

# SUPPORTING INFORMATION

## Evolution of Hierarchically Layered Cu-rich Silicide Nanoarchitectures

Ibrahim Saana Amiin, Nilotpal Kapuria, Temilade Esther Adegoke, Angelika Holzinger,  
Hugh Geaney, Micheál D. Scanlon, and Kevin M. Ryan\*

Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland

Department of Chemical Sciences, University of Limerick, Limerick, V94 T9PX, Ireland

### Experimental section

**Materials and reagents:** All materials and chemical reagents were obtained from various reliable suppliers and used without modifications. Phenylsilane (97.0%) and Squalane ( $\geq 98\%$ ) were supplied by Fluorochem and stored in an argon-filled glovebox ( $< 0.1$  ppm  $O_2/H_2O$ ) until used. High-purity planar Cu-foils ( $\sim 99.9\%$  metal basis) was obtained from Pi-Kem Ltd. Squalane ( $\geq 98\%$ ), reducing agent ( $LiBH_4$ ; 2M in tetrahydrofuran) and copper chloride ( $\sim 99.999\%$ ), as well as methanol and toluene were acquired from Sigma-Aldrich, Ireland.

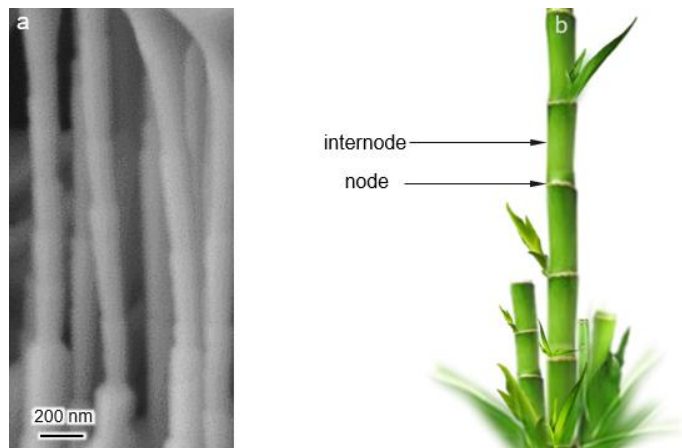
**Synthesis of  $\rho$ -Cu<sub>15</sub>Si<sub>4</sub>:** Typically, a 100  $\mu$ m thick Cu-foil ( $\sim 99.9\%$  metal basis) was surface graded cross-wise with a sand-paper (P-600 grit) and then ultrasonically washed in toluene to remove surface oxide-layers, impurities, and to increase the surface area. A  $3.0 \times 1.0$  cm strip of the treated Cu-foil was then placed in 5.0 mL of HBOS (Squalane:  $\sim 96\%$ ) in a cylindrical glass vial. The solution was mounted on a Stuart CD-162 type hotplate and ramped to  $\sim 450$  °C in an Ar-filled glove box ( $< 0.1$  ppm  $O_2/H_2O$ ). After boiling for  $\sim 15$  min,  $\sim 0.5$  mL of phenylsilane ( $\sim 97\%$ ) was carefully injected followed by adding 2–3 microneedle drops of a reducing agent (2M  $LiBH_4$ ) after 2–5 min of reaction and then allowed to proceed undisturbed for  $\sim 90$  min. The reaction was quenched by directly removing the substrate after switching off the hotplate. The pinkish-orange Cu-foil surface turned to dark-gray in colour, indicating the formation of copper-

silicide (average mass:  $\sim 0.21$  mg). The product was then soaked and rinsed in toluene for  $\sim 30$  min, dried at  $100\text{ }^{\circ}\text{C}$ , and stored in the glovebox until structural characterisation.

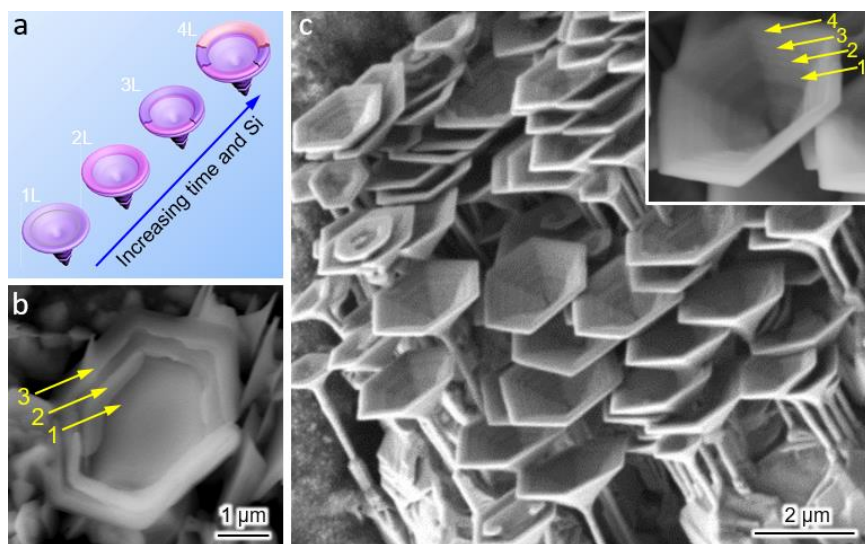
**Electrochemical growth of Cu crystals:** Typically,  $\sim 1.20$  g of copper chloride was first dissolved in  $\sim 45$  mL of methanolic solution by magnetic stirring. Then, 3 mL of the Cu solution was dispensed into toluene to yield 15 mL. The surface graded Cu-foils ( $3.0 \times 1.0$ ) were used as both positive and negative electrodes for the Cu-crystal growth. A potential of 150 V was then applied for 5 min using a high voltage power supplier (TECHNIX SR-5-F-300). The obtained samples were rinsed in toluene and dried at  $100\text{ }^{\circ}\text{C}$  and then used as the substrate for the synthesis of  $p\text{-Cu}_{15}\text{Si}_4$  in a similar procedure as described above.

**Materials Characterisation Techniques:** Field emission scanning electron microscopy (SEM) analysis was performed using SU-70 Hitachi (MSB011) operated at 5–20 kV with a built-in energy dispersive spectrum (EDX) analyser (Oxford instruments). All samples were directly analysed soon after synthesis without any further treatment. Cross-sectional analysis was carried out on a double-beam focused ion beam (FIB)-SEM on a FEI Helios G4 CX microscope at 30 kV. A thin layer of Pt/C was deposited by ion beam induced deposition (IBID) on the sample surface as a protector. A JEOL JEM-2100F (MSB005) equipped with a Gatan Ultrascan CCD camera and an EDAX Genesis EDX detector and operated at 200 kV was used for the transmission electron microscopy (TEM) analysis. The  $p\text{-Cu}_{15}\text{Si}_4$  was harvested from the Cu-foil by gently scraping into methanolic solution and drop cast onto a grid of lacey carbon film (200 Mesh Nickel) for the TEM imaging and analysis. An X-Pert (MSG-006) PRO MRD instrument equipped with an X'celerator detector and a Cu  $K\alpha$  radiation source ( $\lambda = 1.5418\text{ \AA}$ ) was used to collect the X-ray diffraction patterns. Electrochemical synthesis of Cu-crystal was carried out largely in a toluene solution with the positive and negative electrodes separated 2 mm apart. A high voltage power unit (TECHNIXSR 5-F-300, S/N: BU-08/04971) equipped with a voltage monitoring device (Black Star 3225 MP milliammeter) was used to induce the Cu crystal growth.

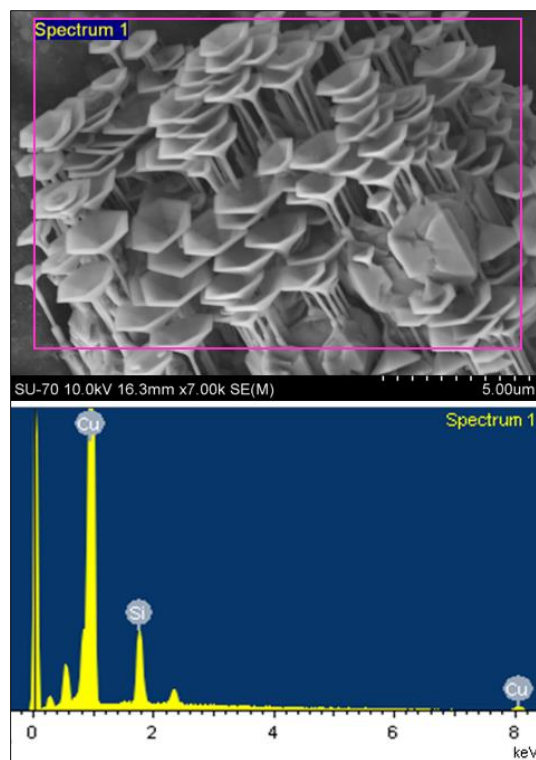
## Supplementary Figures



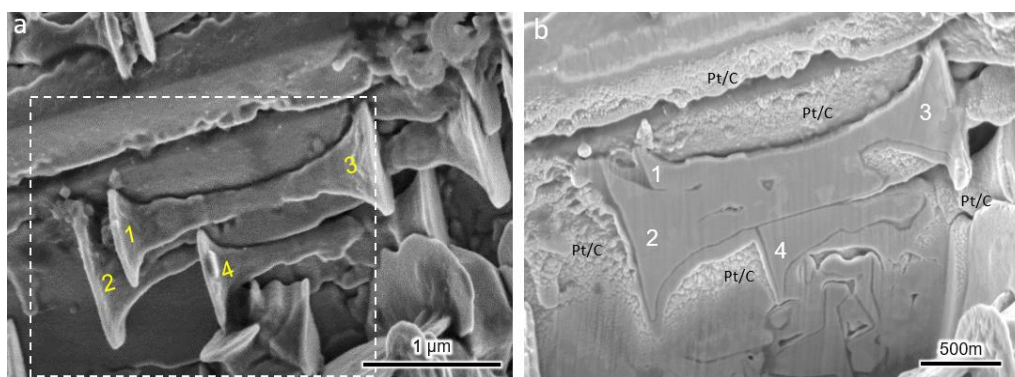
**Figure S1.** (a) SEM image showing the node-internode-like features of  $\rho\text{-Cu}_{15}\text{Si}_4$  compared to that of (b) a bamboo stalk.



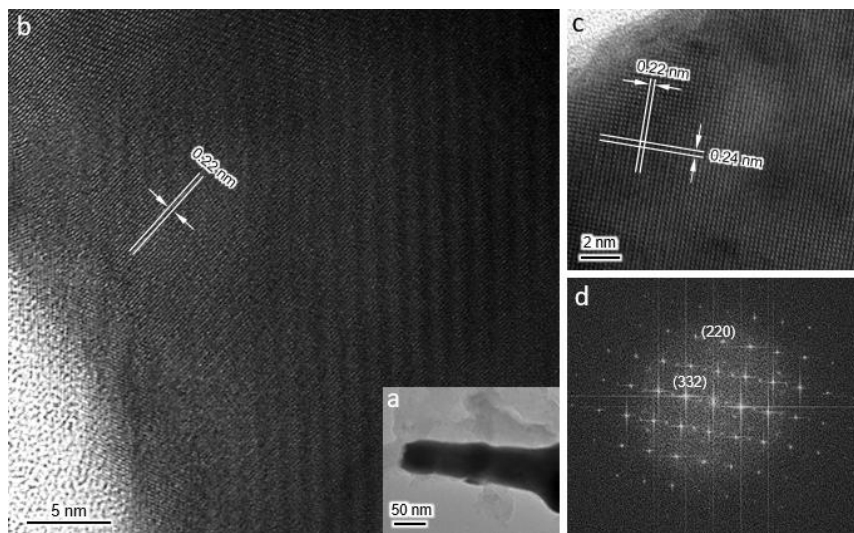
**Figure S2.** Model illustration (a) and SEM images (b, c) of the formation of the layered features of the cap section.



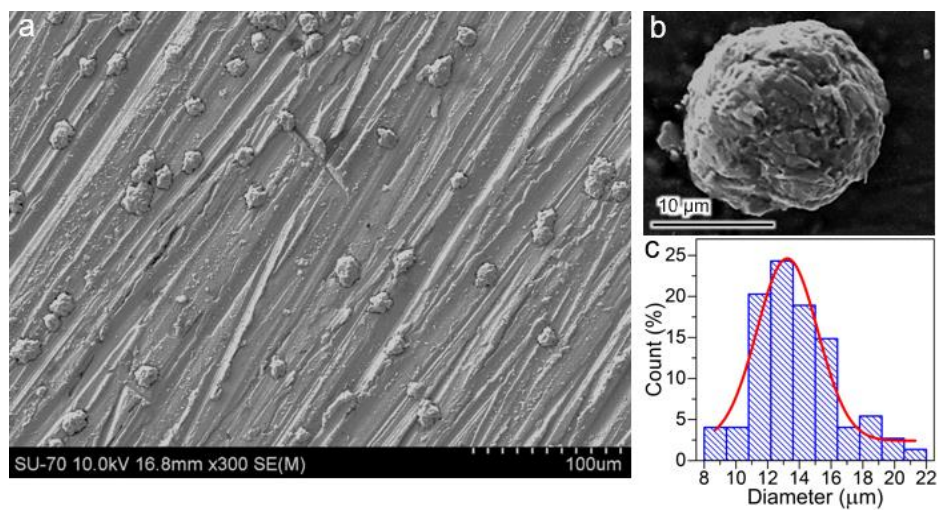
**Figure S3.** SEM image of the  $\rho\text{-Cu}_{15}\text{Si}_4$  and energy dispersive X-ray spectrum confirming the presence of Cu and Si.



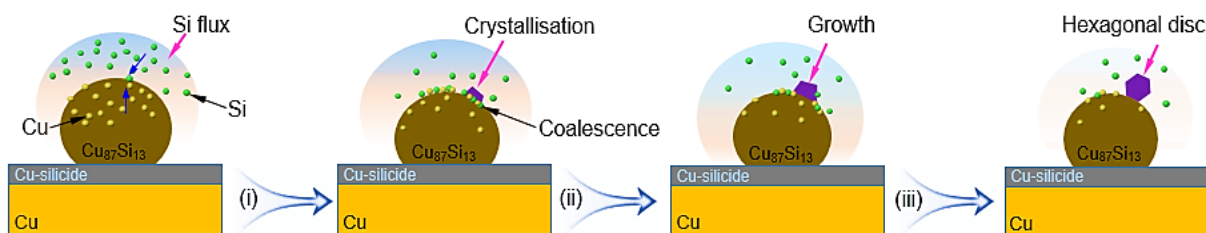
**Figure S4.** SEM image of  $\rho\text{-Cu}_{15}\text{Si}_4$  (a) before and (b) after FIB sectioning.



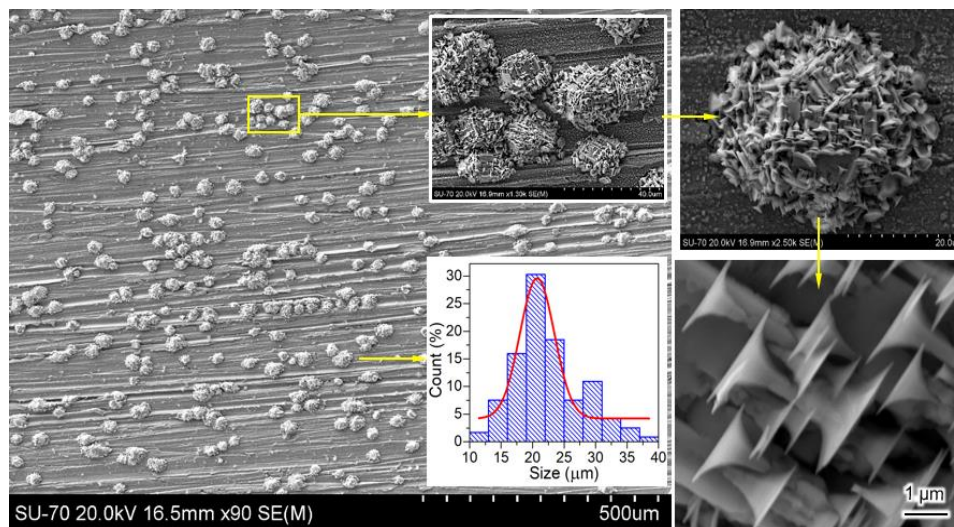
**Figure S5.** (a-c) TEM images and (d) selected area electron diffraction pattern of the stem section of  $\rho\text{-Cu}_{15}\text{Si}_4$ .



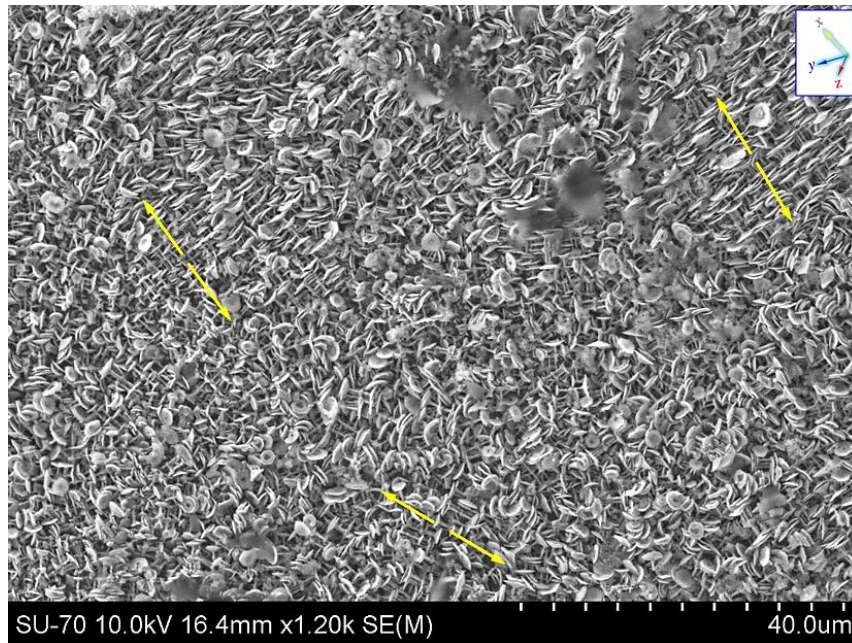
**Figure S6** (a, b) SEM images of the initially formed Cu-silicide grains, that served as islands for growth of the  $\rho\text{-Cu}_{15}\text{Si}_4$  and (c) Gaussian-fitted size distribution histogram (average size:  $\sim 13.7 \pm 6.7 \mu\text{m}$ ).



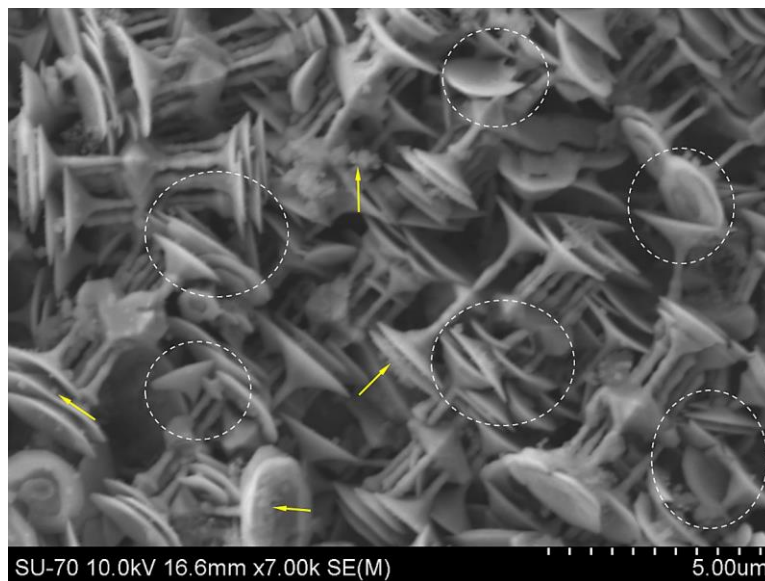
**Figure S7** A schematic illustration of the potential mechanism for the disc formation on the spherical grains: (i) Cu atoms diffuse into atomic Si precipitates at the interface between spherical grains and Si flux, (ii) interdiffusion leads to coalescence and crystallisation and (iii) continuous diffusion of Cu and Si atom leads to growth of the discs.



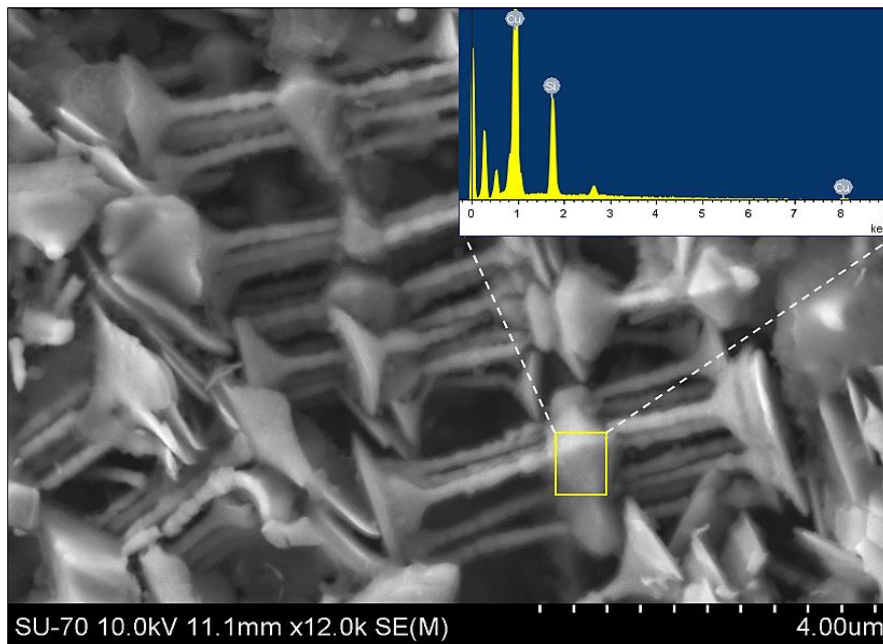
**Figure S8** SEM images of the grown  $\rho$ - $\text{Cu}_{15}\text{Si}_4$  on the spherical crystallite grains at different magnifications and Gaussian-fitted size distribution histogram. (average size:  $\sim 22.46 \pm 14.2 \mu\text{m}$ ).



**Figure S9** SEM image of dense  $\rho$ - $\text{Cu}_{15}\text{Si}_4$  grown in high yield using pre-grown Cu crystals. Yellow arrows show the growth alignment.



**Figure S10** SEM images of high density  $\rho$ - $\text{Cu}_{15}\text{Si}_4$  showing the phenomenon (dashed circles) of grow hindrance and fracture/displacement, and the formation of small surface nanoparticles (arrows).



**Figure S11** EDX spectrum (inset) of  $\rho$ - $\text{Cu}_{15}\text{Si}_4$  indicating the presence of Cu and Si in the growth crystal base, confirming that the pre-grown Cu crystals have also been converted to Cu silicide.