Plasma-induced pre-oxidation of ultrathin aluminum layers for enhanced oxidation resistance of copper nanofilms

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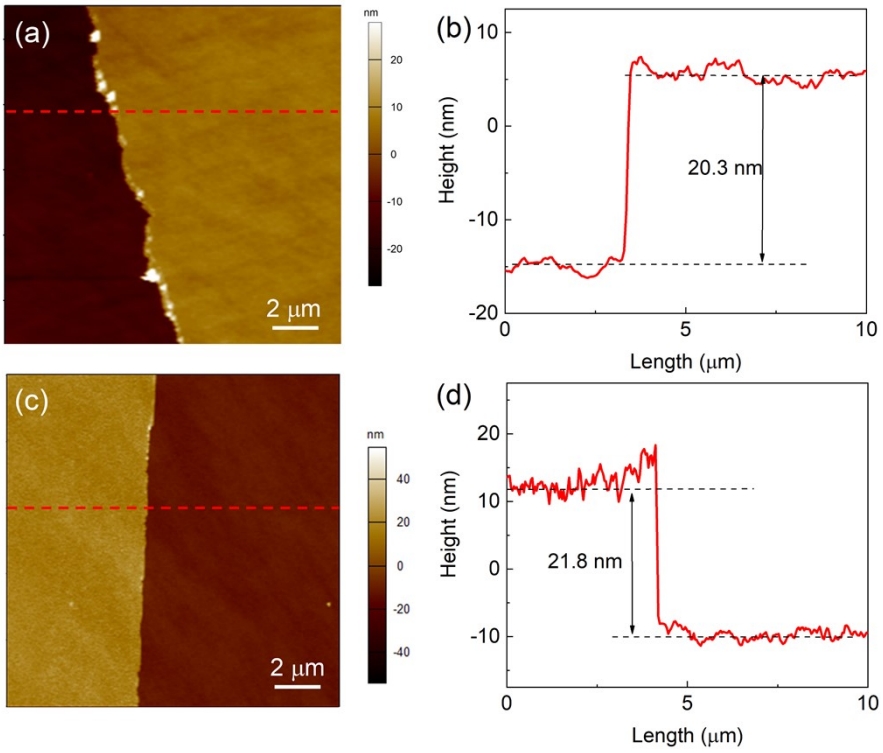

Fig. S1 (a) AFM image of Au electrode; (b) height profile measured along the red dashed line in (a). (c) AFM image of Cu nanofilm; (b) height profile measured along the red dashed line in (d).

The AFM characterization confirmed that the thickness of the deposited Au electrode and Cu nanofilm was 20.3 and 21.8 nm, respectively.

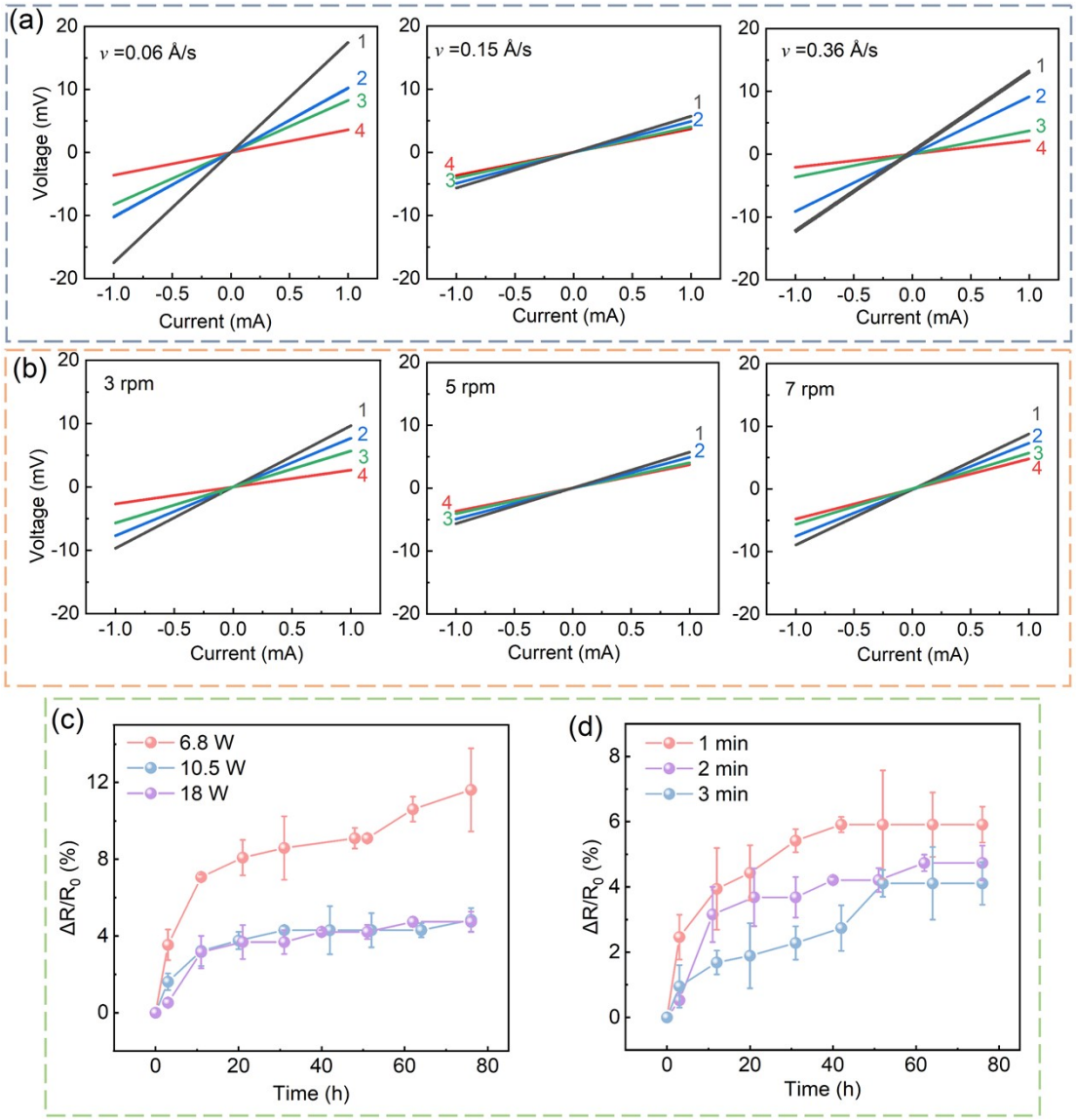

Fig. S2 The I-V curves of 20 nm copper films deposited at (a) different rates and (b) different rotational rates of substrates. The time-dependent $\Delta R/R_0$ of Cu@Al 3 nm under HTHH conditions after plasma treatment with (c) different powers for 2 min and (d) different durations at power of 18 W.

The deposition rate and substrate rotation speed significantly affect the electrical performance and film uniformity. As shown in Fig. S2(a), excessively low or high deposition rates lead to increased resistance fluctuation, suggesting reduced film uniformity and compactness. Similarly, Fig. S2(b) shows that inappropriate substrate rotation speeds also deteriorate the electrical uniformity of the films. Among the investigated conditions, the lowest resistance variation was obtained at a deposition rate

of 0.15 Å/s and a substrate rotation speed of 5 rpm. Based on these results, the optimized deposition conditions were selected for subsequent fabrication of the Cu@Al films.

The influence of plasma parameters on the oxidation resistance of Cu@Al 3 nm films was investigated under HTHH conditions. As shown in Fig. S2(c), increasing the plasma power from 6.8 W to 10.5 W significantly improves the oxidation resistance, indicating that insufficient plasma power results in incomplete oxidation of the Al layer and limited barrier effectiveness. Further increasing the power to 18 W results in comparable protection performance. Similarly, Fig. S2(d) shows that increasing the treatment duration from 1 min to 2 min significantly enhances the protection performance, while further increasing the duration to 3 min leads to only marginal improvement, suggesting that a sufficiently stable oxide barrier can already be established under moderate plasma-treatment conditions.

Importantly, comparable protection performance was obtained under both 10.5 W and 18 W plasma power, as well as for treatment durations of 2 min and 3 min. This indicates that the identified critical thickness of ~3 nm is not restricted to a single narrowly defined processing condition, but remains effective within a reasonably broad plasma-processing window under the present experimental system. Based on the above results, 18 W and 2 min were selected as the standard plasma-treatment conditions for subsequent experiments to ensure stable and reproducible oxidation behavior.

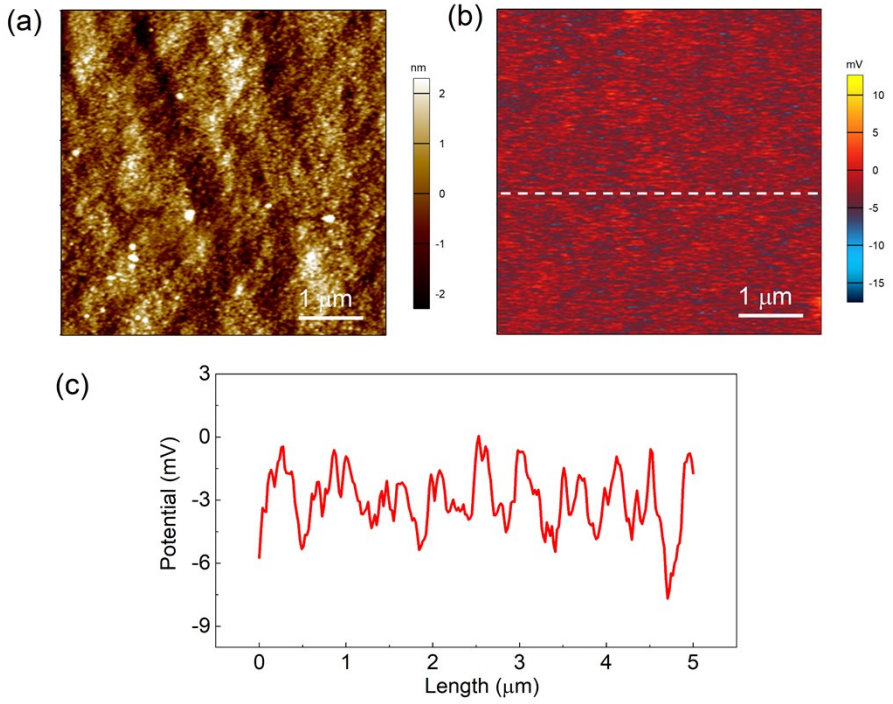

Fig. S3 (a) Surface morphology and (b) surface potential of freshly cleaved HOPG, (c) surface potential profile along the white dashed line in (b).

As shown in Fig.S3, the work function of the probe (HQ NSC8/Cr-Au) was calibrated using freshly cleaved HOPG. The contact potential difference (CPD) between the probe and HOPG was approximately -3 mV. Given that the work function of HOPG is known to be 4.475 eV, thus the work function of the probe was accordingly determined to be 4.478 eV based on Equation (1). According to Equation (2), the surface potential of the probe was set to 4.478 V.

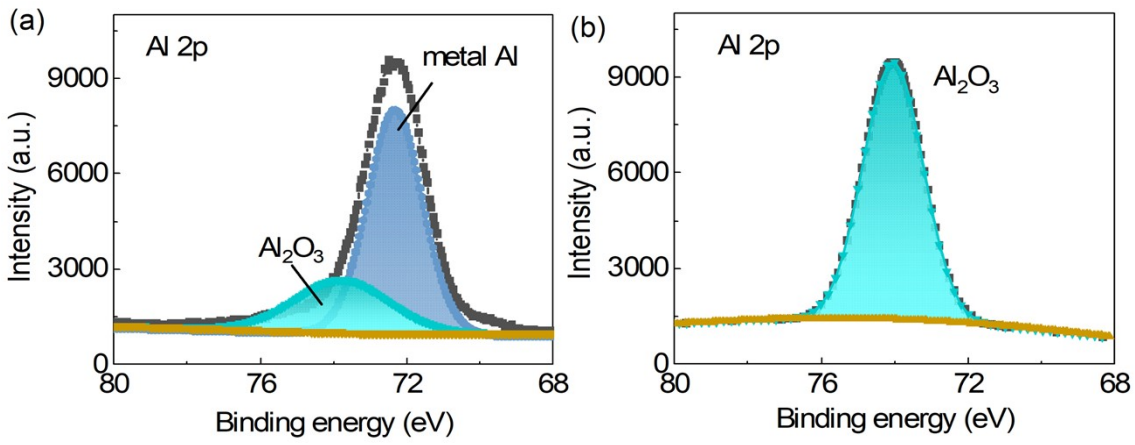

Fig. S4 Al 2p spectra of (a) Cu@Al 3 nm and (b) Cu@Al 3 nm-P.

Table S1. Relative Al_2O_3 and metallic Al peak contributions derived from Al 2p XPS spectra of Cu@Al films before and after plasma treatment.

Sample	Metallic Al (%)	Al_2O_3 (%)
Cu@Al 3 nm	~71.2%	~28.8%
Cu@Al 3 nm-P	Below detection limit	Dominant

For the Cu@Al 3 nm sample, binding energies at 72.4 eV and 73.8 eV are associated to metal Al and Al_2O_3[1, 2]. The oxide layer thickness of untreated sample was calculated using Strohmeier[3], assuming that the oxide and metal phases are spatially separated.

$$d = \lambda_0 \sin\theta \ln\left[\frac{N_m \lambda_m I_0}{N_0 \lambda_0 I_m} + 1\right] \quad \text{(S1)}$$

where d is the thickness of oxide layer, λ_m and λ_0 represent the inelastic mean free paths of photoelectrons in the metal and oxide layer, with values of 30.85 Å and 32.56 Å[4], respectively. The photoelectron emission angle θ relative to the sample surface was set to 90°. The volume densities N_m and N_o are of the metal and oxide layer were taken as 2.7 and 3.99 g/cm[34]. I_m and I_o are the peak intensity of the metal and oxide layer.

Based on this calculation, the oxide layer on the surface of Cu@Al was approximately 0.64 nm, which is consistent with the literature report[5]. Peak fitting results summarized in Table S1 further show that the untreated sample contains approximately 71.2% metallic Al and 28.8% Al_2O_3. After plasma treatment, the Al_2O_3 signal is dominant becomes dominant, while the metallic Al signal becomes nearly undetectable. Under this condition, the Strohmeier method is no longer reliable because the metallic Al intensity required for thickness calculation becomes too weak for accurate analysis. Considering the initial Al thickness of only 3 nm, the strong suppression of the metallic Al component together with the dominant Al_2O_3 signal suggests that plasma treatment promotes oxidation throughout most of the ultrathin Al layer.

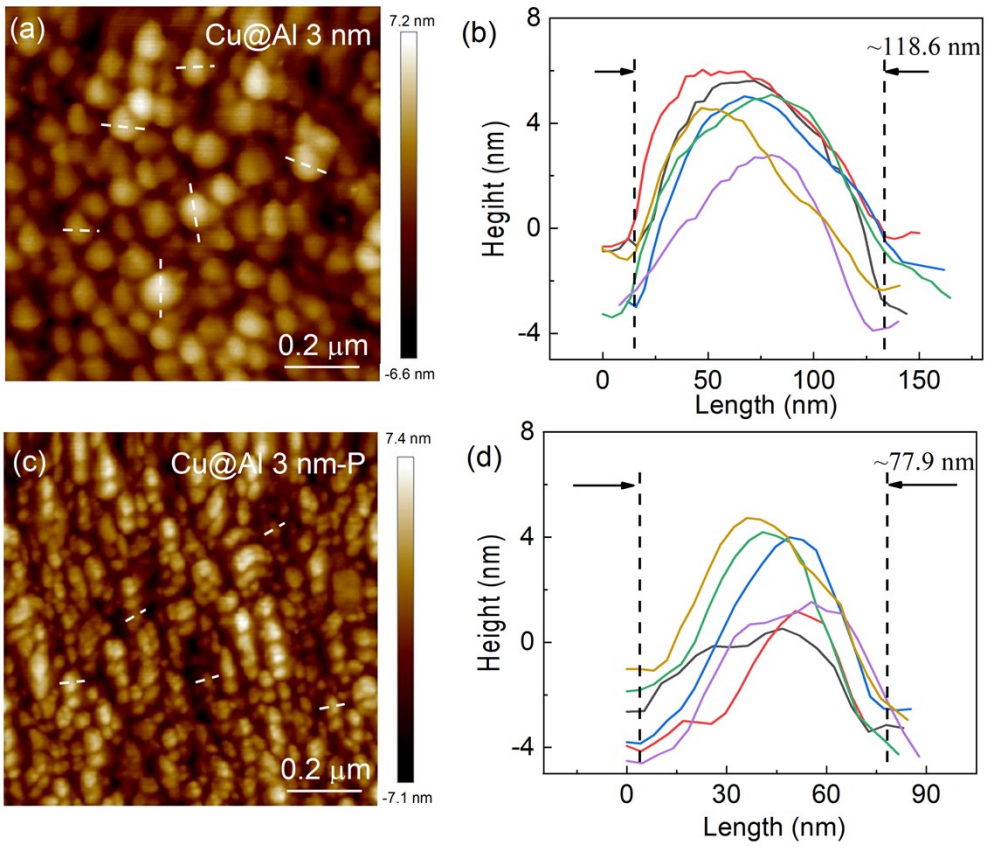

Fig. S5 (a) Surface morphology of Cu@Al; (b) the height profile along the white dashed line in (a). (c) Surface morphology of Cu@Al-P; (d) the height profile along the white dashed line in (c).

Due to the plasma etching effect, the average particle diameter decreased from ~118.6 nm to ~77.9 nm after treatment.

References

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