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A novel method to synthesize high purity, nanostructured copper

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Abstract

Nanostructured high purity (99.999%) copper foils, 10 cm in diameter and 22-25 microns thick were produced using nanoscale multilayer technology. The foils were produced using five different layer thicknesses ranging from 1.25 to 43.6 nm (18,000 to 520 layers). This process delivers the ability to produce multiple large-scale samples during a single deposition run with very small residual stresses. Tensile and indentation tests demonstrate that the material produced is a high strength copper ($\sigma_y \sim 540$-690 MPa).

Keywords: nanostructured copper, multilayers, sputtering

1. **Introduction**

Nanoscale multilayer technology has been used to produce many types of two-dimensional nanocomposites with fine alternating layer structures (<100 nm); by controlling the bilayer thickness, the mechanical properties of these multilayers can be highly tailored. Many types of nanoscale multilayers, such as Cu/Zr, Ni/Cu and Ag/Cu have been fabricated [1,2] for applications such as protective coatings, mirrors, and sensors [1-8]. However, this type of technology, to our knowledge, has not been used to produce single element nanostructured materials.

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The production of new and improved nanocrystalline materials is an endeavor that has been the subject of research for over two decades, with a strong focus on the production of nanocrystalline copper and nickel [9]. Nanocrystalline copper has been produced by a variety of techniques such as electrodeposition, equal channel angular extrusion (ECAE) and ball milling [10-12]. These processes present a wide range of problems, including impurity, porosity, texturing, high surface roughness, film thickness limitations and lack of grain size uniformity [9, 13, 14].

Recently, the processing of copper has focused on improving the ductility while maintaining the high strength of nanocrystalline Cu by the introduction of nano-twins, which act as strengthening agents in Cu with ultra-fine grain sizes (> 200 nm to 1 μm) [10, 15]. Lu et al. and Ma et al. have shown that electrodeposited copper with grain sizes of 400 nm to 1 μm having medium to high density nano-twins exhibits higher strength (600 to 900 MPa) than nanocrystalline Cu (~360 MPa) [16].

Early work by Dahlgren and Maerz [17, 18] demonstrated that, by using a DC triode sputtering chamber, one can make ultrafine grain Cu and nanocrystalline Cu containing twins by increasing the sputtering rate above 11nm/s. More recent work performed by Zhang et al. [19] on nanoscale multilayers of Cu/330 stainless steel has demonstrated that the Cu layers show twins without having to go to very high deposition rates (0.30 nm/s). However, twins in the Cu layers were found in only in about half of the Cu grains.

Even though many advances have been made in processing techniques and improving the mechanical behavior of nanocrystalline and nanostructured Cu, it is difficult to compare results among current data. Overall, there is a large scatter in the data as shown by Cheng et al. [12] which could be attributed to the different processing techniques, sample quality and testing procedures. Questions still remain about the overall purity and porosity of the nano-Cu already reported on. Furthermore, in order for nanostructured Cu to be widely used, more feasible production methods with high reproducibility and scalability need to be devised.

This study presents the large-scale production of nanostructured Cu foils processed by using nanoscale multilayer technology. To our knowledge this is the first time that nanoscale multilayer technology has been used to produce a single element nanostructure material. The Cu samples present 200 nm grain size, medium twin density, high strength (540 to 690 MPa), good ductility and no strain hardening. We compare the properties of our high purity Cu to current data on nanocrystalline and nanostructured Cu. Furthermore, we report that this technology produces ultra-fine and nanostructured grain materials with superior mechanical properties.

2. Experimental Procedures

Cu/Cu foils 20-25 μm thick with individual deposition layer thicknesses ranging from 1.2 to 43.6 nm were deposited on 10 cm diameter (100) silicon wafers by DC magnetron sputtering. Table 1 presents the sample numbers and layer information. Films were prepared using two 150 mm diameter magnetron sputtering sources using ultra high purity Cu (99.999%), operated with 600W of power each, at a pressure of 2 mTorr. The deposition rate was 0.197 nm/s for all samples; however, the substrate rotation speeds were changed in order to acquire the desired layer thickness. Fourteen wafers were coated per run. Substrate temperature was monitored during the deposition process and reached ≈ 90^{o}C for all 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. The films were removed from the substrate and were handled as free standing foils which were characterized by chemical analysis, Archimedes method, XRD, SEM, plan-view and cross-sectional TEM.

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 ^{o}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 to 4 test per sample) were performed at room temperature using an Instron 4444 table-top universal testing machine at a constant cross-head speed of 0.508 mm/min. Samples were cut from a die at room temperature in order to prevent grain growth. The gauge length of the dogbone-shaped samples is 6 mm, width 3 mm with thickness of 22-25μm. 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. Additionally, Vickers microhardness tests were performed using a 5 gram load.

3. Results and Discussion

Residual stresses in coatings and foils is an area of major concern since the development of large residual stresses, due to intrinsic and extrinsic factors, significantly hinders the ability to produce thick films [20, 21]. Multilayer technology allows the synthesis of samples with large thickness (>100 μm) and relative low residual stresses [3]. In this particular case, the nanostructured copper foils were grown by an interrupted process using multilayered technology as described in the experimental procedures. This process has been shown to allow the relaxation of the film stress [22] and thus allow for the synthesis of thick (>25μm) foils with residual stresses <100 MPa. Figure 1 shows the overall shape and size of the coated sample on the substrate (a), and a free-standing foil placed perpendicular to the first (b). Note the smooth surface finish as the reflection of both foil (a) and the coin can be seen on foil (b). Note that foil (b) lays very flat, which further demonstrates the small residual stresses of the foils. All samples had a smooth, mirror-like surface with a top surface roughness of approximately 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 must be analyzed. It can be observed in Figure 2 that the plan-view grain size is very similar for all deposition layer thicknesses and is ~ 200 nm. The cross-sectional TEM shown in Figure 3 was performed for the smallest layer size (1.2 nm), the intermediate layer size (5.4 nm), and the largest layer size (43.6 nm). The cross-sectional TEM reveals elongated columnar grains with up to 5 microns grain length (note growth direction). There was no clear evidence of differences in the layer thickness; however, the samples with layer thickness of 1.2 and 5.4 nm appear to have an effect in suppressing the columnar structure (1-3 microns length) while the 43.6 nm layer thickness has columnar grains of 4-5 microns length. All three samples had grain widths of ~ 200 nm. The twin density was measured for the three samples and shown to increase as the layer thickness decreased (see table 1). This type of increase in the twin density has been shown in previous findings by Zhang et al. on Cu/330 stainless steel, which demonstrated that as the Cu layer thickness decreased, more twins were present [19]. However, the mechanisms that control the twin density in the Cu/330 stainless steel and our Cu/Cu system are quite different.

Another critical method in assessing nanostructured 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 [10]. Density measurements performed on our samples show a fully dense material with density values of 8.93 ± 0.05 g/cm^3.

At this point, the nanostructured copper foils have been shown to have very similar microstructure given a particular deposition layer thickness. However, there are changes in the overall twin density which will affect the mechanical behavior.
Tests by Vickers and nanoindentation were performed to depths of about 2-3 microns (about 10% of the total sample thickness). The hardness values obtained by both methods range between 1.8 to 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 [11].

Tensile tests were performed on samples at a constant strain rate of 1.4×10^{-3}/s. As can be seen in Figure 4**,** the ductility varies as a function of the deposition layer thickness which relates to the overall sample twin density (Table 1). Sample A, which has the smallest layer thickness (1.25nm) and a higher twin density, has on average a larger ductility than any of the other samples. Sample E, which has the largest layer thickness (43.6 nm), has the lowest ductility of all of the samples. Similar trends on the copper ductility as a function of the twin density have been observed by other researchers [10, 23]. Note that the 0.2% offset yield strength is very similar for all five type of samples and falls between 540 and 690 MPa, a high strength for high purity copper **[12].** The stress-strain curve also shows a wavy pattern as the strain increases after reaching σ_{max}. The wavy pattern was present in all tests and is believed to be due the deformation mechanisms [24, 25] which will be further discussed in a future publication. Another interesting feature of the tensile test is the fact that after reaching a maximum stress, the stress-strain curve shows a downward slope (i.e. no strain hardening). This downward slope in the stress-strain curve is similar to Cu samples processed by dynamic plastic deformation (DPD) performed by Zhao et al. [26]. Previous stress-strain curves for ultra-fined grain Cu have shown some strain hardening after a maximum stress was reached **[10, 23]**, and nanocrystalline Cu has shown brittle like fracture [16].

Figure 5 shows the Hall-Petch relationship for Cu as stated by Meyers and Chawla [27] including data from this study. Note the yield strength of all of our materials is higher than that predicted for 200 nm grain size copper. The range of values for the yield strength is nearly independent of the initial layer deposition thickness. The only noticeable difference is between sample **A** (smallest layer deposition thickness of 1.2 nm and the highest strength) and sample **E** (largest layer deposition thickness of 43.6 nm and the lowest strength). Overall, the differences are minimal, which is similar to previous research on Cu-based multilayer materials [28] for which the strength vs. deposition layer thickness plot has shown a plateau for layer thicknesses less than 50 nm.

4. Conclusions

We have demonstrated that nanoscale multilayer technology can be used for large scale production of fully dense-high purity (99.999%) nanostructured copper (14 samples per run, 10 cm diameter foils). Five different layer thicknesses were used ranging from 1.25 to 43.7 nm (18000 to 520 layers). Sample characterization revealed a nanostructured material with medium twin densities. The overall yield strength for all five types of samples was in the range of 540 to 690 MPa, demonstrating that these materials are in the range of high strength copper. Overall the mechanical behavior of the nanostructured copper presented in this paper compares well to samples process by other methods. However, our process has many advantages, such as large-scale production abilities, reproducibility, fully-dense samples, a high surface finish as well as assurance of material purity.

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Table 1. Characterization of Cu/Cu samples*

Sample #	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

*all samples are 22-25 μm thick

Figure Caption:

Figure 1. Copper foils (a) attached to the substrate and (b) free-standing and placed perpendicular to foil (a). Note the smooth surface finish as both foil (a) and the coin reflect on foil (b).

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

Figure 3. Cross-sectional TEM micrographs for deposition layer thickness a) 1.2nm, b) 5.4 nm and c) 46.3 nm and inset showing relatively high dense growth-twins inside columnar grains.

Figure 4. Stress-strain curves for all samples at room temperature from uniaxial tension tests at $1.4\text{x}10^{-3}\text{s}^{-1}$ strain rate. Curves are label by the deposition layer thickness.

Figure 5. Hall-Petch relationship for the yield strength of Cu by Meyers and Chawla [27] including data from present study (200nm grain size).

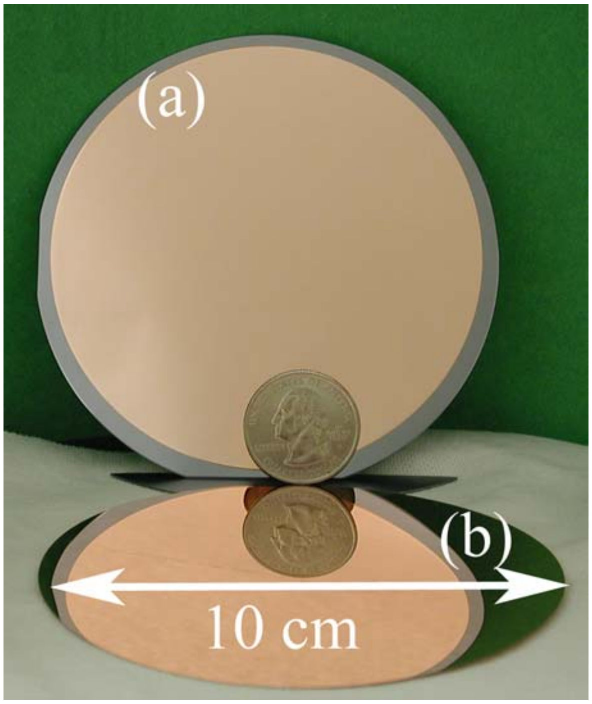

Figure 1

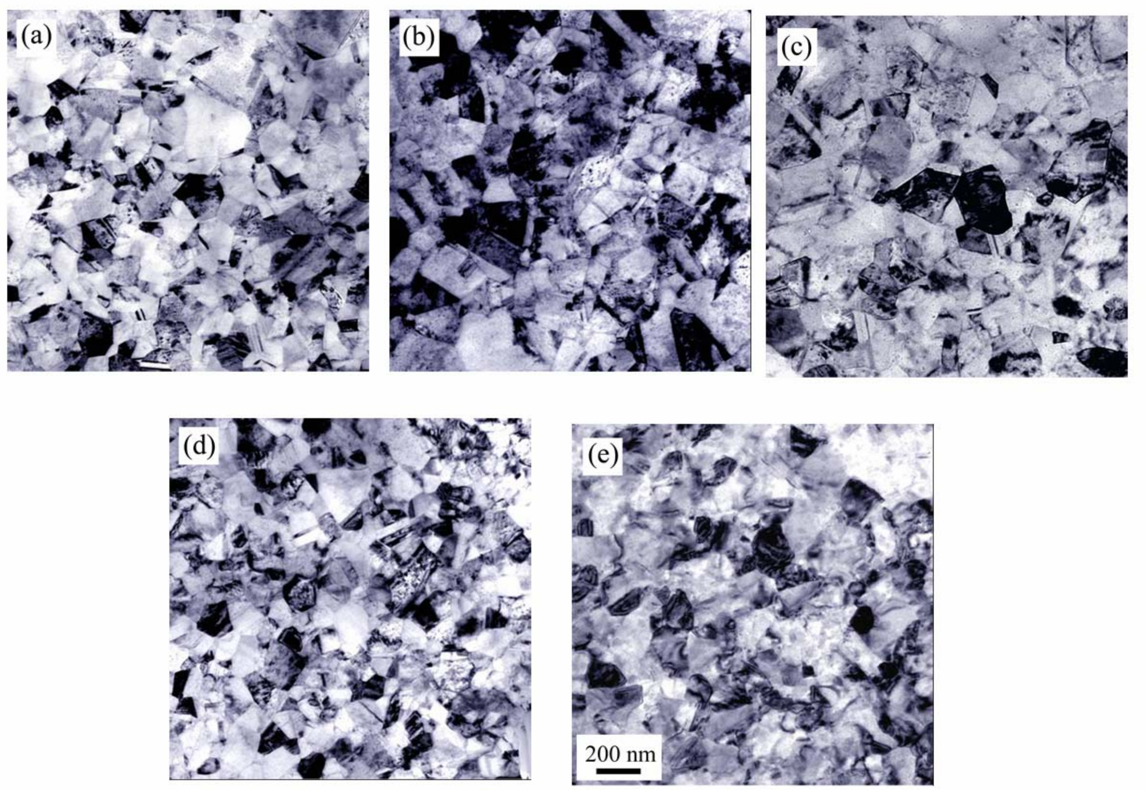

Figure 2

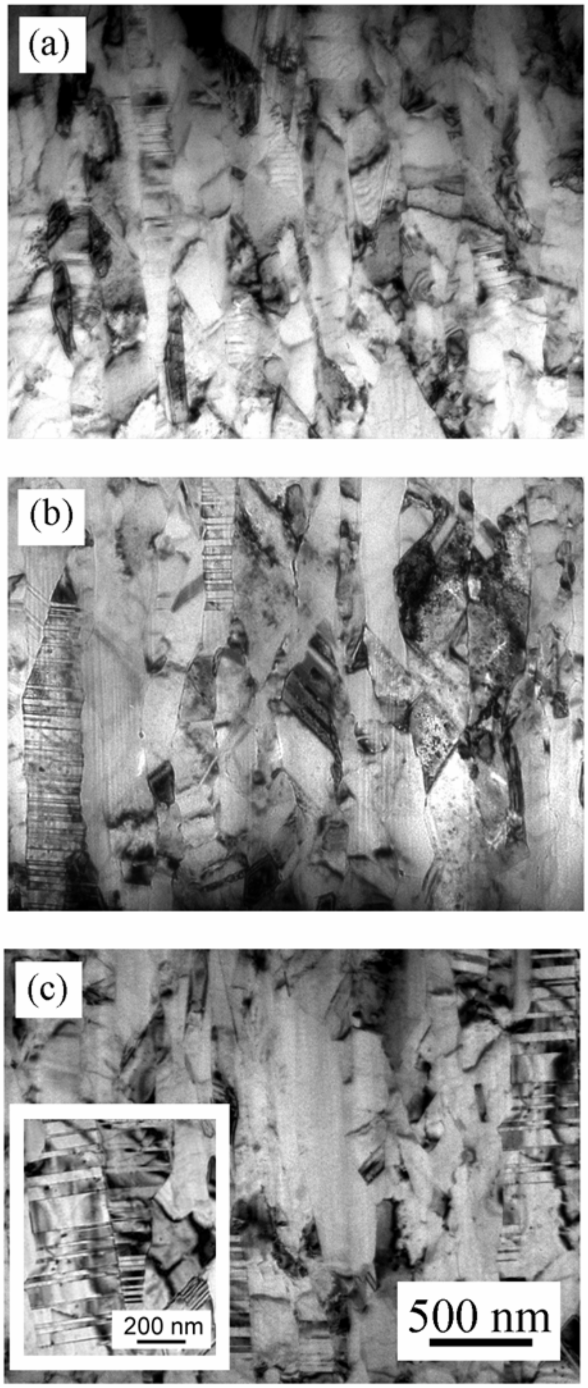

Figure 3

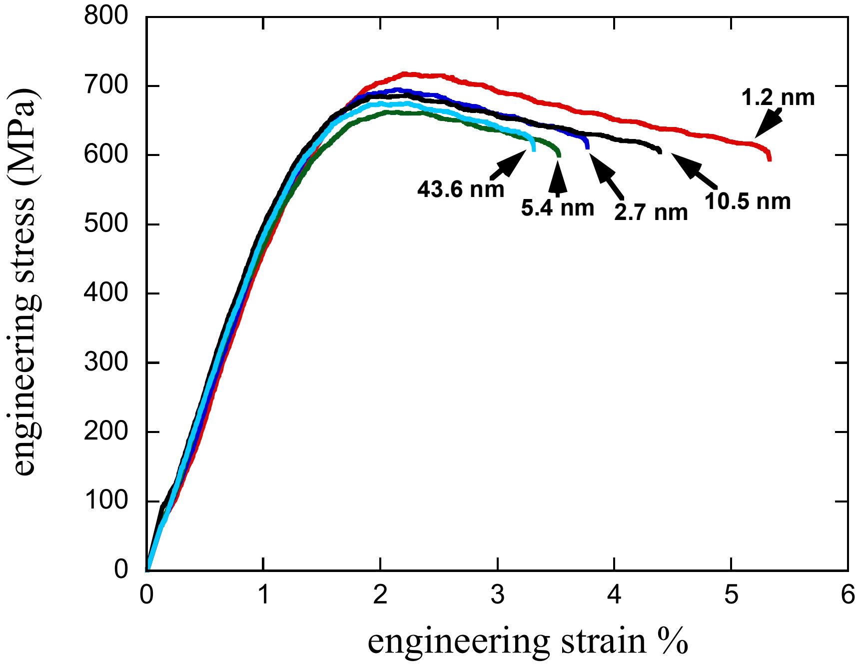

Figure 4

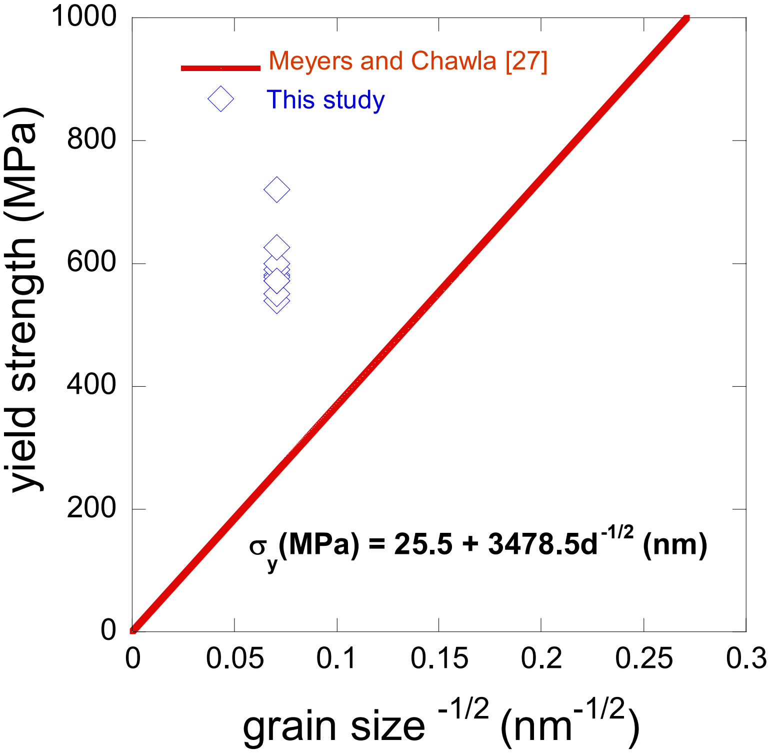

Figure 5