Available online at www.sciencedirect.com
SCIENCE @ DIRECT®
Thin Solid Films 504 (2006) 227 – 230
www.elsevier.com/locate/tsf

Characterization of copper chemical mechanical polishing (CMP) in nitric acid–hydrazine based slurry for microelectronic fabrication

M. Surya Sekhar, S. Ramanathan *

Particle Science Laboratory, Department of Chemical Engineering, Indian Institute of Technology-Madras, Chennai-600036, India

Abstract

Chemical mechanical polishing of copper in nitric acid based slurry, with hydrazine as inhibitor was investigated. The polish rate and static etch rate decreased with the addition of hydrazine. Electrochemical corrosion studies confirm the inhibiting effect of hydrazine. The roughness of the polished copper surface improved with the addition of hydrazine.

Keywords: Chemical–mechanical polishing; Copper; Hydrazine

1. Introduction

The chemical mechanical polishing (CMP) of copper is one of the key processes in the microelectronic industry [1,2]. It is influenced by numerous process parameters, including pressure, velocity, type of abrasive, concentrations of various chemicals and pH. Cu CMP can be performed in acidic or neutral or alkaline media [2–5]. Typical alkaline slurries contain ammonia and ammonium salts and the removal is primarily mechanical [2,4]. Slurries containing hydrogen peroxide and glycine have been investigated in acidic media [6,7]. In acidic media, nitric acid is also commonly used due its high dissolution rates of copper and its ability to hinder the redeposition of the removed copper species [8].

Typically a corrosion inhibitor is added to acidic slurries, in order to avoid isotropic etching of copper, so that better planarization may be obtained. Frequently, Benzotriazole (BTA) is used as an inhibitor for the nitric acid based slurries [4,9–11]. Citric acid has also been used as an inhibitor for Cu CMP in HNO_3 slurries [8].

Hydrazine is known as an inhibitor of copper corrosion in nitric acid [12]. In this paper, the effect of addition of hydrazine to slurries containing silica abrasives and various concentrations of nitric acid was investigated. Electrochemical methods, static etch rate and polish rate measurements were used to study the additive effect. The polished surface was characterized using atomic force microscopy (AFM).

2. Experimental

2.1. Chemical mechanical polishing

The polishing experiments were carried out using a bench top Labpol-5/Laboforce-3 polisher (Struers), with SUBA IV pads (Rodel Inc). Electrochemical grade copper disks of 25.4 mm diameter were used for all the polishing and static etch rate experiments. The slurry contained 5% (wt./vol.) fumed silica abrasives (Cab-o-sil, EH-5 with a surface area of 380 m^2/gm, from Cabot-Sanmar, India). All the polishing runs were carried out for 3 min and the slurry flow rate was maintained at 100 ml/min. The applied down force was 30 N (2.15 psi). The sample was rotated at 250 rpm while the turn table with the pad was rotated at 150 rpm. Static etch rate experiments were carried out for a period of 20 min.

The polish rates and the etch rates were calculated by measuring the weight loss of the disks using Citizen Balance (0.1 mg accuracy). At least three identical runs were conducted and the average removal rate or etch rate is reported in nm/min.

2.2. Electrochemical measurements

Electrochemical studies were performed using an Advanced Electrochemical System (PARSTAT 2263, Princeton Applied

---

* Corresponding author. Tel.: +91 44 2257 4171; fax: +91 44 2257 0509.
E-mail address: srinivar@iitm.ac.in (S. Ramanathan).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.09.128

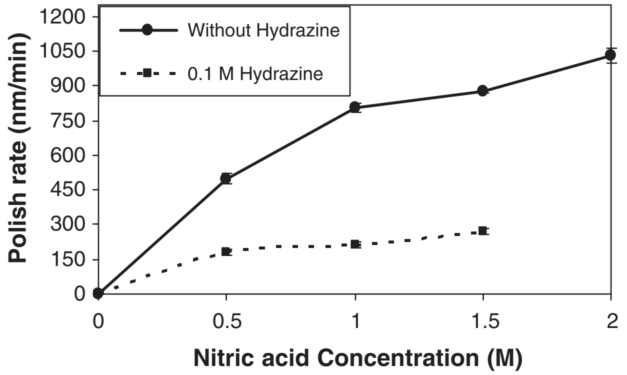

Fig. 1. Removal rate of copper as a function of nitric acid concentration. Polisher settings: 2. psi, 150 rpm table rotation speed, 250 rpm sample rotation speed, 100 ml/min slurry flow rate. Slurry used: 5% (wt./vol.) Fumed Silica.

Research). A standard three electrode cell was used with a platinum wire of 1 mm diameter (99.99% purity, Aldrich) as counter electrode and a saturated calomel electrode (pH products, India) as reference electrode. A copper rod of 11 mm diameter (99.9999% purity, Aldrich) was used as the working electrode. Prior to each experiment, the working electrode was mechanically polished with successively finer grades of alumina down to 0.05 micron in diameter, followed by rinsing and sonication in ultrapure water to remove any attached alumina particles.

Potentiodynamic polarization curves were obtained by scanning the potential at a rate of 1 mv/s from −250 to 250 mV versus open circuit potential. Impedance measurements were made by superimposing a 10 mV sinusoidal potential over the frequency range of 10 to 100 kHz.

2.3. AFM studies

Surface morphology studies of the copper were carried out by Atomic Force Microscopy (Dimension series 3100 AFM, Digital Instruments) using contact mode Si probe.

3. Results and discussions

The CMP removal rate of copper as a function of nitric acid concentration in silica slurries, with and without hydrazine is shown in Fig. 1. As expected, the removal rate increases with increase in acid concentration, in the absence of hydrazine. Addition of 0.1 M hydrazine decreases the removal rate significantly. In presence of 0.1 M hydrazine, increase in nitric acid concentration leads to only a marginal increase in the polish rate. The increase in the polish rate shows a nonlinear behavior, and tends to saturate at high acid concentrations. The polish rate data compare well with those reported in literature using nitric acid based slurries [13].

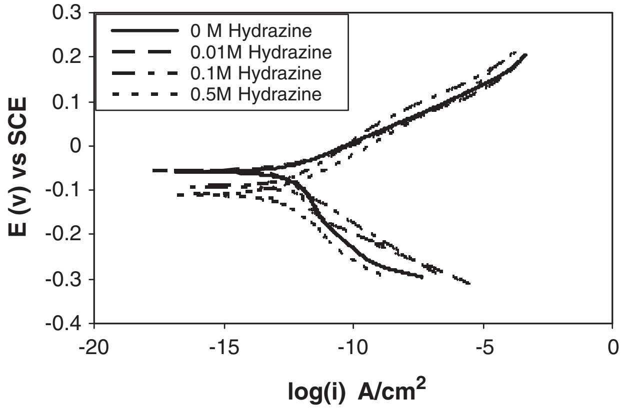

Fig. 2. Polarization curves of copper in 1 M nitric acid and various concentrations of hydrazine.

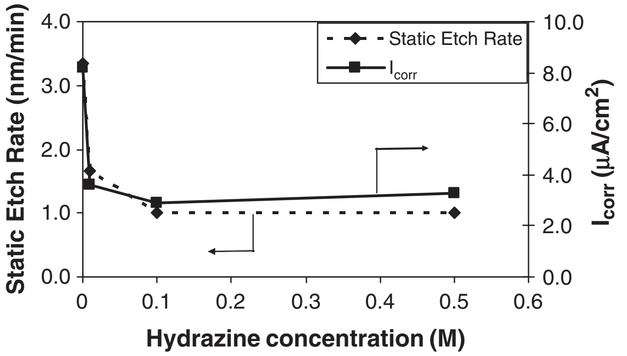

Fig. 3. Corrosion current and static etch rate of copper as a function of hydrazine concentration in 1 M nitric acid.

Tafel plots for the copper electrode in 1 M nitric acid and various concentrations of hydrazine are shown in Fig. 2. The curve shape does not change significantly with the addition of hydrazine. The corrosion potential (E_{corr}) and the corrosion current density values (I_{corr}) were calculated by linear interpolation of the cathodic and anodic branches of the Tafel plots, using the *Powercorr* software (Princeton Applied Research). The corrosion potential shows a shift of about 100 mV in the cathodic direction with the addition of 0.5 M Hydrazine. A shift in the anodic direction would indicate the formation of a passivating film [7,8,14,15]. Hence there is no evidence that the addition of hydrazine leads to the formation of a passivating film on copper surface.

The I_{corr} values and the static etch rates of copper in 1 M nitric acid as a function of hydrazine concentrations are shown in Fig. 3. The I_{corr} and etch rate decrease significantly with the addition of 0.01 M hydrazine. The reduction in I_{corr} corre-

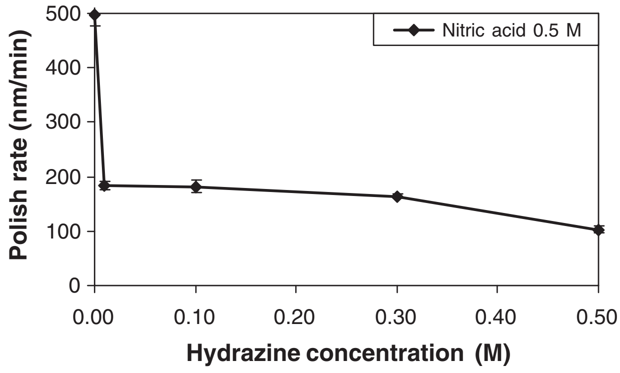

Fig. 4. Removal rate of copper as a function of hydrazine concentration in 0.5 M nitric acid slurry. Polisher settings: 2. psi, 150 rpm table rotation speed, 250 rpm sample rotation speed, 100 ml/min slurry flow rate. Slurry used: 5% (wt./vol.) fumed silica.