Supporting Information

Patterning of Metal Oxide Thin Films using H_2/He Atmospheric Pressure Plasma Jet

*M. Emre Sener, Sanjayan Sathasivam, Robert Palgrave, Raul Quesada Cabrera, Daren J. Caruana**

Sample preparation:

The copper oxide (Cu_2O) films were depostied electrochemically on ITO coated glass substrate. Electrodeposition solution comprised of 0.4 M $CuSO_4 \cdot H_2O$ and 3 M Lactic Acid (>85%, Sigma-Aldrich, UK), the pH of the plating solution was brought to pH 12 by addition of 5 M NaOH solution. The Cu_2O layer was grown potentiostatically (PGSTAT100, Autolab, Windsor Scientific, UK) at −0.5 V vs. Ag/AgCl reference electrode using a large area copper wire counter electrode. The total deposition time was 30 minutes at 55°C.

All other films were deposited on SiO_2 (~50 nm) barrier coated float glass (NSG, UK) by atmospheric pressure aerosol assisted chemical vapour deposition on a horizontal bed reactor. The precursor solution was atomised using a piezoelectric ultrasonic humidifier (Johnson Matthey, UK) and passed over the substrate using a carrier gas at a flow rate of 1 L min^{-1}. A stainless steel top plate was positioned 8 mm above the glass substrate to promote laminar flow of gases. The glass substrates were positioned on a heated graphite block with the deposition temperature monitored using platinum-rhodium thermocouples connected to a temperature controller (Eurotherm, UK).

All precursors and solvents were procured from Aldrich and used as received. The glass substrates were cleaned with detergent/water followed by propan-2-ol, then dried in an oven 80 °C. For TiO_2, the precursors solution contained Titanium ethoxide (0.2 g) in toluene (20 mL) was aerosolized and transferred to the CVD chamber at a flow rate of 1 Lmin-1 using N_2 (99.99%, BOC) carrier gas. For SnO_2, coating the precursor solution contained butyltin trichloride (0.2 g) in methanol was aerosolized and transferred to the CVD chamber at a flow rate of 1 L min^{-1} using compressed air (BOC) carrier gas. For ZnO, the precursors were zinc acetate hydrate (0.2 g) in methanol was aerosolized and transferred to the CVD chamber at a flow rate of 1 L min-1 using N_2 (99.99%, BOC) carrier gas. For WO_3, tungsten hexacarbonyl (0.05 g) in a mixture of acetone (20 mL) and methanol (5 mL) was aerosolized and transferred to the chamber at a flow rate of 1 $Lmin^{-1}$ using N_2 (99.99%, BOC) carrier gas. For all the coatings the deposition temperature was 500 °C, except for tungsten oxide which was carried out at 375 °C. The as deposited tungsten oxide films were then annealed under flow (0.5 L min^{-1}) of air in the AACVD reactor at 500 °C to ensure complete oxidation and formation of WO_3.

Table S1: Operating parameters of the plasma jet.

Parameter	**Value**
Generator power	50 W
Electrode voltage amplitude	2 – 3 kV
Plasma power	0.5 - 2 W
Excitation frequency	13.56 MHz
Modulation frequency	20 kHz
Duty cycle	20 %
Temperature	350 - 380 K

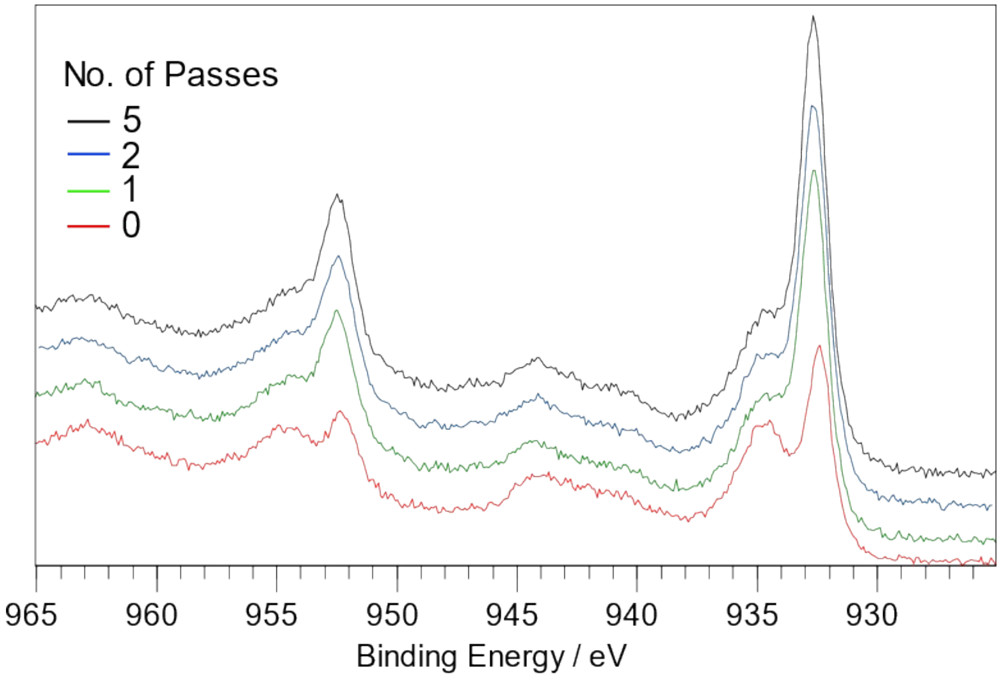

Figure S1: Cu 2p X-ray photoelectron spectra of the Cu_2O film before / after plasma treatment and increasing plasma jet passes over the surface.

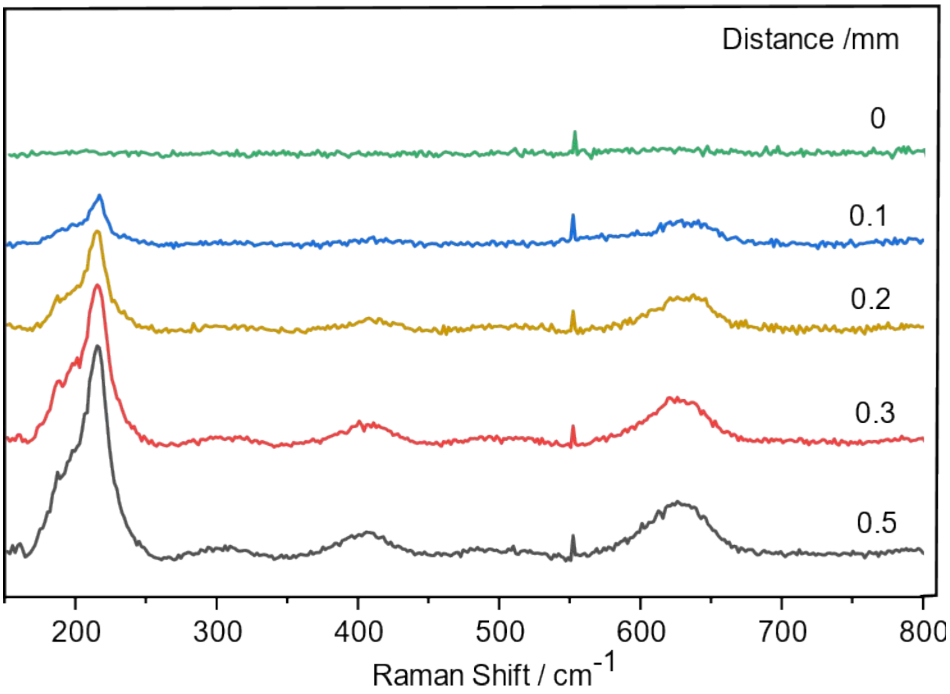

Figure S2: Raman spectra of the plasma treated copper track after 5 passes. Spectra taken along a 0.5 mm line extending out from the track centre(0 mm) into the Cu_2O pristine (0.5 mm) surface.

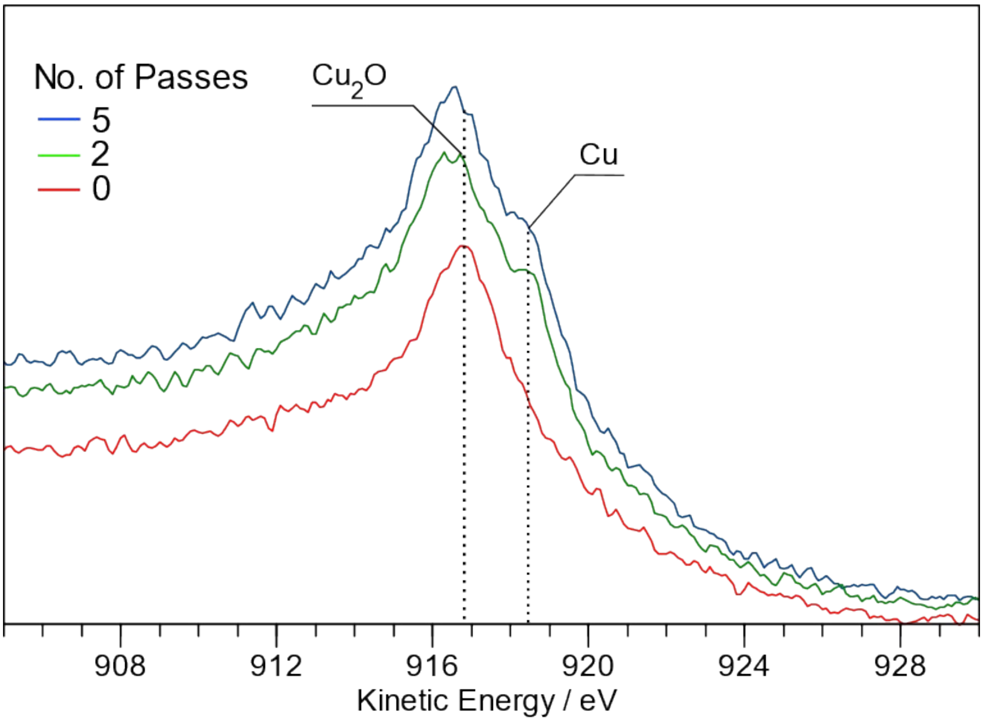

Figure S3: Auger electron spectra of the Cu_2O film before and after plasma treatment.

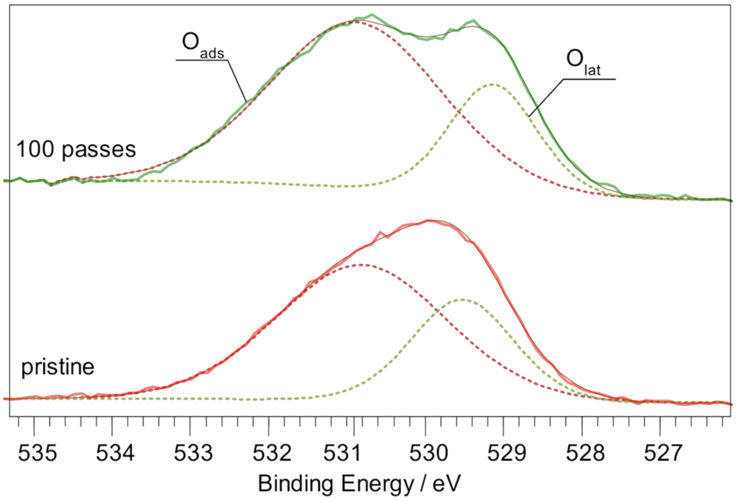

Figure S4: O 1s X-ray photoelectron spectrum of the pristine and reduced TiO_2 surface with deconvoluted lattice (O_{lat}) and adsorbed (O_{ads}) oxygen components.

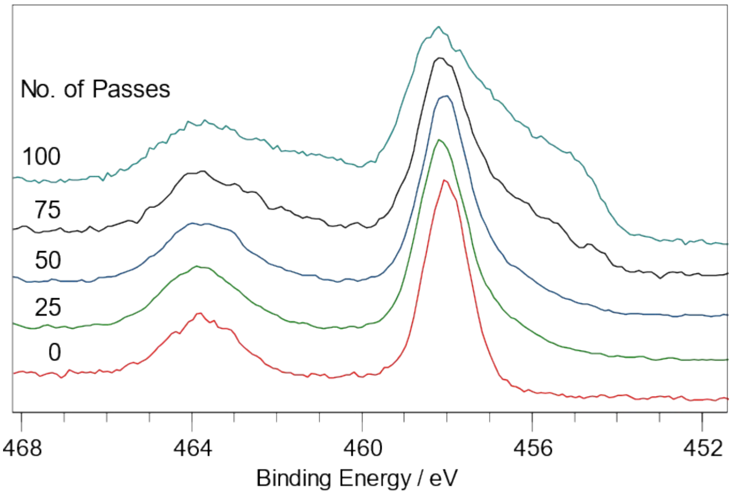

Figure S5: Ti 2p X-ray photoelectron spectra TiO_2 film before / after plasma treatment and increasing plasma jet passes over the surface.

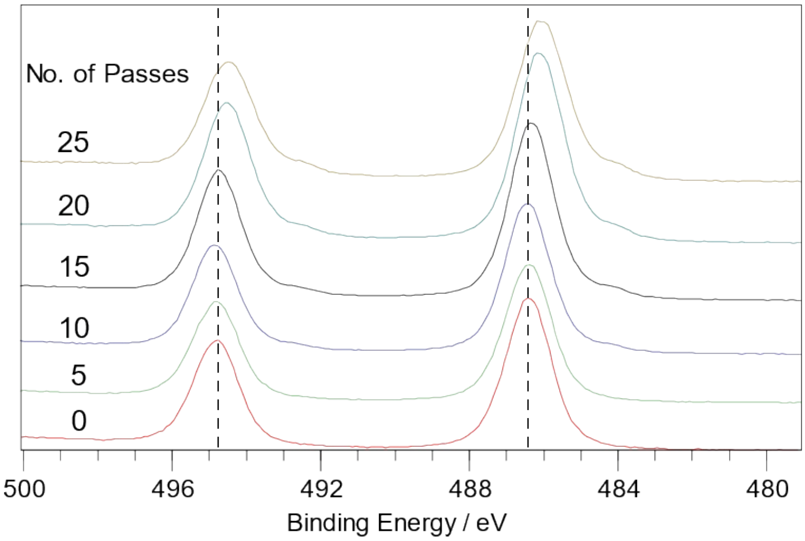

Figure S6: Sn 3d X-ray photoelectron spectra of the SnO_2 surface before / after plasma treatment and increasing plasma jet passes over the surface.

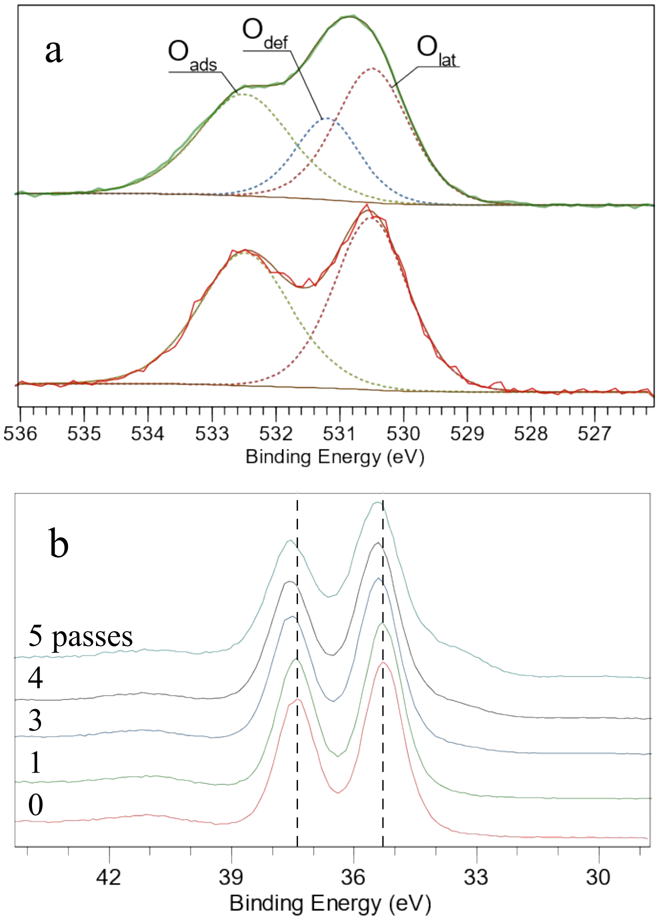

Figure S7: XPS spectra of O 1s from treated (green) and pristine (red) (a) and high-resolution W 4f XPS spectra from WO_3 surfaces as a function of number of passes.

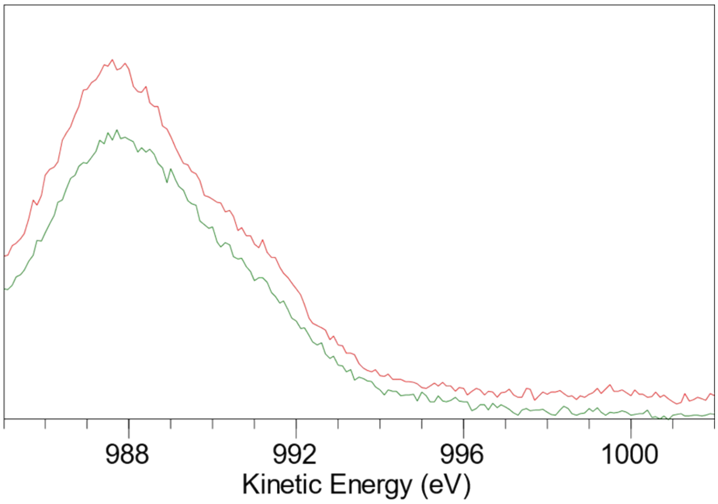

Figure S8: Zn LMM Auger electron spectra for treated (green) and pristine (red).

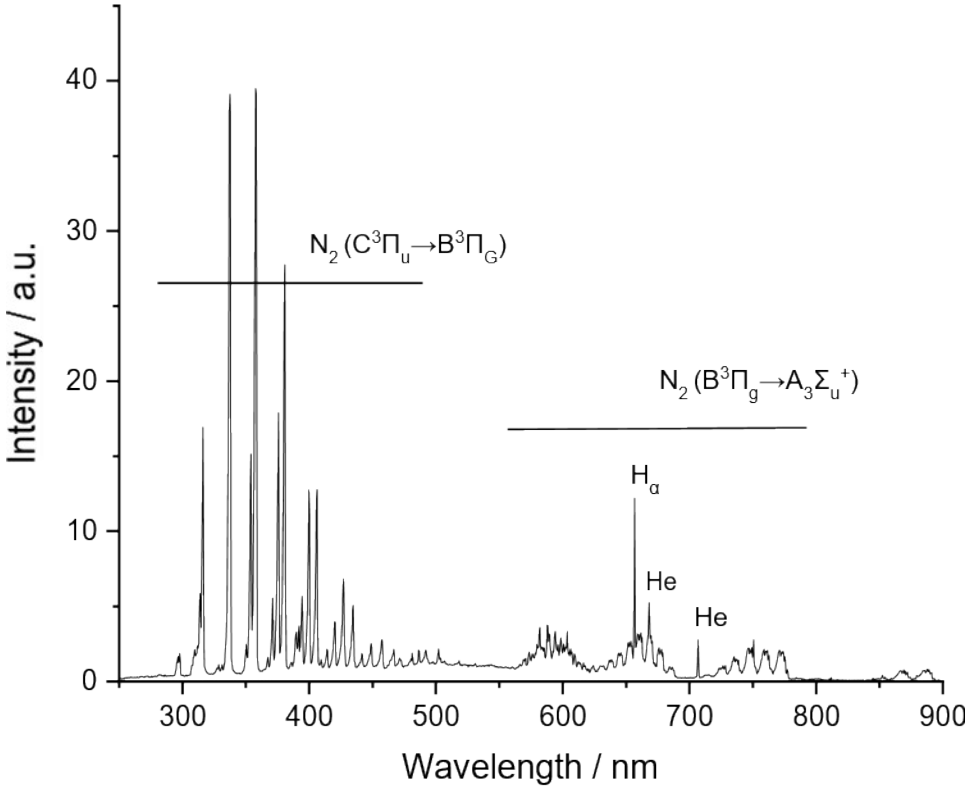

Figure S9: Optical emission spectrum of the plasma plume in the UV/Vis range.