Recent Advances in Copper Polycrystal Film’s Grain Boundaries Behavior and Its Influence in Properties with Molecular Dynamic Simulation

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Abstract. Copper polycrystal film (CPF) is accepted as a promising material for electroplated film in semiconductor devices for its outstanding conductivity and ductility as well as the good resistance to elector-migration. However, the film material attains a rapid failure in the working environment, and hence the failure mechanism and the fabrication methods require more exploration. In previous studies, it is convinced that grain boundaries (GBs) movement and its interaction with twinning boundaries (TBs) and dislocations have a great influence on the failure process. In this study, the applications of Molecular Dynamic (MD) Simulation in the research of CPF have been introduced. The GBs behaviour including deformation of the GBs and the interaction between GBs and TBs that is observed by dislocation extraction algorithm (DXA) has been summarized, and its relation to the properties such as yield strength and the roughness of growth has been discussed. And the best condition to construct a CPF with magnetron sputtering method is concluded to have substrates in 700K as well as low misorientation with grains under incident atoms of large enough kinetic energy and vertical incident angle.

1. Introduction

Nowadays semiconductor devices have been promoted in both integration density and the minimization of transistors. Copper is a crucial material used in those electronics devices due to its promising conductivity and ductility as well as the good resistance to elector-migration, allowing the copper film to keep stable even when it becomes extraordinarily tiny. Hence, Cu film has been a good material to be equipped as an electroplated film in advanced semiconductor devices. However, it is very hard to have a sustainable copper thin film for its high density of grain boundaries strongly affect the stress migration and the electron migration. So it is very important to understand how the working environment can affect the GBs behaviour and the properties.

MD Simulation is a promising method to analyze the deformation activity at atomic scale and therefore the grain behaviour during the deformation process can be revealed. With MD Simulation, some concerning aspects such as coppers grain or twining boundaries formation and extinction, grains interaction during the growth of the thin film and the mechanism of how grain boundaries interact to affect the properties are discussed in this study. Combining the researches, the evolution of GBs can be better understood and therefore serve for better fabrication of copper film and benefit the future use of copper polycrystal film.
2. Molecular Simulation Research Aspects

2.1. Grain boundaries behaviour during tensile environment

During the study where MD Simulation is used to explore grain boundaries behaviour, the model of grains are usually constructed by phase field method. Phase Field Method is a powerful simulation method for studying multi-scale microscopic evolution, in which the grain boundaries are not necessarily to be calculated as a gradient of order parameter is used to track the grain boundaries. Therefore, Phase Field Method is suitable for studying GBs movements.

The model is often created in two steps. First is to solve the evolution equation of order parameter to construct a phase field:

\[
\dot{\phi}_i = - \sum_{j=1}^{n} \frac{2M_{ij}}{n} \left[ \sum_{k=1}^{n} \left( W_{ik} - W_{jk} \right) \phi_k + \frac{1}{2} \left( a_{ik}^2 - a_{jk}^2 \right) V^2 \phi_k \right] - \frac{8}{\pi} \sqrt{\phi_i \phi_j} \Delta E_{ij}
\]

where \( \phi_i \) is order parameter of grain i, and \( a_{ij}, W_{ij}, \) and \( M_{ij} \) are, respectively, related to the grain boundary thickness \( \delta \), grain boundary energy \( \gamma_{ij} \), and grain boundary mobility \( M_{ij} \):

\[
a_{ij} = \frac{2}{\pi} \sqrt{2\delta \gamma_{ij}}, \quad W_{ij} = \frac{4\gamma_{ij}}{\delta}, \quad M_{ij} = \frac{\pi^2}{8\delta} M_{ij}.
\]

Secondly, the outline of the grains is built and after being filled with atoms in FCC which are of random crystallographic orientation, the model is finally accomplished. The atoms near the GBs are removed and a gap with a width of 3A is created between the adjacent grains in order to allow the GBs to have more time to relax during the MD Simulation.

To test if the model is available for the following tests on grain behaviour, Meng Zhang[1] first measure two parameter, Elastic Young’s modulus at a specific strain rate and the strain rate sensitivity, which reflects the deformation kinetics. Comparing the parameters with experimental results, the fact that this model shows a high capability of testing and observation has been confirmed. That is, with the model some questions about grain boundary behaviour can be answered.

With the model built by phase field method and through the common neighbor analysis and dislocation extraction algorithm(DXA), the formation of twining structures and the interaction between twining boundaries and grain boundaries can be studied. Meng Zhang[2] performs the simulation where the twinning boundaries are considerably studied. Comparing the strain when twinning boundaries come into existence with the strain when the fracture appears, it appears that they are in proportional relation, which can be explained by the mechanism that twinning formation causes the stagnation of the Shockley Partial Dislocation and hence the plastic deformation process is blocked which lead to an early fracture formation. Also, the Grain Boundaries are studied as well. The series of Meng Zhang’s [2][3] researches all show that curved GBs tend to deform more easily compared to the flat GBs in the initial stage. With the comparison between consequences after strain test of different grain construction----one is built in Phase Field Method with curved GBs and the other is shaped in exactly hexagon(Fig.1)----it reveals that the curved GBs are capable of mediating the force between adjacent grains with the deformation of curved GBs because the forces cast on the boundaries are changing according to the curvature of different parts out of Laplace equation, which leads to the phenomenon that the movements of the atoms in the same grain are different. In addition, the expansion of the twinning crystal has been discussed. The motion of the partial dislocation on defective twinning structure is sometimes blocked by the GBs or other defects and hence results in the stress-concentration which drives other nearby partial dislocation to appear and move along the adjacent atom plane(Fig.2). As a consequence, the twining layer start to propagate as it is showed at a strain of 4.90% of Fig.2(a) and 5.24% of Fig.2(b).
Fig. 1 Deformation behaviour of the GBs for the two models:
(a) built with Phase Field Method; (b) built in regular-hexagonal.

Fig. 2 Mechanism of twinning propagation in the 10.85 nm model:
(a) Shockley partial dislocation gliding on the adjacent plane of TBs,
(b) Shockley partial dislocation gliding in the twinned region.
(c) The colors denote the local atomic structure: HCP (red) and unknown structures (white).

2.2. Growth
With MD simulations, the evolution of GBs during the growing process under magnetron sputtering can also be studied. By building boundary layer, thermostat layer and newtonian layer, the kinetic energy of Cu atoms can react with the newtonian layer and conduct the heat to the temperature-stable thermostat layer. With an adatom plane that will release atoms in random spot with a specific regulation, Xuegang Zhu[4] is able to reconstruct the process of epitaxial growth of Cu film. The result shows that under the circumstance that misorientation of the crystal film is low and the impulse kinetic energy is large enough to spread the Cu atoms for further diffusion (which in the research has been measured to be $\geq 5\text{eV}$), the Cu film tend to grow via a layered-island model, which indicates it grows layer by layer and the surface is rather smooth (Fig. 3(a)). Alone ground boundaries with low misorientation that attain less density of dislocation, the dislocations tend to expand remaining their previous morphology during the coming growth, while on the ground boundaries with high misorientation, the dislocations expend parallel to the GB plane with bending structure out of the dislocation interaction. Also, with the increasing rotation angle from 0° to 15°, the crystal ratio keeps decreasing while 15° to 30° keeps increasing (Fig. 3(b)), which can be interpreted by the fact that the Cu face-centered cubic (FCC) structure has a six-degree rotational symmetry operation axis along the [1] crystal direction. Also, by changing the incident angle, it shows a great difference in a surface that when the incident angle is above 30°, there would be a valley structure.
on the grain boundary, making it rough and the surface ratio increase. The increasing temperature of the substrate is found to promote the atoms dispersion as well as to keep the surface smooth. Therefore, by controlling the misorientation between grains, the temperature of the substrate, the kinetic energy of the incident atom and the incident angle, high-quality Cu films with specific density of defects can be produced.

Fig. 3(a) The layer-island model growth of Cu films. The color of the atoms in the figure corresponds to the height of the z-axis. The red atoms represent those at the greatest height, and the blue atoms represent those at the lowest height.

(b) DXA analysis of Cu films crystal ratio with different substrates

Similarly, Zhiqiang Chen[7] runs the simulation and analyzes the result with an RMS roughness value $R_q$ is defined as

$$ R_q = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - \overline{Z})^2}{N}} $$

Where $Z_i$ is the height of the $i$th exposed Cu atom in the z axis perpendicular to the film surface, $\overline{Z}$ is the average height, and $N$ is the total number of exposed Cu atoms.

In the research the connection between surface roughness and temperature of substrate has been discussed. The surface roughness decreases when the temperature of the substrates increases. It can be attributed to the enhanced surface diffusion of deposited atoms due to the increasing substrate temperature. However, high temperature can as well lead to excessive diffusion between Cu atoms and Si substrates, damaging the quality of the Cu film. So comparing the circumstances under different substrate temperature, 700K should be the best choice according to the simulation. The trend corresponds with the research of Xuegang Zhu[4], that the excitation and diffusion of substrate atoms are more likely to occur with increasing substrate temperature. Another discovery has also been mentioned in Xuegang Zhu’s work that at high temperature the high-angle boundaries can change to a low-angle GB, which indicates that under high substrate temperature conditions, the film tends to grow into uniform crystalline structures.

2.3. The mechanism of grain behaviour affects properties

With MD simulation, we can simulate some grain behaviour that could play an important part in the properties such as strength and ductility to understand their roles and mechanism they function in a special structure. Kai Zhou[5] use MD simulation to study gradient nanograin Cu(GNC) film’s tensile behaviours, in which the grain behaviour and the dislocation have also been discussed. Kai Zhou constructs a model with grain size from $\sim 2.5$ nm to $\sim 10.5$ nm, perform the simulation and compare the strain test consequences with that of normal Cu film(Fig.4(a)). It reveals that the gradient distribution of grain size can contribute to the promotion of the film. This is because the gradient lead to an inhomogeneous distribution of tensile stress, which can be predicted by the snapshots (Fig.4(b)) that small size of grains dislocations tend to nucleate and expand first in small size of grains’ boundaries and
later in the larger grains. During this deformation pattern, with relatively low stress concentration in small grains, the grain boundaries keep stable and synergetic strengthening the film with other parts. In contrast, in homogeneous nanograin films the dislocations occur simultaneously in different sizes of the grains and with high stress concentration in small-size grain, the grain boundaries can be break by the interaction between GBs and twinning boundaries or dislocations, causing the grain coarsening and the strength of the material is totally confirmed to the inverse Hall-Petch relation.

At the same time, Ken Suzuki[6] performs a simulation of bicrystal Cu film specimens and mostly focuses on the interaction between vacancies and the grain boundary and the influence of which to the tensile behaviour. Comparing the yielding stress of vacancy and no-vacancy models with the model where vacancies are only distributed in a range within 25 Å from the grain boundary, it is found that the grain boundary vacancy model attains relatively low elongation. Applying the common neighbor analysis to analyze dislocations and slip bands, some HCP structures can be seen, indicating the stacking faults generated by the slip deformation. The analysis shows that with the strain become severe no-vacancy model start to have slippage all over the structure that can not cross the grain boundaries because of the high density of defects near the grain boundary. On the other hand, it is said that in the grain boundary vacancy model, small slip occurred around the grain boundary when the stress is still slightly smaller than the yield stress and the slippage can not propagate away from the grain boundary because of the high density of defects, while the slippage did not occur in the regions outside the high-defect (vacancy) region around the grain boundary. As a consequence, the necking rapidly occurred around the grain boundary and caused the final fracture.

3. Conclusion
In this paper, various aspects about copper polycrystal film that MD Simulation can be used to research have been discussed including the grain boundaries behaviour during tensile environment, the factors during growth that affect the quality of the film as well as the mechanism of how grain behaviour affects properties. The combination of Phase Field Methods and Molecular simulation can significantly benefit the observation of grain boundaries for the growth of grain depends on the free energy and interfacial energy so that grain boundaries in this model are more realistic. With the model the insight of the interaction among GBs, TBs and dislocations is perceived. Also, the substrates temperature and the misorientation between grains play important parts in the growth of the Cu film, and a solution of best was concluded. The mechanism of how grain gradients benefit the yield stress of the material and how the vacancies worsen the ductility are explained in the work as well. So this paper concludes several ways to explore the Cu polycrystal film GBs behaviour, properties and their relation to the working condition and hopefully can inspire future discovery.
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