8th. World Congress on Computational Mechanics (WCCM8)
5th European Congress on Computational Methods in Applied Sciences and Engineeering (ECCOMAS 2008)
June 30 –July 5, 2008
Venice, Italy

Ab initio DFT calculations of surface stress and stretch of charged Au films

*** Y. Umeno[1,2], C. Elsässer[3], B. Meyer[4], P. Gumbsch[2,3] and J. Weissmüller[5,6]**

[1] Institute of Industrial Science, The University of Tokyo
4-6-1 Komaba Meguro-ku, Tokyo 153-8505, Japan
umeno@iis.u-tokyo.ac.jp

[2] Institut für Zuverlässigkeit von Bauteilen und Systemen, University of Karlsruhe
Kaiserstrasse 12, 76131 Karlsruhe, Germany

[3] Fraunhofer-Institut für Werkstoffmechanik IWM
Wöhlerstrasse 11, 79108 Freiburg, Germany

[4] Friedlich-Alexander-University of Erlangen-Nürnberg
91054 Erlangen, Germany

[5] Institut für Nanotechnologie, Forschungszentrum Karlsruhe
76021 Karlsruhe, Germany

[6] Technische Physik, Universität des Saarlandes
66041 Saarbrücken, Germany

Key Words: *Ab initio calculation, Surface stress, Electric charge, Mechanical properties, Deformation.*

ABSTRACT

Recent experiments have revealed that nanometer-sized porous materials expand or contract when they are electrically charged [1,2]. This is explained as an effect of surface charge on surface stress, which has been observed in experiment on macroscopic single crystal metal surfaces [3,4]. With the aim to theoretically study the effect of charging on surface stress, we performed *ab initio* density funcional theory (DFT) calculations of Au thin films with (111) and (100) surfaces within the local density approximation (LDA)[5] by means of the mixed basis pseudopotential method (MBPP)[6-8]. First, we showed that derivative of surface stress (f) with respect to surface excess charge (q) corresponds to and can be obtained by derivative of surface work function with respect to in-plane lattice parameter, which can be calculated simply using uncharged thin film models with varying lateral strain [9]. Calculated derivative of f with respect to q for (111) at q = 0, $(\partial f/\partial q)_{q=0} = -1.86$ V, compares well with experimental results [10]. It was also elucidated that the value of the (100) surface is about a factor of two smaller ($(\partial f/\partial q)_{q=0} = -0.90$ V). Secondly, we conducted *ab initio* DFT calculations of charged Au films to examine the role of surface stretch, ε_s, (outward or inward relaxation of the top surface layer) on change in surface stress in response to charging, which was suggested by Weigend et al. [11] in their DFT simulation of Au cluster. We found ε_s is a nearly linear and monotonically decreasing function of q for both (111) and (100). Calculated values of $d\varepsilon_s/dq$ for (111) and (100) are -7.7×10^{-12} m^3/C and -5.2×10^{-12} m^3/C, respectively, which are in good agreement with an experiment for Au (111), -6×10^{-12} m^3/C [12]. Charge density analysis of unrelaxed surface indicated that change in surface stress due to charging stems not only from indirect effect of stretch causing transverse expansion or contraction as was previously pointed out [11], but also from direct effect of charging on bonding orbitals in between ion cores.

REFERENCES

[1] D. Kramer, R. N. Viswanath and J. Weissmüller. “Surface-Stress Induced Macroscopic Bending of Nanoporous Gold Cantilevers”. *Nano Letters*, Vol. **4**, 793–796, 2004.

[2] J. Weissmüller, R. N. Viswanath, D. Kramer, P. Zimmer, R. Würschum and H. Gleiter. “Charge-Induced Reversible Strain in a Metal”. *Science*, Vol. **300**, 312–315, 2003.

[3] H. Ibach. “The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures”. *Surf. Sci. Reports*, Vol. **29**, 193–263, 1997.

[4] W. Haiss. “Surface stress of clean and adsorbate-covered solids”. *Rep. Prog. Phys.*, Vol. **64**, 591–648, 2001.

[5] L. Hedin and B. I. Lundqvist. “Explicit local exchange-correlation potentials”. *J. Phys. C: Solid State Phys.*, Vol. **4**, 2064–2083, 1971.

[6] C. Elsässer, N. Takeuchi, K. M. Ho, C. T. Chan, P. Braun and M. Fähnle. “Relativistic effects on ground state properties of 4d and 5d transition metals”. *J. Phys. Condens. Matter*, Vol. **2**, 4371–4394, 1990.

[7] K. M. Ho, C. Elsässer, C. T. Chan and M. Fähnle. “First-principles pseudopotential calculations for hydrogen in 4d transition metals: I. Mixed-basis method for total energies and forces”. *J. Phys. Condens. Matter*, Vol. **4**, 5189–5206, 1992.

[8] B. Meyer, K. Hummler, C. Elsässer and M. Fähnle. “Reconstruction of the true wavefunctions from the pseudowavefunctions in a crystal and calculation of electric field gradients”. *J. Phys. Condens. Matter*, Vol. **7**, 9201–9217, 1995.

[9] Y. Umeno, C. Elsässer, B. Meyer, P. Gumbsch, M. Nothacker, J. Weissmüller and F. Evers. “Ab initio study of surface stress response to chargin”. *Europhys. Lett.*, Vol. **78**, 13001, 2007.

[10] W. Haiss, R. J. Nichols, J. K. Sass and K. P. Charle. “Linear correlation between surface stress and surface charge in anion adsorption on Au(111)”. *J. Electroanal. Chem.*, Vol. **452**, 199–202, 1998.

[11] F. Weigend, F. Evers and J. Weissmüller. “Structural Relaxation in Charged Metal Surfaces and Cluster Ions”. *Small*, Vol. **2**, 1497–1503, 2006.

[12] R. J. Nichols, T. Nouar, C. A. Lucas, W. Haiss and W. A. Hofer. “Surface relaxation and surface stress of Au(111)”. *Surf. Sci.*, Vol. **513**, 263–271, 2002.