



SURFACE-STRESS-INDUCED STRUCTURAL TRANSFORMATION AND PSEUDOELASTIC EFFECT IN PALLADIUM NANOWIRES

Jijun Lao
Ph.D. Candidate

Faculty Advisor: Dorel Moldovan

ABSTRACT

With the miniaturization of electrical, optical, thermal, and mechanical systems the feature size of relevant device components are reduced down to several nanometers. As the scale of the material is reduced to just a few interatomic distances across at least one of the three spatial dimensions both the structure and properties can be quite different from those of bulk materials. Many (001) oriented surfaces in fcc metals reconstruct to denser quasi-hexagonal packed layers. The reconstruction is driven by the reduction of the surface energy which should be large enough to compensate for the corresponding mismatch strain between the original and the reconstructed atomic layers. When two spatial dimensions of the systems are in the nanometer range (i.e. nanowire or nanobeam structures) the structural characteristics and stability are strongly influenced by both surface energy and surface stress. Several novel structures have been identified in metallic nanowires including: multishell helical gold nanowires,^{1,2} “weird” aluminum and lead nanowires,³

In this study we investigate the fundamentals of surface-stress-induced phase transformation and pseudoelastic deformation processes in palladium nanowires using molecular dynamics (MD) simulation. For a $\langle 100 \rangle$ initial crystal orientation and wire cross-sectional area below $2.18 \text{ nm} \times 2.18 \text{ nm}$, our studies indicate that the surface stress can cause palladium wires to undergo a spontaneous phase transformation from fcc structure to a bct structure, provided that the temperature is above a critical value $T_c = 22.5 \text{ K}$. Upon tensile loading of the bct wire the initial fcc, $\langle 100 \rangle$ oriented wire is reached via a novel stress-strain behavior that is drastically different from those corresponding to bulk metals. The reversible phase transformation driven by the externally applied tensile stress is mediated by short range atomic rearrangements similar to those found in martensitic transformations. The recoverable strain is up to 50%.

The MD simulations were performed using the embedded-atom method (EAM) potential for Pd.⁴ Single crystalline Pd [100] nanowires with a square cross section and surface orientation of [100], [010], and [001] were

created with initial atomic positions corresponding to the bulk fcc Pd crystal. Free boundary conditions were used in all directions.

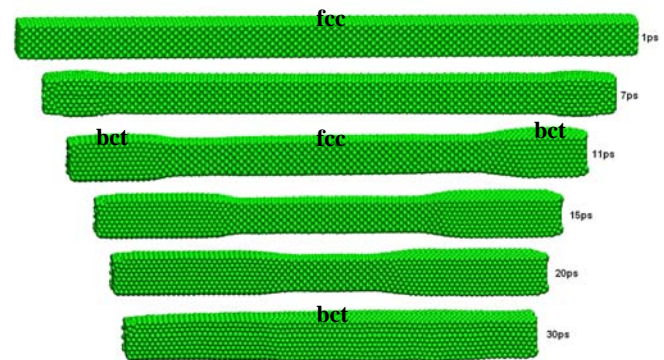


Figure 1. Six snapshots depicting the time evolution of a Pd nanowire during the fcc to bct phase transformation at 100K. Snapshots of the $1.78 \text{ nm} \times 1.78 \text{ nm}$ Pd nanowire at 1, 7, 11, 15, 20, 30 ps respectively are shown here.

At 100K the MD simulations show that the fcc, initially $\langle 100 \rangle$ oriented, Pd nanowire undergoes a spontaneous phase transformation to a bct crystalline structure. As result of the crystal structure change the nanowire exhibits an axial contraction accompanied by a corresponding lateral expansion. Figure 1 shows the dynamic progression of the phase transformation in the Pd nanowire. During the first 3.0 ps the wire relaxes elastically and contracts longitudinally by about 6%. After the elastic contraction a new bct crystalline phase nucleates at the ends and propagates with a speed of approximately 538 m/s toward the center of the nanowire. The fcc to bct phase transformation is completed in about 30ps and leads to a further wire longitudinal contraction of about 31%.

Both tensile loading and unloading studies were conducted under simulated quasistatic conditions. Namely, in each load step the coordinates of all atoms were modified according to a prescribed uniform strain increment of 0.125% in the length direction. To allow the wire to reach local microscopic equilibration, after each straining step the

wire was relaxed for 15ps at 100K holding the wire ends at fixed positions consistent with the newly prescribed wire length. The relaxation process usually takes less than 10ps and the stress evaluated and averaged over the subsequent 5ps was taken as actual stress in the wire at the corresponding strain state. The unloading process followed a similar protocol with a strain decrement of -0.125% at each unloading step.

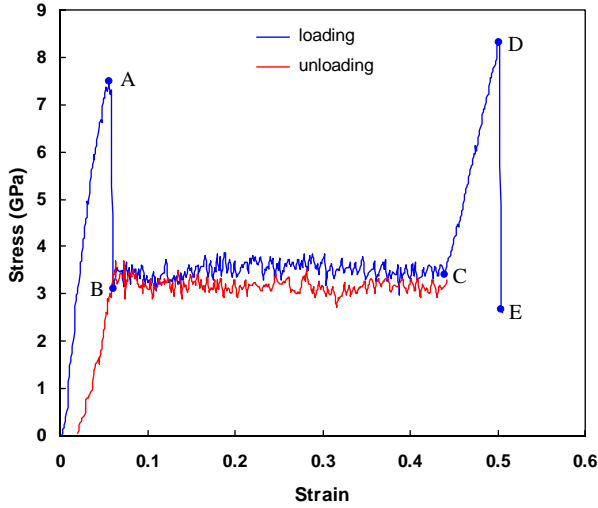


Figure 2. Stress-strain curve for the 1.78 nm x 1.78 nm nanowire during loading and unloading at 100K

Figure 2 show the stress-strain curve of the bct/fcc wires during loading and unloading at 100K. The curves indicate that the Pd wire is very ductile with fracture strains of approximately 50%. Along the loading part of the stress-strain curve one can identify the following stages: i) During the stage delimited by points O and A on the loading curve the wire maintains its bct crystalline structure while undergoing elastic straining. ii) When the tensile stress reaches 7.5 GPa, corresponding to point A on the curve, the nucleation of the fcc phase starts at the ends of the wire, which is also associated with a sudden drop of the applied stress from 7.5GPa to approximately 3.5 GPa. iii) Between points B and C the linear portion of the curve corresponds to wire elongation caused by the steady advance of the bct to fcc phase change from the ends toward the center of the wire. At point C the entire wire has been converted to the fcc structure. iv) The portion between C and D corresponds to the elastic linear stretching of the new fcc wire. v) Further loading beyond point D at a stress leve exciding 8.2 GPa, causes the fcc wire to neck and ultimately to fracture at point E. One can quantify the overall straining by using the following equation: the total strain = elastic strain of the bct wire + plastic strain due to bct to fcc phase change + elastic strain of the fcc wire = 5.6% + 38.5% + 6.1% = 50.2%.

The 1.78 nm × 1.78 nm fcc wire transforms spontaneously back to the 2.196 nm × 2.196 nm bct configuration via phase change mediated by short range atomic rearrangement processes in reverse to what is described above when the temperature is above a certain value. The reversible fcc to bct phase transformation results from a cooperative and collective motion of atoms over distances smaller than a lattice parameter in the absence of any diffusive processes. The absence of diffusion renders the fcc to bct phase transformation almost instantaneous. These characteristics are similar to those present in traditional shape memory alloys (SMA) that commonly involve austenite to martensite phase transformation. The reversible phase change in Pd nanowire has temperature dependence. The spontaneous fcc to bct phase change happens only when the temperature is above a critical value T_c . If the temperature is below T_c , the fcc wire configuration is stable. However, when heated above T_c , the wire spontaneously transform to bct structures. Our MD simulations indicate that the critical temperature T_c , for the Pd nanowire investigated is around 22.5K.

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