Effectiveness of a periodic annealing method to coarsen Cu grains in very narrow trenches

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ABSTRACT

We developed a new annealing method, periodic annealing, to effectively coarsen Cu grains in very narrow trenches. In the periodic annealing method, the temperature of the specimen is elevated at a rapid rate to a target temperature and the temperature is oscillated at a certain periodicity. We identified the best oscillation conditions for the system temperature using the phase field simulation method. The best conditions achieved a 98% increase in the grain diameter of the Cu trench model. A preliminary experiment using an actual 70 nm width wire showed about a 10% increase in the grain diameter, confirming the effectiveness of the periodic annealing method to coarsen Cu grains in very narrow trenches.

1. Introduction

In recent years, wiring delay has become more and more significant with downsizing of large-scale integrated circuits. The wire resistance, which is one of the main causes of wiring delay, increases significantly with decreasing wire width. This is attributed to the refinement of grain size and broadening of the grain size distribution [1-3]. To solve this problem, the grain size should be large and its distribution should be uniform and for that, grain size coarsening by heat treatment is necessary. Recently, we have developed a new heat treatment process, rapid thermal annealing using an infrared lamp (RTA), to effectively coarsen the grain diameter [4-6]. Cu thin films were produced by an electroplating method using nominal 9N anode and nominal 6N $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ electrolyte. These specimen films were heat treated by two procedures: conventional isothermal annealing in a hydrogen atmosphere (H_2 annealing) and the RTA. After heat treatment, the average grain diameters and the grain orientation distributions were estimated by electron backscatter diffraction pattern (EBSP). The RTA specimens (400 °C for 5 min) had a larger average grain diameter, more uniform grain distribution and higher ratio of (111) orientation than the H_2 annealing specimens (400 °C for 30 min) had. This meant that the RTA could produce films with coarser and more uniformly distributed grains than H_2 annealing within the short time of only a few minutes. To clarify the grain coarsening mechanism, we simulated grain growth by RTA using the phase field method. The simulated grain diameter reached the maximum at the same order of heating rate as in the actual RTA experiment. The distribution of misorientation of the grains was analyzed and it led us to propose a grain growth model for the RTA process. In the most appropriate heating rate conditions, the coalescence of grains in the heating stage did not occur as frequently as in the low heating rate annealing process. Therefore a large misorientation energy remained in the sample and the grains coarsened rapidly by utilizing the misorientation energy at the isothermal heating stage as suggested by the change of the misorientation distribution.

In the present study, we modified the RTA method and developed a new annealing method, periodic annealing, to effectively coarsen Cu grains in very narrow trenches. The periodic annealing method is such that the temperature of the specimen is elevated at a rapid rate to a target temperature (the same as RTA) and is oscillated at a certain periodicity (while in RTA the temperature is kept at a target temperature). Figure 1 shows a schematic of the RTA and periodic annealing methods. We identified the best conditions of the oscillation of the system temperature using the phase field simulation method. Then a preliminary experiment was performed to confirm the effectiveness of the periodic annealing method to coarsen Cu grains in very narrow trenches.

2. Simulation method

To clarify the effectiveness of the periodic annealing method to coarsen Cu grains in very narrow trenches, we simulated grain growth by the periodic annealing method using the phase field method. The simulation was done for two-dimensional systems to reduce calculation time and deduce a simple picture for grain coarsening.

2.1. Phase field method

As the model for the simulation, the Kobayashi-Warren-Carter poly crystal model [7-9] was used in which the phase field and the orientation field are considered. In this section, the time evolution equation, which should be solved numerically, is briefly described. Rotation of a crystal grain is described by the orientation field θ and by the phase field ϕ . $\phi = 0$ and 1 represent non crystal and perfect crystal phases, respectively. θ and ϕ are both functions of location in space and time and their time developments are described by the governing equations as follows. For the orientation field θ :

$$\begin{aligned} P(\phi, \nabla\theta) \tau_\theta \frac{\delta\theta}{\delta t} &= -\frac{\delta F}{\delta\theta} \\ &= \nabla \cdot \left[h \varepsilon^2 \nabla\theta + g s \frac{\nabla\theta}{|\nabla\theta|} \right] \quad ; \end{aligned} \quad (1)$$

and for the phase field ϕ :

$$\begin{aligned} Q(\phi, \nabla\theta) \tau_\phi \frac{\delta\phi}{\delta t} &= -\frac{\delta F}{\delta\phi} \\ &= \alpha^2 \nabla^2 \phi - \frac{\partial f}{\partial \phi} - \frac{\partial g}{\partial \phi} s |\nabla\theta| - \frac{\partial h}{\partial \phi} \frac{\varepsilon^2}{2} |\nabla\theta|^2 \quad ; \end{aligned} \quad (2)$$

where δF is the variation of the free energy of the system, f is the homogeneous free energy density as a function of ϕ , and g and h are monotonically increasing functions of ϕ that become 0 at $\phi = 0$ ($g = h = \phi^2$ is assumed here). P and Q are kinetic coefficients related to θ and ϕ respectively, τ_θ and τ_ϕ are relaxation times, ε is interface thickness, and s and α represent gradient correction factors of θ and ϕ , respectively. P is expressed as

$$P = P(\varepsilon |\nabla \theta|) \quad (3)$$

$$P(w) = 1 - e^{-\beta w} + \frac{\mu}{\varepsilon} e^{-\beta w},$$

where β and μ are correction factors for the misorientation field, $\varepsilon |\nabla \theta|$. $Q = 1$ is assumed according to Ref. [10].

2.2. Simulation of the heat treatment process

The system used for the simulation was 4.41 μm long and 1.32 μm high. The system was divided into many areas by Voronoi division such that the average area of the grains was the same as that of the Cu ultra fine wire before annealing, and for each divided area, the initial orientation was randomly set. This lattice, shown in Fig. 2(a) as the gray scale representation of an orientation field, was used as the initial structure of the poly crystal before heat treatment. The phase field parameters of Cu ultra fine wire as determined by using the method of Ref. [10] were used here and they are shown in Table 1. The system was divided into 1000×300 meshes (the length of a mesh was 4.41 nm) and equations (1) and (2) were numerically solved where the time was discretized by 1/300 s.

In order to investigate influence of periodic annealing on grain diameter, the heat treatment process was simulated in such a way that a constant rate heating was followed by isothermal annealing or sinusoidally changing the temperature around the target temperature. Two values of heating rates, 0.5 and 5 K/s, were examined, and target temperature of isothermal annealing was 673 K. The heating rates 0.5 and 5 K/s were typical for the conventional heating and RTA processes, respectively. The two types of specimen models, thin film and wire in trench models, were set as follows. For the thin film model, all the meshes had the same phase field parameters as in Table 1. For the wire in the trench model, however, the parameter τ_θ at the peripheral region of the trench was set as one-tenth of that at the inner region of the trench. The boundary of the peripheral and inner regions of the trench is indicated by solid lines in Figs. 2 (d) and (e). Figures 2 (b), (c), (d) and (e) show the phase fields just after the heating stage from 373 to 673 K. The heating rates and models were: (b) 5 K/s, film; (c) 0.5 K/s, film; (d) 5 K/s, wire; (e) 0.5 K/s, wire. It should be noted that the grains were finer for RTA than for conventional heating when comparing the same model, and they were finer for the wire than for the film when comparing the same heating rate.

For the phase field $\phi(\vec{r}, t)$ obtained by the present simulation, cluster analysis was performed using the Hoshen-Kopelman algorithm [11]. This procedure identifies

individual grains in the simulation specimen. The average grain radius, assuming a perfectly circular grain, could be estimated from the average area of one grain obtained by dividing the calculated area by the total number of grains. Thus the average grain diameter was obtained as a function of the heating rate.

3. Experimental method

Cu thin films were deposited by an electroplating method into a trench coated with Ta/TaN barrier metals and Cu seed layers in that order. The thickness of the Cu seed layer was 50 nm and that of the electroplated Cu thickness was 200 nm. Figure 3 shows a cross-sectional view of the trench. The areas deposited on the top and bottom of the trench, indicated by the open ovals, were examined by EBSP analysis. Field ion beam (FIB) was utilized to remove the over layer. Figure 4 shows a schematic of the electroplating apparatus. A chip was attached on the top of a rotating electrode and electroplated at a rotation speed of 1000 rpm. The rotation allowed sufficient stirring of electrolyte and led to uniform plating of Cu onto the substrate. In the conventional plating method, nominal purities of the electrolyte and anode plate were 3N and 4N, respectively, and the plate contained phosphorous. In the present plating method (hereafter abbreviated as the 6N9N process), however, the nominal purities of electrolyte and anode plate were 6N and 9N, respectively, and the plate was phosphorous free. Electrolyte bath additives were used for the 6N9N process. We found that the additives lowered the purity of the Cu deposits and suppressed the grain growth of Cu. However, the effect of the additives on the Cu deposits was the same for the conventional and the 6N9N processes. Therefore we concluded that purification of electrolyte and anode plate made it possible to suppress impurity segregation at the grain boundary which would otherwise disturb the grain growth as reported in Ref. [12].

The obtained specimens were annealed by two procedures, RTA and periodic annealing, and their temperature diagram is shown in Fig. 5. The specimens were heated very rapidly (3 K/s) to a target temperature of 450 °C in a vacuum of 3×10^{-3} Pa using an infrared lamp in the heating process. Then the periodic annealing was continued for 12 min and the temperature was changed in 3 periods of a trapezoidal pattern, such that the average temperature was 450 °C and the amplitude of the temperature change was 100 K and the time kept at the maximum and minimum temperatures was 1 min each. It should be noted that the applied thermal energy was the same between the RTA and periodic annealing processes. After annealing, the average grain diameters and the grain orientation distributions were examined by EBSP analysis.

4. Results and discussion

4.1. Simulation experiment

Figure 6 shows the square of the average grain diameter for the specimens shown in Fig. 2 as a function of the amplitude and the periodicity of the sinusoidal cyclic temperature variation. The heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire. For each case we found the most appropriate conditions to obtain the largest average grain diameter, as presented in Table 2. The appropriate conditions were in the range of 40 – 70 K for the temperature amplitude and 10 – 30 s for the periodicity. Figure 7 shows the time change of the square of the average grain diameter for each specimen at its most appropriate conditions (Table 2), and after isothermal annealing. The two lower images of each figure part represent the final states of the phase field for the most appropriate conditions and the isothermal treatment, respectively. We saw from the phase field maps that the small grains merged to form larger grains in the most appropriate conditions, compared to the grains formed in the isothermal treatment. It was also noteworthy that the RTA wire model showed abnormal grain growth at the end of the annealing as seen in Fig. 7 (c).

4.2. Actual experiment

Figure 8 shows the cross-sectional SEM images of the wires buried in the trenches with widths of 70 nm. The overlayers were removed by chemical mechanical polishing after annealing. The top layers were removed gradually using FIB and the average grain diameters and the grain orientation distributions were examined by EBSD analysis. The distances where the measurements were done from the bottom were 75 and 160 nm, where the depth of the trench was 200 nm.

Figure 9 shows the typical EBSD observation results for the specimens: (a) trench width 70nm, the distance from the bottom 160nm, periodic annealing (abbreviated as W70D160P), (b) trench width 70nm, the distance from the bottom 160nm, isothermal annealing (abbreviated as W70D160I), (c) W70D75P, and (d) W70D75I. Table 3 summarizes the average grain diameter obtained from the EBSD data. From Table 3, we saw that the periodic annealing increased the average grain diameter of a narrow wire (70 nm width) near the bottom (distance from the bottom 75 nm) by about 10 % compared to the isothermal annealing.

4.3. Discussion

For the narrow wire, which is important for the next generation LSIs, the experimental results can be interpreted as follows (Fig. 10). Initially, the grains are very fine, on the order of 30 nm, throughout the whole wire. Then the specimen is rapidly heated. At the end of the heating stage, a difference between the upper and bottom parts of the wire appears: the diameter of the grains at the bottom still remains small, while that at the upper part becomes large. This is attributed to the strong attractive force that the bottom walls have on the Cu grains in the wire. Because of this effect, grain growth at the bottom part is attenuated under isothermal annealing. In contrast, the periodic annealing frees the constraints on grain growth by using the high temperature in the temperature pattern. Therefore we get larger grains by periodic annealing than by isothermal annealing.

The results for an actual preliminary experiment showed about a 10% increase in the grain diameter, confirming the effectiveness of the periodic annealing method to coarsen Cu grains in very narrow trenches. Unfortunately, we have no data to compare conventional anneal with the new periodic anneal at the present. For that purpose, we are now working on the measurement and will report elsewhere. The discrepancy of the increase ratio of the grain diameter between the simulation and the actual experiment can be attributed to impurity atoms. In the previous research, we analyzed by glow discharge mass spectrometry (GDMS) the impurities in Cu films formed by plating with and without additives using high-purity and low-purity plating materials [13]. The result showed that the total impurities in Cu films were decreased clearly by using the high purity plating materials. Especially, the amount of impurities like O, C, Cl, Ti and Fe, which may suppress grain growth during annealing, were reduced (see Table I in reference [13]). Resistivities as a function of holding time at the peak temperature for the 60 nm wide Cu wires made with additive-free plating using high-purity plating materials (6N electrolyte/8N anode process) and high-heating rate annealing at 1.7 K/s were also measured (see Fig. 10 in reference [13]). Resistivities of 60 nm wide Cu wires formed with additive-free plating and high-heating rate annealing to both 573 K and 673 K decrease with increasing holding time and they have almost the same value for 10 min holding at peak temperature. These resistivities are about 14% lower than those of Cu wires made with additives and high-heating rate annealing for 10 min holding at 573 K, and more than 50% lower than those for Cu wires made by plating with additives using low-purity plating materials (3N electrolyte/4N anode process) and by conventional H₂ annealing with low heating rate of 0.1 K/s and longtime holding of 30 min at peak temperature of 573 K. We also found that Fe and Ti atoms segregated at the grain boundaries of a very narrow Cu wire using *C_s*-corrected STEM. Based on the ab initio calculation, we estimated the segregation energy for the impurities at the Cu grain boundary and found the pinning mechanism to suppress the grain boundary movement. These results will be reported

elsewhere.

Smaller top opening or deeper trench will reduce the grain size. Concerning the effects of trench depth on the grain size, we have evaluated the grain size distributions of less than 100 nm wide Cu interconnects made by DC electroplating by the X-ray diffraction method [14]. The mean grain size of the annealed Cu interconnects was found to be expressed as a linear function of the product of the overburden Cu film thickness times the ratio of the interconnect trench width to depth. This linear relationship describes how to use the interconnect parameters like the thickness of the overburden Cu film and the depth and width of the trench to evaluate the mean grain size in narrow annealed Cu interconnects up to 50 nm wide. For the effects of smaller top opening of the trench, we found that the effects of the electrolyte flow on the void generation in the narrow trenches with small and large top opening were investigated both by an actual electrodeposition experiment and numerical simulation [15]. We observed the Cu film formation process as a function of time and found that the flow of Cu electrolyte solution is not homogeneous in the trench, resulting in void formation at one side of the trench wall during plating. Numerical analysis of the Cu electrolyte solution flow clarified that Cu ion transportation is lowered substantially by the generation of two vortices in the wire trench when the wire width is less than 50 nm. We proposed a method to enhance transportation of Cu ions by enlarging the open angle at the top edge of the trenches to prevent void formation. The effect of the method for void-free filling was predicted by the numerical analysis of the Cu electrolyte solution flow and confirmed by the actual filling experiment of Cu into the wire trench with 60nm width. We also found that the grain size can be enlarged using the trench with large opening by phase field simulation, and will report elsewhere.

5. Conclusions

We developed a new annealing method, periodic annealing, to effectively coarsen Cu grains in very narrow trenches. The periodic annealing method raises the temperature of a specimen at a rapid rate to the target temperature and then the temperature is oscillated at a certain periodicity. We searched for the best conditions for the oscillation of the system temperature using the phase field simulation method. The best conditions achieved a 98% increase in grain diameter for the simulation Cu trench model. The results for an actual preliminary experiment showed about a 10% increase in the grain diameter, confirming the effectiveness of the periodic annealing method to coarsen Cu grains in very narrow trenches.

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References

- [1] T. Fujikawa, T. Onishi, and T. Sato, Jpn. J. Appl. Phys. 40 (2001) 2191.
- [2] W. Steinhögl, G. Schindler, G. Steinlesberger, and M. Engelhardt, Phys. Rev. B 66 (2002) 075414.
- [3] The International Technology Roadmap for Semiconductors (ITRS), 2012 edition, 2012.
- [4] J. Onuki, K. Khoo, Y. Sasajima, Y. Chonan, and T. Kimura, J. Appl. Phys. 108 (2010) 044302.
- [5] J. Onuki, K. Tamahashi, T. Namekawa, and Y. Sasajima, Mater. Trans. 51 (2010) 1715.
- [6] Y. Sasajima, J. Kageyama, K. Khoo, and J. Onuki, Thin Solid Films 518 (2010) 6883.
- [7] R. Kobayashi, J. A. Warren, and W. C. Carter, Physica D 119 (1998) 415.
- [8] R. Kobayashi, J. A. Warren, and W. C. Carter, Physica D 140 (2000) 141.
- [9] J. A. Warren, R. Kobayashi, A. E. Lobkovsky, and W. C. Carter, Acta Mater. 51 (2003) 6035.
- [10] J. Kageyama, Y. Sasajima, M. Ichimura, and J. Onuki, Mater. Trans. 48 (2007) 1998.
- [11] J. Hoshen, and R. Kopelman, Phys. Rev. B 14 (1976) 3428.
- [12] J. Onuki, S. Tashiro, K. Khoo, N. Ishikawa, T. Kimura, Y. Chonan, and H. Akahoshi, J. Electrochem. Soc. 157 (2010) H857.
- [13] J. Onuki, Y. Sasajima, K. Tamahashi, Y. Q. Ke, S. Terada, K. Hidaka, and S. Itoh, J. Electrochem. Soc. 160 (2013) D3266.
- [14] T. Inami, K. Hidaka, S. Terada, and J. Onuki, ECS Electrochem. Lett. 2 (2013) D49.
- [15] Y. Sasajima, T. Satoh, K. Tamahashi and J. Onuki, Materials Transactions 53 (2012) 1507.

Table 1

Phase field parameters for grain growth simulation of Cu [10].

$$\varepsilon = 0.0125$$

$$\alpha = 0.0135$$

$$s = 0.0235$$

$$\tau_{\phi} = 0.1$$

$$\tau_{\theta} = 20.5 \exp(-0.0907 \times 2950 \exp(-2630/T))$$

Table 2

The most appropriate conditions to obtain the largest average grain diameter for each model shown in Fig. 2.

specimen model	heating time [s]	maximum average grain diameter [nm] by periodic annealing	average grain diameter [nm] by isothermal annealing	ratio	most appropriate annealing conditions	
					amplitude of temperature variation [K]	period [s]
Film	60	414	292	1.42	50	10
Film	600	382	342	1.12	70	20
Wire	60	402	203	1.98	40	30
Wire	600	316	221	1.43	55	30

Table 3

Average grain diameters of a narrow wire with trench width 70 nm obtained from the EBSP data.

distance from the bottom [nm]	grain diameter [nm] after periodic annealing	grain diameter [nm] after isothermal annealing	ratio
160	114	112	1.02
75	97.7	88.0	1.11

Figure captions

Fig. 1. Schematic of RTA and periodic annealing methods.

Fig. 2. Gray scale representation of phase field. (a) The initial structure of the polycrystal specimen before heat treatment. (b)-(e) Representation for specimens after the heating stage from 373 to 673 K. Heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Fig. 3. Cross-sectional view of the trench.

Fig. 4. Schematic of the electroplating apparatus.

Fig. 5. Temperature patterns of (a) RTA and (b) periodic annealing for the actual experiment.

Fig. 6. Square of the average grain diameter for the specimens shown in Fig. 2 as a function of the amplitude and the periodicity of the sinusoidal cyclic temperature variation. The heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Fig. 7. Time change of the square of the average grain diameter and the final phase field maps for the specimens shown in Fig. 2. The heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Fig. 8. Cross-sectional SEM images of the trenches with width 70 nm.

Fig. 9. Typical EBSD observation results for the specimens: (a) trench width 70nm, the distance from the bottom 160nm, periodic annealing (abbreviated as W70D160P); (b) trench width 70nm, the distance from the bottom 160nm, isothermal annealing

(abbreviated as W70D160I); (c) W70D75P, and (d) W70D75I. The graphs (c') and (d') show the respective grain size distributions of W70D75P and W70D75I.

Fig. 10. Schematic to explain the actual experiment for a narrow wire.

Figure(s)

Figure 1. Schematic of (a) RTA apparatus and (b) periodic annealing methods.

(a)

(b)

(c)

Figure 2

(d)

(e)

Figure 2. Gray scale representation of phase field. (a) The initial structure of the poly crystal specimen before heat treatment. (b)-(e) Representation for specimens after the heating stage from 373 to 673 K. Heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Figure 3 Cross-sectional view of the trench.

Figure 4 Schematic of the electroplating apparatus.

Fig.5 Temperature patterns of (a) RTA and (b) periodic annealing for the actual experiment.

Fig.6 (a)

Fig.6 (b)

Fig.6 (c)

Fig.6 (d)

Fig. 6 Square of the average grain diameter for the specimens shown in Fig. 2 as a function of the amplitude and the periodicity of the sinusoidal cyclic temperature variation. The heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Fig.7 (a) FilmRT60s

FilmRT60s_50K10s

FilmRT60s_isothermal

Fig.7 (b) FilmRT600s

FilmRT600s_70K20s

FilmRT600s_isothermal

Fig.7 (c) WireRT60s

WireRT60s_40K30s

WireRT60s_isothermal

Fig.7 (d) WireRT600s

WireRT600s_55K30s

WireRT600s_isothermal

Fig. 7 Time change of the square of the average grain diameter and the final phase field maps for the specimens shown in Fig. 2. The heating rates and models were: (a) 5 K/s, film; (b) 0.5 K/s, film; (c) 5 K/s, wire; (d) 0.5 K/s, wire.

Fig.8 Cross-sectional SEM images of the trenches with the width70 nm.

Fig. 9 Typical EBSD observation results for the specimens: (a) trench width 70nm, the distance from the bottom 160nm, periodic annealing (abbreviated as W70D160P) ; (b) trench width 70nm, the distance from the bottom 160nm, isothermal annealing (abbreviated as W70D160I); (c) W70D75P, and (d) W70D75I.

Fig.10 Schematic to explain the actual experiment for a narrow wire.

Periodic annealing

Isothermal annealing