Room temperature melting of gold observed with atomic resolution

Electric field-controlled reversible order-disorder switching of a metal tip surface [3]


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References

Overview
- Surface melting: Effect of temperature on metal surfaces is well known.
- Our motivation: To better understand the behavior of metal surfaces under intense electric fields.
- Our discovery: Electric-field-induced order-disorder phase transition at electric fields of around 20 V/nm, a few surface layers of a gold (Au) nanocone switched from order to disorder. Such loss of crystallinity (i.e., a phase transition) of the surface layer is typical for surface melting.
- Reversibility: Decreasing the electric field reverts the disordered layer back to its original crystalline form.
- Field evaporation: At electric fields of around 30 V/nm we observed field evaporation with atomic resolution.
- Theory: Ab initio molecular dynamics simulations reveal that the disordering effect can be attributed not to an increase in temperature, but, to a vanishing energy cost to form surface defects.

In situ TEM images will be shown here

Ab initio molecular dynamics simulations

Order → disorder → field evaporation

Evolution of a gold nanocone apex with and without an electron beam and an intense electric field
(a) Graph showing the number of atomic layers removed from the nanocone with the electron beam on and the bias at 0 V (time t = 0 – 4 min), with the electron beam off and the bias at 0 V (t = 4 – 32 min), and with the electron beam on and the bias increased from 0 to 140 V (t = 21 – 41 min).
(b) – (g): TEM micrographs illustrating the change in the structure of the nanocone apex at different electric fields. F is the applied bias and r is the nanocone tip radius. (h) – (i): During the crystalline phase some atomic layers are removed over time but the nanocone structure remains ordered. (a) – (g): At an electric field of around 20 V/nm, the disordered phase starts to appear. (h) – (j): The field evaporation phase. The nanocone is rapidly becoming shorter and the tip radius r is increasing. [3]

A ring in the FFT

TEM micrographs and fast Fourier transformations (FFTs)
(a) – (b): At an electric field F = 12 V/nm, an FFT of the apex of the nanocone that is characteristic for a crystalline face-centered cubic metal can be seen (100 frames average).
(c) – (d): At F = 25 V/nm, a ring appears in the FFT of the apex, most likely originating in the disordered phase (single frame).
(e) – (f): The TEM micrograph is the same as in (c), but with 100 frames averaged.
(g) – (h): The TEM micrograph is the same as in (a), but with the FFT obtained after the apex and the disordered phase. The ring overlaps with the face-centered cubic [111] diffraction spots and the reciprocal radius of the ring corresponds to a spatial distance of 2.5 ± 0.2 Å (inverted gold has 2.38 Å). The ring is quite sharp, which could indicate that some medium-range order remains in the structure. [3]

Reversibility

When decreasing the applied electric field, the disordered layer re-crystallizes. In (a), at an electric field of F = 20 V/nm, the disordered phase is clearly seen. In (b), at F = 17 V/nm, the disordered layer is smaller and in (c), at F = 14 V/nm, the disordered layer has reverted back to its original crystalline form. [3]

Ab initio molecular dynamics

(a) Surface melting according to Lindemann, i.e., relation melting point and atom mean square displacement? Thermal displacement at 30 0 V/nm corresponds to a 25% increase of the MSD. This only corresponds to a 50-100 K temperature increase for the field-free case, so no.
(b) – (d): Simulations of Au nanoparticles as a function of electric field and temperature showing the (i) crystalline, (ii) disordered and (iii) field evaporation phases. The electric field induces a very localized charging at the surface (b). The crystalline stage (at electric fields up to ~15 V/nm) was characterized by spherical shapes and constant surface areas. At higher fields, during the disordered stage, the particles elongated, the surface area increased and individual atoms occurred at the surface, which can be seen as a surface roughening, or disordering.
Conclusion: The observed disorder comes from a vanishing cost to form surface defects in high electric fields. [3]

Experimental setup

– Imaging using transmission electron microscopy (TEM)
– Manipulating sample and applying bias with an in situ TEM sample holder
– Sub-nm spatial resolution with nanomanipulator and up to ±140 V bias
– Au nanocone samples, produced by hole-mask colloidal lithography

Summary & conclusions

– A reversible order-disorder switching mechanism in a few atomic layers of gold has been discovered.
– The disordering can be seen as a surface-melting-like process. Not from an increase in temperature, however, but, from it becoming more energetically favorable to introduce surface defects in intense electric fields.
– Such direct structural control of a few atomic layers could be utilized in e.g. nanophotonics and field-effect transistor technology as well as in fundamental research in materials characterization and of yet unexplored low-dimensional phases of matter.