

## Supplementary Information

### Deep X-Ray Lithography on "Sol-Gel" Processed Noble Metal Mesoarchitected Films

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#### Materials and Methods

##### Chemicals

The metallic precursors were Rhodium (III) chloride hydrate ( $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ , Rh 38.5-45.5%, Alfa Aesar), Ruthenium(III) chloride hydrate ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , Sigma Aldrich) and he Pluronic F127 was provided by from Sigma Aldrich. 6 inch -diameter p-type (100) Si wafer with a resistivity of 1-10 ohm-cm was purchased from Siltronix Silicon Technologies.

##### Preparation of the films

At first, 0.020g of F127 was dissolved in a EtOH/H<sub>2</sub>O (7/1 w/w) solution. To induce complete dissolution of the block-copolymer, the solution was warmed at 70°C for several minutes. After cooling, 0.122g of salt metal precursor was added to the solution. The silicon wafer was cleaned with ethanol solution and oxygen plasma. The substrate was coated via dip-coating. The films were obtained by dip-coating at 10 mm.s<sup>-1</sup>.<sup>1</sup>

##### Deep X-Ray Lithography

After deposition the films were patterned using the deep X-ray lithography (DXRL) beamline at Elettra synchrotron facility (Trieste, Italy).<sup>2</sup> The ring was working at an energy of 2 GeV with a current of 310 mA. The samples were exposed through an X-ray

mask containing patterns of different sizes (4.5-450 micron), shapes, and geometries. The exposure time and the corresponding dose values are reported in the table hereafter:

dose J/cm <sup>2</sup>	exposure time (s)
168	68.1
336	136.2
841	340.5
1683	681
4148	2272

The masks had a gold absorber of 20  $\mu\text{m}$  thick and a titanium transparent membrane with a thickness of 2.2  $\mu\text{m}$ . After exposure the films were developed in a water for 30 seconds. Pure ethanol was also used as developer. The developed films were dried under nitrogen flow. The so-formed patterned system was then annealed at 300°C under H<sub>2</sub>/N<sub>2</sub> atmosphere to ensure the metallic conversion.

### **Characterization**

The films were analyzed by a Woolam ellipsometer IR-VASE equipped with an environmental chamber. The measurements cover the spectral range from 1.7 to 30 microns (333 to 5900 wavenumbers). The GISAXS/WAXS analysis were performed at the Austrian SAXS beamline at the ELETTRA synchrotron in Trieste (Italy) at a photon energy of 8 keV.<sup>3</sup> The beam size was set to 1x0.2 mm<sup>2</sup> (HxV). SAXS images were collected in grazing incidence (0.236°) using Pilatus3 1M detector (Dectris AG, Switzerland) at a distance of 1942.3 mm from the sample. WAXS diffraction patterns were collected simultaneously with Pilatus 100K detector placed 197.6 mm from the sample. The patterns have been corrected for the fluctuations of the primary intensity.<sup>4</sup> SEM imaging was performed on a SU-70 Hitachi FESEM. Voltage acceleration setup was 5 kV and usually upper detector was used for secondary electron acquisition. XPS

spectra were recorded using a K-Alpha+ spectrometer from Thermofisher Scientific, fitted with a microfocused, monochromatic Al  $K_{\alpha}$  X-ray source ( $h\nu = 1486.6$  eV; spot size = 400 micrometers). The pass energy was set at 200 and 40 eV for the survey and the narrow regions, respectively. Spectral calibration was determined by setting the main C1s (C-C, C-H) component at 285 eV.

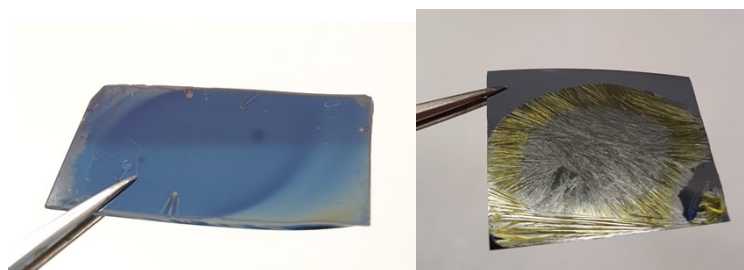


Figure S1 (left) Photograph of a spin-coated homogenous  $\text{RhCl}_3$  xerogel film of optical quality, (right) Photograph of a film made of  $\text{HAuCl}_4$  crystals (recrystallized)

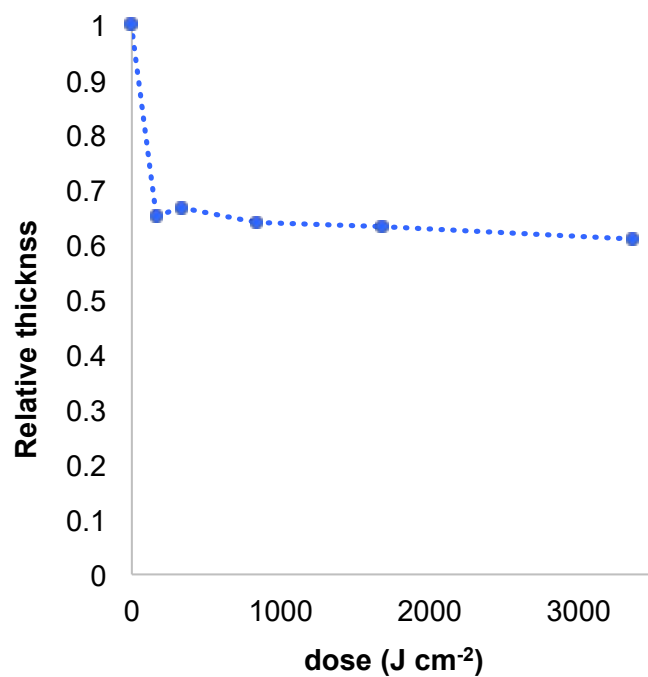


Figure S2 Evolution of the relative thickness of a RuCl<sub>3</sub> xerogel without F127 as function of the X-Ray dose

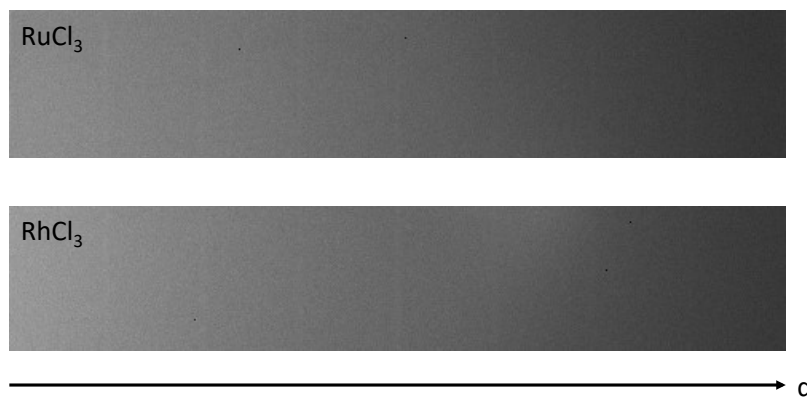


Figure S3 GI-WAXS pattern of the xerogels after deposition. No diffraction spots/rings are visible indicating that the materials are amorphous

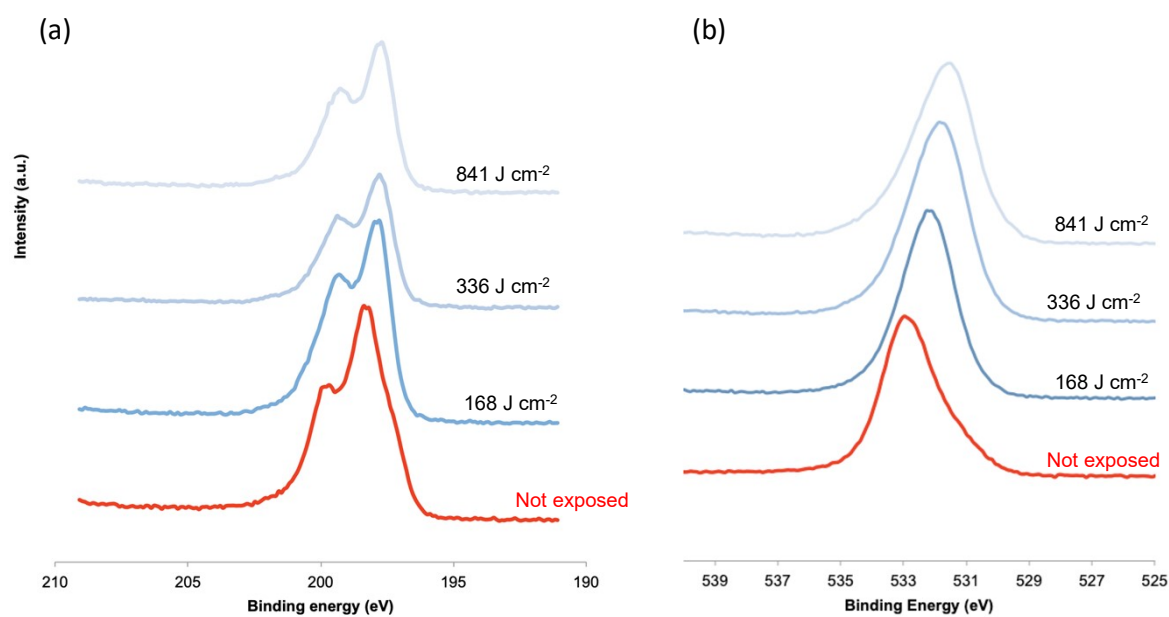


Figure S4 XPS spectra of (a) Cl 2p<sub>3/2</sub> and 2p<sub>1/2</sub> region and (b) O1s region

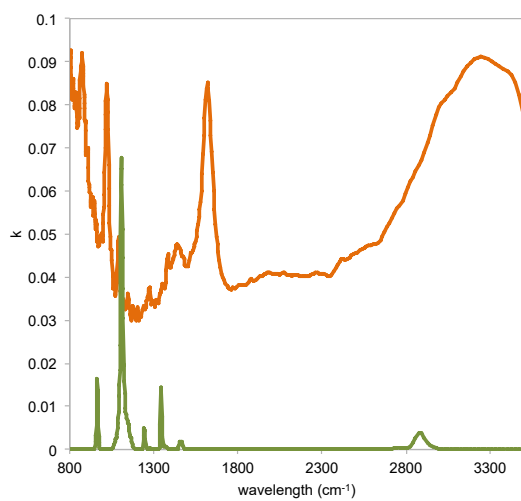


Figure S5 Extinction coefficient  $k$  of a RuCl<sub>3</sub> (orange line) and F127 (green line) films before exposure

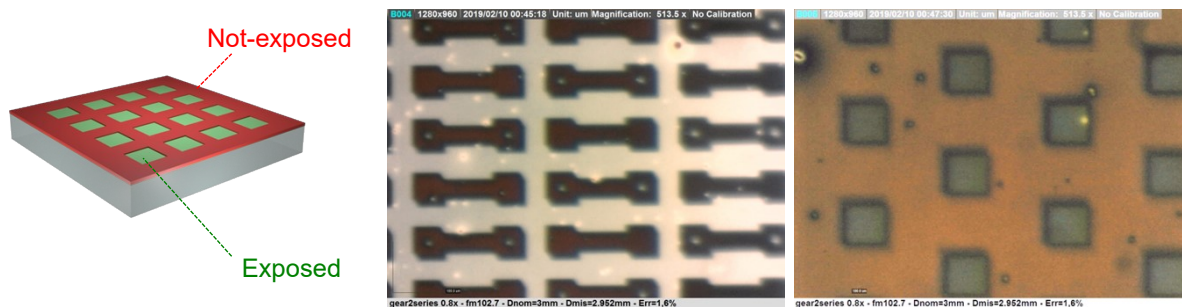


Figure S6 Optical micrographs of the samples after X-Ray exposure Ru-based samples (lateral size of the photographs  $\sim 0.8$  mm)

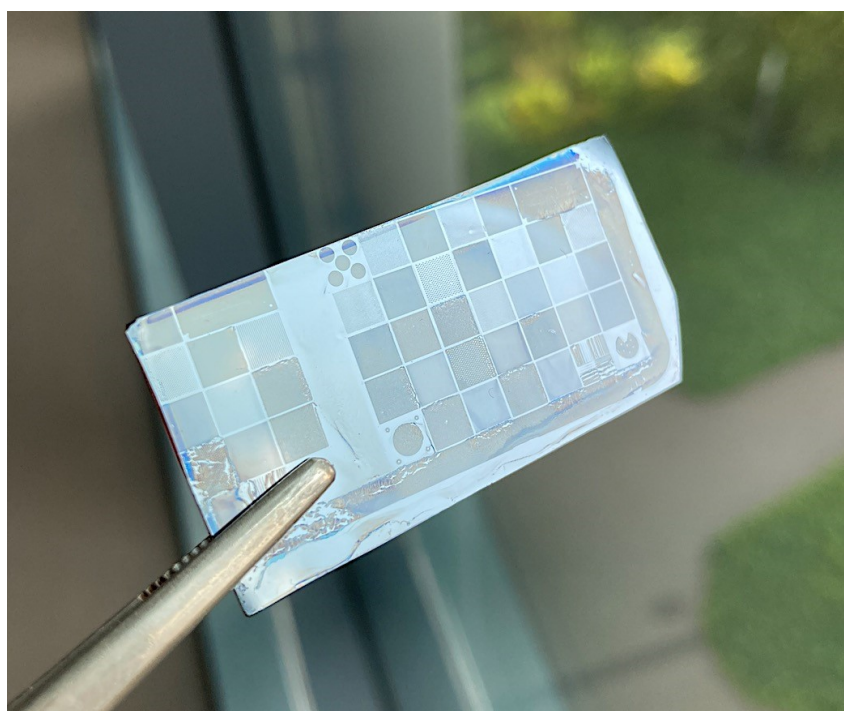


Figure S7 Macroscopic view of a  $\text{RuCl}_3/\text{F127}$  sample after development. The surface is composed of multiple patterned regions

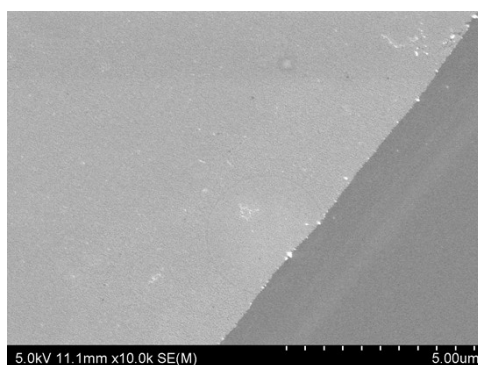


Figure S8 SEM micrograph of a pattern's edge of a Ru film after annealing.

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2. F. Pérennès, F. De Bona and F. J. Pantenburg, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 2001, 467, 1274-1278.
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