

In situ imaging of reversible order-disorder switching of a few Au atomic layers and field evaporation using atomic resolution TEM

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Catalysis, electrical contacts and plasmonic sensors illustrate the importance of surface structure for properties and device performance. A change in surface structure will change the characteristics. In this work we use *in situ* dynamic TEM studies at atomic resolution to reveal how a few atomic surface layers in gold (Au) can be reversibly switched between ordered and disordered structures by changing an applied electric field.

An *in situ* TEM biasing and nanomanipulation holder [Fig 1(a)] was used to bias a Au nanocone and to position it 100 nm from a negative cathode. At fields of around 25 V/nm the outmost atomic layers changed from a crystalline to a disordered state [cf. apex areas of the nanocone in Figs. 1(c) and 1(d)]. When decreasing the field, the disordered layers reverted back to a crystalline state.

Fast Fourier transformation (FFT) of the apex area of the nanocone before the disordered phase appear show a pattern typical for a crystalline material [inset in Fig. 1(c)]. Upon increasing the electrostatic potential from $V = 48$ V to $V = 80$ V (25 V/nm) the FFT have a ring [inset in Fig. 1(d)], overlapping with the $\{111\}$ diffraction spots and corresponding to a spatial distance to the center of the ring of 2.4 ± 0.5 Å. This matches well with that expected for melted bulk Au. However, the *in situ* high resolution imaging of the nanocone reveals an ordered structure below the disordered surface layers, characteristic of surface roughening. By increasing the electric field further (29 V/nm), field evaporation occurred resulting in a shortening and broadening of the nanocone apex area with an increase in tip radius from 3.0 to 4.3 nm. Figure 1(e) is obtained at the onset of the field evaporation whereas Fig. 1(f) displays the nanocone at the end of the field evaporation.

The Au nanocones [Fig. 1(b)] were prepared with hole-mask colloidal lithography [1] and transferred [2] to a Nanofactory Instruments *in situ* TEM holder [3]. Finite element method modeling was used to find an experimental set-up where cold-field emission (a few V per nm [4]) was prevented from the cathode while simultaneously creating a field around the nanocone apex strong enough to switch the outmost layers and after further increase of the field to enable field evaporation.

To better understand the mechanism of the observed structural changes, extensive *ab initio* molecular dynamics calculations were performed. These ascribe the mechanism behind the observed disordered state to a vanishing energy cost for creating surface defects at intense electric fields.

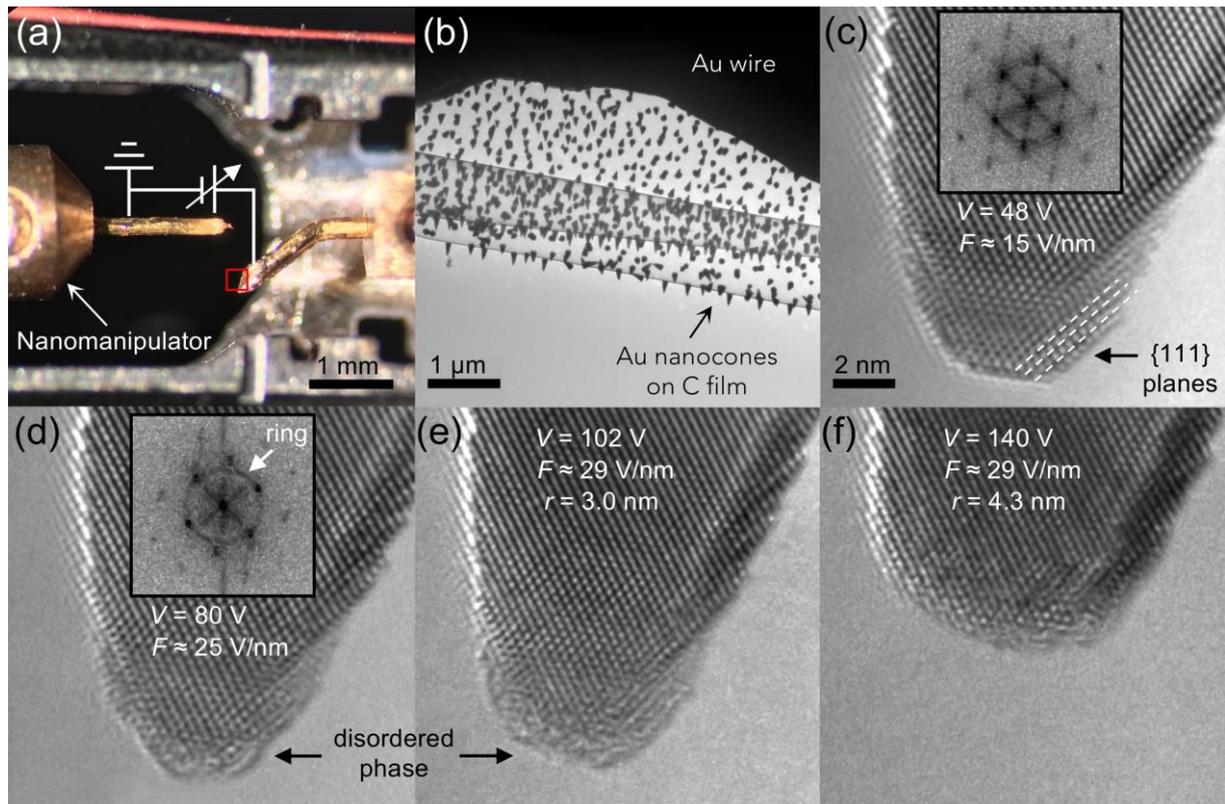


Figure 1 (a) Photograph of the front part of the *in situ* TEM holder showing the nanomanipulator and sample with an electrical circuit schematic overlaid. The red square indicates the area displayed in (b). (b) TEM micrograph of Au nanocones on a C film that is wrapped around a Au wire. (c) At an applied voltage $V = 48$ V corresponding to an electric field of $F \approx 15$ V/nm, the nanocone remains in a crystalline state, which is confirmed from the crystalline-typical fast Fourier transformation (FFT) of the apex of the nanocone. In (d), at $V = 80$ V and $F \approx 25$ V/nm the outmost atomic layers have switched to a disordered state. The FFT in the inset displays a ring, overlapping the $\{111\}$ diffraction spots, which is indicative of a disordered phase. By increasing the field more, the atoms are ionized and evaporated, starting in (e) and ending in (f), which is seen as a shortening and blunting of the nanocone [5]. The scale bar in (c) also applies for (d) - (f).

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