Supplementary Information

Enhanced Electrical and Thermal Conduction in Graphene-Encapsulated Copper Nanowires

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High temperature growth of graphene was carried out following an erstwhile described process of atmospheric pressure chemical vapor deposition\textsuperscript{1}. After loading the copper film and wire samples into the furnace, the temperature was ramped from room temperature to 1000 °C. Upon reaching 1000 °C, the sample was annealed for 15 minutes in a constant 460 sccm flow of argon and hydrogen followed by introduction of 40 sccm flow of diluted methane (8 ppm in Ar) for 25 minutes. Upon completion of growth, the furnace was opened for cool-down to room temperature and the samples were removed. Optical micrographs show that the high temperature processing results in severe damage to thin copper structures (Figure S1). So, a low temperature CVD process is essential for graphene deposition on copper nanostructures.

\textbf{Figure S1 :} High temperature (1000 °C) graphene deposition on copper films. Severe dewetting observed in copper film and wire structures made of 500 nm thick copper.
We employ a plasma-enhanced chemical vapor deposition process for graphene deposition. Before loading the samples into the deposition system (Figure S2), all growth substrates were cleaned using a solvent triple wash consisting of toluene, acetone and isopropyl alcohol for 5 minutes each to remove organic contaminants. The clean substrates were loaded into a deposition system that consisted of a 6-inch diameter quartz tube surrounded by a resistive heating furnace. The design of our system allows inductively coupled RF plasma to be generated upstream from the location of the copper nanowires to avoid ion bombardment damage. Furnace temperature was ramped up to 650 °C in a constant flow of argon (50 sccm) at 300 mTorr and allowed to stabilize for a few minutes. Graphene deposition was initiated by flowing methane (2 sccm) and hydrogen (2 sccm) while keeping the same argon flow. The total pressure was stabilized to 150 mTorr. A 550W RF plasma was ignited and the reflected RF power was

**Figure S2:** Illustration of the Plasma-enhanced Chemical Vapor Deposition setup. The copper nanowire samples were placed on a quartz holder and inserted at the center of the furnace while the RF plasma is inductively generated far from the copper nanowires.
minimized using a matching network for maximum plasma efficiency. Graphene deposition was carried out for 15 minutes after which the process gases were turned off. The chamber was evacuated and allowed to naturally cool down in a flow of argon. Samples were unloaded upon reaching 200 °C by venting the chamber back to atmospheric pressure.

Majority of the copper samples achieved full coverage of graphene after 15 minutes of deposition using the aforementioned optimized process parameters. For lower deposition times, the Raman peaks either disappeared or became less sharp (Figure S3), indicating incomplete graphene coverage on the copper surface. It is critical to keep the time of deposition as low as possible to avoid structural damage to the copper nanowires at elevated temperatures.

Figure S3: Raman spectra of graphene deposited on copper films at 650 °C for various deposition times, with all other process parameters kept identical.
Figure S4: X-ray diffraction 2θ scans of a 60 nm thick Cu film sample before (black) and after (red) undergoing a PECVD process (650 °C for 15 minutes). Only counts from the (111) Cu orientation at 44.2° were observed while counts from (220) Cu or (200) Cu orientations at around 51° and 75° were missing. The (111) Cu peak from the as-deposited film (black) is wider and has lower intensity compared to the (111) Cu peak after PECVD processing (red) which is sharper and higher in intensity. This is explained by the ultra-small grain sizes in as-deposited Cu whereas annealing during the PECVD process increases the grain sizes. This confirms the preferential (111) orientation of the Cu grains during PECVD graphene growth. The silicon background peaks are marked with (*) symbols.
Cu nanowires were fabricated on silicon substrates covered with 5 µm thick thermal SiO$_2$ using an erstwhile described process$^2$. The substrates were thoroughly cleaned with piranha solution before further processing. The steps of fabrication as shown in Figure S5 are: (1) Physical Vapor Deposition of a stack of 10 nm thick Ta and 60 nm thick Cu onto the SiO$_2$ covered silicon substrates. (2) The Cu film samples were then spin coated with poly(methyl methacrylate) (PMMA) and baked at 180 °C for 2 minutes, followed by spin coating with hydrogen silsesquioxane (HSQ) and baked at 180 °C for 2 minutes. Thickness of PMMA and HSQ layers were 180 nm and 100 nm respectively. (3) 4-probe nanowire devices were patterned into the
HSQ negative resist layer using e-beam lithography at 30 keV. Afterwards the unexposed HSQ was removed using TMAH. (4) With the HSQ layer acting as a mask, the PMMA layer was etched using reactive ion etching with a directional 50 W oxygen plasma. This was followed by argon sputter etching of the Cu/Ta stack. This step was timed closely to avoid etching any underlying SiO$_2$. (5) Following the inspection of complete etching, the HSQ/PMMA bilayer was stripped off in a hot bath of N-Methyl-2-pyrrolidone kept at 100 °C and ultra-sonication to remove any residue.

### S4 Atomic force microscopy of Cu-G and Cu-NG wires

![Atomic force microscopy scans of graphene-coated Cu (Cu-G) and uncoated Cu (Cu-NG) nanowires. The similarity in the height scans for graphene-coated and uncoated nanowires reveals the ultra-thin nature of the graphene coating.](image)

**Figure S6:** Atomic force microscopy scans of graphene-coated Cu (Cu-G) and uncoated Cu (Cu-NG) nanowires. The similarity in the height scans for graphene-coated and uncoated nanowires reveals the ultra-thin nature of the graphene coating.
S5  Extent and nature of Cu oxidation in Cu-NG NWs

X-ray photoelectron spectroscopy was performed on Cu samples after graphene removal to study the amount and chemistry of the oxide species on the Cu surface. The O1s and Cu2p\textsubscript{3/2} spectra from the Cu-NG film along with appropriate peak fitting curves are shown in Figure S7a. The O1s spectrum is highly symmetric with a single peak centered at 531.9 eV. This binding energy is attributed to hydroxyl and hydroxide type compounds.\textsuperscript{3} This points to the formation of Cu(OH)\textsubscript{2} on the Cu surface. Note that there is no shoulder visible on the spectrum in the range of 529.8 eV to 530.6 eV, which is the reported binding energy range for CuO and Cu\textsubscript{2}O. Therefore, Cu(OH)\textsubscript{2} seems to be the dominant oxide species on the Cu surface in Cu-NG samples. Such passivation with Cu(OH)\textsubscript{2} has been reported earlier for Cu foils\textsuperscript{4} and could be a result of the increase in hydrophilicity and wettability of the Cu surface from the O\textsubscript{2} plasma used for graphene removal.

Further proof of Cu(OH)\textsubscript{2} formation is obtained from the Cu2p\textsubscript{3/2} spectrum. The major peak in the spectrum is shifted to higher BE values compared to Cu peak, which is common for Cu(OH)\textsubscript{2} coverage on Cu.\textsuperscript{5} Peak fitting shows a majority peak at 934.9 eV, which is a signature of hydroxide formation, along with the background Cu peak at 932.7 eV. Peak fitting was tried for CuO peak at 933.5 eV without success, confirming a predominance of Cu(OH)\textsubscript{2} in the overlayer.

For estimating the thickness of Cu consumed during oxidation after graphene removal, it is important to quantify the thickness of the Cu(OH)\textsubscript{2}. We use the well known Strohmeier equation, as shown in Supplementary equation (1), to calculate the hydroxide thickness based on the fitted peak area ratio of Cu(OH)\textsubscript{2} / Cu. Inelastic mean free paths of electrons from Cu and Cu(OH)\textsubscript{2} layers are calculated as per Seah & Dench\textsuperscript{6}, as shown in Supplementary equation (2).
\[ d_{\text{ox}} \text{(nm)} = \lambda_{\text{ox}} \sin \theta \ln \left( \frac{N_{\text{Cu}}\lambda_{\text{Cu}}}{N_{\text{ox}}\lambda_{\text{ox}}I_{\text{Cu}}} + 1 \right) \]  

(1)

\[ \lambda_{\text{Cu}} = 538E^{-2} + 0.41(aE)^{0.5}, \lambda_{\text{ox}} = 2170E^{-2} + 0.72(aE)^{0.5} \]  

(2)

where \( a(\text{nm}) = 10^8 \times \frac{M}{\rho nN_A} \)

\[
\begin{align*}
N_{\text{Cu}} / N_{\text{ox}} &= \rho_{\text{Cu}} M_{\text{ox}} / \rho_{\text{ox}} M_{\text{Cu}} = 4.09 \text{(ratio of volume density of Cu atoms in the bulk to the hydroxide)}, \\
a_{\text{Cu}} &= 0.0228 \text{ nm (monolayer thickness for Cu)}, \\
a_{\text{ox}} &= 0.0213 \text{ nm (monolayer thickness for Cu(OH)$_2$)}, \\
\theta &= \text{the electron take-off angle of the detector (45°),} \\
E &= \text{the kinetic energy in eV.}
\end{align*}
\]

The calculated inelastic mean free paths for Cu and Cu(OH)$_2$ are \( \lambda_{\text{Cu}} = 1.12 \text{ nm} \) and \( \lambda_{\text{ox}} = 1.9 \text{ nm} \), respectively. Peak fitting in Figure S7b was performed using mixed functions of the type Gaussian (20%) / Lorentzian (80%) along with the Shirley background correction. The ratio \( I_{\text{ox}} / I_{\text{Cu}} = 3002 / 1050 = 2.86 \) was calculated from the fitted peak areas. This calculation yields a value of \( d_{\text{ox}} = 3 \pm 0.5 \text{ nm} \) for the hydroxide thickness. The thickness of Cu consumed due to hydroxide formation is calculated as \( d_{\text{Cu}} = d_{\text{ox}}\rho_{\text{ox}}M_{\text{Cu}} / \rho_{\text{Cu}} M_{\text{ox}} = 0.75 \pm 0.1 \text{ nm} \). So, the conductive cross-sectional area of a graphene-coated CuNW of dimensions 180 nm wide and 60 nm thick NW reduced by only 2% after the removal of graphene.
Figure S7: (a) Peak fitting of the O1s spectrum for the Cu-NG film sample. Only a single peak centered at 531.9 eV can be fitted to the raw data. The dashed line helps to visualize the symmetric nature of the O1s spectrum. (b) Peak fitting of the Cu2p$_{3/2}$ spectrum for the Cu-NG film sample. The two fitted peaks are centered at 932.7 eV (Cu) and 934.9 eV (Cu(OH)$_2$). Copper hydroxide appears to be the dominant oxide species on the Cu surface after graphene removal.
S6  First order approximation of the exact solution of heat equation

To analyze the temperature rise due to Joule heating in a non-suspended copper nanowires with finite heat loss to the substrate, we use the following heat equation from ref. 33 in the main text:

\[ \kappa_s A \frac{\partial^2 T(x)}{\partial x^2} + \frac{I^2 R_0}{L} \left[ 1 + \beta_R (T(x) - T_0) \right] - Q_{\text{sub}} (T(x) - T_0) = 0 \]  

(3)

where \( \beta_R \) is the temperature coefficient of resistivity, \( \kappa_s \) is the thermal conductivity, \( A \) is the cross-sectional area of the wire, \( L \) is the length of the wire, \( I \) is the electric current, \( R_0 \) is the initial resistance prior to Joule heating and \( Q_{\text{sub}} \) is the heat loss to the substrate per unit length.

The individual heat terms are depicted in Figure S8 for a section of the graphene-copper hybrid nanowire.

**Figure S8**: Illustration of the various entities in the heat diffusion equation adapted for Cu nanowires on a substrate. From the Supplementary equation (1), the first term is depicted by in-plane thermal conduction (blue arrow), the second term is depicted by Joule heat generation (red arrow) and last term is depicted by the substrate heat loss per unit length (green arrow).
The expression for the solution to the heat equation (from ref. 35 in the main text) is as follows:

\[
\Delta T(x) = \frac{\Delta T(x)}{p R_l (Q_{sub} - p)} \left( 1 - \frac{\cosh(mx)}{\cosh(mL/2)} \right)
\]  

This expression is used for estimating the temperature profile along the length of the nanowire (Figure 3d in main text). By integrating the Supplementary equation (4) along the length of the wire, we obtain the average temperature rise in the wire (equation (2) in the main text):

\[
\frac{R - R_0}{R_0} = \beta_R \left( \bar{T} - T_0 \right) = \frac{p}{(Q_{sub} - p)} \left( 1 - \left( \frac{2}{mL} \right) \tanh \left( \frac{mL}{2} \right) \right)
\]  

with \( p = \beta_R \left( \frac{I^2 R_0}{L} \right) \) and \( m = \sqrt{\frac{Q_{sub} - p}{\kappa_s A}} \)

This expression is suited for numerical fitting but is cumbersome for gaining basic insight into the problem of heat dissipation in nanowires. For sufficiently small values of \( p \) (small range of \( I \)), the expression for \( m \) can be approximated as follows:

\[
m = \sqrt{\frac{Q_{sub} - p}{\kappa_s A}} \approx \sqrt{\frac{Q_{sub}}{\kappa_s A}} \left( 1 - \frac{p}{2Q_{sub}} \right)
\]  

The hyperbolic tangent function (tanh) is a smooth function and for a small range of values of \( m \) (or \( p \) or \( I \)), it can be approximated as a constant \( c \). Using the approximate expression for \( m \), we can simplify the expression in Supplementary equation (5) as follows:
\[
\frac{R - R_0}{R_0} = \beta_R (\bar{T} - T_0) = \frac{p}{Q_{sub}} \left[ 1 - \frac{p}{Q_{sub}} \left( 1 - \frac{2c}{L \sqrt{Q_{sub}}} \left( 1 - \frac{p}{2Q_{sub}} \right) \right) \right]
\]

(7)

\[
\frac{R - R_0}{R_0} \approx \frac{p}{Q_{sub}} \left( 1 - \frac{2c}{L} \sqrt{\frac{\kappa_A}{Q_{sub}}} \right)
\]

\[
\frac{R - R_0}{R_0} \approx \frac{\beta_R \rho_0}{Q_{sub} A} \left( 1 - \frac{2c}{L} \sqrt{\frac{\kappa_A}{Q_{sub}}} \right)
\]

From the last identity in Supplementary equation (7), we can clearly see that relative change in resistance due to Joule heating is directly proportional to \( R \). Note that this approximation is only valid for small range of values of \( p \) such that \( p \ll Q_{sub} \), which is true for our samples.

### S7 Estimation of temperature coefficient of resistance (\( \beta_R \))

**Figure S9**: (a) Resistance as a function of substrate temperature for calibrating the temperature coefficient of resistance (\( \beta_R \)) of a copper nanowire with \( L=20\mu m \) and \( W=180nm \). (b) Relative change in measured resistance plotted as a function of substrate temperature for the nanowire in (a). The slope gives the average value of \( \beta_R \). Both Cu-G and Cu-NG versions of the nanowire have approximately the same \( \beta_R=0.48x10^{-3} \, K^{-1} \).
S8 Thermal conductivity extraction of wires with different dimensions

The measured increase in wire resistance with increasing drive currents is shown in Figure 3a in the main text. As the measured resistance increases linearly with $I^2$, we can extract the initial resistance $R_0$ (low currents) and the slope of the curves (Figure S10a) for the two different lengths. Interestingly, the slope of the curve (degree of Joule heating) is proportional to the initial resistivity. So, graphene-coated wires of a given length have a lower slope than the uncoated wires, as expected from the measured resistivity data and Supplementary equation (7). Additionally, the slope also depends on other important parameters like thermal conductivity of the nanowires and heat loss to the substrate.

We extract the thermal conductivity of individual nanowires with and without the graphene coating by carefully measuring the dimensions and $\beta_R$ values of each nanowire. As the graphene coating covers the three exposed faces of the nanowire, the heat dissipation across the nanowire-substrate interface is independent of the presence of graphene coating. So, we assume $Q_{sub}$ to be identical for the two cases while fitting the data for a given nanowire. In addition to the data shown in Figure 3b of the main text, Figures S10b - S10d show the measured and fitted Joule heating curves for CuNWs of other dimensions.
Figure S10. (a) Extracted initial resistance and slope of the Joule heating curves for graphene-coated and uncoated copper nanowires of two different lengths. (b)-(d) Relative change in measured resistance (spheres) plotted as a function of $I^2$ for individual copper nanowires of different dimensions. Equation (2) from the main text was used to fit the observed values with minimized $R^2$ fitting error (solid lines).
S9 Supplementary references


