

Contact Compression of Self-assembled Nano- and Micro-scale Pyramid Structures on Au (100) Surface

J. Wang, D. Ward, W.A. Curtin and K.-S. Kim
Division of Engineering, Brown University, Providence, Rhode Island

ABSTRACT

A process of self-assembly induced by electro-chemical etching was used to produce nano and micrometer scale pyramid-structures on (100) surfaces of gold. The pyramids grew in a self-similar fashion with the facets aligned in (114) plane. Using the unique characteristics of the self-similar pyramid structure, plastic compression of the pyramids by a flat-surface platen was performed to study length scale effects in the plastic deformation. A continuum limit analysis and a finite element simulation as well as molecular dynamics simulations were carried out to predict the deformation and load-displacement behavior of the pyramid compression. The limit analysis predicts that the load of compression is proportional to the square of the contact-compression displacement. The continuum analysis provides estimation on the asymptotic behavior of the elastic-plastic load-deflection response of the pyramid under compression for a large value of displacement. The three dimensional molecular dynamics simulation was utilized to study the dislocation activities during the early stage of the pyramid compression. Experiments were also carried out by pressing the pyramids with an atomically flat mica surface. The deformation of the compressed pyramid was measured using an Atomic Force Microscope (AFM). The continuum analyses predict size independent values of the slope change of the pyramid facets near the contact edge, caused by plastic deformation. However, atomistic simulation predicts an opposite value of the slope change to the prediction of the continuum analyses. The AFM measurements of the slope change show size dependent transition from the prediction of the continuum analyses to that of the atomistic simulations. The transition data provide an apparent characteristic length of the size dependence of plastic deformation in a small volume. Molecular dynamics show that at very small length scale the size effect is strongly influenced by surface adhesion effects.

INTRODUCTION

Rapid advances in electronics and structural materials are enabling the development of ever-smaller micro- and nano-electromechanical (MEM and NEM) devices. When materials and structures are scaled down from tens of micron to a fraction of a micron, metals display a strong size-dependence when deformed non-uniformly into the plastic range due to the inhomogeneous plastic flow in crystalline solids. Conventional plasticity theory, which has no length scale, can no longer sufficiently characterize the behavior of the materials and structures. This phenomenon has motivated a large effort in the mechanics and materials communities to develop both experiments and theories to investigate the material behavior at micron and nanometer scales. These include the recent established strain gradient plasticity theory [1] at micrometer scale, discrete dislocation plasticity theory [2] at tens of nanometer scale, etc. However, due to the difficulty in manufacturing sub-micron structures systematically, experimental characterization of the length scale effect across micron to nanometer is challenging. At the nanometer scale, much of the fabrication process is controlled by the self-assembly of material. Thus the

development of a single experiment that can measure the size-dependence across several length scales is highly desirable.

In this paper, a novel electro-chemical etching approach was adopted to produce nano and micrometer scale pyramid-structures on (100) surfaces of single crystal gold. The pyramids grew in a self-similar fashion with the facets aligned in (114) plane. Using the unique characteristics of the self-similar pyramid structure, contact compression experiments were performed on the single crystal gold surface to study the length scale effect in the plastic deformation of the pyramids. A continuum limit analysis was used to characterize the self-similar deformation of the pyramid compression, while molecular dynamics simulations were used to see the origin of the scale dependence in plastic deformations at a very small length scale.

SELF ASSEMBLY AND CONTACT COMPRESSION OF (114) GOLD PYRAMIDS

The self assembly of four sided square pyramids on Au (100) surface was recently discovered when a mechanically polished surface was immersed in a certain Au electrolyte. Even the eventual function of the electrolyte was to remove the scratches from mechanical polishing, it was found that under center conditions (current, temperature and etching time), the (11 n) ($n = 4$ in most cases) facets can be reconstructed during the etching and form very well defined pyramid structures. The electrolyte consists of 25% hydrochloric acid, 25% ethylene glycol and 50% ethanol. Self-assembly of the pyramids was highly dependent on the etching parameters. The best pyramids were usually achieved at an electrical current of 2.5 amperes at an elevated temperature of 60 °C for duration around 2 minutes. Under this condition, complete pyramids of different sizes across nanometer to micrometer were obtained. Under other conditions (varying current or etching time), either no pyramids were observed or the pyramids became too big that the nearby pyramids start to coalesce with each other and the peaks got etched away.

Figure 1 shows an AFM scan of the self-assembled pyramids on top of Au (100) surface grown using the aforementioned method. Figure 2 shows the line profiles across the ridge direction of 6 pyramids shown in Figure 1. The line profiles show that the pyramids grew in a self-similar manner. Regardless of their individual sizes, the facets of most of the pyramids are aligned in the (114) plane, although (113) and (115) orientations were observed in some other measurements. Measurements on different areas of the sample indicate that the size of these self-similar pyramids range from tens and hundreds of nanometer to a few microns.

Given the self-similar nature, these pyramids serve as perfect samples for experimentally characterizing the size effect across micron to nanometer scales. Therefore, contact compression experiments were conducted to see the length scale effect in the plastic deformation of these pyramid structures. To apply a contact pressure loading, an

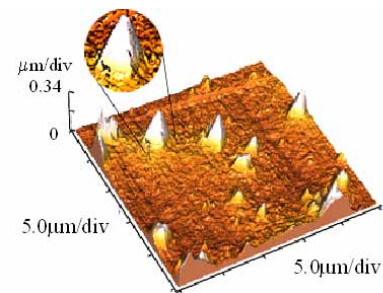


Figure 1. 25 μm by 25 μm AFM scan of pyramid structures produced from electro-chemical polishing on a single crystal Au (100) surface.

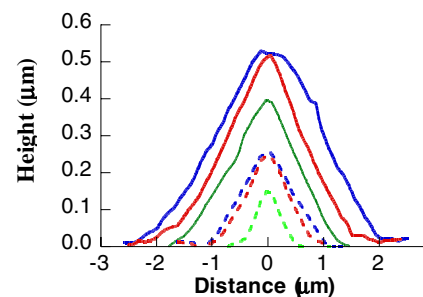


Figure 2. Height profile across the ridges of the pyramids.

atomically flat mica sheet was used to transfer the load applied by an Instron 4502 machine to the (100) Au sample surface. Different nominal pressure corresponding to 1/6, 1/3, 1/2, 2/3 of the yielding load of gold were applied. The initial and deformed pictures for a 25 μm by 25 μm area are shown in Figure 3a and 3b. A line scan across the two symmetric ridges of one of the deformed pyramids before and after compressing is shown in Figure 3c. By compression, the peaks of the pyramids were flattened. Material was crushed downwards and sideways. The ridge angle became smaller after compression, although the amount of change was measured to be different for different sizes of pyramids.

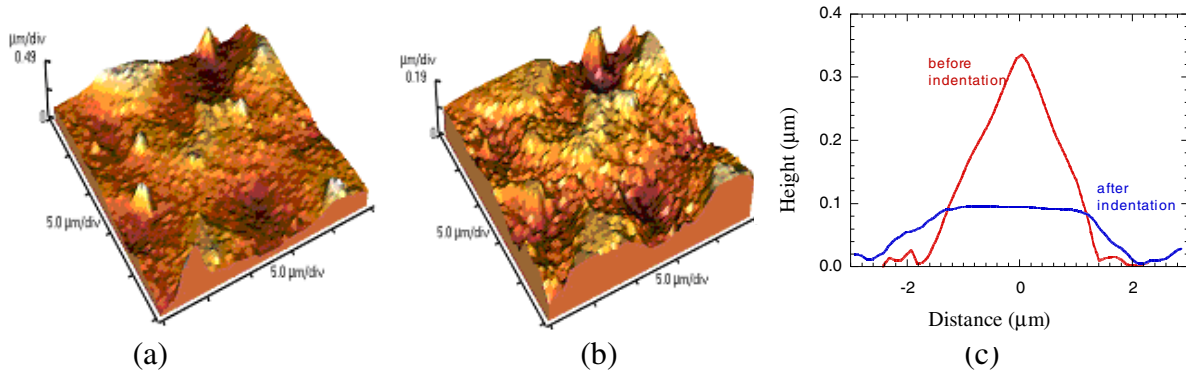


Figure 3. Pyramid deformations: (a) AFM scan before compression; (b) AFM scan after deformation; (c) line scan along the ridge of one pyramid before and after compression.

CONTINUUM MODELING

In order to model the deformation of a single pyramid under contact pressure, continuum limit analysis was used to analyze the rigid-perfect-plastic punching of a single pyramid structure. Upper bound theorem was adopted to predict the pressure loading at which the system starts to slip [3]. It was assumed that no friction exist at the contact surface and relative sliding was allowed between the punch and pyramid top surface.

Following the procedure used by R.T. Shield [4], the slip system was chosen to be that shown in Figure 4. The square area LMNO in Figure 4a stands for the top surface of the pyramid, and is punched down under a velocity of v under a uniform pressure q . The top surface is divided into four equal triangles by the diagonal LN and MO. Due to symmetry, only one triangle CMN is considered. The downward movement of the triangle is accommodated by the flow in CDEFMN. The polyhedra DCMN and EFMN are tetrahedral. Points D, E are vertically below line CF. MBDE and NBDE are two symmetric sections of

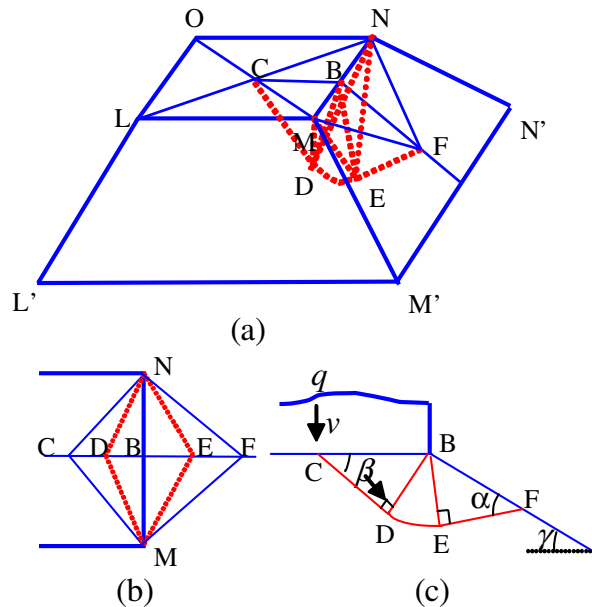


Figure 4. Schematic of the pyramid slip system.

right circular cones with MN as the axis. Fig.4b and 4c are the plane and vertical sections through CF. The stream lines of the flow are along CDEF. Assuming $\angle BCD = \beta$, the stream velocity $= v/\sin \beta$. The downward motion of the lower three triangles of MNCD is accommodated in the same way while the remainder material being at rest. Energy is dissipated in the discontinuity surfaces between the material at rest and the material moving in volume CDEFMN and also in the conical regions MBDE and NDBE where the plastic strain rate is not zero. Other parameters of the slip kinematics, the angles α and γ ; are shown in Figure 4c.

By using the upper bound and slip-line theorem [5], the contact pressure q was found to be a function of the flow stress k and the angles of the pyramid and the slip line system, α , β , and γ

$$q(\alpha, \beta; \gamma) \geq k \left\{ (\alpha + \beta - \gamma) + \sqrt{1 + \sin^2 \beta} (\alpha + \beta - \gamma + \cot \alpha + \cot \beta) \right\},$$

with the minimum value corresponds to the upper bound. For a given value of initial angle γ , one can solve for α and β by minimizing q . For $\gamma = \pi/12$ (15°) which is close to experimentally observed angle, $\alpha = 47^\circ$, $\beta = 35^\circ$ and $q = 5.2384 \cdot k$.

Thus from Figure 4c, the contact area between the punch and pyramid will expand with a velocity $v_{CB} = v \cot \beta = 1.46v$ as the punch moves down with a speed of v . Assuming that changes in β is negligible, the geometric relations in Figure 4c further provide the relations between the contact area A , punching load P and the punch displacement δ as

$$A = \left[\sqrt{A_0} + 2.92(\delta - \delta_0) \right]^2,$$

$$P = q \cdot A = 5.24k \left[\sqrt{A_0} + 2.92(\delta - \delta_0) \right]^2,$$

where A_0 and δ_0 are the initial contact area and the punch displacement, respectively. Thus, continuum limit analysis predicts that the deformation of the pyramid abides a parabolic relation between the normal loading and displacement. The macroscopic behavior of the plastic deformation of the pyramid was also analyzed with finite element methods; however, due to space limit the results of FEM will be reported else where. The continuum analysis provides self similar shape changes of the pyramid deformation, and thus constant ridge-angle change caused by plastic bulging effect is expected for large compression displacement. At a small displacement of compression some size effects are expected to be observed.

ATOMISTIC SIMULATIONS

Atomistic simulations were performed to catch the early period of the deformation of the pyramid under compression. In order to compare with the experimental results, Au pyramids of (114) facet orientations were considered for the molecular dynamics simulation of the deformation at 300K. The punch was created out of Ir atoms. The Sutton Chen potential [6], a Finnis-Sinclair many body potential, that includes long range van der Waals interactions in the form of a pair potential was used to model the interactions between the punch and pyramids. The Ir atoms were held fixed to simulate a rigid punch. A bi-material alloy combination rule was used to determine the interaction between the punch and pyramid [7].

The size of the system consists of 9736 atoms corresponding to 9 atomic layers of atoms with an initial contact area consisting of 9 atoms by 9 atoms. The bottom layer was held fixed creating an unnatural boundary condition but the system was large enough to capture the important features that occur during the initial stages of the contact compression. Figure 5 shows the load-displacement curve for this simulation. It can be seen that as the punch moves close to the pyramid the surface atoms jump to the punch. At room temperature, the atoms have enough velocity that helps to overcome the energy barrier holding the atoms to the pyramid. This reaction causes the pyramid relocate the volume from the lower part of the pyramid to the top changing the over all geometry in a manner that is the inverse of that seen in macroscopic experiments.

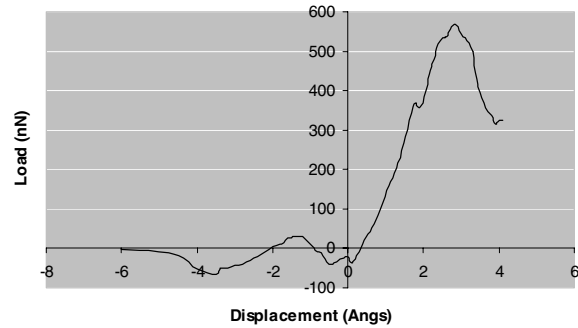


Figure 5. Load vs. displacement curve.

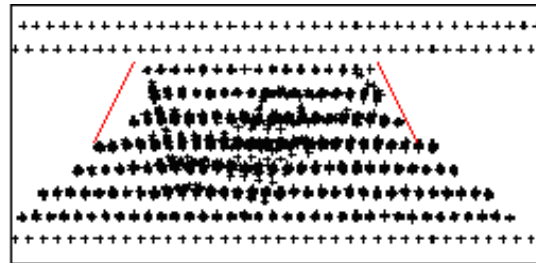


Figure 6. 2D projection of a deformed configuration of (114) pyramid on (110) plane.

The deformed configuration is shown in Figure 6, in which each plus sign represents the projection of an atom on a (110) plane. The image is taken from the increment step at which the first layer of the punch is at the initial position for the top layer of the pyramid. Due to an attraction between punch and pyramid, the top layer of the pyramid atoms move along the surface of the pyramid towards the punch. Since the atoms are accepting deformation and moving to positions that are in a lattice structure, the stress on the system is very low at any given time. The atoms are free to move and are free to accommodate the migration of other atoms to previously occupied sites. As a result, an initially (114) pyramids finally approaches a structure more closely representing that of the (113) plane. The ridge angle change is increased for an amount of 4.2° , which is opposite to what was observed in experiment of larger length scale.

SIZE EFFECT

In order to see the size effect in the plastic deformation of the pyramids under contact pressure, the ridge angle change (initial angle subtract the final angle) of different sizes of pyramids vs. the contact areas are plotted in Figure 7 for both experiments and atomistic simulations. The experimental data show that the change of ridge angle remains constant, with some scattering, with respect to the change of contact area for the contact deformation with contact area larger than

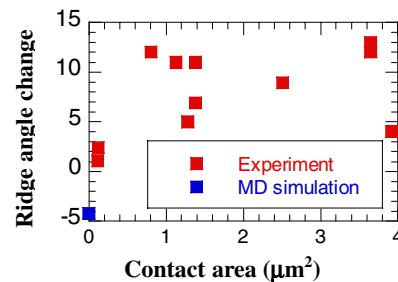


Figure 7. Angle change vs. contact area from experiment and atomistic simulations.

approximately $0.7 \mu\text{m}^2$, while the angle change decreases with decreasing contact area at very small contact area less than $0.2 \mu\text{m}^2$. Amazingly, the only available atomistic simulation result converges to the trend of experimental observation.

DISCUSSIONS AND CONCLUSIONS

A novel electro-chemical etching technique was used to produce self-organized pyramid structures on a single crystal gold (100) surfaces. The facets of the pyramid have a preferred orientation of (114) plane. Due to the self-similar nature and their size distribution, these pyramids serve as unique samples for investigating the size effect in the plastic deformation of the single crystals. Contact compression experiments as well as continuum limit analysis and molecular dynamics simulations were conducted to study the deformation of the pyramids. The limit analysis predicts a parabolic relation between the load and displacement. It provides an estimate on the asymptotic behavior of the elastic-plastic load-deflection response of the pyramid under compression for a large value of deflection. The three dimensional molecular dynamics simulation reveals the very small volume deformation process during the early stage of the pyramid compression. The continuum analyses predict size independent values of the slope change of the pyramid facets near the contact edge, caused by plastic deformation. However, atomistic simulation predicts opposite value of the slope change to the prediction of the continuum analyses. The AFM measurements of the slope change show size dependent transition from the predictions of the continuum analyses to that of the atomistic simulations. The transition data provide an apparent characteristic length of the size dependence of plastic deformation in a small volume. The simulation shows that the deviation from a continuum behavior at a very small length scale is clearly due to interface interaction and surface effects, while the transition at a larger scale may be due to dislocation mechanisms.

ACKNOWLEDGEMENTS

This work was supported by Brown/General Motors Collaborative Research Laboratory. Valuable discussions with Dr. Y. Qi and Dr. Y.T. Cheng are gratefully acknowledged.

REFERENCES

1. Hutchinson, J.W., *Int. J. Solids Structures*, 37, 225-238 (2000)
2. Bitterncourt, E., Needleman, A., Gurtin, M.E., and Van der Giessen, E., *JMPS*, 51, 281-330 (2003)
3. Johnson, K.L., Cambridge University Press (1984)
4. Shield, R.T., Drucker, D.C., Technical report, A11-75. Division of Applied Mathematics, Brown University (1975)
5. Rice, J.R., Technical report, AT (11-1)-3084, no.13. Division of Engineering, Brown University (1972)
6. Sutton, A.P., Chen, J., *Phil. Mag. Lett.*, 61 (3), 139 (1990)
7. Rafii-Tabar, H., Sutton, A.P., *Phil. Mag. Lett.*, 63 (4), 217 (1991)