

Probing the Nanoscale Onset of Plasticity in Electroplated Copper for Hybrid Bonding Structures via Multimodal Atomic Force Microscopy

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Abstract

The slowdown of Moore's law has elicited a paradigm shift whereby shrinking of in-plane dimensions is being replaced by 3D-stacking advanced packaging approaches to satisfy the ever-increasing demands for power, performance, area, and cost. Driven by the widespread use of metallic interconnects with submicron pitches, robust metrology for probing mechanical behavior at the nanoscale emerges as a key area of interest in the semiconductor industry. Here, we develop an Atomic Force Microscopy (AFM)-based protocol for characterizing the incipient stages of plasticity and illustrate it on hybrid bonding-ready (prior to bonding) copper pads. We combined AFM's high-resolution imaging with contact resonance and indentation techniques (including single- and multi-step indentation) to characterize the mechanical heterogeneity of the material, quantify the nanoscopic yield stress statistics, and derive indentation stress-strain curves. From these measurements, we have clarified the mechanisms of early plasticity and determined the elastoplastic constitutive response of polycrystalline copper, including parameters such as elastic modulus, yield stress, and strain-hardening slope. Besides providing metrology relevant to various length scales, our approach offers a pathway to utilize an industry-standard instrument for characterizing the thermomechanical properties that are essential for the development of semiconductor structures.

1. Introduction

The advancement of semiconductor technology cannot continue solely under the paradigms of Moore's and More Moore's laws, as dimensions approach the physical limits of transistor scaling. Nonetheless, ongoing developments in fields such as artificial intelligence, large-scale computing, big data, and robotics are driving the need for improvements in power, performance, area, and cost (PPAC)¹. In this context, various advanced packaging techniques (an umbrella term for different architectural accelerators) have emerged as potential solutions to sustain miniaturization trends and meet PPAC requirements² (Fig. 1a). One promising approach is hybrid bonding technology, which enables direct metal-metal and dielectric-dielectric connections with interconnect pitches $<10\text{ }\mu\text{m}$, without the need for wires or bumps in the circuit³. In a general hybrid bonding process (Fig. 1b), two identical dies made of silicon (Si) and silicon dioxide (SiO_2) are prepared with embedded copper (Cu) pads⁴. During a chemical-mechanical polishing (CMP) step, the dielectric is smoothed and the copper on each die is recessed slightly (i.e., dishing) to ensure it does not impede the dielectric-dielectric bonding. Heat and pressure are subsequently applied, causing the Cu pads to expand, fill the recesses, and contact the opposing Cu pads. These contacts lead to copper migration and bonding of the two dies. Thus, two of the most critical steps in hybrid bonding, CMP and annealing plus bonding phase, involve nanoscale mechanical and thermomechanical processes. During CMP, the copper is deformed and abraded by contact with silica particles in a slurry^{5,6}. In the annealing and bonding phase, the asperities at the mating interfaces come into contact and plastically deform, increasing the effective merging area for an enhanced diffusion-assisted bonding⁷. Therefore, understanding and improving these processes requires a thorough characterization of the elastic and plastic properties of bonding-ready copper at the nanoscale^{1,8,9}, which differ from those measured at the macro-, meso- and micro-scale due to the emergence of size¹⁰ and processing effects^{11,12}.

Fundamental micro- and nano-scale plasticity studies in copper have primarily been conducted using conventional nanoindentation^{13–16}, atomic force microscopy (AFM) indentation¹⁷, miniaturized uniaxial testing^{18,19}, and forward and inverse computational methods^{13,20–22}.

Despite the versatility and advanced capabilities of modern AFMs for nanoscale mechanical mapping²³, there is a significant lack of studies leveraging AFM for the characterization of nanoscale incipient plasticity in materials specific to the semiconductor industry. Most studies using AFM for mechanical characterization in heterogeneous integration and advanced packaging have primarily focused on topographic imaging to infer the mechanical response of the samples^{24–26}, rather than directly probing their nanomechanical properties. For example, observation of thermoplastic deformation in hybrid-bonding-ready Cu-SiO₂ structures can be simply observed by AFM topographical scans as a function of temperature²⁴. However, to understand and accurately model the thermomechanical response of these structures, we require direct measurements of their material parameters at the nanoscale, rather than relying on values obtained from macroscale tests. These needs align with the continued downward trend in size-scaling and the critical need for application-relevant robust metrology as identified in the International Roadmap for Devices and Systems¹.

We address these gaps by introducing a multimodal AFM-based metrology framework designed to characterize the nanoscale elastic and plastic response of copper at room temperature, specifically within actual hybrid bonding patterns prior to the bonding process (Fig. 1b). In this framework, we utilize contact resonance (CR-AFM, Fig. 1d) and AFM-indentation (Figs. 1e, 1f) together with the topographic capabilities of AFM to measure local moduli, determine yield stresses, and derive indentation stress-strain curves at room temperature. Our multimodal AFM approach, with tip radii less than 40 nm, enables probing the mechanics of nanoscale volumes on precise nanostructural surface features such as grain boundaries, without requiring additional sample preparation. A key advancement of this work is the ability to resolve sub-nm size pop-in events taken at force increments $< 1 \mu\text{N}$. Furthermore, our

AFM-based strategy lays the groundwork for future nanoscale hybrid-metrology that combines topographic, mechanical, electrical, and thermal capabilities²⁷. These types of measurements and corresponding data pertaining to structures prepared for integration are essential for enhancing predictive manufacturing in hybrid bonding applications.

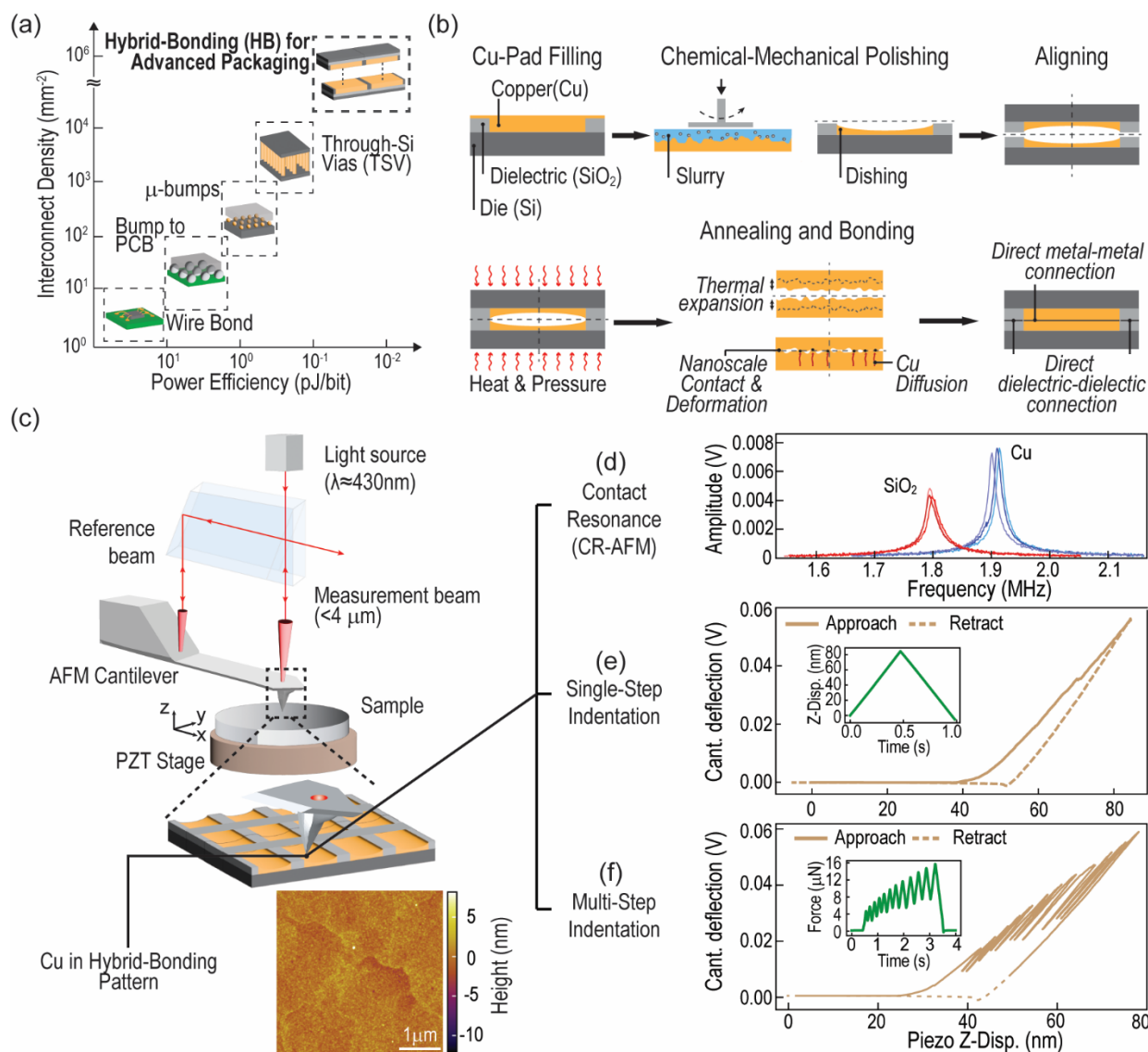


Figure 1. (a) Overview of scaling trends in 3D-interconnect technologies in terms of energy efficiency and interconnect density; (b) Schematic representation of the main steps involved in a typical hybrid bonding process. Multimodal AFM experiments on hybrid-bonding ready patterns: (c) Experimental setup for interferometric AFM, along with a topographic image of copper in a hybrid bonding pattern (prior to bonding); Representative experimental curves obtained through (d) CR-AFM, e) single-step, and f) multi-step AFM indentation. Insets in (e) and (f) show the imposed displacement/load profiles as a function of time.

2. Experimental

2.1. Hybrid Bonding Samples

Samples were collected from wafers featuring hybrid bonding SiO₂/Cu patterns (Intel Corporation, Hillsboro, OR, USA) that underwent chemical-mechanical polishing. The surface of the polycrystalline Cu pads exhibits micrometer-sized grains. In AFM topographic images, these grain boundaries are visible to varying extents, with height differences across them measuring a few nanometers.

2.2. AFM – Topographic Imaging

AFM experiments were performed using an environmental Vero AFM (Oxford Instruments/Asylum Research, Santa Barbara, CA, USA). The Vero AFM features a built-in Quadrature Phase Differential Interferometer (QPDI)⁵⁶, which directly measures the vertical displacement of the tip based on the wavelength λ of the light (Fig. 1c). In addition to benefiting from low-noise measurements through interferometric detection, the QPDI provides two significant advancements: 1) the vertical deflection measurement directly reflects the AFM tip displacement, improving the characterization of the tip-sample interaction, and 2) the cantilever deflection is converted into displacement without requiring contact with the sample, enabling stiffness calibration through the thermal tune method prior to contact. Furthermore, unlike the optical beam deflection method commonly used in AFM, QPDI minimizes crosstalk between lateral and vertical forces. All experiments were conducted in air at room temperature. The uncertainties reported correspond to the experimental standard deviation of the measurements taken during each experiment (see Supporting Information, Notes S1 and S4-S6).

Topographic imaging of selected areas within the hybrid bonding patterns was conducted in non-contact mode, both before and after AFM indentations, using the same tip for both operations. For high-resolution imaging following the indentations, sharper AFM tips were utilized. In these instances, PPP-SEIH silicon cantilever tips (Nanosensors, Neuchâtel, Switzerland) were used, with cantilever stiffness

of around 8.5 N/m and tip radius less than 10 nm. All topographic images were processed using first-degree polynomial flattening.

2.3. Contact Resonance AFM

CR-AFM measurements were conducted using photothermal excitation of the cantilever in dual AC mode. A DT-NCHR probe (Nanosensors, Neuchâtel, Switzerland), with a resonance frequency in air $f_1^{\text{air}} = 415.8$ kHz and a spring constant $k_c = 9.2$ N/m, was used. Frequency maps were generated over a Cu pad surrounded by SiO₂, with an applied force of 750 nN, a frequency scan rate of 0.5 Hz, and a resolution of 512 px $\times$ 512 px. During the mapping, the two driving frequencies were kept apart at a constant difference of 120 kHz. A complete description of the experimental and analysis methodology is presented in Supporting Information Note S1.

2.4. AFM-Indentation

Single-step and multi-step AFM-indentation measurements were performed using silicon probes with conospherical diamond tips (Adama Innovations Ltd., Dublin, Ireland), and spring constants k_c ranging between 508 N/m and 528 N/m. The shape of the tips was regularly assessed against a TGT1 test grating (K-TEK Nanotechnology, Wilsonville, OR, USA) in between indentation arrays to check for significant wear or damage. Throughout the measurements, the tips maintained a spherical end, with only a slight increase in tip radius observed after hundreds of measurements (see Supporting Information, Note S7). Force versus indentation depth, P vs h , curves were derived from the cantilever deflection voltage V versus piezo displacement d curves, V vs d , with $P = k_c h$ and $h = d - VS$, S being the deflection sensitivity of the cantilever in nm/V. The processing of the force-spectroscopy data was carried out using an in-house developed script in Python, which utilized the SciPy⁵⁷ and Scikit-learn⁵⁸ packages.

2.4.1. Single-Step AFM-Indentation

Single-step indentations were performed as square arrays over areas of approximately $4\ \mu\text{m} \times 4\ \mu\text{m}$, at a given maximum applied load. The loading and unloading segments of the indentations were carried out at a velocity of 200 nm/s, with a sampling rate of 500 Hz, and a scan rate of 1 Hz. Force-displacement curves were analyzed for several metrics like pop-ins, total work, plastic work, residual depth, and cumulative excursion length. Pop-ins (i.e., small displacement excursions on the loading curves) were identified with the aid of an in-house developed algorithm. A subsequent visual inspection was conducted to detect any potentially overlooked pop-ins and to ensure accuracy. The force-displacement coordinates of all identified pop-ins, as well as the total number of pop-ins, were recorded for statistical analysis. A complete description of the experimental methodology and analysis is presented in Supporting Information Note S2.

2.4.2. Multi-Step AFM-Indentation

Multi-step AFM-indentation experiments were performed over selected areas within Cu pads. Typically, the maximum load used for these tests was around 15 μN , with approximately 20 partial loading-unloading cycles made to gradually reach the desired maximum load. Partial unloading was performed up to 25 % of the cycle's maximum load to maintain a conformal tip-sample contact during unloading. The loading and unloading segments were executed at velocities of 50 nN/s, and with a sampling rate of 500 Hz. Indentation stress-strain curves were derived following the formalism developed by Pathak and Kalidindi⁵⁰, based on the analysis of the unloading segments. A complete description of the experimental methods and analysis is presented in Supporting Information Note S3.

3. Results and Discussion

3.1. Elastic Modulus Characterization

The elastic modulus of polycrystalline Cu pads was determined using contact resonance atomic force microscopy (CR-AFM) mapping, with results presented in Figure 2. In essence, CR-AFM utilizes the resonant frequency shift of the AFM cantilever while in elastic contact with the sample to quantify the elastic and viscoelastic properties of materials at the nanoscale^{23,28}. We performed CR-AFM measurements on both Cu pads and adjacent SiO₂ regions, over areas of about 25 μm^2 on each material. The measurements taken in the SiO₂ regions served as a reference for converting the measured CR frequencies into indentation moduli^{28,29} (Fig. 2a-b). The indentation modulus M is defined as $M = E/(1 - \nu^2)$, where E and ν represent the Young's modulus and Poisson's ratio, respectively. For the reference SiO₂ material, a Young's modulus $E_{\text{SiO}_2} = 72$ GPa and a Poisson's ratio $\nu_{\text{SiO}_2} = 0.17$ were assumed, which correspond to an indentation modulus of $M_{\text{SiO}_2} = 74.1$ GPa. The indentation modulus of the tip (diamond) was taken as $M_{\text{Tip}} = 1250$ GPa, obtained from $E_{\text{Tip}} = 1200$ GPa and $\nu_{\text{Tip}} = 0.2$. Using these values, we calculated the reduced elastic modulus of the SiO₂ as $E_{\text{eff,SiO}_2} = (1/M_{\text{SiO}_2} + 1/M_{\text{Tip}})^{-1}$.

The modulus profile shown in Fig. 2a exhibits minimal variation across the reference SiO₂ regions, with an indentation modulus of $M_{\text{SiO}_2}^{\text{Exp}} = 74.1 \text{ GPa} \pm 4.1 \text{ GPa}$. The uncertainty in the measurements of SiO₂ is ascribed to the inherent variability of the contact area during CR-AFM mapping. In contrast, a more pronounced variation in indentation modulus is observed on the profile of the Cu area ($M_{\text{Cu}}^{\text{Exp}} = 136.4 \text{ GPa} \pm 11.5 \text{ GPa}$), as also evidenced in the histogram of Fig. 2b. This distinct contrast within the Cu pad can be attributed to its polycrystalline structure. The range of indentation moduli shown in Fig. 2b can be correlated with the indentation moduli of the three main crystallographic directions of Cu, whose theoretical indentation moduli are 129 GPa, 138 GPa, and 141 GPa, for $\langle 100 \rangle$, $\langle 110 \rangle$, and

$\langle 111 \rangle$, respectively³⁰. Although a predominance of the $\langle 111 \rangle$ texture is generally expected due to its greater diffusivity (as Cu-Cu hybrid bonding is a diffusion-based process), the observed heterogeneity is not surprising because the process parameters associated with various fabrication steps of the Cu pads (such as Cu-seeding via physical vapor deposition, Cu-electroplating, annealing, and CMP) are known to influence their texture^{31–33}. Establishing a clear association between the mechanical properties and specific crystallographic orientations is less important for the purposes of this work. Instead, we focus on using these results to develop an elastic-plastic characterization that is highly localized and can be effectively performed at specific locations on samples of interest.

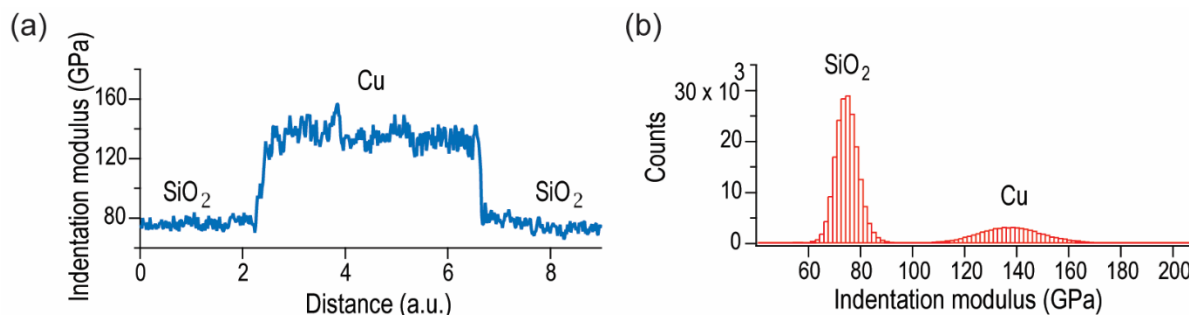


Figure 2. CR-AFM measurements. (a) Single-line profile of indentation moduli across SiO₂ and Cu regions as determined by CR-AFM mapping; (b) Histogram of the indentation moduli obtained from CR-AFM over the mapped SiO₂ and Cu regions.

3.2. Incipient Plasticity Characterization

With the indentation moduli determined from CR-AFM, we now turn our attention to the onset of plastic deformation, also known as incipient plasticity. As briefly noted in the introduction, AFM-based force-spectroscopy is particularly well-suited for studying the onset of plasticity due to its ability to probe material volumes on the nanometer scale, where the likelihood of encountering and moving

dislocations is relatively low³⁴. In turn, AFM-indentation allows for the investigation of dislocation nucleation mechanisms¹⁰ and defect-induced plastic mechanisms.

Single-step indentations were first performed on the center region of two separate Cu pads from the same batch of fabrication. Fig. 3a shows a topographic scan of the surface of one of the pads after indentation, where the pad's polycrystalline structure and some surface defects can be observed. Individual grains in the AFM topography can be distinguished from one another due to the slight misalignment of their polished surfaces. The significant non-uniformities observed across polycrystalline copper grains arise from the varying mechanical wear rates during CMP, which depend on the crystallographic orientation of the grains^{35,36}. Additionally, small, thin ridges (measuring less than 1 nanometer) can be observed along the grain boundaries, resulting from the mechanical mismatch between the grains. As shown in Fig. 3a, the post-imaging AFM offers high spatial resolution for locating indents with respect to the interior of the grains and their boundaries. Force-depth curves, one of which is presented in Fig. 3a, display similar characteristics, featuring a jagged loading segment and a relatively smooth unloading curve. The former is associated with the occurrence of pop-in events related to plastic deformations (indicated by black arrows in Fig. 3a), while the latter is indicative of elastic unloading without additional effects, such as pop-outs.

Averaging the force-depth curves obtained from each pad (Fig. 3b) provides a clearer understanding of their behavior under load and shows that our AFM indentations are consistent across pads. In the average curves, the pop-ins are smoothed out, and an inflection is observed at approximately 7.5 μN force (black dashed arrow in Fig. 3b). Before reaching this point, the (average) loading curve resembles the unloading path. After the inflection at 7.5 μN , the material exhibits a significantly more compliant response. By comparing the average curves with the individual ones, we find that the inflection region corresponds to the occurrence of the largest pop-in events recorded during the experiments. Given that these are not the first pop-ins, the largest pop-ins likely reflect a collective motion of dislocations³⁷

resulting from the interaction between pre-existing dislocations and those generated around the AFM tip³⁸. The fluctuations observed at the maximum load of the averaged profile in Fig. 3b result from the sparse averaging of force-distance curves that reach the same maximum load at various indentation depths. Additional examples of individual force-distance curves are provided in the Supporting Information. Other plasticity metrics (Fig. 3c) derived from individual force-depth curves also show good consistency across pads. The number of pop-in events per curve generally ranges from 8 to 15, with an average plasticity index and plastic work around 0.6 and 0.012 pJ, respectively.

As shown in the individual indentation curve (Fig. 3a) and the curves in Supporting Information Note 4, the actual departure from elasticity occurs considerably earlier in the loading path than the aforementioned inflection around 7.5 μN . This departure can be assessed by fitting the elastic segment up to the first pop-in with the classical Hertz expression for the contact of a paraboloid onto a flat, elastic half-space³⁹:

$$P = \frac{4}{3} E_{\text{eff}} \sqrt{R} h^{3/2} \quad (1)$$

where P , E_{eff} , R , h are the load, the effective modulus, the tip radius, and the displacement, respectively. The elastic modulus values obtained from CR-AFM measurements were used to fit Eq. (1), leading to an estimate of the tip radius $R = 12.3 \text{ nm} \pm 1.4 \text{ nm}$ (see Supporting Information, Notes 2 and 7). In our analysis, we disregarded any existing native oxide layer on the surface of Cu due to the lack of a distinct compliant region at the contact, which suggests that this layer may be very thin, possibly within the nanometer range. After fitting, the maximum shear stress ($\tau_{\text{max}}^{\text{pop}(1)}$) at the point of departure from the Hertzian response (marked with a circle in Fig. 3a), can be calculated as³⁹:

$$\tau_{\text{max}}^{\text{pop}(1)} = 0.31 \sqrt[3]{\frac{6E_{\text{eff}}^2 P^{\text{pop}(1)}}{\pi^3 R^2}} \quad (2)$$

where $P^{\text{pop}(1)}$ is the load at the first pop-in. The maximum shear stress in Eq. (2) represents the onset of plasticity (i.e., incipient plasticity) and can be regarded as the nanoscopic yield stress. Furthermore, by

analyzing various force-depth curves (refer to Figures S4 and S5 from Supporting Information), it is evident that pop-ins occur at different load-depth pairs, highlighting their stochastic nature. In this context, Fig. 3d presents the empirical cumulative distribution function of the maximum shear stresses calculated at the 1st pop-in events from each indentation experiment. For both Cu pads examined, the distributions are narrow, ranging from 5 GPa to 12 GPa, with median maximum shear stress ($\tilde{\tau}_{\max}^{\text{pop}(1)}$, tilde denoting median) of 8.4 GPa and 8.9 GPa, respectively. These values are of the order of the theoretical shear strength of copper, generally estimated to be about $G/2\pi$ (with G the shear modulus of the material, which for Cu $\langle 111 \rangle$ is about 48 GPa)⁴⁰. Previous experimental studies by Suresh et al.¹⁵ and Gouldstone et al.⁴¹ reported shear strengths of 20.8 GPa and 15 GPa, respectively, through nanoindentation of primarily (111)-copper thin films on Si substrates. More recent computational⁴² and experimental³⁸ works found lower shear strengths around 4.56 GPa and 4.20 GPa under spherical nanoindentation, respectively. As such, our values fall within these upper and lower bounds, reflecting both our methodology and the characteristics of copper in hybrid bonding patterns.

To gain mechanistic insight into the nature of the 1st pop-in, the empirical cumulative distributions (f) are fitted using⁴³:

$$f = 1 - \exp \left[-\frac{\eta k_B T}{\dot{\tau} v^*} \exp \left(\frac{\tau v^*}{k_B T} \right) \right] \quad (3)$$

where k_B , T , v^* , η , τ , $\dot{\tau}$ are Boltzmann's constant (1.380649×10^{-23} J/K), temperature, activation volume, defect nucleation rate, and the shear stress and rate (where $\tau_{\max}^{\text{pop}(1)}$ has been denoted τ , for brevity), respectively. The fit is performed after using Eq. (3) to write $\ln[\ln(1/(1-f))]$ as a linear function of τ , to obtain v^* and η from the slope and intercept, respectively. From the fits (dashed lines in Fig. 3d), an average value of $3.5 \times 10^{-3} \text{ nm}^3$ for the activation volume is obtained, on the order of 20 % the atomic volume of copper ($1.182 \times 10^{-2} \text{ nm}^3$), and consistent with the values reported for other face-centered cubic (FCC) metals^{44,45}. This correlation suggests that the plastic events, which

appear as the first pop-in in the force-depth curves, are associated with the homogeneous nucleation of dislocations caused by the reconfiguration of a small number of atomic bonds, rather than a larger-scale reconfiguration of the lattice^{10,46}. Although this topic is beyond the scope of this work, future studies employing computational modeling (such as molecular dynamics) and experimental techniques (like transmission electron microscopy) could provide deeper insights into the dislocation nucleation phenomena. Additionally, the similarity between the cumulative excursion lengths (δ , Fig. 3c) and the sum of abrupt displacements in the force-depth curves indicates that the plastic dissipation is primarily driven by shear.

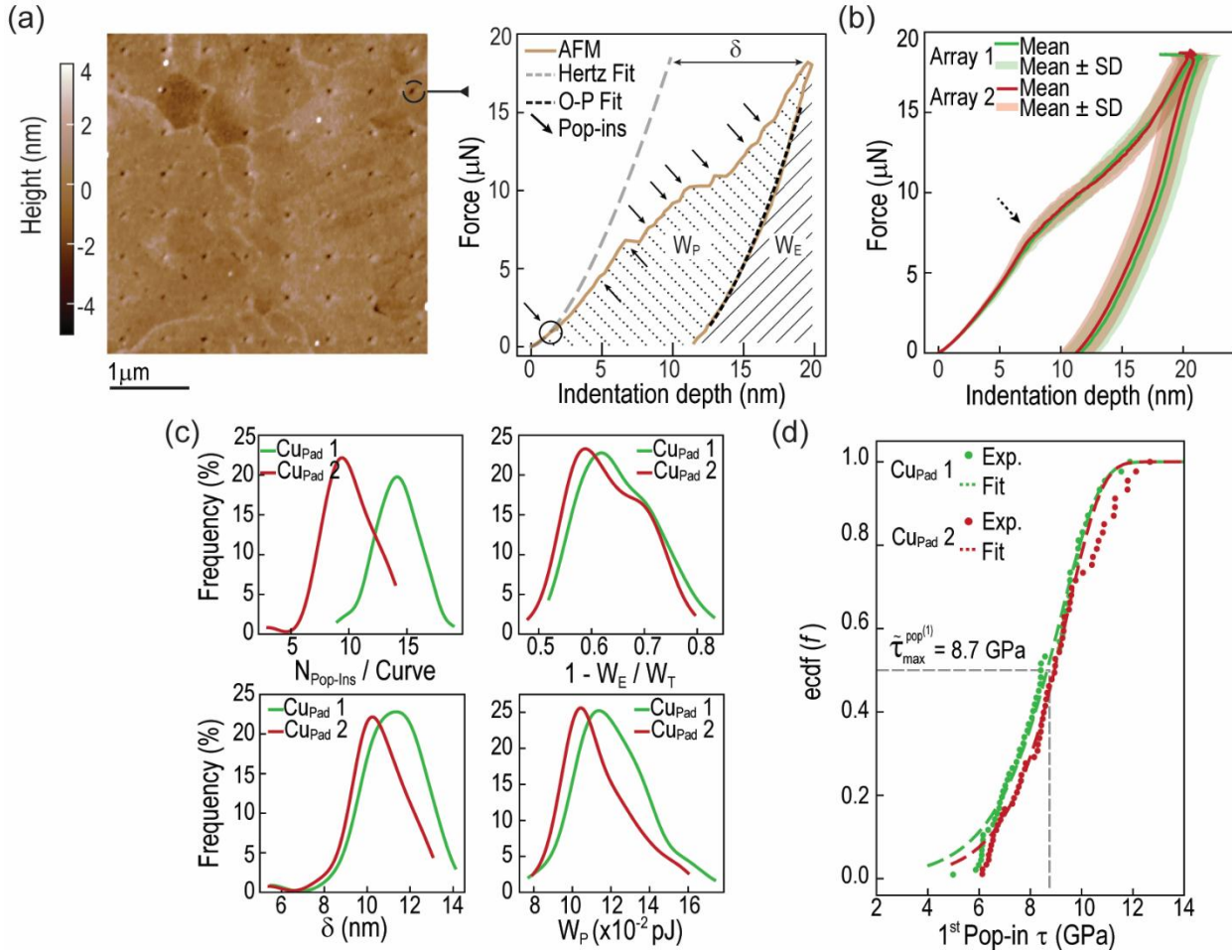


Figure 3. AFM single-step indentation characterization on Cu pads. (a) Post-indentation topographic scan with a selected force-displacement curve shown; (b) Average force-indentation depth curves, with the shaded region covering curves within one standard deviation; (c) Histogram fits for plastic metrics

including the number of pop-ins per indentation curve, plasticity index, cumulative excursion length, and plastic work; (d) Empirical cumulative distribution (ecdf) of maximum shear stress at the first pop-in event, as defined by Eq. (2).

3.3. Influence of Grain Boundaries

As discussed in the previous sections, Cu pads in hybrid bonding patterns are polycrystalline, raising the question of how grain boundaries influence the onset of plasticity in these samples. It is well established that grain boundaries play a significant role in accommodating deformation, controlling strength, and regulating diffusion, with mechanisms often differing from those within the grains^{47,48}. However, the reduced size of grains and their boundaries make it challenging to examine their local mechanics. In this context, the topographic capabilities of AFM and the ability to use sharp tips for force-spectroscopy enable the precise positioning of the indenter to probe grain boundary properties and compare them to those of the grains themselves. To achieve this, the plastic behavior of copper grain boundaries in hybrid bonding patterns was studied using a methodology similar to that described in Section 3.2. On a different copper pad, a set of indentations was performed on both grain boundaries and within grains, as shown in the topographic scan in Fig. 4a.

The average force indentation-depth curves (Fig. 4b) show comparable loading behavior up to nearly 7.5 μN (as indicated by the black dashed arrow in Fig. 4b), consistent with the onset of plasticity discussed in Section 3.2. Additionally, the unloading paths appear parallel yet shifted, illustrating similarity in elastic behavior. The difference arises in the behavior following the kink in the average loading curve, wherein the grain boundaries exhibit a stiffer response and reduced ductility compared to the grain interiors. The latter is clearly seen when comparing the plasticity index, plastic work and

cumulative departure length metrics, as shown in Fig. 4c. In all cases, these metrics indicate increased plasticity for points within the grains compared to boundaries, which is consistent with the notion that grain boundaries act as barriers to dislocation motion⁴⁹.

Notably, in the early stages of plasticity, the differences between boundary and interior points are not as pronounced, with the median maximum shear stress differing by less than 3 % (8.00 GPa and 7.83 GPa, respectively), resulting in distributions that nearly overlap around the theoretical shear strength (Fig. 4d). Therefore, the influence of grain boundaries appears to be more prevalent at the level of dislocation motion rather than at the level of dislocation nucleation.

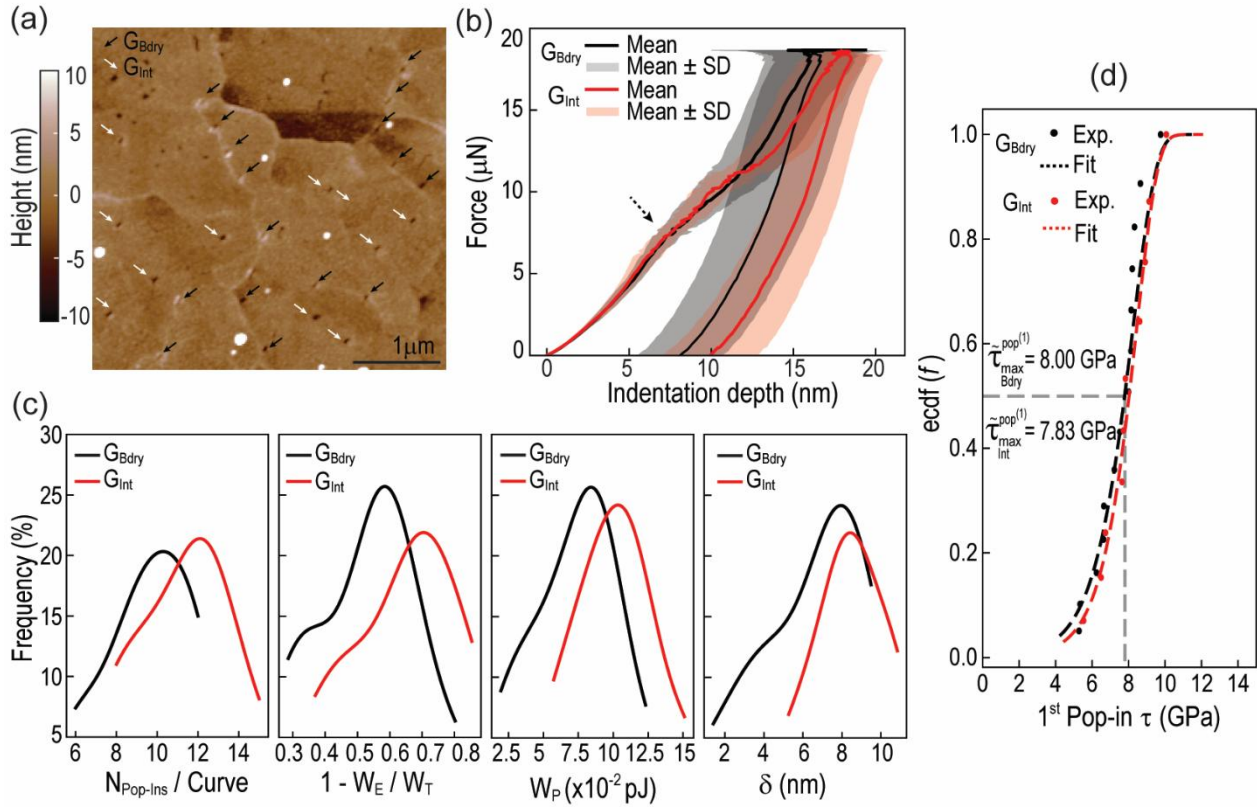


Figure 4. AFM single-step indentation comparison between grain boundary (G_{Bdry}) and grain interior (G_{Int}) plasticity. (a) Post-indentation topographic scan with indents on grain boundaries and grain interiors highlighted; (b) Average force-indentation depth curves (shaded region signifies one standard deviation); (c) Histogram fits for plastic metrics: number of pop-ins per indentation curve,

plasticity index, cumulative excursion length, and plastic work; (d) Empirical cumulative distribution (ecdf) of maximum shear stress at first pop-in, as defined by Eq. (2).

3.4. Stress-Strain Curves

We utilized our AFM multi-step indentations to obtain the constitutive relations for copper in the form of indentation stress-strain (ISS) curves. To achieve this, we followed the methodology developed by Pathak and Kalidindi⁵⁰ and fitted the unloading segments (i.e., elastic reloading segments) of multi-step indentations using a more general Hertz expression:

$$P^{(i)} = \frac{4}{3} E_{\text{eff}} \sqrt{R_{\text{eff}}^{(i)}} h^{(i)3/2} \quad (4)$$

where (i) represents a given unloading segment. It is important to note that Eq. (4) differs from Eq. (1) in the effective radius term $R_{\text{eff}}^{(i)}$. This is because, in multi-step experiments, an effective tip radius must be used to account for the plastic deformation of the sample. To fit Eq. (4) with $R_{\text{eff}}^{(i)}$ as the sole fitting parameter, it was assumed that the elastic moduli remained constant. The value of the effective radius was used to compute the contact radius as $r_c^{(i)} = (3P_t^{(i)} R_{\text{eff}}^{(i)} / 4E_{\text{eff}})^{1/3}$, with $(P_t^{(i)}, h_t^{(i)})$ the maximum load and depth at the maximum load of each segment⁵¹. From this, pairs of stress-strain values were ultimately obtained as⁵⁰:

$$(\epsilon_{\text{ISS}}^{(i)}; \sigma_{\text{ISS}}^{(i)}) = \left(\frac{4h_t^{(i)}}{3\pi r_c^{(i)}}; \frac{P_t^{(i)}}{\pi r_c^{(i)2}} \right) \quad (5)$$

Fig. 5a presents topographic images of the surface of Cu pads before and after multi-step indentations. These indentations were performed within grains (i.e., not on grain boundaries) and the residual indentations with depths reaching nearly 20 nm. It is important to note that the post-indentation residuals

of multi-step indentations in Fig. 5a appear somewhat elongated. This effect is likely due to the material's crystallographic anisotropy and the uneven distribution of the pile-up around the rim. More pile-up material was observed around the multi-step indents compared to the single-step ones. Associated with the indents shown in Fig. 5a, Fig. 5b depicts two individual multi-step force-indentation depth curves, with the Hertzian fits superimposed on the unloading segments (more curves presented in Supporting Information Note 6). The force-depth data is well captured by the expression in Eq. (4), which facilitates the conversion to indentation stress-strain values. This is justified by virtue of the non-overlapping loading-unloading segments, which indicate plastic deformation. In contrast, the unloading and reloading segments, on the other hand, appear overlapped, indicating negligible hysteresis.

By analyzing the force-depth curves from all multi-step indentation experiments, a collection of indentation stress-strain pairs was obtained, as shown in the combined plot of Fig. 5c. Overall, the stress-strain data aligns well with a linear trend of slope E_T , which is smaller than the elastic slope E_E . This indicates that the response is not solely elastic. This is further evidenced by the force-indentation depth curves, where no overlap between loading and unloading was observed during the cycles. Consequently, the slope E_T represents the linear strain-hardening behavior of the Cu pads, also referred to as tangent stiffness. We calculated the median E_T from each indentation stress-strain curve (Fig. 5c) to obtain an average $E_T = 20.3$ GPa. From this value, by computing the intersection of the plastic path (dashed blue line in Fig. 5b) with the 0.2 % offset elastic path, a median indentation yield stress of $\bar{\sigma}_{ISS}^{Y_{0.2\%}} = 0.64$ GPa was determined. Thus, by deriving the yield stress and tangent stiffness through multi-step indentations, we can elucidate the elastic-plastic constitutive behavior of the Cu pads.

The yield stress obtained is consistent with the values reported by Niu et al.⁵² (200 MPa to 600 MPa) and Ramachandramoorthy et al.⁵³ (about 400 MPa), both of whom investigated micropillar compression. It must be noted, however, that the former⁵² examined single crystal copper and the latter⁵³ micro additive-manufactured copper pillars. These materials are expected to differ from

the copper used in our study, which comes from hybrid bonding-ready patterns. Moreover, the discrepancy observed between yield stress values derived from indentation stress-strain curves and those obtained from micropillar testing is similar to previously reported comparisons⁵⁰.

Further analysis of the force-depth curves reveals that the average envelopes from the multi-step indentations resemble those from the average curves presented in Sections 3.2 and 3.3. In particular, the inflection around 7.5 μN persists, but can now be quantified in terms of stress using the indentation stress-strain formalism. As a result, we can determine that the transition observed in the force-depth curves, coinciding with the largest pop-ins, occurs at a stress of approximately 3.75 GPa.

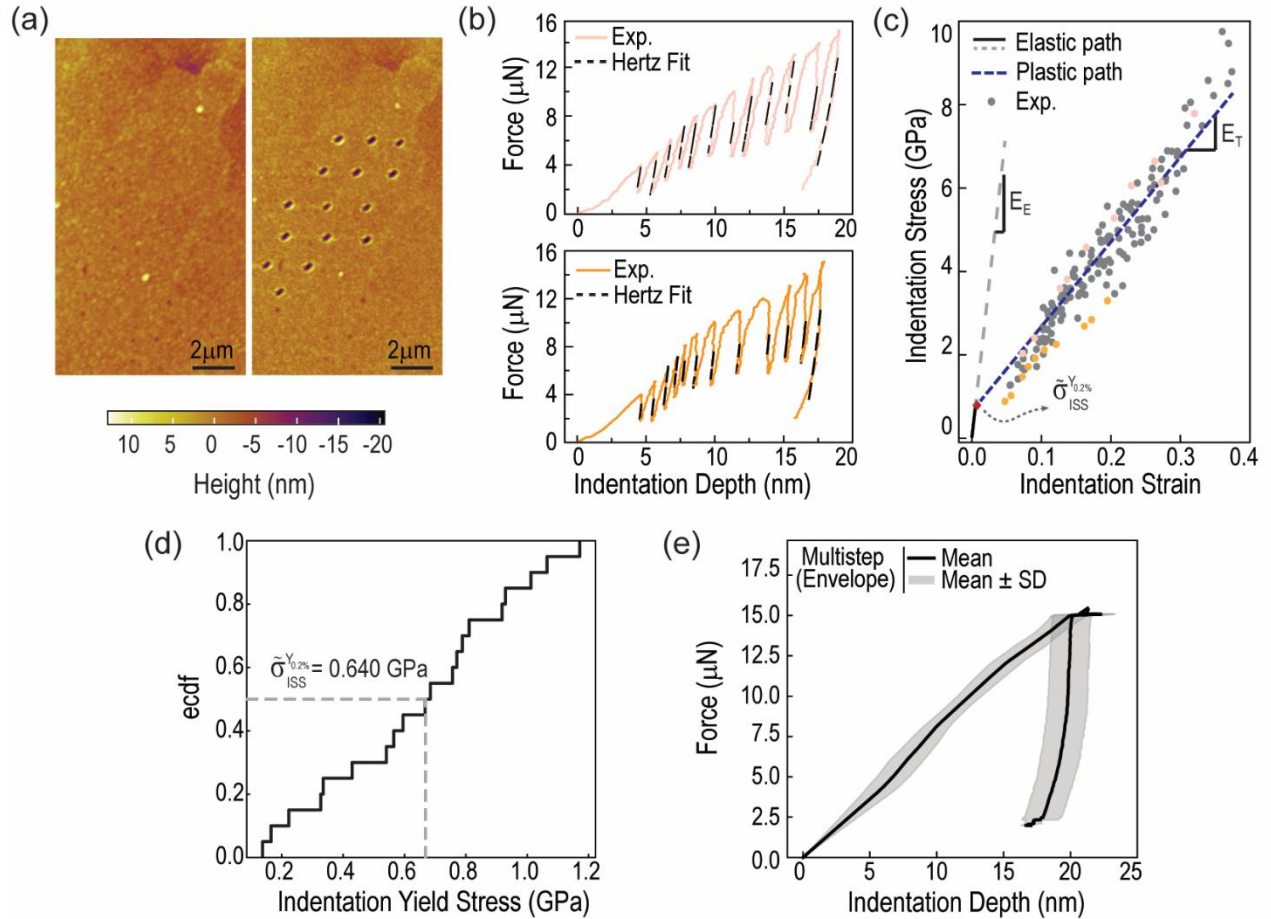


Figure 5. Multi-step AFM-indentation experiments. (a) Before and after multi-step indentation topographic scans within a Cu pad; (b) A subset of force-indentation depth curves with the Hertzian fits superimposed on the unloading segments; (c) Indentation stress-strain curve with stress-strain pairs from all experiments (grey markers) and the ones derived from the force-depth curves from (b) (orange and

pink markers); (d) Empirical cumulative distribution function of the indentation yield stress from all the experiments, with the median indentation yield stress ($\tilde{\sigma}_{\text{ISS}}^{\text{Y}_{0.2\%}}$) highlighted; (e) Average force-depth envelope curve for multi-step indentation experiments (shaded region signifies one standard deviation).

4. Conclusions

The push for smaller and more efficient semiconductor devices requires lengthscale- and condition-relevant metrology techniques that can inform on the mechanical and thermomechanical properties of the materials involved. Herein, we have demonstrated an AFM-based protocol to gain insight into the room-temperature, nanoscale—mechanical properties of Cu in hybrid bonding-ready patterns. Specifically, we have i) quantified the statistics and characteristics of incipient plasticity and obtained nanoscale constitutive behavior for the Cu pads, and ii) developed a multimodal AFM-based methodology for characterizing these materials at the nanoscale. The parameters obtained (Young's modulus, yield stress, strain-hardening slope) can be effectively utilized in the design and modeling of key hybrid bonding processes, such as chemical-mechanical polishing⁵ and diffusion-bonding⁹. Furthermore, we have outlined a roadmap for integrating an additional AFM-based material property characterization into existing AFM metrologies in the semiconductor industry. Unlike other techniques, AFM does not require extra sample preparation, allows for high-precision positioning, and can be used in- or near-line metrology applications.

Building on the findings of this study, several avenues for future research emerge. Along these lines, we emphasize the integration of CR-AFM and AFM-indentation experiments with microstructural correlative measurements such as electron backscatter diffraction and transmission electron microscopy. This integration can enhance our understanding of the relationship between microstructural states and deformation mechanisms observed in AFM experiments. Additionally, our multimodal experiments

could be used to inform and compare with multiscale computational modeling approaches (e.g., molecular and discrete dislocation dynamics, crystal-plasticity finite elements) aimed at both forward and inverse material property prediction⁵⁴. Finally, expanding the multimodal capabilities of AFM into a high-throughput and high-speed experimental framework holds significant potential in the context of data-driven approaches, where big-data-generating experiments are increasingly demanded^{23,55}.

ASSOCIATED CONTENT

Supporting Information

Additional information on methodology, and measurements (CR-AFM, single-step indentation, multi-step indentation, AFM probe geometry) (PDF).

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Author Contributions

G.S. and N.A.A. conceived the research. G.S. performed AFM measurements. N.A.A. performed data analysis, software, and visualization tasks. The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

NOTES

The authors declare no competing financial interest.

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Supporting Information

Probing the Nanoscale Onset of Plasticity in Electroplated Copper for Hybrid Bonding Structures via Multimodal Atomic Force Microscopy

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Details of the contact resonance AFM (CR-AFM) on SiO₂ and Cu pads

CR-AFM measurements were performed using photothermal excitation of the cantilever in the dual AC mode with a Vero AFM (Oxford Instruments/Asylum Research, Santa Barbara, CA, USA). A DT-NCHR probe (Nanosensors, Neuchatel, Switzerland) with a resonance frequency in air $f_1^{\text{air}} = 415.8$ kHz and a spring constant $k_c = 9.2$ N/m was used in these measurements. CR-AFM frequency maps were generated over a $9\ \mu\text{m} \times 9\ \mu\text{m}$ square area encompassing a single Cu pad surrounded by SiO₂. The mapping was carried out with an applied force of 750 nN, a frequency scan of 0.5 Hz, and a resolution of $512\ \text{px} \times 512\ \text{px}$. The fast-scan direction in CR-AFM was the same as that used in topography scanning, specifically along the cantilever's long axis. The two driving frequencies were kept apart during CR mapping at a constant difference of 120 kHz. Several CR frequency sweeps from the initial tuning states on SiO₂ and Cu regions are shown in Figure S1.

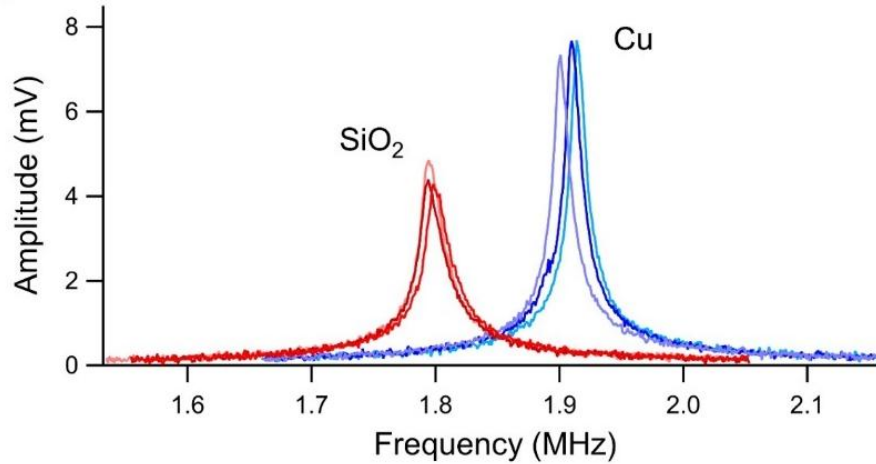


Figure S1. Measured contact resonance frequency f_c : sweeps over SiO₂ and Cu regions.

The measured CR frequencies were converted into indentation moduli M by following the CR-AFM analysis procedure based on a single reference material^{1–3}. Briefly, we used the equation for flexural vibration along a clamped-spring coupled beam to relate the measured CR frequencies to the vertical contact stiffness, k_{vert} , of the tip-sample contact^{4,5}. We modeled our cantilever as a beam with a length $L_c = 125\ \mu\text{m}$, clamped at its base, and tilted at an angle of 12° . The tip has a length of $14\ \mu\text{m}$, and is

coupled to the sample through normal k_{vert} and lateral k_{lat} springs attached at the end of the tip. We have taken $k_{\text{lat}} = 0.85k_{\text{vert}}$ for both SiO_2 and Cu. By numerically solving these equations, we determined $k_{\text{vert}}(f_c)$ at any point of the scanned domain. We have also calculated the average value of k_{vert} over the reference SiO_2 material, $k_{\text{vert}}^{\text{ref}} = k_{\text{vert}}(f_c^{\text{SiO}_2, \text{avg}})$. Finally, under the assumption of a spherical tip in contact with a flat, elastic substrate, we used Hertz contact mechanics to determine the indentation modulus M_{sample} at any point on the map relative to the indentation modulus of SiO_2 , M_{ref} , as⁵:

$$M_{\text{sample}} = \frac{M_{\text{ref}}(k_{\text{vert}}/k_{\text{vert}}^{\text{ref}})^{3/2}}{1 + (M_{\text{ref}}/M_{\text{tip}})(1 - (k_{\text{vert}}/k_{\text{vert}}^{\text{ref}})^{3/2})}. \quad (\text{Eq. S1})$$

The indentation modulus M is defined as $M = E/(1 - \nu^2)$, where E and ν represent the Young's modulus and Poisson's ratio, respectively. For the reference material, SiO_2 , a Young's modulus $E_{\text{SiO}_2} = 72$ GPa and a Poisson's ratio $\nu_{\text{SiO}_2} = 0.17$ were assumed, which correspond to an indentation modulus of $M_{\text{SiO}_2} = 74.1$ GPa. For the diamond tip, the indentation modulus was taken as $M_{\text{Tip}} = 1250$ GPa, with $E_{\text{Tip}} = 1200$ GPa and $\nu_{\text{Tip}} = 0.2$. The interested reader is encouraged to consult supporting references 1-4 for varied and unique applications of CR-AFM.

Details of the Single-Step Indentation Analysis Methodology

Fig. S2 outlines our procedure to fit the elastic portion of the single-step indentation force-depth, P vs h , curves. First, we identified the pop-ins along the loading curve using an in-house developed algorithm, which was then visually checked to ensure accuracy and completeness. This algorithm selects the pop-ins based on the expected value ($\mu(\Delta P(h))$) and the standard deviation ($\sigma(\Delta P(h))$) of the difference between the actual curve and a loess-smoothed version of the curve ($\Delta P(h)$). As such, the algorithm is designed to search for departures that exceed the experimental noise. A sensitivity parameter k controls the threshold for these departures. Once the pop-ins are identified, we proceed with conducting

Hertz fitting of the loading curve up to the elastic limit. As described in the main text, there are two fitting parameters: E_{eff} and R . Measuring the radius of the AFM tip directly is challenging (see Supporting Information Note 7 for details), so we treated R as a fitting variable. It is important to note that different combinations of E_{eff} and R can yield the same force-depth curve, which necessitates setting upper and lower bounds for these parameters. To achieve that, we employed a two-step approach. First, we fitted the unloading segment, which is assumed to represent pure elastic unloading, between $0.9P_{\text{max}}$ and $0.2P_{\text{max}}$ following the well-established Oliver-Pharr (OP) procedure⁶. This fitting enables us to obtain the upper and lower bounds for the tip radius. In the OP procedure, the unloading curve is fitted as a power law of the form⁶:

$$P = A(h - h_f)^m, \quad (\text{Eq. S2})$$

where A , h_f , m are all fitting variables and represent a scaling factor, the final depth, and the exponent of the power law, respectively. The slope of the unloading curve (dP/dh) can be calculated from the OP fitting. The relationship between the contact area, stiffness, and effective modulus is given by⁶:

$$E_{\text{eff}} = \frac{\sqrt{\pi}}{2} \frac{dP/dh}{A} \quad (\text{Eq. S3})$$

Here, for a spherical tip, the contact area A can be computed as:

$$A = \pi(2h_c R - h_c^2), \quad (\text{Eq. S4})$$

with the contact depth $h_c = h_t - \varepsilon[P_t/(dP/dh)]$, and ε a geometric constant⁶. By substituting Eqs. S2 and S4 into Eq. S3, we can calculate the tip radius R by bounding E_{eff} with values from the CR-AFM measurements, $E_{\text{lb(ub)}} = \tilde{E}_{\text{CR-AFM}} \pm \sigma(E)_{\text{CR-AFM}}$. Here, $\tilde{E}_{\text{CR-AFM}}$ and $\sigma(E)_{\text{CR-AFM}}$ are the mean and standard deviation of the modulus measurements from CR-AFM with the subscripts lb and ub for the upper and lower bounds, respectively. Additionally, the fitted exponent m from the Oliver-Pharr procedure was used as a check for the overall shape of the indenter, with values of 0, 1.5, and 2 for flat, paraboloid, and conical indenters, respectively. In summary, the Oliver-Pharr methodology was used only to establish bounds for the solution space during the subsequent Hertzian fitting of the loading curve

up to the first pop-in. The Hertzian fitting was conducted via least-squares minimization with variable starting points (up to the first pop-in) to determine the effective point of initial contact. This approach minimizes artifacts that may arise from surface conditions at the initial point of contact, such as roughness or oxide layers⁷.

Once the values for the modulus and tip radius are obtained, the maximum shear stress at the first pop-in event can be calculated, along with the cumulative plastic excursion length δ . This is defined as the difference in displacement between the elastic response of the material and its actual elastic-plastic response:

$$\delta = h_t - \left(\frac{3P_t}{4E_{\text{eff}}\sqrt{R}} \right)^{2/3} \quad (\text{Eq. S5})$$

The analysis workflow is summarized in the flowchart of Fig. S2a with the relevant variables from the indentation force-depth curves highlighted in Fig. S2b.

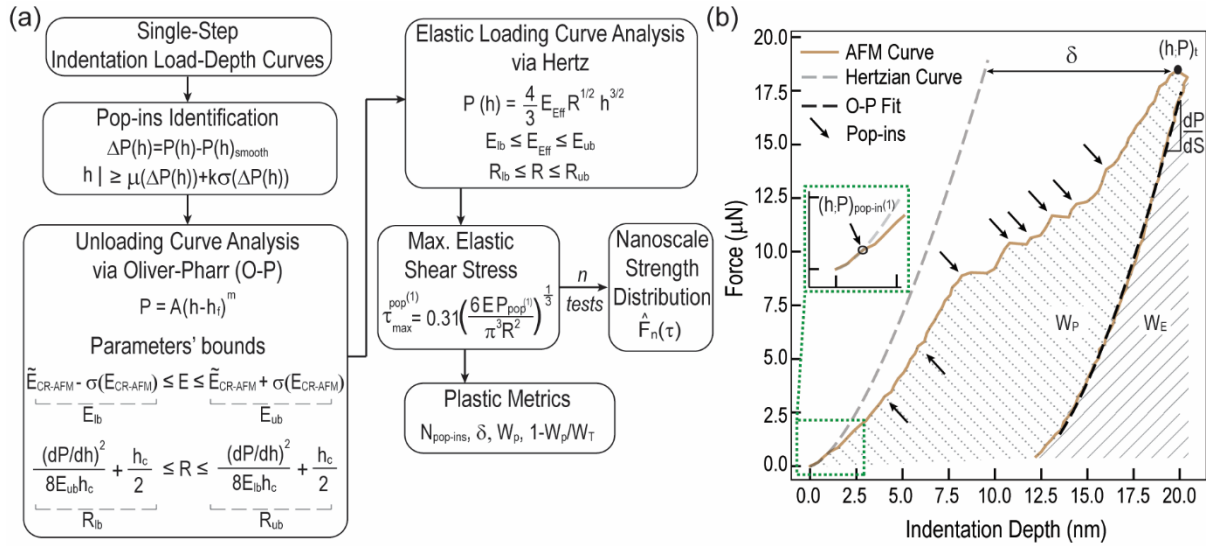


Figure S2. (a) Analysis workflow for single-step indentation curves; (b) AFM-based single-step indentation force-depth curve with relevant fits, events and variables of interest (see (a)) highlighted.

Details of the Multi-Step Indentation Analysis Methodology

The procedure summarized in Fig. S3 was followed to obtain indentation stress-strain curves from multi-step AFM-indentation experiments. Each unloading segment $(P - h)^{(i)}$ of a multi-step indentation curve was fitted between $0.9P_t^{(i)}$ and $0.2P_t^{(i)}$, with the general Hertz expression:

$$P^{(i)} = \frac{4}{3} E_{\text{eff}} \sqrt{R_{\text{eff}}^{(i)}} h^{(i)3/2}, \quad (\text{Eq. S6})$$

where $P_t^{(i)}$ is the maximum load for each step, and E_{eff} is the effective indentation modulus and $R_{\text{eff}}^{(i)}$ the effective radius. In fitting Eq. S6, with $R_{\text{eff}}^{(i)}$ as a sole fitting parameter, it was assumed that the moduli of the sample and tip remained constant (i.e., constant E_{eff}). The value of the effective radius was then used to calculate the contact radius as $r_c^{(i)} = (3P_t^{(i)} R_{\text{eff}}^{(i)} / 4E_{\text{eff}})^{1/3}$, with $(P_t^{(i)}, h_t^{(i)})$ being the maximum load and depth at the maximum load for each segment⁸. Pairs of stress-strain values were ultimately obtained as⁹:

$$\left(\varepsilon_{\text{ISS}}^{(i)}, \sigma_{\text{ISS}}^{(i)} \right) = \left(\frac{4h_t^{(i)}}{3\pi r_c^{(i)}}; \frac{P_t^{(i)}}{\pi r_c^{(i)2}} \right). \quad (\text{Eq. S7})$$

It is important to note that only the stress-strain pairs obtained from unloading fits with scores $R^2 \geq 0.7$ were retained, which means the number of stress-strain pairs may differ from the number of steps. For each experiment, a robust Theil-Sen linear regression was performed to determine the tangent stiffness, also referred to as the plastic slope E_T . From this, the indentation yield stress was calculated as the intersection of the plastic linear path and the 0.2 % offset elastic path. The analysis workflow is summarized in the flowchart of Fig. S3a. An example of a multi-step indentation curve is shown in Fig. S3b with fits on unloading steps and marked stress-strain pairs. The stress-strain curve obtained from this experiment is plotted in Fig. S3c along with its elastic and plastic path fits.

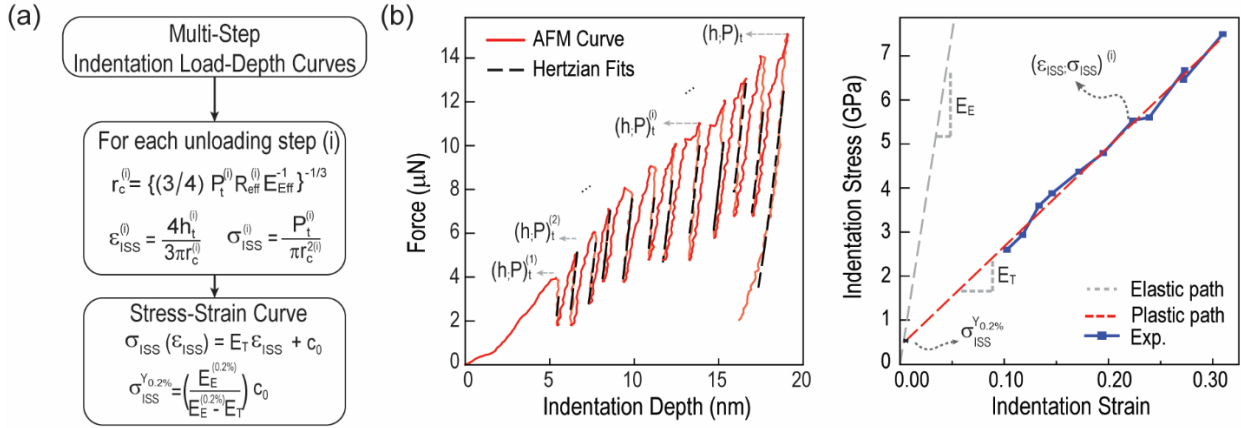


Figure S3. (a) Analysis workflow for multi-step indentation curves; (b) AFM-based multi-step indentation force-depth curve with relevant fits, events, and variables of interest highlighted; (c) the determined stress-strain curve obtained from the multi-step indentation curve shown in (b), with its elastic and plastic path fits.

Incipient Plasticity Characterization

Table S1 presents the experimental parameters during force-spectroscopy measurements on CuPad-1 and CuPad-2 arrays as described in Section 3.2 of the main text.

Table S1. Experimental parameters for AFM single-point indentation tests.

Array	Sensitivity (nm/V)	Cantilever Stiffness (nN/nm)	Approach/Retract Velocity (nm/s)	Number of indents	Spacing between indents (nm)
CuPad-1	510.45	527	200	64	500
CuPad-2	510.45	529	200	62	500

Figures S4 and S5 present 14 randomly selected force-indentation depth curves with parameters specified in Table S1. The detected pop-ins are highlighted with black arrows along each of these curves. The first pop-in is specifically marked with a circle, and the corresponding shear stress, indicating the

initiation of plastic deformation, is annotated. Additionally, we show the Hertzian and Oliver-Pharr fits for both the loading and unloading segments of each curve.

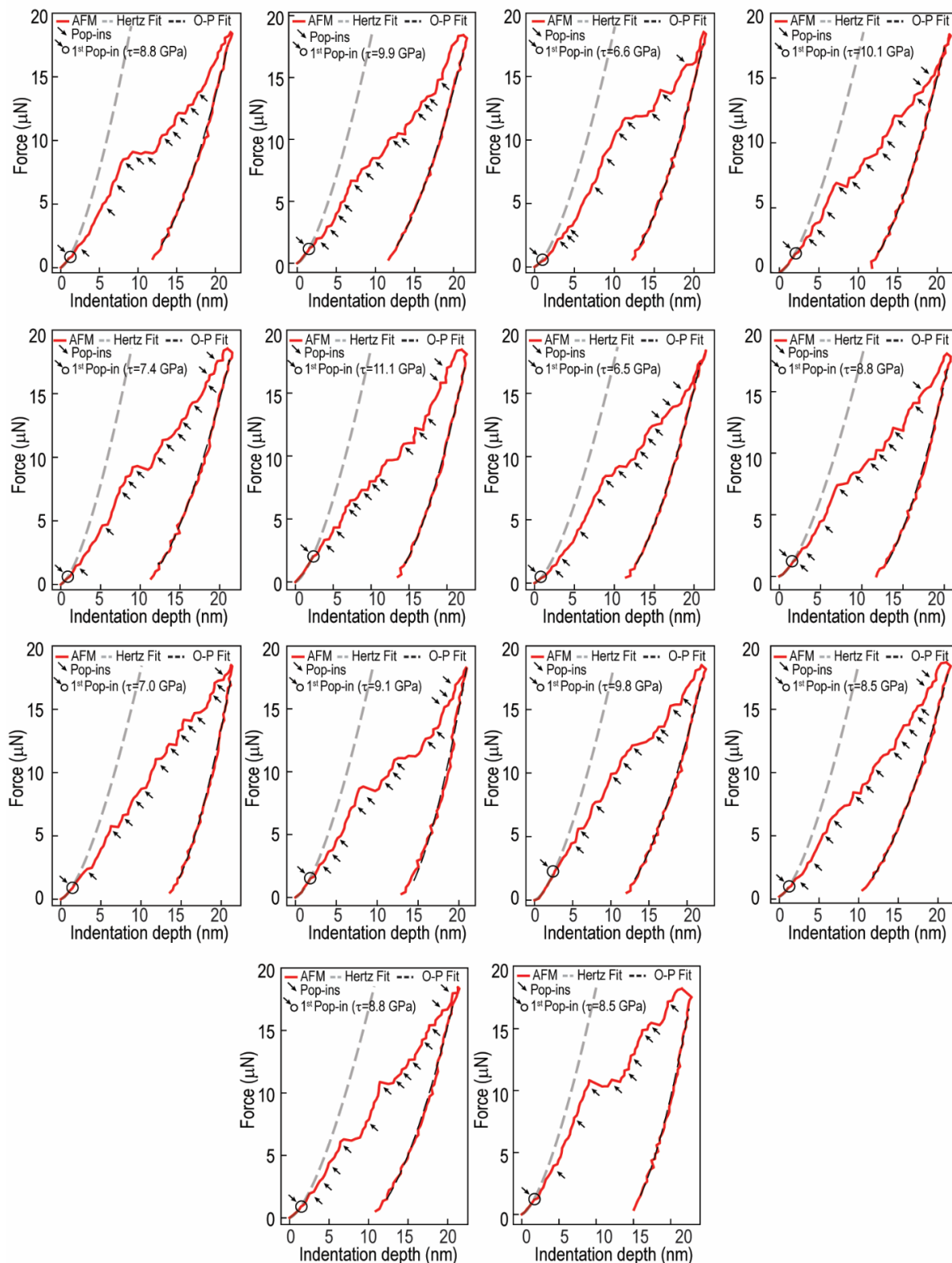


Figure S4. Force-displacement curves of single-step indentations on CuPad-1.

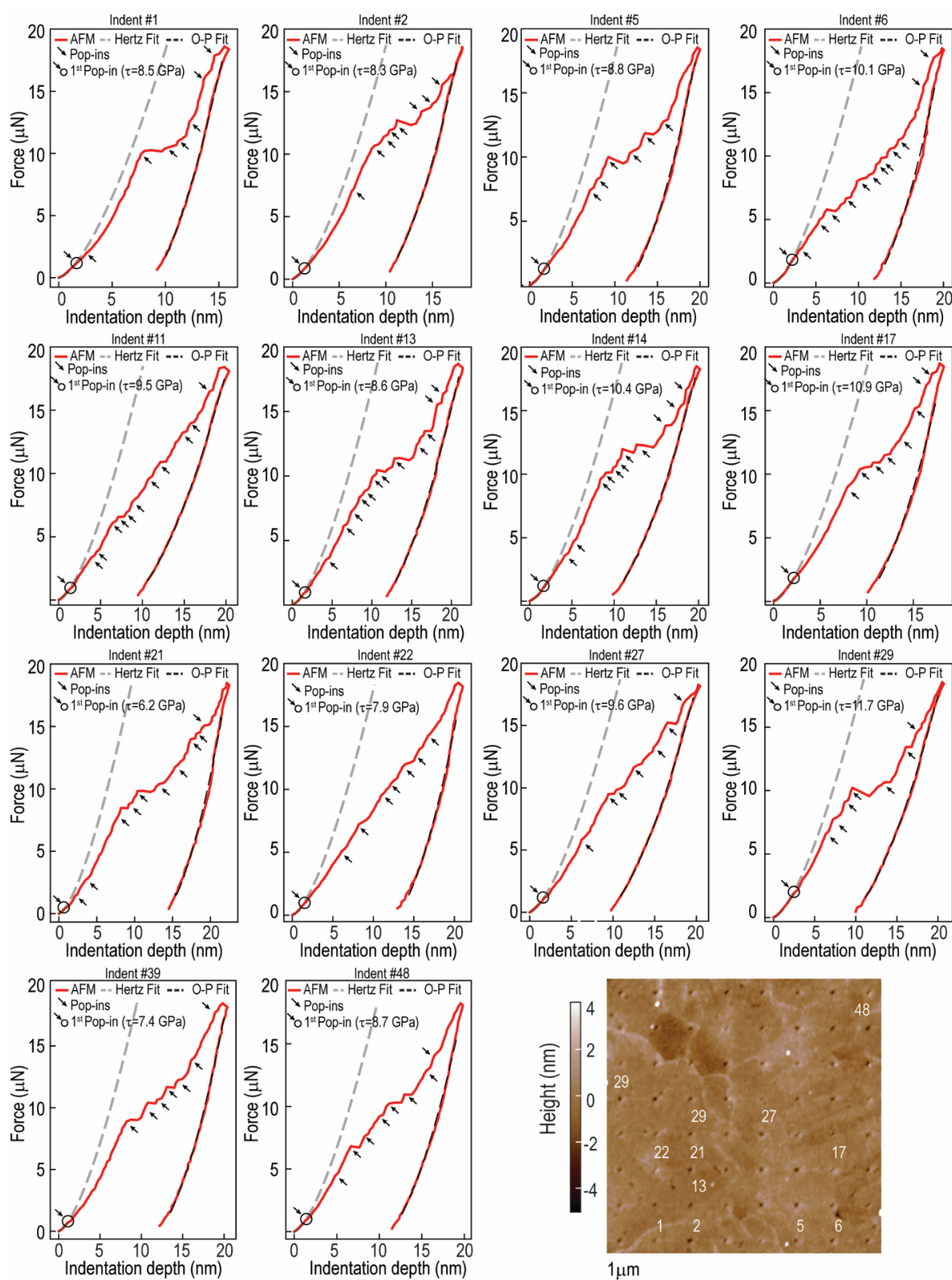


Figure S5. Force-displacement curves of single-step indentations on CuPad-2. The locations of these indents are indicated in the AFM topography image included in the figure.

Influence of Grain Boundaries

Table S2 presents the experimental parameters used during single-step indentation measurements to assess the effect of grain boundaries on the response of copper in hybrid bonding patterns.

Table S2. Experimental parameters for AFM single-step indentation tests within grains and on grain boundaries.

Location	Sensitivity (nm/V)	Cantilever Stiffness (nN/nm)	Approach/Retract Velocity (nm/s)	Number of indents
Grain Interior	510.45	529	200	12
Grain Boundary	510.45	529	200	17

Figure S6 and Figure S7 present a subset of randomly selected force-displacement curves from the indentation measurements performed within grains and on grain boundaries, respectively. The determined pop-ins are highlighted with black arrows along each of these curves. The first pop-in is specifically marked with a circle, and the corresponding shear stress shear, indicating the initiation of plastic deformation, is annotated. Additionally, we show the Hertzian and Oliver-Pharr fits for both the loading and unloading segments of each curve. Topographic maps after indentation are shown, with the locations of the indents corresponding to the curves highlighted.

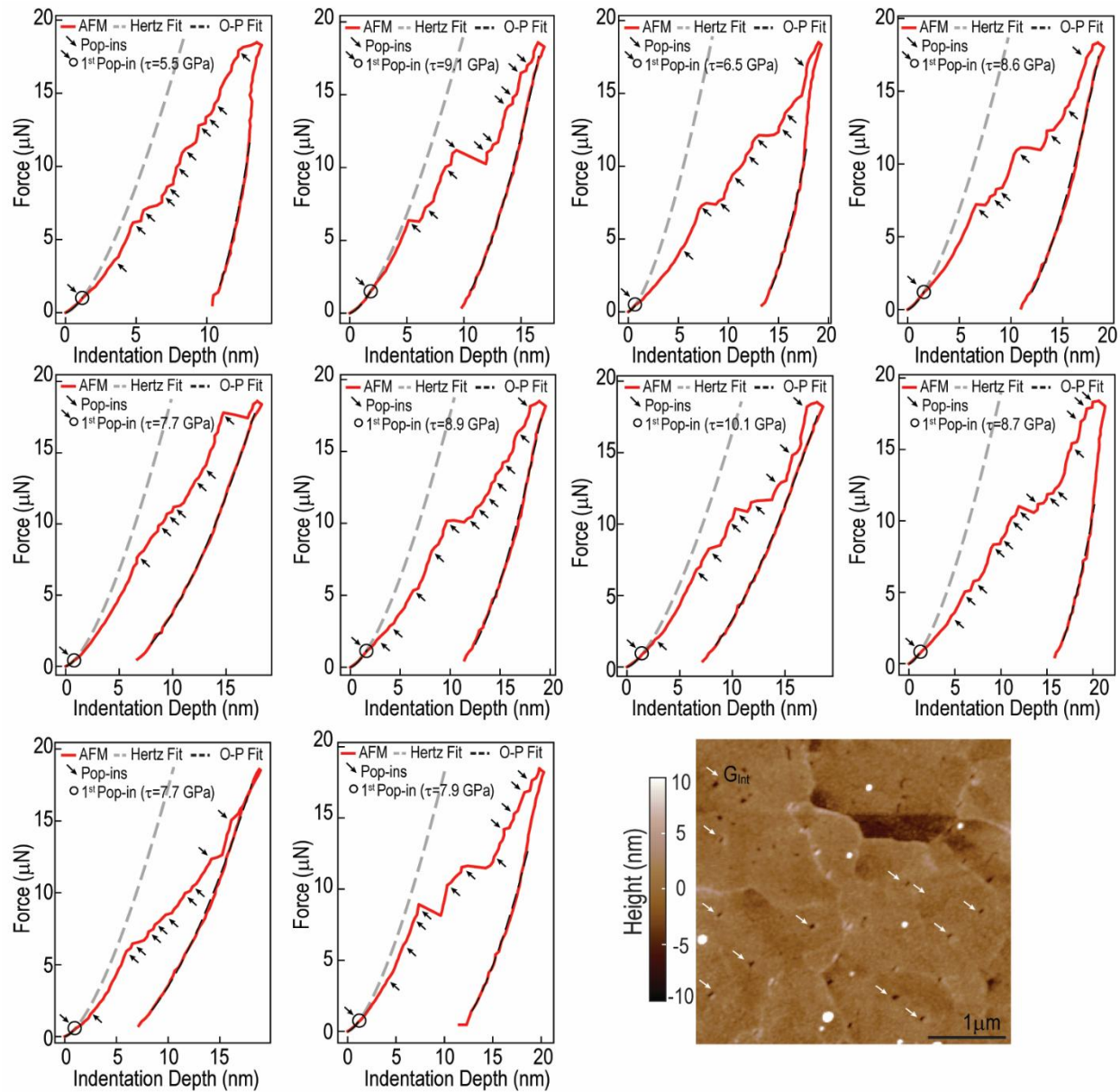


Figure S6. Force-displacement curves of indentations within grains.

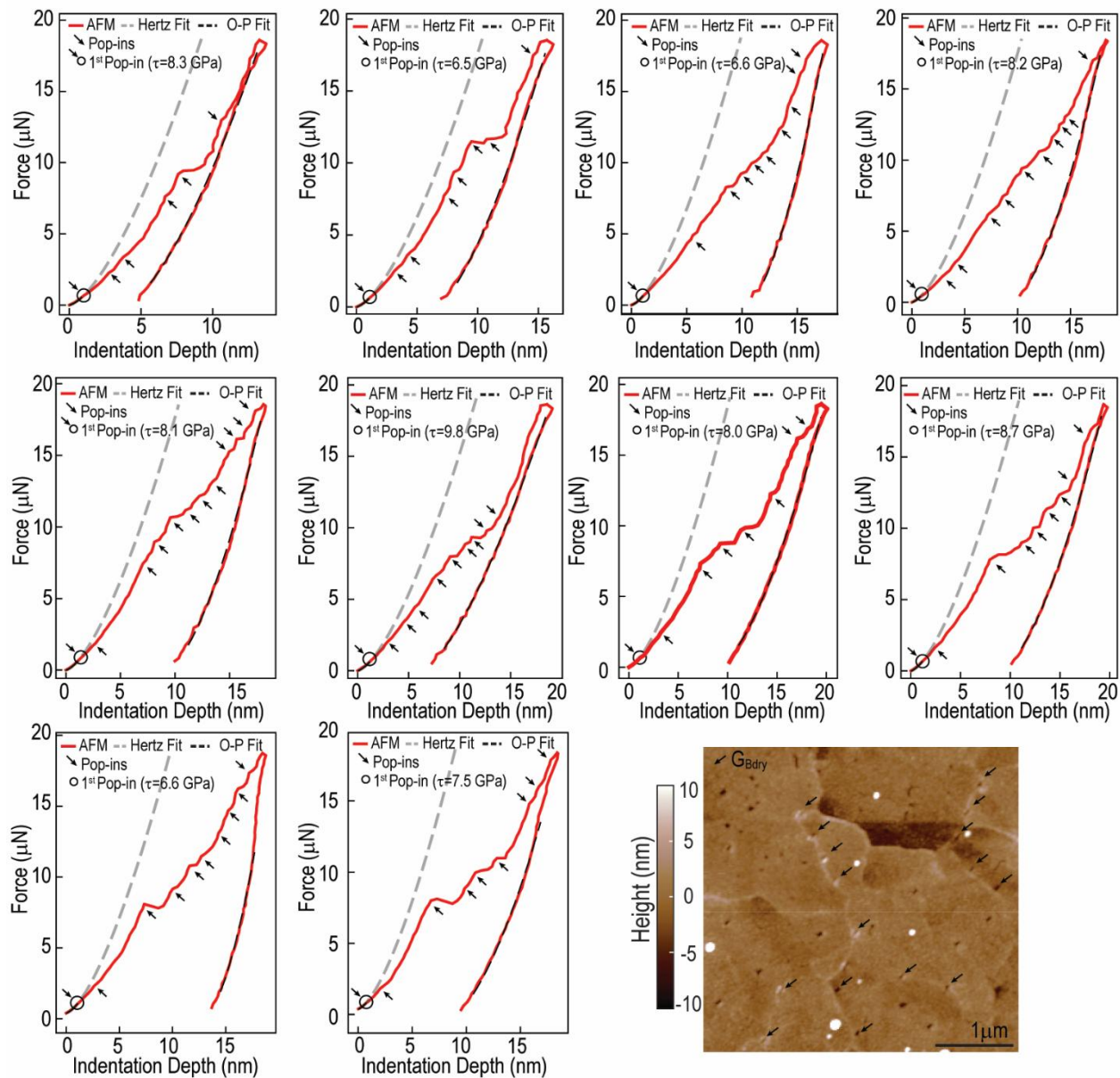


Figure S7. Force-displacement curves of indentations on grain boundaries.

Indentation Stress-Strain Curves

Table S3 presents the experimental parameters during multistep force-spectroscopy measurements performed to obtain the indentation stress-strain pairs presented in Section 3.4 of the main text.

Table S3. Experimental parameters for AFM multi-step indentation tests.

Inverse Optical Lever Sensitivity (nm/V)	Cantilever Stiffness (nN/nm)	Approach/Retract Velocity (nm/s)	Number of Indents
510.45	514	200	20

Figure S8 presents 6 randomly selected force-indentation depth curves, along with their derived indentation stress-strain curves, based on the parameters specified in Table S3. In addition to the AFM curves, the Hertzian fits on the unloading segments are also included. The derived stress-strain curves are shown with their elastic and plastic paths, as well as the indentation yield stress.

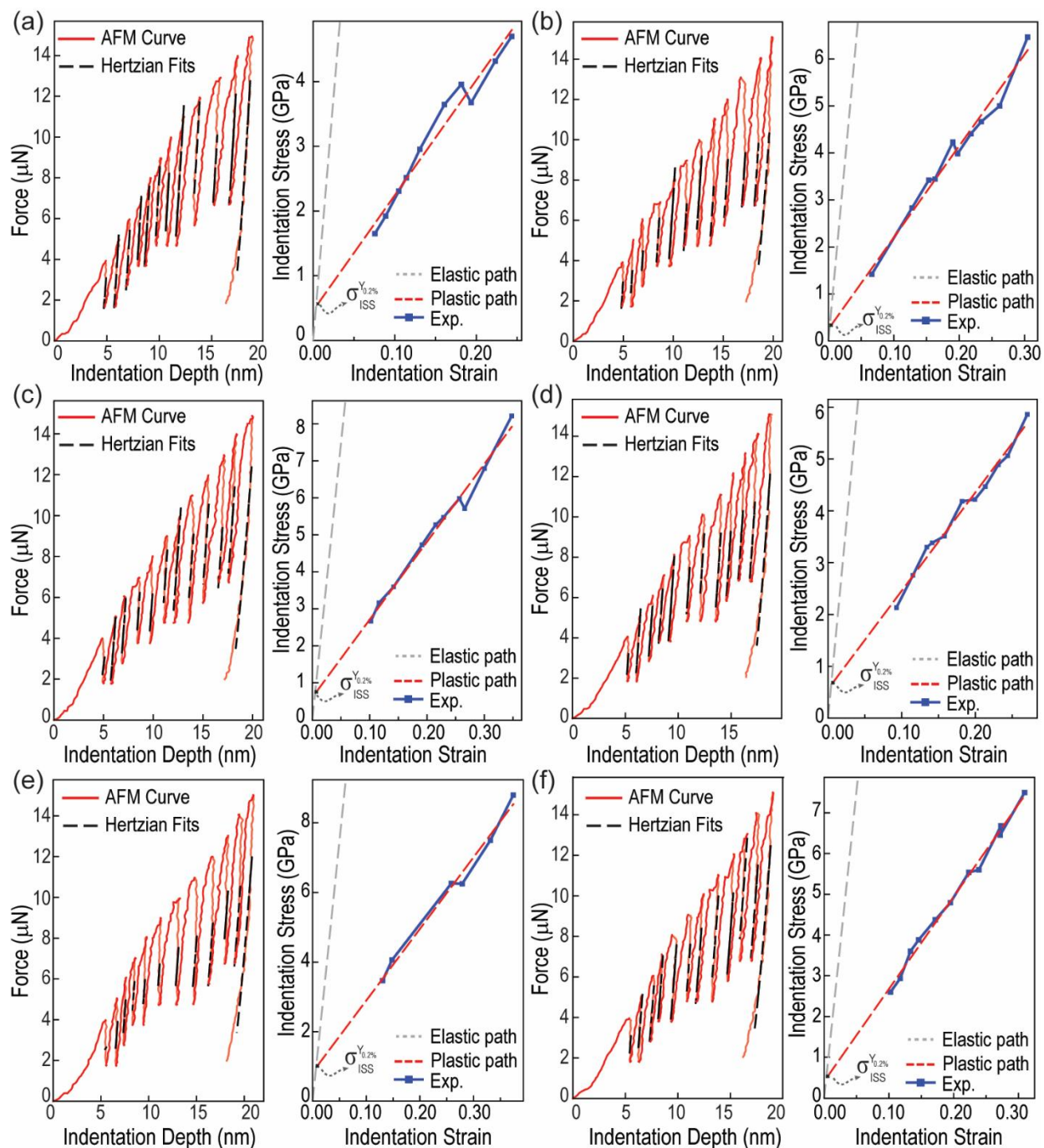


Figure S8. Force-displacement curves and derived indentation stress-strain curves from multi-step indentation measurements.

AFM Probe Tip-Shape Assessment

The analysis used for both single-step and multi-step indentation measurements assumes that the indenter's tip is spherical. However, ex-situ characterization of the tip before indentation is quite challenging, as handling and imaging can carry uncertainty, and more critically, they can deform and damage the tip¹⁰. To address this, we have opted to: i) determine the radius of the tip by fitting the elastic region of the force-indentation depth curves (as explained in Supporting Information Note 2 and Section 3.2 in the main text), and ii) characterize the shape of the tip by imaging it against a TGT1 test grating (K-TEK Nanotechnology, Wilsonville, OR, USA).

Figure S9a presents 2D and 3D AFM topographic images of the TGT1 test grating obtained before and after the single-step indentations. It can be observed that throughout our measurements, which numbered in the hundreds, the tip maintained a spherical end, with only a slight increase in tip radius observed after these numerous measurements (see also cross sections of Fig. S9b). Additionally, Figure S9c presents the statistical distribution of the tip's radius, as obtained from the Hertzian fits of the single-step indentation measurements (Sections 3.2 and 3.3 of the main text). The distribution of the radius from these fits is centered around 12.3 nm with a standard deviation of 1.4 nm. These values align with those reported by the vendor. In the case of our multi-step indentation experiments, we used a different tip than the one employed for the single-step indentations. Alongside the multi-step experiments, we also carried out a series of single-step indentations to determine the physical radius of the tip. From these measurements, we obtained a statistical distribution for the tip radius, centered at 22.0 nm with a standard deviation of 2.5 nm (see Fig. S9d). Consequently, the tip used for the multi-step indentations discussed in Section 3.4 is slightly larger than the one used for the single-step indentations reported in Sections 3.2 and 3.3 of the main text.

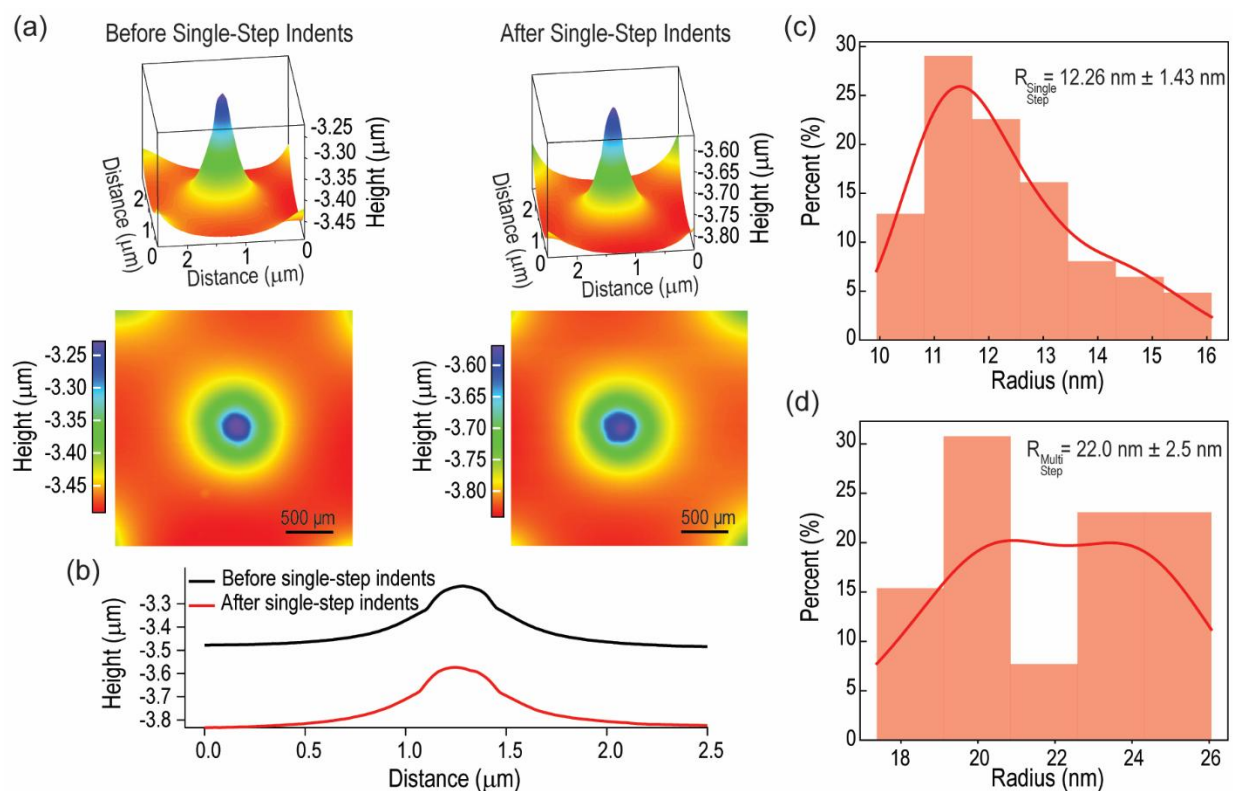


Figure S9. Shape characterization of the tip used in single-step and multi-step indentation measurements. (a) 2D and 3D topography scans of TGT1 test grating before (left) and after (right) indentations; (b) 1D height profile from a transverse cross section across the topographies shown in (a); (c) Statistical distribution of tip radius used for single-step indentations, obtained from analyzing the elastic region of the force-depth curves from single-step indentation experiments; (d) Statistical distribution of tip radius used for multi-step indentations, obtained from analyzing the elastic region of force-depth curves from several single-step indentations conducted alongside the multi-step indentation experiments.

NOTES

Certain commercial equipment, software, instruments, and materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

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