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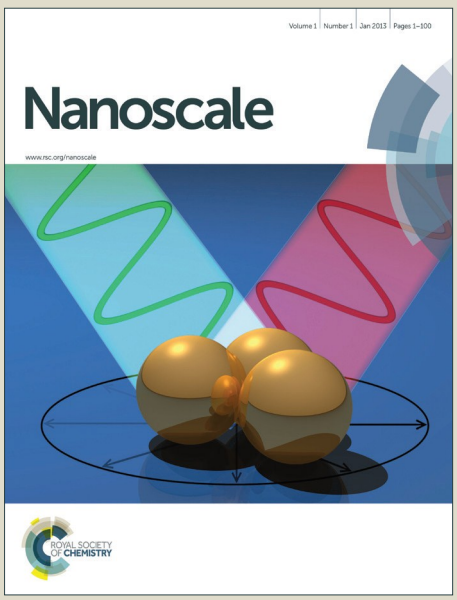

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Optimization of the nanotwin-induced zigzag surface of copper by electromigration

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By adding nanotwins to Cu, the surface electromigration (EM) slows down. The atomic mobility of the surface step-edges is retarded by the triple points where a twin meets a free surface to form a zigzag-type surface. We observed that EM can alter the zigzag surface structure to optimize the reduction of EM, according to Le Chatelier's principle. Statistically, the optimal alternation is to change an arbitrary (111)/(hkl) zigzag pair to a pair having a very low index (hkl) plane, especially the (200) plane. Using in-situ ultrahigh vacuum and high-resolution transmission electron microscopy, we examined the effects of different zigzag surfaces on the rate of EM. The calculated rate of surface EM can be decreased by a factor of ten.

Introduction

In Al interconnect technology, electromigration (EM) occurs by grain boundary diffusion at the device operation temperature. To slow down EM in Al, the alloying of approximately 1 at. % Cu solute has been found to be effective[1]. In Cu interconnect technology, EM occurs by surface diffusion, and solutes, such as Sn, Si, P, Al, and Mn, have been proposed to reduce the EM, which follows the same alloying approach taken in Al technology[2-4]. The main problem with the use of alloying is a performance penalty owing to the increase in Cu resistivity, which is not desirable, as the device dimensions continue to shrink. We report here that instead of solute alloying, a high density of nano-twins can serve the same purpose without sacrificing the electrical conductivity of pure Cu[5-10]. More importantly, we found that EM can alter the nanotwin-induced zigzag surface structure. The normal evolution of the zigzag surface suggests a statistically optimal orientation of nanotwins in a polycrystalline Cu interconnect to further slow EM. When introducing nanotwins into Cu, the free surface where a twin intersects is transformed to a zigzag surface because a valley and a ridge are formed by the two triple points at the intersections of the pair of twin planes with the free surface. Typically, the zigzag surface consists of two sets of alternating surface planes, for example, (111)/(422) /(111) /(422)… It has been reported that the triple points can slowdown the net rate of surface diffusion when the EM-induced surface step migrates from the (111) surface plane to the (422) surface plane on the zigzag surface[11]. This is because of the necessity of the change of the surface step on the (111) surface to that on the (422) surface and the long incubation time that is needed to nucleate a new step. However, in addition to the delay of step migration across triple points, local surface structures are also believed to significantly affect the EM behaviors of surface steps[12-16]. In turn, how EM can alter the local surface structure and how feedback based on Le Chatelier's principle can reduce EM further are addressed in this paper.

On different orientations of Cu grains, the zigzag surface is different, and a different reduction rate of EM is found. Generally speaking, we found that on a zigzag surface, while one set of the alternating surface plane tends to be (111), the other set can be a low-index (hkl) plane. The selection is based on the surface energy from thermodynamics, yet under EM, the selection based on kinetics is more favorable. For comparison, we have also measured the rate of EM on a (111) surface that has no nano-twins; the rate is orders of magnitude faster than that on a zigzag surface having nano-twins. In this report, the effect of the configuration of the surface structures of nanotwin-modified Cu on EM has been observed by an *in-situ* TEM-EM technique. We correlate the magnitude of the EM-induced mass flux to the specific geometry of the surface step-edges on the zigzag surfaces.

Results and discussion

We performed a direct comparison between the EM-induced migration of step-edges in a $(0\bar{1}1)$-oriented Cu grain with and without nanotwins. A detailed description of the experimental procedure is provided in the supplementary materials. The two regions of examination are indicated in the schematic diagram of a Cu grain in Figure 1a. A void with a new free surface is formed in this grain when atomic layers are gradually removed from the right side of the Cu grain under EM. The new free surface has two regions of different surface planes with step edges, as seen in Figure 1b and 1c, depending on whether there are nanotwins. Figure 1b is the region of a free surface of the

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(111) plane without nanotwins, and there are some surface step-edges on the (111) plane that form a curved surface.

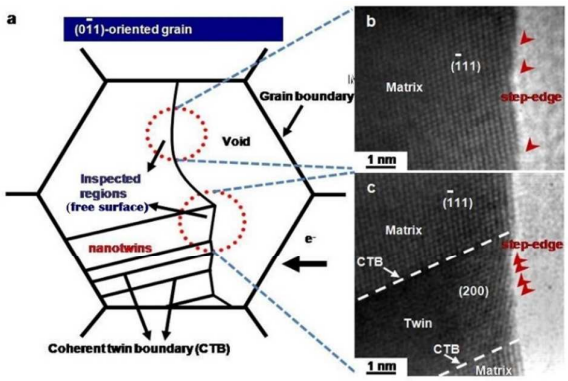

Figure 1. EM-induced Cu surface planes. (a) A schematic diagram of a $(0\bar{1}1)$-oriented Cu grain without and with nanotwin-structured regions. (b) and (c) Corresponding HRTEM images of the evolved step edges at unnano-twinned and nano-twinned surfaces under EM.

Figure 1c is the region of a free surface with nanotwins that form a zigzag shape. The zigzagged surface consists of alternating (111) and (200) planes, and surface step-edges are inherent in the (200) plane to maintain the zigzag surface. The evolution of the surface structure, morphology, and EM rate on these two regions were examined. In Figure 1b, we observe that under EM, the upper edge of the Cu without nanotwins has a single step-edge and developed into an array of surface step-edges with (111) terraces in changing a smooth surface to a slightly curved (111) surface, see Figs. 2a-d. When electron carriers are scattered by the surface step-edges, they transfer their momentum and provide the energy needed for the change of the surface morphology in Figure 2e-g. Later, the array of surface step-edges fades away and becomes a flat(111) surface again, as seen at the top of Figure 2h. The curved surface at the bottom of the image in Figure 2h is connected to a twin boundary. As a consequence, the free surface recedes deeper into the remaining grain, as shown by the schematic diagram in Figure 1a. It is reported that (111) surface planes have the lowest activation energy and are the preferred diffusion plane over any other surface plane[17,18]. In addition, the electrons flowing in <110> directions have less resistance than those in <100> or <111> directions, indicating that the current density in <110> directions is higher when an electrical field is applied [21]. Repeating step-edge diffusion on the (111) surface along the <110> directions observed in Figure 2 leads to a unique stepped atomic structure in crystalline Cu. After long periods of surface EM, there was a substantial change in surface morphology of a Cu grain. Movie S1 shows the real time movement of the step-edges on the nanotwin-free region during the first 24 seconds in Figure 2. Additional evidence of concurrent EM-induced multiple step-edge migration in a twin-free $(0\bar{1}1)$-oriented Cu grain is shown in movie S2.

In contrast to the nanotwin-free surface, the lower part of the surface of this $(0\bar{1}1)$-oriented Cu grain, which has a pair of twin boundaries, has evolved into a surface with a zigzag shape as shown in Figure 3. The zigzag surface was found to have alternating $(\bar{1}11)$ and (200) planes, see Figure 3a. Under EM we observe that the migration of step-edges in the region between triple points is similar to that in the twin-free region. The surface step-edges indicated on the (200) plane (Figure 3b) are locations to see the initiated migration of the surface step-edge and the removal of atomic layers with the current stressing time (Figs. 3a-c).

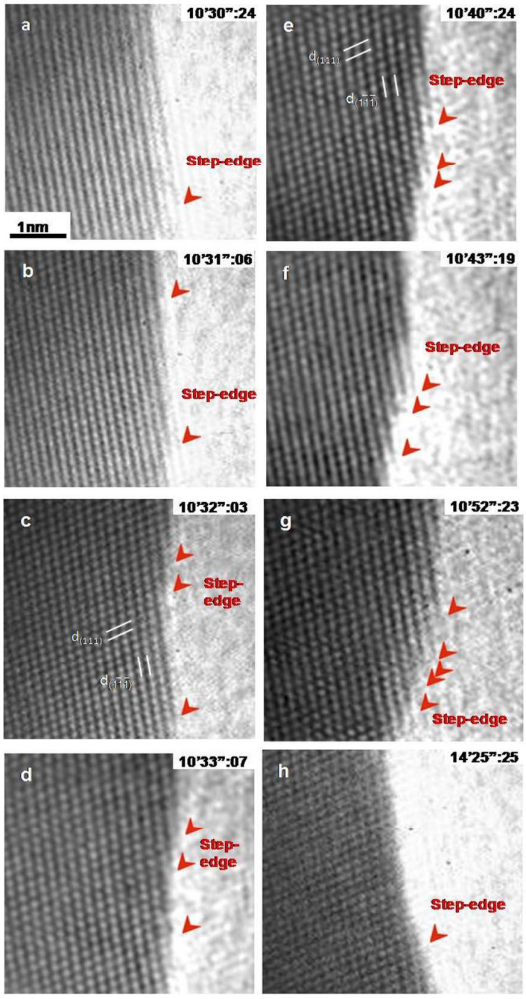

Figure 2. Step-edge migrations with no nanotwins. (a-h) HRTEM images of the $(0\bar{1}1)$-oriented Cu grain under current stressing as a function of time. The time of the image capture is given in the rectangular box at the upper-right corner. The first two numbers are in units of minutes, the second two numbers are in units of seconds, and the following two smaller numbers are in units of 1/30 seconds.

Under EM, the zigzag surface and the triple points tend to persist. As shown in Figs. 3c-d, the zigzag surface has evolved into $(\bar{1}11)$ and $(\bar{3}11)$planes. From Figs. 3c to 3d, the change of alternating $(\bar{1}11)$ /(200) to alternating $(\bar{1}11)$ / $(\bar{3}11)$ planes seems to have been affected by the advancing sunken (111) planes in the upper untwinned region (Figure 1b) due to the faster rate of EM. It led to a change in the relative orientation of the normal grain surface with respect to the flow direction of electrons. The change indicates that the geometry of the triple point or the three surface forces at the triple point may not be in thermodynamic equilibrium as given by the classical Young's equation. It is a kinetic effect of EM to alter the surface planes of the zigzag. Furthermore, it is assumed that a free surface has no normal stress. However, whether there is a normal strain in a

ridge-type triple point is uncertain, and it is a subject that needs further study. Movies S3 and S4 show the direct observation of the step-edge migration on a meta-stable zigzag surface of alternating $(\bar{1}11)$ and (200) planes and on alternating $(\bar{1}11)$ and $(\bar{3}11)$ planes, respectively.

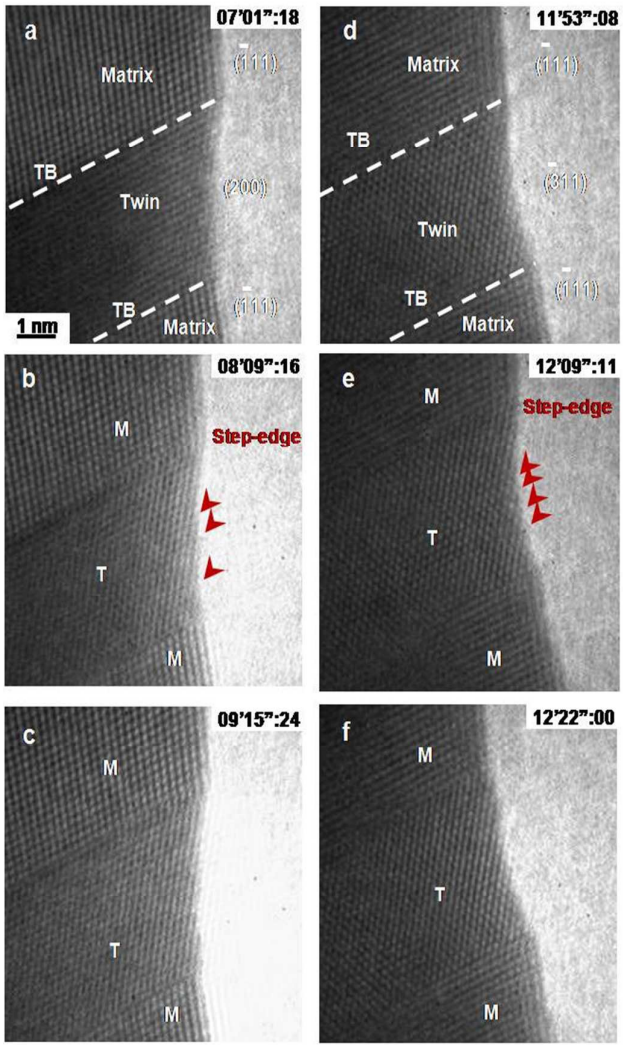

Figure 3. Step-edge migrations and pinning of triple points with nanotwins. (a-f) HRTEM images of the $(0\bar{1}1)$-oriented Cu grain with nanotwins under current stressing as a function of time. The time of the image capture is given in the rectangular box at the lower-left corner. The first two numbers are in units of minutes, the second two numbers are in units of seconds, and the following two smaller numbers are in units of 1/30 seconds.

Figure 4a shows the number of removed {111} atomic layers as a function of the current stressing for different Cu surface planes. It quantitatively indicates EM-induced step-edge migrations at the surfaces with and without nanotwins. The effect of the nanotwinned surface on the EM rate is demonstrated by the significant change of the slope of the measured curves compared to those of the untwinned surface, see insets in Figure 4a. The EM rate to remove Cu atomic layers at the free surface without nanotwins has a very sharp slope (Line a) compared to the gradual slopes of the nanotwin-modified zigzag surfaces. Because the nanotwinned region has a zigzag surface, Line b-1 and Line b-2 are the numbers of removed Cu atomic layers counted from two $(\bar{1}11)$ planes separated by a $(\bar{3}11)$ plane, and similarly, Line c-1 and Line c-2 are for the $(\bar{1}11)/(200)/(\bar{1}11)$zigzag surface. In each of these step-wise curves, we can break each step into two periods: the very narrow width of the vertical line and the very wide width of the horizontal line. The very short period of the width of the vertical line represents the time of the propagation of an atomic layer, which shows no significant difference for all curves and it is less than 0.1 sec per atomic layer. However, the long period of the width of the horizontal line represents a stagnation time or incubation time between two vertical steps (the time it takes for the electromigration of a new free surface layer to occur); it is this long waiting time that greatly reduces the rate of EM. More twin boundaries can increase numbers of wide widths of the horizontal line and therefore are expected to slow down the EM-induced voiding.

The incubation time depends on the triple point configuration; the (111)/(200) pair has the longest incubation time and, in turn, the slowest EM rate. This is because it is harder to nucleate a step-edge on a low-index plane than on a high-index plane.

By taking the reciprocal of the slope of the curves, the average time required to remove one {111} Cu atomic layer in the nanotwinned regions can range from 3 times (3.85 sec) per atomic layer for the $(\bar{1}11)$ / $(\bar{3}11)$zigzag pairs to one order of magnitude larger (12.2 sec) per atomic layer for the $(\bar{1}11)$ /(200) zigzag pairs, compared to that (1.34 sec) per atomic layer on the $(\bar{1}11)$ planes without nanotwins. By computing the incubation period in the different stepwise curves captured in Figure 4a, frequency distribution curves of the incubation period for the step-edge migration are plotted in Figure 4b. The zigzag surfaces lead to an increase as well as a wider frequency distribution in the incubation period and consequently, a decrease in the rate of EM. Clearly, there is a strong dependence of the EM on the two alternating atomic planes of the zigzag surface. We found that the EM induces a feedback selection of the zigzag surface. The $(\bar{1}11)$ /(200) combination appears to be one of the most meta-stable zigzag pairs under EM, as is further demonstrated in the process of the refilling of a void of nanotwinned Cu (supplementary materials Figure S2).

In the classical theory of EM, the atomic flux equation is

$$J_{EM} = CMF = C\frac{D}{kT}Z^{*}e\rho j$$

where C is the Cu concentration ($C=1/\Omega_{Cu}$ atomic volume of Cu, $\Omega_{Cu}=1.182\times10^{-23}$ cm^3), M is the atomic mobility and F is the EM force. From the step-edge displacement in Figure 4a, the atomic flux J can be calculated by the total atoms crossing a unit area per unit time (Crossing area A=thickness$\times\delta$, where $\delta\approx0.3$ nm is the effective diameter of the Cu atom). The divided time is the average period to remove one Cu atomic layer, which is the reciprocal of the slope of the stepwise curves (Figure 4a). The Cu step-edge diffusivity D can be obtained by giving the measured atomic flux and the defined driving force F. Here, we assume ρ_{Cu} (resistivity of Cu) $=1.68\times10^{-8}$ ohm·m, Z^* (effective charge number) is -5, and an average current density of 2×10^6 A/cm^2 for computing the driving force. Our calculated step-edge diffusivity for the free surface without a nanotwin-modified structure is 3.8×10^{-10} cm^2/sec, whereas for the nanotwin-modified surface, it ranges from 1.61×10^{-10}

cm^2/sec to 5.07×10^{-11} cm^2/sec for the $(\bar{1}11)/(\bar{3}11)$ and the $(\bar{1}11)/(200)$ pairs of the zigzag surface, respectively. Such a lowered diffusivity indicates that the step-edge diffusion is much more difficult on the nanotwin-modified surface. The diffusivities are 1.8×10^{-10} cm^2/sec and 4.1×10^{-12} cm^2/sec for the high-symmetry (straight) and low-symmetry (rough) step-edges reported in the literature, respectively[16,19,20]. In the case of partial symmetry[16], the effective diffusivity can be calculated as 1.4×10^{-11} cm^2/sec.

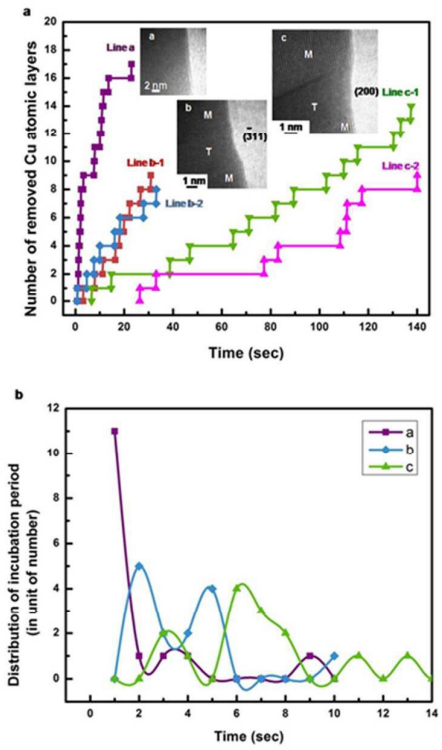

Figure 4. Measurement of EM rate in three surface planes. (a) Plot of the number of removed {111} Cu atomic layers as a function of current stressing time in regions without and with nanotwins. (b) Frequency distribution curves of incubation period for step-edge migration computed from (a). The insets are the three corresponding HRTEM images of the $(0\bar{1}1)$-oriented Cu grain edges under EM.

It can be seen that our calculated results agree well with the literature data, indicating that the assumptions used in this calculation are reasonable.

Conclusions

In conclusion, we have demonstrated that the nanotwin-induced zigzag surface structures of Cu can be altered by EM. The alternation by the feedback of EM can produce a high density of the (111)/(200) pairs of zigzag surfaces on a polycrystalline Cu interconnect. The correlation between the specific zigzag surfaces and the magnitude of the mass flux driven by EM has been studied by direct observations using *in-situ* ultrahigh vacuum and high-resolution TEM.

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