Abstract—Nanocrystalline Pd films were produced by electron-beam evaporation and sputter deposition. The electron-beam-evaporated films reveal randomly oriented nanograins with a relatively high density of growth twins, unexpected in view of the high stacking fault energy of Pd. In contrast, sputter-deposited films show a clear (111) crystallographic textured nanostructure without twins. These results provide insightful information to guide the generation of microstructures with enhanced strength/ductility balance in high stacking fault energy nanocrystalline metallic thin films.

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**Keywords:** Nanocrystalline palladium films; Growth twins; Formation mechanism; In situ annealing TEM

1. Introduction

Nanocrystalline (nc) thin metallic films are widely used in a variety of technologies ranging from flexible electronics, microelectromechanical systems (MEMS), microelectronics and thin functional coatings. In these applications, a high strength is often desirable to avoid permanent deformation under different loading conditions. The small grained size combined with other effects related to the small film thickness usually lead to large strength levels [1–3], thus meeting this requirement. However, in some applications, good ductility is also needed. This is the case in flexible electronic devices in which the thin conductive metallic lines must sustain several percentages of deformation without failure [4–6] or with thin functional coatings on metallic substrates that must undergo forming operations after deposition. Another example specific to Pd film concerns its use as a thin membrane in hydrogen technologies, in which sufficient ductility is needed to avoid failure during operation [7]. Unfortunately, most thin nc films suffer from a lack of ductility [8–11]. Ductility is indeed directly connected to the ability of a material to deform plastically without plastic localization or without damage. Often the limited resistance to plastic localization is the main concern in thin films [4]. The resistance to plastic localization is inherently related to the strain-hardening capacity, i.e. the capacity of metals to harden with plastic deformation, and to the presence of imperfections [12,13]. The reasons for the low strain-hardening capacity essentially relate to the absence of forest hardening mechanisms when the grain size is in the submicron range [8]. The challenge is thus to adapt the recent success in the ductilization of bulk or thick layers of nc metals with bimodal grain size distribution [14] or nanotwins [15–17], to the deposition of functional nc thin films with well-controlled populations of crystallographic defects while avoiding imperfections.

Recently, highly textured and twinned nc metallic bulk samples and layers have been successfully produced using pulsed electrodeposition [15–17] and sputter deposition [18–22]. All these studies confirm that the introduction of nanoscale twins considerably improves the strength/ductility balance. In order to facilitate the formation of growth twins, the efforts were intentionally focused on metals with low and moderate stacking fault energy (SFE), such as Cu [15–18] and stainless steels [19–22]. However, although the technological needs for other nc twinned metallic films with higher SFEs are clear, for instance, in the case of Pd membranes to be used for hydrogen technologies, such materials have not as yet benefited much from similar efforts.
Very recently, Pd films with ~30 nm grain size, deposited using electron-beam evaporation, have been characterized in detail by transmission electron microscopy (TEM) [23]. These analyses proved that more than 20% of the grains contain growth twins. The mechanical properties of these films were measured [23,24] using a novel concept of on-chip nanomechanical tensile testing, devoted to the characterization of the mechanical behavior of freestanding thin films or wires [25–27]. This method involves microfabrication techniques as used for microelectronic devices and MEMS for the measurements of the tensile response of thin films. The basic idea is illustrated in Figure 1a. It consists of the use of internal stresses present in a long actuating beam, the “actuator”, to deform another material, the “specimen”, attached to it after removing the sacrificial layer underneath. Figure 1b shows the stress $\sigma$ vs. strain $\varepsilon$ curves corresponding to 310, 160 and 80 nm thick Pd films, extracted from the on-chip nanomechanical tensile tests [23]. From these curves, an unexpectedly large strain-hardening capacity compared to what is currently reported for nc materials was observed (in the present example leading to fracture strains as large as 8% and more than 1 GPa strength) [23]. This large strength/ductility balance was attributed to the presence of the nanotwins. These nanotwins act as barriers to dislocation motion as well as sources for dislocation storage and multiplication via specific twin boundary/dislocation reactions (see Ref. [23] for more details), providing an isotropic hardening contribution to the strain-hardening capacity. In addition, the presence of the nanotwins leads to significant back-stresses at the levels of the grain interior as well as heterogeneities at the level of the grains (grains with no twins being softer than grains with twins), both effects contributing to a significant kinematic hardening [24]. A semi-analytical grain aggregate model has been developed [24] in order to investigate the impact of these different contributions on the flow behavior of the Pd films, involving the effect of the twins, of the grain size and of the presence of a thin surface layer. This model provides guidelines for optimizing the strength/ductility ratio of the films, showing a potential for significant improvement. It is indeed important to note that the experimentally observed high strain-hardening capacity is obtained with only one-fifth of the grains containing nanotwins, revealing a huge potential to improve the strength/ductility balance even further. These results provided the motivation to study in more detail the twin formation mechanisms in Pd with the ambition to control this process and optimize the film properties.

The central question concerns the origin of the nanotwins in the electron-beam evaporated films, a priori not expected because of the high SFE of Pd. Indeed, from the literature, twins were only reported in bulk Pd subjected to severe plastic deformation such as cold rolling [28] or high-pressure torsion (HPT) [29]. The high strain and stress levels attained in these processes can overcome the effect of the high SFE and provide the necessary driving force for the formation of deformation twins. There is very little experimental evidence in the literature of twin formation during the growth of nanocrystalline Pd thin films. Recently, Zhang et al. [30] have studied strain relaxation in heteroepitaxial films by misfit twinning in Pd. However, the authors observed the formation of twins in single-crystal 10 nm thick Pd epitaxial layer electroplated on a Si substrate, which is different from the nanocrystalline and relatively thicker Pd films used in the present study.

In the present work, nc Pd films were deposited using two methods based on physical vapor deposition (PVD): electron-beam evaporation and sputter deposition, the latter being extensively used in the literature to produce well-controlled populations of twins in Cu layers [18,20,31] and stainless steels layers [19–22]. TEM analysis shows that sputter-deposited films have no twins, while a significant number of nanograins contains growth twins in the films deposited by electron-beam evaporation. The primary aim of the present study is to understand this difference through the characterization of the structure and the thermal stability of the twinned films.

### 2. Experimental procedures

Pd films 173 nm thick were sputter-deposited at room temperature with a deposition rate of 0.3 nm s$^{-1}$. The Pd films were deposited on top of a SiO$_2$ intermediate layer lying on a Si wafer. A thin Ti adhesion layer (25 nm) separating the Pd film from the SiO$_2$ layer was used to improve the adhesion of the films. Pd films 310 nm thick were deposited using electron-beam evaporation. In this case, a very thin Cr layer (5 nm) was used to enhance the adhesion. The temperature of the substrate was limited to 100°C, and the deposition rate was equal to 0.1 nm s$^{-1}$. For both of these two deposition processes, the Pd target used for the evaporation of the films is of high purity (>99.995%), and as a high vacuum ($1 \times 10^{-8}$ Torr) is created using a cryogenic...
pump inside the chamber deposition, no pollution effect is expected inside the Pd films. It should also be noted that the deposition rates used here are in the same range as those found in the literature [32, 33]. To ensure the good quality of the film, an evaporation rate about 0.1 nm s\(^{-1}\) is usually used. This evaporation rate can be increased but will produce films with high internal stress which can be harmful for the integrity of the films.

Conventional TEM characterization of the films was carried out using a Philips CM20 microscope (LaB\(_6\), 200 kV), while a TECNAI G2 (FEG, 200 kV) was used for high-resolution TEM (HRTEM) analysis. Focused ION BEAm (FIB) thinning with the “lift-out” procedure was used for the preparation of cross-sectional TEM thin foils. A protective Pt layer was deposited on the Pd beam prior to FIB thinning. This prevents the surface of the Pd beam from damage caused by the incident Ga\(^+\) ions in the FIB instrument.

3. Results

3.1. Formation mechanism of growth twins

Figure 2a shows a bright-field (BF) micrograph of the sputter-deposited film revealing columnar nanograin morphology. The average lateral grain size measured from BF and dark-field (DF) images is equal to 41.6 ± 5.3 nm with an elongated aspect ratio (grain height/lateral grain size) of ~4. The selected-area diffraction pattern (SADP) shown in the upper left part of the image reveals that the film exhibits strong (1 1 1) face-centered cubic (fcc) crystallographic texture similar to the microstructure of sputter-deposited, textured and highly twinned Cu and stainless steel layers [18–22, 31]. Zhang et al. [20] reported that, for a deposition rate of 0.3 nm s\(^{-1}\) and an average lateral columnar grain size of around 50 nm (i.e. similar to the deposition rate and the grain size for the Pd film of Fig. 2a), no sputter-deposited Cu films not only exhibit a clear (1 1 1) texture but about 40% of the grains contain nanoscale growth twins. In contrast, no twins can be observed within the grains of Figure 2a. This lack of twins can be attributed to the high SFE of Pd, hence to the too small driving force for the formation of twins. Indeed, it has been shown that the formation of nanoscale growth twins in sputter-deposited Cu and stainless steel films depends mainly on the SFE and the deposition rate, with an increase in twin nucleation probability as the SFE decreases and the deposition rate increases [20]. Thus, at SFE of a few hundred mJ m\(^{-2}\), twin or stacking fault formation becomes very unlikely and high SFE metals such as Al (160–200 mJ m\(^{-2}\)) or Pd (150–180 mJ m\(^{-2}\)), even when deposited at rates of a few nm s\(^{-1}\), are unlikely to show any stacking faults or twins, in agreement with the result shown in Figure 2a. In other words, the mechanism responsible for the formation of growth twins in sputter-deposited Cu and stainless steel films, attributed to the nucleation and growth of twin nuclei which form accidentally during the layer-by-layer deposition [18–22, 31], cannot operate in the Pd films.

Figure 2b shows a BF micrograph of the electron-beam evaporated Pd film. The film again exhibits a morphological texture with columnar grains elongated parallel to the growth direction and is homogeneous through the entire beam. The ring-shaped SADP shown in the upper left reveals the fcc Pd crystalline structure. However, in contrast to the sputter-deposited sample, no preferential crystallographic orientation of the grains can be observed, indicating the absence of a clear crystallographic texture. The analysis of the statistical distribution of the lateral grain size and of the aspect ratio of the grains using BF and DF micrographs yields an average grain diameter of 25.6 ± 7.3 nm and an aspect ratio of ~7. It is worth mentioning that, in some cases, due to the small grain size, stereographic effects associated with the FIB cross-sectioning process could lead to an apparent grain size different from the real one.

A significant density of planar defects was observed inside the grains as indicated by white arrows in the BF micrograph of Figure 2b. These defects were identified as {1 1 1} nanotwins using nanodiffraction with an example provided in the lower left part of Figure 2b. Indeed, the diffraction pattern obtained from the twin boundary (TB) region indicated by white circle in Figure 2b and oriented along a (1 1 0) zone axis reveals the typical superposition of two mirrored (1 1 0) diffraction patterns with respect to the {1 1 1} plane. Figure 2b also shows that most twins are not parallel to the surface of the film and their orientation changes randomly from one grain to another, confirming the absence of crystallographic texture in the growth direction. Also, the twins are heterogeneously distributed within the grains and their thickness, i.e. the distance between two subsequent
Twin nuclei, which form accidently during the layer-by-layer faces using HRTEM is presented in order to investigate rated films has an effect on the formation of the twins. In the crystallographic texture in the electron-beam-evaporation Figure 2, it can be anticipated that the absence of electron-beam evaporation. By comparing the images ble for the twin formation in the Pd films deposited by deposition[18–22,31], was excluded in the present work due to the high SFE of Pd. Thus, other elementary mechanism(s) involved in the formation of twins should be invoked. In the literature, several fundamental mechanisms have been proposed to explain the formation of annealing and mechanical twins in nanostructured fcc metals. These mechanisms can be categorized into two main groups depending on the characteristics of the nucleation process of the twins.

(i) The successive [34] and random [35] emission of Shockley partial dislocations (SPDs) from grain boundaries (GBs): in this case, one SPD nucleates from the disordered structure of the GB. This partial glides in one {111} plane and will be absorbed by the opposite GB, leaving one SF behind it. The repetition of this process on a consecutive immediately adjacent {111} close-packed plane forms a twin. Other twinning mechanisms were proposed in the literature for nc materials based on the coincidental overlapping of wide SF ribbons inside a grain interior [36], the overlapping of dissociated dislocations with a SF from a GB [37], the self-propagation via cross-slip [38] or the sequential twinning to produce multifold twins [39]. However, all these mechanisms also involve nucleation and glide of SPDs in the twinning plane.

(ii) The GB migration mechanism initially proposed by Ashby and Harper [40] and also described by Gleiter [41]: this model is based on the splitting and the subsequent migration of a GB segment, leaving behind two coherent TBs. Fullman and Fisher [42] proposed that twins form by GB migration during grain growth as a result of a decrease in the interfacial free energy of GBs that would not be achieved in the absence of twinning. Very recently, Huang et al. [43] demonstrated that this mechanism is responsible for the formation of 5-fold twins in nc Cu.

In principle, deformation and/or annealing twins are not expected here. Indeed, due to the high SFE of Pd, deformation twins in Pd would require severe plastic deformation [28,29] not present in the as-received deposited films (a minute amount of plasticity could develop due to internal stress, but this would remain very small). Annealing twins can also be excluded, since the Pd films were deposited at low temperature (<100 °C) and no subsequent annealing was performed. In order to investigate the participation of the mechanisms cited above to the formation of the growth twins in the electron-beam-evaporated Pd films, several twins shown in Figure 2b were carefully analyzed using HRTEM.

Figure 3 shows a HRTEM image of a typical Σ3 (111) type TB. The inserted fast Fourier transform (FFT) shows a typical twin relationship of (111) twins in the fcc structure. The TB of Figure 3 is perfectly coherent and atomically sharp without steps. Further HRTEM analysis on other TBs showed the same feature. This exact lattice coherency of TBs excludes the mechanisms based on the emission and the glide of SPDs [34–39] as being responsible for the formation of growth twins. Indeed, in the latter case some twinning SPDs are expected to be left at the TBs by segregation when meeting obstacles during their movement, producing several atomic steps at the twin interface, not observed here. Indeed, Lu et al. [17] observed steps related to SPDs lying at TBs in as-received ultrafine-grained Cu samples produced by pulsed electrodeposition. A feature like this can be explained by the low SFE of Cu (30–40 mJ m⁻²). Furthermore, isolated stacking faults lying in the (111) planes and bounded by SPDs were also not observed in the Pd films, thus excluding the twinning mechanisms based on the overlapping of wide SFs [36,37]. Again, these results illustrate the difficulty of producing SFs and twins in high SFE metals by the nucleation and glide of SPDs.

The alternative twin formation mechanism proposed by Ashby and Harper [40] is based on the splitting and the subsequent migration of a GB segment. This mechanism can provide perfectly coherent TBs in the Pd films, since it is based on the excess energy of GBs and does not involve the nucleation and glide of SPDs from GBs. Moreover, the driving force for this mechanism, which is found in the excess energy of the GBs, immediately points towards a difference between textured and non-textured films.

Figure 3. HRTEM image of one TB in a 310 nm thick Pd film deposited by electron beam evaporation. Note the perfect coherency of the twin/matrix interface.
Based on these results, the following scenario can be envisaged to explain the formation of the growth twins observed in the Pd films deposited by electron-beam evaporation. During the deposition of the films, columnar nanograins with random orientations are formed. The absence of (111) crystallographic texture results in large misorientation between the grains. Thus, GBs with high energy are formed which provide the driving force for twin nucleation by GB splitting and migration thereby decrease the total interfacial energy. Twins prefer to nucleate at GBs or triple junctions to reduce GB energies through orientation changes and a high twin density leads to a lower average GB excess energy. It is worth mentioning that the moderate temperature of the substrate (≤100 °C) as well as the film internal stress (350 MPa as measured by the Stoney method) might also enhance the formation of the observed nanoscale twins by accelerating GB splitting and migration, initiated by the Ashby and Harper mechanism. A recent study shows that the formation of growth twins in sputter-deposited 330 stainless steel films indeed depends slightly on the sign and the magnitude of the residual stress [21].

Finally, it is worth mentioning that the role of impurities for the enhancement of twin formation by reducing the SFE [44] was excluded in the present work based on extensive analytical TEM measurements using energy-dispersive X-ray (EDX) analysis (see Supplementary Data). In addition, the high purity of the films was confirmed using electron energy loss spectroscopy (EELS) in TEM as well as inductively coupled plasma emission spectroscopy (ICP) [45]. In the latter case, no contaminant was detected in the Pd films in concentrations exceeding 10 ppb. Furthermore, no native oxide layer is present on the Pd surface, as confirmed by energy-filtering TEM (see Supplementary Data) in agreement with other reports for standard atmospheric conditions [46].

In the next step, an in situ annealing experiment was performed in order to directly observe any variation in twin density and morphology during grain growth. Such an experiment provides additional information concerning the thermal stability of the growth twins which can affect the mechanical properties of the films at elevated temperatures. Moreover, the observations confirm the above conclusions on the formation mechanism of the TBs.

### 3.2. Thermal stability of growth twins

Figure 4 reveals the evolution of the microstructure of a Pd film deposited by electron-beam evaporation, observed during in situ TEM heating. Figure 4a shows the initial microstructure of the film. In this figure, growth twins can be clearly observed within several nanograins. Grain A has a diameter of 68 nm and contains several growth twins on different families of {111} planes. The thicknesses of the twins labeled “T1” and “T2” are 10.8 and 5.3 nm, respectively. In the same figure, grain B has a diameter of 26 nm and contains several growth nanotwins shown by a small white arrow. The latter are less visible than those observed in grain A because of the difference between the diffraction conditions in the two grains, indicating again the difficulties in obtaining good statistics on twin densities.

Figure 4b shows the same region as Figure 4a after annealing at 500 °C for 20 min. Figure 4b clearly shows that grain A has undergone significant growth during annealing. Its diameter increased from approximately 68 to 131 nm. However, no variation in the twin thickness inside this grain was detected; the initial thickness of the twins “T1” and “T2” remains the same before and after annealing, while the length of the twin lamellae increased following the grain growth. Furthermore, emission of SPDs from TB–GB intersection and/or glide of pre-existing SPDs in the twinning plane was not observed during the in situ TEM heating experiment.

On the other hand, these results confirm the absence of SPDs in the twinning plane which again excludes the contribution of the mechanisms based on the emission of SPDs from GBs. Indeed, the activation of this mechanism would induce shrinking (detwinning) or thickening of the twin lamellae during the in situ heating experiment, as reported recently in nc twinned Cu films [31]. On the other hand, the correlation between the change of the grain size and the expansion of the twin lamellae in length indicates that this expansion is controlled by GB migration, in agreement with the mechanism proposed by Ashby and Harper [40]. In addition, it is worth mentioning that the twin density considerably decreased after annealing. For example, growth twins of grain B in Figure 4a were eliminated due to the shrinking and final disappearance of grain B after annealing at 500 °C.

In summary, we demonstrated that sputter deposition does not induce growth twins in (111)-textured Pd films. However, the absence of crystallographic texture in electron-beam-evaporated films allows the formation of nanoscale growth twins in these films via GB migration, even though Pd has a high SFE. Furthermore, it can be argued that, in spite of the high thermal stability of growth twins, GBs with higher energy which are highly mobile at elevated temperatures will control the twin density and the related mechanical behavior of the Pd films deposited by electron beam evaporation. These results constitute the first step towards a better control of nanoscale growth twins in high-SFE metallic thin films which can improve the strength/ductility balance. Follow-up experiments are under way in order to optimize this deposition process to produce Pd films with well-controlled populations of nanoscale growth

![Figure 4. Microstructure evolution of a Pd film deposited by electron beam evaporation during in situ TEM heating at 500 °C for 20 min.](image)
twins by varying parameters such as substrate temperature, internal stress, deposition rate, adhesion layer and alloying elements.

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