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Copper thin films by ion beam assisted deposition: strong texture, superior thermal
stability and enhanced hardness

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Abstract

Nanocrystalline metals generally exhibit exceptionally high strength. However, their susceptibility to grain growth restricts their applications in high temperature environments. The current study presents that nanocrystalline Cu thin films produced by ion beam assisted deposition (IBAD) are able to sustain their as-deposited microstructure and high hardness upon annealing at high temperatures. IBAD-Cu films exhibit a strong (111) fiber texture, which is caused by the ion beam induced effects of substrate cleaning, preferential damage and preferential sputtering. The microstructure of the IBAD-Cu films is stable at temperatures up to 800°C (80% of the melting point of Cu). The hardness of the as-deposited IBAD-Cu films can reach a maximum value of 3.85 GPa. Even after annealing, their hardness is still much higher than that of the normally deposited (without ion beam) films as well as their bulk nanocrystalline counterparts before heat treatment. The excellent thermal stability of microstructure is attributed to the formation of nanometer-sized voids and their pinning effect on grain boundary migration. The kinetics of void formation, the contribution of twin boundaries and ion beam induced defects to the hardness are analyzed and discussed. The findings in this study demonstrate that IBAD is an effective method for the stabilization of microstructure and mechanical properties of nanocrystalline metal thin films.

Keywords: Thin film; Ion beam processing; Defects; Microstructure; Hardness

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1. Introduction

For conventional polycrystalline metals, the mechanical strength is mainly controlled by dislocation pile-up at the grain boundaries (GBs) and, therefore, can be described by the empirical Hall-Petch relation [1]. This relation is valid even down to nanometer regime and the nanocrystalline (nc) metals have been found to exhibit significantly higher mechanical strength than that of their coarse-grained counterparts [2-5]. However, a main drawback for nc metals is their microstructural susceptibility: rapid grain coarsening and, consequently, a strength reduction are commonly observed in nc metals due to the high volume fraction of GBs [6-8]. This microstructural instability is a challenge for high temperature applications of nc metals.

Several strategies have been explored to surmount the issue of poor thermal stability in nc metals: (i) The introduction of secondary phase particles through alloying and subsequent precipitation. The mobility of dislocations and GBs is reduced by the Zener drag force [9]. Both simulations [10, 11] and experiments [12, 13] have shown that particle drag is effective to retain the initial fine-grained microstructures upon annealing. (ii) The minimization of free energy by GB segregation. Recently, Chookajorn et al. [14] developed a nanostructure stability map based on a thermodynamic model. According to the map, there are certain alloy systems, in which nanocrystalline structure is the most stable microstructure due to the minimization of free energy by GB segregation. The validity of this map was demonstrated by the successful synthesis of a nanocrystalline W-Ti alloy with substantially enhanced stability against high temperature and long duration annealing. (iii) The introduction of low energy phase interfaces. By severe plastic deformation, Zheng et al. [15] developed a nanolayered Cu/Nb composite, which exhibited extremely high strength even after annealing at high temperatures. The authors attributed this high post-annealing strength to the atomically well-ordered Cu/Nb phase interfaces, which prevented the coarsening of the
nanolayered structure. (iv) The introduction of high density of nanoscale twin boundaries (TBs). Similar to GBs, coherent TBs are also strong barriers for dislocation transmission and can contribute to the strength of materials [16]. Since the excess energy of TBs is much lower than that of GBs, the driving force for twin coarsening is much lower than that for grain coarsening. The nanotwinned (nt) microstructure in Cu [17, 18] and Ag [19] has been found to be stable at temperatures as high as 0.8 $T_m$, where $T_m$ is the melting point of the materials.

Although all the above mentioned strategies are able to stabilize nanostructures, there are some limitations. For the strategies (i - iii), alloying systems have to be carefully selected in order to ensure the occurrence of particle precipitation, GB segregation and the formation of sharp and low energy phase interfaces, respectively. In the meantime, the strategy (iv) is only applicable for materials with very low TB energies. Now, the question arises: is there a universal way, which is material independent, for the stabilization of microstructure? Ion beam irradiation seems to have this potential. Upon irradiation, point defects are generated in materials. Their migration results in the formation of complex defect clusters [20-22]. For example, nanometer-sized voids have been found to form in irradiated fcc [23, 24], bcc [25] and hcp [26] metals. Due to their low formation energy at GBs [27, 28], voids are preferentially formed along GBs [24] and they are very stable even at very high temperatures [29]. These voids could act as pinning centers, similar to secondary phase particles, for GB migration and stabilize the microstructure. In addition, irradiation-induced defects in materials also act as barriers for dislocation motion and, hence, are able to additionally improve the mechanical properties [30-33].

Defects can be simultaneously introduced into materials during processing by means of ion beam assisted deposition (IBAD). The effect of IBAD on microstructure and mechanical properties of as-deposited films have been intensively studied [34-36]. However, only few studies [37] have been reported to reveal the stability of microstructure and mechanical
properties at high temperatures. In the present study, the microstructure evolution and hardness change in IBAD-Cu films upon annealing was investigated and compared to Cu films deposited without the assistance of ion beam. The effect of IBAD on thermal stability and hardness of Cu films was analyzed and discussed.
2. Experimental

Polycrystalline Cu thin films with thickness of ~500 nm were deposited at room temperature (RT) on (100) silicon wafers coated with 50 nm SiO₂ and 50 nm Si₃N₄ (Si-Mat Silicon Materials) by both normal DC magnetron sputtering and IBAD. For simplicity, the films deposited by the former method are named as “ND-Cu” while the latter as “IBAD-Cu”. Prior to Cu deposition, a 10 nm thick Ta layer was DC sputter-deposited onto Si wafers in order to improve the adhesion of Cu films. The IBAD system consists of a grided broad ion beam source (KRI KDC 40) attached to the DC magnetron sputtering system (PVD Products, Inc.). The incident angle of ion beam was 35° with respect to the substrate surface normal. The base pressure in the sputter chamber was better than 3 × 10⁻⁷ Torr. Deposition was carried out under Ar atmosphere with a constant pressure of 3 × 10⁻³ Torr. For IBAD, the ion beam energy was varied from 0.05 to 1.2 keV while the current was kept constant at 5 mA. The ion beam was neutralized by a hot W filament. During deposition, the substrate was kept rotating with a speed of 12 rpm in order to achieve a homogeneous film thickness. For the thermal stability studies, films were annealed at temperatures between 400 and 800°C for 1 h in a rapid thermal annealing oven (RTA, CreaTec) under ultra-high vacuum of 5 × 10⁻⁹ Torr.

The film hardness was measured using a nanoindenter (TriboIndenter, Hysitron Inc., USA) equipped with a standard Berkovich tip. The measurements were carried out in a load-controlled mode with loads varying from 1 to 10 mN (increment of 1 mN). The loading, unloading and dwell time were 10 s for each. The load function for each measurement consists of a loading, a holding and an unloading segment. In order to minimize the effect of thermal drift on measurements, the time for each segment was kept short and constant, i.e. 5, 1 and 5 s, respectively. For each load, hardness of 5 different positions was measured, and the average value was taken as the final hardness. The indentation depth varied with loads and film microstructure. Overall, it is in the range of 50 - 350 nm. The reduced Young’s modulus
and the hardness were determined at indentation depth ~ 150 nm (30% of film thickness) by the Oliver and Pharr method [38]. For soft film on hard substrate, this indentation depth is still safe to avoid substrate effect [39, 40].

The electrical resistivity of the films were measured by the Van der Pauw method [41] using a Jandel four point probe. The four pins on the probe are arranged in a square array with a spacing of 0.635 mm. A DC current of 50 mA was applied and the resulting voltage was recorded in order to calculate the resistivity. For each film, 50 measurements were carried out and the average value was calculated. All the measurements were controlled and evaluated with LabView 8.2 software.

The surface morphology of the films was measured by means of atomic force microscope (AFM) (Cypher S, Oxford Instruments). The texture and grain size of the films were analyzed using a scanning electron microscope (SEM) (Quanta 200 FEG, FEI) operated at 20 kV and equipped with an electron backscatter diffraction (EBSD) detector (AMETEK-EDAX). The microstructures on the film cross sections were studied using a transmission electron microscope (TEM) (Tecnai F30, FEI) operated at 300 kV in both TEM and STEM (scanning transmission electron microscope) modes. The size distribution of voids in the IBAD-Cu films was analyzed with ImageJ routines, where the outline of voids was first extracted from STEM micrographs based on the contrast difference between void areas and matrix and the statistics of void size distribution was subsequently generated by the “Analyze particles” function. The TEM cross section lamellas were prepared by a focused ion beam (FIB) dual station (NVision 40, Zeiss) operated at 30 kV of Ga⁺ and 2 kV of electron sources.
3. Results

3.1. Film microstructure

The out-of-plane EBSD orientation maps and corresponding {111} pole figures of the as-deposited films are shown in Fig. 1a-c. The ND-Cu film exhibits a nearly random texture, indicated by the spread of grain colors in the orientation map (Fig. 1a). However, there are still weak texture components present, i.e. (111), (511) and (5713) fiber textures indicated by the rings in the pole figure. The last two textures are known to result from twinning and multiple twinning [42], respectively. For the IBAD-Cu films (Fig. 1b and c), the effect of ion beam is to promote the formation of (111) fiber texture. The area fraction of texture components as a function of ion beam energy in the as-deposited films is summarized in Fig. 1g. An energy threshold of 0.2 keV is observed. Below 0.2 keV, the area fraction of the (111) fiber texture steeply increases from ~16% to more than 90%. Above 0.2 keV, it continues to increase, but very slowly, until the entire film becomes (111) fiber textured. After 1 h annealing at 400˚C, all the films are dominated by a very strong (111) fiber texture, as shown in Fig. 1h. For the ND-Cu (Fig. 1d) and 0.05 keV IBAD-Cu (Fig. 1e) films, small amount of (511) fiber texture is retained after annealing. For the high energy (≥ 0.2 keV, the same hereinafter) IBAD-Cu films (Fig. 1f), there is no obvious change in texture upon annealing.

The influence of ion beam energy on the grain sizes are summarized in Fig. 2a. For the as-deposited films, the grain size increases from ~60 nm in the ND-Cu film to ~90 nm in the 0.2 keV IBAD-Cu film. Above 0.2 keV, the grain size gradually decreases until a grain size of ~70 nm is reached at 1.2 keV. Upon annealing at 400˚C, the ND-Cu and 0.05 keV IBAD-Cu films show significant grain growth with final grain size close to the film thickness. Interestingly, no obvious grain growth is observed in the high energy IBAD-Cu films. The 1.0 keV IBAD-Cu film was annealed up to 800˚C (~0.8 Tm) and the evolution of its grain size as a function of annealing temperature is presented in Fig. 2b, where literature values for nt-
Cu [17] and ufg (ultra-fine grained)-Cu [43] samples are also shown for comparison. More than one order of magnitude increasing in grain size is observed in nt-Cu, ufg-Cu as well as the ND-Cu film. In contrast, the grain size of the 1.0 keV IBAD-Cu film keeps almost constant even up to 800°C.

The surface morphologies of the as-deposited films are presented in Fig. 3a-c. All the films exhibit granular surface features, with modulations corresponding to grain sizes. The 1.0 keV IBAD-Cu film (Fig. 3c) exhibits deeper and wider grooves between the features than that of the ND-Cu (Fig. 3a) and 0.05 keV IBAD-Cu (Fig. 3b) films. The groove formation most likely indicates the preferential ion beam damage at GBs. All the films become porous after 1 h annealing at 400°C, as shown in Fig. 3d-f. Cross-sectional TEM micrographs shown in Fig. 3h and i indicate that the pores are confined at the surface of the films. The pore morphologies suggests that the pores in the ND-Cu and 0.05 keV IBAD-Cu films might result from thermal grooving at GBs during grain growth (Fig. 3h) while that in the high energy IBAD-Cu films are most likely caused by the accumulation of ion beam induced defects (i.e. vacancies) at the surface (Fig. 3i). The evolution of surface roughness as a function of ion beam energy is presented in Fig. 3g. For both the as-deposited and annealed films, the surface roughness increases with increasing ion beam energy. The roughness saturates when the ion beam energy becomes higher than 0.2 keV. Due to the formation of surface pores, the roughness of the annealed films is slightly higher than that of the as-deposited films.

The Dark-field TEM micrographs in Fig. 4 reveal the interior microstructure of the films. The ND-Cu film consists of nearly equiaxed grains before annealing (Fig. 4a). The random distribution of grain orientations is indicated by the 111 ring in the electron diffraction pattern. Annealing at 400°C led to significant grain growth in the ND-Cu film (Fig. 4d). In contrast, both the as-deposited and annealed 1.0 keV IBAD-Cu films exhibit similar microstructures,
consisting of columnar grains with high density of nanotwins, as shown in Fig. 4b and e, respectively. Most of the TBs are $\Sigma 3\{111\}$ coherent TBs (CTBs) indicated by the inserted selected area diffraction patterns [18, 44, 45]. The average twin variant thickness is ~16 nm before annealing (Fig. 4c) and is not affected much by annealing (Fig. 4f).

The cross-sectional STEM micrographs shown in Fig. 5 reveal the defect (mainly voids) distribution in the films. The as-deposited films (Fig. 5a and b) are dense. After 1 h annealing at 400°C, the ND-Cu film (Fig. 5d) retains the dense structure while the IBAD-Cu film (Fig. 5e) shows the formation of high density of voids (small black dots in the image). The arrangement of voids can be more clearly seen in the contrast-enhanced image in Fig. 5f. The threshold fitted image in Fig. 5g indicates that the voids are preferentially arranged along GBs and TBs. The void size distribution shown in Fig. 5c gives an average diameter of 4 nm.

3.2. Electrical resistivity and defect concentration

The resistivity of the films was modeled using the combined Fuchs–Sondheimer (FS) and Mayadas–Shatzkes (MS) method (see [46] for details), which takes into account the resistivity contribution from the grains, surface/interface and GB scattering. The measured and modeled resistivity as a function of ion beam energy is summarized in Fig. 6a. The difference between measured and modeled values reflects the contribution from scattering at point defects (i.e. vacancies and incorporated Ar atoms) [46]. For the as-deposited films, the measured resistivity values of the ND-Cu and 0.05 keV IBAD-Cu films are very close to the modeled ones, indicating that these films are virtually free of point defects. Starting from 0.2 keV, the difference increases and saturates at 1.0 keV, indicating that the efficiency of point defect production is proportional to ion beam energy. Moreover, the annealed films show much lower resistivity than the as-deposited films due to defect annihilation.
On the basis of the difference between the measured and molded resistivity values, one can calculate the point defect concentration if the resistivity increment per point defect is known [46]. The values for a single vacancy and Ar atom were experimentally measured to be 1.3 - 1.5 × 10^{-8} Ohm m at.%^{-1} [47, 48] and 1.74 × 10^{-8} Ohm m at.%^{-1} [35], respectively. An average value of 1.5 × 10^{-8} Ohm m at.%^{-1} was used for the calculation in this study. The calculated defect concentration as a function of ion beam energy is presented in Fig. 6b with a maximum concentration of 4.5 at.% obtained for the as-deposited 1.0 keV IBAD-Cu film.

3.3. Film hardness

The evolution of film hardness as a function of ion beam energy is presented in Fig. 7a. The hardness of the as-deposited ND-Cu film is 2.46 ± 0.06 GPa. It slightly decreases to 2.23 ± 0.05 GPa in the 0.05 keV IBAD-Cu film. Above 0.2 keV, the hardness increases with ion beam energy until the maximum value of 3.85 ± 0.04 GPa is reached at 1.2 keV. After annealing, all the films show lower hardness than the as-deposited ones. The relative decrease in hardness is ~40% for the low energy (0 and 0.05 keV) IBAD-Cu films but less than 20% for the high energy IBAD-Cu films.

The change in reduced Young’s modulus $E_r$ as a function of ion beam energy is shown in Fig. 7b. The Young’s modulus $E_f$ is related to $E_r$ by the following equation [38]:

$$\frac{1}{E_r} = \frac{1 - \nu_f^2}{E_f} - \frac{1 - \nu_i^2}{E_i}$$

(1)

where $\nu_f = 0.33$ is the Poisson’s ratio of Cu; $\nu_i = 0.07$ and $E_i = 1140$ GPa are the Poisson’s ratio and Young’s modulus of the diamond indenter, respectively. According to Eq. (1), $E_f$ is 118 - 132 and 116 - 125 GPa for the as-deposited and annealed films, respectively. Those values are in good agreement with the literature values of 108 - 131 GPa for Cu [49]. For the high energy IBAD-Cu films, the $E_r$ after annealing is lower than that before annealing. The
decreasing modulus upon annealing is believed to be caused by void formation in the film (Fig. 5f) [50].

A series of annealing with temperatures up to 800°C were carried out on the 1.0 keV IBAD-Cu film. Fig. 8 shows the evolution of its hardness as a function of annealing temperature. The hardness continuously decreases from 3.78 ± 0.07 GPa to 2.5 ± 0.07 GPa upon annealing. A similar annealing behavior was observed in polycrystalline nt-Cu films [17]. In comparison, the hardness of the ND-Cu film, ufg-Cu [6] and nc-Cu [7] rapidly decreases to ~1.5 GPa or even below upon annealing at 400°C.
4. Discussion

4.1. IBAD induced texture formation

Because of surface/interface energy minimization, fcc metals deposited on amorphous substrates commonly show (111) fiber texture [51]. However, the as-deposited ND-Cu film (Fig. 1a) in this study exhibits a nearly random texture, which was also frequently observed in Cu films deposited on various substrates by different deposition techniques [52, 53]. Substrate surface contamination was considered to be responsible for the formation of the random texture due to strong affiliation of Cu with O adsorbed by the substrate surface [53].

Cu thin films deposited on clean Ta interlayer commonly show strong (111) texture [51, 52] due to the heteroepitaxial growth of hexagonal close-packed Cu (111) planes on β-Ta (002) planes with pseudohexagonal atomic arrangement [53]. However, it seems not to be the case in this study. Although the as-deposited ND-Cu film on Ta interlayer shows the trace of (111) fiber texture (Fig. 1a), the majority of texture is still random (more than 40% of texture components are random while only 20% are (111), see Fig. 1g). This contradiction could be due to surface contamination of substrates, because the quality of Cu films is found to be strongly affected by substrate surface condition [54]. Since the substrates used in this study were not routinely cleaned prior to film deposition, the Ta interlayer could be partially oxidized by the substrate contamination and, therefore, partially hindered the heteroepitaxial growth of Cu on Ta.

During IBAD, the substrate surface (Ta interlayer) is directly exposed to ion beam at the beginning of deposition. As a consequence, the oxide formed on Ta substrate surface contamination could be removed by ion bombardment. This cleaning effect could promote the heteroepitaxial growth of Cu on Ta increase the mobility of arriving Cu adatoms and, therefore, promote the nucleation enhance the formation of (111) fiber texture. The texture evolution shown in Fig. 1g could be related to the efficiency of the cleaning effect.
beam energy of 0.2 keV is probably an approximate threshold below which the ion beam is not strong enough to completely remove the substrate surface contamination and, therefore, the area fraction of (111) fiber texture is proportional to ion beam energy in this range. Above this threshold, the area fraction of (111) fiber texture is saturated, since the surface of the Ta interlayer substrate surface is fully cleaned.

In addition to the substrate cleaning effect, the ion beam itself can also contribute to texture formation. During IBAD, the growing film is continuously bombarded by energetic ions. The energy transfer between ions and film atoms occurs through elastic (nuclear) and inelastic (electronic) collisions. Fig. 9a presents the stopping power, i.e. the amount of energy transferred, of Ar ions in a Cu target calculated by SRIM (stopping and range of ions in matter) [55]. It is clear, that the nuclear stopping power dominates in the entire energy range employed here. This implies that the main effects of ion bombardment on the growing film are defects production and sputtering. Considering the geometrical setup of IBAD (Fig. 10) with the ion beam inclined at 35˚ to the substrate normal, the ion beam is actually parallel to the <110> channeling directions in a subset of grains provided the film is (111) fiber textured. As the substrate is rotating, all (111) fiber textured grains are at some point in channeling condition during deposition. Therefore, the grains in the growing film can be divided into two groups: those with the (111) planes parallel to the substrate surface and, therefore, are in channeling condition and those with random orientations. Compared to the channeling oriented grains, the randomly oriented grains are characterized by higher defect concentration and higher sputter yield due to the preferential damage and preferential sputtering processes, respectively. Simulations [56, 57] have shown that both of the processes are able to promote texture formation. The preferential damage process, driven by the minimization of the volume free energy between the channeling oriented and randomly oriented grains, will lead to the growth of channeling oriented grains. For the preferential sputtering process, randomly
oriented grains will be eliminated by shadowing and the subsequent pinch-off effects. Overall, the IBAD films will finally consist only channeling oriented grains and, therefore, exhibit a strong texture. This is an alternative mechanism accounting for the formation of strong (111) fiber texture in the IBAD-Cu films (Fig. 1).

The energy threshold of 0.2 keV in Fig. 1g suggests that the efficiency of preferential damage and preferential sputtering is also ion beam energy dependent. Fig. 9b presents the average penetration depth, defect (vacancy) production as well as sputter yield as a function of ion beam energy for irradiation of a Cu thin film with Ar ion beam based on SRIM simulations [55]. The effective ion-film interaction range is less than 2 nm. With ion beam energy below 0.2 keV, both the defect production rate and sputter yield are close to zero, indicating that the film growth is not affected much by the ion beam. This is consistent with the only slight enhancement of the (111) fiber texture in the 0.05 keV IBAD-Cu film, compared to the ND-Cu film (Fig. 1g). With ion beam energy above 0.2 keV, both the defect production rate and sputter yield, especially the former, increase steeply. This makes both processes, especially the preferential damage, efficient enough to completely eliminate the randomly oriented grains. This is in a perfect accordance with the substantial enhancement of the (111) fiber texture in high energy IBAD-Cu films, as shown in Fig. 1g.

It should be noted that in our experiments, the (511) and (5713) texture components in the as-deposited IBAD-Cu films almost completely disappear when the ion beam energy exceeds 0.2 keV (Fig. 1c and g). This is, however, in contrast to the results in [52]-[54], where only substrate cleaning effect was activated and the (511) and (5713) texture components were clearly visible after film deposition the texture formation in Cu is solely caused by clean Ta interlayer and the (511) and (5713) texture components are still presented. This contrast strongly implies that the vanishing of the two texture components in this study is caused by the preferential damage and preferential sputtering processes. Since the grains showing (511)
and (5713) textures are not in channeling condition (Fig. 10), their growth is energetically unfavorable during IBAD.

Therefore, based on the above discussion, we can conclude that both the substrate cleaning effect and ion beam induced preferential damage as well as preferential sputtering processes are responsible for the texture formation during IBAD of Cu films in this study. The latter two processes are essential for getting a pure (111) fiber texture.

4.2. Void formation in IBAD-Cu films

Upon ion beam irradiation, point defects (i.e. Frenkel-pairs) are generated by atomic displacements. The deposition temperature (RT) of IBAD-Cu films in this study falls in the range of stage III recovery temperatures (−40 - 100°C) of irradiated Cu [58], where vacancies are mobile with a migration energy of 0.71 eV [59]. Cu interstitials are even more mobile with a very low migration energy of 0.12 eV [60]. The migration and interactions of point defects can lead to the change in defect concentration and the generation of new types of defects. The exact defect dynamics is complicated. However, it can be summed up in three scenarios. First, mutual annihilation of vacancies and interstitials; second, formation of defect clusters (e.g. dislocations loops, stacking fault tetrahedra); third, absorption by sinks (e.g. GBs, surface/interface, dislocations). The concentration of the surviving defects will be much lower compared to the production rate and most of them are in the cluster form. Nevertheless, the existence of biased sinks and the incorporation of Ar atoms into the IBAD films make the situation even more complicated. On one hand, the large local lattice distortion around interstitials leads to a preferential adsorption of interstitials at dislocations [61]. This biased sink efficiency leaves excess vacancies in the film, which is probably the main driving force for void formation upon annealing. On the other hand, a certain amount of Ar atoms are incorporated into the film during IBAD [34, 35]. Due to their limited solubility in Cu, Ar
atoms are mainly trapped at vacancies. The vacancy-Ar clusters are characterized by a high binding energy (> 2.87 eV) and a high migration energy (> 2.55 eV), indicating that they are very stable and immobile even at high temperatures [29]. By considering all these situations, it is reasonable to assume that the main surviving defects in the as-deposited IBAD-Cu films are interstitial clusters, vacancy clusters and vacancy-Ar clusters. The number of vacancies is much higher than that of interstitials due to the effect of biased sinks. Unfortunately, these defect clusters in the as-deposited films are usually too small to be visible by TEM/STEM, as shown in Fig. 5b.

Due to the relatively low binding energy of vacancy clusters [20], single vacancies or small vacancy clusters can dissociate from large clusters [22]. Some of them move to sinks and annihilate there. This process could account for the more than 50% reduction of point defect concentration in IBAD-Cu films upon annealing (Fig. 6b). The remaining are continuously incorporated into immobile vacancy-Ar clusters and finally give rise to Ar-filled voids. Due to the strong binding energy of Ar atoms to vacancies, those voids are very stable even close to 800°C [29]. Since the formation energy and diffusion barrier for vacancies in GBs are much lower than those in the bulk [27, 28], mobile vacancies have higher tendency to diffuse to GBs. This is in accordance with the high density of voids arranged along GBs (Fig. 5f). In addition, voids also form along TBs, as shown in Fig. 5f, even though previous studies [23, 24] have shown that TBs have no crucial effect on the void formation. However, since atomic diffusion is strongly hindered at TBs [62], it is likely that the implanted Ar atoms are kinetically arrested at TBs and, afterwards, serve as nucleation sites for the formation of vacancy-Ar clusters and subsequent Ar-filled voids.

A simple model is proposed here to reveal the kinetics of void formation. As will be shown in the next section, voids are the main obstacles to grain growth in IBAD-Cu films. Therefore, the kinetics of void formation should be much faster than that of grain growth, i.e.
voids have to be already existed before significant grain growth can occur. For the 1.0 keV IBAD-Cu film, the grain size increased by 18 nm after 1 h annealing at 400°C (Fig. 2a). The kinetics of normal grain growth usually obeys the following relation:

\[ d - d_0 = (Mt)^{1/n} \]  

(2)

where \( d_0 \) is the average initial grain size, \( d \) is the average grain size after a time \( t \), \( n \) is the grain growth exponent and \( M \) is a constant related to the GB mobility. For nanocrystalline Cu thin films annealed at 400°C [63], the \( n \) and \( k \) values were determined to be 2.8 and 43 nm\(^n\) s\(^{-1}\), respectively. Applying these parameters to Eq. (2), the effective time for a 18 nm increase in grain size is less than 2 min (\( \sim 76 \) s) and, accordingly, the void formation in the IBAD-Cu films should be completed in this time period.

Since the nucleation and growth of voids require migration of point defects, they are essentially diffusion-controlled processes. According to the solutions of the Fick’s second law, the position of the diffusion front can be expressed as [1]:

\[ X^2 = 6Dt \]  

(3)

where \( X \) is the position of the diffusion front at time \( t \), \( D \) is the self-diffusion coefficient, given by:

\[ D = D_vC_v = D_0\exp\left(-\frac{E}{kT}\right)C_v \]  

(4)

where \( D_v \) is the diffusion coefficient of vacancy, \( C_v \) is the atomic concentration of vacancies, \( D_0 \) is the pre-exponential factor, \( E \) is the activation energy for self-diffusion, \( k \) is the Boltzmann constant and \( T \) is the temperature. Actually, both vacancies and interstitials contribute to diffusion, especially in irradiated materials. However, the concentration of interstitials is usually much lower than that of vacancies, because of the existence of biased sinks. Therefore, the diffusion processes in IBAD-Cu films here are still considered to occur mainly through vacancy-driven mechanisms. If we simply take the average void spacing, measured to be \( \sim 20 \) nm from STEM micrographs, as \( X \) and the effective grain growth time
The self-diffusion coefficient for IBAD-Cu films $D^{IB}$ is calculated (by Eq. (3)) to be $8.8 \times 10^{-15}$ cm$^2$/s, which is more than one order of magnitude higher than that for unirradiated Cu ($D^* \sim 2.2 \times 10^{-16}$ cm$^2$/s) [64]. According to Eq. (4), the relation between $D^{IB}$ and $D^*$ can be expressed as:

$$\frac{D^*}{D^{IB}} = \frac{C_v^*}{C_v^{IB}} \exp\left(-\frac{E^* - E^{IB}}{kT}\right)$$  \hspace{1cm} (5)

where $C_v^*$ and $C_v^{IB}$ are the atomic concentration of vacancies at thermal equilibrium and IBAD conditions, respectively. $E^*$ and $E^{IB}$ are the activation energies for self-diffusion in ND-Cu and IBAD-Cu, respectively. The $C_v^*$ in ND-Cu at 400˚C is in the order of $10^{-9}$ and the $C_v^{IB}$ is in the order of $10^{-2}$ (Fig. 6b). The activation energy $E^*$ is equal to the migration energy of single vacancies 0.71 eV [59]. Consequently, $E^{IB}$ is determined by Eq. (5) to be 1.43 eV. The diffusion parameters for the ND-Cu and IBAD-Cu films are summarized in Table 1. Due to the significant supersaturation of vacancies, diffusion in the IBAD-Cu film is enhanced by more than one order of magnitude compared to that in the ND-Cu film. The activation energy for diffusion in the IBAD-Cu film is 0.72 eV higher than that in the ND-Cu film. The higher activation energy indicates that mobile single vacancies are not presented in the as-deposited IBAD-Cu film. They have to be first dissociated from vacancy clusters by thermal activation. The value of 0.72 eV corresponds to the dissociation energy of one single vacancy from a vacancy cluster containing about 20 vacancies [20].

### 4.3. Thermal stability of microstructure

The microstructure of the IBAD-Cu films shows exceptional thermal stability, compared to that of the ND-Cu film. No obvious grain growth was discerned even at temperature as high as 800˚C, as shown in Fig. 2b.

One possible explanation for the superior thermal stability of microstructure is the limited GB mobility due to triple junction drag force. At equilibrium, the dihedral angles at a triple
junction, where three GBs meet, are determined by the balance of GB energies. During GB migration, the dihedral angles were often observed to deviate from the equilibrium values, indicating that the mobility of triple junctions is finite and can be sufficiently small to retard GB migration [65, 66]. In the IBAD-Cu films, large amounts of triple junctions are generated by intersecting the GBs with high density of coherent TBs (Fig. 4b and e). The TB-GB triple junctions have been found to be able to stabilize the microstructure of Cu samples, which was plastically deformed at low temperatures, at RT [67]. On the contrary, significant grain growth has been observed in nt-Cu films upon annealing at high temperatures, despite the existence of large amounts of TB-GB triple junctions [17]. These seemingly contradictory observations are however reasonable, since the mobility of triple junctions is strongly temperature sensitive, i.e. their dragging effect on GB migration is large at low temperatures, but it becomes trivial at high temperatures [65, 66]. Therefore, by considering the high annealing temperatures applied (400 - 800˚C), the contribution of TB-GB triple junctions to the microstructure stability of the IBAD-Cu films is very limited in the current study.

Another possible reason for the extraordinary thermal stability is the orientation pinning effect due to the presence of large amounts of low-angle GBs [68]. The grain boundary character distribution in materials essentially depends on texture [69]. Materials with strong fiber texture contain higher fraction of low-angle GBs than those with random texture [70]. As a result, the boundary of a grain in the IBAD-Cu films consists of, on average, more low-angle GB segments than that in the ND-Cu film. Since the mobility of low-angle GBs is low, they could serve as obstacles pinning the movement of neighboring GBs and, therefore, slowing down grain growth. However, this orientation pinning effect is not strong enough to completely hinder grain growth, as observed in [17], where the grain size of the nt-Cu film increased by more than one order of magnitude upon annealing at 800˚C even though the film showed very strong (111) fiber texture. As a result, the completely absence of grain growth in
the IBAD-Cu films in this study could not be solely accounted for by the orientation pinning effect.

A more plausible explanation for the enhanced thermal stability is the Zener drag force. It is well known that, finely dispersed secondary phase particles exert strong Zener drag force on GB migration [9]. Normal grain growth is expected to stagnate once the driving force (i.e. the minimization of GB curvature) is balanced by the Zener drag force. As shown in Fig. 5e, the GBs in the IBAD-Cu films are decorated with high density of nanometer-sized voids. Those voids serve as secondary phase particles to pin the GB migration. The critical maximum grain size ($R_c$), above which normal grain growth would be completely inhibited by the Zener drag force, can be predicted by the general form [12]:

$$R_c = K \frac{r}{f_v^m}$$

where $r$ and $f_v$ are, respectively, the average radius and the volume fraction of the secondary phase particles, $K$ is a dimensionless constant and $m$ is the exponent. Statistical analysis on void size distribution in Fig. 5c yields a value of ~2 nm for $r$. The value of $f_v$ is estimated from STEM micrographs to be ~0.4% by assuming a thickness of 80 nm for the TEM lamella. The values of $K$ and $m$ vary with different theories. However, Eq. (6) with $K = 0.17$ and $m = 1$ has been found to be able to fit most of the experimental grain growth data in material systems with $f_v < 5\%$ very well [12]. With all these values, $R_c$ is estimated to be ~85 nm, which is comparable with the grain size (~92 nm) of the 1.0 keV IBAD-Cu film after annealing. Therefore, we conclude that the enhanced thermal stability of microstructure in the IBAD-Cu films in this study is mainly caused by the Zener drag force by voids.

### 4.4. IBAD induced hardening

The yield strength of polycrystalline materials is generally related to grain size by the Hall-Petch relation [5]:

\[
\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}
\]  
(7)

where \(\sigma_y\) is the yield strength, \(\sigma_0\) and \(k_y\) are material dependent constants and \(d\) is the grain size. Since the yield stress \(\sigma_y\) is usually related to the hardness \(H\) by the Tabor’s relation as \(H \sim 3\sigma_y\) [71], the hardness can also be expressed in the Hall-Petch form:

\[
H = H_0 + \frac{3k_y}{\sqrt{d}}
\]  
(8)

The hardness of the Cu films is plotted as a function of \(d^{1/2}\) in Fig. 11. Literature values for Cu samples prepared using different methods [72-75] are also shown for comparison. With some scatterings, all the literature values follow the Hall-Petch relation. The hardness of the ND-Cu and 0.05 keV IBAD-Cu films is in the scattering range and also follow the Hall-Petch relation. The fit Eq. (8) to both data sets yields \(H_0\) and \(k_y\) to be 1.01 GPa and 0.11 MPa m\(^{-1/2}\), respectively. By contrast, the hardness values for the high energy IBAD-Cu films are significantly higher than those expected using the Hall-Petch relation. This deviation implies that there are additional mechanisms contributing to the hardness: (i) Similar to GBs, TBs also acts as strong barriers to dislocation transmission and, therefore, strengthen the materials [16]. The existence of high density of TBs (Fig. 4b and e) is expected to increase the hardness of the IBAD-Cu films. (ii) A large amount of defects were generated during IBAD, as shown in Fig. 6b. Since defects are barriers for dislocation movement, they are also expected to contribute to the hardening of the IBAD-Cu films. These two contributions are discussed respectively in the following parts.

4.4.1. Hardening due to twin boundaries

Compared to conventional metals, nt-fcc metals show very different Hall-Petch slope when only twin spacing \(l_{\text{twin}}\) or grain size \(d\) is considered in Eq. (7) and (8) [17, 19]. An
effective domain size \( (d_{\text{eff}}) \) has been suggested, with which the Hall-Petch relation for the conventional metals can be extended to nt-metals [19], as:

\[
d_{\text{eff}} = d \left[ 1 - \frac{t_{\text{twin}}}{d} + \left( \frac{t_{\text{twin}}}{d} \right)^2 \right]
\]  

(9)

The grain size of each IBAD-Cu film is known, as shown in Fig. 2a. The twin spacing is measured to be 16 and 17 nm for the 1.0 keV IBAD-Cu film before and after annealing (Fig. 4c and f), respectively. By assuming the same twin spacing in other high energy IBAD-Cu films, the effective domain size for each IBAD-Cu film is determined by Eq. (9). Using these values, together with the \( H_0 \) and \( k_y \) values (1.01 GPa and 0.11 MPa m\(^{1/2}\), respectively) determined above, the hardness due to GB and TB strengthening can be calculated by Eq. (8). The calculated values are 2.3 and 2.16 GPa for the 1.0 keV IBAD-Cu film before and after annealing, respectively. They are only slightly higher than that calculated when grain size, instead of the effective domain size, is applied (2.19 and 2.07 GPa, respectively). The TB corrected hardness of IBAD-Cu films is presented in Fig. 11b. They are much lower than the measured values. Therefore, TBs only contribute a small portion of the total hardness and the main hardening effect has to be attributed to the irradiation-induced defects.

4.4.2. Hardening due to irradiation-induced defects

As discussed in section 4.2, a large amount of vacancy clusters are generated in the film during IBAD. They evolve into large voids (Fig. 5e) upon annealing. All these defects are dispersed barriers for dislocation motion and, therefore, lead to strong hardening. The change in hardness \( \Delta H \) due to defects can be evaluated by a dispersed barrier hardening model [32]:

\[
\Delta H = 3 \Delta \sigma_y = 3T \alpha G b \sqrt{N d}
\]

(10)

where \( \Delta \sigma_y \) is the change in yield stress, \( T \) is the Taylor factor (set to be 3.06 [76]), \( \alpha \) is the obstacle strength, \( G \) is the shear modulus of Cu (44.7 GPa), \( b \) is the Burger’s vector in Cu (0.256 nm), \( N \) is the volume density of obstacles and \( d \) is the obstacle size. By assuming that
all the vacancy clusters and voids are in spherical shape, then the above equation can be modified to be:

$$\Delta H = 3\Delta \sigma_y = 3T \alpha G b n_s^{-1/3} \sqrt{N_s d_s} \qquad (11)$$

where $N_s$ is the volume density (can be calculated from the atomic density in Fig. 6b) of defects in the form of single vacancy, $d_s = (3/2\pi)^{1/3} a$ (with $a = 0.362$ nm is the lattice constant in Cu) is the diameter of a single vacancy and $n_s$ is the number of single vacancies in a vacancy cluster or a void. For the as-deposited IBAD-Cu films, $n_s$ is estimated to be $\sim 20$ in section 4.2. In case of the annealed IBAD-Cu films, the average void diameter of $\sim 4$ nm (Fig. 5c) corresponds to a $n_s$ of $\sim 300$. By adding Eq. (11) to Eq. (8), the total hardness can be modeled with the follow equation:

$$H_{total} = H_0 + 3k_y + 3T \alpha G b n_s^{-1/3} \sqrt{N_s d_s} \qquad (12)$$

All parameters, except $\alpha$, in Eq. (12) are known. The modeled total hardness of the IBAD-Cu films is then calculated with varying $\alpha$ values. With $\alpha = 0.15$ and 0.1 for the as-deposited and annealed IBAD-Cu films, respectively, the modeled hardness values are found to best match the experimental measured values (Fig. 11b). The values of $\alpha$ are in the low range compared to literature values for different types of obstacles [32], which implies that the vacancy clusters and voids are very weak barriers for dislocation motion. However, it should be noticed that the density of GBs and TBs is high in the IBAD-Cu films. Due to the low formation energy at GBs and the low diffusivity across TBs, the defects are preferentially form along GBs and TBs (Fig. 5e), especially at high temperatures. As a consequence, the density of obstacles in the grain interior for dislocation motion is correspondingly reduced. Therefore, the calculated obstacle strengths, especially for the annealed films, are greatly underestimated.
5. Summary

In this study, the effect of IBAD on the thermal stability of microstructure and hardness of Cu thin films was revealed. IBAD-Cu films are strongly textured, which is caused by the ion beam induced effects of substrate cleaning, preferential damage as well as preferential sputtering. The grain structures in the films are stable at temperatures as high as 800°C (80% of the melting point of Cu). This superior microstructure stability is mainly attributed to the formation of nanometer-sized voids and their pinning effect on grain boundary migration. We developed a simple model for analyzing the kinetics of void formation and found out that the clustering of vacancies made the activation energy for self-diffusion in the IBAD-Cu films much higher than that in the ND-Cu film. However, the increase in activation energy was compensated by the supersaturation of vacancies, which in turn enhanced the diffusivity by more than one order of magnitude. With regards to mechanical properties, the maximum achieved hardness of the as-deposited IBAD Cu-films is approximately 1.4 GPa higher than that of the ND-Cu film and about 2 to 5 times higher than their bulk nanocrystalline counterparts. This enhanced hardness in the IBAD-Cu films is attributed to twin boundary formation and ion beam induced defects. Upon annealing, their hardness decreases slightly due to the annihilation of point defects, nevertheless, the hardness is still much higher than that of the ND-Cu films, because of their highly stabilized microstructure. On the other hand, the void formation at high temperatures in the IBAD-Cu films might assist crack initiation and, therefore, reduce the tensile properties. However, it is not a big issue for the application, for instance as metallization in microelectronic systems on rigid substrates, where the metallization will be most probably in compressive stress state due to the large thermal expansion coefficient of Cu.

Overall, our results demonstrate that the stability of microstructure and mechanical properties of Cu thin films can be greatly improved by means of IBAD. Although the current
study is focused on Cu films, similar results could be also expected in other metals and alloys, since the ion beam induced defect generation is material independent. This indicates that IBAD is promising for the production of stable nanocrystalline metallic systems for structural and functional applications.
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References

Figure captions

Fig. 1. Out-of-plane EBSD orientation maps and corresponding {111} pole figures of the ND-Cu (a and d) and IBAD-Cu (b, e, c and f) films. The insert in the upper right corner of (a) is the color legend of EBSD orientation maps. The arrows in the pole figure of (a) indicate the texture components of (111), (511) and (5713) fiber textures, respectively. (a - c) As-deposited films. (d - f) Films annealed at 400˚C for 1 h. (g and h) Evolution of the area fraction of different texture components in the as-deposited and annealed films, respectively, as a function of ion beam energy.

Fig. 2. (a) Evolution of grain size as a function of ion beam energy. The curves connecting the individual data points do not represent fitting, they are just smooth connections to show the trend of change. (b) Evolution of grain size of the ND-Cu and 1.0 keV IBAD-Cu films as a function of annealing temperature. For comparison, literature data from nt-Cu and ufg-Cu are also shown.

Fig. 3. AFM micrographs of the ND-Cu (a and d) and IBAD-Cu (b, e, c and f) films. (a - c) As-deposited films. (d - f) Films annealed at 400˚C for 1 h. (g) Evolution of surface roughness as a function of ion beam energy. (h - i) Bright-field TEM micrographs of the ND-Cu and 1.0 keV IBAD-Cu films after annealing at 400˚C for 1 h. The arrows in (h) and (i) indicate the grain boundary thermal grooving and the void formation resulted from vacancy accumulation, respectively.

Fig. 4. Dark-field TEM micrographs of the ND-Cu (a and d) and 1.0 keV IBAD-Cu (b and e) films. (a and b) As-deposited films. (d and e) Films annealed at 400˚C for 1 h. The inserts are selected area diffraction patterns which were taken inside the image area. (c and f) Statistical distributions of twin variant thickness of the as-deposited and annealed 1.0 keV IBAD-Cu films, respectively.
Fig. 5. STEM micrographs of the ND-Cu (a and d) and 1.0 keV IBAD-Cu (b and e) films. (a and b) As-deposited films. (d and e) Films annealed at 400°C for 1 h. (f) The same STEM micrographs as shown in (e). The contrast of this image is enhanced by ImageJ in order to more clearly distinguish voids from the matrix. (g) Threshold fitted images of the area marked with dashed line square in (f). The black dots indicate voids. The red and green dashed lines indicate grain boundaries and twin boundaries, respectively. (c) Statistical distribution of void size of the annealed 1.0 keV IBAD-Cu film. The size of voids is measured on threshold fitted images using the “Analyze particles” function of ImageJ.

Fig. 6. (a) The measured and modeled resistivity of the Cu films as a function of ion beam energy. (b) Evolution of the point defect concentration as a function of ion beam energy.

Fig. 7. (a) Hardness and (b) reduced Young’s modulus of the as-deposited and annealed (1h at 400°C) Cu films as a function of ion beam energy.

Fig. 8. Evolution of hardness of the ND-Cu and 1.0 keV IBAD-Cu films as a function of annealing temperature. Literature data for nt-Cu, ufg-Cu and nc-Cu are also included for comparison.

Fig. 9. (a) Nuclear and electronic stopping power of Ar ions in a Cu target obtained by SRIM simulations. (b) Penetration depth, vacancy production as well as sputter yield for Ar ions irradiation of Cu thin films as a function of ion beam energy, obtained by SRIM simulations.

Fig. 10. Schematic illustration of the IBAD setup.

Fig. 11. (a) The variation in hardness with d^{1/2} for the as-deposited and annealed (1h at 400°C) Cu films. The dashed line is the linear fitting for the low energy (0 and 0.05 keV) IBAD-Cu films. Literature data of hardness of Cu samples are also included for comparison. The solid line represents the Hall-Petch relation extrapolated from the coarse grain Cu. (b)
Modeled hardness of IBAD-Cu films by considering the contribution from TBs and irradiation-induced defects.

Table captions

Table 1: Diffusion parameters for the ND-Cu and 1.0 keV IBAD-Cu films.