Planarization properties of an alkaline slurry without an inhibitor on copper patterned wafer CMP*

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Abstract: The chemical mechanical polishing/planarization (CMP) performance of an inhibitor-free alkaline copper slurry is investigated. The results of the Cu dissolution rate (DR) and the polish rate (PR) show that the alkaline slurry without inhibitors has a relatively high copper removal rate and considerable dissolution rate. Although the slurry with inhibitors has a somewhat low DR, the copper removal rate was significantly reduced due to the addition of inhibitors (Benzotriazole, BTA). The results obtained from pattern wafers show that the alkaline slurry without inhibitors has a better planarization efficacy; it can planarize the uneven patterned surface during the excess copper removal. These results indicate that the proposed inhibitor-free copper slurry has a considerable planarization capability for CMP of Cu pattern wafers, it can be applied in the first step of Cu CMP for copper bulk removal.

Key words: planarization; alkaline copper slurry; inhibitor free; copper pattern wafer
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1. Introduction

As the semiconductor industry drives towards faster circuits, resistive capacitive (RC) delay due to metallization layers needs to be reduced. Its low-resistivity and high-electromigration properties have made copper the material of choice for the fabrication of interconnects in present-day integrated circuit (IC) chips. The integration of copper into an IC manufacturing process can be implemented by using the dual damascene technique. Chemical mechanical planarization (CMP) of copper is a critical step in damascene processing[1−3]. Generally, a typical multistep Cu CMP process involves three steps: in the first step, the overburden copper is rapidly removed and achieves initial planarization, which is followed by a Cu clearing step for copper residue removal, the third step involves the clearing of the barrier metal. The initial planarization is key to the CMP process[4]. If the surface of the copper pattern wafer cannot be planarized in the first step, the height may propagate throughout the polishing process in the initial step and leave significant dishing after the barrier removal.

Recently, a great deal of research has been carried out on planarizing the copper pattern wafer surface, most of which are slurry investigations. Typical Cu CMP slurries consist of a chelating agent, a surfactant, an oxidizer (most frequently H_2O_2), a corrosion inhibitor, and abrasive particles. Benzotriazole ($C_6H_4N_3H$, BTA) is widely used as a corrosion inhibitor to increase planarization and prevents dishing in Cu CMP[6−10]. However, it reduces the copper removal rate and sacrifice throughout. The Cu–BTA complexes cannot be easily or completely removed and also produce organic residues. On the other hand, the used copper slurry is commonly acidic and may cause corrosion of the polishing equipment. In this paper, we have developed a kind of alkaline copper slurry. The key characteristic of the slurry is that it does not contain inhibitors. Firstly, we investigate the dissolution rate and polish rate of the slurry as compared with slurries containing a certain BTA, and then the planarization versus polishing time is studied. To estimate the planarization efficacy of the alkaline slurry, the surface topography of pattern wafer is measured by using an atomic force microscopy (AFM) technique. The mechanism of the slurry for Cu CMP is also discussed.

2. Experiment details

Polishing experiments were carried out by using E460E polishing equipment, produced by the French Alpsitec Company. The polishing pad was an IC 1000^{TM} provided by Rohm and Haas, and before each experiment started, the pad was conditioned by using a diamond conditioner for 60 s. An MIT 854 pattern wafer was used for evaluating the planarization performance of the alkaline slurry. The cross sectional view of the pattern wafer is shown in Fig. 1. The alkaline copper slurry under investigation consisted of colloidal silica (SiO_2 mean particle size 20 nm), an FA/O chelating agent (obtained from the Institute of Microelectronics, Hebei University of Technology), and nonionic surface active agents. Hydrogen peroxide 3.3 vol% (H_2O_2, wt30%) was used as an oxidizing agent. Slurries with 1 mM BTA and 3 mM BTA were also used in the experiment for comparison. The experimental conditions are

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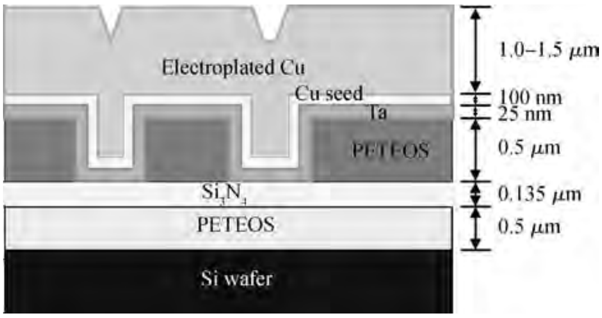

Fig. 1. Cross section view of the MIT 854 pattern wafer.

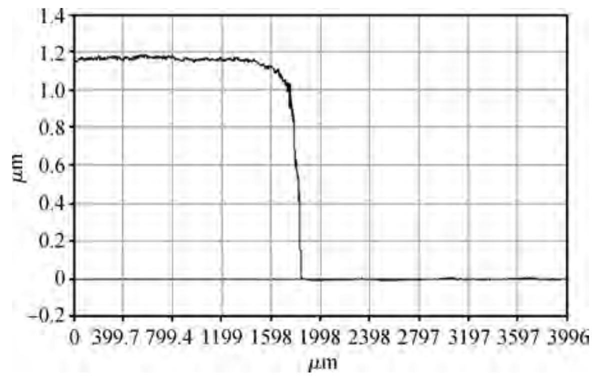

Fig. 2. A typical sample of copper film measurement.

Table 1. Experimental conditions for copper CMP.

Parameter	Condition
Working pressure	1.5 psi
Back side pressure	1.5 psi
Plate speed	60 rpm
Head speed	65 rpm
Slurry flow rate	150 mL/min
Sweeping external position	185 mm
Sweeping internal position	150 mm

listed in detail in Table 1.

All experiments were performed at room temperature in a super-clean laboratory. Before and after polishing, the surface morphology of the pattern wafer was characterized by atomic force microscopy (Agilent, 5600LS) in taping mode at a scan rate of 0.01 in/s. An Xp-300 profiler was used to measure the thickness of copper films. Based on it, we can calculate the removal rate of Cu. A 200 mm copper blanket wafer was used in order to test the material removal rate and within-wafer non uniformity (WIWNU). A typical sample of copper film measurement is shown in Fig. 2.

Copper dissolution rates were measured in a 1000 mL glass beaker containing 500 mL of three different slurry solutions, using a piece of a copper wafer as the sample. The solution containing the sample was stirred with a rotary electromagnetic stirrer at 1000 rpm. The Cu sample was taken out after 5 min, washed with de-ionized (DI) water, and dried in a N_2 air stream. The sample was weighed in an analytical balance (Mettler Toledo AB204-N). The rate of dissolution was calculated by measuring the weight loss of the piece of copper. The reported data were obtained by averaging three experiments.

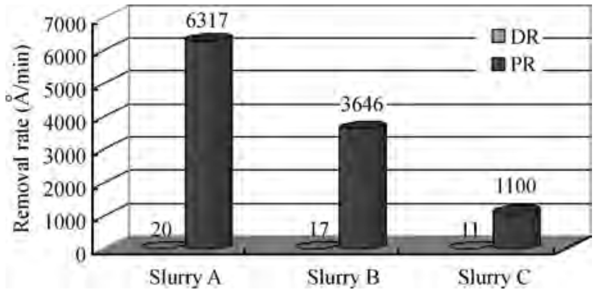

Fig. 3. The polish rate and dissolution rate of copper measured using different slurries.

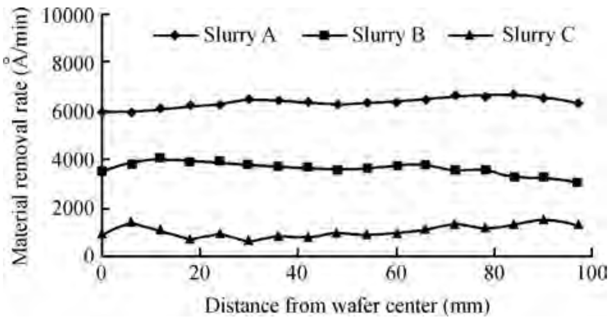

Fig. 4. The removal rate profile of copper films polished by using three different slurries.

3. Results and discussion

Figure 3 shows the polish rate (PR) and dissolution rate (DR) of copper after treatment using three different slurries. Slurry A was inhibitor-free slurry, denoted here as "Ref.". Slurry B was Ref. +1 mM BTA and slurry C was Ref. +3 mM BTA. With the addition of 1 mM BTA to Ref. slurry, the polish rate sharply decreased to 3646 Å/min, but the dissolution rate does not change significantly using slurry B. Although the dissolution rate was suppressed to 11 Å/min by using slurry C, the polish rate further decreased down to 110 Å/min. Thus, the addition of BTA may sacrifice the Cu removal rate significantly. The results reveal that slurry A without an inhibitor has a relatively high removal rate and a considerable dissolution rate. The removal rate profile of the three different slurries is presented in Fig. 4. As shown in Fig. 4, the WIWNU of slurry A, slurry B, and slurry C is 3.3%, 6.9%, and 23.5% respectively. The copper blanket wafer polished by slurry A has good uniformity. However, BTA prohibits chemical dissolution of copper film in copper CMP slurry by generating a Cu–BTA complex on the copper film. The addition of BTA in copper CMP slurry not only changes the DR and PR of copper, but also the WIWNU, as shown in Fig. 4. The WIWNU drops significantly due to the addition of BTA. Figure 5 shows images of the copper blanket surface before and after polishing by using slurry A, we can see that the surface has a good quality after polishing and no corrosion was found.

Figure 6 shows a schematic diagram indicating the step height test regions on the pattern wafer, the experimental wafer samples are labeled (a), (b), and (c), the step height value is the average of the three points. In order to demonstrate the planarization properties of the slurry, the experiment was carried

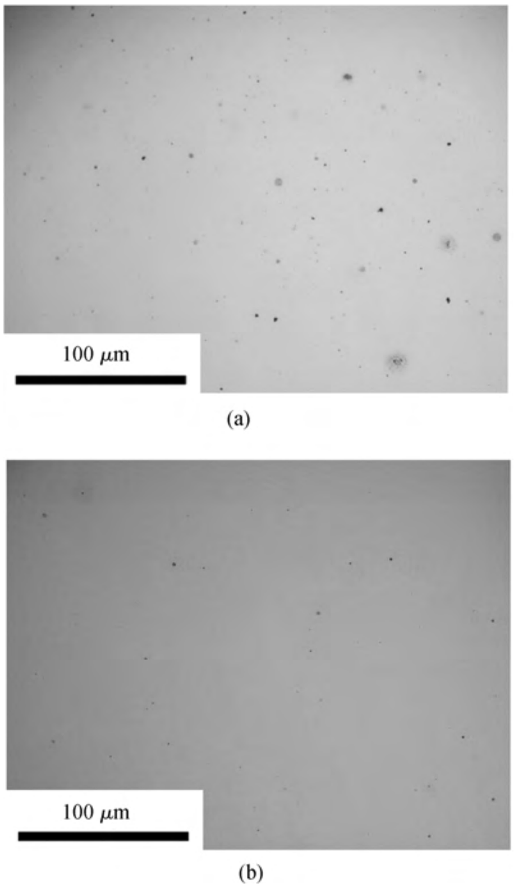

Fig. 5. Images of copper blanket wafer surface before and after polishing, captured from an optical microscope (200X). (a) Before polishing. (b) After polishing.

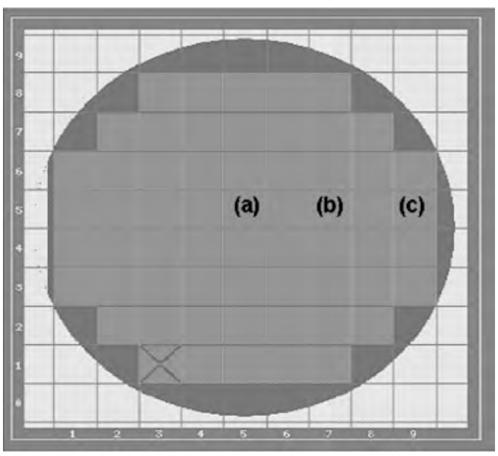

Fig. 6. Schematic illustration of a copper pattern wafer, used to examine step height reduction by using the alkaline slurry. Three different test surface regions are marked as (a), (b), and (c).

out on copper wiring with 100 μm pitch and 50% density. The step height as a function of polishing time is shown in Fig. 7. The initial step height of the test line is nearly 4780 Å, and the initial copper film thickness is 1.15 μm. The CMP of the patterned wafer was performed under the same process condition as the copper blanket wafer. The results presented in Fig. 7 indicate that all of the three different slurries can reduce the step

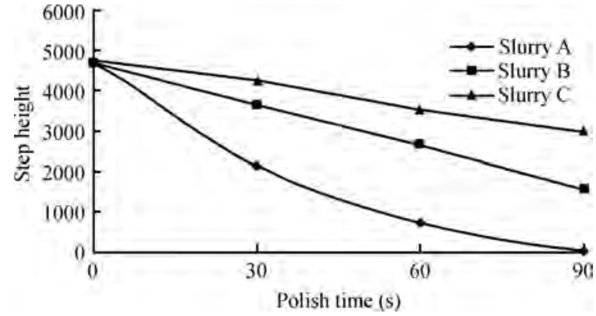

Fig. 7. The step height as a function of polish time.

height of the test line as the polishing process proceeds. When the polish time is 90 s, the step height of the copper wiring polished by using slurry A is nearly completely eliminated, the surface topography was planarized. However, the copper pattern wafer polished by slurry B and slurry C still have 1565 Å and 3034 Å step heights.

The AFM results of the copper patterned wafer polished by using slurry A is presented in Fig. 8. Figure 8 shows the profile of the copper line (100 μm pitch, 50% density) extracted from the AFM image before CMP and after planarization. From Fig. 8, we can see that the initial non-planarity surface with 4780 Å step height was planarized and the step height across the copper line was below 75 Å. Figure 9 shows the three dimensional AFM image of the copper line with 100 μm pitch and 50% density before CMP (Fig. 9(a)) and after planarization (Fig. 9(b)), it can be seen that the maximum peak valley distance was 7600 Å before CMP, but it dramatically reduced to 425 Å after planarization, which further demonstrated that the slurry A without inhibitors has a considerable planarization capability.

As is well known, Cu, CuO, Cu_2O and $Cu(OH)_2$ films can be dissolved in acidic solution, thus most acidic slurries contain one or more kinds of inhibitors to avoid state corrosion and obtain high planarization efficiency. The FA/O alkaline copper slurry applied in the experiment contained no inhibitor but consisted of a FA/O chelating agent, a surfactant and a silica sol as abrasive, which added 3.3 vol% H_2O_2 before use. The planarization performance of the slurry can be explained as follows: in the alkaline condition, the films of Cu, copper oxide and $Cu(OH)_2$ cannot be dissolved inherently and forms a passivation film on the pattern wafer surface with the presence of H_2O_2 during CMP process. However, in the elevated regions, the passivation layer was abraded mechanically, meanwhile the slurry complexing with Cu ions forms an easily soluble reaction product and is rapidly taken away from the copper surface, then a fresh surface appears and the process is repeated again. But in the recess regions, the passivation films protect the copper surface from direct dissolution, then a high removal rate ratio of elevated regions to recess areas was achieved, finally the surface was planarized.

In general, the copper CMP process can be divided into three steps: (1) most of the excess copper film is removed; (2) the adherent copper film on the barrier layer is totally abraded and leaves the barrier layer unpolished; and (3) the barrier layer is removed from the substrate. Slurry A proposed in this report can be applied in the first step of Cu CMP, it can re-

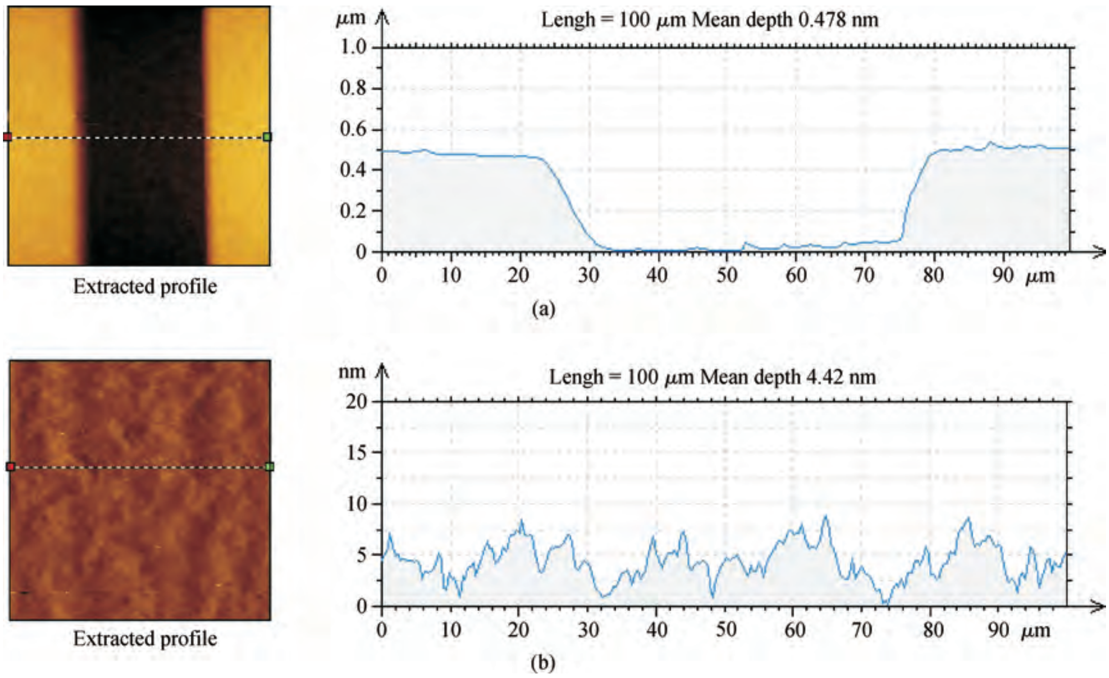

Fig. 8. The profile extracted from the AFM image test on the copper line with 100 μm pitch and 50% density. (a) Before CMP. (b) After planarization.

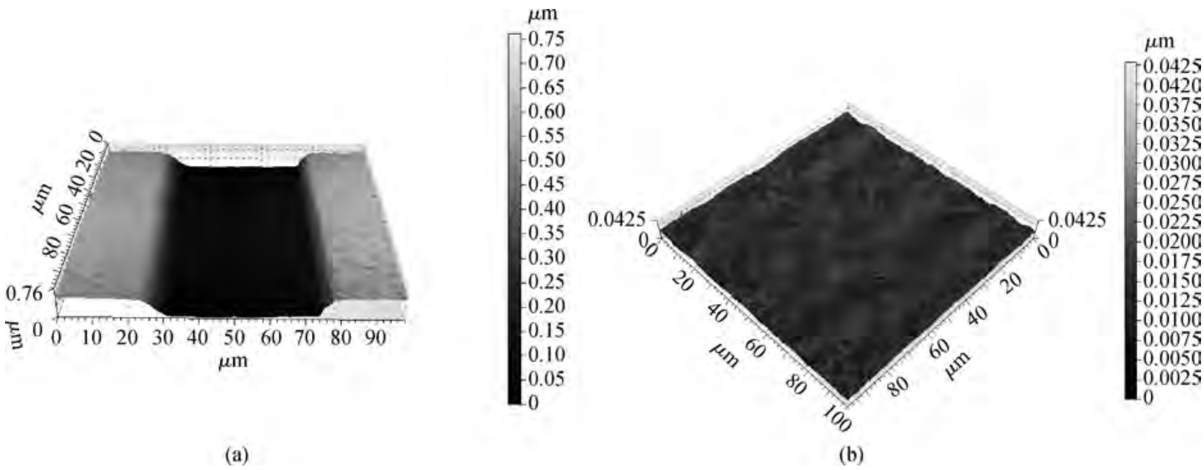

Fig. 9. Three dimensional AFM image of a copper line with 100 μm pitch and 50% density. (a) Before CMP. (b) After planarization.

move the bulk copper under a relatively high removal rate (~6317 Å/min), and can effectively planarize the pattern wafer surface. The optimization of the alkaline slurry and polishing process will be researched in the near future on 300 mm pattern wafer.

4. Conclusion

In this experiment, we have proposed an inhibitor-free alkaline slurry to remove excess copper and planarize an uneven pattern surface, it can be applied in the first step of Cu CMP. Through the static etching rate test and polishing experiment on a copper blanket wafer, it is indicated that the alkaline copper slurry hardly reacts with copper in a state situation, but the removal rate of copper was accelerated during CMP conditions. In addition, the planarization capability of the slurry was also demonstrated on MIT854 copper pattern wafers. The results reveal that the slurry has good planarization properties, the step height is effectively eliminated, and the surface is planarized. It can be applied in the first step of Cu CMP for copper bulk removal.

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