Engineering the grain boundary network of thin films via ion-irradiation: Towards improved electromigration resistance

Huan Ma^a, Fabio Lamattina^b, Ivan Shorubalko^b, Ralph Spolenak^a, Matteo Seita^{c,*}

^aLaboratory for Nanometallurgy, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland

^bLaboratory for Reliability Science and Technology, EMPA, 8600 Dübendorf, Switzerland

^cDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, MA 02139, USA

Abstract

Controlling the grain boundary network of small-scale materials—such as coatings and thin films—is an ambitious goal that would ultimately enable the production of components with tailored properties and improved reliability. In this work we present a new technique—which we term ion-induced grain boundary engineering (iGBE)—to engineer the character distribution and connectivity of grain boundaries in gold films *in situ*, as they are being deposited. iGBE consists of a repeated sequence of ion-induced material removal and material deposition which results in the selection and growth of crystal grains in twinned relationship. This phenomenon yields **a substantial increase in the density and connectivity of $\Sigma 3$ twin boundaries**, which have renowned beneficial effect on the material's resistance to intergranular degradation. We confirm the improved reliability of iGBE microstructures by assessing their resistance to electromigration—one of the most common causes of failure in integrated circuit interconnects. We find that, through iGBE, interconnect lifetime increases by three orders of magnitude at standard operating conditions. Since iGBE is material-insensitive and compatible with standard microfabrication technology, we expect it to have significant impact on microelectronics industry.

Keywords: Grain boundary engineering; Thin films; Ion-irradiation; Microstructure design; Electromigration

* Correspondence should be addressed to Matteo Seita (E-mail: matteos@mit.edu; Tel.: 00-1-617-258-8038).

1. Introduction

Most engineering materials are polycrystalline: they consist of an aggregate of differently oriented crystal grains joined along grain boundaries (GBs) [1]. Although they typically comprise a small fraction of the material's volume, GBs have tremendous impact on its properties, including strength and ductility [2-4], diffusion [5-7], resistance to environment-assisted failure [8, 9] and radiation tolerance [10, 11]. Indeed, by engineering **the distribution and connectivity of GBs—namely the GB network**—such properties can be improved by many orders of magnitude [12-15]. In metals and metal alloys, the GB distribution can be tailored by processing raw materials through specific thermo-mechanical treatments—a sequence of cold work and anneal—which take the name of *grain boundary engineering* (GBE) [16-20]. GBE yields an increased proportion of “special” GBs in the microstructure—primarily $\Sigma 3$ boundaries—which have the effect of improving the material's performance and its resistance to intergranular degradation [21].

While GBE is largely employed for the fabrication of high-performance bulk materials, its use at the small-scale—such as on coatings or thin films—is still limited, due to the challenge of selectively deform and anneal small volumes of material [22]. Here we present a new method to engineer the GB network of as-deposited films and thus improve their performance. Our method consists of a combination of ion-irradiation and material deposition processes to selectively control the crystal grain orientation distribution, *in situ*, during sputter-deposition. We demonstrate the method—which we refer to as *ion-induced grain boundary engineering* (iGBE)—using gold (Au) films and we prove the beneficial effect of iGBE by assessing the material's resistance to electromigration (EM)—a GB-controlled degradation phenomenon which causes failure of interconnects in integrated circuits [23].

2. Experimental

Au deposition is performed by DC magnetron sputtering (PVD Products, Inc.) at room temperature on (100) silicon wafers coated with 50 nm of SiO₂ and 50 nm of Si₃N₄. To improve the adhesion of the film to the wafer, a 10 nm thick Ti layer is deposited prior to Au. The base pressure in the sputter chamber is better than 10⁻⁶ mbar. During deposition, the pressure is increased to 10⁻³ mbar by flowing pure argon (Ar) in the chamber and the silicon substrate is kept in rotation (with a speed of 12 rpm) in order to obtain a homogeneous film thickness. Ion-irradiation is carried out by means of a gridded ion-source (KRI KDC 40) with collimated and neutralized Ar⁺ beam. The ion-source is installed directly in the sputter tool at a fixed angle of 35° with respect to the film surface normal. This configuration allows for *in situ* ion-irradiation of the deposited films. The ion-energy, ion-current, and irradiation time are kept constant throughout the experiments presented here at 1.2 keV, 5 mA, and 8 minutes, respectively. Upon irradiation, the base pressure in the chamber is increased to $\sim 4 \times 10^{-4}$ mbar and the substrate rotation is turned off.

The film microstructure is characterized by means of a high-resolution scanning electron microscope (SEM, Magellan 400 FEI) using both secondary electron (SE) and backscattered electron (BSE) detectors. Grain orientation information is assessed via electron backscatter diffraction (EBSD) using a FEI Quanta 200 FEG SEM. Only EBSD data with confidence index (CI) larger than 0.1 is considered. Quantities such as crystallographic texture spread, average grain size, and area fraction of specific grain orientations are measured from EBSD data using the OIM Analysis Software (EDAX, Inc). The GB character distribution and the triple junction (TJ) distribution are measured from cleaned EBSD data using MTEX 3.4.1 [24]—a free software for the MATLAB environment. The cleanup procedure used is similar to others found in the literature [25-27] and consists of grain CI standardization, neighbor orientation correlation with level 1, and a single iteration of grain dilation using grain

tolerance angle of 5° and minimum grain size of 2 pixels. GBs are classified according to the coincidence site lattice model [28], using Brandon's criterion [29, 30]. The film grain structure is characterized along the cross-section using high-resolution SEM, transmission electron microscopy (TEM, FEI Tecnai F30 and FEI Talos F200X). The TEM analysis is carried out in both bright field (BF) and high-angle annular dark-field (HAADF) modes. Cross-sections and TEM lamellae are prepared using a focused ion beam (FIB) microscope (NVision 40, Carl Zeiss).

EM tests are carried out using a four-point probe method [31] on arrays of Au lines, patterned from 500 nm thick films via lithography. The lines are 10 µm wide and 700 µm long. All lines are coated with a 200 nm SiN_x layer by plasma enhanced chemical vapor deposition (Plasmalab 80 Plus, Oxford Instruments) at 300°C. EM tests are performed in a shielded wafer prober at controlled temperature, ranging from 125 to 200°C. The current density used for all tests is 1.3×10^7 A/cm². All lines are tested until open circuit failure.

3. Microstructure control via iGBE

Fig. 1 illustrates the elements of iGBE via schematics as well as EBSD maps taken from representative samples. First, a 50 nm thick Au film—hereafter referred to as the *reference*—is sputter-deposited onto a substrate. The reference microstructure consists of columnar grains with an average size of ~60 nm and strong (111) fiber texture normal to the film surface. The fiber texture—a common feature in the microstructure of thin FCC films [32]—is clearly visible from the (111) pole figure in Fig. 1a, where the central peak and the continuous ring at $\sim 70^\circ$ indicate that all grains have the same surface normal, but random in-plane orientation, respectively.

After deposition, the reference film is irradiated at a fixed angle of 35° with respect to the surface normal (see schematics in Fig. 1b). As the energetic ions strike the film surface, two different phenomena take place in the crystal grains, depending on their orientation: *ion-milling* and *ion-channeling*. Grains that are randomly-oriented with respect to the ion-beam direction undergo ion-milling and thus are progressively removed from the sample surface [33]. Conversely, those oriented such that their open-most crystal-axis is parallel to the ion-beam undergo ion-channeling and thus survive ion-irradiation [34]. We refer to the combination of both phenomena as *selective grain milling* (SGM). The EBSD measurement of the reference after SGM is reported in Fig. 1b. Notably, the (111) pole figure now exhibits three symmetric peaks at $\sim 70^\circ$ from the normal, which suggests that all grains left on the surface have similar crystallographic orientation [35, 36].

In FCC materials, such as Au, the easiest channeling-axes coincide with the $\langle 110 \rangle$ crystallographic directions [37]. Owing to the pre-existing (111) out-of-plane texture in the reference film, all grains in the microstructure exhibit three possible $\langle 110 \rangle$ channeling axes at an angle of 35° from the surface normal—exactly the angle at which the ion-beam is set. However, since the reference film is held steady during SGM, only one specific subset of

grains is found in channeling-orientation and thus survives SGM. These are the grains appearing in the EBSD map in Fig. 1b. The orientation spread of the surviving grains is $\sim 20^\circ$, as measured by EBSD. This value is in good agreement with the maximum angular deviation from the nominal channeling-axis that is allowed for the ion-energy, ion-species, and target material used in this study. In fact, following the model proposed by Lindhard [34], we compute a maximum deviation of:

$$\psi_c = \left(\frac{3a^2 Z_a Z_b e^2}{E_i d^3} \right)^{1/4} = 21^\circ \quad (1)$$

where Z_a and Z_b are the atomic numbers of ions and target atoms, respectively, $e^2 = 14.4$ eV Å (the square of the elementary charge), E_i the ion energy (1.2 keV), d the distance between two atoms along the $\langle 110 \rangle$ channel wall in Au (2.9 Å), and $a = a_B 0.8853 (Z_a^{2/3} + Z_b^{2/3})^{-1/2}$, where a_B is the Bohr radius. The agreement between the measured orientation spread and ψ_c confirms that the grains remaining on the sample surface after SGM are in channeling-orientation and that all the other randomly-oriented grains were selectively removed. In our experiments, 8 minutes is the shortest irradiation time that yields complete removal of randomly-oriented grains. In fact, after 8 minutes the material's coverage on the sample surface is measured to be 25.3%, which is very close to the measured fraction of channeling-oriented grains (25.7%, see Table 1) in the reference film and the predicted values in a fiber textured film (27.5%, see reference [35]).

In the next step of iGBE, a supplemental 50 nm Au film is sputter-deposited onto the irradiated reference without breaking the vacuum. The resulting microstructure—hereafter referred to as $I \times iGBE$ —exhibits a higher fraction of channeling-oriented grains ($\sim 39.7\%$, see Table 1) as well as a large proportion of twinned grains ($\sim 26.4\%$, see Table 1). This can be seen from the pole figure in Fig. 1c, where the six-fold symmetry about the (111) fiber texture suggests the presence of two twinned orientations rotated by 60° . The increased

fraction of channeling-oriented grains is due to the epitaxial growth of the pre-existing channeling-oriented grains—namely those which survived the first SGM [38]. At the same time, the favorable conditions for twin nucleation onto (111) crystal planes during physical vapor deposition of FCC materials leads to the preferential growth of grains in twinned orientation [39, 40]. This means that upon the supplemental deposition of 50 nm of Au, the adatoms diffusing to the channeling-oriented grains can arrange themselves in two—equally favorable—crystallographic orientations: one which follows the parent orientation (namely the channeling-orientation), and one that is in a twinned relationship to them, which results into the nucleation of a new grain. However, not all new grains fall in the latter category. In fact $\sim 6.3\%$ of the grains in $1\times iGBE$ exhibits no crystallographic relationship to the channeling-orientation, besides displaying the same (111) fiber texture (see Table 1). These are the grains that nucleated in areas that were depleted of material after SGM. **Because we only consider EBSD data with $CI > 0.1$, a large fraction of material is not assigned a crystallographic orientation and appears in the EBSD scans in black color. We believe that the low CI in these regions is due to the small grain size of the films, which approaches the resolution limit of EBSD. As a result, during the EBSD scan it is often the case that multiple diffraction patterns from different grains are superposed and not recognized by the EBSD software. Such a shortcoming leads to uncertainties in the evaluation of the area fraction of different grains.**

Fig. 1e shows the EBSD map of a Au film subjected to two cycles of repeated SGM and deposition of 50 nm Au supplement—hereafter referred to as $2\times iGBE$. The resulting film comprises $\sim 48.7\%$ of channeling-oriented grains and $\sim 22.2\%$ of twinned-oriented grains (see Table 1). This yields a microstructure that is predominantly bi-crystalline, since it is composed for $\sim 70.9\%$ by only two crystallographic orientations in a twinned relationship (Fig. 1e). The origin of the bi-crystalline microstructure stems from the higher fraction of

channeling-oriented grains that is induced through the first iGBE cycle. In fact, despite SGM removes all grains that are not in channeling-orientation—including the twinned ones—the higher fraction of channeling-oriented grains in 1×iGBE compared to the reference (from 25.7% to 39.7%, see Table 1) ensures that fewer grains will nucleate with random crystallographic orientation upon the second Au supplement.

In Fig. 2 we show how Au coverage in 50 nm thick films changes during the entire iGBE process (as depicted in Fig. 1) by means of SE and BSE micrographs. Since the SE and BSE signals are function of surface morphology and material's atomic number, respectively, the information carried by the corresponding micrographs is complementary and can be used to reliably assess film integrity. From Fig. 2a,c,e, it is clear that all films after both initial and supplemental deposition are continuous. Conversely, after SGM, the films are removed with exception of the channeling-oriented grains (in bright contrast against the dark contrast from the substrate), which survive the ion-milling process (see Fig. 2b and d). The area fractions of the channeling-oriented grains from the SE and BSE analysis are ~23.9% and ~46.1% after the first (Fig. 2b) and second (Fig. 2d) SGM step, respectively. These values are in good agreement with those measured by EBSD in Fig. 1b and d (~25.3% and ~44.9%, respectively).

The GB type that joins two twinned grains is called $\Sigma 3$ boundary [28]. $\Sigma 3$ boundaries are the foremost type of boundaries among the “special” GBs which are purposefully introduced in the microstructure during conventional GBE [41]. The large proportion of twinned-grains induced through the iGBE cycles leads to a progressive increase in the number fraction of $\Sigma 3$ boundaries: from 15.7% (in the reference) to 17.5% (in 1×iGBE) to 18.4% (in 2×iGBE), as can be seen from the GB character distribution reported in Fig. 3. This means that after only two cycles of iGBE the total number fraction of $\Sigma 3$ boundaries can be increased by 17%. Beside $\Sigma 3$ boundaries, other “special” GBs are also engineered through iGBE (see Fig. 3).

Typically, “special” GBs are those with $1 < \Sigma < 29$, according to the coincidence site lattice model [28]. However, owing to the (111) fiber texture in the films produced in this study, only a few of such GBs exist, namely those whose misorientation axis lays parallel to the $\langle 111 \rangle$ fiber axis: $\Sigma 1$ (low-angle GBs with misorientation angle below 15°), $\Sigma 3$ (twin boundaries), $\Sigma 7$, $\Sigma 13b$, $\Sigma 19b$, and $\Sigma 21a$. As can be seen from Fig. 3, both $\Sigma 3$ and $\Sigma 1$ boundary fractions show a significant increase through the iGBE cycles, while the other GB types decrease or remain constant. We attribute the increase in $\Sigma 1$ boundaries to the higher fraction of channeling-oriented grains from $1 \times \text{iGBE}$ to $2 \times \text{iGBE}$. Since the orientation spread of channeling-oriented grains is 20° , there is a high chance that when two of such grains meet, they will be separated by a $\Sigma 1$ boundary.

To assess how the GB network—and thus the connectivity of different GB types—changes as a result of iGBE, we analyze the triple junction (TJ) distribution [42, 43] in all 50 nm thick films. The distributions are reported in Fig. 4. For reasons that will be explained in Section 6, we consider only $\Sigma 1$ and $\Sigma 3$ boundaries as “special GBs”. According to this definition, there can be four different types of triple junctions, which we call $\text{TJ}i$. Here $i = 0, 1, 2, 3$ denotes how many $\Sigma 1$ and $\Sigma 3$ GBs intersect at the TJ. Fig. 4 shows that the TJ distribution changes significantly through the iGBE process. Specifically, we find that in just two iGBE cycles, $\text{TJ}2$ ’s increase from 16.7% to 31% and $\text{TJ}3$ ’s from 4.4% to 18.4%. This increase implies that through the iGBE process, $\Sigma 1$ and $\Sigma 3$ boundaries tend to be connected together, changing the overall GB network topology. This phenomenon is attributed to the uniform distribution of channeling-oriented grains across the film microstructure (see Fig. 2b and d). During SGM and supplemental deposition, the progressive increase of grains in both channeling- and twinned-orientation results in a GB network with increasing connections of $\Sigma 1$ and $\Sigma 3$ boundaries. We therefore conclude that, besides providing the capability to

1 engineer the GB character distribution in thin metal films, iGBE also allows engineering GB
2 connectivity by promoting “special GBs” to connect.
3

4 Because of the large fraction of material that cannot be indexed by EBSD (see Fig. 1a,c,e
5 and Table 1), we note that the GB character and TJ distributions presented in Fig. 3 and Fig.
6 4, respectively, contain uncertainties. As a result, rather than focusing on the absolute number
7 fraction of specific GB types (such as $\Sigma 3$ boundaries) or TJs (such as TJ2 and TJ3), we
8 highlight their relative change through iGBE.
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4. Templated growth of iGBE films

All the different samples—reference, 1×iGBE, and 2×iGBE—can be used as “microstructure templates” to grow thicker films that inherit the same texture and grain structure. This is accomplished by depositing an additional 450 nm of material on each microstructure template without breaking the vacuum. High-resolution SEM images from the cross-section of the newly produced films (now 500 nm thick) confirm that most grains are columnar and that the GBs extend through the entire film thickness (see Fig. 5). The EBSD orientation maps and corresponding (111) pole figures for all 500 nm thick films are presented in Fig. 6a. The grain orientation distribution in 500 nm thick films is reported in Table 1 for comparison with that in the microstructure templates. In general, we find that the thicker films exhibit a bi-crystalline microstructure similar to that of microstructure templates, with strong out-of-plane and in-plane textures. This finding confirms that thin iGBE films can be used as microstructure templates to grow thicker films with controlled microstructure. Some differences can be found in the average grain size and grain orientation distribution when comparing 50 nm to 500 nm thick films. In fact, thicker films comprise grains that are about double the size of those in microstructure templates (the average grain size increases from ~60 nm to ~120 nm). Moreover, upon thickening we measure a larger fraction of twinned-oriented grains and a decreased fraction of randomly-oriented grains. Both the increase in average grain size and the change in grain orientation distribution may be attributed to competitive grain growth upon sputter-deposition [32]. During competitive grain growth, grains with orientations that are more energetically favorable (e.g. for FCC materials, those with surface normal parallel to the $\langle 111 \rangle$ direction), or grains with larger diameter grow faster than others [32]. Since during sputter-deposition of FCC metal films, such as Au, grains are known to grow even at room temperature [44], we expect competitive grain growth to occur in all our samples upon deposition of the additional 450 nm. All grains in our films

have surface normal parallel to the $\langle 111 \rangle$ direction and thus are, presumably, equally favorable to grow. However, some grains in iGBE films (i.e. 1×iGBE and 2×iGBE) have different size, depending on their in-plane orientation. In fact we can classify all grains into three groups based on their in-plane orientation with respect to the incident ion beam direction during SGM: channeling-, twinned- and randomly-oriented grains. Upon film thickening, channeling-oriented grains grow larger because they survive SGM (as we explained in Section 3). When a twinned-oriented grain nucleates over a channeling-oriented grain during supplemental deposition, presumably it will inherit the same (large) size. Moreover, the probability of twin nucleation increases with increasing grain size [27]. Conversely, all randomly-oriented grains nucleate in areas that are depleted of material. As a result, randomly-oriented grains are smaller and, therefore, they will be gradually overgrown by the channeling- and twinned-oriented grains during competitive grain growth. Following these arguments, upon film thickening we expect a decrease in the fraction of randomly-oriented grains while an increase in that of the twinned-oriented grains, which is indeed the trend reported in Table 1. However, the observed differences in grain orientation distribution may also be partially attributed to the large fraction of material that cannot be indexed by EBSD in 50 nm thick films (see Fig. 1a,c,e and Table 1), which may introduce uncertainties in the measured area fraction of the different grain families.

Because of their columnar grain structure (see Fig. 5), we treat all the 500 nm thick films as 2-D microstructures, whose GB character distribution and network can be directly characterized at the film surface by EBSD. Fig. 6b shows that the fraction of $\Sigma 1$ and $\Sigma 3$ boundaries in 500 nm thick films progressively increases through the iGBE cycles. This trend is comparable to what we find in the microstructure templates (see Fig. 3). However, the absolute number fractions are significantly different than those in the microstructure templates, especially in the iGBE samples. The fraction of $\Sigma 3$ boundaries reaches 16.1% in

reference (compared to 15.7% in the microstructure templates), 23.6% in 1×iGBE (compared to 17.5%) and 28.2% in 2×iGBE (compared to 18.4%). This means that after only two cycles of iGBE on the microstructure template, a thicker film can be grown with 75% more $\Sigma 3$ boundaries than what it would naturally comprise. This result is justified by the higher fraction of twinned-oriented grains in 500 nm thick films (see Table 1). We may speculate that the decrease in $\Sigma 1$ boundaries from 44.5% to 40% upon film thickening of the 2×iGBE sample is the result of the increased probability for channeling-oriented grains to turn into twinned-oriented ones for the reasons outlined in the foregoing. As a result, fewer channeling-oriented grains will be adjacent.

The analysis of the TJ distributions in 500 nm thick films is reported in Fig. 7. When compared to microstructure templates (Fig. 4), 500 nm thick films show similar trends in the evolution of GB network topology. TJ0's and TJ1's decrease, while TJ2's and TJ3's increase up to 38.1% and 31%, respectively, in just two iGBE cycles. As we will show in Section 5 and 6, this change has profound effects on the properties of iGBE materials.

5. Electromigration testing of different microstructures

To prove that iGBE is an effective strategy to enhance the performance of small-scale materials, we assess the EM resistance of all three microstructures using accelerated EM tests. EM consists in the progressive deterioration of interconnects in microelectronic circuits, when they carry high current densities [23]. Over time, the electrons drive the atoms of the crystalline material to diffuse across the interconnect line from cathode to anode. This atomic migration results in the formation of voids (at the cathode side) and hillocks or whiskers (at the anode side), which ultimately result into the failure of the interconnect (i.e. in the form of an open or short circuit) [23]. Since atomic diffusion is faster along GBs than across the crystal lattice [45], materials' resistance to EM damage is function of their GB character distribution and connectivity—namely the GB network [46].

We perform EM testing on arrays of interconnect lines which we patterned from the 500 nm thick reference, 1×iGBE, and 2×iGBE films by lithography (see schematics in Fig. 8a). We design the interconnects to be ~80 grains wide to ensure that there are no size-effects to affect the line's EM behavior, such as when the line width is comparable to the average grain size (i.e. “bamboo-like microstructures”) [47]. Since Au does not form a stable surface oxide layer, we coat the lines with 200 nm of SiN_x to prevent atomic surface diffusion from dominating EM damage [23]. Because we see no grain growth in the lines for temperatures as high as 400°C (see Fig. 9)—nor we see changes in the grain structure of the tested lines (see Fig. 8c-e)—we conclude that the crystallographic texture, GB character and TJ distribution do not evolve during EM testing. For each of the microstructures produced, we test from 3 to 5 lines at each test-temperature considered. Each line is tested to open circuit failure and the corresponding *time to failure* (*TTF*) is plotted versus the inverse of the test-temperature in the Arrhenius plot shown in Fig. 8b. To account for the Joule heating induced in the lines when the current is applied, the following procedure is routinely carried out. Before EM testing, the

line's resistivity, ρ_0 , is measured at room temperature ($T_0 = 25^\circ\text{C}$). Then the line is heated up to the test-temperature T and the corresponding resistivity $\rho(T)$ is measured. The line is stabilized at the temperature T for 10 minutes to minimize fluctuations in the measured resistivity. The current is then applied to the line using a constant ramp rate of 4 mA/sec. The new resistivity $\rho(T')$ is measured at the end of the current ramp. These values are used to calculate the temperature coefficient of resistance α from Eq. (2) [48] and the temperature increment ΔT resulting from Joule heating from Eq. (3) and (4):

$$\rho(T) = \rho_0[1 + \alpha(T - T_0)] \quad (2)$$

$$\rho(T') = \rho_0[1 + \alpha(T' - T_0)] \quad (3)$$

$$\Delta T = T' - T = \frac{\rho(T') - \rho(T)}{\alpha\rho_0} \quad (4)$$

Electron micrographs of the failed lines confirm that catastrophic failure occurred via EM-induced damages: in the form of voids at the cathode side and hillocks/whiskers at anode side (see Fig. 10). FIB cross-sections of the failed lines confirm that no EM-induced damage occurred at the interfaces between the metal line and the SiN_x passivation layer or the substrate (see Fig. 8c-e). Finally, we verify that atomic diffusion is fastest along GBs in the range of test-temperatures employed in this study. We compare the magnitude of lattice and GB diffusion using equations (5) and (6) [23], respectively:

$$D_l = 0.5\exp\left(-\frac{142.3T_m}{RT}\right) \quad (5)$$

$$D_{gb} = 0.3\exp\left(-\frac{74.5T_m}{RT}\right) \quad (6)$$

where D_l and D_{gb} are the lattice and GB diffusivities, respectively. T_m is the melting point of the material considered and $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ the gas constant. We find that GB diffusion is several orders of magnitude faster than lattice diffusion (see Table 2). By virtue of the

foregoing analysis, we conclude that the EM behavior of the tested microstructures is function only of the GB network.

To quantify EM resistance and compare the behavior of the different microstructures, we calculate the effective activation energy for EM, E_a , using Black's formula [49]:

$$TTF = Aj^{-n} \exp\left(\frac{E_a}{k_B T}\right) \quad (7)$$

where A is a pre-exponential factor, k_B the Boltzmann constant, j the current density, and n the acceleration factor. Both reference and 1×iGBE lines have similar activation energy of ~0.55 eV, while 2×iGBE lines exhibit a much higher value of ~1.22 eV (see Fig. 8b). Differences in EM behavior are also noticeable in the lines' TTF . For instance the extrapolated TTF of 2×iGBE at 100°C—the typical operating temperature in integrated circuits [23]—is 2 and 3 orders of magnitude longer than that of 1×iGBE and reference lines, respectively (see Fig. 8b). These findings demonstrate that iGBE allows for the production of interconnects with improved resistance to EM. Moreover, the drastic increase in E_a after two iGBE cycles suggests a change in the kinetics of EM-induced damage. Indeed, the value of 0.55 eV is comparable to what is reported in literature for GB-mediated EM in Au (0.42 – 0.98 eV) [50-53]. Conversely, the higher value of 1.22 eV in 2×iGBE indicates slower atomic migration, approaching that of lattice diffusion (~1.8 eV) [54].

6. Discussion

The change in GB character distribution and GB connectivity induced through iGBE may be at the origin of the measured difference in EM behavior of the interconnect lines—and thus of their improved resistance to EM. Indeed, both $\Sigma 1$ and $\Sigma 3$ boundaries are known to be low-energy interfaces and to exhibit low atomic diffusivity [45, 55, 56]. The highest number fraction of $\Sigma 1$ and $\Sigma 3$ boundaries obtained in 2×iGBE and the tendency for such boundaries to be connected together (as shown from the TJ distribution analysis) could be enough to force atomic migration through low-diffusivity paths, yielding a measurable difference in E_a . In the following, we are going to use percolation theory to interpret our EM results and test this hypothesis. Following the work by Kononenko et al. [46] we consider only $\Sigma 1$ and $\Sigma 3$ to be low-diffusivity GBs and we compute their cumulative number fraction, p , in the different microstructures that we tested. We then define two percolation thresholds, p_H and p_L , corresponding to having a connected path of high- and low-diffusivity GBs across the interconnect line, respectively. We use the two thresholds to study which microstructures comprise percolating network of GBs with similar diffusivity. If $p < p_H$, a connected path of high-diffusivity GBs must exist in the line, while if $p > p_H$ then no such path exists. Conversely, if $p > p_L$ a connected path of low-diffusivity GBs exists across the interconnect. The values of p_H and p_L are taken from the theoretical work by Frary and Schuh [57, 58], who calculated percolation thresholds in 2-D microstructures for both fiber textured and twinned microstructures. Indeed, because our films comprise columnar grains (see Fig. 5 and Fig. 8c-e), they can be considered as 2-D microstructures. Moreover, since the iGBE microstructures are both textured and twinned, we define p_H and p_L as a range of values between the corresponding theoretical thresholds (reported in Table 3). The connectivity of high- and low-diffusivity GBs for the different microstructures is reported in Fig. 11a. Our analysis indicates that none of the samples produced in this study comprises a percolating path of

high-diffusivity GBs (i.e. all microstructures exhibit $p > p_H$). However, percolation of low-diffusivity GBs is expected in 2×iGBE—exactly the sample showing the highest E_a .

To interpret this result, we first correlate the measured EM behavior of our lines to their effective diffusivity, considering only GBs as the atomic migration pathway. Simulations of GB networks have shown that the effective diffusivity of a GB network is determined by the effective atomic flux across the network and, therefore, that it is sensitive to the percolation of high-diffusivity GBs [6]. Since $p > p_H$ for all the three microstructures we tested, we expect their effective diffusivities to be similar [6]. If the EM resistance of a line were function of the effective diffusivity of its microstructure, then we would expect all the three microstructures to exhibit similar EM behavior. That is clearly not the case. The activation energy for EM that we measured in 2×iGBE lines is more than twice that of the reference and 1×iGBE lines. Moreover, the effective diffusivity of a microstructure does not depend on the percolation of low-diffusivity GBs. However our EM tests show that the microstructure with highest resistance to EM is 2×iGBE, which is the only one exhibiting a percolating network of low-diffusivity GBs.

We conclude that EM resistance must be evaluated on the basis of p_L , not p_H . The rationale to support our conclusion is that EM-induced damage forms at locations—or nodes—in the microstructure where there is a strong difference in the atomic migration flux—namely where the flux diverges. In our interconnect lines, flux divergence nodes are the interfaces between clusters of high- and low-diffusivity GBs [59]. Since both reference and 1×iGBE lines have no percolating network of GBs with similar diffusivity ($p_H < p < p_L$), we expect them to consist of a series of high- and low-diffusivity GB clusters—and thus to contain flux divergence nodes from the cathode to the anode. The only type of lines that exhibit a connected path of GBs with similar (low) diffusivity across the entire interconnect is indeed 2×iGBE ($p > p_L$). Based on this argument we can explain why 2×iGBE exhibits the highest

1 resistance to EM damage (i.e. higher E_a). This concept is schematically illustrated in Fig.
2 11b, using an electric circuit model. Here, clusters of low- and high-diffusivity GBs are
3 represented as low- and high-conductivity resistors, respectively. Nodes of large divergence
4 in the atomic flux can be found when both types of resistors are connected in series across the
5 interconnect line.
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11 Using this simple model, we can speculate on the origin of the measured difference in TTF
12 between the reference and 1×iGBE samples. Because of the higher number fraction of low-
13 diffusivity GBs in 1×iGBE, we can expect a lower density of flux divergence nodes across
14 the lines. Intuitively, this translates into a slower degradation of the 1×iGBE lines and thus
15 into an improved lifetime, which is superior to that of the reference sample by a factor 2
16 across the entire range of test-temperatures (see Fig. 8b). However, because $p_H < p < p_L$ in
17 both reference and 1×iGBE microstructures, EM kinetics—and thus E_a —is similar in both
18 types of microstructures.
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31 One interesting case is that of $p < p_H$ (see schematics in Fig. 11b), namely when a
32 connected path of high-diffusivity GBs exists across the interconnect line. While we have no
33 experimental assessment of the EM behavior of such a microstructure, based on the foregoing
34 discussion it might be tempting to conclude that it should have high resistance to EM (owing
35 to the lack of flux divergence nodes across an hypothetical interconnect). However, the
36 presence of a high-diffusivity path across the line would make its use in microelectronic
37 devices impracticable. In fact, any interface between the interconnect and other functional
38 units or diffusion barriers in the device would turn into a flux divergence node [23]. Owing to
39 the fast atomic diffusion across the percolating path of high-diffusivity GBs, the interconnect
40 lifetime would thus be comparable to—if not shorter than—that of the reference-type lines.
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56 Another important aspect to consider when comparing the EM behavior of the reference,
57 1×iGBE and 2×iGBE lines is that different processing conditions are used to produce the
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three microstructures. 1×iGBE, and 2×iGBE samples are ion-irradiated, while the reference sample is not. Ar⁺ ion-irradiation is known to introduce void-like damage in metal thin films [60]. However, since the ion-irradiation is only carried out in the microstructure template during iGBE, the damage should be confined within the first 50 nm. Fig. 12 shows cross-sectional TEM micrographs of the tested lines. The TEM micrographs show that grains have homogeneous structure throughout the entire thickness. Moreover, they show uniform distribution of defects (such as dislocations) and no indication of voids or bubbles at the interface with the substrate, the interface between the 50 nm microstructure template and the additional 450 nm material (marked in micrographs in red color), or at GBs [61, 62]. We conclude that ion-induced damage during iGBE can be ignored. This result is not surprising. In fact, only the first 50 nm thick channeling-oriented grains have experienced ion-beam damage during iGBE. The remainder material was never irradiated. Moreover ion-matter interactions in channeling-oriented grains are expected to be very mild, hardly inducing extensive damage.

Another aspect to account for is that the interrupted sequence of ion-irradiation and supplemental material deposition may have induced a different stress state in the 50 nm thick microstructure templates, which could have propagated to the 500 nm thick lines. Indeed, residual stresses are known to play an important role in the EM behavior of interconnects [63]. Furthermore, the change in EM kinetics from 1×iGBE to 2×iGBE may also cause the establishment of back stresses of different magnitude in the lines, which would be caused by the migration and accumulation (or depletion) of material [59, 64]. Both the effects of residual and back stresses on the EM behavior of interconnects are not captured by Black's formula. To estimate how stresses influence atomic diffusion we consider [65]:

$$D' = D \exp \left(\left(\frac{\Omega}{k_B T} + \frac{1}{B} \right) \sigma \right) = D_0 \exp \left(\frac{\sigma}{B} \right) \exp \left(-\frac{Q - \sigma \Omega}{k_B T} \right) \quad (8)$$

where D' and $D = D_0 \exp(-Q/k_B T)$ refer to the atomic diffusivities with and without stresses, respectively. D_0 is a pre-exponential factor, Q the activation energy for diffusion without stresses, Ω the atomic volume, B an effective modulus, which depends on the passivation conditions as well as the material tested, and σ the hydrostatic stress. $Q - \sigma\Omega$ represents the activation energy for diffusion considering the effect of stresses. Assuming that Q is the same for all tested microstructures and that the measured difference in activation energy ($0.67 \text{ eV} = 1.22 - 0.55 \text{ eV}$) stems solely from the effect of stresses, a stress of 3.4 GPa would be required to explain the difference in the activation energy (0.67 eV), according to Eq. (8). However, 3.4 GPa is much greater than the yield strength of Au [66, 67] and even the fracture strength of the passivation layer of SiN_x [68]. Therefore it would be impossible for the metal lines to sustain such level of stress. Consequently, we conclude that the mentioned difference in activation energy cannot be attributed to the effect of stresses, rather to the change of the GB network in the microstructures.

Interestingly, the foregoing analysis suggests that our EM test—performed on nominally identical interconnect lines, except for their GB network—is capable of measuring GB diffusion in both high- and low-diffusivity GBs. In fact, while in reference and 1×iGBE samples EM kinetics is governed by high-diffusivity GBs, in 2×iGBE it must be a function of the atomic flux divergence between low-diffusivity GBs and the crystal grains (i.e. lattice diffusion). Therefore the measured value of 1.22 eV must result from the average between $\Sigma 1$ and $\Sigma 3$ boundary self-diffusivities. On the other hand, the value of 0.55 eV must be the average self-diffusivity of all other GB types in the microstructure.

7. Summary

In summary, we have proved that iGBE is a novel method to engineer the GB network of thin metal films, *in situ*, to an unprecedented level of detail. iGBE is based on the repeated sequence of SGM and supplemental material deposition which enables the production of microstructures comprising controlled fraction of low-diffusivity GBs—specifically, $\Sigma 1$ and $\Sigma 3$ boundaries. We showed that iGBE markedly affects GB connectivity. By applying different iGBE cycles, it is in fact possible to produce films with tailored GB network topology, which show completely different behavior. To prove the beneficial effect of iGBE, we tested the EM resistance of three differently processed Au interconnects and found a progressive improvement in the lines' lifetime. By designing the EM tests to only probe the role of the GB network, we were able to explain the origin of the improved performance using percolation theory and to estimate atomic self-diffusivity of different GB types. Since iGBE is a material-insensitive method, it can be readily applied to a variety of different cubic materials—both FCC and BCC—with no requirements for additional treatments—such as annealings—or for specific substrates. Most importantly, the method is readily integrable in standard microfabrication technology for the production of interconnects with superior resistance to EM.

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Figure captions

Fig. 1. Schematics, in-plane orientation EBSD maps, and (111) pole figures illustrating the film microstructure evolution during iGBE. (a) Initial (111) textured microstructure (reference). First iGBE cycle comprising SGM (b) and supplemental deposition (c). Both the channeling-oriented grains and those in twinned orientation are represented in green color in the schematics as well as in the EBSD maps. Upon supplemental deposition, new grains in twinned orientation nucleate, as evidenced by the six-fold symmetry in the corresponding pole figure. (d and e) Second iGBE cycle.

Fig. 2. Secondary electron and backscattered electron micrographs showing Au coverage in 50 nm thick films through the entire iGBE process.

Fig. 3. GB character distribution in the 50 nm thick microstructure templates.

Fig. 4. Evolution of TJ distribution in 50 nm thick films as a function of iGBE cycles.

Fig. 5. SEM cross-sections of as-produced 500 nm thick films. (a) reference, (b) 1×iGBE and (c) 2×iGBE films.

Fig. 6. (a) EBSD in-plane orientation maps and corresponding (111) pole figures of 500 nm thick reference, 1×iGBE, and 2×iGBE films. (b) Corresponding GB character distribution in 500 nm thick films, showing a substantial increase in the number fractions of $\Sigma 1$ and $\Sigma 3$ boundaries upon iGBE cycles.

Fig. 7. Evolution of TJ distribution in 500 nm thick films as a function of iGBE cycles.

Fig. 8. (a) Layout of the Au interconnect lines for EM test. (b) Arrhenius plots of the TTF versus $1/T$. Each data point represents the average TTF of 3 to 5 tested lines. (c-e) SEM cross-sections of EM tested 500 nm thick lines. (c) reference, (d) 1×iGBE, and (e) 2×iGBE. The micrographs are from regions near to the cathode end. The arrows indicate the EM-induced damage.

Fig. 9. EBSD in-plane orientation maps and corresponding (111) pole figures of the 2×iGBE microstructure (a) before and (b) after a 3 hour thermal annealing at 400°C.

Fig. 10. Representative SEM images of line failure at (a) cathode and (b) anode in the 500 nm thick reference sample after EM test.

Fig. 11. (a) Comparison of the low-diffusivity GB number fraction, p , in the tested microstructures. The ranges of the defined percolation thresholds for the 2-D microstructure with both fiber texture and twins are also presented. (b) Electric circuit models of the GB networks in microstructures with different p . (top) $p > p_L$, low-diffusivity boundaries percolate; (middle) $p_H < p < p_L$, neither low-diffusivity nor high-diffusivity boundaries percolate; (bottom) $p < p_H$, high-diffusivity boundaries percolate.

Fig. 12. Representative TEM micrographs of EM tested lines. (a-c) are bright-field (BF) micrographs taken from (a) reference, (b) 1×iGBE and (c) 2×iGBE sample. (d) is a high-angle annular dark-field (HAADF) STEM micrograph taken from the 2×iGBE sample. The

TEM lamellae are cut from regions near the cathode end by FIB. The red dashed lines indicate where the interface between the 50 nm thick microstructure template and the remainder 450 nm thick material.

Table captions

Table 1. Average grain size and the area fraction of channeling-, twinned- and randomly-oriented grains as well as non-indexed areas in the 50 nm and 500 nm thick reference, 1×iGBE, and 2×iGBE films, respectively.

Table 2. Calculated lattice and grain boundary diffusivities in Au from [23].

Table 3. Summary of the total number fraction of low-diffusivity GBs, p , in reference, 1×iGBE, and 2×iGBE. The simulated values of the percolation thresholds for the existence of high- (p_H) and low-diffusivity GBs (p_L) in 2-D microstructures with either fiber texture or twins are also listed.

Figure 9(s)

Figure(s)

Figure(s) reference

a.

b.

1xiGBE

c.

2xiGBE

Figure(s)

a.
as-deposited

b.
annealed

111

111

a. Cathode

b. Anode

Figure(s)

a. reference

b. 1xiGBE

c. 2xiGBE

d. 2xiGBE

Table(s)

	Sample	Grain size [nm]	Channeling- oriented grains	Twinned- oriented grains	Randomly- oriented grains	Non-indexed area
50 nm thick	reference		25.7%	-	-	31.9%
	1×iGBE	~ 60	39.7%	26.4%	6.3%	27.6%
	2×iGBE		48.7%	22.2%	1.7%	27.4%
500 nm thick	reference		32.8%	-	-	9.5%
	1×iGBE	~ 120	45.3%	43.1%	4.2%	7.4%
	2×iGBE		47.4%	44.5%	1.4%	6.7%

Table(s)

Au	Diffusivity [cm ² /s]		
	100 °C	200 °C	300 °C
Lattice	1.2×10^{-27}	4.9×10^{-22}	2.3×10^{-18}
Grain boundary	3.4×10^{-15}	3.0×10^{-12}	2.5×10^{-10}

Sample		$\Sigma 1$	$\Sigma 3$	Others	p	$p_H(2-D)$	$p_L(2-D)$
500 nm thick	reference	28.6%	16.1%	55.3%	44.7% $\pm$ 0.4%	-	-
	1 $\times$ iGBE	35.3%	23.6%	41.1%	58.9% $\pm$ 1.2%	-	-
	2 $\times$ iGBE	39.6%	28.2%	32.2%	67.8% $\pm$ 2.6%	-	-
Fiber textured [57]		-	-	-	-	39.9%	68.9%
Twinned [58]		-	-	-	-	34.1%	66.6%

*Graphical Abstract