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Chemical mechanical polishing and electrochemical characteristics of tungsten using mixed oxidizers with hydrogen peroxide and ferric nitrate

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Abstract

In this paper, the interaction between the tungsten surface and the oxidizer was discussed by potentiodynamic polarization test in order to compare the chemical mechanical polishing (CMP) performances and electrochemical behavior of the tungsten film as a function of mixed oxidizers. The potentiodynamic polarization results indicated that the corrosion current densities of 5 wt.% $Fe(NO_3)_3$ + 5 wt.% H_2O_2 were higher than the other mixed oxidizers. Such an electrochemical corrosion effect implies that slurries with the highest removal rate (RR) have high dissolution rate.

Keywords: Chemical mechanical polishing (CMP); Mixed oxidizer; Potentiodynamic polarization; Electrochemical corrosion; Removal rate (RR); Dissolution rate

1. Introduction

Chemical mechanical polishing (CMP) process has been widely used in semiconductor fabrication and microelectronics industry. Especially, it is an essential technique for fabrication of tungsten (W) plug, which tungsten has been mainly used as a plug for the multi-level interconnection structures [1–3]. The CMP process must provide a high removal rate (RR) and good planarity through the simultaneous action of chemical dissolution with mechanical abrasion [4,5]. The tungsten CMP slurry is playing a very important role in increasing the RR, because the passive tungsten-oxide layer formed by the oxidizer is softer than tungsten to be removed easily [6]. Therefore, it is important to understand the effect of oxidizer on passive tungsten-oxide layer in order to obtain a higher RR and very low within-wafer non-uniformity (WIWNU%) during the W-CMP process [7–11]. In this paper, the W-CMP process using $Fe(NO_3)_3$, KIO_3, and H_2O_2 as an oxidizer was performed so as to examine the influence of passive tungsten-oxide layer with the different kinds of oxidizers [12,13]. We have investigated the potentiodynamic polarization curves for slurry compositions in order to investigate the correlations between the kinetics of passive tungsten-oxide and the removal action of tungsten film. Eventually, tungsten dissolution rate derived from electrochemical measurements was compared with the actual polish rate.

2. Experiments

2.1. Chemical mechanical polishing

Blanket wafers of W/TEOS (tetra-ethyl ortho-silicate)/Si structure were prepared and Al_2O_3-based W-slurry (RODEL, MSW 2000A) was used as a starting slurry. As listed in Table 2, each oxidizer such as $Fe(NO_3)_3$, KIO_3, and H_2O_2 was adopted by 5 wt.%. In addition, a new mixed oxidizer was fabricated with a different mixing ratio by adding KIO_3 and $Fe(NO_3)_3$ into the best stable H_2O_2 concentration with excellent corrosion effect. Table 3 summarized the mixing ratio of different oxidizer additive and their pH value. To prevent the aging effect and precipitation of mixed slurry, the slurry was dispersed using a stirrer before polishing. The CMP experiments were performed using a G&P POLI-380 CMP polisher and the polishing pad was a double pad with stack-type IC-1300/Suba-IV from

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Table 1
Summary of RR and RMS roughness as function of H_2O_2 oxidizer concentrations

No.	Solution	RR [nm/min]	RMS [nm]
1	H_2O_2 1 wt.%	10	12.7
2	H_2O_2 3 wt.%	14	11.5
3	H_2O_2 5 wt.%	70	3.4
4	H_2O_2 7 wt.%	5	17.8
5	H_2O_2 9 wt.%	15	20.2

RODEL Company. The process conditions of polisher are as follows; the rotation speed of table and head were both set to 70 rpm, and head pressure was set to 60 gf/cm^2. Also, polishing time was fixed as 60 s. After post-CMP cleaning, the sheet resistance was measured for the calculation of the removal rates using 4-point probe (Chang Min Co.). The surface morphology of a sample was measured using AFM (PSIA XE-200).

2.2. Potentiodynamic polarization test

The potentiodynamic polarization test was performed using a potentiostat CMS-100 model of Gamry Company. During the potentiodynamic scans, the working electrode potential was varied with a scanning rate of 1 mV/s from −500 mV/SCE to +1000 mV/SCE, in order to measure the electrochemical corrosion behavior such as corrosion potential or corrosion current density. A carbon rod and a saturated calomel electrode (SCE) were used for the counter and reference electrodes, respectively. The electrode rod was used to investigate the tungsten dissolution behavior under hydrodynamic conditions.

3. Results and discussion

The RRs and root mean square (RMS) roughness of tungsten surface as a function of H_2O_2 contents are listed in Table 1. As the H_2O_2 contents increased from 1 to 9 wt.%, the RR reached a maximum value at 5 wt.%, whereas the RR decreased as the H_2O_2 oxidizer over 5 wt.% is added. It can be seen that it is consistent with the result reported by Hernandez et al. [14]. Also, the RMS roughness of W film decreased to minimal value of 3.4 nm as the H_2O_2 contents increased from 1 to 5 wt.%. Whereas, the RMS roughness linearly increased to maximum value of 20.2 nm as the H_2O_2 contents increased from 5 to 9 wt.%.

Table 2
Summary of RR and RMS roughness in various oxidizer solutions

No.	Solution	RR [nm/min]	RMS [nm]
1	H_2O_2 5 wt.%	70	3.4
2	KIO_3 5 wt.%	18	24.3
3	$Fe(NO_3)_3$ 5 wt.%	320	2.6

Fig. 1 shows the potentiodynamic polarization curves for tungsten in different oxidizers with 5 wt.% concentration. As shown in Fig. 1, the E_{corr} showed the lowest value in the condition of 5 wt.% H_2O_2 and the highest value of the I_{corr} was obtained from the content of 5 wt.% Fe $(NO_3)_3$. This indicates that the corrosion effect was dominant in the 5 wt.% $Fe(NO_3)_3$. On the other hand, the highest value of the E_{corr} and the lowest value of the I_{corr} were showed in addition of 5 wt.% KIO_3, which means that this oxidizer results the relatively little corrosion behavior. The RRs for different kinds of each oxidizer are listed in Table 2. The 5 wt.% H_2O_2-added slurry shows the RR of 70 nm/min. However, 5 wt.% $Fe(NO_3)_3$-mixed slurry revealed an excellent RR of 320 nm/min. This implies that $Fe(NO_3)_3$ is the most suitable oxidizer for this W-CMP application. It was consistent with the potentiodynamic results of Fig. 1 that showed the most excellent corrosive characteristics for the case of $Fe(NO_3)_3$. We can guess for this reason that the addition of $Fe(NO_3)_3$ hastened the formation of passive film and then, increased the dissolution rate.

Fig. 2 shows the comparison of AFM image for the different oxidizers. The corrosive surface was notably observed in the case of 5 wt.% KIO_3-added slurry. This problem can be alleviated by fine controlling with a small amount of adjustment as reported in other work [10]. In terms of oxidizer additive, it is very important to minimize the defects due to the corrosion effects by finding the proper amount of oxidizer, without compromising a high RR. Although the WIWNU% was more improved after polishing, there was no great difference in the modified slurries with KIO_3 and H_2O_2 as an oxidizer,

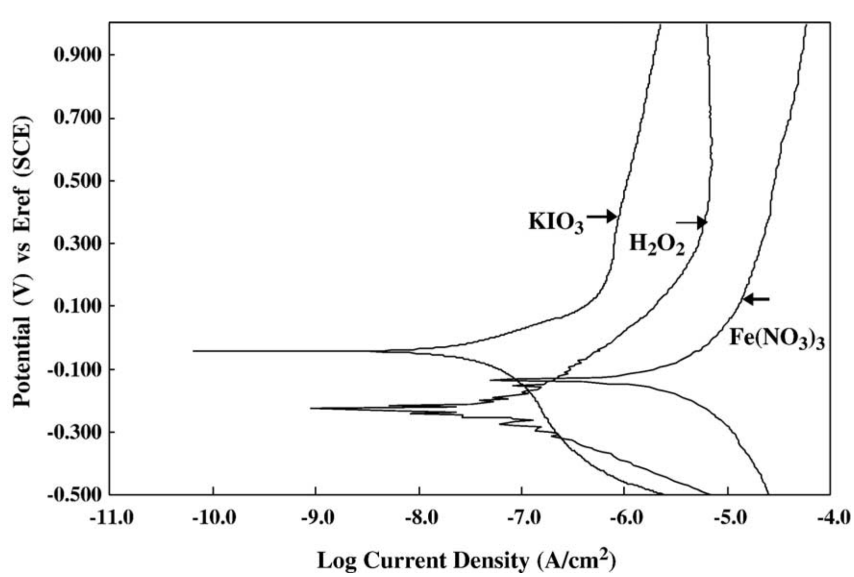

Fig. 1. Potentiodynamic polarization curves of different oxidizers with 5 wt.% contents.