Applied Surface Science 256 (2010) 2583–2595

Contents lists available at ScienceDirect

Applied Surface Science

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

Electrochemical characterization of surface complexes formed on Cu and Ta in succinic acid based solutions used for chemical mechanical planarization

Christopher M. Sulyma, Dipankar Roy *

Department of Physics, Clarkson University, Potsdam, New York 13699-5820, USA

ARTICLE INFO

Article history:
Received 2 June 2009
Received in revised form 2 October 2009
Accepted 31 October 2009
Available online 10 November 2009

PACS:
68.08.−p
68.43.−h
81.20.−n
81.65.−b
82.45.Bb

Keywords:
Copper
CMP
Impedance spectroscopy
Rotating disc
Surfactant
Tantalum

ABSTRACT

Open-circuit potential measurements, cyclic voltammetry and Fourier transform impedance spectroscopy have been used to study pH dependent surface reactions of Cu and Ta rotating disc electrodes (RDEs) in aqueous solutions of succinic acid (SA, a complexing agent), hydrogen peroxide (an oxidizer), and ammonium dodecyl sulfate (ADS, a corrosion inhibitor for Cu). The surface chemistries of these systems are relevant for the development of a single-slurry approach to chemical mechanical planarization (CMP) of Cu lines and Ta barriers in the fabrication of semiconductor devices. It is shown that in non-alkaline solutions of H_2O_2, the SA-promoted surface complexes of Cu and Ta can potentially support chemically enhanced material removal in low-pressure CMP of surface topographies overlying fragile low-k dielectrics. ADS can suppress Cu dissolution without significantly affecting the surface chemistry of Ta. The data analysis steps are discussed in detail to demonstrate how the D.C. and A.C. electrochemical probes can be combined in the framework of the RDE technique to design and test CMP slurry solutions.

1. Introduction

The newer interconnect structures are designed to have low-k dielectrics underlying Ta/TaN barrier layers and Cu lines [1,2]. Many of these dielectrics consist of mechanically fragile, Si-based porous materials that disintegrate in alkaline media due to carbon-depletion and/or deformation of their Si–H bonds [3]. Avoiding these low-k damages is an important criterion of the chemical mechanical planarization (CMP) technique used for damascene processing of interconnects structures. Meeting this criterion requires low down-pressure (low-P) polishing as well as non-alkaline slurry solutions, where single-dispersion slurries could offer several additional advantages [4–6]. For instance, in the single-dispersion chemically enhanced CMP (CE-CMP) approach, removal of both Cu lines and Ta/TaN barrier layers can be controlled by adjusting the slurry pH, without changing the complexing agent(s) and the oxidizer of the polishing slurry. By controlling the pH and the H_2O_2 content of such a slurry it is also possible to tune the rates of bulk and residual Cu removal, which can minimize dishing [6]. Recent efforts to address these issues have identified certain carboxylic/di-carboxylic acids as potentially useful complexing agents for CMP of both Cu and Ta/TaN in non-alkaline media [5–7]. Among these acids, SA (H_2Su, $Su = C_4H_4O_4$) has yielded satisfactory values of polish rate (PR) to dissolution rate (DR) ratios for Cu (typically, $PR/DR \approx 3–5$ at pH 2–5 for a polish pressure at ~6 psi using fumed silica abrasives and H_2O_2) [7]. SA also serves as a stabilizer of H_2O_2 in Cu-CMP [8], and is used in Ta and TaN barrier CMP slurries [9,10]. Due these reasons, SA is an attractive complexing agent for single dispersion CMP of Cu and Ta.

Most CMP slurries include an oxidizer (typically H_2O_2) to generate oxides and hydroxides that would react with the complexing agents more efficiently than the bare metals [11,12]. Dissolution and/or mechanical disintegration of these complexes provide the main routes to low-P material removal in CMP. For Cu CMP, a dissolution inhibitor is also necessary to regulate excessive chemical etch and maintain good planarization efficiency [13]. Ammonium dodecyl sulfate (ADS) is an effective dissolution inhibitor for Cu [13,14], which can easily be removed during post-CMP cleaning [13–15]. The combination of SA, H_2O_2,

* Corresponding author. Tel.: +1 315 268 6676; fax: +1 315 268 6610.
E-mail address: samoy@clarkson.edu (D. Roy).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.10.108

and ADS chosen in the present work is based on the above considerations. In comparison with Cu, Ta is far less reactive, because in air-saturated aqueous solutions Ta surfaces generally are covered with inert Ta_2O_5 films [16,17]. In the single-dispersion approach, however, the same slurry components are exposed (at different pH settings) to both Cu and Ta [5,6], and hence, the corrosion inhibitor of Cu in such a system must not interfere with the CMP of Ta. The present study addresses these issues of Cu and Ta CMP in SA and ADS based solutions.

The experiments reported here combine D.C. and A.C. electrochemical techniques, using Cu and Ta rotating disc electrodes (RDEs) as model systems. Since the surface reactions of CMP occur at open-circuit potentials (OCPs), the slurry- and metal-dependent OCPs are analyzed in detail. D.C. voltammetry is employed to study the reaction characteristics of these RDEs, and the reaction mechanisms are examined further using Fourier transform electrochemical impedance spectroscopy (FT-EIS). A substantial part of this work focuses on the analytical aspects of studying such CMP systems by combining D.C. and A.C. electrochemical techniques. Application of FT-EIS to RDE systems has rarely been reported in previous studies of CMP slurry chemistries [14,18]. Furthermore, the corrosion and surface passivation steps in CMP are governed by mixed potential effects [19–21], and this specific aspect of CMP also has remained relatively underexplored in the published CMP literature. Therefore, certain essential elements of these subjects are discussed in the next section to outline the analytical techniques and the strategies used here for combining these techniques. The experimental procedures and results, and the implications of these results are discussed in subsequent sections.

2. Background and theoretical considerations

2.1. Considerations for OCP analysis

Surface reactions on metals in the CMP environment frequently are composed of faradaic steps, where an anodic process is balanced by a cathodic one. According to the mixed potential theory [20,21], the relative strengths of these mutually coupled electrochemical reactions, which occur in the absence of external voltage activation, are manifested in the characteristic behavior of the OCP of the metal–liquid interface. Thus, OCP measurements provide a convenient method for studying the detailed reactive features of metals in CMP solutions. The strategy for applying this technique to the presently used Cu and Ta systems is illustrated below from an examination of the expected surface reactions supported by these systems.

Depending on the solution pH, SA exists as H_2Su, HSu^- or Su^{2-}. H_2Su and HSu^- tend to electrochemically react with Cu [22] as follows:

$$Cu + H_2Su = CuHSu^+ + H^+ + 2e^- \quad (E^0 = 0.16\,V), \tag{1}$$

$$Cu + HSu^- = CuSu + H^+ + 2e^- \quad (E^0 = 0.17\,V), \tag{2}$$

where E^0 denotes standard potentials [22,23]. The main cathodic reactions on Cu in the presently used system are those of H_2O_2 and O_2 reduction [11,12,22,23]:

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \quad (E^0 = 1.53\,V), \tag{3}$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad (E^0 = 0.99\,V), \tag{4}$$

where in a strict sense, the H^+ should be considered as H_3O^+. The reversible formal potentials (E_r) for the above reactions can be obtained by using the corresponding E^0 values in the Nernst Equation. If H_2Su is the predominant solution species of SA, and if the OCP (E_{OC}) of Cu exhibits a value between those of E_{r3} and E_{r1} (reversible potentials for reactions (3) and (1), respectively) then reactions (1) and (3) will be coupled, with the net reaction having the form: $Cu + H_2Su + H_2O_2 + H^+ = CuHSu^+ + 2H_2O$. Likewise, if E_{OC} of Cu in a solution of HSu^- is located between E_{r3} and E_{r2} (reversible potentials for reactions (2)), then a net reaction, composed of reactions (2) and (3) will be expected: $Cu + HSu^- + H_2O_2 + H^+ = CuSu + 2H_2O$. The last two reactions do not involve any net charge transfer across the metal–solution interface, and could be sustained at the OCP without activation voltages.

For freshly polished, oxide-free Ta in aqueous solutions, the main anodic reaction is [17]:

$$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10e^- \quad (E^0 = -0.99\,V), \tag{5}$$

which might be driven by reactions (3) and/or (4), since the standard potentials of both the latter reactions are considerably higher than that of reaction (5). For example, if reactions (4) and (5) are coupled, then the effective step is: $4Ta + 5O_2 = 2Ta_2O_5$ [4,24]. Previously, this mixed potential mechanism has been suggested as a possible origin of the native Ta_2O_5 commonly found on Ta under ambient conditions [4,24,25]. In the context of our present study, this oxidation mechanism might play a significant role when a fresh Ta sample is first introduced in the experimental cell [4].

In actual CMP, mechanical abrasion of the sample removes the loosely bound surface species [1], but laboratory scale electrochemical measurements (as those reported here) often are performed in the absence of surface abrasion [4,14,26]. RDEs are useful for OCP measurements in the latter situation [14,18], as the rotational motion of the RDE helps to remove the physisorbed species from the sample surface [27] minimizing their effects on the recorded OCP data.

2.2. Factors affecting excess surface charges of Cu and Ta in CMP solutions

Electrostatic adsorption/desorption of charged species plays an important role in controlling the surface chemistry (and hence the removal rates) of Cu and Ta in CMP [4,11–15]. Therefore, to study the chemical mechanisms of Cu and Ta CMP, it is necessary to examine the factors that dictate the surface charges of these metals in the slurry solutions used. Typically, the metal surface subjected to CMP contains both bare and oxide covered sites, where the latter might be native species and/or those formed by an oxidizer in the CMP solution. The excess surface charge density q (E_{OC}) of Cu at the OCP has the form [13,15]:

$$q \approx (E_{oc} - E_{PZC}^{eff})\bar{C}, \tag{6}$$

where E_{PZC}^{eff} is the effective potential of zero charge (PZC) of the partially oxide covered "amphifunctional" surface, determined by both the intrinsic PZC of the bare metal and the isoelectric point (IEP) of the surface oxide sites [28]. Phenomenologically, q can be split in two parts, q_M and q_{ox}, representing the excess charges arising from the bare metal and the oxidized surface sites, respectively. A substantial component q_{ox} originates at the hydroxylated oxide sites (M–OH), $(M–O)^-$ and $(M–OH_2)^+$ [4]:

$$q_{ox} = F\{[(M - OH_2)^+] - [(M - O)^-]\}, \tag{7}$$

where M denotes the metal under study; F is the faraday constant; $q_{ox} = 0$ at the IEP. In Cu-CMP, H_2O_2 is a commonly used oxidizer that partially oxidizes the metal: $2Cu + H_2O_2 = Cu_2O + H_2O$; $Cu_2O + H_2O_2 = 2CuO + H_2O$. The net surface charge on the resulting Cu/Cu-oxide surface is controlled by both the PZC of Cu and the IEP of Cu-oxides, and hence, follows the description of Eq. (6).

As noted in the context of Eq. (5), Ta surfaces in aqueous solutions generally are covered with native Ta_2O_5 films. In