Observation of Atomic Diffusion at Twin-modified Grain Boundaries in Copper

Atomic diffusion at grain boundaries in copper driven by electric current can be slowed down greatly by modifying the grain boundary structure with the introduction of nanometer scale twin defects.

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Abstract: Grain boundaries affect the migration of atoms and electrons in polycrystalline solids, thus influencing many of the mechanical and electrical properties. By introducing nanometer scale twin defects into copper grains, we show that we change the grain boundary structure and atomic diffusion behavior along the boundary. Using in-situ ultrahigh vacuum and high resolution transmission electron microscopy, we observe electromigration induced atomic diffusion in the twin-modified grain boundaries. The triple point where a twin boundary meets a grain boundary was found to slow down grain boundary and surface electromigration by one order of magnitude. We propose that it is due to the incubation time of nucleation of a new step at the triple points. The long incubation time slows down the overall rate of atomic transport.

Grain boundaries affect many physical properties of polycrystalline solids. For example, reduction of grain size is known to improve the mechanical strength of metals, governed by the Hall-Petch equation (*1, 2*). A large angle tilt-type grain boundary can short-circuit atomic diffusion, which has been the most serious reliability issue in Al interconnects in microelectronics technology. The atomic structure of a grain boundary is controlled by the misorientation between the two grains forming the grain boundary. Balluffi and co-workers have made bicrystals of Au thin films and varied systematically the tilt or twist angle in the bicrystals for studying the correlation between formation energy and atomic structure of grain boundaries (*3, 4*). Generally speaking, the higher the grain boundary misorientation angle, the higher the atomic diffusivity. Thus by modifying the structure of a grain boundary, it should be possible to control the atomic diffusion along the grain boundary.

Lu and co-workers have synthesized a high density of nano-twins in pure Cu foils by pulsed electro-deposition (*5*). The average grain size in the Cu foils is about 400 nm and the high density twins have a peak at 15 nm in twin lamella size distribution. The Cu foil shows a ten-fold improvement of the mechanical strength relative to a large grained Cu and the foil remains ductile, but its electrical resistance did not significantly change. High mechanical strength and low electrical resistivity are desired properties for interconnecting wires in integrated circuits from the consideration of the resistive-capacitive delay, electromigration (EM), and stress migration (*6-8*). EM is enhanced atomic diffusion under a high-density electric current. Stress migration is creep and is atomic diffusion driven by a normal stress potential gradient. With the increase in density of electric current in integrated circuits, EM-induced voids and hillocks in conductors can lead to circuit

reliability failure (*9*). EM-induced mass transport, in principle, can take place along different diffusion paths such as lattices, grain boundaries, surfaces, and interfaces (*10, 11*). It is now generally accepted that free surfaces or interfaces are principal EM paths in Cu interconnects at the device operation temperature around 100 ºC, and grain boundaries become preferential EM paths at high temperatures (*12*). Conventional EM investigations of interconnects were conducted by measuring the changes in electrical resistance or monitoring morphological changes due to void or hillock formation in the current-stressed metal lines (*13, 14*). The mass transport can be observed indirectly by marker displacement (*15*). However, no direct observations of EM-induced atomic scale mass transport have been conducted.

To study atomic-scale EM in the nano-twin modified grain boundaries requires in-situ high resolution transmission electron microscopy (TEM) and it requires ultrahigh vacuum to prevent oxidation of the Cu under high temperature and high current. Our previous studies of Cu have revealed that the EM-induced mass transport occurs preferentially on the {111} surface planes and along the <110> directions, leading to a unique stepped atomic surface structure in crystalline Cu (*16, 17*). In the present study, we introduced nano-twins into the test samples of Cu (*18*). The specimens for in-situ TEM observation were prepared through conventional thin film deposition and patterning processes (Figs. S1, A to E). A scanning electron micrograph of the test specimen around the observation window is shown in Fig. S1F.

Figure 1 shows a set of high-resolution TEM (HRTEM) images of a twin-modified grain boundary at different stages during electric current stressing. A twin has two twinning planes, so it will intersect a grain boundary with two triple points. Since a grain

boundary is formed by two grains, we should have twins to intersect the grain boundary from both sides. We inspected only one of the two grains forming the grain boundary, the grain in the lower part of the image, which is $(01\bar{1})$-oriented or it has $[01\bar{1}]$ as the surface normal. This grain has several {111}/<112> type coherent twin boundaries which appear to have an angle of 70.5° with respect to the (111) lattice planes. Under the influence of electromigration, the edge of this $(01\bar{1})$-oriented grain in the grain boundary plane has evolved into a zig-zag shape. The zig-zag edges in the grain boundary were found to be $(1\bar{1}\bar{1})$ and $(4\bar{2}\bar{2})$ atomic planes that are separated by the thickness of the twin lamellae, as shown in Figs. 1, A to D.

The direction of electron flux is from the right to the left of the inspected grain. We observed that an atomic step appeared at the triple point of the twin boundary (TB1) in Fig. 1 and moved rather rapidly on the $(1\bar{1}\bar{1})$ plane towards the other triple point of the twin boundary (TB2). The results indicate that the Cu atoms move on the $(1\bar{1}\bar{1})$ surface along the direction of electron flux, from the right to the left, resulting in the atomic step moving in the opposite direction. Once the atomic step reached TB2, we observed that it was trapped for a while before moving out onto the $(4\bar{2}\bar{2})$ plane. Movie S1 shows the atomic step movement and the effect of the twin boundary on slowing down EM (*18*). By tracing the atomic steps moving along the $(1\bar{1}\bar{1})$ and $(4\bar{2}\bar{2})$ facet surfaces, we can plot the distances of different atomic steps respectively from TB1 and TB2, with respect to time, as shown in Fig. 2. We found that there exists a time lag of ~ 5 seconds for the atomic steps to cross the triple points under electric current stressing with an average current density of 2.5×10^6 A/cm^2. The moving speeds of the atomic steps on the $(1\bar{1}\bar{1})$ and $(4\bar{2}\bar{2})$ surfaces

were calculated to be 5.7 ± 0.4 and 3.4 ± 0.3 nm/s, respectively, based on the plots in Figs. 2A and 2B. Since the {111} crystal planes have the lowest atomic migration energies among the major low-index planes in Cu, it would not be surprising to find that the moving speed of atomic steps on the $(1\,\bar{1}\,\bar{1})$ surface is faster than that on the $(4\bar{2}\bar{2})$ surface (*19*). Nevertheless, the most important finding is that the triple points can slow down or block the EM-induced atomic migration in the twin-modified grain boundaries of Cu.

Now, the question is why can the triple points of twin boundaries block the EM-induced atomic diffusion. In general, atoms are released from a kink site on a stepped surface of $(1\,\bar{1}\,\bar{1})$ and $(4\bar{2}\bar{2})$ planes. At a triple point, if we assume that the atomic arrangement is close to a coincidence site, it is energetically less favorable to form a step and kink site at the triple points. More importantly, in a transition from a $(1\,\bar{1}\,\bar{1})$ to a $(4\bar{2}\bar{2})$ surface, for example, the nucleation of a new step and a kink site on the $(4\bar{2}\bar{2})$ surface is required, so an incubation time is needed. Overall, the nucleation of steps from the triple points would be the rate-limiting step, resulting in a time lag for the atomic diffusion across the triple points, as shown in Fig. 2A and 2B. When we recorded the atomic step moving along the facet surfaces and plotted the moving distance of an atomic step as a function of time, we find a stair-type curve as shown in Fig. 2C. We interpret that the horizontal part of a step is the incubation time spent to nucleate a new step on the $(1\,\bar{1}\,\bar{1})$ or $(4\bar{2}\bar{2})$ surface and the vertical part of a step is the propagation or growth of the step across the $(1\,\bar{1}\,\bar{1})$ or $(4\bar{2}\bar{2})$ surface. We obtained similar stair-type curves when we followed electromigration along the grain boundary over several triple points.

With the Cu atoms continuously drifting away under electric current stressing, the atomic steps in the $(01\bar{1})$-oriented grain were found to disappear gradually and a void eventually formed along the entire grain boundary. This is because EM-induced grain boundary diffusion is non-conservative (*20*). As it is an irreversible process, we cannot assume vacancy to be at equilibrium everywhere in the sample. Figure 3 shows a set of schematic diagrams of the grain boundary and twin boundaries of one of the Cu grains with $(01\bar{1})$ crystal planes in parallel to the surface of the Cu line sample at different stages during electric current stressing. The HRTEM images were obtained from a local spot of the inspected Cu grain to highlight the evolution of the atomic-scale EM-induced voiding along the grain boundary. We found that the atomic steps gradually vanished from the upper left corner of the grain in Fig. 3A. With time, the void grows to the right against the electron flow direction and also grows downward. The upper free surface of the void is the original grain boundary plane on the top side, and the lower free surface of the void becomes a zig-zag type of free surface consisting of $(1\bar{1}\bar{1})$ and $(4\bar{2}\bar{2})$ edges of twins, as shown in Fig. 3B and 3C. The size of the void was about 10 to 20 nm wide. Finally, the whole grain almost completely disappeared after electrically stressing the specimen for 30 min, as revealed in Fig. 3D.

In dual damascene Cu interconnect technology, surface and interfaces have been found to be the dominant kinetic paths of electromigration in device operation temperature. It is generally accepted that grain boundaries become the more active EM paths for copper when the surface and interfacial paths are blocked or if the temperature reaches above 300 ºC (*12*). However, as a void is formed (Fig. 3), surface diffusion occurs. We have performed an independent experiment to measure the heating of the Cu specimen induced

by the transmission electron beam using a thermocouple attached to the TEM specimen holder, and no significant temperature rise was found for the specimen exposed to the electron beam for 3 hrs. One may argue that the local temperature of the specimen due to electron beam heating might be much higher than the overall temperature measured. In fact, we also found lots of EM-induced grain boundary voids elsewhere in the specimen without direct electron beam exposure. It indicates that the observed EM-induced voiding is not directly affected by the electron beam heating. If the electron beam heating is not severe, it seems that grain boundary diffusion in large angle grain boundaries can still be active EM paths at low temperatures.

The measured speed of a moving atomic step and the triple point induced incubation time lag can be used to evaluate the kinetics of EM-induced voiding in the twin-modified Cu. Figures 3E and 3F show a schematic of a twin-modified Cu grain of dimension L with an average twin lamella width of l and a HRTEM image of the grain edge with a zig-zag feature. It is noted that surface diffusion becomes the active EM path once the void is formed in the upper part of the image as shown in Fig. 3F. We can calculate the time required to remove a layer of Cu atoms from the edge of the twin-modified grain as follows.

$$t_{tw} = \frac{L}{l} \times 5 + \frac{(L/2)\csc(70.5^\circ)}{v_{\{111\}}} + \frac{(L/2)\csc(61.9^\circ)}{v_{\{422\}}} \qquad (1)$$

where $v_{\{111\}}$ and $v_{\{422\}}$ are the moving speeds of atomic step on the {111} and {422} crystal planes, respectively, and L and l are the grain size and twin lamellar thickness, respectively. In the right-hand side of the equation, the 5 in the first term reflects the delay time of 5 sec associated with each triple point of the twin boundaries, while the second and third terms account for the time of the atomic step moving along the {111} and {422} facets, respectively. Equation (1) is established with the reasonable assumption that the twinned

region is approximately equal in extent to the untwinned region in the grain. On the other hand, the time required to remove an atomic layer from a twin-free Cu grain of dimension L will be $t_0 = (L \cdot \csc(70.5^o))/v_{\{111\}}$, since the {111} planes are the most favorable EM surfaces. The EM-induced void is expected to grow in the direction normal to the facets with a rate that is inversely proportional to the above estimated time (t_{tw} and t_0). With the measured $v_{\{111\}}$ and $v_{\{422\}}$ values, the EM-induced void growth rate for the twin-modified Cu grain (l = 5 nm) is calculated to be approximately one order of magnitude lower than that for the twin-free Cu grain. The effect of twin boundaries on slowing down the EM-induced voiding is expected to decrease with an increase of the twin lamella width, i.e. a decrease in the twin density. The twin boundary induced atomic migration delay may also decrease with rising temperature since the EM-induced atomic diffusion is a thermally activated process. However, typical integrated circuit devices usually operate at temperatures around 100 °C.

In conclusion, we have observed the atomic-scale EM process in twin-modified Cu grains near room temperature using high resolution and ultrahigh vacuum TEM technique. The EM-induced atomic migration along a twin-modified grain boundary was observed and the presence of the triple point of a coherent twin boundary meeting a grain boundary was found to retard the EM-induced atomic transport.

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21. The work was supported by the National Science Council through grants No. NSC 96-2120-M-007-006 and 96-2628-E-007-018-MY3. KNT acknowledges the support of NSF-NIRT contract No. CMS-0506841.

Figure legends

Fig. 1. HRTEM images of the $(01\bar{1})$-oriented Cu grain under electric current stressing as a function of time. The time of the image capture is given in the rectangular box at the lower-left corner in minutes and seconds. The direction of electron flow is from right to the left. The labeled arrows indicate the atomic steps on the lattice planes. The cross refers to a fixed point for ease of inspection. The HRTEM image was analyzed by fast Fourier transform technique.

Fig. 2. Movement of different atomic steps on (A) the $(1\bar{1}\,\bar{1})$ surface, (B) the $(4\bar{2}\bar{2})$ surface and (C) the surface between TB1 and TB3 as a function of time. The inset images show the moving trace of the atomic steps.

Fig. 3. Schematic diagrams of the grain boundary and twin boundaries of a $(01\bar{1})$-oriented Cu grain at different stages during electric current stressing. (A to D) The time of the HRTEM image capture is given in the rectangular box at the lower-right corner. The direction of electron flow is from right to the left. (E) A cartoon of a twin-structured Cu grain of dimension L with an average twin lamella width of l. (F) HRTEM image of the grain edge revealing the direction of EM-induced voiding, respectively.

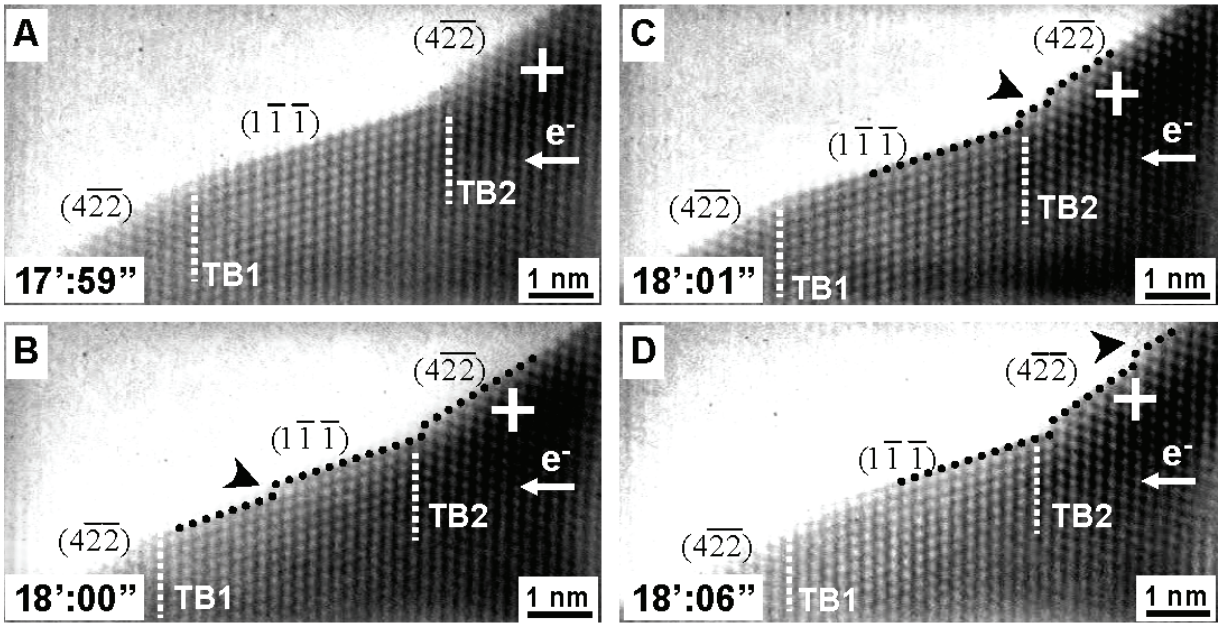
A
(4$\bar{2}\bar{2}$)
(1$\bar{1}\bar{1}$)
e⁻
(4$\bar{2}\bar{2}$)
TB2
17':59"
TB1
1 nm
C
(4$\bar{2}\bar{2}$)
(1$\bar{1}\bar{1}$)
e⁻
(4$\bar{2}\bar{2}$)
TB2
18':01"
TB1
1 nm
B
(4$\bar{2}\bar{2}$)
(1$\bar{1}\bar{1}$)
e⁻
TB2
(4$\bar{2}\bar{2}$)
18':00"
TB1
1 nm
D
(4$\bar{2}\bar{2}$)
(1$\bar{1}\bar{1}$)
e⁻
TB2
(4$\bar{2}\bar{2}$)
18':06"
TB1
1 nm

Fig. 1.

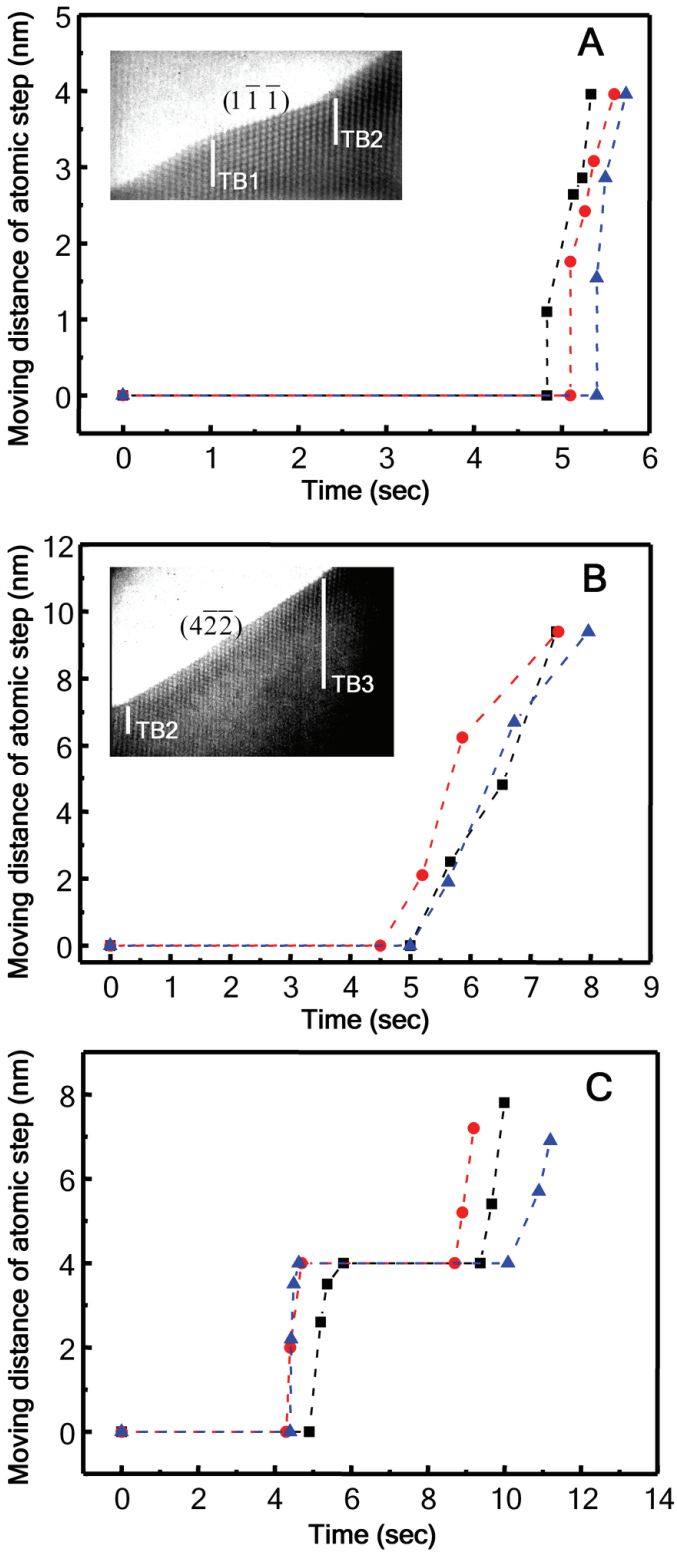
A
$(1\bar{1}\bar{1})$
TB1
TB2
Moving distance of atomic step (nm)
Time (sec)
B
$(4\bar{2}\bar{2})$
TB2
TB3
Moving distance of atomic step (nm)
Time (sec)
C
Moving distance of atomic step (nm)
Time (sec)

Fig. 2.

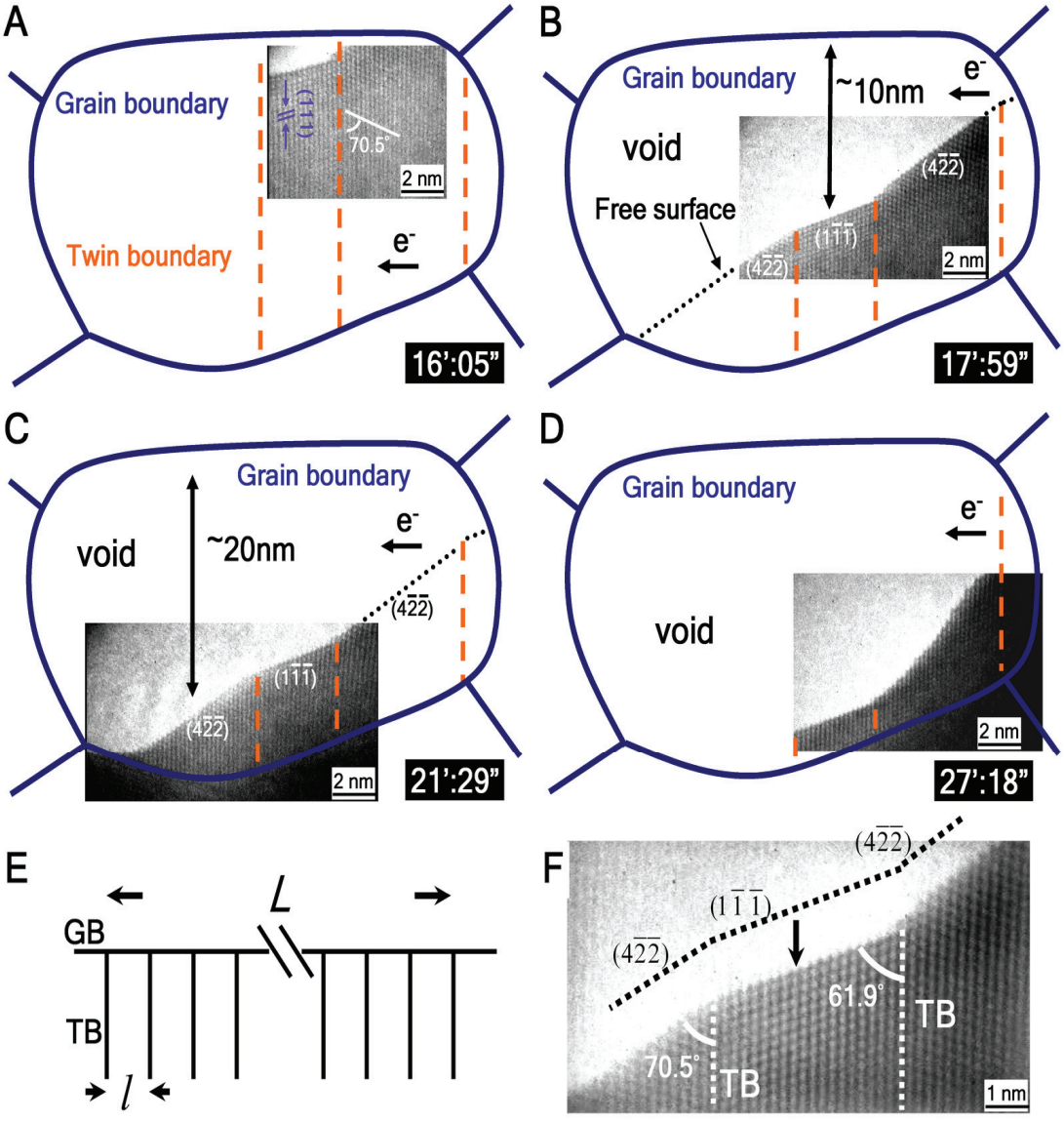
A
Grain boundary
Twin boundary
70.5°
2 nm
e⁻
16':05"
B
Grain boundary
~10nm
e⁻
void
Free surface
2 nm
17':59"
C
Grain boundary
void
~20nm
e⁻
2 nm
21':29"
D
Grain boundary
e⁻
void
2 nm
27':18"
E
L
GB
TB
l
F
61.9°
70.5°
TB
TB
1 nm

Fig. 3.