Supporting information

The Kirkendall Effect in Binary Alloys: Trapping Gold in Copper Oxide Nanoshells

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1. Selective area electron diffraction of nanowires annealed for 5 min at 300°C

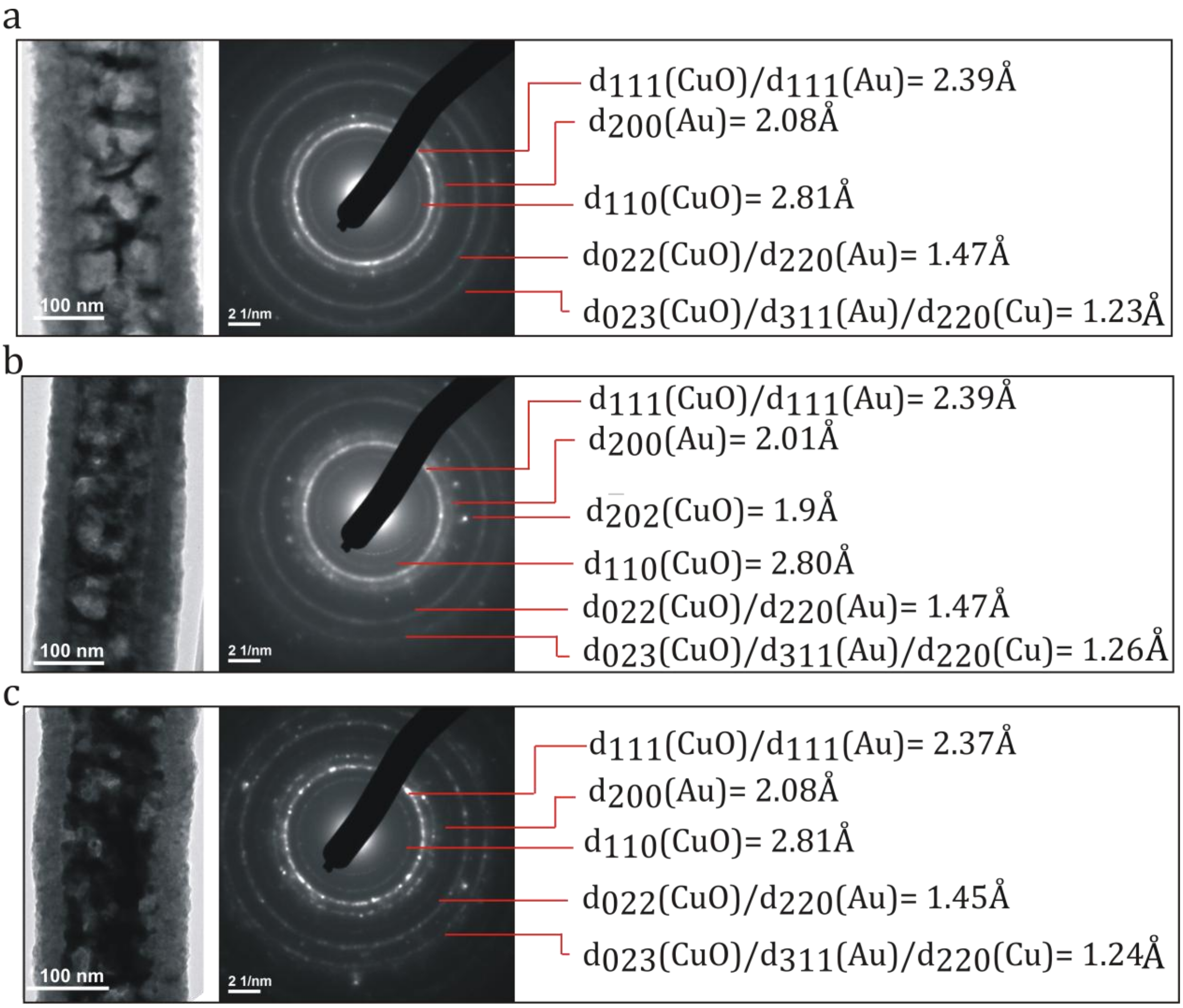

Figure S1. Bright-Field TEM micrographs and the associated selective area electron diffraction patterns of Au-Cu nanowires with various Au contents after thermal oxidation during 5 min for an annealing temperature of 300 °C: (a) 4 at. %, (b) 8 at. % and (c) 16 at. %. The electron diffraction patterns have been indexed according to the monoclinic CuO (JCPDS 89-5895), cubic Au (JCPDS 65-2870) and cubic Cu (JCPDS 85-1326).

2. Evolution of the total diameter and the oxide shell thickness of the nanotube for an annealing temperature of 300°C

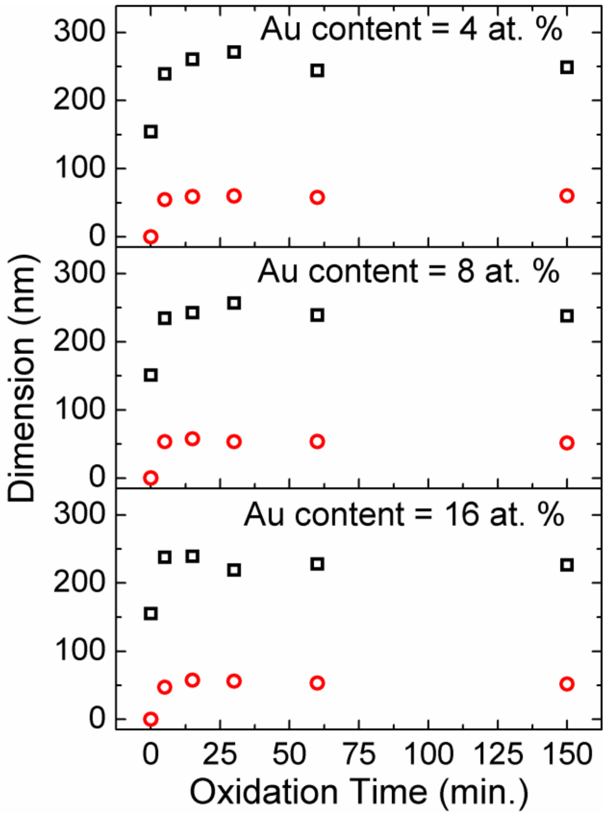

Figure S2. Evolution of the total diameter of the nanotubes (open black squares) and the oxide shell thickness (open red circles) as a function of the oxidation time for an annealing temperature of 300°C. The standard deviation deduced from three measurements is about 4 nm.

3. Description of the method employed to estimate the gold content using the TEM micrographs

In order to calculate the atomic gold content from the TEM micrographs in Figure 1**,** it is assumed that the material inside the nanowire is entirely constituted of gold and has the geometrical form of a cylinder surrounded by a CuO oxide shell. This calculation has been applied on the samples exhibiting a wire-in-tube structure obtained after thermal oxidation for 150 min (Figure 1 b-c), *i.e.*, for an Au content of 8 and 16 at. % as determined experimentally by EDS on the non-oxidized samples.

The volume of the gold wire (V_{Au}), the volume of the inner part ($V_{inn.}$) and the one of the entire tube ($V_{tot.}$) can be calculated by following equation S1:

$$V_X = \pi \frac{d_X^2}{4} L \quad (cm^3) \quad \textbf{Equation S1}$$

where V_x and d_X (cm) represent the volume and the diameter of the considered 1D object, respectively. They can be deduced from the TEM micrographs presented in Figure 1. L stands for the length of the1D object.

The volume of the copper oxide shell (V_{CuO}) can be calculated as follow:

$$V_{CuO} = V_{tot.} - V_{inn.} \quad (cm^3) \quad \textbf{Equation S2}$$

On the other hand, the number of moles of Au (n_{Au}) and CuO (n_{CuO}) in the considered volume can be calculated using equation S3:

$$n_X = \frac{\rho_X V_X}{M_X} \quad (mol) \quad \textbf{Equation S3}$$

where ρ_X (g/cm^3) and M_X (g/mol) represent the density and the molar mass of the considered material X (here Au or CuO), respectively. The density, ρ , is equal to 6.31 g/cm^3 and 19.3 g/cm^3 for CuO and Au, respectively. The molar mass, M, is 79 g/mol and 197 g/mol for CuO and Au, respectively.

From the geometric data deduced from TEM, the atomic gold content (at_c. % Au) can be estimated from the following equation:

$$at_c.\%Au = \frac{n_{Au}}{n_{Au} + n_{CuO}} .100 \quad (\%) \qquad \textbf{Equation S4}$$

Finally, the estimated gold content can be calculated according to equation S5:

$$at_c.\%Au = \frac{1}{(1 + \frac{\rho_{CuO}}{\rho_{Au}} . \frac{M_{Au}}{M_{CuO}} . \frac{(d^2_{tot.} - d^2_{inn.})}{d^2_{Au}})} .100 \quad (\%) \qquad \textbf{Equation S5}$$

4. Evolution of the total diameter of the nanotube for an annealing temperature of 600°C.

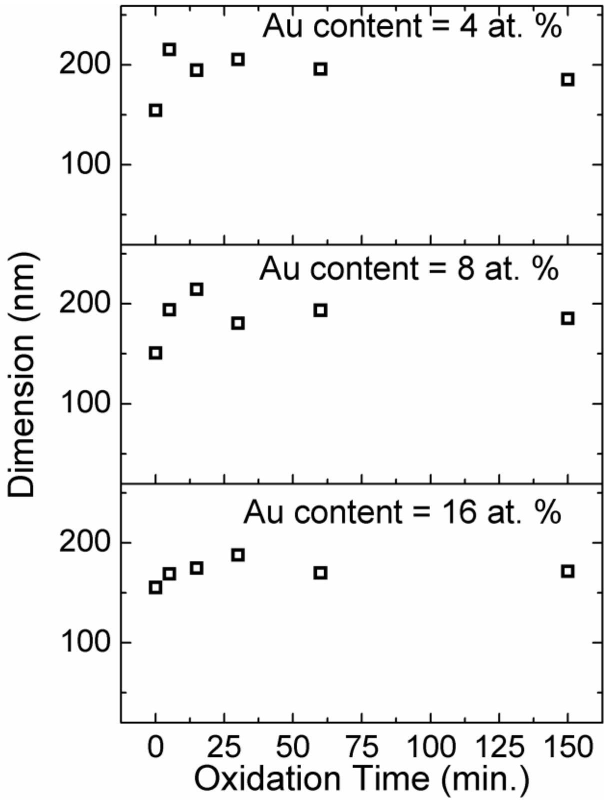

Figure S3. Evolution of the total diameter of the nanotubes as a function of the oxidation time for an annealing temperature of 600°C. The standard deviation deduced from three measurements is about 9 nm. As the wall thickness of the nanotube is irregular, the evolution of the oxide shell thickness is not represented.

5. TEM image of an as-grown Au-Cu nanodot

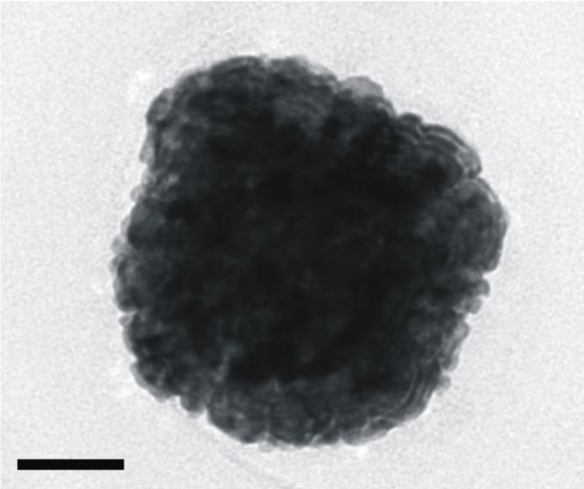

Figure S4. TEM micrograph of an as-deposited Au/Cu alloy nanodot for an Au content of at. % = 8 %. Scale bar: 50 nm.

6. Evolution of the diameter and the oxide shell thickness of the nanodots

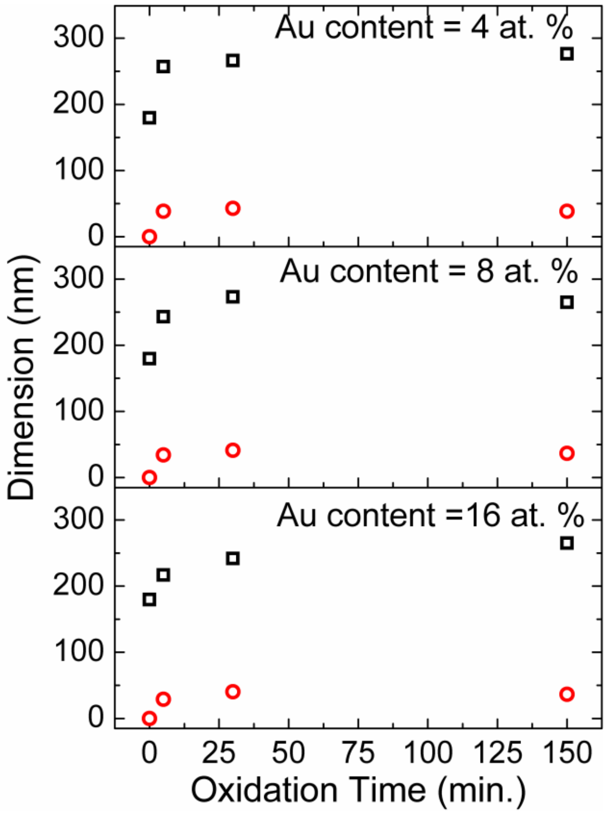

Figure S5. Evolution of the total diameter of the nanodots (open black squares) and the oxide shell thickness (open red circles), evaluated from the TEM micrographs, as a function of the oxidation time for an annealing temperature of 300°C. The standard deviation deduced from three measurements is about 7 nm.

7. Description of the method employed to estimate the gold content in nanodots

In order to estimate the atomic gold content in the samples after 150 min of oxidation using the TEM micrographs in Figure 6a-c, it is assumed that (i) the nanodot and the inner particle have a spherical form and that (ii) the interior core is entirely constituted of gold surrounded by a CuO oxide shell.

The volume of the interior gold particle (V_{Au}), the inner part ($V_{inn.}$) and the entire nanodot ($V_{tot.}$) can be calculated using equation S6:

$$V_X = \pi \frac{d_X^3}{6} \quad (cm^3) \qquad \textbf{Equation S6}$$

where d_X (cm) represents the diameter of the considered sphere and is deduced from the TEM micrograph in Figure 6a-c.

The volume of the copper oxide shell (V_{CuO}) can be calculated as follow:

$$V_{CuO} = V_{tot.} - V_{inn.} \quad (cm^3) \qquad \textbf{Equation S7}$$

The number of mol of Au (n_{Au}) and CuO (n_{CuO}) in the considered volume is calculated following equation S8:

$$n_X = \frac{\rho_X V_X}{M_X} \quad (mol) \qquad \textbf{Equation S8}$$

where ρ_X (g/cm^3) and M_X (g/mol) represent the density and the molar mass of the considered material X (here Au or CuO). ρ is equal to 6.31 g/cm^3 and 19.3 g/cm^3 for CuO and Au, respectively. M is equal to 79 g/mol and 197 g/mol for CuO and Au, respectively.

The estimated atomic gold content (at_c. % Au) is defined as follow:

$$at_c.\%Au = \frac{n_{Au}}{n_{Au} + n_{CuO}} .100 \quad (\%) \qquad \textbf{Equation S9}$$

Finally, the estimated gold content can be calculated according to equation S10:

$$at_c.\%Au = \frac{1}{(1 + \frac{\rho_{CuO}}{\rho_{Au}} . \frac{M_{Au}}{M_{CuO}} . \frac{(d^3_{tot.} - d^3_{inn.})}{d^3_{Au}})} .100 \quad (\%) \qquad \textbf{Equation S10}$$