Nano-Mechanics towards Advanced Structured Functional Materials

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Abstract—*In this paper, we will discuss our recent progress in Nanomechanics. While unique mechanical properties of nano-materials have been reported for past decade, the affirmative mechanism behind wasunresolved for many cases. The recent evolution of in-situ electron-microscopyhas enabled us to observe the real time nano-mechanical behavior, which opens up new insight into the nano-mechanics. By using in-situ mechanical testing, we elucidated the fundamental deformation mechanism of single crystalline FCC metallic nano wires showing the size dependency of unprecedentedultra-strongand ductile behavior. Our group also took advantage of the unique mechanical properties of nanostructures to design and fabricate advanced structured functional materials such as fatigue damage free metal electrode and pulverization damage free nanostructured Si anode based on the fundamental understanding of nano-mechanics.*

Keywords: *Nano-mechanics, Nanowire, Nanostructure, In-situ testing, Advanced Structure Materials*

INTRODUCTION

Among our recent works in nanomechanics, this paper hassummarized a couple of interesting works related to deformatin of nanometals [1, 2]. The first section will discuss a fundamental mechanism of unique deformation behavior of metallic nanowires [1]. This study was the first to identify the size and surface dependent atomistic deformation mechanisms that enable high strength and high ductility to simultaneously be achieved in 1D metal nanostructures across a wide range (40-250 nm) of nanowire sizes. The second section will deal with how a nanostructured metallic thin film enhanced the fatigue damage resistance [2].Wedemonstrated a new and facile approach to solve the reliability issues of metal electrodes under continuous bending deformation in flexible devices.

ULTRA STRONG AND DUCTILE BEHAVIOR OF SINGLE CRYSTALLINE METALLIC NANO-WIRES

It has been experimentally observed that the mechanical properties of metallic materials change as their characteristic sizes are reduced to nanometer dimensions. The mechanism behind this size dependency has attracted significant scientific interest [3-5]. In an attempt to answer this fundamental question, the mechanical behavior of nanomaterials has been extensively studied primarily using classical molecular dynamics [3,6]. Many resulting predictions of unique mechanical behavior emerges specifically as a result of the nanometer dimensionality. However, experimental confirmation of a certain predictions still remains unresolved due to significant experimental challenges.The recent evolution of in-situ electron-microscopy has enabled us to observe the real time nano-mechanical behavior, which opens up new insight into the nano-mechanics. In particular, our recent study using in-situ and defect free single crystalline metallic nanowires could elucidate the fundamental deformation mechanism of single crystalline FCC metallic nanowires showing unprecedented ultra-strong and ductile behavior.Furthermore, we identified"Smaller is Stronger" behavior of the ultra-strong and ductile nanowires and providediscreet answers for the size dependent twin propagation stress originated from a combination of lattice and surface reorientations.

Figure 1 shows arepresentative in-situ tensile testing of a Pd single crystalline NW. The NWs all have a <110> axial growth direction and a rhombic cross-section bounded by four equivalent close-packed {111} transverse surfaces. The *in-situ* tensile tests were carried out in a dual beam electro-microscope (FEI).

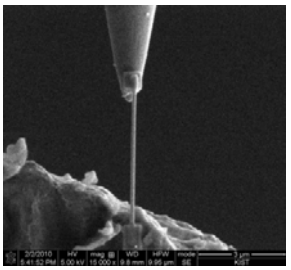

Fig. 1: Are Presentativein-situ Tensile Testing of a Pd Single Crystalline NW in the Dual Beam FIB Chamber by Nanomanipultors

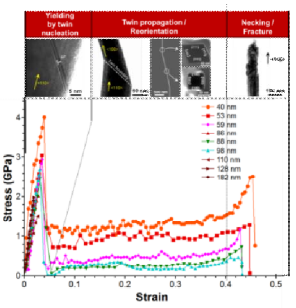

Fig. 2: The Three-stage Stress-strain Curves of Pd NWs with the Diameter Ranging from 40 nm to 182 nm. The NWs all have a < 110 > Axial Growth Direction and a Rhombic Cross-section Bounded by four Equivalent Close-packed {111} Transverse Surfaces

The three-stage stress-strain curves of Pd NWs with the diameter ranging from 40 nm to 182 nm were presentedin Figure 2: In the stage 1 (yielding stage), the rhombic cross section of the <110> NW with {111} transverse surfaces (<110>/{111}NW) elastically deforms until the stress dropsdue to the nucleation of a twin. The stress value before this stress drop corresponds to the yield stress. The stage 2 exhibited the unique plateau stress-strain region which is induced by the twin propagation. The twin boundary propagates along the NW length of more than 1 μm at a constant stress (the twin propagation stress). The stress-induced twin propagation results in the reorientation of the initially {111} surfaces to {100} surfaces with a transformation of the NW cross section changing from rhombic to square. The NW eventually is transformed to a <100>/{100}NW after ~ 40% tensile strain. Finally, after the reorientation process is complete, the stage 3 becomes linear elastic deformation of the resulting <100>/{100} NW before fracturing. (For more detailed mechanism, please see the ref [1])

Our defect free single crystalline noble metallic FCC NWs are appropriate to investigate the size dependent mechanicaal properties because of no grain boundary effect, strong surface oxidation resistance, andtheir deformation mechanism given. Hence,we were able to report, for the first time,a clear size-dependence of yielding and twin propagation behavior.Due to limited space, the size dependcy of twin propagation is summarized in this paper. The twin propagation stresses for three different <110>/{111} NWs, i.e. Au (red stars), Pd (gray solid circles), and AuPd (orange diamonds) with different diameters were ploted in Figure 3. At a critical diameter of about 100 nm, the twin propagation stressbegins to increase substantially. Specifically, the twin propagation stress increases nearly five-fold from about 0.2 GPa to about 1 GPa as the NW diameter decreases from 100 to 30 nm. Furthermore, we find that if the twin propagation stress is analyzed in power-law format, i.e. $\sigma_{tm} \propto d^{-n}$, where σ_{tm} is the twin propagation stress, the exponent we find is n close to unity ($n = 0.93$). The $1/d$ dependence for the twin propagation stress was predicted but never been observed experimentally before. The origin of this high exponent value can be explained by the micromechanical theory presented by Liang et al. [7]and the surface energy differential model of Li *et al.* [8]. In a similar manner, we derived the analytical form of twin propagation stressbased on the surface energy differntial model and can write as $\sigma_{tm} = \frac{K}{d}$, where K is a geometric factor of the surface reorientationas

$$K = \frac{4\sqrt{3}(\gamma_{100} - \frac{\sqrt{3}}{2}\gamma_{111})}{(\sqrt{2}-1)} \quad (1)$$

Figure 3 also showed a comparison between the analytical surface energy differential model in equation (1), i.e. Pd (gray solid line) and Au (red dotted line) with the twin propagation stress measured experimentally in the present work for three different <110>/{111} NWs, i.e. Au (red stars), Pd (gray solid circles), and AuPd (orange diamonds). The surface energy obtained from atomistic simulationsfor the {111} and {100} surfaces of Pd are 1.92 J/m^2 and 2.33 J/m^2, while the same surfaces of Au have energies 1.28 J/m^2 and 1.63 J/m^2, respectively [9]. As can be seen, the analytical model with the inverse diameter relationship captures the size-dependent twin propagation stress very accurately.

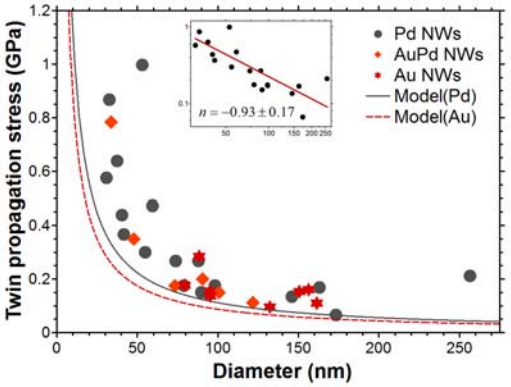

Fig. 3: Comparison between the Analytical Surface Energy Differential Model in Equation (1), i.e. Pd (Gray Solid Line) and Au (Red Dotted Line) with the Twin Propagation Stress Measured Experimentally in the Present Work for Three Different <110>/{111} NWs, i.e. Au (Red Stars), Pd (Gray Solid Circles), and AuPd (Orange Diamonds) The Inset Confirms the 1/d Dependence of Twin Propagation Stress

We should note that while the surface energies of Pd are about 50% higher than those of Au for a given orientation, the K value for Pd (11.16 J/m^2) is closer (~ 28% difference) to that for Au (8.72 J/m^2), which results in the similar twin propagation stress at a given diameter as illustrated by the gray solid line and red dotted line in Figure 3. Our model explains why the experimentally measured twin propagation stress for three different <110>/{111} NWs, i.e. Au (red stars), Pd (gray solid circles), and AuPd (orange diamonds) falls on the similar twin propagation values and also demonstrates the increasing importance of surface energy on the twin propagation stress with decreasing NW diameter.In conclusion,this study clarified the size-dependent twin propagation behavior of metal NWs. The key findings can be summarized as follows: First, for defect-free single crystalline PdNWs, we observed ultra-strong and ductile behavioras a result of coherent twin propagation regardless of the NW diameter. Second,we showed that the twin propagation stress increases more dramatically with decreasing NW diameters (size dependent exponent n ~ 1) than the yield stress, demonstrating the

fundamental role that surface reorientations play in enhancing the size-dependent mechanical behavior and properties of metal NWs according to our surface energy differential model.

HYBRID NANOSTRUCTURE FOR FATIGUE DAMAGE RESISTANT CU ELECTRODE

Taking advantage of unique properties of nanostructured metals, we could design advanced funtional materials. Among those, we presented the detailed illurstration of fatigue damage free flexible Cu electrode for application of flexible devices in this paper.Typically, fatigue damage is the most commonly identified failure in metal films that are subjected to repeated deformation [10-11]. Fatigue damage evolution in a metal thin film is characterized by two subsequent processes: crack initiation and crack propagation. Crack initiation related to collective dislocation motions is followed by crack propagation, which degrades theelectrical properties of the metal electrode, conductivity. Therefore, in order to realize highly stable flexible metal electrodes, it is necessary to control crack initiation and suppress crack propagation.

Here, we demonstrate a novel nanostructured metal electrode that has dramatically improved fatigue damage resistance. Figure 4 shows the nanohole Cu electrode fabricated using a nanorod polyimide (PI) substrate. A 125-μm-thick PI substrate (Dupont, Kapton) was etched by the RF glow discharge of CF_4 plasma using the plasma-assisted chemical vapor deposition (PACVD) method to form nanoscale rods on the PI surface. Subsequently, a 200-nm-thick Cu thin film was deposited on the etched PI with nanorod structure by thermal evaporation. For comparison, a conventional 200-nm-thick Cu thin film was also deposited on a bare (non-etched) PI film with the same deposition conditions.

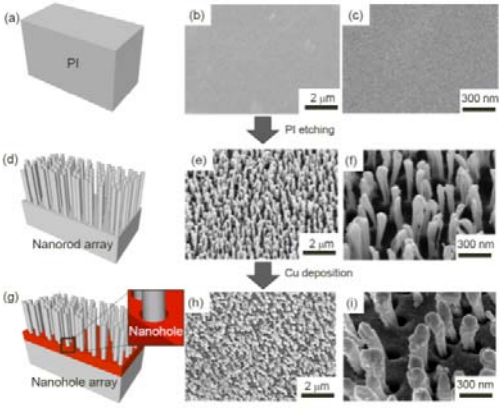

Fig. 4: Fabrication of the Nanohole Cu Electrode using a Nanorod Polyimide (PI) Substrate. A 125-μm-thick PI Substrate (Dupont, Kapton) was Etched by the RF Glow Discharge of CF4 Plasma using the Plasma-assisted Chemical Vapor Deposition (PACVD) Method

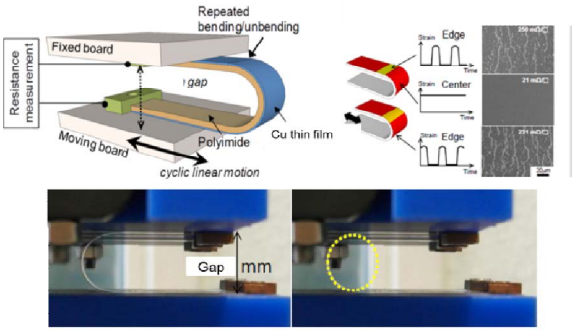

Fig. 5: Bending/ Sliding Testing with Real-time Detection of the Change in Electrical Resistance. The Linear Motion of the Lower Board form Two Fatigue Damage Zones (Yellow Region on Top Right) which Increased the Resistance of Cu Thin Film. The Gap between Boards Determines the Bending Fatigue Strain

We used a new bending/sliding test system that can mimic repeated cycles of real bending deformation with real-time detection of the change in electrical resistance as illustrated in Fig. 5. The metal film on the flexible substrate was located between two parallel boards and the edges of the specimen were fixed with metal grips. While the top board was fixed, the bottom board was moved for repeated sliding motion, as indicated by the arrow in Figure 5. The linear motion of the lower plate produces two fatigue-damaged zone (yellow region on the top right side figure) which causes resitance increase. By changing the gap between the two boards, we can vary an applied bending strain on the metal thin film. Metal electrode samples with 60 mm length and 4 mm width were prepared. The gap between the two plates was 7.8 mm, which should applya bending strain of 1.6% on the metal layer. A cyclic sliding test was performed with a sliding distance of 10 mm and frequency of 5 Hz at room temperature in air. The changes in the electrical resistance were measured during cyclic bending by using a current and voltage meter (Agilent 34410A) for up to 500,000 bending cycles.

Figure 6 showed comparision of the fatigue behavior of the nanohole Cu structures with the traditional Cu thin film.The electrical resistance of the nanohole metal electrode increased by less than 10% even after 500,000 fatigue cycles, whereas that of a conventional metal electrode having the same thickness increased by more than 300%. The nanohole-structured Cu electrode had significantly improved electrical stability and it enabled the realization of fatigue-damage-free metal electrodes. Based on the microstructural observations and the FE simulation, we explained the fatigue resistance mechanism of the nanohole structures as follows. First, the nanohole structure can inhibit crack initiation by suppressing protrusion formation by collective dislocation slips with many dislocation sink sites. Second, the nanoholes in the electrode act as a buffering

structurethatdecreases the strain distribution at the crack tips so as to retard the crack propagation throughcrack blunting and shorten the crack length. Hence, thesenovel nanohole electrodes guarantee long-term stability against bending fatigue without losing their high electrical conductivity. Our resultsprovide a key guideline for a new design principle for fatigue-free flexible metal electrodes thatprevent mechanical and electrical failure of the metal layer during repeated bending deformation.

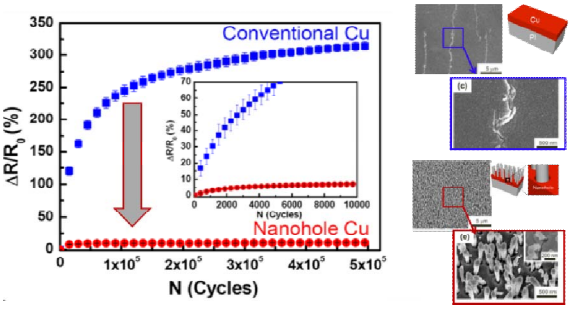

Fig. 6: Bending/ Sliding Testing with Real-time Detection of the Change in Electrical Resistance. The Linear Motion of the Lower Board form Two Fatigue Damage Zones (Yellow Region on Top Right) which Increased the Resistance of Cu Thin Film. The Gap between Boards Determines the Bending Fatigue Strain

CONCLUSION

In summary, this paper briefly introduced two representative examples of our recent nanomechanics research works; unique mechanical properties of metallic nanowires and an application of nanostructured metals. We believe that the novel in-situ characterization methodolgy has enabled us to unveil the mechanism of nanomechanical properties. Moreover, fundamental understanding of nanomechanics helped us to find a breakthrough design in nanostructured materials for advanced devices.

REFERENCES

[1] J.H. Seo, H. Park, Y.D. Yoo, J. Li, J.P. Ahn, B.S. Kim, I.S. Choi, 'Origin of size dependency in coherent-twin-propagation mediated tensilede formation of noble metal nanowires,' Nano Letters, 2013,Vol. 13, pp. 5112-5116

[2] B.J. Kim, M.S. Jung, M.W. Moon, H.N. Han, K.T. Nam, Y.C. Joo, I.S. Choi,'Fatigue-free, electrically reliable Copper electrode with nanohole array,' Small, 2012, Vol.8, pp. 3300-3306.

[3] H. S. Park, W. Cai, H.D. Espinosa, H. Huang, 'Mechanics of crystalline nanowires', MRS Bull. 2009, 34, pp. 178-183.

[4] J. R. Greer, J. Hosson, Th. M. D. 'Plasticity in small-sized metallic systems: Intrinsic versus extrinsic size effect', Prog. Mater. Sci., 2011, Vol.56, pp. 654-724.

[5] O. Kraft, P.A. Gruber, R. Mönig, D. Weygand, 'Plasticity in confined dimensions', Annu. Rev. Mater. Res., 2010, Vol.40, pp. 293-317.

[6] C.R. Weinberger, W. Cai, 'Plasticity of metal nanowires', J. Mater. Chem., 2012, Vol.22, pp. 3277-3292.

[7] W. Liang, D.J. Srolovitz, M.J. Zhou, 'A micromechanical continuum model for the tensile behavior of shape memory metal nanowires', J. Mech. Phys. Solids, 2007, Vol. 55, pp. 1729-1761

[8] S. Li, X. Ding, J. Li, X. Ren, J. Sun, E. Ma, ' High-Efficiency Mechanical Energy Storage and Retrieval Using Interfaces in Nanowires', Nano Letters, 2010, Vol.10, pp. 1774-1779

[9] J. Wan, Y.L. Fan, D. W. Gong, S. G. Shen, X.Q. Fan, 'Surface Relaxation and Stress of FCC Metals: Cu, Ag, Au, Ni, Pd, Pt, Al and P', Model. Simul. Mater. Sci. Eng., 1999, Vol. 7, pp. 189-206.

[10] O. Kraft, R. Schwaiger, P. Wellner, 'Fatigue in thin films: lifetime and damage formation', Mater. Sci. Eng., A 2001, Vol. 319, pp. 919-923.

[11] R. Schwaiger, O. Kraft, 'High cycle fatigue of thin Ag films investigated by dynamic microbeam deflection', Scr. Mater., 1999, Vol. 41, pp. 823-829.