Microelectronic Engineering 87 (2010) 174–179

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Acetic acid and phosphoric acid adding to improve tantalum chemical mechanical polishing in hydrogen peroxide-based slurry

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ARTICLE INFO

Article history:
Received 3 April 2009
Received in revised form 3 July 2009
Accepted 9 July 2009
Available online 15 July 2009

Keywords:
CMP
Acetic acid
Phosphoric acid
Slurry
Tantalum
Electrochemical measurement

ABSTRACT

Tantalum (Ta) is difficult to polish mechanically because of the formation of the hard oxide, Ta_2O_5, on its surface. In the IC metallization process, increasing the chemical removal rate of the barrier metal, tantalum (Ta), during chemical mechanical polishing (CMP) is essential to achieve global planarity and enhance the efficiency of the process. This study explores how the addition of acetic acid (CH_3COOH) and phosphoric acid (H_3PO_4) accelerates Ta CMP in hydrogen peroxide (H_2O_2) slurries. Experimental results indicated that CH_3COOH and H_3PO_4 were adsorbed on Ta, modifying its surface; in particular, the time taken for the Ta surface to be passivated into dense Ta_2O_5 was effectively increased, enabling Ta to be easily etched and removed. An impedance study further confirmed that the addition of CH_3COOH or H_3PO_4 changed the reaction mechanism between Ta and H_2O_2 slurries and displayed the lack of dense oxide film to be formed. Therefore, the chemical removal rate of Ta was substantially enhanced. After Ta CMP in H_2O_2-based slurries with CH_3COOH or H_3PO_4, the surface roughness from 32.52 nm could be decreased to 16.21 or and 13.81 nm, respectively.

1. Introduction

Because of the ongoing development of interconnects toward the nano-scale, increases in the degree of device integration, and the evolution of multilayer interconnects on chips, ultra large-scale integrated circuit (ULSI) manufacturers are paying considerable attention to Cu as a potential interconnect material because it exhibits excellent intrinsic electromigration resistance and a lower resistivity than conventional Al and Al alloys [1–3]; thus, it is therefore associated with a greatly reduced RC delay. However, some problems must yet be solved in order to successfully integrate Cu metallization into IC manufacturing. Much effort has been devoted to the development of Cu CMP [4–8]. Barrier layers, such as layers fabricated with Ta and tantalum nitrides, that are thermodynamically stable and have low film resistivity have been introduced to prevent the diffusion of Cu atoms into dielectrics and to prevent problems of adhesion [9,10]. In recent years, many studies have focused on the investigation of barrier layer materials [11,12]; however, few have addressed barrier CMP. In this work, Ta, which is regarded as the barrier material with most potential in Cu metallization, was adopted for an experimental CMP study.

The Cu CMP process that is currently employed in general semiconductor processes has two main steps [13]. The first is the rapid removal of the excess deposited Cu to achieve initial planarization; in this stage, Cu is polished and removed rapidly until the underlying barrier layer is exposed. The study and applications of the first step of Cu CMP have become more mature in recent years; even electro-CMP, which is associated with electropolishing applications, has been developed to improve the traditional CMP process [14]. The second step focuses on the simultaneous polishing of the barrier and Cu. Since the polishing properties of Ta differ greatly from those of Cu, overpolishing, which causes erosion and scratches on Cu, must be avoided. Therefore, the slurry that is adopted in the second step for enhancing the performance of Ta CMP is key factor to global planarization. Metal CMP involves complicated surface chemistry and electrochemical reactions between metal and slurry. They include passivation, dissolution, adsorption and accelerated etching during polishing. Additionally, if several metals or dielectrics are simultaneously polished, then galvanic coupling effect among metals, the removal selection ratio, and the corrosion and adsorption characteristics of the different materials must all be considered. Since Cu is soft and can be corroded easily, the hardness of the barrier layer material is typically markedly exceeds that of Cu, and so, controlling the mechanical action alone will not suffice to yield an appropriate removal selection ratio. Accordingly, controlling the chemical reactions is far more important than controlling the mechanical characteristics. All of the aforementioned issues are related to the slurry; therefore, to improve Ta CMP performance, to increase planarization effective-

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0167-9317/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2009.07.009

ness, and to reduce surface defects, the chemical composition of the slurry must be controlled.

In previous studies of Ta CMP, Pourbaix diagrams show that Ta, with very low chemical activity, could be spontaneously oxidized to a Ta_2O_5 passivation layer of high hardness in slurries of all compositions at all pH values [15]; this hinders further chemical dissolution and mechanical removal. However, the electrochemical reaction mechanisms of Ta in different slurries, such as dissolution and passivation, are not yet clearly understood; Babu and Li et al. performed a series of studies on Ta CMP [16–18], and proved that Ta was oxidized to Ta_2O_5 in DI water. Open-circuit potential (OCP) results revealed that the passivation effects were more pronounced when oxidizers such as H_2O_2 and $Fe(NO_3)_3$ were added to the slurry, reducing the removal rates. The pH of H_2O_2-based slurries importantly affected the removal rate; for pH > 8, the removal rate increased significantly when either alumina or silicon abrasives were added. The lower removal rates of Cu CMP in natural solution help in identifying favorable slurry compositions. Stavreva and Zeidler et al. found that galvanic coupling occurred between Cu and a barrier (Ti, TiN) during CMP [19], making difficult the determination of the end of polishing, which is disadvantageous in the simultaneous polishing of different materials. Lu et al. [20], Wrschka et al. [21], Ahn et al. [22], and Mazaheri and Ahmadi [23] all published results of Cu and barrier CMP with silicon abrasives, which are softer than alumina particles. They observed fewer scratches and obtained a larger barrier to Cu removal ratio. Chelating agents such as citric acid and oxalic acid have been used to increase barrier removal rates. However, published results concerning Ta CMP are still insufficient, and the further development of Ta CMP is worthy of study.

Since Ta CMP involves complicated reaction mechanisms and dynamic processes, there are numerous chemical reaction parameters that are associated with the slurry; the best approach to study the chemical behaviors between metal and solution is by electrochemical techniques. In this work, the effects of CH_3COOH and H_3PO_4 on Ta CMP in H_2O_2-based slurries were investigated. Polarization curves were plotted, and an electrochemical impedance analysis performed to discuss the reaction mechanisms in Ta CMP. XPS and AFM were used to study the surface compositions and roughness after polishing.

2. Experimental

2.1. Slurry preparation and specimen pretreatment

α-Al_2O_3 particles with diameters of 50 nm and a fixed solid concentration of 5 wt% were used as abrasives in all experiments. The colloid slurries were prepared with high shear stress and were agitated continuously until the α-Al_2O_3 particles were fully suspended in the slurries. The chemical constituents of the slurry were prepared using analytical grade reagents – hydrogen peroxide (H_2O_2), acetic acid (CH_3COOH), and phosphoric acid (H_3PO_4).

The specimens made from 99.99% pure Ta plate were used for electrochemical measurements. Additionally, wafers with a PVD Ta film with a thickness of 5000 Å were prepared for surface analysis after CMP. Before the experiments were conducted, all specimens had to be precleaned in 3 wt% H_2SO_4 and then rinsed by deionized (DI) water, and dried with nitrogen gas.

2.2. Electrochemical measurements

A designed cell for simulating the Ta CMP process was used for electrochemical measurements, as described elsewhere [5]. The cell was connected to a potentiostat/galvanostat (Eco Chemie, model no. Autolab PGSTAT 30) to perform electrochemical tests. The dc polarization curves were obtained at a voltage scan rate of 5 mV/s to measure the corrosion current densities and potentials. The effects of abrasion on OCP were also investigated under stationary conditions and during CMP. General purpose electrochemical system (GPES) software of the potentiostat was adopted to calculate the electrodynamic parameters.

Electrochemical impedance spectroscopy (EIS) was employed to characterize the Ta/slurry interface. The equivalent circuit for simulating interfacial behaviors was also established. A sinusoidal perturbation potential with a small amplitude (10 mV) was applied at frequencies in the range 100 kHz–0.01 Hz at OCP. The EIS results were then plotted as Nyquist plots. Frequency response analyzer (FRA) software was adopted to fit the EIS results to the equivalent circuit.

2.3. Morphological analysis

An atomic force microscope (AFM; Digital Instruments, Model no. Nanoscope IIIa) was used along with a probe (Silicon-MDT, U.S.A, Model no. NSC15) to analyze the morphological characteristics of the surface. The selected operational mode was the non-contact tapping mode, the amplitude and scanning speed were approximately 1.2 V and 1 Hz, respectively. The software package that was used for analysis was applied to calculate the root mean square roughness of the surface, R_{rms}.

X-ray photoelectron spectroscopy (XPS) (VG Microtech, Model no. MT-500) was adopted to conduct a chemical analysis of the surface before and after CMP. Excitation was performed using Mg Kα radiation ($h\upsilon$ = 1253.6 eV); the energy detection range was from 1000 to 0 eV. All spectra were calibrated with respect to the C 1s electron peak at 284.6 eV. The quantitative analysis was performed by employing the software to calculate the atomic concentration of each peak. The quantitative ratios of Ta-metallic/Ta oxide on the Ta surface could be obtained.

3. Results and discussion

3.1. Polarization curves and OCP measurements

The effects of CH_3COOH addition under static conditions and during Ta CMP in 5 wt% H_2O_2-based slurries on the polarization curves are shown in Fig. 1. Fig. 1 indicates that under static conditions, the cathode curve moved to the right more than did the anode curve when CH_3COOH was added , and thus the corrosion

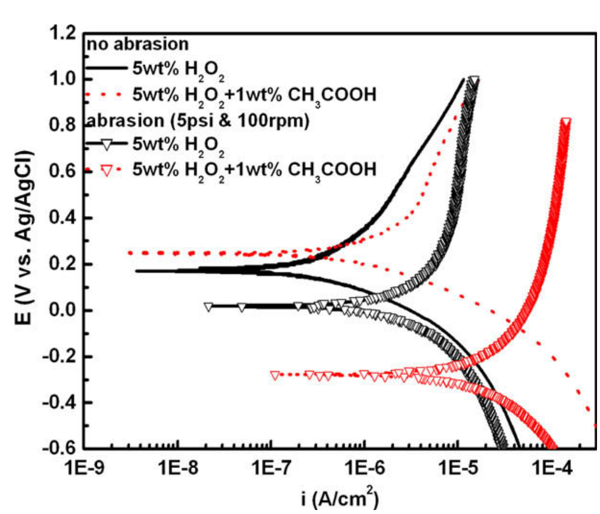

Fig. 1. Polarization curves of Ta in 5 wt% H_2O_2 and 5 wt% H_2O_2 + 1 wt% CH_3COOH slurries without and with abrasion (5 psi and 100 rpm).