrum confirms this hypothesis because no features belonging to MoO_3 can be identified while the broad peak suggests that the material is amorphous and multiple phases randomly distributed cohesist. A comparison with the Raman spectrum of an amorphous MoO_3 film (Figure 2) deposited using the PVD method shows a shift of about 15 cm^{-1} in the peak position. This shift confirms that the two deposition techniques, produce MoO_3 films with different amorphous structures. The comparison between different amorphous materials using Raman spectroscopy, is a complex task. However, we suggest that because the two deposition methods produce MoO_3 with different oxygen vacancies, the two films growth with different disordered configurations. In the right panel in Figure 2 the most intense peak around 920-950 cm^{-1} does not match the pattern of the MoO_3 peaks, nor those of other Mo oxides known[8]. The analysis of the samples confirms the coexistence of multiple phases of molybdenum hydroxide and other organo-metal oxides of molybdenum. As seen above, single crystalline samples growth at the Seoul university, have been also investigated using Raman spectroscopy. The preliminary results (not showed here) report

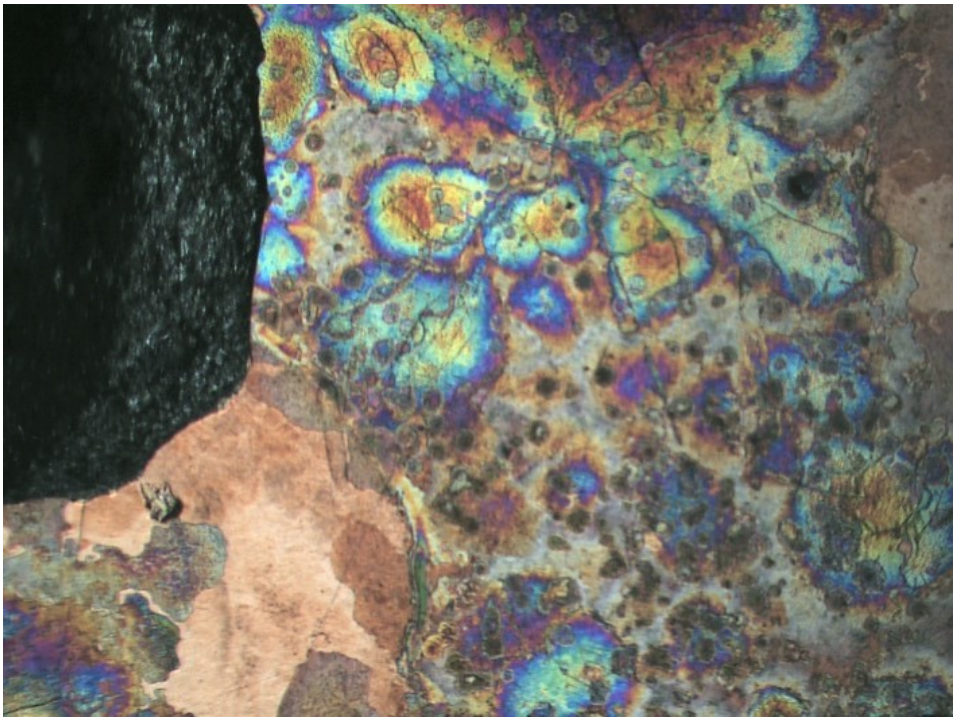

FIG. 1 : Optical image ($500x300\mu m$) of the sample R26 acquired with a x5 objective

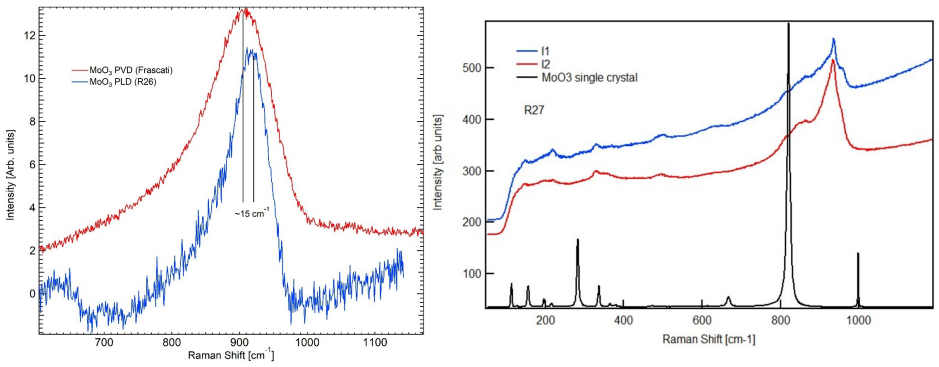

FIG. 2 : (Left) Comparison between the Raman spectrum of a MoO_3 sample deposited using the physical vapour deposition and the sample R26 with PLD. (Right) Raman spectra in two different locations and of the MoO_3 single crystal.

an anisotropic behaviour of Raman spectra. As reported by Wang and co-workers[9], the intensity of the Raman peak at 820 cm^{-1} reaches the maximum, when the polarization vector is parallel to the lattice parameter.

A. Cylindrical RF cavity coated prototype

In order to test the coating performance on a structure similar to a real cavity we assembled a copper-coated device with a cylindrical shape. A copper cylinder 100 mm long with an internal diameter of 60 mm and 80 mm of external diameter, was properly sectioned. Each section was diamond milled to obtain a roughness less than 10 nm (Figure 3).

Each section was PVD evaporated with our HV chamber, which can cover areas up to 150 mm wide. After the evaporation of a 100 nm MoO_3 layer, the four sections were assembled together with TIG welding. The process was performed keeping temperature as low as possible in order not to damage the coating. The entire procedure will be described in an INFN report in preparation.

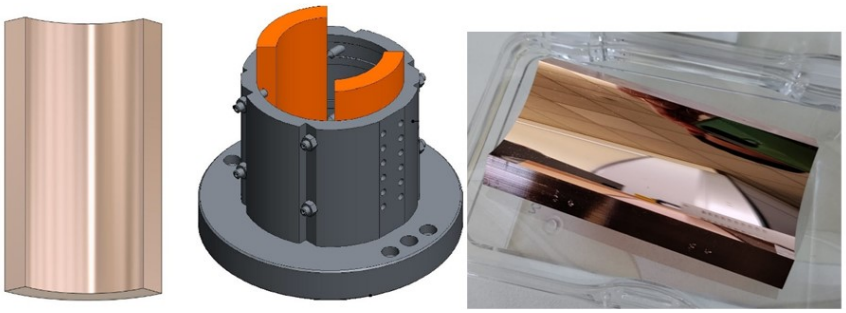

FIG. 3 : CAD scheme of the copper cylindrical sections and on the right the copper section before the evaporation.

IV. THZ, IR AND UV SPECTROSCOPY

Characterization of MoO_3 and SnO thin films was performed in the THz-UV range. The THz-FIR region down to 30 cm^{-1} was collected with a reflectance setup in a vacuum environment inside the sample compartment of the Vertex 70v Bruker interferometer. Specular reflectance IR spectroscopy was performed using a Hyperion 3000 Bruker FTIR Microscope paired with the Vertex 70v interferometer. The microscope setup allows measuring from 400 to 8000 cm^{-1} collecting the MIR part of the spectra. To extend the transmittance measurements in the visible and in the ultraviolet region, we used the spectrophotometer Jasco V-770. It incorporates two gratings and two detectors to fully cover the wavelength range from 190 to 3200 nm (UV-VIS-NIR). As shown in Figure 4, the thin film of MoO_3 and SnO deposed on Cu substrate seems almost "invisible" at lower frequencies, as we don't see any differences in the FIR region, while at higher frequencies we see differences between the coatings. SnO-coated sample reaches the highest reflectivity, in the NIR is even higher than the copper one. The Reflectance of the MoO_3 coated samples in the NIR-UV range exhibits a band gap lower (1.8 eV) for the 200 nm film with respect to the 100 nm film (3 eV). This behavior could be related to the occurrence of more disorder in the thicker film [7, 10].

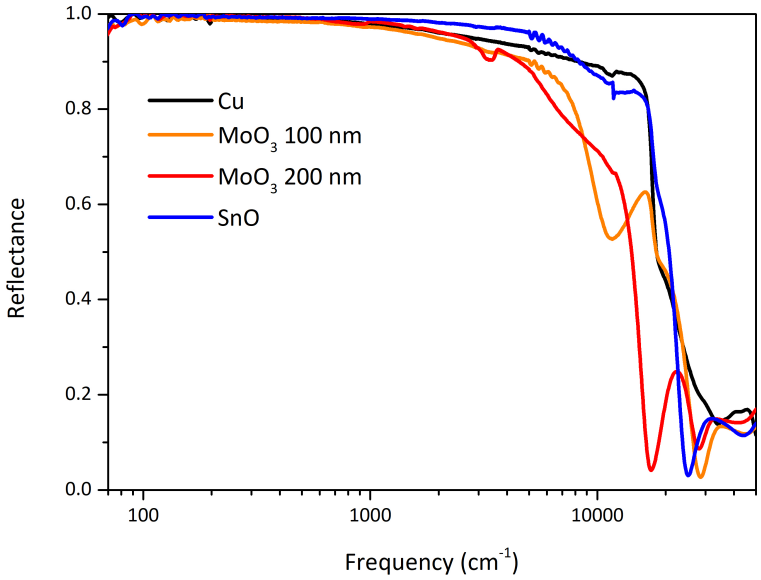

FIG. 4 : THz-UV spectra of the Cu substrate, 100 nm MoO_3, 200 nm MoO_3 and 100 nm SnO

V. IRRADIATION AT THE ISIR FEL FACILITY

In order to test the resistance of the MoO_3 coating at high intensity electric fields we performed damage tests at the ISIR Free Electron Laser of the Osaka University. This FEL generates a coherent EM radiation at 4 THz (120 μm) [4, 5]. The testing protocol consisted in the reproducible irradiation of the sample surface by several THz pulses with different intensities and time structures. This approach makes possible to generate and measure the surface damage on a well-defined sample region and, in addition, allows to measure and compare copper with different coated surfaces in a reproducible way. We calculated that with the ISIR figures, the electric field on the sample surface may reach values as high as 5 GV/m, i.e., allowing us to compare the aftermath of the exposure to electric field gradients higher than the target electric fields required by the most demanding RF devices [4, 5]. Here we present the results of irradiations performed on a smooth Cu substrate and different MoO_3 films deposed on copper using PVD. The analysis of the damaged area and of the coating resistance has been performed using Raman spectroscopy and imaging. THz radiation is generated by the ISIR Free Electron Laser, a coherent source where a LINAC accelerates the electron beam up to 15 MeV [4, 5]. The pulsed electron beam travels an undulator that emits radiation in the THz range. A series of optics extract the highly coherent beam outside the accelerator hutch, focusing it on the sample position for different kinds of experiments. The time-structure of the emitted radiation is characterized by "macro" and "micro" pulses. The macro pulse is 4 μs long and has a repetition rate of 5 Hz. Each macro pulse contains 108 micro pulses (repetition rate of 27 MHz) each one 20 ps long. For these irradiation experiments, we measured with the calibrated Coherent® energy meter the energy of a single macro pulse (12 mJ). The focal spot of this THz beam after the undulator and the optical system has a Gaussian distribution with a $\sigma \sim 75$ µm and we estimated that 95.5% of the beam intensity lies in a circular spot with a diameter of 260 µm. The electric field generated at the center of the spot was estimated to be 5 GV/m [4, 5].

Different tests were performed on different samples to clarify if the observed damage depends by the incidence angle; the beam intensity, i.e., with the macro-pulse energy; the number of shots, i.e., with the number of macro-pulses; by irradiation with s or p polarization. As mentioned before, to evaluate the copper damage, we looked at the oxides generated by the irradiation. Two type of copper oxides are mainly observed after the irradiation: copper (II) oxide (CuO) and copper (I) oxide (Cu_2O). Due to heating inhomogeneities in the irradiated area, the two oxides appear in different regions where damage occurs. In the left panel in Figure 5 we compare the two spectra of the copper oxides observed in two locations within the same damaged area. The intensity of the peak at 230 cm^{-1} (black arrow) was used to study the Cu_2O spatial distribution, while for CuO oxide we used the intensity of the peak at 300 cm^{-1} (red arrow). In the right panel in Figure 5 is reported the Raman spectra of a disordered phase of MoO_3 deposited on Cu. We used the wide Raman peak at about 800 cm^{-1} to build the intensity maps of MoO_3 in the coated samples.

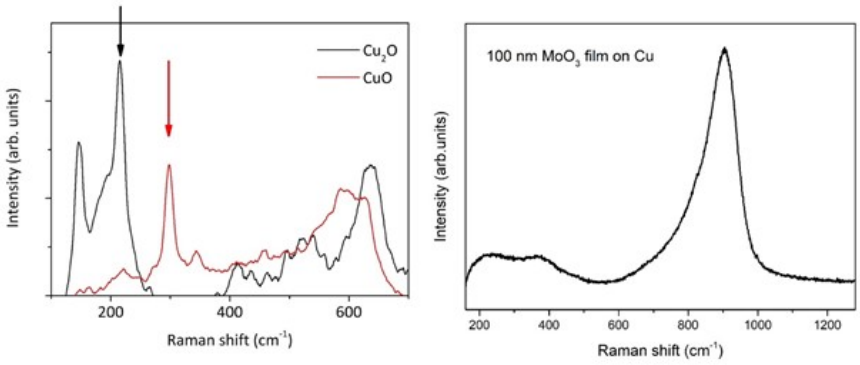

FIG. 5 : Left: comparison of the Raman spectra of the two copper oxides observed in the irradiated regions. Cu_I2O is mainly formed in the external corona surrounding the focal spot, while CuO oxide is detected in the central region. The red and black arrows point features used to map CuO and Cu_2O distributions. Right: The Raman spectrum of a MoO_3 film (100 nm) deposed on Cu.

Looking at the damaged areas observed on the copper substrate, Raman maps of copper oxides clearly show how CuO and Cu_2O occurs in different regions of the exposed region. CuO is mainly present in the central spot where higher temperatures are reached by the metal, while Cu_2O is mainly detected in the external corona of the spot. Tests as a function of the incidence angle on the Cu substrate return damages compatible with previous tests always performed at ISIR. Different results were obtained irradiating coated surfaces. Both 100 nm and 200 nm thick MoO_3 films show damaged regions and the partial removal of the film occurs in the central region of the spot [Macis,

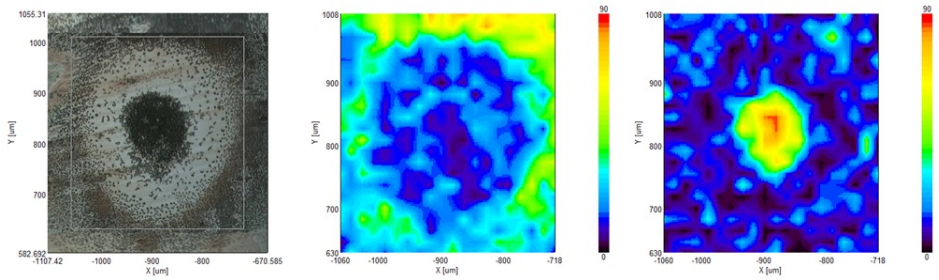

FIG. 6 : Microscope image of the central region of the damaged area obtained with irradiation at 40° of incidence angle, incidence energy 6 mJ and 5000 shots. On the central- and right-panel the two Raman maps of the copper oxides: the Cu_2O and the CuO, respectively

2022]. The removal of the film was not observed in previous irradiation tests. The different behavior could be due to the 20% increase of the energy of the THz beam in the new set used for irradiation. Several approaches can be considered to explain the damage phenomena. All of them do not consider electric-related effects, e.g., discharges and/or breakdowns occurring in air due to light pulses. They are also unable to explain the angular dependence and the negligible or no damages observed on samples coated by thin Mo oxides films.

VI. IRRADIATION SETUP AT SAPIENZA TERAHERTZ LABORATORY

Sapienza Terahertz laboratory aims to produce a high-intensity THz radiation by means of optical rectification process from a ultra-short 800 nm laser source. A 15 femtoseconds high-intensity pulse at 800 nm, as generated by a Vitara-UBB modelocked Ti:Sapphire Laser from Coherent, which is amplified by a chirped pulse amplificator (Coherent Verdi G-series), reaching a final power of nearly 7 W with a repetition rate of 1 kHz, while shortening the pulse in down to 35 fs. This same pulse is used as an input in a collinear optical parametric amplifier (OPA) (TOPASprime from Light Conversion), allowing the production of femtosecond pulses at tunable IR wavelengths, going from 1100 nm up to 2300 nm. By fixing the wavelength emission at 1500 nm, in accordance with the phase matching condition for the THz generation in DSTMS crystals, the emitted pulse from the OPA, with a power of nearly 800 mW (with a fluence nearly 4 mJ/cm^2), is used to pump the organic crystal. The intensity of the generated field can reach up to 5 MV/cm when focused on dimensions lower than 1 mm in diameter. The setup scheme is shown in Figure 7. The setup is also equipped with a box made in plexiglass which allows purging the experimental setup removing the water absorption and increasing the overall intensity. Respect to the ISIR radiation this setup allows covering a wider spectral range (0.2 - 4 THz), has an higher repetition rate (1kHz) and can be tuned and controlled more easily.

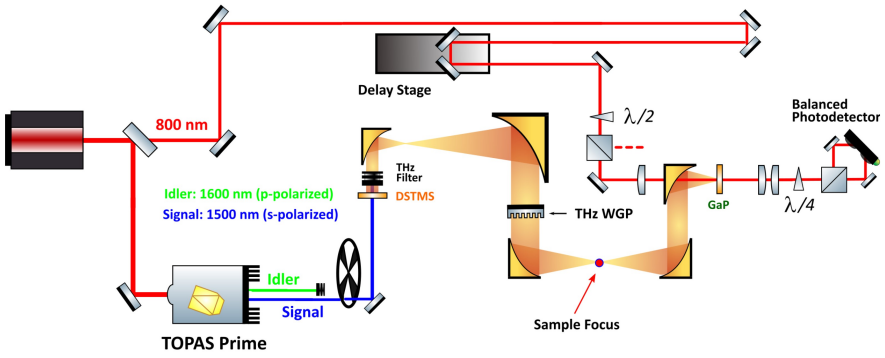

FIG. 7 : Optical setup for the generation of high-fluence THz pulses from the optical rectification in a DSTMS organic crystal.

The same setup will also be used for the pump-probe measures in the second year of the project.

VII. ACKNOWLEDGEMENTS

We acknowledge the Ministero degli affari esteri e della cooperazione internazionale for support, within the framework of the Italian-Chinese collaborative research in 3D graphene and Italian-Japanese bilateral project "Spettroscopia THz lineare, non lineare e risolta in tempo con sorgenti di radiazione di ultima generazione". We acknowledge Ivan Davoli of Tor Vergata University for the evaporation setup. We also acknowledge the Osaka University for providing beamtime at the ISIR facility and Akinori Irizawa for the experimental support at Osaka.

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VIII. PUBLICATIONS

- S. Macis, A. D'Elia, A. Irizawa, M. Carillo, B. Spataro, Z. Ebrahimpour, L. Mosesso, J.S. Rezvani, S. Lupi and A. Marcelli, "High electric field induced damage using a pulsed THz source: a new technique to test metallic surfaces" INFN-22-05-LNF, 14-11-2022

IX. ORAL CONTRIBUTIONS

- S. Macis, "Thin conducting MoO_3 films on copper for technological applications: a new route for improved RF devices" Symposium of Quantum Materials for Quantum Technologies QMQT, Frascati 14 February 2022