Electronic Supplementary Information For

Surface oxygen vacancy defect engineering of p-$CuAlO_2$ via Ar&H_2 plasma treatment for enhancing VOCs sensing performances

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Experimental Section

1.1 Synthesis of $CuAlO_2$ particles

First of all, 0.04 mol $Cu(CH_3COO)_2 \cdot H_2O$ (Alfa Aesar, 99.9%) was dissolved in 160 mL absolute alcohol with vigorous stirring, and then 16 mL HNO_3 (Sinopharm Chemical Reagent, 99.7%), 0.2 mol $C_6H_8O_7 \cdot H_2O$ (Sinopharm Chemical Reagent, 99.8%) and 0.04 mol $Al[OCH(CH_3)CH_2CH_3]_3$ (Alfa Aesar, 97%) were added into the above solution in sequence. After stirring for 6 hours, 16 mL HNO_3 was added to the solution drop by drop to obtain a well-mixed precursor solution. The precursor solution was dried at 100 °C overnight. In order to remove the organics, the condensed solution was heated to 300 °C for 6 hours. After that, the dried powders were milled for 24 h using a planetary ball miller and then annealed at 1100 °C for 10 h under air atmosphere. Subsequently, the powders were reground and heated to 950 °C under flowing N_2 atmosphere for 6 hours to form delafossite $CuAlO_2$ particles. To ensure the pure phase of delafossite $CuAlO_2$, trace (excess) Cu_xO was washed with 1 M diluted hydrochloric acid, [11] deionized water and absolute alcohol in sequence several times, and the final products were dried in an oven at 80 °C for 24 h.

1.2 Fabrication of $CuAlO_2$ sensors

The $CuAlO_2$ slurry was prepared by dispersing the powders in appropriate isopropyl alcohol. $CuAlO_2$ sensors were prepared by brushing the above paste onto a thin alumina substrate with micro-interdigital Pt electrodes. $CuAlO_2$ films on slide glass substrates were fabricated simultaneously for characterization. After naturally drying, the $CuAlO_2$ sensors and films were heated at 350 °C under flowing air atmosphere for 3 hours. Afterwards, the samples were treated by Ar&H_2 plasma in KT-S2DQX (150 W, 13.56 MHz, Zhengzhou) plasma etching system at 10 sccm 4% H_2 in Ar and the pressure of ~ 99.8 Pa for 30 min, 60 min and 90 min, herein are referred to as pristine, PT-30, PT-60 and PT-90.

1.3 Characterization and gas sensing test

$CuAlO_2$ samples were characterized by X-ray diffraction (XRD, Rigaku Smartlab), scanning electron microscope (SEM, VEGA3 TESCAN), field emission high resolution transmission electron microscope (HRTEM, Talos F200X), X-ray photoelectron spectroscopy (XPS, Thermo Scientific Esca Lab 250Xi spectrometer), photoluminescence (PL, JY Fluorolog-3-Tou) and Electron spin resonance (ESR, JEOL, JES-FA200 ESR spectrometer). Mott-Schottky measurements were carried out on an electrochemical work-station (Zahner Company, Germany) in 1M NaOH solution (pH=12.5) with frequency of 5000 Hz. Platinum sheet, Ag/AgCl electrode and pristine/ PT-30 $CuAlO_2$ samples were used as counter electrode, reference electrode and work electrode, respectively. Gas sensing tests were examined in SD101 (Hua Chuang Rui Ke Technology Co., Ltd.) sensing system. The response was defined as $\Delta R/R_a$, $\Delta R = R_g - R_a$, where R_a and R_g are sensor resistance in

flowing drying air and synthetic VOCs, respectively. During gas sensing test, the total flow rate of the dry air and VOCs gas were adjusted to be 1000 sccm by mass flow controllers (MFCs).

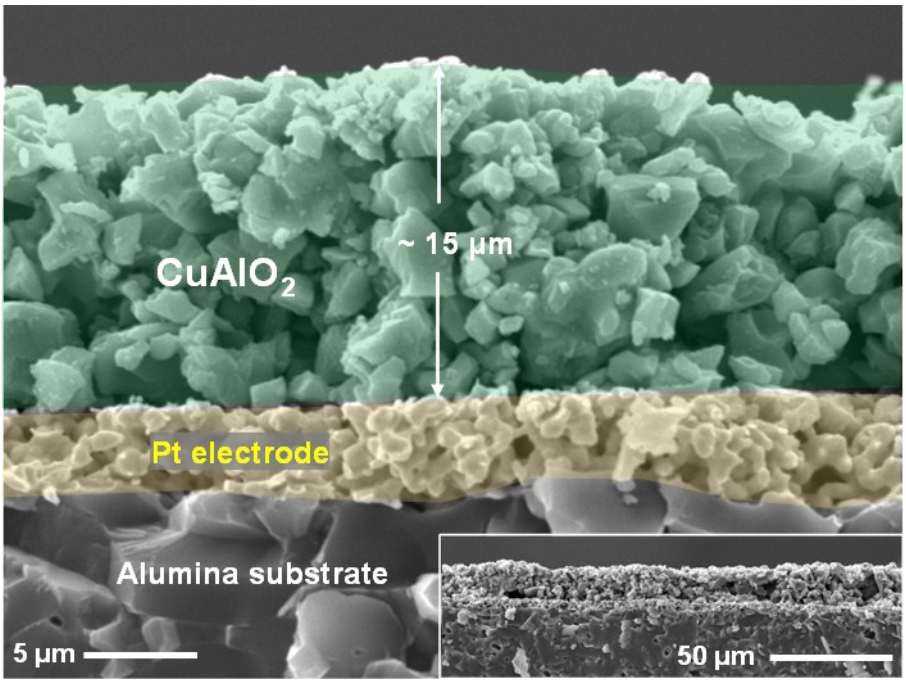


Fig. S1. Cross-sectional SEM image of typical $CuAlO_2$ sensors. The inset shows a low-magnification image. The sensing layer is comprised of loosely packed $CuAlO_2$ particles, with a thickness of ~ 15 μm.

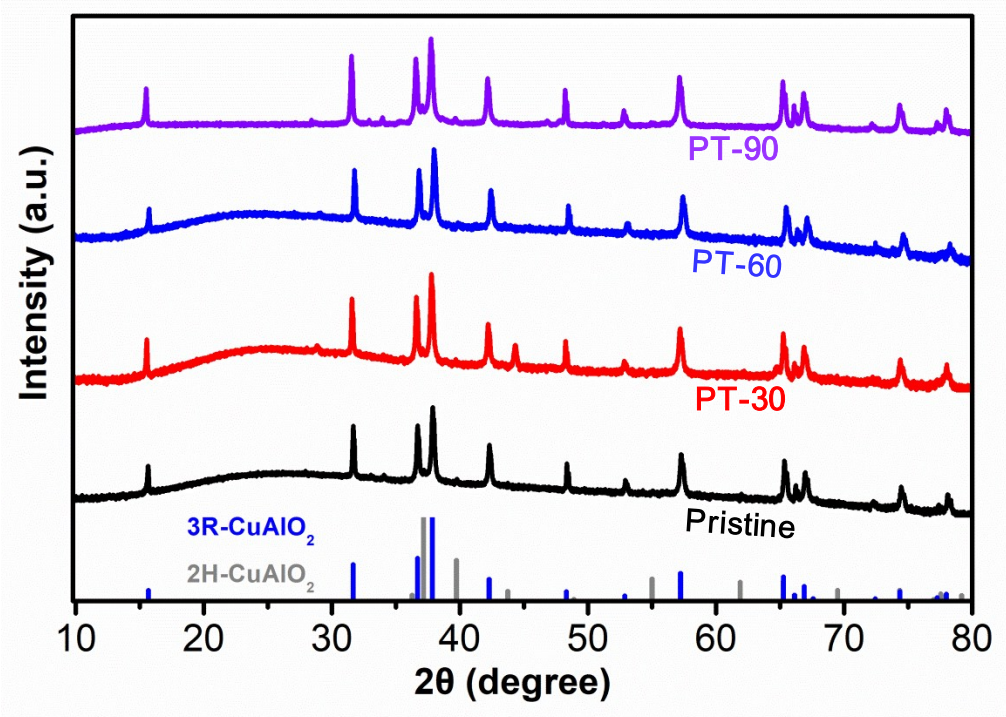


Fig. S2. XRD patterns of pristine and Ar&H_2 plasma treated $CuAlO_2$ sensors. Ar&H_2 plasma treatment didn't cause any detectable impurity phase. All the samples show a 3R (dominent) and 2H mixed $CuAlO_2$ phase.

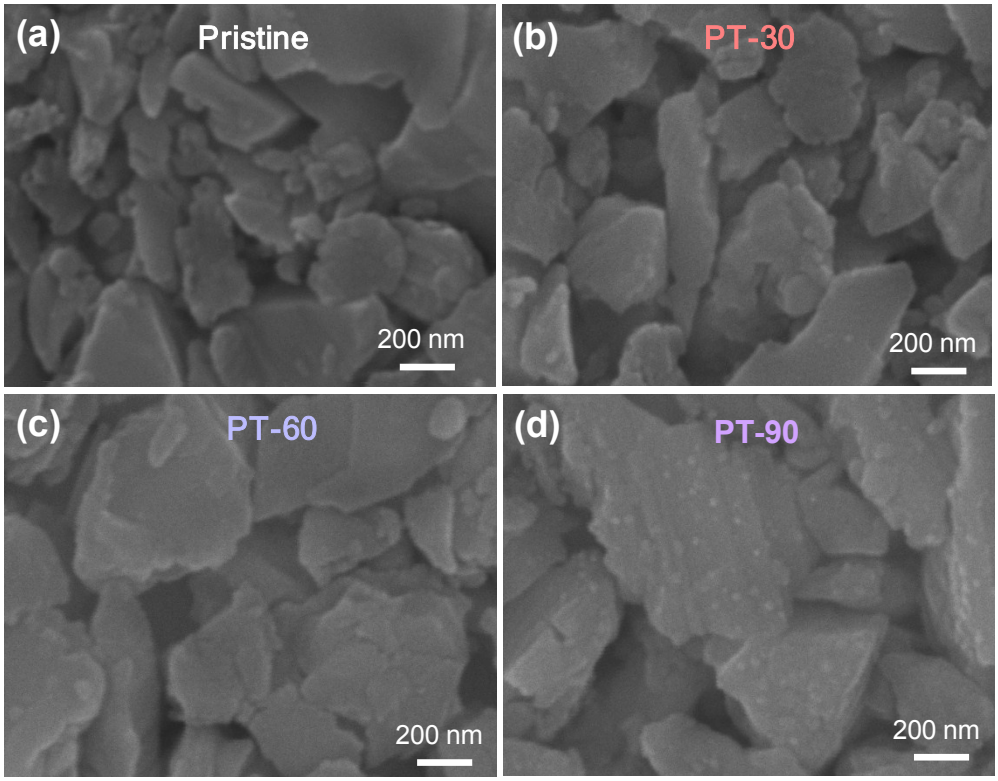


Fig. S3. SEM images of pristine (a) and Ar&H_2 plasma treated PT-30 (b), PT-60 (c) and PT-90 (d) $CuAlO_2$ sensors. Except for 90 minitues treated sample (PT-90) with appearance of small nanodots, no obrvious change of surface morphology was obervered via Ar&H_2 plasma treatment.

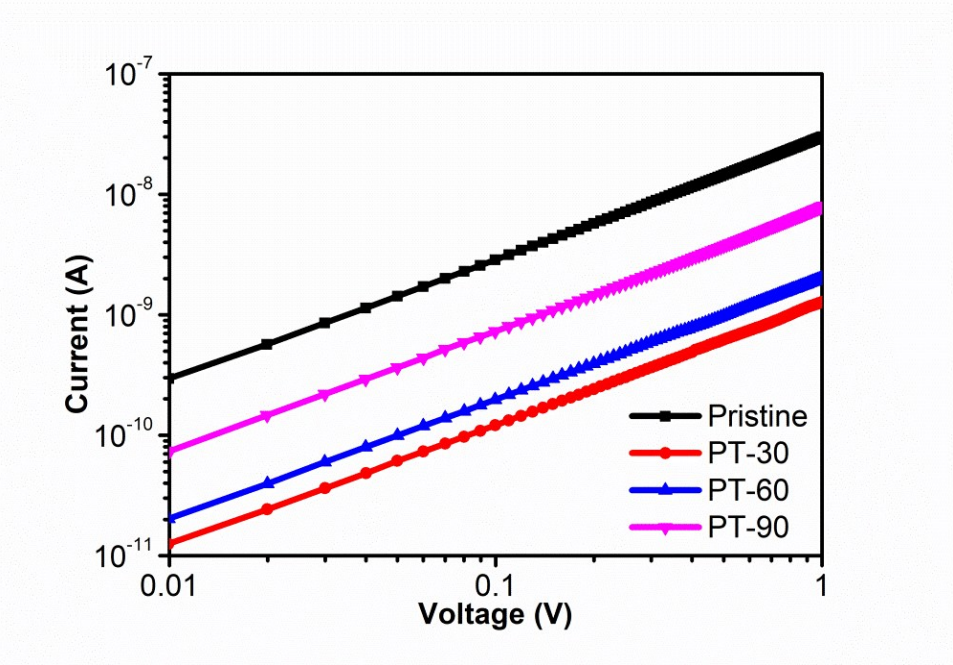


Fig. S4. *I-V* curves of pristine and Ar&H_2 plasma treated CAO sensors, measured under ambient environment at room temperature. All the sensors exhibit linear (Ohmic) contact behavior.

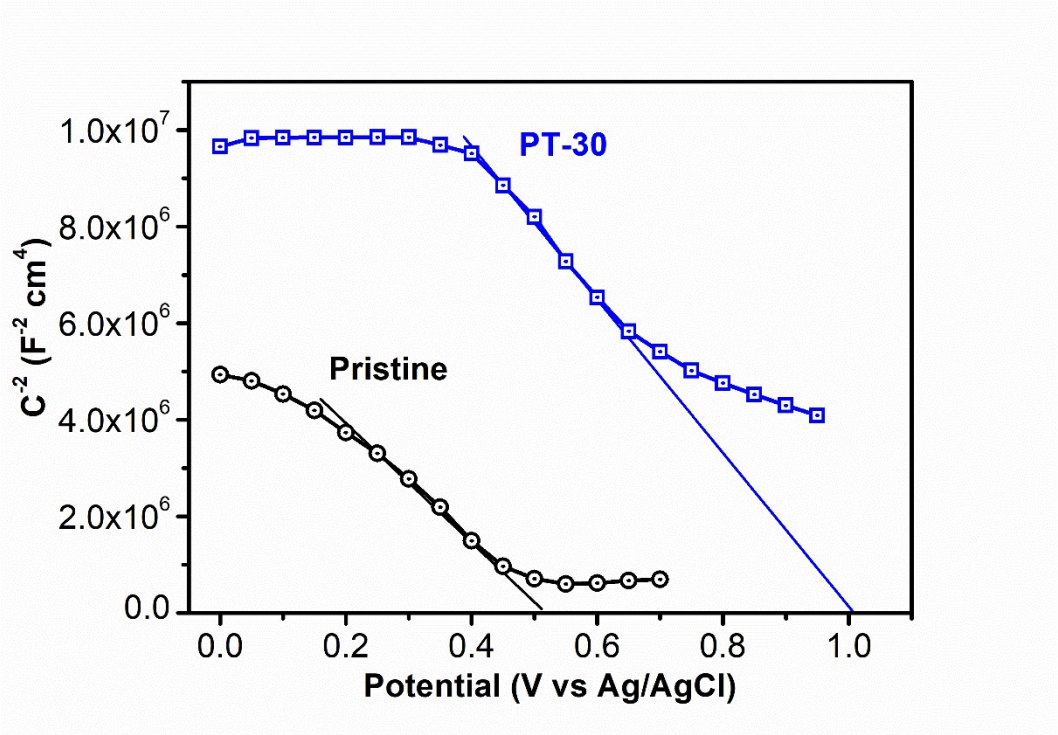
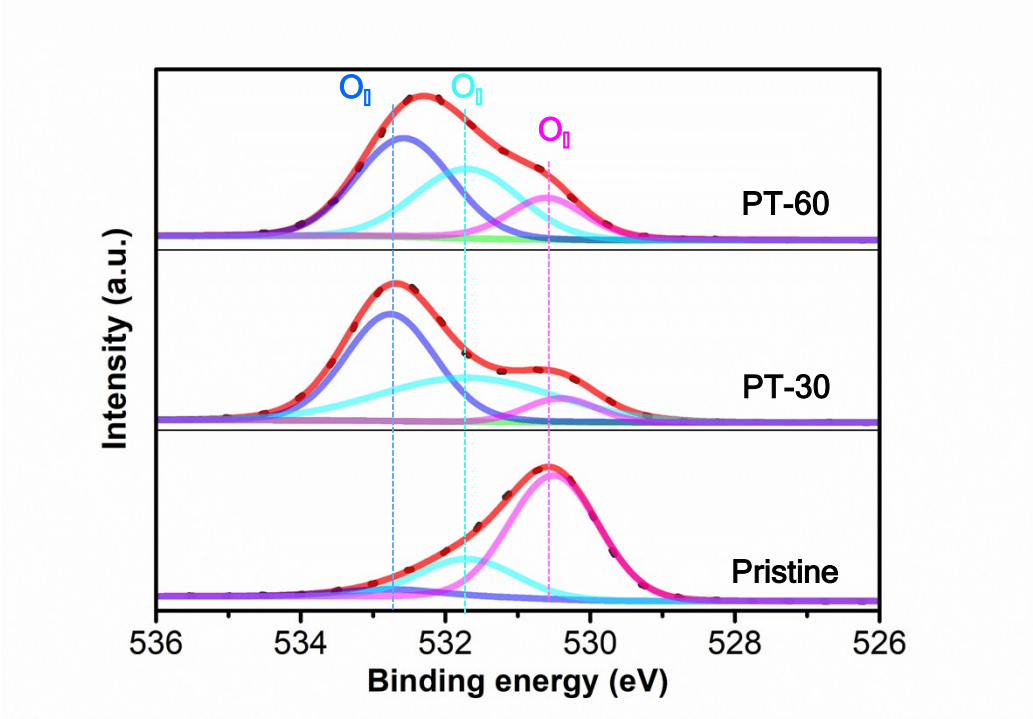


Fig. S5. Mott-Schottky plot of pristine and PT-30 $CuAlO_2$ sensors. Negative slope of $1/C^2$ versus V infers p-type conductivity. [2, 3]



Samples	Peak O_{I} lattice oxygen	Peak O_{II} oxygen vacancy	Peak O_{III} surface absorbed oxygen
Pristine	71.5% (530.5 eV)	23.4% (531.7 eV)	5.1% (532.76 eV)
PT-30	8.7% (530.4 eV)	39.7% (531.7 eV)	51.6% (532.76 eV)
PT-60	17.9% (530.6 eV)	35.7% (531.7 eV)	46.4% (532.57 eV)

Fig. S6. XPS O 1*s* spectra of pristine, PT-30 and PT-60 $CuAlO_2$, and the fitting results of three compositions.

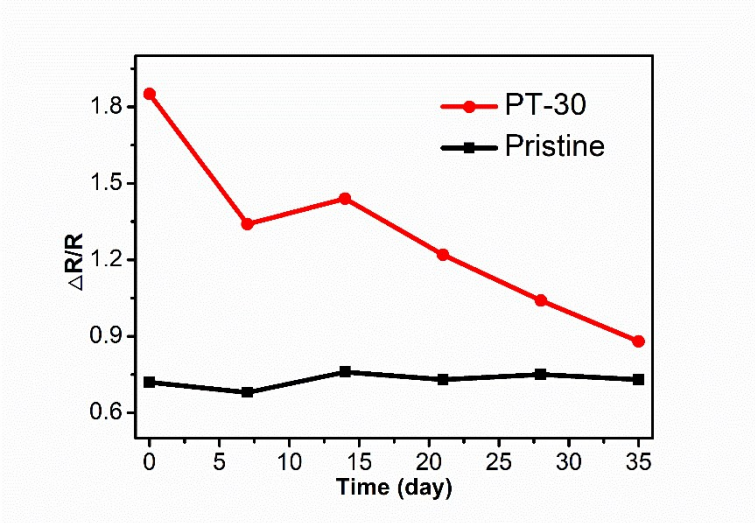


Fig. S7. Stability test of pristine and PT-30 $CuAlO_2$ sensors toward 100 ppm ethanol at 300 °C.

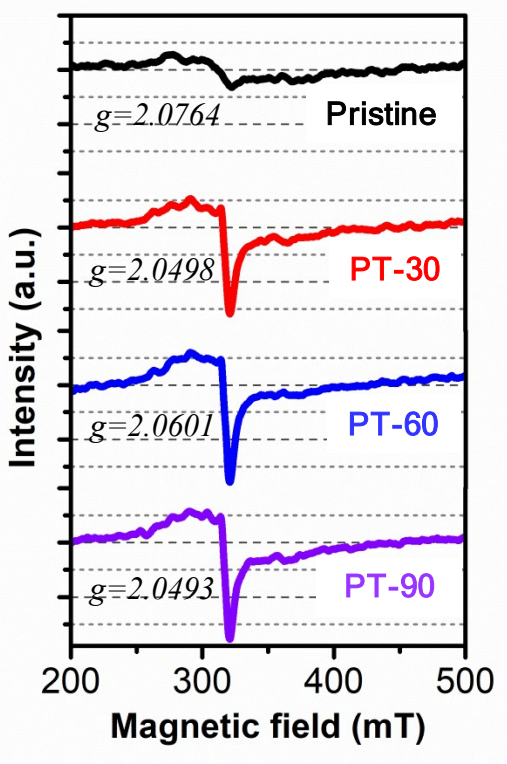


Fig. S8. ESR signals of pristine and Ar&H_2 plasma treated CAO samples. Ar&H_2 plasma treatment results in a significant increase of unpaired electron resonance. The asymetric ESR profiles of PT-30, PT-60 and PT-90 $CuAlO_2$ may arise from weakend surfce crystalllinity induced by ion bombardment.[4]

References

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