Preliminary white paper – Eric Stach *9/6/01*
DOE BES "Workshop on New Materials Science Enabled by In-situ Microscopies"
September 13-15, 2001

In-situ TEM – a tool for quantitative observations of deformation behavior in thin films and nano-structured materials

E.A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory

Abstract

This paper highlights future developments in the field of in-situ transmission electron microscopy, as applied specifically to the issues of deformation in thin films and nanostructured materials. Emphasis is place on the forthcoming technical advances that will aid in extraction of improved quantitative experimental data using this technique.

What is scientifically interesting?

The deformation response of thin films and nano-structured materials is fundamentally different than that of bulk materials. This is due to the confining effects of small sizes and geometrical boundaries on the kinetics of dislocation behavior. In the case of thin film materials, the fact that the substrate is significantly thicker than the film causes it to be, in effect, perfectly elastically rigid. As a result the film is constrained, and any differences in lattice parameter between the two – be they due to heteroepitaxial growth, differential thermal expansion or induced by internal transformations – result in the incorporation of strain into the film. Because of the elastic constraint, this strain induces stresses in the film, and concomitantly increases the internal strain energy. The magnitudes of these stresses can be very large (from many hundreds of MPa to 1 – 2 GPa in some cases) and the resulting strain energy is highly thermodynamically unfavorable. This causes large driving forces for strain relaxation, which compete with the kinetics of dislocation nucleation, propagation, multiplication and interaction in complex ways to determine the mechanical properties of these structures. These kinetic effects fundamentally control the performance of strained layer semiconductor heterostructure devices[1] and can cause very high yield strengths and hardness in thin metal films.[2,3]

Similarly, in the case of nanostructured materials – 'nano' tubes, wires and particles – the presence of small volumes, free surfaces and strong bonding can dramatically alter mechanical behavior.[4,5] Additionally, because of unique bonding configurations and quantum mechanical size effects, coupling between mechanical and electronic properties can be observed in many of these systems.[6,7]

Why in-situ TEM?

In general, the technique of *in-situ* transmission electron microscopy (TEM) allows real time observations of the interplay between processing / property / microstructure relationships in materials. In this technique, some form of active stimulus is applied to a sample inside the electron microscope during simultaneous imaging. This allows quantitative observations to be made of the microstructural response (and in some cases material properties) to changing conditions. Common stimuli included thermal, mechanical, electrical, and magnetic, while less common (but demonstrated) stimuli include electrochemical, gaseous and liquid fluxes and optical irradiation.

Transmission electron microscopy is ideally suited to the task of characterizing dislocation and deformation behavior in thin films and nano-structures. TEM allows direct imaging at high resolution of the configuration of high densities of dislocations in materials, be they within a single crystal, an individual grain or at a grain boundary or bi-material interface. Additionally it allows characterization of the Burgers vector and slip systems of dislocations – their key geometrical signatures.

In the case of thin film studies, the imaging capabilities of TEM allow one to *quantitatively* characterize the kinetics of dislocation nucleation, propagation, multiplication and interaction during *in-situ* experiments. These parameters control the rate of strain relaxation in thin films, and can, individually and collectively, determine 7mechanical behavior. Some summary examples of these quantitative kinetic measurements extracted from our work are shown as Figures 1 through 3.[8,9,10]

In the case of nanostructured materials, TEM is one of the few tools with sufficiently high resolution and magnification to image these structures. Recent efforts by several groups have adapted the technology of scanning probe microscopy techniques to measure the mechanical behavior of various nanostructured materials as well as the interplay between mechanical behavior and electronic structures. Several examples culled from the literature are shown as Figures 4 through 6.[11,12,13]

What are the inherent difficulties?

In-situ TEM studies are subject to strong experimental constraints. Primary among these is concerns regarding sample preparation. A TEM sample has to be prepared in such a way as to be electron transparent at the intended operating voltage. The exact thickness at which a material is 'electron transparent' depends on both the atomic weight of the material, the accelerating voltage of the microscope and the intended experimental study. It is, generally, on the order of 1 – 5 μm for deformation studies in intermediate to high voltage TEM's and less than a hundred Angstroms for atomic resolution studies. In the case of thin film studies a substrate thickness of > 10 times the film thickness is required to prevent excessive strain relaxation[14] – this generally means that films thickness no greater than 500 nm can be observed without substantial concerns about thin foil relaxation. Additionally, the more traditional methods of sample preparation – ion beam and chemical thinning – do not create particularly uniform or reproducible sample geometries and may introduce artifacts that affect dislocation kinetics. All of these problems produce significant data reproducibility concerns when attempting quantitative work.

Additionally, the objective lens of the transmission electron microscope is a very small laboratory within which to conduct experiments! In the case of very high-resolution lenses, the gap between the pole pieces is on the order of 1.5 mm – this increases to only about as large as 5 mm to 1 cm in the most favorable cases. This puts very significant design constraints on sample manipulation devices for *in-situ* experimentation. These constraints dramatically increase the time to build working devices, require very talented and patient toolmakers and can be considerably expensive. This difficulty should in no way be underestimated.

What are the new opportunities and directions?

Advances in Sample Preparation

One of the most important developments in the field of *in-situ* TEM concerns the application of advanced lithographic techniques to create samples of uniform thickness and geometry. The techniques of photolithography, electron lithography and focused ion beam lithography are now well developed, relatively easy to use and increasingly available. Two examples of lithographic methods used in thin film deformation studies are shown as Figures 7 & 8.[15,10] The creation of uniform samples through lithographic methods allows the creation of many well-suited samples, reduced artifacts and generally more data. All of these give greater data reliability.

Sample 'Nano-manipulation'

The adaptation of scanning probe techniques in the design of sample holders has already produced significant breakthroughs in the field of nano-structured materials. Several of these were demonstrated in Figures 4 through 6. At present, a number of different research groups through the world are exploiting these developments with holders manufactured in-house. At LBNL, we have built five of these for different microscopes in the facility. Two of these are dedicated to the study of the mechanical and electrical properties of nanostructured materials, while three are dedicated to the technique of *in-situ* nanoindentation, both at room temperature and elevated temperatures. Additionally, a commercial manufacturer of these devices has recently appeared.[16]

Integration of Microelectromechanical Systems (MEMS)

Coupled with the development of lithographic processing technologies has been the development and exploitation of increasingly sophisticated MEMS devices. These devices are of appropriate size to be operated within the objective lens regions of electron and ion microscopes. In addition to creating large numbers of samples of fixed geometry, MEMS also allow mechanical actuation to be incorporated into the experimental design directly. Additionally, coupling of mechanical, electrical and magnetic stimuli can be achieved within the same experimental apparatus. Even more dramatic applications of MEMS can be envisioned in the areas of microfluidics, *in-situ* sensing, optoelectronic biasing and bio-molecular and bio-material probes.

Improvements in microscope performance – Abberation correction

The ultimate resolution limit of the transmission electron microscope is a function of the spherical aberration (C_s) of the objective lens and the electron wavelength. In the past, reduction of C_s has been intimately connected with reducing the size of the objective lens pole gap – the opposite of what is best for *in-situ* experimentation. Recent research has demonstrated that it is possible to electron optically correct the C_s of microscope.[17] It is anticipated that within the very near future, one will be able to design microscopes with very large pole gaps (1 to 2 cm) with low spherical aberration and high resolution.[18] Significantly, C_s correction has the additional benefit that it eliminates electron delocalization effects. This allows one to exploit the extended coherence envelope of a field emission gun without having to confront the problem of image blurring at interfaces and edges. Some examples of how this aids in real time imaging are shown as Figure 9. Here individual columns of gold atoms migrate along a foil edge due to beam heating.

Within the context of deformation studies, this increased pole gap size will significantly aid the process of sample holder creation and allow the incorporation of more elaborate

micromachines to bias samples and measure properties. Even greater benefits may be found in the area of *in-situ* crystal growth and environmental cell microscopy, where the increased pole gap should allow further types of real time characterization.

Improvments in microscope performance – Energy Filtering and STEM

The past five years have seen the steady development of both energy-filtered imaging and high angle annular dark-field imaging techniques. These techniques have become both sophisticated and easier to accomplish, thereby allowing quasi-real time imaging of compositional changes in materials.[19,20] It is anticipated that they will be used increasingly in *in-situ* experimentation in the next several years.

Improvements in microscope performance – High Voltage TEM

As mentioned above, the inherent resolution of the electron microscope is a function of the electron wavelength and thus the TEM accelerating voltage. High voltage electron microscopy is a proven technology for resolution extension (present machines have capabilities on the order of 1 Å point-to-point).[21] Additionally, the increased electron energy allows significantly greater specimen penetration (many microns) allowing *in-situ* experimentation to probe truly bulk-like behavior.[22,23] US capabilities in the area of HVEM significantly lag those of other countries, with seven new machines installed in Japan, one in Germany and one in South Korea over the last decade or so and none in the US. With the decommissioning of the Argonne HVEM Tandem facility in April 2001, the only HVEM dedicated to *in-situ* experimentation in America is at LBNL. It is microscope based on 1960's technology and has proven unreliable over the past several years. The installation of a new HVEM coincident with new MEMS and scanning probe based deformation capabilities as well as energy-filtered imaging techniques would provide the US with truly world class facilities for *in-situ* deformation studies.

Improvements in data analysis

In-situ experiments produce tremendous amounts of data – 30 minutes of videotape contains 54,000 individual frames of data. However, at present, computational power has progressed to the point where a relatively inexpensive desktop computer can batch process a full 30 minutes of video in only several hours. It is anticipated that we will be able to automate certain types of data analyses in the near future, allowing increasingly quantitative *in-situ* analyses.

Breakthrough science?

In conclusion, *in-situ* transmission electron microscopy is uniquely well suited to the study of fundamental deformation processes in thin films and nanostructures. Recent advances in sample preparation methodology, sample manipulation devices, microelectromechanical systems and improvements in microscope performance all point towards exciting developments in the near future.

Expected breakthrough research includes:

(a) Quantitative characterization and control of strain relaxation in heteroepitaxial films, leading to templated quantum dot structures and better design rules for heteroepitaxial devices,

(b) An understanding of the relevant dislocation mechanisms behind the high strengths in thin metal films,

(c) Understanding of the deformation processes during indentation of hard materials, the origing of the high hardness of thin metal films and dislocation behavior in wide band gap semiconductors and

(d) Exploration of the mechanical behavior and complex coupling between strain and electronic structure in nanostructured materials.

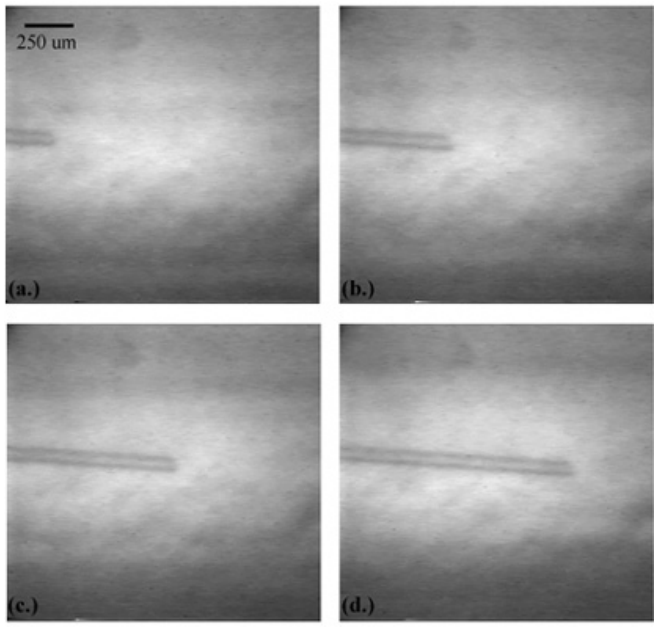

Figure 1(a) A time sequence of images obtained from video recording of dislocation motion. Each frame is 1 second apart. Bright field **g** = 220.

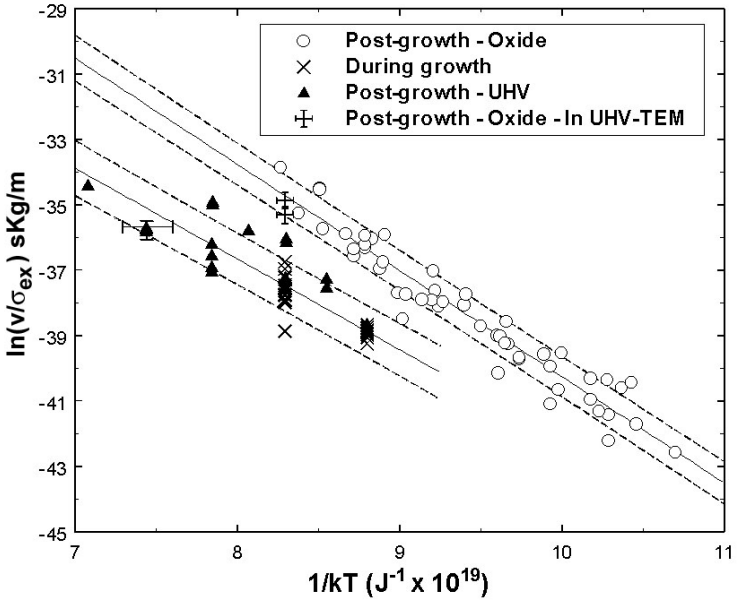

Figure 1(b) Quantitative measurements of dislocation velocities in strained layer SiGe heterostructures. Measurements made during crystal growth, post-growth in ultrahigh vacuum and post-growth after native oxide formation. Adapted from Reference 8.

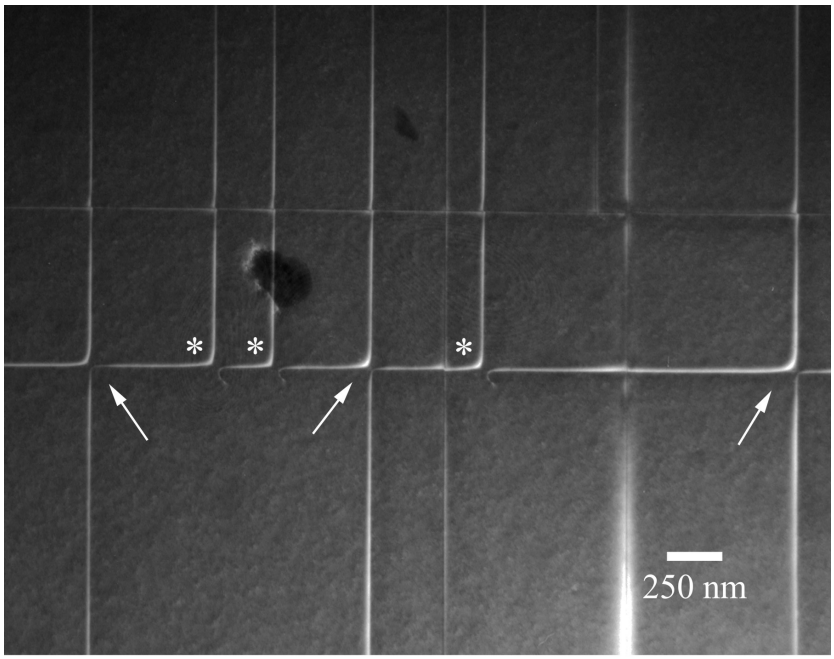

Figure 2(b) Dark field **g** = 400 *s* << 0 image showing dislocation interactions in a 70 nm $Si_{80}Ge_{20}$ / Si (001) heterostructure. Dislocation pairs with parallel Burgers vectors are indicated by a (*) if the reaction results in blocking and are arrowed in the cases where the interaction does not result in blocking.

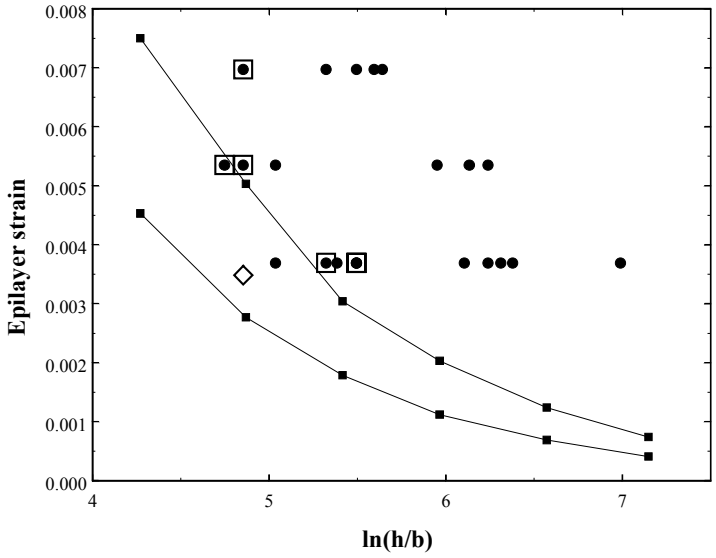

Figure 2(b) Quantitative determination of the epilayer thickness and strain at which various types of dislocation interactions are observed. The upper curve shows the limits of reactive blocking calculated by a dislocation dynamics simulation; the lower curve shows the critical thickness computed by the same methods. Figures reprinted from Reference 9.

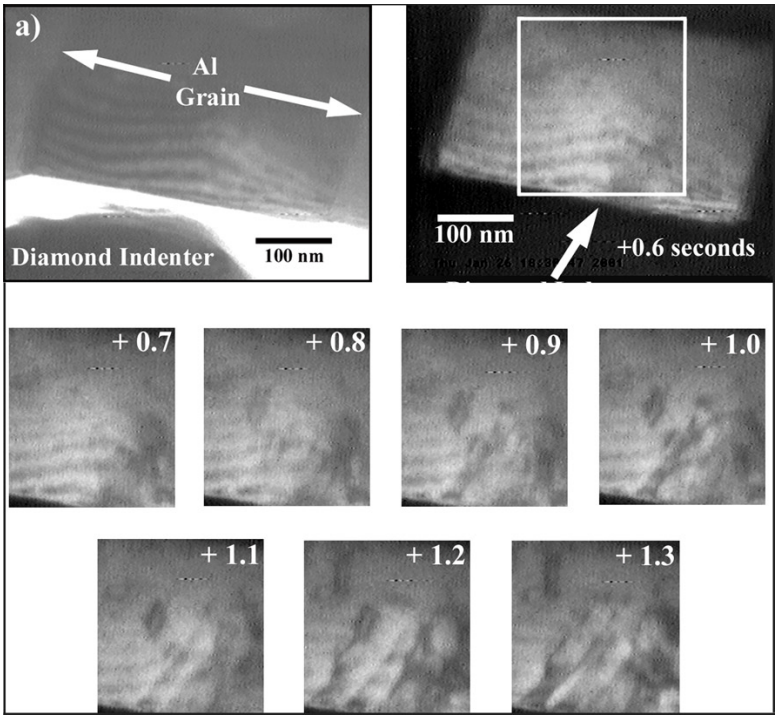

Figure 3(a) Series of dark field **g** = $1\bar{1}1$ micrographs taken from an *in-situ* TEM nanoindentation of a <113> oriented aluminum grain. As indentation proceeds, the introduction of dislocations into the grain is clearly visible.

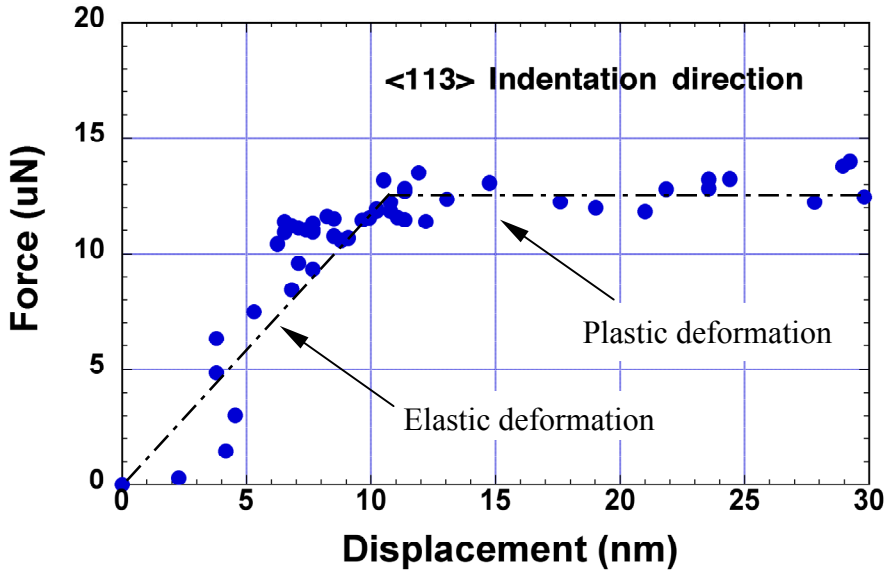

Figure 3(b) Quantitative force – displacement determined during the experiment shown as Figure 3(a). The onset of plastic deformation is observed to coincide with the introduction of surface prismatic dislocation loop nucleation and propagation into the grain. Adapted from Reference 10.

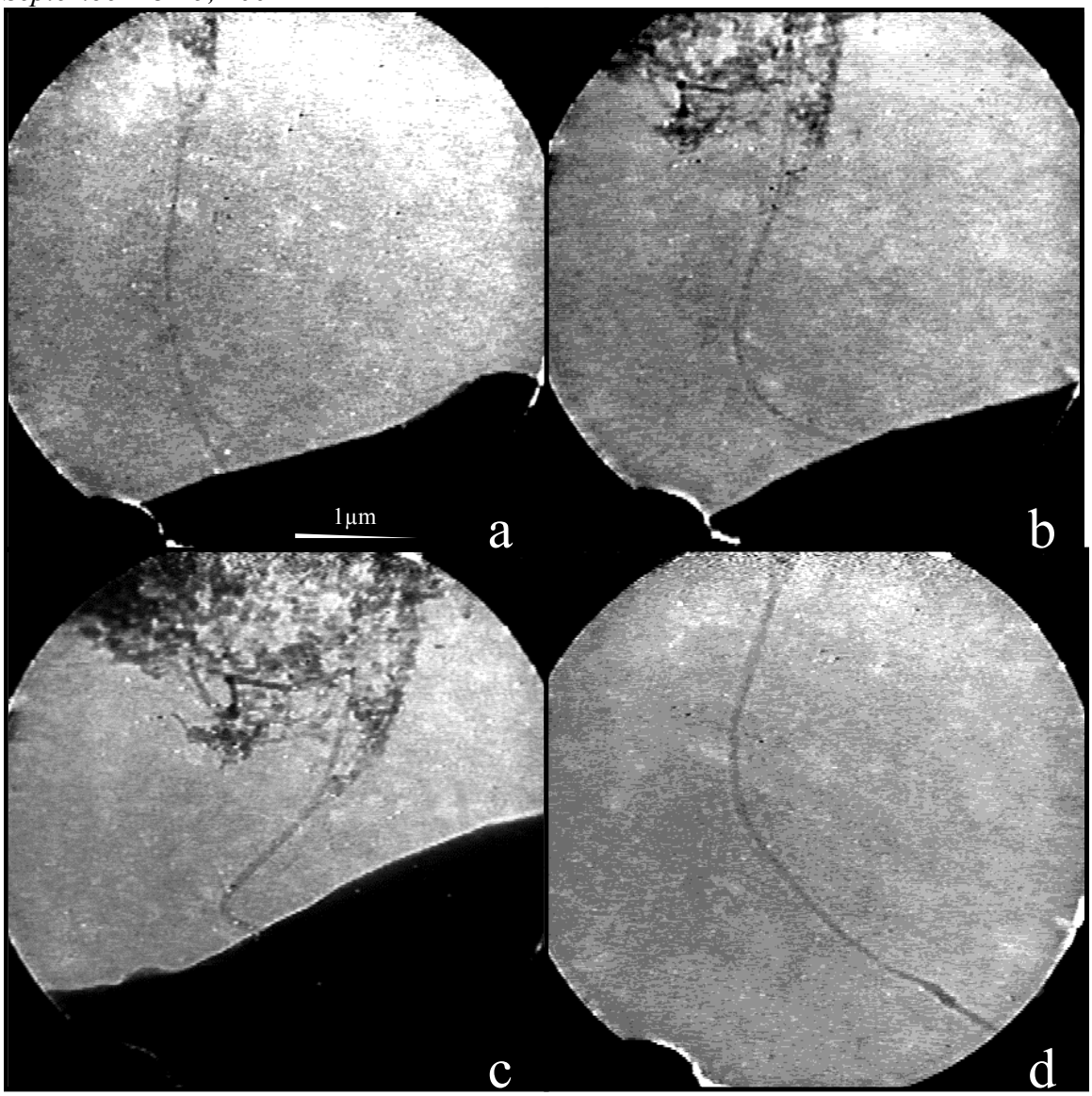

Figure 4 *In-situ* bending experiment conducted in the LBNL HVEM showing carbon nanotube kinking (c) at large deformation and recovery (d) upon release. From Reference 11.

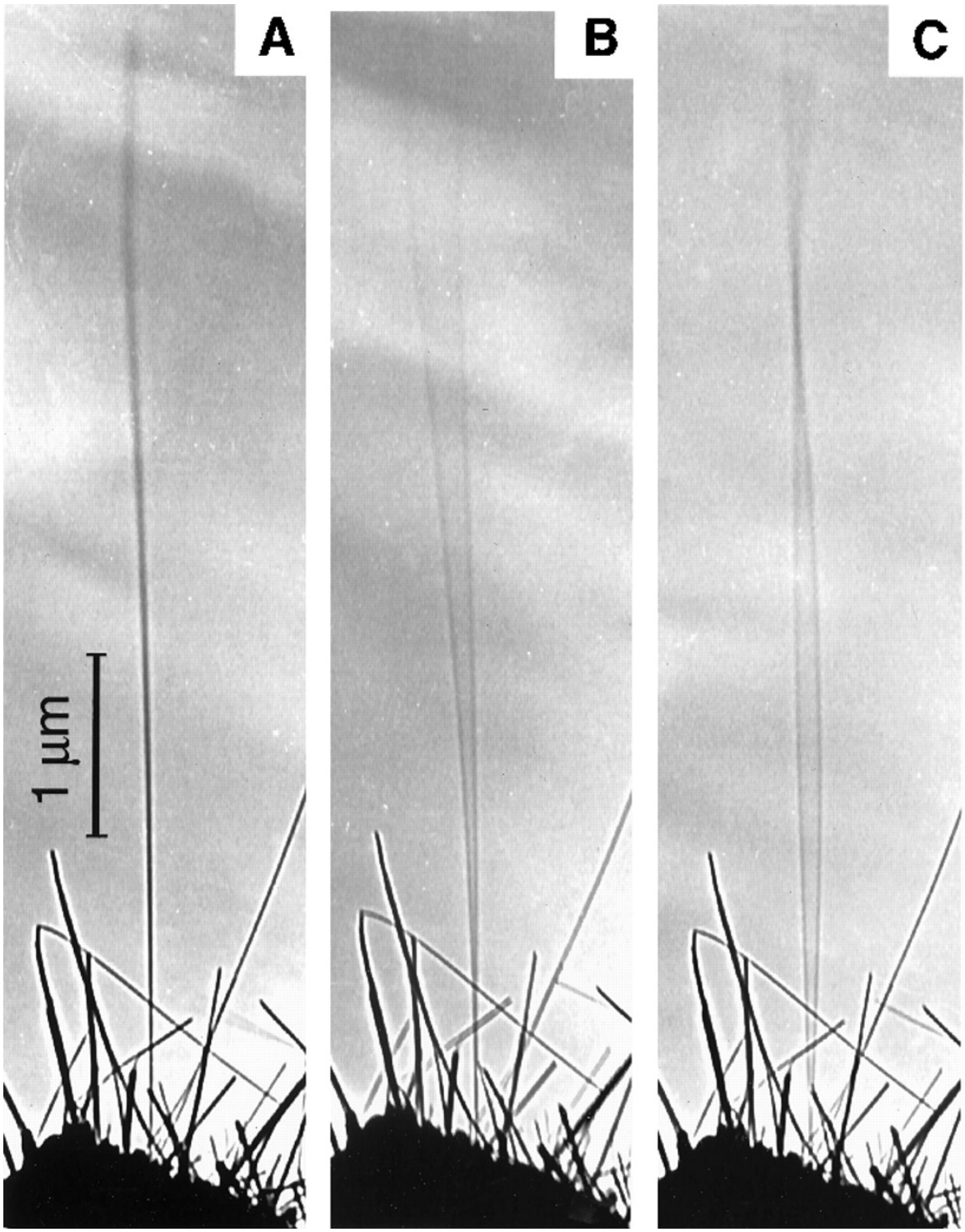

Figure 5 Carbon nanotube response to resonant alternating applied potentials. In (b) and (c) resonant excitation is used to determine the fundamental modes of the tube and determine the bending modulus. Reprinted from Reference 12.

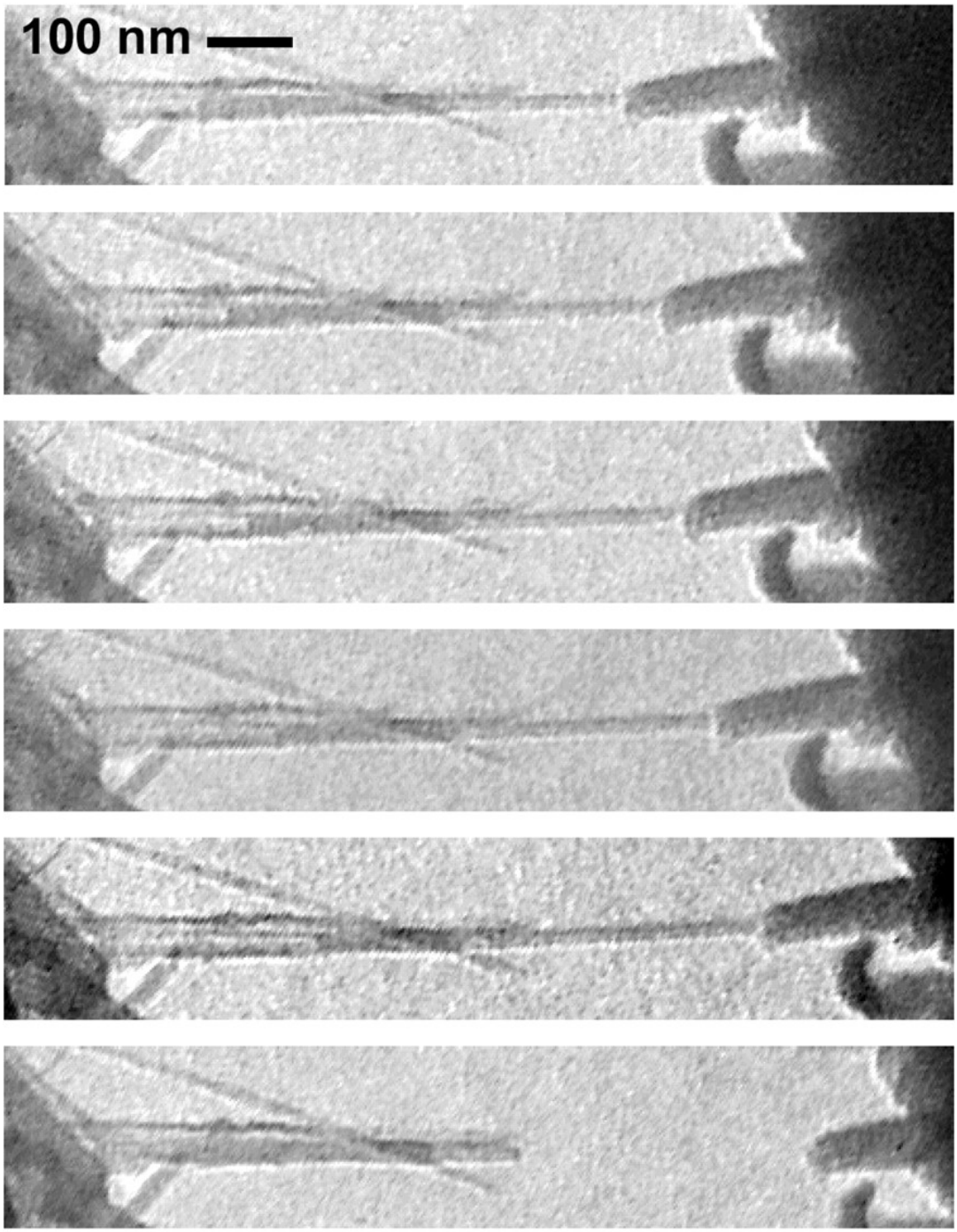

Figure 6 Selected frames of a video recording of the *in-situ* telescoping of a multi-walled carbon nanotube. In the first five frames, the core nanotubes are slowly withdrawn to the right. In the sixth image, which occurred one video frame after the core was released, the core has fully retracted into the outer nanotube housing as a result of the attractive van der Waals force. Reproduced from Reference 13.

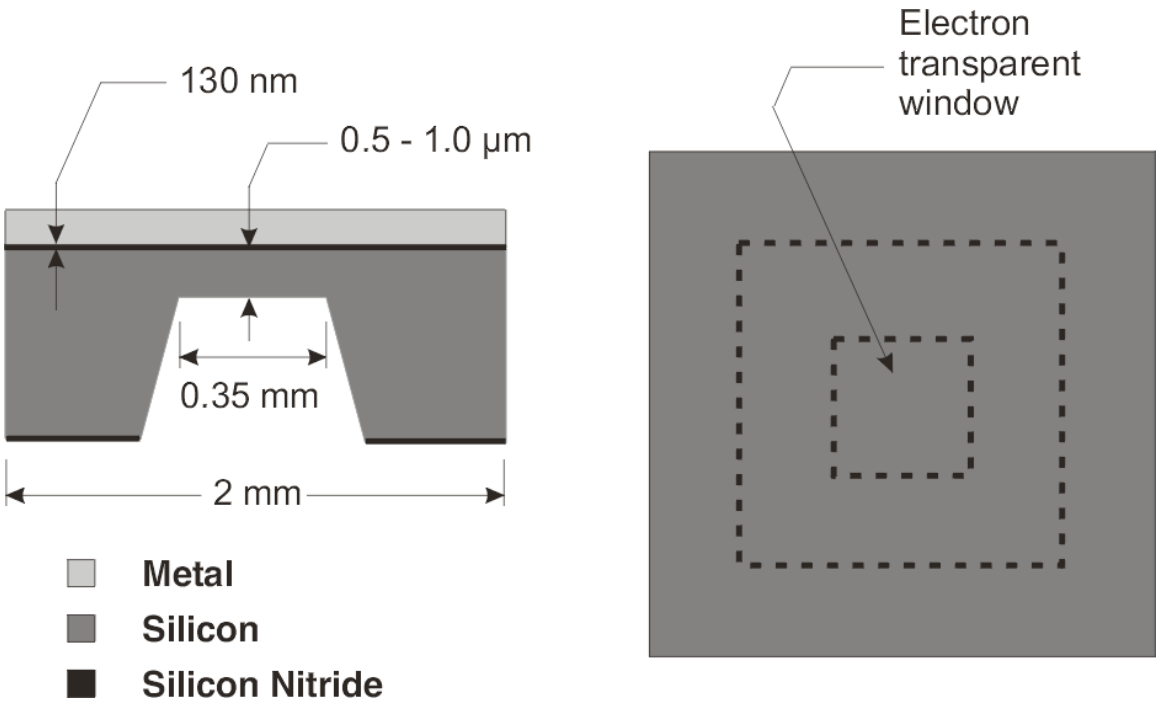

Figure 7 Schematic of micromachined 'window' samples developed for *in-situ* thermal cycling studies. Adapted from Reference 15.

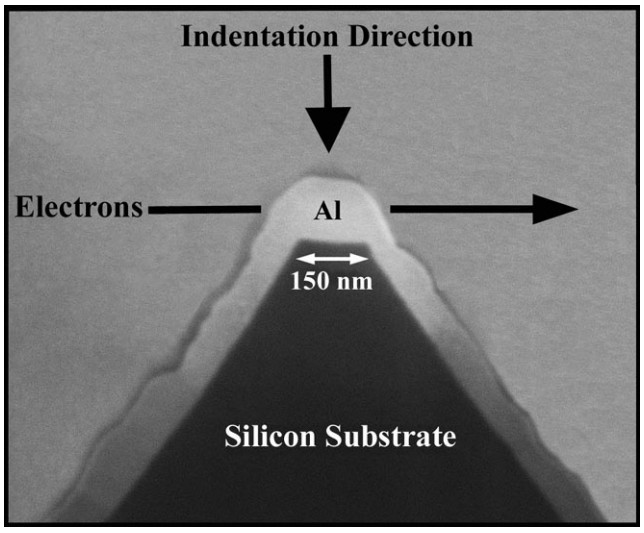

Figure 8 Scanning electron micrograph of a lithographically patterned wedge sample used in *in-situ* nanoindentation studies of thin film deformation. Reproduced from Reference 10.

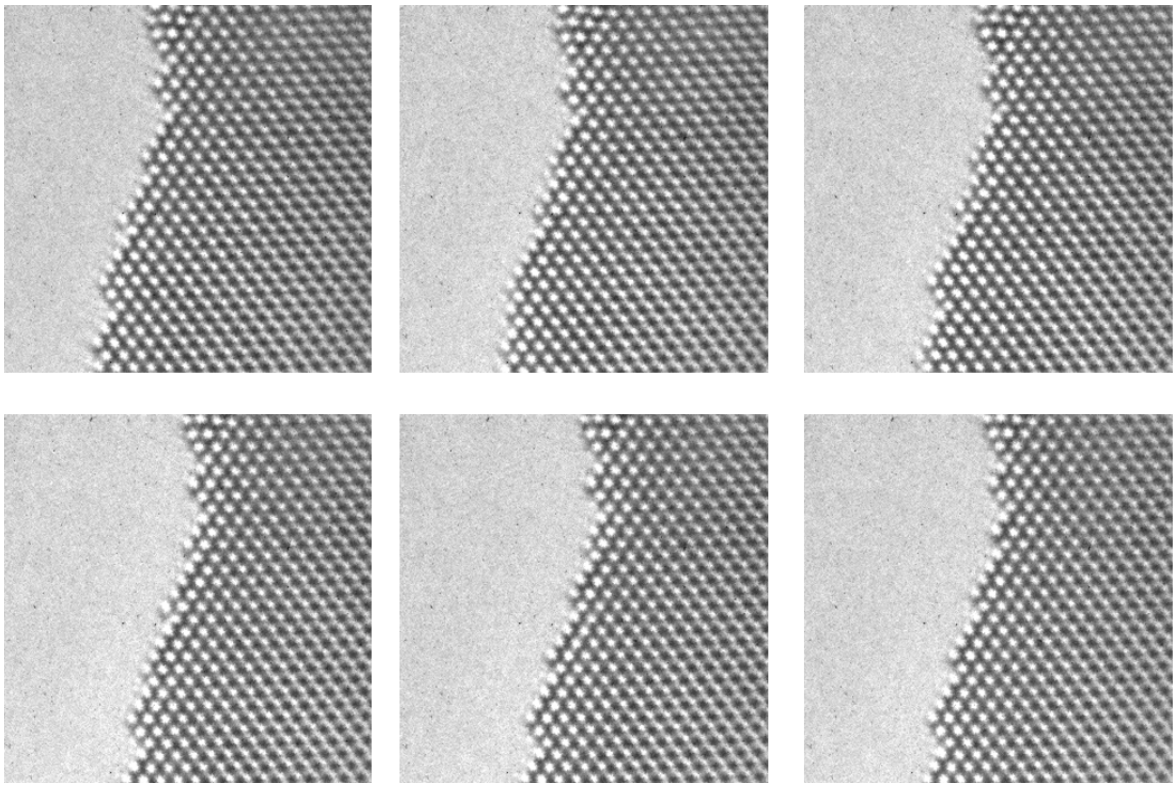

Figure 8 A time sequence of images taken along the Au <110> zone axis using the C_s corrected microscope at Jülich. Atomic column migration to and from kink sites is visible. What is interesting about these images is that they are single images (not focal series reconstructions) which do not show electron de-localization effects, despite the fact they were taken with a field emission gun microscope. This means that one can exploit the resolution gain inherent in field emission microscopes due to the increased coherence, without suffering the effects of image delocalization at boundaries and interfaces. Data courtesy C. Kisielowski of NCEM.

References:

[1] R. Hull and E.A. Stach; "Strain accommodation and relief in SiGe / Si heteroepitaxy" in *Heteroepitaxy, Thin Film Systems*, edited by A.W. Liu and M.B. Santo (World Scientific Publishing Co., Inc., Rivers Edge, NJ 1999).

[2] W.D. Nix, "Mechanical properties of thin films", Met. Trans. A **20**, 2217, 1989.

[3] W.D. Nix, "Elastic and plastic properties of thin films on substrates: nanoindentation techniques", Mat. Sci. Eng. A **234-236**, 37, 1997.

[4] M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson, "Exceptionally high Young's modulus observed for individual carbon nanotubes", Nature, **381**, 678-80 1996.

[5] Z.W. Pan, S.S. Xie, L. Lu, B.H. Chang, L.F. Sun, W.Y. Zhou, G. Wang, D.L. Zhang, "Tensile tests of ropes of very long aligned multiwall carbon nanotubes", Appl. Phys. Lett., **74**, 3152-4, 1999.

[6] S. Paulson, M.R. Falvo, N. Snider, A. Helser, T. Hudson, A. Seeger, R.M. Taylor, R. Superfine, S. Washburn, "In situ resistance measurements of strained carbon nanotubes" Appl. Phys. Lett., **75**, 2936-8, 1999.

[7] D. Tekleab, D.L. Carroll, G.G. Samsonidze, B.I. Yakobson, "Strain-induced electronic property heterogeneity of a carbon nanotube" Phys. Rev. B, **64**, 35419, 2001.

[8] E.A. Stach and R. Hull, "Enhancement of dislocation velocities by stress assisted kink nucleation at the native oxide / SiGe interface", Appl. Phys. Lett., **79**, 335, 2001.

[9] E. A. Stach, R. Hull, K. W. Schwarz, F. M. Ross and R.M. Tromp "A new mechanism for dislocation blocking in strained layer epitaxial growth", Phys. Rev. Lett. **84**, 947, 2000.

[10] A.M. Minor, J.W. Morris Jr. and E.A. Stach "Quantitative in-situ nanoindentation of aluminum thin films", Appl. Phys. Lett., accepted for publication, 2001.

[11] S.-J. Chen, R. Ritchie, A. Zettl and U. Dahmen "In-situ bending deformation of carbon nanotubes in a HVEM", Proc. ICEM 14, **I**, 75, 1998.

[12] P. Poncharal, Z.L. Wang, D. Ugarte and W.A. de Heer, Science, **283**, 1513, 1999. Z.L. Wang, "Nanomechanics of fiber-like nanomaterials", J. of Mat. Sci. & Tech., **17**, 303-5, 2001.

[13] J. Cumings and A. Zettl; "Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes", Science, **289**, 602-4, 2000.

[14] R. Hull, Appl. Phys. Lett. **63**, 2291 (1993).

[15] M.J. Kobrinsky and C.V. Thompson, "Activation volume for inelastic deformation in polycrystalline Ag thin films" Acta Mater., 48, 625-33, 2000.

[16] Nanofactory Instruments, Göteborg, Sweden. http://www.nanofactory.com

[17] M. Haider, H. Rose, S. Uhlemann, E. Schwan, B. Kabius, and K. Urban; "A spherical-aberration-corrected 200 kV transmission electron microscope." Ultramicroscopy, **75**, 53-60, 1998.

[18] K. Xiu and J.M. Gibson; "Aberration corrected microscope design for large gap *in-situ* electron microscopy", oral presentation at the Spring 2001 Materials Research Meeting, San Francisco, CA.

[19] J.M. Howe, T.M. Murray, K.T. Moore, A.A. Csontos, M.M. Tsai, A. Garg and W.E.

Benson, "Understanding interphase boundary dynamics by in situ high-resolution and energy-filtering transmission electron microscopy and real-time image simulation", Microscopy and Microanalysis, **4**, 235-47, 1998.

[20] N.D. Browning, I. Arslan, Y. Ito, R.F. Klie, P. Möck, S. Sivananthan, K. Sun and T. Topuria, "Atomic scale analysis of the structure-property relationships at interfaces and defects in thin film materials", oral presentation at IUMRS Meeting, Singapore, 2001.

[21] G. Dehm, F. Ernst, J. Mayer, G. Möbus, H. Muellejans, F. Phillipp, C. Scheu, and M. Rühle; **"**Transmission electron microscopy at the Max-Planck-Institut für Metallforschung**".** Zeitschrift für Metallkunde, **87**, 898-910, 1996.

[22] E.P. Butler and K.F. Hale; "Dynamic experiments in the electron microscope", Elsevier / North-Holland, New York, 1981.

[23] U. Messerschmidt, D. Baither, M. Bartsch, B. Baufeld, B. Geyer, S. Guder, A. Wasilkowska, A. Czyrska-Filemonowicz, M. Yamaguchi, M. Feuerbacher, and K. Urban; "High-temperature in situ straining experiments in the high-voltage electron microscope" Microscopy and Microanalysis, **4**, 226-34, 1998.