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Platinum chemical mechanical polishing (CMP) characteristics for high density ferroelectric memory applications ☆

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Abstract

The key component of ferroelectric random access memory (FeRAM) is a capacitor including a ferroelectric thin film and electrode materials. Platinum is one of the suitable metals which meet requirements such as low resistivity, high thermal stability, and good oxygen resistance. Generally, the ferroelectric and the electrode materials were patterned by a plasma etching process. The application possibility of chemical mechanical polishing (CMP) processes to the patterning of ferroelectric thin film instead of plasma etching was investigated in our previous study for improvement of an angled sidewall which prevents the densification of FeRAM. In this study, the characteristics of platinum CMP for FeRAM applications were also investigated by an approach as bottom electrode materials of ferroelectric material in CMP patterning. The removal rate was increased from 24.81 nm/min by the only alumina slurry (0.0 wt% of H_2O_2 oxidizer) to 113.59 nm/min at 10.0 wt% of H_2O_2 oxidizer. Electrochemical study of platinum and alumina slurry with various concentrations of H_2O_2 was performed in order to investigate the change of the removal rate. The decreased particle size in the alumina slurry with an addition of 10.0 wt% H_2O_2 oxidizer made the improved surface roughness of the platinum thin films. Micro-scratches were observed in all polished samples.

Keywords: Chemical mechanical polishing (CMP); Platinum (Pt); FeRAM; Electrode

1. Introduction

Ferroelectric random access memory (FeRAM) will be expected to replace the current dynamic random access memory (DRAM) in the near future due to its ideal memory properties such as non-volatility, low power consumption, high speed, and almost unlimited endurance [1–4]. The key component of FeRAM is a ferroelectric capacitor consisting of a ferroelectric thin film sandwiched between top and bottom electrodes [5]. In order to fabricate optimum capacitors, electrode materials should obey several requirements such as low resistivity, high thermal stability, and good oxygen resistance. Platinum is one of the suitable metals which satisfy all these requirements. Generally, the ferroelectric and the electrode materials are patterned by a plasma etching process. The application of chemical mechanical polishing (CMP) to the patterning of ferroelectric thin film instead of plasma etching process was investigated in our previous study, which is aimed at the improvement of an angled sidewall which prevents the densification of FeRAM [1–6]. In this study, platinum CMP for FeRAM applications was investigated by an approach as bottom electrode of ferroelectric material in CMP patterning [6]. Good surface morphology for bottom electrode was necessary. Generally, the CMP slurry is playing a very important role in controlling the removal rate for

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metal CMP, because the passive layer formed by the oxidizer is softer than the metal to be removed [7,8]. Therefore, it is important to understand the effect of oxidizer on the passive layer in order to control the removal rate and to lower a within-wafer non-uniformity (WIWNU%) during the platinum CMP process.

2. Experiments

All the platinum specimens in this study were deposited on Ti/SiO_2/Si substrates. P-type (100) orientation, 6-in. diameter silicon wafers (1–30 Ω cm) were used as the starting substrates. The substrate was cleaned by rinsing with the solution of H_2SO_4:H_2O_2 (1:4), H_2O:HF (DHF; 10:1), and de-ionized water in order to eliminate the native silicon oxide. Dry thermal oxide of 100 nm was grown by electric furnace in O_2 gas flux at 1100 °C. Titanium of 30 nm for the adhesion and platinum of 120 nm were deposited by DC sputtering at room temperature under the conditions of Ar gas flux, 1.0×10^6 Torr vacuum, 300 W of DC power with a 4-in. Ti target (99.999% purity) and a 4-in. Pt target (99.99% purity) respectively. All test samples were polished by a POLI-450 CMP polisher of G&P Company. IC-1400 of Rohm and Haas Electronic Materials Company was used for polishing pad. The commercially developed alumina-based tungsten slurry (alumina slurry) was used as CMP slurry. The slurry was agitated before CMP to prevent aging effects. To investigate the effect of oxidizer on platinum CMP, an oxidizer of H_2O_2 was adopted by 1.0, 3.0, 5.0 and 10.0 wt% to the alumina slurry. The process parameters were fixed as follows: table speed, head speed, slurry flow rate, down force, and polishing time were 40 and 60 rpm, 90 ml/min, 100 gf/cm^2, and 30 s, respectively, which were summarized in Table 1. The conditioning pressure was fixed at 2 kg/cm^2 to exclude the effects of pad conditioning. The polishing pad was used without change because of its good stability. The post-CMP cleaning was proceeded by the sequence of 3 min in SC-1 chemicals (NH_4OH:H_2O_2:H_2O = 1:2:7), and 4 min in ultrasonic cleaning. The surface morphology of platinum thin films after CMP process was measured with AFM (PSIA XE-200). The sheet resistance of platinum thin films was measured by using four-point probe (Chang Min Co.) for calculation of removal rates. Electrochemical curves were recorded with a potentiostat (EG&G 273A) in order to measure the electrochemical corrosion behavior such as corrosion potential or corrosion current density. Particle size was measured using Zetasizer (Malvern Instruments Ltd., Nano ZS).

Table 1
Process parameter ranges of platinum CMP

Head speed	60 rpm	Polishing time	30 s
Down force	100 gf/cm^2	Slurry flow rate	90 ml/min
Table speed	40 rpm	H_2O_2 oxidizer	0, 1, 3, 5, 10 wt%

3. Results and discussion

In our previous study [9], platinum thin films were polished by both silica and alumina slurry. The improvement of surface roughness was main goal in platinum CMP process in the study. AFM gave 3D images over a 3×3 μm scan of platinum thin films before and after polishing by silica or alumina slurry. In the AFM surface morphology of platinum thin films before CMP, the root mean square (RMS) surface roughness of the oxide film before CMP was 271.5 nm. After polishing, both the RMS surface roughness of platinum thin films was improved, in which the RMS surface roughness of the specimen polished by silica slurry was 242.2 nm. Most of the spire-features were observed to be stumpy. The RMS surface roughness of the specimen polished by alumina slurry was improved more to 182.0 nm. The removal rate of platinum thin films by alumina slurry was also higher than that by silica slurry. Therefore, alumina slurry was selected for the base slurry in this study.

It is generally known that platinum is an acid-resistant metal. According to C. Marie, platinum can be oxidized at room temperature by only some oxidizers such as $K_2S_2O_9$, K_2Cr_2O7, $KClO_3$, concentrated HNO_3, $K_3Fe(CN)_6$, and $KMnO_4$ in sulphuric or caustic solution [10]. H_2O_2 was employed as an oxidizer for platinum CMP, because H_2O_2 is a wide-used oxidizer in metal CMP in spite of not mentioning by C. Marie. Fig. 1 shows the removal rate of platinum thin films by alumina slurry with an addition of H_2O_2 oxidizer. The removal rate of platinum thin films was 24.81 nm/min by the only alumina slurry without oxidizer. The removal rate rapidly increased with an addition of 1.0 wt% H_2O_2 to 67.41 nm/min, and then it increased linearly to a maximum value of 113.59 nm/min at 10.0 wt% of H_2O_2 as shown in Fig. 1. Non-uniformity after CMP process with an increase of H_2O_2 oxidizer was also shown in Fig. 1. Non-uniformity was 54.65% with only alumina slurry, which is a very inferior value to apply to fabrication process. With an addition

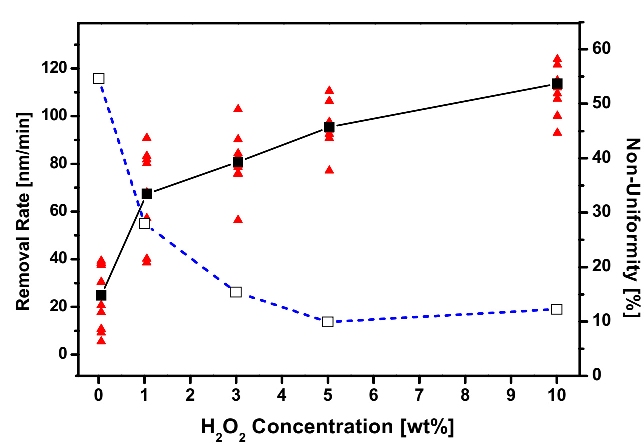

Fig. 1. Removal rate and non-uniformity of platinum thin film after CMP with an addition of H_2O_2 oxidizer to alumina slurry.