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Glycolic acid in hydrogen peroxide-based slurry for enhancing copper chemical mechanical polishing

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Abstract

The effects of glycolic acid (GCA) added into hydrogen peroxide (H_2O_2) or urea-hydrogen peroxide (U-H_2O_2) slurries on Cu-CMP performance were investigated. Experiments showed that GCA could prevent H_2O_2 or U-H_2O_2 from rapid decomposition and increase the active peroxide lifetime of the slurries. In addition, electrochemical studies from polarization and impedance experiments verified that copper removal efficiency could be enhanced by use of GCA. Meanwhile, a valid equivalent circuit for Cu-CMP system was proposed, and the fitting results provided a good index to surface planarization. Furthermore, GCA could shorten the range of isoelectric points between Cu film and α-Al_2O_3 abrasives. After a post cleaning, the particle contamination thus could be reduced due to the electrostatic repulsion. Our study proved that adding GCA into the U-H_2O_2 slurries with BTA could further improve the Cu-CMP performance.

Keywords: Glycolic acid; Urea-hydrogen peroxide; Slurry; Copper; Chemical mechanical polishing

1. Introduction

Chemical mechanical polishing (CMP) of metal is widely recognized as the key technique to obtain global planarization for copper multilevel interconnection in IC manufacturing [1]. However, the planarization mechanisms of metal CMP involve complicated chemical reactions and physical actions. So it is difficult to control the CMP performance, especially for a high corrosion-sensitivity metal like Cu. According to different slurry components, the planarization mechanisms of metal CMP can be summarized as the following two types. The first one is that the metal surface may be polished with a dissolution-type slurry in which no surface film forms. In this case, the CMP

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process proceeds by the mechanical removal and chemical dissolution of metal itself [2]. In the second type of mechanisms, a thin abradable layer is continuously formed on metal surface by the reactions of metal and slurry components. These slurry components may include oxidants, inhibitors and other film-forming agents. The thin abradable layer is then scanned away rapidly by the mechanical action or dissolves in the slurry with a chelating agent. Once the mechanical polishing process has stopped, a thin passive film remains on the surface and inhibits the proceeding of wet etching [3]. Therefore, controlling CMP process to reach global planarization is much easier due to this mechanism.

The chemical components and properties of slurry determine the Cu-CMP performance principally. As a result, many studies devoted to the development of copper slurries with high planarization ability and CMP efficiency. According to the second mechanism mentioned above, oxidants with high oxidizing ability and low contamination should be required to form a passive film on Cu surface. Hydrogen peroxide (H_2O_2) is a widely used example at present [4,5]. However, H_2O_2 decomposes to H_2O and O_2 easily, and this decomposition will result in the slurry transport issues, unstable CMP performance and short shelf lifetime. Recently, urea-hydrogen peroxide (U-H_2O_2) has been proposed as the oxidant for Cu-CMP slurries due to its less self-decomposition and better oxidizing performance during CMP [6].

Also, Kaufman and Kistler [7] reported that organic acids can be added into metal slurries to enhance CMP performance by acting as pH adjusters or chelating agents. On the other hand, many researchers have examined the further efficiency of organic acids, and it was found that the action of organic acids would depend on the different CMP conditions. For instance, in 1999, Hu et al. [8] indicated that citric acid can inhibit Cu corrosion in HNO_3 slurries, and Zhang et al. [9] found that citric acid can prevent the alumina-particle deposition on tungsten surface. Even though many organic acids, such as acetic acid [10], oxalic acid [11], ethylenediamine tetraacetic acid (EDTA) [12] and amino acid [13,14] have been extensively studied, glycolic acid (GCA) has never been used. As known, GCA is easy handling, water-soluble, biodegradable, non-volatile and can efficiently chelate the metal. Therefore, the objective of this paper is to investigate the effect of GCA added into U-H_2O_2 slurries on electrochemical behaviors of Cu CMP. In addition to the measurement of polarization curves, the electrochemical impedance spectroscopy (EIS) was also obtained, and the equivalent circuit of surface reactions during Cu CMP was proposed. Although the equivalent circuits of Al have been discussed [15], fewer studies examined that in Cu CMP. In this study, the specific role of GCA and the information of the equivalent circuit for CMP in U-H_2O_2-based slurries were explored. Our experiments proved that GCA could improve Cu-CMP efficiency, and the planarization mechanisms of Cu CMP could be described well by the electrochemical methods.

2. Experimental

Commercial pure Cu sheets with 0.3-mm thickness were used, and the dimension of each specimen was 1×1 cm^2 for electrochemical measuring. In addition, 3-in. wafers with an electroplated Cu film were polished to obtain removal rates and surface roughness. All specimens were degreased by the cathode electrochemical method at 6 V for 20 s, and then were cleaned in 3 wt% H_2SO_4 solution followed by deionized (DI) water rinsing. Afterward, the samples were dried in nitrogen gas and transferred to the electrochemical measuring equipment or polishing machine. The slurry was prepared by use of 50-nm alumina particles (α-Al_2O_3), and its solid concentration in the slurry was fixed at 5 wt% for all of the experiments. To investigate the effects of different chemical components on Cu CMP, we prepared the slurries by analytical grade reagents, including urea-hydrogen peroxide (U-H_2O_2), benzotriazole (BTA) and glycolic acid (GCA).

For the purpose to compare the stability of solutions, 5 wt% U-H_2O_2 and 1.8 wt% H_2O_2, with the equal level of peroxide in solutions, were periodically analyzed by titration with 1 wt% potassium permanganate solution to determine the peroxide activity. An acoustic spectrometer, model