Materials Science and Engineering A 429 (2006) 272–276

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Large-scale production of nano-twinned, ultrafine-grained copper

A.M. Hodge [a,b,*], Y.M. Wang [a,b], T.W. Barbee Jr. [a]

[a] *Materials Science and Technology Division, Lawrence Livermore National Laboratory, P.O. Box 808, L-352, Livermore, CA 94550, USA*

[b] *Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, P.O. Box 808, L-352, Livermore, CA 94550, USA*

Received 5 January 2006; received in revised form 11 May 2006; accepted 11 May 2006

Abstract

Large-scale production of high purity (99.999%), nano-twinned, and ultrafine-grained copper foils (22 μm thick) was successfully implemented by the use of nanoscale multilayer technology. The process allows the production of up to fourteen 10 cm diameter foils during a single deposition run with high levels of reproducibility. Mechanical tests demonstrate that the strength of the Cu foils ($\sigma_y \sim 540$–690 MPa) compares favorably to ultrafine-grained copper samples produced by other methods.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ultrafine-grained copper; Nano-twinned; Multilayers; Sputtering

1. Introduction

The production of new and improved high strength nanocrystalline (NC) and ultrafine-grained (UFG) materials is an endeavor that has been the subject of research for over two decades, with a strong focus on metals such as copper and nickel [1]. In order for NC or UFG materials to be widely used, it is necessary to study feasible production methods with high reproducibility and scalability.

Even though many advances have been made in processing techniques and improving the mechanical behavior of NC and UFG materials, the subject of large-scale production remains one of the biggest challenges in nanostructured materials research. For a pure metal, such as copper, a variety of techniques have been employed to synthesize small grain structures, including electrodeposition, equal channel angular extrusion (ECAE), ball milling, and inert gas condensation [2–4]. One common issue of these processing techniques is that the sample dimensions are very small, typically in millimeter sizes. Moreover, these processes present a wide range of problems, such as impurity, porosity, texture, high surface roughness, and film thickness limitations [1,5,6] that lead to a large scatter in the mechanical behavior data. In many cases, such discrepancies could be attributed to the different processing techniques. This signifies the importance of large-scale production of high quality NC or UFG specimens for meaningful comparison results.

Historically, nanoscale multilayer technology is a process that uses a physical vapor deposition (PVD) technique to produce two-dimensional nanocomposites with fine alternating layer structures (<100 nm). Many types of nanoscale multilayers, such as Cu/Zr, Ni/Cu, and Ag/Cu alloys [7,8], have been synthesized for applications such as protective coatings, mirrors, and sensors [6–15]. Currently, this type of technology has not been used to synthesize single element nanostructures (having nanoscale size features). This particular technique presents many advantages over conventional processing methods for nanoscale materials production: (a) control of the bilayer thickness in order to tailor the mechanical properties, (b) fabrication of large samples (diameter >10 cm), (c) production of multiple samples during a single deposition run, and (d) creation of samples with highly reproducible mechanical properties.

Early work by Dahlgren and Merz [16,17] illustrated the possibility of using a sputtering technique (dc triode sputtering chamber) to synthesize NC or UFG Cu by continuous deposition of copper materials at extremely high sputtering rates (above 11 nm/s). The development of highly columnar grain structures and relatively high residual stresses, however, prevented them from producing large-scale, smooth, and high quality samples. Nonetheless, this early work indicates that nanoscale twins are one of the common microstructural features formed in PVD pro-

* Corresponding author. Tel.: +1 925 424 3715.
E-mail address: hodge4@llnl.gov (A.M. Hodge).

0921-5093/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2006.05.109

cesses. Recently, Zhang et al. [18] developed a model for the formation of nanoscale twins during sputter deposition on Cu/330 stainless steel nanoscale multilayers. The model implements factors such as stacking fault energy and deposition rate for the formation of nanoscale twins. The study demonstrates that using multilayer technology allows the formation of nanoscale grains containing twins while using much lower deposition rates (0.30 nm/s). Understanding the development of nanoscale twins (nano-twins) in Cu produced by multilayer technology will further enhance the ability to improve the mechanical properties. Lu et al. and Ma et al. [2,19] have shown that an electrodeposited copper with ultrafine grain sizes (400 nm to 1 μm) and medium to high density nano-twins (which act as strengthening agents) exhibits high strengths (600–900 MPa) when compared to the strength of nanocrystalline Cu (360–1100 MPa) [20,21].

This study presents the large-scale production of UFG Cu foils with nanoscale twins processed by nanoscale multilayer technology. The synthesized foils are not considered multilayers since they are made of a single element. However, the techniques for processing the Cu foils arrived from multilayer technology, i.e., the foils were fabricated using five different layer thicknesses ranging from 1.25 to 43.6 nm (18,000 to 520 layers) for a total foil thickness of ∼22 μm. We compare the effects of the deposition layer thickness to sample microstructure and mechanical behavior, all of which are unknown since this is the first time that multilayer technology has been adapted to process large-scale single element foils.

2. Experimental procedures

Cu/Cu foils 22 μm thick with individual deposition layer thicknesses ranging from 1.2 to 43.6 nm were deposited on 10 cm diameter (1 0 0) silicon wafers by dc magnetron sputtering. Table 1 presents the sample number and layer thickness information. Films were prepared using two 150 mm diameter magnetron sputtering sources using ultrahigh purity Cu (99.999%), operated with 600 W of power each, at a pressure of 2 mTorr. The deposition rate was 0.197 nm/s for all samples. The substrate rotation speeds were changed in order to acquire the desired individual layer thickness. Fourteen wafers were coated in a single run. Substrate temperature was monitored during the deposition process and reached ∼90 °C for all of the foils.

Once the samples were removed from the chamber, the residual stress was measured using a Tencor FLX-2320 Thin Film Stress Measurement Instrument. Then the films were removed from the substrate and handled as free standing foils, which were characterized by chemical analysis, Archimedes method, XRD, SEM, plan-view and cross-sectional TEM. Uniformity in sample thickness was verified by measuring at least five different locations in a single foil, using a digital micrometer with a precision of 0.1 μm. The standard deviation for five measurements is less than 0.5 μm. Additionally, stylus profilometry (Veeco-Sloan Dektac 3) was used to check coating thickness by scanning the step height between the mask and unmasked region of a witness wafer.

The microstructures of as-deposited samples were characterized using a Philips CM300-FEG transmission electron microscope (TEM) at 300 kV. The plan-view TEM samples were thinned to transparency using an E.A. Fischione (PA, USA) twin-jet electropolisher in an electrolytic solution of 10 vol.% nitric acid and 90% methanol at a temperature of −25 °C. The cross-sectional TEM samples were prepared using a dual focused ion beam (FIB) technique. Both bright-field and dark-field techniques have been applied in order to better resolve the structural information of the copper samples.

Tensile tests (2–4 tests per sample) were performed at room temperature using a computer controlled Instron 4444 table-top universal testing machine at a constant cross-head speed of 0.508 mm/min. Samples were knife-cut from a die without any thermal heating in order to prevent grain growth. The gauge length of the dogbone-shaped samples is 6 mm, width 3 mm, and thickness of 22 ± 0.5 μm. A special fixture was designed in order to minimize handling of the samples and prevent bending during mounting.

Nanoindentation tests were performed on the samples using a XP-nanoindenter (MTS, Oak Ridge, TN) with depth control mode. Additionally, Vickers microhardness measurements were performed using a 5 g load.

3. Results and discussion

The residual stress in Cu foils is an area of major concern since the development of large residual stresses, due to intrinsic and extrinsic factors, could significantly hinder the ability to produce thick films [22,23]. Multilayer technology allows the synthesis of samples with large thickness (>100 μm) and relative low residual stresses [13]. In this particular case, the UFG copper foils were grown by an interrupted process using multilayered technology as described in Section 2. This process has been shown to allow the relaxation of the film stress [24] and thus facilitate the synthesis of thick (>100 μm) foils with low residual stresses (<100 MPa). Fig. 1 shows the overall shape and size of

Table 1
Characterization of Cu samples[a]

Sample number	Number of layers	Deposition layer thickness (nm)	Cross-sectional grain size (μm)	Twin density (m^2/m^3)	Plan-view grain size (nm)
A	18000	1.2	∼1–3	3.0×10^6	195
B	8350	2.7	Not measured	Not measured	179
C	4168	5.4	∼1–3	2.0×10^6	177
D	2084	10.5	Not measured	Not measured	178
E	520	43.6	∼4–5	1.2×10^6	175

[a] All samples are 22 μm thick.

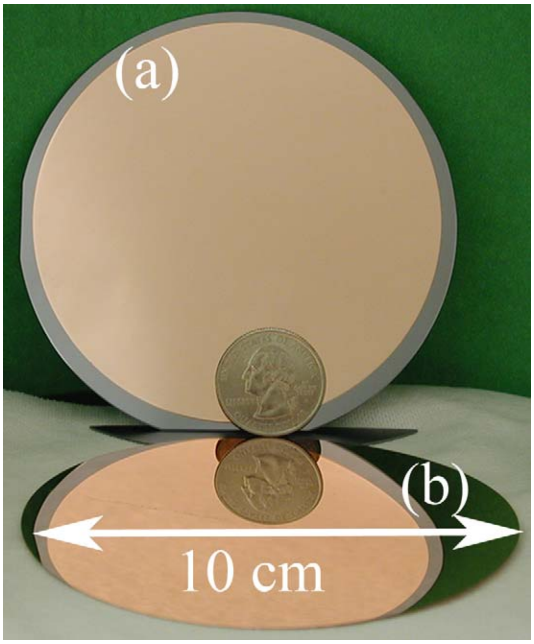

Fig. 1. Free-standing copper foil processed by using multilayer technology. Coin is placed to emphasize the large foil size.

a free-standing foil. A coin (US$ 0.25) has been placed next to the foil to accentuate the large foil diameter. The smooth surface finish, as well as the fact that the free-standing foil lies very flat, implies the small residual stresses in the samples. The mirror-like surface roughness of all samples approximates 10 nm rms over a 1 mm length.

In order to assess microstructure effects due to the processing method, both the plan-view and cross-sectional TEM images were analyzed. It can be observed in Fig. 2 that the plan-view grain size is very similar for all deposition layer thicknesses and is about 200 nm. This suggests that the final grain size of the foils is controlled by the substrate temperature, rather than the individual deposition layer thickness. The cross-sectional TEM shown in Fig. 3 was performed for the smallest deposition layer size (1.2 nm), the intermediate layer size (5.4 nm), and the largest layer size (43.6 nm). Though the columnar grains are still visible in all three samples, cross-sectional TEM suggests that smaller deposition layer thickness does help to suppress columnar grain growth. The samples with layer thickness of 1.2 and 5.4 nm have columnar grains of 1–3 μm length while the 43.6 nm layer thickness has grains of 4–5 μm length. The twin density for the three samples was measured as the twin boundary area per unit volume (m^2/m^3) [19,25] and is shown to increase as the layer thickness decreases (see Table 1). This result is in line with the recent findings by Zhang et al. on Cu/330 stainless steel, which demonstrated that as the Cu layer thickness decreased, more twins were present [18].

Another critical method in assessing UFG materials such as Cu is the study of the sample purity and porosity, which can affect the mechanical behavior. Chemical analysis performed on the Cu/Cu samples showed a purity higher than 99.999%; this purity is difficult to achieve by other methods [2]. Density measurements performed on our samples show a fully dense material with density values of 8.93 ± 0.05 g/cm^3. Nanovoids were not detected in extensive TEM examinations of all foils (Figs. 2 and 3).

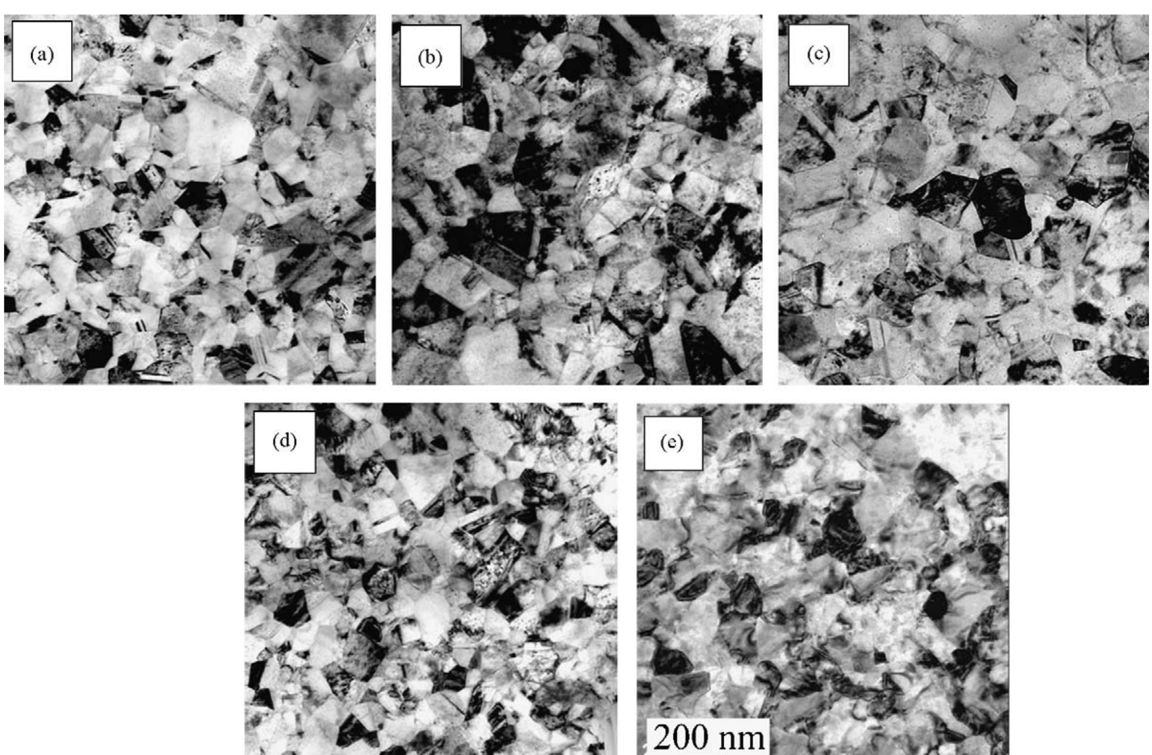

Fig. 2. Plan-view TEM micrographs with deposition layer thickness of (a) 1.2 nm, (b) 2.7 nm, (c) 5.4 nm, (d) 10.5 nm, and (e) 43.6 nm. (All figures have the same scale bar.)

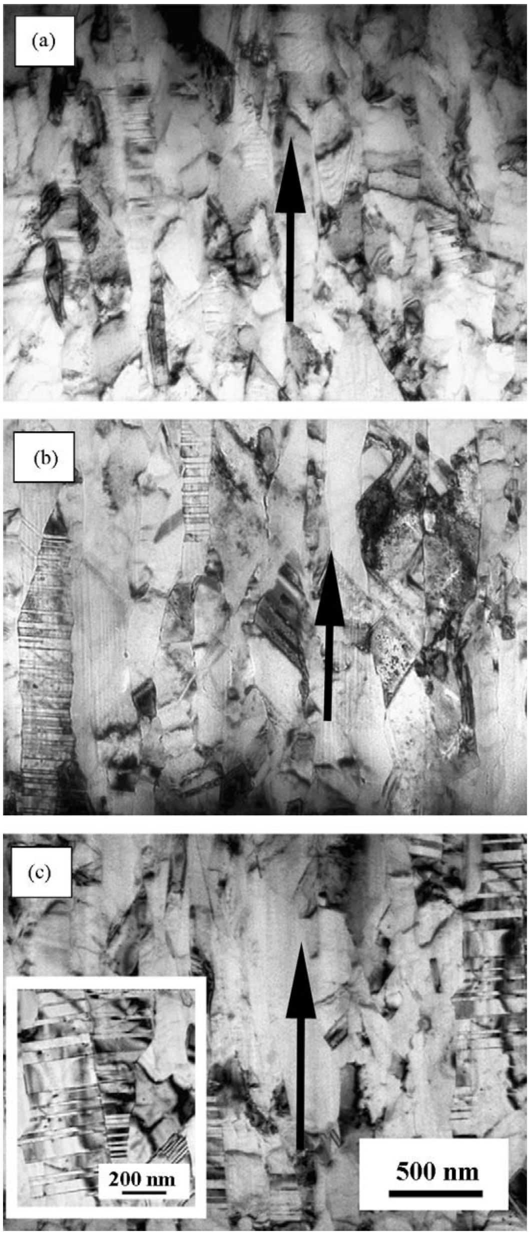

Fig. 3. Cross-sectional TEM micrographs for deposition layer thickness of (a) 1.2 nm, (b) 5.4 nm, and (c) 46.3 nm. The inset shows relatively high density growth twins inside columnar grains (arrows indicate film growth direction).

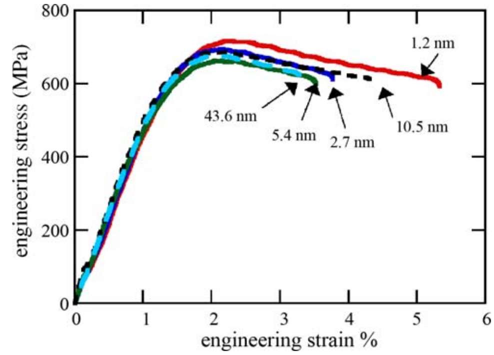

Fig. 4. Representative stress–strain curves for all samples at room temperature from uniaxial tensile tests at a strain rate of $1.4 \times 10^{-3}\,\mathrm{s}^{-1}$. Curves are labeled by the deposition layer thickness.

At this point, the UFG copper foils with nanoscale twins have been shown to have similar plan-view grain sizes given a particular deposition layer thickness. However, there are changes in the overall twin density which has been shown to affect the mechanical behavior [2,19]. Tests by Vickers and nanoindentation were performed to depths of about 2–3 μm (∼10% of the total sample thickness). The hardness values obtained by both methods ranged between 1.8 and 2.2 GPa. From these values one can approximate the yield stress as $\sigma_y \sim 1/3H$, which ranges from 600 to 733 MPa. The elastic modulus was obtained from nanoindentation tests, ranging from 130 to 140 GPa, which are accepted values for randomly oriented Cu [3].

Tensile tests were performed on samples at a constant strain rate of $1.4 \times 10^{-3}\,\mathrm{s}^{-1}$. As mentioned in Section 2, 2–4 tests were performed per sample (A–E). Fig. 4 shows a representative curve for each sample. The tensile data scatter given a deposition layer thickness was less than 1%, thus further demonstrating the sample uniformity. Note that the displacement of these tensile curves is measured by the cross-head movement of the machine; therefore, the elastic slopes of the curves do not represent the true elastic moduli of the samples. The plastic strains, however, indicate a variation in ductility as a function of the deposition layer thickness. Sample A, which has the smallest deposition layer thickness (1.25 nm) has, on average, a larger ductility than any of the other samples. Sample E, which has the largest deposition layer thickness (43.6 nm), has the lowest ductility of all the samples. As Sample A has the highest twin density, the observable increase of the tensile ductility with the decreasing deposition layer thickness seems consistent with the recent results by Lu et al. [2,25], suggesting that high twin density could increase the tensile ductility of the materials. Not surprisingly, high-twin-density Sample A also shows a high yield strength than that of other samples. Overall, the measured yield strength of all five types of samples falls between 540 and 690 MPa. These values are substantially higher than all other ultrafine-grained coppers with similar grain sizes reported in the literature [26]. This emphasizes the importance of the growth twin in strengthening materials. Note that as the majority of elongation in our samples is post necking, a much larger tensile strain is expected if we employed a smaller gauge length such as those typically used for UFG and NC materials (1–5 mm) [26].

Despite the similarity in overall grain sizes, we emphasize the importance of layer-by-layer deposition technique in reducing residual stress to allow large-scale production, in modifying the twin density, and in suppressing columnar grain growth. Smaller deposition layer thickness can be related to higher nanoscale twin density and, therefore, higher strength. The tensile and indentation tests present a high strength Cu material that is attributed to the presence of nanoscale twins and ultrafine-grained structures. The Hall–Petch relationship for Cu as stated by Meyers and Chawla [27] for an average grain size of 200 nm predicts a yield strength of ∼270 MPa, which is much lower than our experimental values: 540–690 MPa. Recently, Youssef et al. [21] and Lu et al. [25] reported two strong NC and UFG copper samples that have strengths over 1 GPa, synthesized by ball-milling and electrodeposition techniques, respectively. In compared with their results, our copper exhibits lower strength due to larger grain sizes and/or lower twin density. However, above-mentioned techniques have severe limitations that could prevent them from being used to produce large scale (over 10 cm in diameter), high finish, and/or low residual stress materials.

4. Conclusions

We have demonstrated that nanoscale multilayer technology can be used for large-scale production of fully dense, high purity (99.999%), nano-twinned, and ultrafine-grained copper (14 samples per run, 10 cm diameter foils). Five different layer thicknesses were used ranging from 1.25 to 43.7 nm (18,000 to 520 layers). Sample characterization revealed similar sample microstructures with medium twin densities. The yield strength for all five types of samples was in the range of 540–690 MPa, demonstrating that these materials are among the high strength coppers. Overall, the mechanical behavior of the UFG copper presented in this paper compares favorably to other UFG samples processed by methods such as ECAE. Our process also has many advantages, such as large-scale production abilities, reproducibility, fully dense samples, a high-quality surface finish, and assurance of material purity.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. The authors thank P. Ramsey, E. Sedillo, D. Freeman at LLNL for sample preparation and characterization, and Dr. A.V. Hamza for helpful discussions.

References

[1] K.S. Kumar, H. Van Swygenhoven, S. Suresh, Acta Mater. 51 (2003) 5743.
[2] L. Lu, R. Schwaiger, Z.W. Shan, et al., Acta Mater. 53 (2005) 2169.
[3] S.R. Agnew, J.R. Weertman, Mater. Sci. Eng. 242A (1998) 174.
[4] S. Cheng, E. Ma, Y.M. Wang, et al., Acta Mater 53 (2005) 1521.
[5] C.J. Youngdahl, J.R. Weertman, R.C. Hugo, et al., Scripta Mater. 44 (2001) 1475.
[6] S.R. Agnew, B.R. Elliot, C.J. Youngdahl, et al., Mater. Sci. Eng. 285A (2000) 391.
[7] T.W. Barbee Jr., D.L. Keith, Proceedings of the Fall Meeting of the Metallurgical Society AIME, Pittsburgh, PA, 1980.
[8] T.W. Barbee Jr., in: L. Chang, B.C. Giessen (Eds.), Synthetic Modulated Structures, Academic Press, New York, 1985, p. 313.
[9] A.B.C. Walker, J.T.W. Barbee, R.B. Hoover, et al., Science 241 (1988) 1781.
[10] T.W. Barbee Jr., Proceedings of the Topical Conference on Low Energy X-ray Diagnostic, Monterrey, CA, 1981.
[11] T.P. Weihs, T.W. Barbee Jr., M.A. Wall, Acta Mater. 45 (1997) 2307.
[12] N. Mara, A. Sergueeva, A. Misra, et al., Scripta Mater. 50 (2004) 803.
[13] T.G. Nieh, T.W. Barbee Jr., J. Wadsworth, Scripta Mater. 41 (1999) 929.
[14] F. Ebrahimi, A.J. Liscano, Mater. Sci. Eng. 301A (2001) 23.
[15] H. Huang, F. Spaepen, Acta Mater. 48 (2000) 3261.
[16] S.D. Dahlgren, J. Vac. Sci. Technol. 11 (1974) 832.
[17] M.D. Merz, S.D. Dahlgren, J. Appl. Phys. 46 (1975) 3235.
[18] X. Zhang, A. Misra, H. Wang, et al., Acta Mater. 52 (2004) 995.
[19] E. Ma, Y.M. Wang, Q.H. Lu, et al., Appl. Phys. Lett. 85 (2004) 4932.
[20] P.G. Sanders, J.A. Eastman, J.R. Weertman, Acta Mater. 45 (1997) 4019.
[21] K.M. Youssef, R.O. Scattergood, L.K. Murty, et al., Appl. Phys. Lett. 87 (2005) 091904.
[22] C.V. Thompson, R. Carel, J. Mech. Phys. Solids 44 (1996) 657.
[23] J.A. Thornton, D.W. Hoffman, Thin Solid Films 171 (1989) 5.
[24] P.R. Guduru, E. Chason, L.B. Freund, J. Mech. Phys. Solids 51 (2003) 2127.
[25] L. Lu, Y. Shen, X. Cheng, et al., Science 304 (2004) 422.
[26] Y.M. Wang, E. Ma, M.W. Chen, Appl. Phys. Lett 80. (2002) 2395.
[27] M.A. Meyers, K.K. Chawla, Mechanical Metallurgy: Principles and Applications, Prentice-Hall, Englewood Cliffs, NJ, 1984, p. 496.