Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Material

Stretching Single Atom Contacts at Multiple Subatomic Step-Length

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Figure 1S

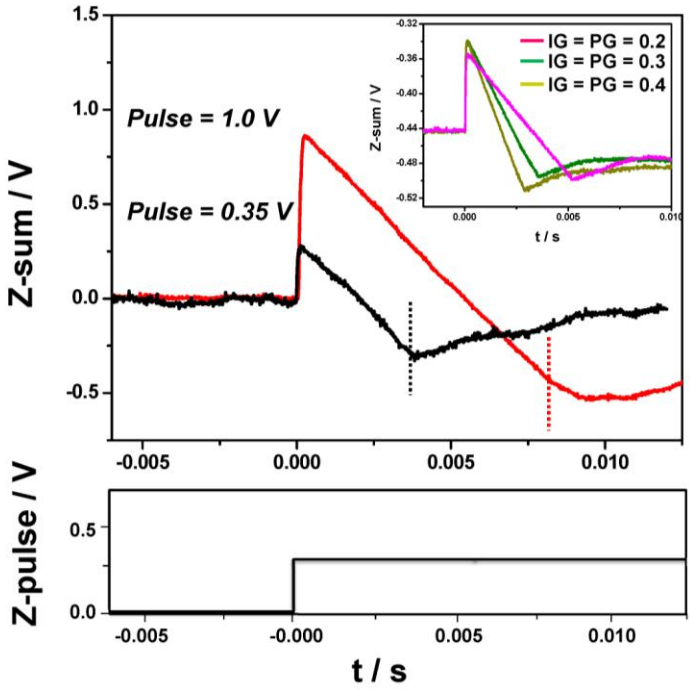

Figure S1. Response curves of sum of Z-piezo voltage (Z-sum) of the STM feedback circuit upon application of external Z-pulse voltage of various heights. These curves were recorded by an oscilloscope during the jump-to-contact STM experiments for creation of Cu NCs. The external Z-pulse voltage starts at 0 s on the time axis with duration of ca. 20 ms. Here, the ending of the Z-pulse voltage is not shown, but is ensured to be sufficiently longer than the time required for STM feedback circuit to respond for the entire jump-to-contact and then break-of-contact processes. The red and pink line corresponds to Z-pulse voltage of 1.0 and 0.35 V, respectively, with integral and proportional gains of 0.1 and current setpoint of 20 nA. The rising part of the Z-sum voltage response curve corresponds to tip approach and decreasing part tip withdrawal process, respectively, the later following a linear relationship with time till the break of the nanocontact. The stretching rate was calculated from the slope of the linear relationship of the response curve after converting the Z-sum voltage to

withdrawal distance according to the z-piezo coefficient of the scanner, which is calibrated using the monoatomic step-height of Au(111) single crystalline surface. The slope of the response curve is insensitive to Z-pulse height and current setpoint, but closely depends on the feedback parameters. As shown in the inset, the purple, green and brown line corresponds to integral and proportional gains of 0.2, 0.3 and 0.4, respectively. The stretching rate is calculated to be 1.3 ± 0.1 $\mu m \cdot s^{-1}$ at fixed proportional and integral gains of 0.1. This value was also calibrated by using Au tip with the same jump-to-contact STM-BJ approach. To maintain constant stretching rate, the integral and proportional gains were kept to be 0.1 throughout the measurements in this work.

Figure S2

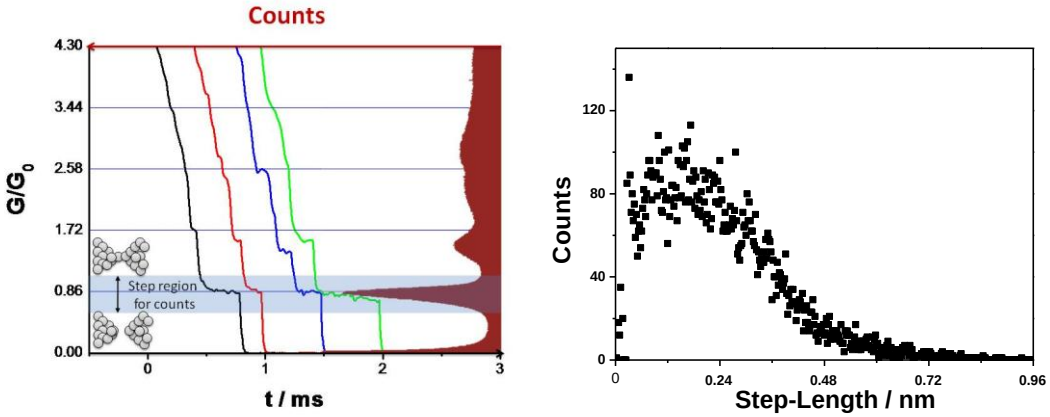

Figure S2. Statistic analysis of thousands of conductance traces to yield the last-step-length histogram. Data analysis was performed following the approach by Yanson et al.[1] Firstly, a conductance histogram was constructured, in order to identify the position of last peak, which corresponds to the most probable conductance of single atom contacts. Second, a conductance boundary region (denoted with blue on the left) was set by the foot of the least conductance peak on the histogram so that subsequent data analysis is focused only on those which fall within this conductance region of a conductance trace, safely including the least conductance plateau if any, see left pannel of the figure. Third, the last plateau in each conductance trace was automatically searched and a stretching length was calculated, considering the duration of the plateau multiplied by the stretching speed. The stretching speed was determined by the responding curve of STM *Z*-piezo voltage, see Figure 1S, which shows a linear relationship with time, meaning a fixed stretching rate. Finally, a last-step length histogram was constructed. This is shown in the right panel, and corresponds to 1600 Fe conductance traces. Statistical probability of different stretching length at single atom contact would be revealed if 10 times more of the conductance traces, *e.g.* 16000, are used.

Figure 3S

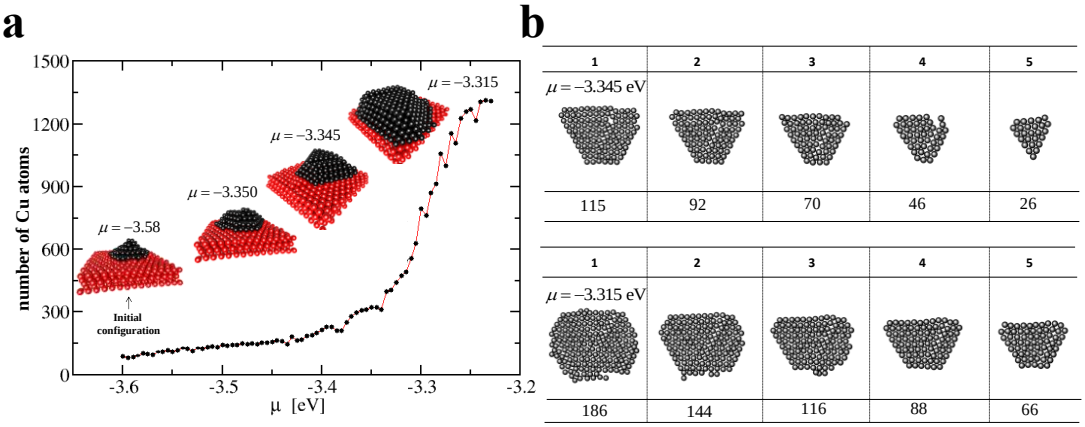

Figure S3. (a) Sample structures taken from a Grand Canonical Monte Carlo simulation for the Growth of a Cu cluster on Au(111). These simulations emulate the growth of a metal cluster -as generated from molecular dynamics simulations, see for example reference2 -at different chemical potentials μ given in eV, what is equivalent to the deposition at different overpotentials η. The relationship between excess of chemical potential $\Delta\mu$ and overpotential is $\Delta\mu = \mu - \mu_0 = -ze_0\eta$, where $\mu_0 = -3{,}58\ \mathrm{eV}$ is the chemical potential of the bulk metal, z is the valence and e_0 the elemental charge. It can be noticed that the Cu cluster grows in an ordered fashion, following the structure of the underlying substrate. This fact becomes more evident in the layer by layer analysis shown in figure (b). For the two samples chemical potentials selected, this figure shows the structure of the different layers, numerated starting from the first layer in contact with the surface. This number is given in the upper part of the figure and the number of atoms in each layer is shown at the bottom. Analogous results were obtained from simulations were the clusters were generated with different structures of the tip. (111, 100 or 110 oriented). When the structure of the Au surface is (100), the clusters are found to grow following the square symmetry of the surface.

Figure S4

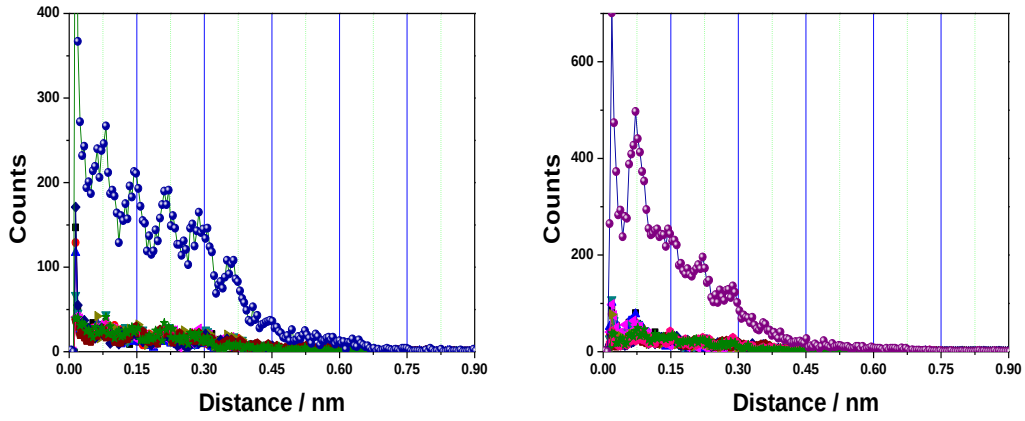

Figure S4. The last-step length histogram of 16000 conductance traces of Fe (left) and Cu (right) single atom contacts on the Au(100) substrate.

Figure S5

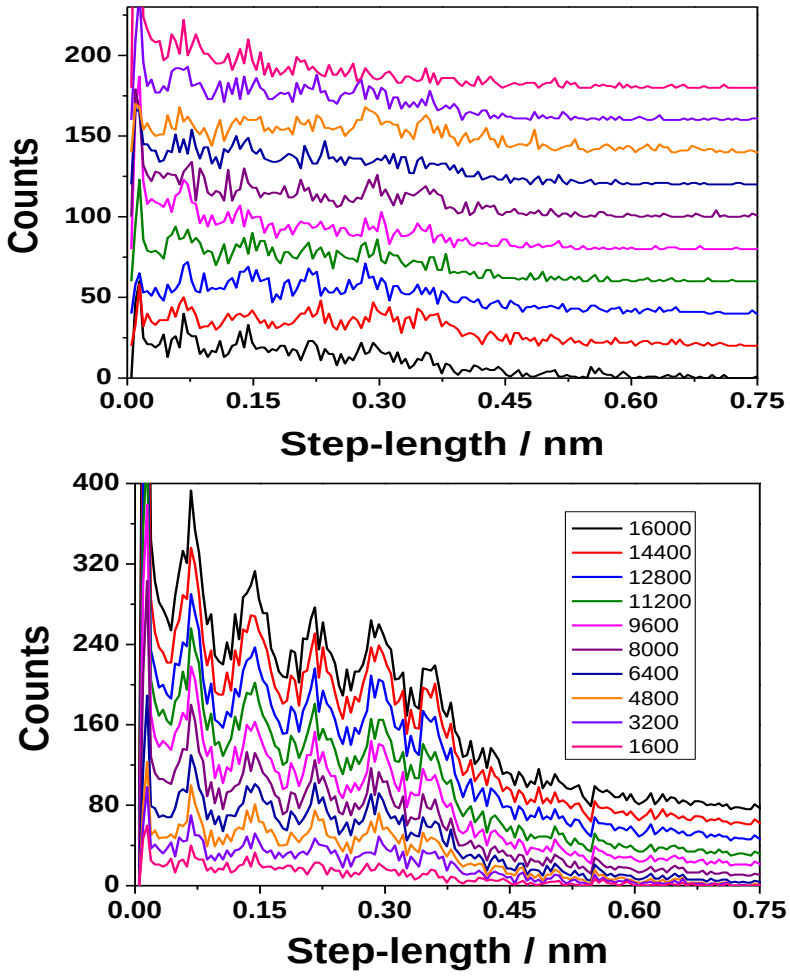

Figure S5. The last-step length histogram of 1600 conductance traces in ten segments of Fe (left) and results indeed show gradual build up of the multiple step-length signals (right).

References

S1. Xing, Y.; Park, T.-H.; Venkatramani, R.; Keinan, S.; Beratan, D. N.; Therien, M. J.; Borguet, E., *J. Am. Chem. Soc.* **2010**, 132, 7946-7956.

S2. Marcelo, M.; Claudio, F. N.; Mario, G. D. P.; Ezequiel, P. M. L., *Nanotechnology* **2005**, 16, 974.