УДК 669.3:539.89:539.25

Влияние температуры отжига на структуру электроосажденной нанокристаллической медной проволоки

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Effect of annealing temperature on structure of electrodeposited nano-scale copper wires

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Высокоразрешающий анализ картин дифракции обратно-рассеянных электронов (EBSD) использован для исследования эволюции структуры электроосажденной нанокристаллической проволоки после отжига в широком диапазоне температур. Показано, что структура проволоки после отжига стабильна в нижней части тренча. Отмечено наличие большой доли малоугловых границ и двойников отжига.

Ключевые слова: электроосаждение; медь; структура; нанокристаллический; EBSD-анализ.

High-resolution electron backscatter diffraction (EBSD) technique was employed to investigate structure evolution of electrodeposited and subsequently annealed nano-scale copper wires. The grain structure was found to be stable in the bottom area of a trench during the annealing process. The material was shown to exhibit a large fraction of low-angle boundaries as well as annealing twins.

Keywords: electrodeposition; copper; structure; nano-crystalline; Electron backscatter diffraction.

Introduction

The pronounced trend towards miniaturization of electronic devises is prompting a reduction of interconnect width down to a nano-scale. For manufacturing of such interconnects, a copper damascene process is currently used. Generally, it involves a preliminary etching of a silicon substrate to form a line pattern (i.e. the damascene trenches) and final electrodeposition of copper to fill them up. The excess of copper is then removed by chemical-mechanical polishing process.

The decrease of the interconnector width, however, gives rise to a notable increase in electrical resistivity. This effect is believed to be associated with expected approaching of the copper grain size to the mean free path of electrons (~40 nm at ambient temperature) and related scattering of electrons on grain boundaries. There is a strong need, therefore, to produce as much as possible coarse grained structure in the interconnectors [1-3]. In this regard, an annealing behavior of the electrodeposited copper wires becomes of particular practical importance. Despite the critical significance of this problem for progress in semiconductors industry, only little works have been reported in this area [e.g. 4-5] and structural behavior of the interconnectors during annealing is virtually unknown. Attempting to fill this gap in our knowledge, this work presents a detailed study of microstructure evolution of the electrodeposited copper wires in a wide range of annealing temperatures.

Experimental procedure

Damascene trenches (80 nm wide and 200 nm height) were patterned in SiO_2/Si dielectric films using electron beam lithography and reactive ion etching. An ultra-thin TaN/

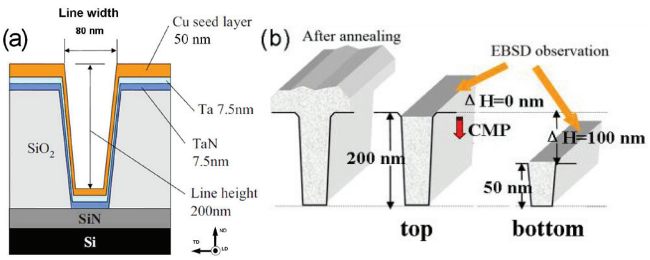


Fig. 1. (a) schematic representation of a trench cross section before electroplating with a superimposed reference frame; (b) schematic drawing of sample preparation by CMP for EBSD observation

Ta (7.5 nm/7.5 nm) layer was first sputter-deposited on the trenches as a diffusion barrier and adhesion layer, followed by sputter deposition of a 50 nm copper seed layer to serve as the cathode for electroplating. Figure 1a is a schematic drawing of the trench structure. The reference directions employed were denoted as longitudinal direction (LD), transversal direction (TD) and normal direction (ND).

The copper interconnectors were made by a normal DC electroplating process at room temperature and a current density of 5 mA/cm^2. In order to eliminate impurities, a high purity 99.999999% (8N) copper anode and 99.9999% (6N) $CuSO_4{\cdot}5H_2O$ copper electrolyte were used. Organic additives were also added to the solution to enhance the filling capability of copper. The total plating time was 162 s, and the thickness of the electroplated layer was 300 nm. After completion of the electrodeposition process, the obtained samples were immediately washed with distilled water and dried with argon gas.

To investigate the influence of annealing at different temperature on the structure of copper wire, the obtained material was annealed at 1.7 deg per second with temperature of 300°C, 400°C, 500°C and 600°C for 10 minutes in vacuum (5x10^{-5} Torr) immediately after the finishing of electrodeposition process. The time between EBSD observation and the annealing was about 18 hours. Samples after annealing were stored in vacuum.

All microstructural observations were made on the longitudinal (i.e. LD-TD) plane. To evaluate the features of microstructure, the observations were made at the trench heights of 50 nm and 200 nm, which correspond to bottom and upper parts of the deposits, respectively (fig. 1b). Chemical mechanical polishing (CMP) was applied to remove the excess copper and TaN/Ta layers from the trenchers as well as to get the EBSD final surface finish.

The high-resolution electron backscatter diffraction (EBSD) analysis was performed with a Hitachi S-4300SE field emission gun scanning electron microscope equipped with a TSL OIM^{TM} EBSD system. A triangular scanning grid was employed for orientation mapping. The EBSD maps were acquired with a scan step size of 30 nm. To improve the reliability of the EBSD data, small grains comprising three or fewer pixels were automatically removed from the maps using the standard grain-dilation option in the TSL software. Due to limited experimental accuracy of EBSD, a lower limit boundary misorientation cut-off of 2° was used. A 15° criterion was used to differentiate low-angle boundaries (LABs) and high-angle boundaries (HABs).

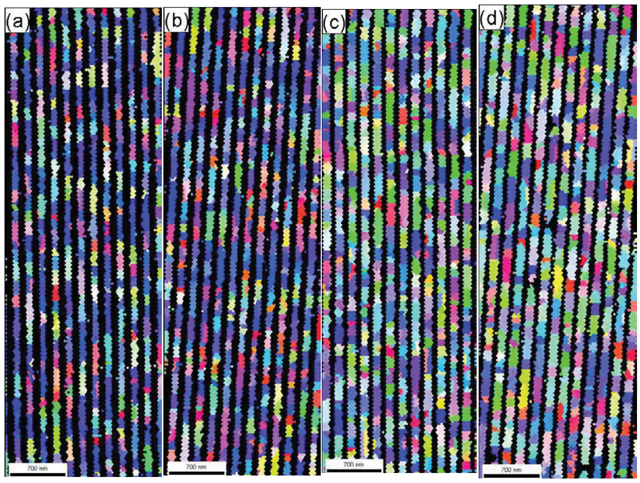
Results and discussion

Structure morphology and grain size

Typical EBSD maps of the electrodeposited copper wires after annealing in wide temperature interval (300–600 °C), obtained from the trench heights of 50 nm and 200 nm, are presented on figs. 2 and 3, respectively. It is seen that the structure of the copper wires resembles a bamboo consisting of a sequence of grains spanning across entire wire width. Moreover, the structure at trench height of 200 nm seems to be coarser than that at 50 nm. This may be evidence that the grain growth was easier in this area. Taking into account that the wire width was 80 nm, the underlying grain structure was nanocrystalline in nature at least in one dimension.

The grain size distributions measured at different heights of the trenches are summarized in fig. 4a and b. In all cases, the grain areas in an EBSD map were measured and the equivalent grain diameters were calculated assuming each grain to be a circle (grain reconstruction method [6]). The term "grain" in the present work refers to a crystallite bordered by a continuous boundary having a misorientation of >15°.

The grain size distributions in case of trench height 50 nm were broadly similar and very close to each other being single-modal and centering near ~ 150 nm (fig. 4a).



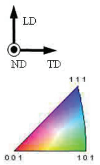


Fig. 2. Inverse pole figure EBSD maps obtained from the electrodeposited copper wires (at the trench height of 50 nm) after annealing at: (a) 300 °C; (b) 400 °C; (c) 500 °C; and (d) 600 °C. A color code triangle is given in the bottom left corner.

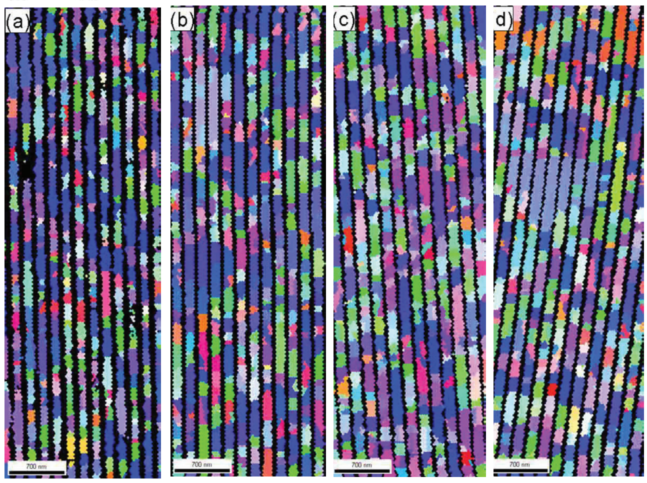


Fig. 3. Inverse pole figure EBSD maps obtained from the electrodeposited copper wires (at the trench height of 200 nm) after annealing at (a)300 °C; (b) 400 °C; (c) 500 °C; and (d) 600 °C.

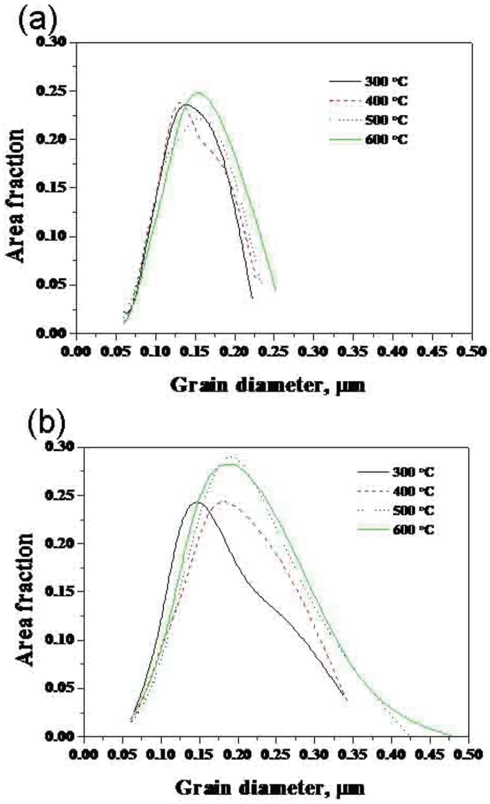


Fig. 4. Distributions of grain size measured at different heights of trench using the grain reconstruction method: (a) height 50 nm; (b) height 200 nm.

In other words, there is no large difference in average grain size after different temperature annealing. That is the structure in the bottom area remains stable after annealing in wide interval of temperature. One of the possible explanations for this phenomenon is stabilization of grain growth by impurities [4,5,7]. On the other hand, the grain-size distributions in case of the trench height of 200 nm shifted towards coarser grain size with annealing (fig. 4b).

Attempting to obtain an additional insight into grain structure evolution process, the grain size was also measured by using the linear intercept method. Taking into account the bamboo morphology of the microstructure, only longitudinal grain size was evaluated. The obtained results were summarized in fig. 5. It is seen that the results were broadly similar to that obtained by the grain reconstruction method (fig. 4). The typical grain lengths in the bottom area of the trench were close to 150 nm (fig. 5a). In the top area, there was a little increase in a fraction of coarse grains with increasing of annealing temperature up to 600 °C (fig. 5b). A muted grain growth is also evident from fig. 5c.

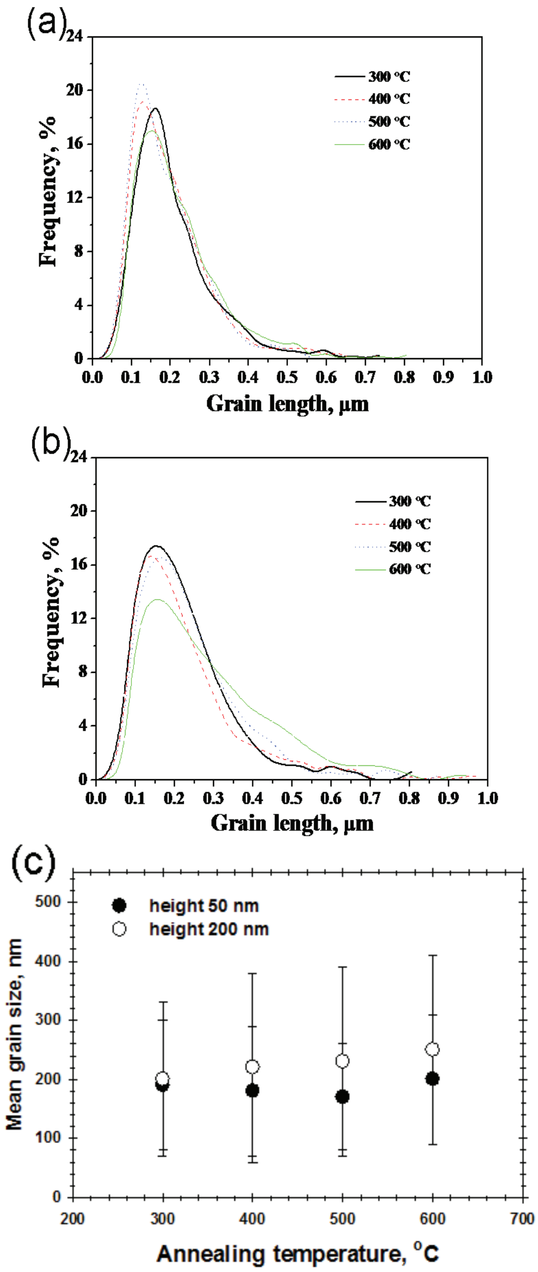


Fig. 5. Distributions of grain size measured at different heights of trench using the linear intercept method: (a) height of 50 nm; (b) height of 200 nm; (c) mean grain size. In (c), error bars show standard deviation of measurements.

Misorientation distribution

The EBSD data were also used to quantify the evolution of the misorientation-angle distribution in the bottom and top areas (figs. 6a and b, respectively). It is seen that the misorientation-angle distributions are broadly similar to each other. In both cases, they were characterized by large fraction of LABs and sharp peaks near 60°. The EBSD measurements revealed that substructure of LABs dominated after 300 °C annealing. With increasing of temperature, however, the LAB fraction decreased significantly. Elimination of some portion of the LABs can be explained by the migrating grain boundaries during annealing. On the other hand, high-angle part of the distributions was featured by a sharp peak near 60°. Grain growth in some face-centered cubic metals is known to be frequently accompanied by the formation of annealing twins [8]. In our study, the annealing twins became more dominant with increasing temperature (fig. 6) thus indirectly indicating grain growth.

In addition to the annealing twinning mentioned above, twinning in copper is also possible during the electrodeposition process. In this regard, it is interesting to examine the nature of twins in present cases. It is believed that the misorientation across the boundaries of the twins originating from the electrodeposition may deviate significantly from the ideal twin–matrix relationship due to significant internal stresses inherent to the material. On

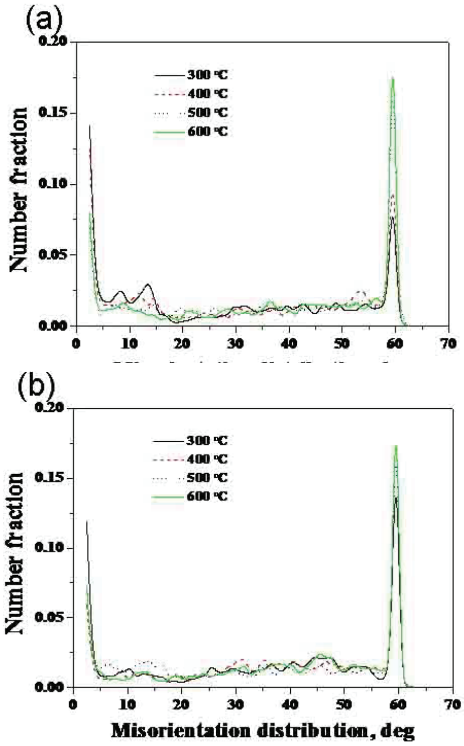


Fig. 6. Misorientation angle distributions: (a) height 50 nm; (b) height 200 nm

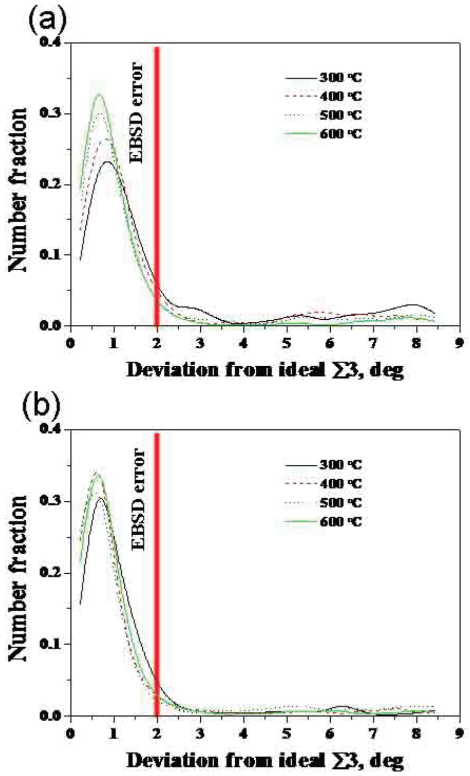


Fig. 7. Deviation of measured twin misorientations from the ideal Σ3 relationship: (a) height 50 nm; (b) height 200 nm.

the other hand, the misorientation across the boundaries of annealing twins would be expected to be close to the ideal 60° rotation about a <111> direction, because such twins do not undergo deformation [9]. Thus, the deviation from the ideal Σ3 misorientation may be used as a criterion to separate mechanical twins from annealing twins. The distributions of the misorientation perturbation along the twin boundaries (within the Brandon interval) for the two areas – the bottom and top parts of the trench – are shown in figs. 7a and b, respectively.

It is seen that in both cases the deviations of the measured misorientations of the twin boundaries from the ideal Σ3 were found to be small and typically lay within the experimental EBSD error (2°). This latter observation indicates that the twin boundaries have primarily originated from annealing.

Conclusions

In present work, high-resolution EBSD technique was used to investigate the influence of annealing temperature on structure evolution in nano-scale electrodeposited copper wires. The main conclusions are as follows.

1) The grain size in the bottom part of the trench was somewhat finer than that in upper part of the trench.

2) In all cases, misorientation angle distribution was characterized by a presence of notable proportion of LABs as well as significant fraction of Σ3 annealing twin boundaries.

2) The structure in the bottom area of a trench remains stable after annealing at 300-600°C whereas some evidences of grain growth were found in the top part of the trench. In general, the microstructure is surprisingly stable despite its very fine grained nature. The reason for this effect is not clear.

Financial support from Grants-in-aid for Science Research (Contract Nos. 17206071 and 20226014) and from JST is gratefully acknowledged. The authors are very grateful to Nippon & Metal Co., Ltd. for supplying the high purity electroplating solution and ultrahigh purity anode copper plate. They also would like to Mr. T. Namekawa for technical assistance.

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