Supporting Information for:

Electrochemical formation and surface characterisation of $Cu_{2-x}Te$ thin films with adjustable content of Cu

Minghua Huang, Artjom Maljusch, Federico Calle-Vallejo, John B. Henry,

Marc T.M. Koper, Wolfgang Schuhmann, Aliaksandr S. Bandarenka

1. Stability of Cu atoms inserted into Te surfaces

The calculated stabilities of Cu atoms at various concentrations and depths of Te surfaces shown in Figure 1 in the main text are presented in Table S1.

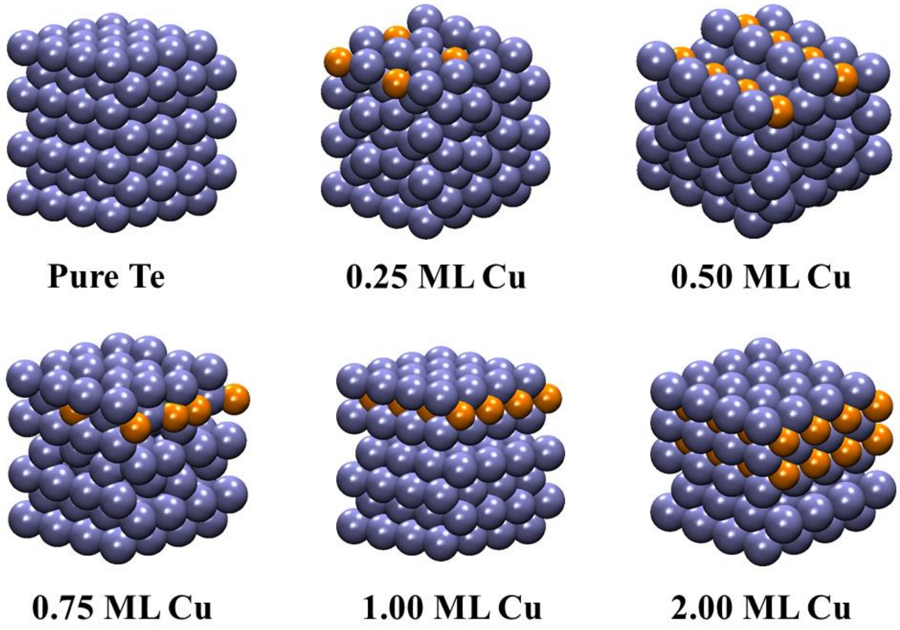
Table S1. Concentration, location and stability of Cu atoms within Te surfaces. The reference (-) for the concentrations up to 1 ML is the energy of Cu atoms in the 2nd layer, whereas for 2 ML it is that of the 1st + 2nd layers. The most stable configuration for a given concentration is marked in bold.

Cu content / ML	Layer	Δ E / eV/Cu
0.25	**1st**	**-0.43**
	2nd	-
	3rd	0.84
	4th	0.48
0.50	**1st**	**-0.31**
	2nd	-
	3rd	0.11
	4th	0.13
0.75	1st	0.15
	2nd	**-**
	3rd	0.31
	4th	0.29
1.00	1st	0.94
	2nd	**-**
	3rd	0.23
	4th	0.35
2.00	1st + 2nd	-
	1st + 3rd	0.05
	1st + 4th	-0.21
	2nd + 4th	**-0.50**

Besides, we calculated the work function and the average number of valence electrons per Cu atom for the most stable configurations in Table S1 (See also Figure 6a in the main text). The results are shown in Table S2 where we also included the data for pure Te and Cu.

Table S2. Work function and valence electron counting for the most stable surface configurations on Table S1.

Cu content / ML	Cu Location	Φ / eV	e^- on Cu atoms
Te(0001)	-	4.766	-
0.25	1st	4.882	10.79
0.50	1st	4.867	10.83
0.75	2nd	4.835	10.88
1.00	2nd	4.749	10.81
1.50	2nd	4.726	10.86
2.00	2nd + 4th	4.584	10.82
Cu(111)	1st	4.703	11.02



Pure Te **0.25 ML Cu** **0.50 ML Cu**

0.75 ML Cu **1.00 ML Cu** **2.00 ML Cu**

Figure S1. Most stable structures for each used (sub)surface Cu concentration at a Te electrode surface.

2. Experimental Details

2.1. Cu intercalation into Te

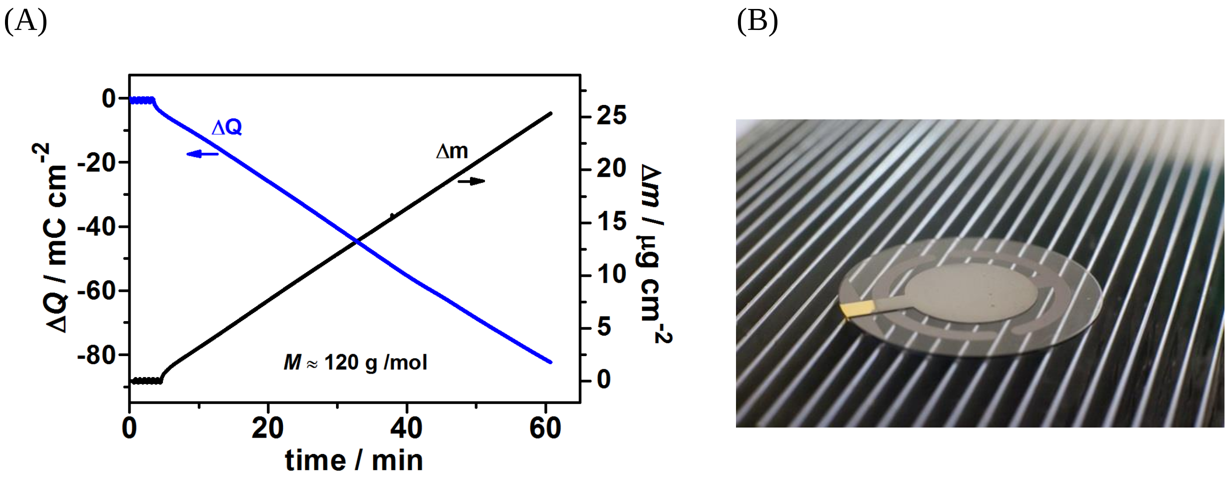


Figure S2. (A) Electrode mass change and the total charge passed during cathodic deposition of a ~100 ML Te film and (B) a photographic image of the resulting sample (a quartz crystal with Au electrodes; the WE-side is coated with a thin film of Te).

2.2. SKP measurements

SKP is a non-contact, non-destructive vibrating capacitor technique which measures the contact potential difference (CPD) between an electrically conductive vibrating reference probe and an electrically conductive sample. Briefly, a conventional SKP used in this work consists of a plane-ended cylindrical electrode vibrating perpendicular to a stationary sample with a frequency ω (Figure S3). In this way, both electrodes form a planar capacitor. If an external electrical contact between the two capacitor plates is formed their Fermi levels start to equalize and the resulting charge flow causes a potential gradient (U_{CPD}). Periodic modulation of the distance between the electrodes, $d = d_0 + \Delta d*\sin(\omega t)$ leads to changes in the capacitance, (dC/dt), thereby causing a so-called Kelvin current (I_{Kelvin}) to flow through the external circuit (Equation S1).

$$\boldsymbol{I_{Kelvin} = \Delta\Psi^{KP}_{Sample} * (\varepsilon * \varepsilon_0 * A * \Delta d * \omega)\frac{cos(\omega t)}{(d_0 + \Delta d(sin(\omega t))^2}} \tag{1}$$

where $\Delta\Psi^{\mathrm{KP}}_{\mathrm{Sample}}$ is the contact potential difference between the Kelvin probe and the sample, ε is the dielectric constant of the medium, ε_0 is the vacuum permittivity, *A* is the active tip area, Δ*d* is the tip oscillation amplitude, *ω* is the tip oscillation frequency, d_0 is the main tip-to-sample distance

In the conventional nulling technique used in this work a variable backing potential (U_0) is adjusted until the Kelvin current (I_{Kelvin}) vanishes. When U_0 is equal to $-U_{CPD}$, the electric field between the capacitor plates is compensated and a zero output signal is recorded (Equation S2). In this case, the contact potential difference between the Kelvin probe and the sample is equal to the applied compensation voltage.

$$\boldsymbol{I_{Kelvin} = (\Delta\Psi^{KP}_{Sample} - U_0) * \frac{dC}{dt} = 0, \quad if\ \Delta\Psi^{KP}_{Sample} = U_0} \tag{2}$$

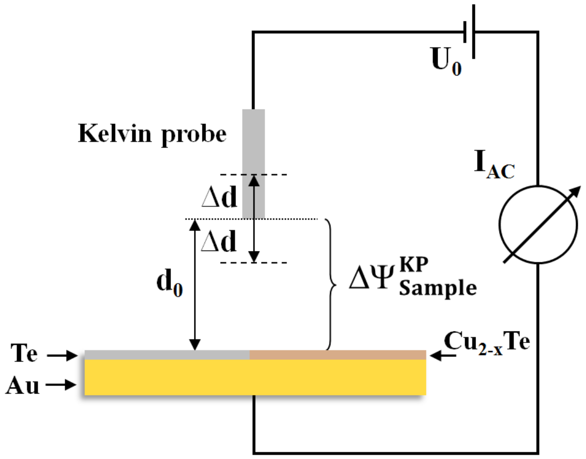


Figure S3. Schematic representation of the set-up for the measurement of the contact potential difference ($\Delta\Psi^{\mathrm{KP}}_{\mathrm{Sample}}$ – the contact potential difference between the Kelvin probe and the sample, d_0 - main tip-to-sample distance, Δd - tip oscillation amplitude, U_0 - variable backing potential, I_{AC} – Kelvin current).

3. The work function and CPD

The work function (Φ) is defined as the minimum work needed to extract electrons from the Fermi level of a solid carrying no net charge [1]. It is assumed that the electron is removed to a position just outside the sample (end position) where the interaction between the solid and the electron is no longer existent, i.e. the contribution from the image forces is eliminated, while the dimension of the surface is large compared to the distance between the surface of the solid and the end point (Fig. S4A).

Connection of two solids with different work functions Φ^A and Φ^B leads to a flow of electrons until a uniform redistribution of electrons at the Fermi levels of both solids is reached. As the work functions of both solids are different, the equilibration of Fermi levels causes charging of one solid relative to the other. This leads to the observation of a Volta potential difference which is also called contact potential difference (CPD, denoted as $\Delta\Psi$) and is equivalent to the difference in the work functions of the two solids. As the work function of the solid is an intrinsic parameter, it remains constant after connection of two different solids while the electrochemical potential of the electrons within both phases become identical (Fig. S4B). Therefore, as the change of the work function of the SKP-SECM tip during the experiment remains negligibly small, the observed changes of the CPD are related to changes of the work function of the sample as a consequence of its modification by intercalation of Cu.

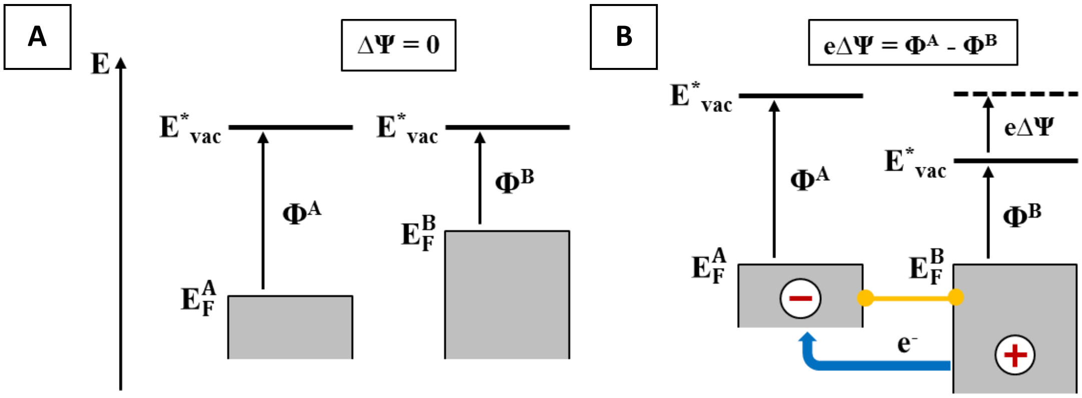


Figure S4. Schematic representation of the relationship between work function (Φ) and contact potential difference (ΔΨ).

[1] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught, A. Wilkinson. Blackwell Scientific Publications, Oxford (1997)