Electrochimica Acta 210 (2016) 512–519

Contents lists available at ScienceDirect

Electrochimica Acta

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

Micro-pattern Corrosion Screening on Bimetallic Corrosion for Microelectronic Application

Kyle Kai-Hung Yu[a], Sirish Rimal[a], Muthappan Asokan[a], Praveen R. Nalla[a], Simon Koskey[a], Karthikeyan S.M. Pillai[a], Oliver Chyan[a,*], Kanwal Jit Singh[b], Satyarth Suri[b]

[a] Interfacial Electrochemistry and Materials Research lab, Department of Chemistry, University of North Texas, Denton, TX 76203, USA
[b] Components Research, Intel Corporation, Hillsboro, OR 97124, USA

ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form 27 May 2016
Accepted 28 May 2016
Available online 28 May 2016

Keywords:
Microscopic corrosion
Bimetallic corrosion
Ammonium citrate
Fluorocarbon residues
Corrosion inhibitor

ABSTRACT

The continued miniaturization of the integrated circuit, leading to minute dimensions (< 10 nm) in microelectronic architecture, can greatly accelerate the on chip corrosion into a severe reliability threat. Particularly, various interfaces between multilayered film stacks create dissimilar contacts with significant galvanic potential difference. This can promote on-chip corrosion under semiconductor processing conditions. In this paper, an efficient micro-pattern corrosion screening metrology combined with electrochemical and x-ray photoelectron scattering techniques, is utilized to study bimetallic corrosion and its inhibition in wafer cleaning solutions. Cu/Ru bimetallic contact was found to exhibit a higher corrosion rate than the Cu/Ta contact. In alkaline ammonium citrate solution, higher dissolved oxygen content significantly accelerated Cu corrosion. The increased alkalinity (pH > 12) at Cu/Ru interface, caused by enhanced oxygen reduction reaction on Ru, is proposed to generate more NH_3 for sustaining fast Cu corrosion. Effects of different plasma chemistries like CF_4, $CF_4 + O_2$, CH_2F_2, C_4F_8 and SF_6 on the Cu corrosion in tetramethylammonium hydroxide (TMAH) were also investigated. Plasma treatments using higher fluorine content gases showed higher Cu corrosion rate in TMAH. Benzotriazole showed limited corrosion inhibition to plasma treated Cu/Ru micro-patterns in pH 14 TMAH solution. Contrastingly, pyrazole demonstrated as an effective corrosion inhibitor suppressing Cu corrosion rate down to the desirable < 1 A°/min level.

1. Introduction

In modern integrated circuit (IC) design, the copper interconnects play a key role as the digital communication superhighway between nanometer size transistors (< 10 nm) on a silicon chip and the external analog functions like audio/visual displays and touch screens. Due to the inability to directly pattern Cu by reactive ion etching (RIE), the intricate Cu interconnects are fabricated indirectly using a damascene patterning process [1]. As highlighted in Fig. 1, the damascene patterning process involves creating a trench/via pattern into a porous low *k* dielectric film by plasma-assisted RIE, followed by bottom up Cu electrodeposition (ECD) on a barrier/liner/Cu seed over layer, and subsequent removal of the Cu overburden by chemical-mechanical planarization (CMP) [1–4]. Finally, post-CMP cleans are needed to completely remove organic and inorganic contaminants left over after the CMP polishing process.

As IC device structures scale down to <10 nm nodes, even a minute materials losses from wafer cleaning can readily impact the device performance through critical dimension (CD) changes and film modification [5]. In particular, exposure to corrosive CMP and cleaning chemicals cause microscopic Cu bimetallic corrosion defects across Cu/barrier/ULK interfaces, which can be highly detrimental to device reliability and production yield [6–8]. The decreasing dimension of copper interconnects can further exacerbate the corrosion damage, as a $20 \times 20 \times 100$ nm Cu line has a mass of 3.6×10^{-16} grams can be completely corroded with an oxidation charge of only 1 pC. Furthermore, the evolving complex microfabrication processes used for making next generation IC devices results in various dissimilar Cu contacts exposed to complex chemical environments, making identification and prevention of microscopic on-chip bimetallic corrosion a technologically challenging task.

In this paper, a new micro-pattern corrosion screening metrology was developed to study Cu bimetallic corrosion in post

* Corresponding author.
E-mail address: Chyan@unt.edu (O. Chyan).

http://dx.doi.org/10.1016/j.electacta.2016.05.189
0013-4686/

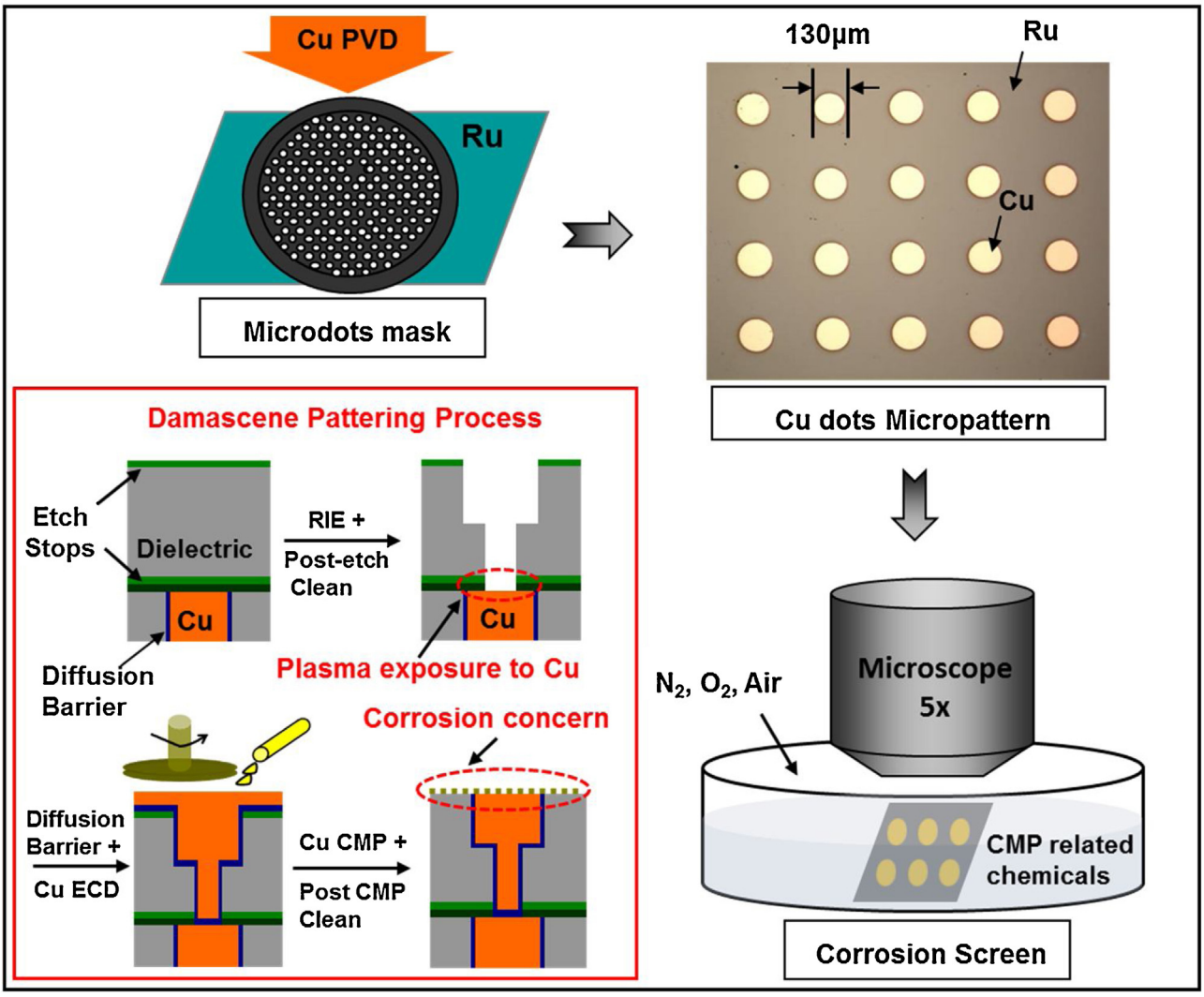

Fig. 1. Micro pattern corrosion screening metrology. Inset shows the dual damascene patterning process for fabricating Cu interconnects.

Cu CMP and post RIE cleans related chemical environments. As illustrated in Fig. 1, patterns of Cu microdots were fabricated by magnetron sputtering through a contact mask on selected barrier/liner metal substrates including Ta, Ru, and TaN. The Cu corrosion on the test pattern was observed and recorded in real time with a digital optical microscope. The relatively small Cu microdots (D = 130 μm) were chosen to permit rapid corrosion screening in different chemical environments with various bimetallic contacts and ambient controls. The micro-pattern corrosion screening results, corroborated with electrochemical and x-ray photoelectron spectroscopy (XPS) measurements, revealed the Cu corrosion mechanism in alkaline ammonium citrate under the influence of Cu/Ru and Cu/Ta bimetallic contacts. Micro-pattern corrosion screening was also used to study the corrosion behavior of Cu in tetramethylammonium hydroxide (TMAH) after five different plasma treatments including CF_4, $CF_4 + O_2$, CH_2F_2, C_4F_8 and SF_6 etching gases. XPS and contact angle were used to examine the effect of Cu surface after plasma treatments. Our micro-pattern corrosion screening data demonstrated that pyrazole is a more effective corrosion inhibitor than commonly used benzotriazole (BTA) for plasma-treated Cu samples in alkaline TMAH.

2. Experimental

The micro-pattern corrosion screening method used in this study was described in detail previously [9,10]. The Cu microdots (ca. 70 nm thick and 130 μm in diameter) were deposited on Ru and Ta substrates through a contact mask by magnetron sputtering. Visual corrosion screening, recorded by a metallurgical microscope (Nikon, Eclipse ME600), was carried out by immersing Cu/Ru and Cu/Ta micro-patterns in a test solution (specific composition detailed in the text). Ambient environmental control was achieved by bubbling N_2, Ar or O_2 gas and subsequently maintaining an ambient blanket over solution. Plasma treatments on micro-patterns using CF_4, $CF_4 + O_2$, CH_2F_2, C_4F_8 and SF_6 plasma etch gases were done using an OXFORD PLASMALAB100 system. The plasma treatment time was 30 sec for all samples, operated at 5 mTorr and 20 °C with 400 W top and 50 W RF bias applied. Water contact angle measurements were used to determine the surface wettability of the plasma treated samples.

All chemicals were ACS reagent grade and used as received. All test solutions, specific composition detailed in the text, were prepared using pre-purified water (> 18.2 MΩ, Millipore integral