The mobility of growth twins synthesized by sputtering: tailoring the twin thickness

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Abstract

The current work presents a protean twin thickness contour zone map that illustrates how the nucleation and the mobility of twin boundaries affects the twin thickness of sputtered films. The twin thickness contour zone map can be used as a versatile guide to synthesize fully nanotwinned films with tailored twin thicknesses in materials with a wide range of stacking fault energies. The nucleation and mobility of twin boundaries was studied in four Cu alloys of different compositions (Cu-6wt.%Al, Cu-4wt.%Al, Cu-2wt.%Al, and Cu-10wt%Ni), having stacking fault energies ranging from 6 mJ/m² to 60 mJ/m². The films were synthesized by magnetron sputtering and characterized by transmission electron microscopy, where the twin thickness varied from 2 nm to 35 nm. Our experimental results show that it is possible to control the twin thickness. Three main mechanisms are explained to describe twin nucleation and twin boundary mobility, which are correlated to the interplay of specific sputtering conditions and the deposition temperature.

Keywords: Copper alloys; Nanotwins; Sputtering; Stacking fault energy; Twinning.

Introduction

Improving a material's properties such as strength, ductility, thermal stability, corrosion resistance, and conductivity need to be taken into account when designing materials at the nanoscale [1]. At the macro-scale the concept of grain boundary engineering is based on the idea that increasing the fraction of special boundaries can be used to enhance the bulk properties of structural and functional materials [2]. At the nanoscale, nanotwinned (nt) materials have been

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4 shown to have a large density of $\Sigma 3$ boundaries, which are a special type of grain boundaries and
5 where the twin thickness (λ) can play the role of the grain size [3-5]. The potential of nt materials
6 has been highlighted in the mechanical testing of nanotwinned Cu, which showed high strength
7 and good ductility compared to UFG or coarse grain Cu [4, 6, 7]. Additionally, nt materials have
8 shown good corrosion resistance, thermal stability, and tolerance to radiation damage [8-10]. To
9 date, nt materials have been synthesized using different metals and alloys systems, such as Cu,
10 Ag, Cu-Al, Cu-Zn, and stainless steel among others [4, 6, 7, 11-18]. However, the synthesis of nt
11 materials has been limited due to stacking fault energy (SFE) restrictions and further
12 understanding of growth twin formation is needed.
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21 Different techniques have been utilized to produce materials with a large density of $\Sigma 3$
22 boundaries, such as annealing twins by heat treatment [19], deformations twins by plastic
23 deformation [18], and growth twins by electrodeposition or sputtering [7, 15]. One of the
24 parameters that is crucial for the synthesis of nt materials by any of the aforementioned methods
25 is the SFE, which is an intrinsic property of the material. The SFE of face-centered cubic (FCC)
26 materials can vary from Al with a high SFE of 166 mJ/m², Cu an intermediate SFE of 45 mJ/m²,
27 and Ag with a low SFE of 20 mJ/m² [13, 20, 21]; the lower the SFE of the material, the highest
28 the probability of twinning [22]. Moreover, the SFE of a material can be reduced by introducing
29 an alloying element. For example, the addition of small amounts of Al or Zn to Cu lead to a
30 significant reduction in the SFE [23], although alloying does not always lead to a reduction of
31 the SFE, as has been shown in the case of Cu-Ni alloys [24].
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42 In previous studies on the synthesis of nt films by magnetron sputtering, an analytical model has
43 been proposed to describe the probability of twin nucleation based on the effects of sputtering
44 rate and SFE; where an increase in the twin nucleation leads to a decrease in λ [17, 22].
45 However, we have reported experimental results which were contrary to what is expected from
46 the model in respect to the deposition rate [25]. This discrepancy can be attributed to the effects
47 of the film's temperature which increases as a function of sputtering time and can also be vary by
48 modifying any of the processing parameters like the deposition rate [26, 27]. In general, when
49 the film temperature is increased boundary mobility increases and changes in the overall
50 microstructure are expected [28]. For example, in heat treated nt films, twin boundary (TB)
51 mobility has been observed, which led to twin coarsening [29-33]. Therefore, it is imperative to
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study the influence of film temperature on the mobility of TBs during the sputtering synthesis period.

In this manuscript, we present a sputtering methodology to tailor λ using four different Cu alloys with varying SFEs. The resulting microstructures presented a high percentage of twins (>95%), where λ is correlated to different SFEs and the deposition temperature. Our experimental results provide a guide to control λ and contribute to optimize microstructural configurations in the synthesis of nt materials.

Experimental details

Four Cu alloys (99.99% purity) were magnetron sputtered (Cu-6wt.% Al, Cu-4wt.% Al, Cu-2wt.% Al, and Cu-10wt.% Ni) onto 1" (25.4 mm) Si (100) substrates; the Cu alloys targets were 3" (76.2 mm) in diameter. The chamber was evacuated prior to deposition to a base pressure < 1.2×10^{-6} Torr, while during sputtering, the Ar working pressure was 2 mTorr and the target-substrate distance 3". In Table 1 the sample name, average deposition temperature, average deposition rate, sputtering power, substrate temperature, and duty cycle for each of the sputtered films are listed; a value of 100% in the duty cycle represents no sputtering interruption (refer as continuous sputtering). For simplicity, the samples were labeled by taking into account the alloy element and its content, and sequentially label from small to large λ within the same Cu-alloy. The average deposition temperature listed was varied by three different methods: (i) changing the power to increase or decrease the deposition rate, (ii) interrupting the flux of sputtered atoms that arrive to the substrate (refer as interrupted sputtering), and (iii) cooling or heating the substrate during sputtering. In the last case, a cooling stage was custom made to cool down the substrates to 16 °C, while a resistivity heating stage (SU-200-IH MeiVac) was used to heat the substrates. Temperature measurements were taken for the different sputtering conditions by means of a K or T type thermocouple embedded in a Si wafer (Thermo Electric) that it is placed as a substrate to monitor the deposition temperature. The films thicknesses were >15 μm , as measured on a JIB 4500 (JEOL) focused ion beam (FIB) and an XP-2 stylus profilometer (AMBiOS). Transmission electron microscope (TEM) sample preparation was conducted by typical film cross-sectioning, bright field, dark field and high resolution TEM images were obtained on a JEM-2100F (JEOL) to characterize the microstructure. λ was calculated by measuring the distance between consecutive twin boundaries. The statistical weighted average

for λ and grain width was obtained by the measurement of more than 1100 twin boundaries and more than 200 grains for each sample.

Results and discussion

A. Microstructural characterization

In table 2, the SFE for each of the alloys, the average twin thickness, the average grain width, the probability of twinning (ρ), the total grain boundary energy (GBE) stored in a film, and the ratio between the total GBE and twin boundary energy (TBE) stored in the film are displayed. The Cu alloys are listed from low to high SFE, 6 mJ/m² for the Cu-6wt.% Al [23], 13 mJ/m² for the Cu-4wt.% Al [23], and 37 mJ/m² for the Cu-2wt.% Al [34]. Although, no SFE values were found in the literature for the Cu-10wt.% Ni alloy, a study conducted by Li *et al* [24] showed that the SFE of Cu-Ni alloys is higher than that of pure Cu, Additionally, the SFE of Cu-Ni alloys increases as the Ni content is increased, for example, for Cu-20wt.% Ni the SFE is 74 mJ/m² [24]. Therefore, one can assume that the SFE of Cu-10wt.% Ni alloy is in the range of 47 - 74 mJ/m². For comparison reasons we will use a value of 60 mJ/m² throughout this paper.

As shown in Table 2, λ is arranged from low to high for each of the Cu alloys, where λ and grain width for each sample were calculated by taking several TEM images and measuring at least 500 TBs and 200 grains in different locations. All samples present highly defined columnar grains and high twin density; where more than 95% of the grains observed are twinned and the TBs are parallel to the film surface. The parameters showed in Table 2, and the sputtering parameters displayed in Table 1 will be discuss further in this manuscript together with the methodology applied to vary λ .

Representative TEM images for the Cu-2wt.% Al alloys presented in Table 2 and their corresponding λ volume fractions are shown in Figure 1, the insets depict representative selected area electron diffraction (SAED) patterns, which show the typical double hexagon pattern of the (110) oriented twinned grain. In the TEM Figures 1a thru 1e, λ variation is observable for the different sputtering conditions, while λ volume fraction plots show the increase in λ from ~5.7 nm to ~35 nm. In Figure 2, representative TEM images and λ volume fractions are shown for the Cu-4wt% Al, Cu-6wt% Al, and Cu-10wt.% Ni. The inset SAED patterns are typical for twinned grains, and the TEM images highlight λ variation. In Figure 2 it is evident that λ and λ volume

fraction were increased for each of the alloys at different sputtering conditions; for example, in Figures 2a and 2b the average λ varied from 2 nm to 19nm for the Cu-6wt.% Al; in a similar way for the Cu-4wt% Al films (Figure 2c and 2d), λ varied from 2.4 nm to 15 nm; and for the Cu-10wt.% Ni (Figure 2e and 2f) λ varied from 15 nm to 31nm.

B. Effect of the average deposition temperature

The average deposition temperature displayed in Table 2 is calculated by collecting temperature profiles at the sputtering conditions for each sample during a time span of 60 min. In Figure 3 representative temperature profiles are displayed, where only one sputtering condition was vary to change the average deposition temperature; Figure 3a compares continuous sputtering with interrupting sputtering; Figure 3b compares the influence of substrate temperature; Figure 3c compares two different sputtering powers; and Figure 3d compares two different duty cycles. By a combination of interrupted sputtering, cooling or heating the substrate, varying the sputtering power, and varying the duty cycle it was possible to sputter films at different average deposition temperatures, which allowed to produce significant changes in λ . Note that in this manuscript we did not take into account the effect of residual stresses, which were relatively small and of the same order of magnitude for all samples.

The methodology used in this study to tailor λ is strongly dependent on the average deposition temperature. First, we will discuss the three main mechanisms that can affect λ when thermal energy is added to the system: twin nucleation; TB mobility; and the effect of free surfaces on TB mobility. Second, λ zone plots will be discussed for different SFEs materials at different sputtering temperatures, followed by a pictorial representation of λ (contour λ zone map), where different SFEs and sputtering conditions are summarized in terms of the average deposition temperature (see section C).

B1. Twin nucleation

The synthesis of fully nt films requires sputtering conditions that facilitates a high rate of twin nucleation. In the case of sputtered growth twins an analytical model developed by Zhang *et al* [22] describes from a thermodynamic point of view the probability of twin nucleation (ρ). The model examines the relative difference between the critical radius of a perfect nucleus $r_{perfect}^*$ and

the critical radius of a nucleus with a stacking fault defect r_{twin}^* , that is, $\frac{\Delta_r}{r} = \left(\frac{r_{twin}^* - r_{perfect}^*}{r_{perfect}^*} \right)$. A

relative difference of less than 5% is considered favorable for high rate of twin nucleation [13].

One can rewrite ρ in a simplified form as:

$$\rho = \frac{\Delta_r}{r} = \left(\frac{\gamma_{twin}}{h\Delta G_v} \right) \text{ equation (1),}$$

where γ_{twin} is the twin boundary energy (TBE $\approx$ SFE/2), h is the {111} interplanar spacing, and

ΔG_v is the bulk free energy per unit volume $\Delta G_v = \frac{KT}{\Omega} \ln \left(\frac{J\sqrt{2\pi mKT}}{P_s} \right)$, K is the Boltzmann

constant, T is the temperature, Ω is the atomic volume, J is the deposition flux, m is the atomic mass of the interacting species, and P_s is the vapor pressure above the solid. The simple form of equation 1 allows one to identify three parameters that will affect ρ ; the SFE, the deposition flux J (proportional to deposition rate), and the deposition temperature T . Therefore, ρ will decrease if the SFE is low and/or the deposition rate is high; additionally, increasing the deposition temperature will also decrease ρ and enhance twin nucleation. We have calculated ρ using equation 1 (displayed in Table 2) by taking into account the average deposition temperature. In general, ρ was $< 5\%$, except for sample 2Al#2. Low ρ values imply that a large number of TBs are nucleated, and λ should decrease as ρ decreases.

B2. Twin boundary mobility

To identify whether nucleated TBs can move and alter λ while the films are being sputtered, we first examine two competing mechanisms that can modify the resulting microstructure, (i) grain growth via grain boundary (GB) mobility; and (ii) λ coarsening via TB mobility. It is possible to identify which mechanism is favored from a thermodynamics point of view, that is by comparing the total energy stored in the film due to GBs and due to TBs [31].

The total GBE stored in the films can be calculated by making two assumptions: first, the columnar grains are cylindrical; and second, the boundaries between columnar grains are high angle grain boundaries (HAGB). For comparison, and due to the lack of HAGB energy values

for the different Cu-alloys used, we use the HAGB energy for nanocrystalline Cu (710 mJ/m²) [35]. In our calculations, we use a film surface area of $5.67 \times 10^{-4} \text{ m}^2$, a film thickness 15 μm , and the average grain width of the samples from Table 2. The total energy stored due to grain boundaries for each of the films is displayed in Table 2 and it is the product of the HAGB energy, the total number of columnar grains in the film, and the lateral surface area of the cylinder. In a similar way, the total TBE stored in the films is the product of the TBE, the total number of TBs in the film, and the surface area that encompasses each TB. To calculate the total number of TBs in the film, we used the smallest λ for each of the Cu-alloys. The ratio between the total GBE and the total TBE stored in the films (GBE/TBE) is shown in Table 2. Overall, the total GBE stored is higher than the total TBE stored, therefore, grain growth is more favorable than λ coarsening. In other words, from a thermodynamic point of view the TBs should not move. However, when nt films have been heat treated, it was commonly observed that grain growth and λ coarsening occurred at the same time [29-31, 33, 36, 37].

During grain growth in annealing twins it has been observed that λ coarsening occurs by the formation and migration of incoherent twin boundaries (ITBs) [38]. In regards to sputtered nt films, it has been reported that the migration of ITBs promotes the lateral propagation and/or elimination of CTBs and increase in λ [36, 37]. The ITB migrates through the glide of Shockley partial dislocations that comprise the ITB [33, 36, 37], where the partials can move in the planes that are perpendicular to the $\{111\}$ growth direction [36, 37]. Thus, CTBs can laterally displace across the grain and λ will increase as thin twins will coarsen faster than thick twins [36]. By combining both the observations for λ coarsening in annealing twins and the migration of ITBs in sputtered nt films, the microstructure evolution during sputtering can be describe as follows:

Sputtering is a non-equilibrium process, where columnar grains grow during film deposition, and where the addition of thermal energy increases columnar GB migration [28]. In Figure 4 a mechanism that displays schematically λ coarsening as the film is being deposited is explained. Figure 4a shows two columnar grains labeled A and B. In grain A there are four CTBs, a wide blue line that indicates a boundary of relatively high interfacial energy, and an arrow showing that grain A will grow at the expense of grain B. As grain A grows, it is possible for a CTB to detach from the high energy boundary and form an incoherent twin boundary (ITB) (see Figure 4b); this will occur if the free energy of the high energy boundary at the end of the CTB is

sufficiently higher than that of the adjacent boundary [38]; thus, a reduction in the overall free energy will take place if:

$$S_{A'B}\sigma_{AB} + S_{ITB}\sigma_{ITB} < S_{A'B}\sigma_{A'B} + S_{A'A}\sigma_{A'A} \text{ equation (2) [38],}$$

where S and σ represent the interfacial area and the interfacial energy per unit area, respectively, of the boundaries indicated by the subscripts [38]. Further increase in the width of grain A may produce more ITBs, and cause the CTBs to fully detach from the high energy boundary, as shown in Figure 4c. After the CTBs are completely detached from the high energy boundary, it is feasible that the addition of thermal energy triggers the migration of the ITB as noted by the green arrow, then the ITB can migrate and sink in a columnar GB, which leads to the disappearance of two CTBs [37] (shown in Figure 4d). Therefore, during the film deposition, the formation of ITBs and the lateral propagation of CTBs will increase the average λ .

B3. Effect of free surfaces on twin boundary mobility

In this section we explain a mechanism that can affect the mobility of TBs, specifically, when the TBs are near to the free surface or near to an interface where their mobility can be affected by the image force. The partial dislocations that comprise ITBs can be drawn to the free surface because the material is more compliant near to the surface and the dislocations do not experience forces associated with the bulk of the crystal [39]. Thus, the image force can draw partial dislocations to the free surface, contribute to ITB migration and increase the mobility of TBs.

The image force can be calculated by $F_x = -\frac{A}{x}$, where A is a constant that relates the shear modulus, the burgers vector, and the dislocation type, while x is the distance of the dislocation to the surface. Further description of the image force can be find elsewhere [21, 39]. From the image force expression, one can identify that the image force decreases as dislocations are deeper inside the film. Therefore the image force will potentially interact with partial dislocations which are near (a couple hundred nm) to the free surface. In the context of this manuscript, the image force contributes to an increase in λ by increasing the migration of the ITBs. This process is enhanced as transient free surfaces are allowed to relax during interrupted sputtering.

C. Protean representation of sputtering conditions: tailoring λ

The interplay of the mechanisms explained in section B allowed for varying λ within a wide range (2 - 35 nm). In Figure 5, we summarized the sputtering conditions in terms of the average deposition temperature and corresponding λ (Figure 5a and 5b); followed by an empirical determined λ contour zone map that can be used to tailor λ as a function of temperature and the SFE (Figure 5c). For visualization purposes, the average λ of the Cu alloys with a SFE < 13 mJ/m² is shown in Figure 5a (Cu-6wt.% Al and Cu-4wt.% Al), while the average λ of the Cu alloys with a SFE > 37 mJ/m² is displayed in Figure 5b (Cu-2wt.% Al and Cu-10wt.% Ni). Three zones are depicted in Figure 5a that correspond to the average deposition temperature, zone I < 90 °C, zone II between 90 and 240 °C, and zone III > 240 °C. Two zones are depicted in Figure 5b, zone II < 240°C and zone III > 240 °C. The mechanisms described in section B allow for an explanation of the different λ trends observed in Figures 5a and 5b as follows:

In zone I, increasing the average deposition temperature allowed λ to decrease monotonically. Although it is expected that λ will decrease as ρ decreases; the ρ values calculated for zone I showed a different trend than the one expected. In this case, the use of interrupted sputtering may allow the image force to trigger ITB migration and increase λ regardless of specific ρ values. At the lowest temperature, low TB nucleation is expected (equation 1) and in combination with interrupted sputtering allows λ to increase.

In zone II, further increase of the average deposition temperature and the use of interrupted sputtering allowed to increase and control λ as follows: first, increasing the temperature increases the nucleation of TBs, which favors the growth of a fully nt film; second, during film deposition, as thermal energy is added to the system, the CTBs can detach from columnar GBs and form ITBs that will migrate, and increase λ ; and third, after each layer is deposited (~200 nm), the ITB migration is enhanced due to the effect of the image force as transient free surfaces are allowed to relax. Based on the interplay of the mechanisms proposed to vary λ , and the effect of temperature in ITBs in zone II [37], the density of ITBs after a sample has been synthesized is expected to be low. The supplementary material Figure S3 shows representative cross-sectional TEM images, where ITBs are observed in only a few grains for samples in zone II, which is in agreement with the proposed mechanisms explained in sections B2 and B3.

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4 In zone III, when the average deposition temperature is increased, λ showed two different trends:
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6 (i) for the Cu-6wt.% Al and Cu-4wt.% Al, λ remained constant or decreased, this λ trend is
7 explained as follows: first, the alloys in zone III have the lowest calculated ρ values, which
8 means that it is expected that a high amount of TBs are nucleated; second, only continuous
9 sputtering was used in zone III, and there is virtually no free surface until the film reaches its
10 final thickness. Hence, the effect of the image force on the migration of ITBs will be minimal
11 and limited to few hundred nms below the film free surface. (ii) for the Cu-2wt.% Al alloy, λ
12 increased which could be attributed to the influence of the Al content in the alloy. In this case,
13 the effect of the Zener drag force [40] in the Cu-2wt.% Al is lower than in Cu-4wt.% Al and Cu-
14 6wt.% Al alloys, and it decreases as the temperature is increased. Therefore, boundary mobility
15 at elevated temperatures can be higher in the Cu-2wt.% Al alloy, promote grain growth, and λ
16 coarsening. In general, ITBs were not observed for the samples in zone III, we attribute the lack
17 of ITBs to the effect of high synthesis temperature on ITB migration in zone III [37]. However,
18 the overall λ trend in zone III is intriguing and needs further investigation.

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21 It is also important to mention that when the average deposition temperature was increased
22 beyond zone III, fully nt structures were not obtained for any of the four Cu-alloys. Instead, the
23 columnar structure was lost, the few twins which formed were not parallel to the film surface,
24 and the texture was random.

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27 In Figure 5c, the data presented in Figures 5a and 5b are depicted in a protean λ contour zone
28 map, generated with a Kriging correlation matrix showing λ in correlation with the average
29 deposition temperature and the SFE of the Cu-alloys. The Kriging correlation is an optimal
30 prediction method that uses known nearby observations; a detailed description can be found
31 elsewhere [41]. The zones depicted in Figures 5a and 5b, are delineated by the dashed lines in 5c.
32 Overall, the λ contour zone map presented in this study can be use as a versatile guide to
33 synthesize fully nt films with different λ . In the case of low SFE materials it is possible to
34 achieve low λ values at low or high temperatures (zone I and III), while in zone II it is possible
35 to obtain higher λ values at intermediate temperatures. As the SFE increases zone II encompasses
36 the ideal sputtering conditions to vary λ within a wide range (from blue to red).

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39 By using interrupted sputtering in combination with low cooling temperatures, it is possible to
40 increase the zone I area and a larger λ variation. Although, this approach may only work for low
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SFE materials. The contour lines highlight that zone III is isolated with respect to the other two zones, probably due to the effect to the Zener drag force in the Cu alloys, which decreases at elevated temperatures. Additionally, it is possible to fuse zone I and II. The transition between the two zones can be marked by an inflection point, where the amount of thermal energy added to the film significantly increases TB mobility, and in the case of the low SFE materials the inflection point can be related to the minimum experimentally achieved λ (~ 2 nm). The λ contour zone map can be adapted to operate at different sputtering conditions, by using zone I and II as starting points to increase or decrease λ as desired. For instance, by keeping the same average film temperature and varying the duty cycle, it is possible to generate variations of the λ contour zone map presented in this study.

Conclusions

Our experimental results show that it is possible to synthesize fully nt films and vary λ in materials with different SFEs. The analytical model can described the early stages of nucleated TBs and can be used to set proper sputtering conditions to obtain a high nucleation of TBs (low ρ values). Two mechanisms were used to explained the mobility of nucleated TBs as the films are synthesized and the mechanisms where correlated to specific sputtering conditions. The resulting film microstructures were analyzed in a comprehensive study that allows to present a protean λ contour zone map. The versatility of the λ contour zone map provides guidance to tailor λ and control the amount of twin boundaries in the film, thus expanding the synthesis space for nanostructure materials.

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Figure(s)

Figure 1. Representative cross-sectional TEM images of the twinned structures within a Cu-2wt.%Al alloy obtained at different sputtering conditions; the inset SAED patterns show the typical double hexagon of the (110) oriented twinned grain. (a) sample 2Al#5, noting the overall columnar grain structure. The twin thickness distributions highlight the volume fraction of twins for each sample in images (b) to (e); , (b) sample 2Al#1, $\lambda \approx 5.7$ nm; (c) sample 2Al#4, $\lambda \approx 10$ nm; (d) sample 2Al#6, $\lambda \approx 27$ nm; and (e) sample 2Al#7, $\lambda \approx 35$ nm. Representative TEM images showing the λ achieved for samples 2Al#2, 2Al#3, and 2Al#5 are presented in the supplementary material (Figure S1). The growth direction is vertical for all the images.

Figure 2. Representative cross-sectional TEM images of the twinned structures for Cu-Al and Cu-Ni alloys obtained at different sputtering conditions. The inset SAED patterns show the typical double hexagon of the (110) oriented twinned grain. The twin thickness distributions highlight the volume fraction of twins for each sample. For Cu-4wt.%Al (a) sample 4Al#2, $\lambda \approx 5.1$ nm, and (b) sample 4Al#5, $\lambda \approx 15$ nm; For Cu-6wt.%Al (c) sample 6Al#2, $\lambda \approx 4.8$ nm, and (d) sample 6Al#7, $\lambda \approx 19$ nm; For Cu-10wt.%Ni (e) sample 10Ni#1, $\lambda \approx 15$ nm, and (f) sample 10Ni#4, $\lambda \approx 31$ nm. Representative TEM images showing the λ achieved for samples 4Al#1, 4Al#3, 4Al#4, 6Al#1, 6Al#3, 6Al#4, 6Al#5, 6Al#6, 10Ni#2 and 10Ni#3 are presented in the supplementary material (Figure S2). The growth direction is vertical for all the images. Sample details are presented in Table 2.

Figure 3. Representative temperature profiles collected at different sputtering conditions for Cu-Al and Cu-Ni alloys during a time span of 60 minutes. The temperature profiles show the change in average deposition temperature by the variation of only one sputtering parameter as follows: (a) comparison between interrupted sputtering and continuous sputtering; (b) comparison between cooling, heating, and as-sputtered; (c) comparison between two different sputtering powers; and (d) comparison between two different duty cycles. (color online)

Figure 4. Schematic representation of λ coarsening as a function of columnar grain growth during film deposition. (a) Grain A will grow at expense of grain B; (b) and (c) CTBs are detached from a high energy boundary and form an ITB; and (d) two CTBs disappeared by the migration of the ITB depicted in Figure 4c. (color online)

Figure 5. Average λ as a function of temperature and SFE. (a) λ as a function of temperature for the Cu-alloys with a $\text{SFE} < 13 \text{ mJ/m}^2$. (b) λ as a function of temperature for the Cu-alloys with a $\text{SFE} > 13 \text{ mJ/m}^2$. (c) Protean λ contour zone map showing the change in twin thickness as a

function of the SFE and average deposition temperature; the three zones depicted in Figures 5a and 5b are delineated by the dashed lines in Figure 5c. (color online)

Table 1. Summary of sputtering conditions used to synthesize highly nt Cu alloys.

Sample label	Material	Average deposition temperature (°C)	Duty cycle (%)	Average deposition rate (nm/sec)	Substrate temperature (°C)	Sputtering power (W)
6Al#1 ^a	Cu-6wt.%Al	80	100	0.92	N/A	65
6Al#2		50	9	1.26	16	1500
6Al#3		350	100	15.00	N/A	1500
6Al#4		100	9	1.25	N/A	1500
6Al#5		28	9	0.06	N/A	65
6Al#6		290	100	12.93	16	1500
6Al#7		140	9	1.31	100	1500
4Al#1 ^a	Cu-4wt.%Al	80	100	0.86	N/A	65
4Al#2		50	9	1.20	16	1500
4Al#3		290	100	11.79	16	1500
4Al#4		350	100	14.49	N/A	1500
4Al#5		100	9	1.21	N/A	1500
2Al#1	Cu-2wt.%Al	36	9	0.74	16	1000
2Al#2		28	9	0.06	N/A	65
2Al#3		50	9	1.10	16	1500
2Al#4		100	9	1.06	N/A	1500
2Al#5		140	9	1.10	100	1500
2Al#6		290	100	12.08	16	1500
2Al#7		350	100	13.49	N/A	1500
10Ni#1	Cu-10wt.%Ni	145	9	1.11	100	1500
10Ni#2		175	9	1.09	150	1500
10Ni#3		190	16.6	2.16	150	1500
10Ni#4		225	9	1.14	200	1500

Average deposition rate = deposition rate $\times$ duty cycle / 100.

^a Samples included from a previous study [25].

N/A no substrate heating or cooling.

Table 2. Average microstructural properties and total stored energy of highly nt Cu alloys samples.

Sample	SFE ^b (mJ/m ²)	Weighted average λ (nm)	Weighted average grain width (nm)	ρ (%)	Total GBE (mJ)	Total GBE/TBE (J/J)
6Al#1 ^a	6	2.1±0.3	40±5	1.1	80	17.7
6Al#2		4.8±0.6	130±20	0.7	93	5.4
6Al#3		6.5±0.8	130±20	0.3	93	5.4
6Al#4		7.4±0.9	130±20	0.6	93	5.4
6Al#5		8±1	110±10	1.5	110	6.4
6Al#6		13±1	190±30	0.4	63	3.7
6Al#7		19±3	300±40	0.5	40	2.3
4Al#1 ^a	13	2.5±0.3	60±7	2.3	53	6.7
4Al#2		5.1±0.6	140±20	1.4	86	2.8
4Al#3		5.1±0.6	130±20	0.8	93	3.1
4Al#4		5.9±0.7	100±10	0.7	120	4
4Al#5		15±2	220±30	1.2	54	1.8
2Al#1	37	5.7±0.7	160±20	4.6	75	2.4
2Al#2		6±0.7	130±20	8.6	93	2.9
2Al#3		8±1	160±20	4.1	75	2.4
2Al#4		10±1	260±30	3.5	46	1.4
2Al#5		10±1	210±30	3.1	57	1.8
2Al#6		27±3	200±30	2.3	60	1.9
2Al#7		35±4	230±30	2	52	1.6
10Ni#1	60	15±2	220±30	5.0	54	3.2
10Ni#2		17±2	330±40	4.7	36	2.1
10Ni#3		20±2	260±30	4.4	46	2.7
10Ni#4		31±4	380±50	4.1	31	1.8

^a Samples included from a previous study [25].

^b SFE values from references [23,24, and 34].