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Fabrication of ruthenium thin film and characterization of its chemical mechanical polishing process

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HIGHLIGHTS

- Ru electrodeposition is a 2e metal ion reduction process with Tafel behavior.
- Ru electrodeposition on Ti RDE fits a quasi Koutecky–Levich equation.
- Metal-free slurry is employed for CMP operation to avoid contamination.
- The Ru CMP process is affected by the surface condition and the pH of slurry.
- The CMP efficacy factor should be high in order to obtain a smooth surface.

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ABSTRACT

The fabrication of Ru thin film is conducted on titanium (Ti)-based rotating disk electrodes (RDE) by electrodeposition and characteristics of its chemical mechanical polishing (CMP) are investigated to be employed for copper diffusion layer applications in various semiconductor-device interconnects. The electrodeposits obtained under different electrodeposition conditions are characterized using atomic force microscope (AFM) and field emission scanning electron microscope (FESEM). Experimental results indicate that the Ru electrodeposition exhibits a Tafel behavior with a 2e metal ion reduction process. Both exchange current density and cathodic transfer coefficient are determined. A quasi Koutecky–Levich analysis is proposed to analyze the electrodeposition processes under different applied current density conditions and the activation overpotentials together with electrodeposition rate constants are obtained. For Ru CMP operations, slurries containing metal-free 2wt% ammonium persulfate and 2wt% silica abrasive at various pH values are employed. Potentiodynamic polarization studies indicate that the corrosion current density varies in the presence of ammonia while the static etch rate remains low. Both chemical and mechanical effects are investigated and analyzed, and the CMP efficacy factors are obtained.

1. Introduction

Ruthenium is recognized as an excellent material for the diffusion barrier between copper and the dielectric layer to be used in next-generation Damascene process of semiconductor-device interconnects. The major advantage of Ru is its lower resistivity (7.60 μΩ-cm) compared to other competitive barrier materials, such as Ta (13 μΩ-cm) and TaN (252 μΩ-cm) [1,2]. In addition, Ru shows negligible solubility with Cu, even after annealing up to 800 °C [3]. In order to explore its characteristics and applications, the preparation of Ru thin film and its CMP have attracted considerable attention. The term “chemical mechanical polishing” implies that this process combines both chemical and mechanical effects on the removal of metal species for surface planarization [4].

A variety of techniques, e.g., electroless deposition (ED) [5], physical vapor deposition (PVD), and chemical vapor deposition (CVD) [6], have been applied to the deposition of Ru thin films. However, the electrodeposition method offers a number of merits compared to other competitive counterparts including being a cost-effective operation. In particular, surface morphology and film thickness of the Ru deposit can be easily modulated by varying the experimental parameters, such as applied current, voltage,

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electrolyte composition, solution pH and deposition time.

Several research articles had reported the electrodeposition of Ru from solutions containing various electrolytes and substrates [7–11]. Jow et al. [9] studied the Ru cathodic deposition from $RuCl_3$ aqueous solutions and pointed out that the species on the deposited film contained ruthenium hydroxides/oxides and some amounts of Ru metal. Reid and Blake [12] proposed the use of ruthenium nitrosyl sulfamate plating bath for Ru electrochemical deposition. However, this bath was unstable in operation and lack of reproducibility in operation. Later, Reddy and Taimsalu [13] used the electrolyte based on the N-bridged complex of ruthenium nitrosyl chloride ($(NH_4)_3(RuCl_4)N(RuCl_4)$) as the source of Ru. The complex had high water solubility and exhibited high current efficiency for Ru electrodeposition, and the ammonium salt was prepared from $RuCl_3$ and sulfamic acid. Finally, Kim et al. [10,11] succeeded in electrodepositing pure Ru thin film by using the electrolyte composed of 20 mM $RuCl_3 \cdot 3H_2O$, 20 mM HCl, 40 mM NH_2SO_3H, and 5 μL/L PEG.

After the deposition of Ru barriers, chemical mechanical polishing (or chemical mechanical planarization) is commonly employed to obtain planar surfaces for the next level metallization in semiconductor processes. The results of Ru CMP using various slurries had been reported in literature. Ceric ammonium nitrate (CAN) was the first species to be used as the oxidizing agent of the Ru CMP slurry at low pH values [14]. Since the CAN species forms a gel-like material when pH is above 2, it is not suitable for practical processing. Periodate salts were also employed as oxidizing agents [15–18]. Kim et al. [15,16] had showed Ru CMP results using sodium periodate ($NaIO_4$) and briefly discussed the potentiodynamic curve, removal rate of Ru, and surface composition as a function of slurry pH. Potassium periodate (KIO_4) with alumina or silica was studied as a slurry for Ru polishing by Peethala and Babu [18]. The removal rate of Ru obtained using the oxidizing agent with silica abrasives was found to be higher than that with alumina. Victoria et al. [19,20] studied potassium bromate ($KBrO_3$) and oxone ($KHSO_5$) as oxidizing agents for Ru CMP, and analyzed the Ru removal rate as a function of pH, oxidizer concentration, and abrasive loading. The systematic investigations into several oxidizers at the same pH value and concentration of oxidizer in Ru CMP had also been reported [21].

In order to further improve the application of electrochemical approaches to Ru-based diffusion barrier formation process, the electrodeposition of Ru thin film and its CMP behaviors are investigated. Since Ti is a metallic material that can be used as an underlying diffusion barrier [10], particularly when the precious Ru metal is to be deposited very thin, it is therefore employed as a substrate for the electrodeposition of Ru. In this study, the Ru thin film is first electrodeposited on a titanium foil RDE substrate in a ruthenium nitrosyl chloride-based bath, and the electrodeposition processes and results under various experimental conditions are analyzed. After the electrodeposition, we are the first to use metal-free slurries containing ammonium persulfate ($(NH_4)_2S_2O_8$) as an oxidant and silica as an abrasive at various pH values for conducting Ru CMP operations. The chemical corrosion rates as well as mechanical removal rates of the electrodeposited Ru films are investigated and measured, and the CMP efficiency factor is determined.

2. Experimental

The ruthenium electrodeposition bath contains 8 mM ruthenium (III) chloride ($RuCl_3$, Alfa Aesar, 99.99%), 40 mM hydrochloric acid (HCl, J. T. Barker, 37.6%), 40 mM sulfamic acid (NH_2SO_3H, Sigma–Aldrich, 99%) with and without addition of 250 ppm polyethylene glycol (PEG, Alfa Aesar). The titanium disk electrode is prepared by attaching a Ti foil (Nilaco, 99.5%) to the Pt disk on a rotating disk electrode (Pine Instrument Company) and the Ti substrate is 0.2 mm in thickness and 12 mm in diameter. Prior to electrodeposition of Ru, each Ti foil substrate is polished successively using an abrasive paper (#1200) and polishing pads (MD–Largo and MD-Chem, Struers Co.). A three-electrode system composed of a divided H-cell and separated with a piece of Nafion® membrane is employed for carrying out electrodeposition experiments to avoid the interferences of the undesired reaction products generated from the counter electrode. The current efficiency is measured based on the weight gain of the Ti foil after electrodeposition. The Ti foil with an electrodeposited Ru thin film (~200 nm) is then employed as a specimen for the chemical mechanical polishing study.

For Ru CMP, the slurry is composed of 2wt% silica (30 nm, Sigma–Aldrich) and 2wt% ammonium persulfate ($(NH_4)_2S_2O_8$, J. T. Barker, 98%). The pH value of the polishing slurry is adjusted using H_2SO_4 or NH_4OH solution. The polishing time is 1 min, and the removal rate of Ru is estimated by measuring the weight loss of the electrodeposited foil. A specially designed experimental cell for the Ru CMP process at a constant applied pressure of 2psi is employed for carrying out electrochemical measurements. The CMP cell is connected to a potentiostat/galvanostat (Eco Chemie, Autolab PGSTAT 30) instrument to conduct electrochemical tests. The dc polarization curves are measured at a potential scan rate of 5 mV s^{-1} for estimating the corrosion current densities and corrosion potentials for Ru CMP.

The surface morphology of the prepared Ru thin films and those after subjecting to CMPs is examined by an atomic force microscope (AFM, Digital Instruments, Nanoscope IIIa) operated in the tapping mode, and the root-mean-square roughness (R_q) of the surface is obtained from the AFM analysis. The surface roughness, or RMS roughness, of the metal surface is defined as the standard deviation of the elevation, z values, within the given area, and is calculated from

$$R_q = \sqrt{\frac{\sum (z_i - z_{ave})^2}{N}} \quad (1)$$

where z_i is the z value for a given point, z_{ave} is the average of the z values within the given area and N is the number of points within the given area (i.e., 512x512 = 262,144 points).

A field-emission scanning electron microscope (FESEM, Nova, NanoSEM230) is utilized to characterize microstructures of sample surfaces, and X-ray diffraction (XRD, Rigaku) analysis is also conducted to obtain crystalline information on the electrodeposited Ru film.

3. Results and discussion

3.1. Electrodeposition of Ru thin film

3.1.1. Effect of current density on Ru electrodeposition

Potential transients recorded at various applied current densities (i.e., -1.0, -3.0, -5.0 and −7.0 mA cm^{-2}) with the RDE speed controlled at 500 rpm are shown in Fig. 1. The inset shows the responses at the early stage of electrodeposition operations, which indicates that the Ru metal can be properly deposited onto the Ti substrate. As results suggest, at an early short time interval the electrode process is mainly the nucleation of Ru clusters on a Ti surface, while at a longer time the electrode process is controlled by electrode kinetics with enough nucleation sites on electrode surface. The nucleation activation energy at the Ru/Ti interface is larger for the initial Ru electrodeposition reaction, so the electrodeposition potential is more negative initially.