Thin Solid Films 518 (2010) 6883–6890

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Grain coarsening mechanism of Cu thin films by rapid annealing

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ARTICLE INFO

Article history:
Received 13 October 2009
Received in revised form 8 July 2010
Accepted 8 July 2010
Available online 14 July 2010

Keywords:
Copper thin films
Rapid thermal annealing
Electron backscattering analysis
Grain growth
Simulation
Phase field method

ABSTRACT

Cu thin films have been produced by an electroplating method using nominal 9N anode and nominal 6N $CuSO_4 \cdot 5H_2O$ electrolyte. Film samples were heat-treated by two procedures: conventional isothermal annealing in hydrogen atmosphere (abbreviated as H_2 annealing) and rapid thermal annealing with an infrared lamp (abbreviated as RTA). After heat treatment, the average grain diameters and the grain orientation distributions were examined by electron backscattering pattern analysis. The RTA samples (400 °C for 5 min) have a larger average grain diameter, more uniform grain distribution and higher ratio of (111) orientation than H_2 annealed samples (400 °C for 30 min). This means that RTA can produce films with coarser and more uniformly distributed grains than H_2 annealing within a short time, i.e. only a few minutes. To clarify the grain coarsening mechanism, grain growth by RTA was simulated using the phase field method. The simulated grain diameter reaches its maximum at a heating rate which is the same order as that in the actual RTA experiment. The maximum grain diameter is larger than that obtained by H_2 annealing with the same annealing time at the isothermal stage as in RTA. The distribution of the misorientation was analyzed which led to a proposed grain growth model for the RTA method.

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 distribution should be uniform and grain size coarsening by heat treatment is necessary.

In the present study, Cu thin films were produced by an electroplating method using nominal 9N anode and nominal 6N $CuSO_4 \cdot 5H_2O$ electrolyte [4]. The plated films were annealed by two different annealing processes, i.e., conventional isothermal annealing in H_2 atmosphere (H_2 annealing) and rapid thermal annealing using an infrared lamp (RTA). The average grain diameter and the grain orientation distribution were estimated by electron backscattering pattern (EBSP) analysis for the obtained samples. Based on the present experiments, the most appropriate annealing process is proposed to obtain Cu wire with uniform and coarsened grains. In addition, grain growth by RTA was simulated using the phase field method to clarify the grain coarsening mechanism and to propose its grain growth model.

2. Experiments

2.1. Sample preparation and experimental procedure

Cu thin films were deposited by an electroplating method onto TEG (test element group) chips coated with Ta/TaN barrier metals and Cu seed layers in this order. The thickness of the Cu seed layer was 50 nm and that of the electroplated Cu thickness was 200 nm. Fig. 1(a) shows a magnified top view of a TEG chip. The area deposited on the voltage and current pad was examined by EBSP analysis. Fig. 1(b) 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 are 3 N and 4 N, respectively, and the plate contains phosphorous. In the present plating method (hereafter abbreviated as the 6N9N process), however, the nominal purities of electrolyte and anode plate were 6 N and 9 N, 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 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 grain boundary which would otherwise disturb the grain growth as reported in [4].

The obtained samples were annealed by two procedures, H_2 annealing and RTA, and schematics of the apparatuses are shown in

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doi:10.1016/j.tsf.2010.07.039

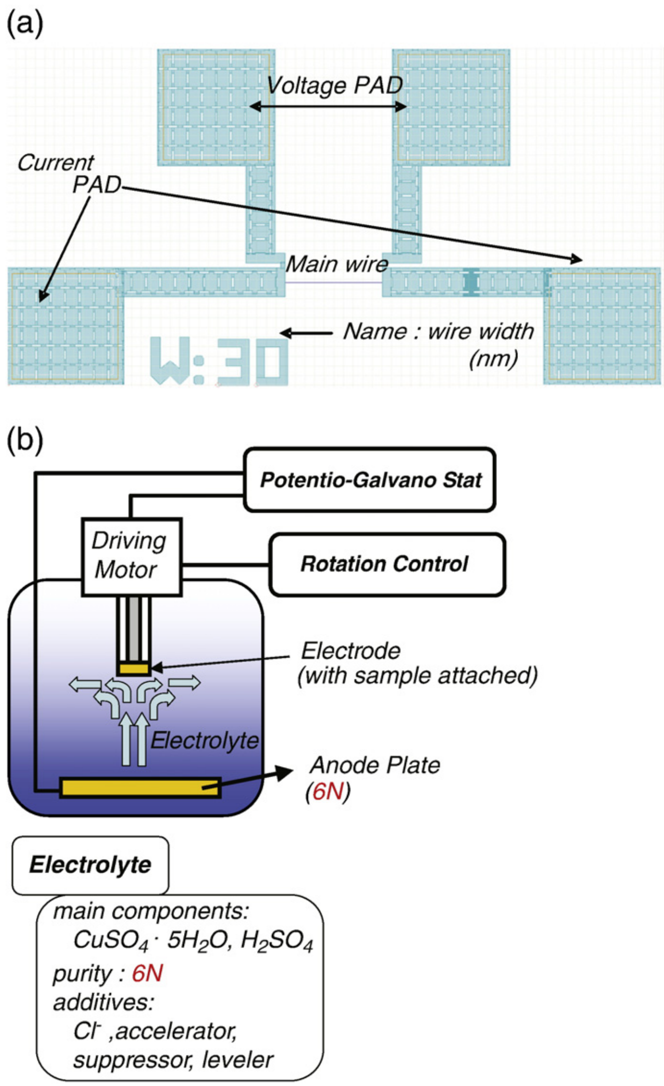

Fig. 1. (a) Magnified top view of a TEG chip and (b) schematic of plating apparatus.

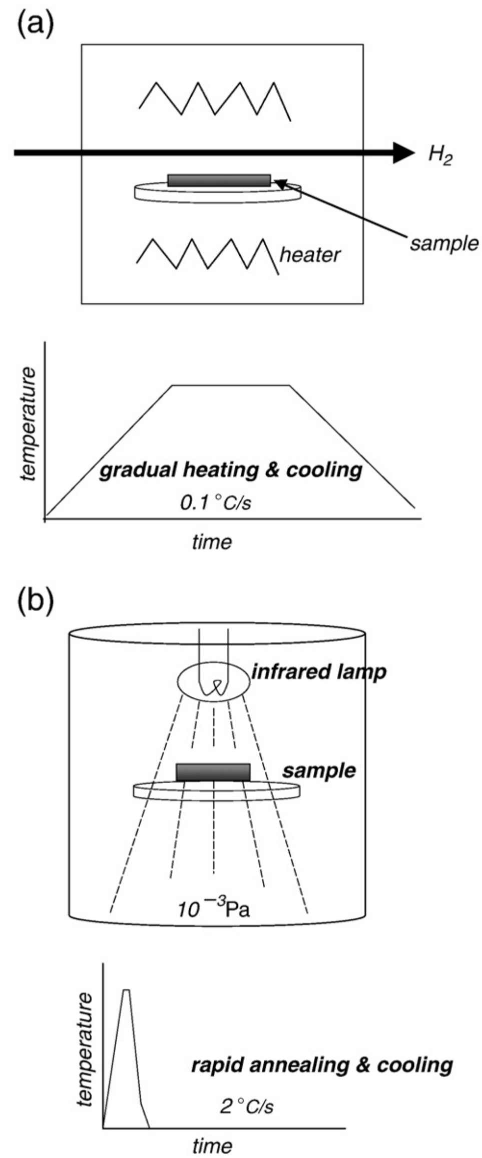

Fig. 2. Schematics of (a) H_2 annealing and (b) RTA.

Fig. 2. The samples could be heated very rapidly (up to 500 °C/min) in a vacuum of 3×10^{-3} Pa using an infrared lamp in the RTA process. The descendent rate of temperature for this process was also rapid, i.e. about 2 °C/s. The heat treatment conditions were set as follows: 400 °C for 30 min in H_2 annealing, 400 °C for 1 min and 5 min in RTA. The times needed for going from room temperature to the target temperature were 30 min for H_2 annealing and 1 min for RTA, i.e., the respective heating rates were 0.211 °C/s and 6.33 °C/s. The times needed for descending from the target temperature to room temperature were 30 min for H_2 annealing and 5 min for RTA. After annealing, the average grain diameters and the grain orientation distributions were examined by EBSP analysis.

2.2. Results of experiments

Fig. 3 shows EBSP observation results for samples heat-treated at (a) 400 °C for 30 min by H_2 annealing, (b) 400 °C for 1 min by RTA, and (c) 400 °C for 5 min by RTA. Table 1 summarizes the results obtained from Fig. 3. The supplied thermal energy to a sample can be estimated as the integrated area of a temperature (°C)–time (min) diagram. According to the amounts of supplied thermal energy, the samples can be sorted in the following order for their integrated areas of temperature (°C)–time (min) diagrams (where the letters refer to the images of Fig. 3): (a) 24,600 > (c) 3260 > (b) 1660. It is noteworthy that the supplied thermal energy in RTA (samples (b) and (c)) is very low compared to that in H_2 annealing (sample (a)).

From the comparison between H_2 annealing and RTA samples in Table 1 regarding average diameter, grain diameter distribution and (111) orientation, the average grain diameter of Cu thin films produced by RTA (400 °C for 5 min) is seen to be larger. In addition, the grain diameter distribution is narrower and the ratio of (111) orientation is higher for RTA samples. This means that RTA can produce coarse grained samples with higher ratios of (111) orientation and narrower grain diameter distributions than H_2 annealing can produce within a short time for the same annealing temperature.

3. Grain growth simulation

To clarify the grain coarsening mechanism for the RTA process, grain growth by RTA was simulated using the phase field method. The