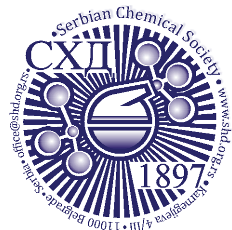

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Urea as a complexing agent for selective removal of Ta and Cu in sodium carbonate based alumina chemical–mechanical planarization slurry

ARPITA SHUKLA, NOYEL VICTORIA SELVAM
and MANIVANNAN RAMACHANDRAN*

Department of Chemical Engineering, National Institute of Technology Raipur, Chhattisgarh-492010, India

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Abstract: This work reports urea as a promising complexing agent in sodium carbonate-based alumina slurry for chemical–mechanical planarization (CMP) of tantalum and copper. Ta and Cu were polished using Na_2CO_3 (1 wt. %) with alumina (2 wt. %) in the presence and absence of urea. The effect of slurry pH, urea concentration, applied downward pressure and platen rotational speed were deliberated and the outcomes conveyed. Prior to the addition of urea, the Ta removal rate (RR) was observed to increase with pH from acidic to alkaline, having a maximum RR at pH 11. However, Cu RR decreases with increasing pH with minimum RR at pH 11. With the addition of urea in the slurry, a Cu to Ta removal rate selectivity of nearly 1:1 was encountered at pH 11. The addition of urea simultaneous boosts the Ta RR and suppresses Cu RR at pH 11, as it adsorbs on the metal surface. Potentiodynamic polarization was conducted to determine the corrosion current (I_{corr}) and the corrosion potential (E_{corr}). Electrochemical impedance spectroscopy of both metals was carried out in the proposed formulation and the obtained outcomes are elaborated.

Keywords: chemical mechanical planarization; corrosion potential; electrochemical study; electrochemical impedance spectroscopy; corrosion current.

INTRODUCTION

In the realm of integrated circuit (IC) industries, chemical mechanical planarization (CMP) has acquired immense attention to date.[1] There are different applications of CMP in the process of IC fabrication, among which front-end-of-line (FEOL) and back-end-of-line (BEOL) processes hold significant importance.[2] The materials used for gap-filling, such as silicon dioxide, are polished during the FEOL stage. The BEOL stage includes the formation of metallic interconnects and

* Corresponding author. E-mail: rmani.che@nitrr.ac.in
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a barrier layer. Copper and tantalum are widely used as interconnect and barrier materials, respectively.[3] Cu having extremely promising characteristics, such as low resistivity and high electron migration resistance, has been given precedence over aluminum for interconnects.[4] Due to its higher mobility, Cu poses a tendency to diffuse in silicon and Si-based materials. A diffusion barrier layer made up of Ta or TaN is incorporated to hinder Cu diffusion between Cu and adjacent Si-based material.[5] Currently, in the integrated circuits fabrication, Cu is employed for BEOL along with materials having a lower value of dielectric constant, such as Ta and nitrides of Ta.[6]

In IC manufacturing industries, it is vital to maintain the polishing rate of Ta as well as Cu consistent.[7] Moreover, a Cu to Ta polishing selectivity ratio of nearly 1:1 is preferable for efficient polishing. The formulation of the polishing slurry is of significant importance in metal CMP. The polishing slurry is mainly a combination of an abrasive, oxidizer dispersed in distilled water. Various additives, such as complexing agents, surfactants, corrosion inhibitor, dispersants *etc*., may be present in the polishing slurry depending on the desired metal to be polished. Fumed silica, colloidal silica, alumina are some of the frequently studied abrasives for metal polishing.[8–11] Numerous oxidizers, such as potassium iodate, quinones, and their derivatives *etc.*, have been intricately studied, among which hydrogen peroxide (H_2O_2) is the most prominent one. A slurry containing H_2O_2 as oxidizer is not stable as it has a decomposition nature. A stabilizer, such as phosphoric acid, must be used in the formulated slurry to overcome the decomposition issue.[12–14] Many researchers have worked on Ta and Cu CMP, but only a few literature reports are available on 1:1 Cu to Ta removal rate selectivity. Jindal *et al.* reported 1:1.7 selectivity in a slurry containing 3 wt. % fumed silica, 5 wt. % H_2O_2 and 1 wt. % glycine as complexing agent at pH 12.[15] Babu *et al.* reported approximately 1:1 selectivity using a slurry formulation of 5 wt. % colloidal silica, 5 wt. % H_2O_2 and 0.13 M tartaric acid at pH 6.[16] Kaufman *et al.* investigated Ta and Cu CMP with slurry comprising of 2 wt.% alumina, 5 wt.% H_2O_2 and 0.5 wt.% tartaric acid at pH 10 and reported a selectivity of 1:1.9.[17] Carter *et al.* studied a Cu and Ta CMP using a slurry composition of 0.5 wt. % fumed silica, 0.5 wt. % cesium carbonate and 5 mM of various organic and inorganic quinon containing compounds as oxidizers at pH 2.2 and obtained a range of selectivity with different oxidizer, *i.e.*, 1,8-disulfonic acid dipotassium salt (≈3:1), 1,5-disulfonic acid disodium salt (≈1.5:1), H_2O_2 (0.17:1) and potassium persulfate (≈1:1).[14] Although few researches has been performed on Ta and Cu CMP incorporating various competent abrasives, oxidizers, and complexing agents, the mechanism of the removal rate selectivity is still not well understood. This study targets the achievement of a Cu to Ta removal rate selectivity of 1:1. Cu and Ta differ highly in their chemical and physical properties, being a mild and hard metal, respectively. The addition of an additive is needed, which can enhance the Ta RR and simultaneously suppress

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Cu RR. Organic acids, such as citric acid, tartaric acid and urea, were tested and better synergy for both the metals with urea was obtained. Hence, urea was selected for further selectivity study in the alkaline region and has also previously been studied as an inhibitor for Cu CMP.[18] Particularly, sodium carbonate as oxidizer and urea as complexing agent have not been studied in any literature to date and this is the first report which uses the above formulation for Ta and Cu CMP.

In this research work, Ta and Cu CMP experiments were performed using a polishing slurry containing alumina as abrasive, sodium carbonate as oxidizer and urea as complexing agent dispersed in distilled water. Static etch rate experiments were performed for both metals in the oxidizer solution at various pH to understand the chemical dissolution behavior. However, the static etch rate of tantalum was found to be practically zero. The influence of numerous parameters, such as pH of the polishing slurry, alteration in the concentration of the complexing agent, increasing the applied downward pressure and increase in rotational platen speed on metal removal rate was studied and the results are conveyed. A metal polishing selectivity of nearly 1:1 is reported, which is desirable for a CMP involving more than one type of metal. Electrochemical analysis, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) of both the metal were performed in 1 wt. % sodium carbonate solution in the presence and absence of urea. An electrical equivalent circuit (EEC) was proposed for the EIS results, and the EIS data were also validated using the Kramer–Kronig transformation.

EXPERIMENTAL

Polishing experiments were executed using a benchtop polisher assembly of Labopol 5 and Laboforce 3 purchased from Struers Denmark. A Suba IV polishing pad, constructed of polyurethane, obtained from Eminess Technology, USA, was used for the CMP experiments. All the experiments were performed using Ta (≈99.9 % pure) and Cu (≈99.9 % pure) coupons, which were purchased from Alfa Aesar and Industrial Engineering Store, India, respectively. Both the coupons had 2.5 cm diameter and 1.25 cm thickness. Polishing slurry composed of alumina as abrasive along with sodium carbonate as oxidizer, with and without urea as the complexing agent dispersed in distilled water was employed for the CMP experiments. All the used chemicals were of analytical reagent grade and obtained from Loba Chemie. Unless otherwise stated, the concentration of abrasive, oxidizer and complexing agent were maintained at 2, 1 and 0.1 wt. %, respectively. The speed of the coupon holder was fixed at 250 rpm. The platen rotational speed and downward pressure were kept at 100 rpm and 40680 Pa, respectively, unless specified otherwise. The flow rate of the polishing slurry was maintained at 100 ml min^{-1} with the help of a peristaltic pump throughout the experiment. Potassium hydroxide or nitric acid was used to regulate and reach the desired slurry pH. All the polishing experiments were conducted at ambient temperature. The polishing pad was hand conditioned using 600 grade silicon carbide paper employing the same slurry prior to each polishing cycle to ensure consistency of the polishing pad surface. Both the coupons were washed with distilled water and subsequently air dried. The samples were weighed before and after polishing using an analytical balance (Sartorius, BSA 2245-CW). The rate of material removal was calculated from weight loss of the specimen, metal density, area and the polishing time. The

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average removal rate and the standard deviation were calculated from three polishing runs performed under identical conditions.

A PARSTAT MC 1000 electrochemical workstation (Ametek, USA) was used for all the electrochemical experiments. Open circuit potential (OCP), potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) were executed and the outcomes were studied. The cell consisted of the studied metal electrode (Cu/Ta), a saturated Ag/AgCl electrode and a platinum wire, employed as the working, reference and counter electrode, respectively. All potentials in the paper refer to Ag/AgCl scale. The working electrode for both the metals was prepared by covering small cylindrical metal sample with a Teflon casing giving a circular cross section of the exposed surface. The electrical connection between the electrochemical cell system and working electrode were established with the aid of copper. The working electrodes were polished with 0.3 μm alumina powder followed with 0.05 μm alumina powder procured from Buehler (USA). Both the electrodes were then washed and sonicated with distilled water. The electrolyte used in this study was Na_2CO_3. HNO_3 or KOH were used to maintain the pH of the electrolyte solution. Open circuit potential (OCP) measurements were performed for 3 min to stabilize the electrochemical system preceding all the electrochemical experiments. A potential range of –250–250 mV was applied with respect to the value obtained from the OCP for the Tafel experiments at a scan rate of 1 mV s^{-1}. After extrapolation of the anodic and cathodic branches of the tafel curves using PARSTAT software, the E_{corr} and I_{corr} values were found. A frequency range of 0.1 Hz to 100 kHz with respect to the OCP value was applied for the EIS studies. An EEC was identified using ZSimpWin (Princeton Applied Research, USA) software which gives more insight into the results obtained from EIS.

RESULTS AND DISCUSSION

Effect of pH on material removal rate

The effect caused by change in pH of the slurry on the removal rate of Ta and Cu is illustrated in Fig. 1a and b. The CMP experiments were executed using a slurry containing 2 wt. % alumina and 1 wt. % sodium carbonate (Fig. 1a) without urea (Fig. 1b) with 0.1 wt. % urea. Without urea, the Ta removal rate increases when the pH moves from acidic to alkaline side with maximum metal removal rate at pH 11.[19] Ta reacts with the water present in polishing slurry forming a stable Ta_2O_5 layer, which is challenging to remove from metal surface. This oxide layer is relatively weaker at alkaline pH values than at acidic ones.[20]

The Ta removal rate was enhanced at all the pH with the introduction of urea to the polishing slurry. The resulting enhancement was perhaps because urea forms a complex with the formed oxide layer. In the absence of urea, the Cu removal rate decreases with increasing pH, with a maximum removal rate at pH 3. In the presence of urea, Cu removal rate was suppressed at all the pH values. This behavior could be attributed to the adsorption of urea on the surface of polished metal. Enhancement in Ta removal rate and suppression in Cu removal rate with the addition of urea yields nearly 1:1 Cu removal rate to Ta removal rate selectivity at pH 11, which is desirable for barrier layer CMP. Henceforth, all the further experiments were conducted at pH 11.

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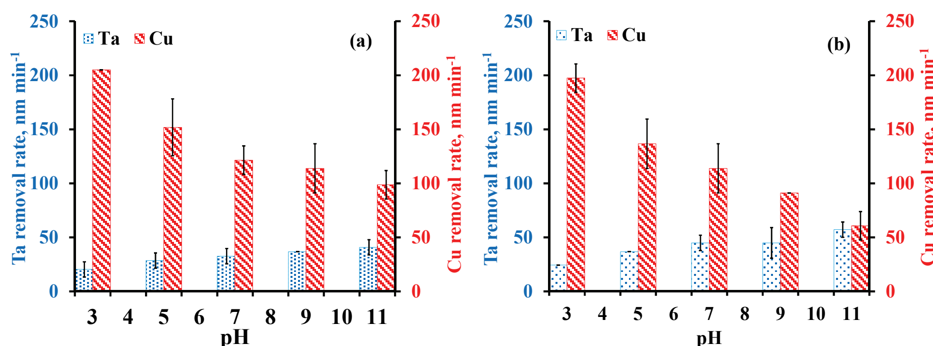

Fig. 1. Effect of pH on material removal rate of Ta and Cu using 2 wt. % alumina and 1 wt. % Na_2CO_3; a) without and b) with urea.

A Cu dissolution study was also performed with and without urea in the solution. A 2 wt. % sodium carbonate solution, a 0.1 wt. % urea and a 2 wt. % sodium carbonate along with 0.1 wt. % urea solution were taken for the dissolution study. Cu showed no dissolution with urea. A decrease in the dissolution rate of copper was observed with increasing pH, ≈12 nm min^{-1} at pH 3 to 3 nm min^{-1} at pH 11 in 2 wt. % sodium carbonate + 0.1 wt. % urea. Nearly the same dissolution was encountered prior to the introduction of urea.

Effect of urea concentration

Effect of urea concentration with 2 wt. % alumina slurry containing 1 wt. % Na_2CO_3 on the Ta and Cu metal removal rate at pH 11 were studied and the outcomes are presented in Fig. 2. As the urea concentration increases from 0.05 to 0.5 wt. %, an increase in the Ta removal rate was observed. A similar trend was also observed for the Cu removal rate. On increasing the urea concentration, the ratio of the Cu to Ta removal rate was observed to decrease initially from 1.5:1 to 1.1:1 and then increases from 1.1:1 to 4:1. The desired polishing selectivity of ~1:1 was observed with 0.1 wt. % urea concentration. Polishing experiments were not performed beyond 0.5 wt. % urea concentration, as the selectivity ratio between Ta and Cu removal rate was higher than the desired range.

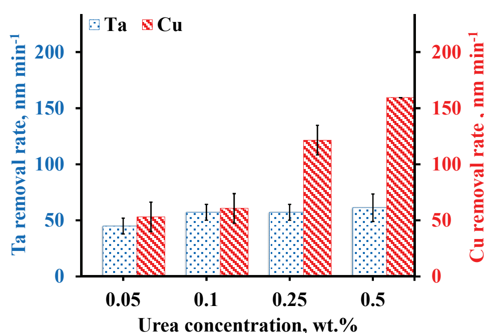

Fig. 2. Effect of urea concentration on material removal rate of Ta and Cu.

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Effect of pressure and platen speed

The influence of the applied downward pressure and platen rotational speed on the removal rate of Ta and Cu are portrayed in Fig. 3a and b, respectively. The experiments were conducted with 2 wt. % alumina + 1 wt. % Na_2CO_3 + 0.1 wt. % urea slurry and a constant pH of 11 was maintained throughout. The applied downward pressure ranged from 19995 to 81359 Pa.

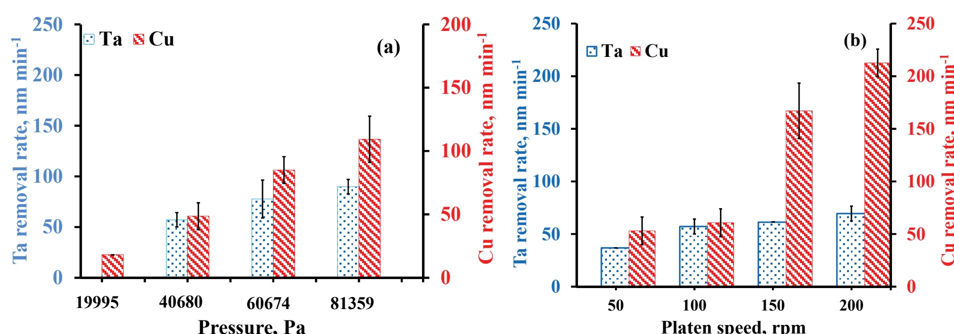

Fig. 3. Effect of: a) applied pressure and b) platen speed on material removal rate of Ta and Cu.

The selectivity of the removal rate was noticed to enhance from 0 to 1.5:1 with increasing applied downward pressure. This could possibly be due to increase in the contact area between metal surface and polishing pad.[21] The rotational speed of the platen was varied from 50 rpm to 200 rpm having same polishing slurry composition mentioned earlier, with a constant pressure of 40680 Pa and the results are reported in Fig. 3b. The removal rate selectivity ratio increased from 1.5:1 to 3:1.

Potentiodynamic polarization study (Tafel)

Tafel experiments were conducted with an electrolytic solution containing 1 wt. % Na_2CO_3 with and without 0.1 wt. % urea for both the metal coupons (Ta and Cu). The studies were performed for various odd pH values from 3 to 11. The results are shown in Fig. 4a and b, which depict the Tafel plot for Ta without and with the addition of urea, respectively. It can clearly be seen that the shift in anodic current density towards the left with increasing pH from 3 to 11 confirms the maximum dissolution at pH 11 for both cases.[3] However, the obtained current density in the latter case is slightly increased. The obtained pattern matches well with the results obtained from the CMP experiments with and without incorporation of urea.

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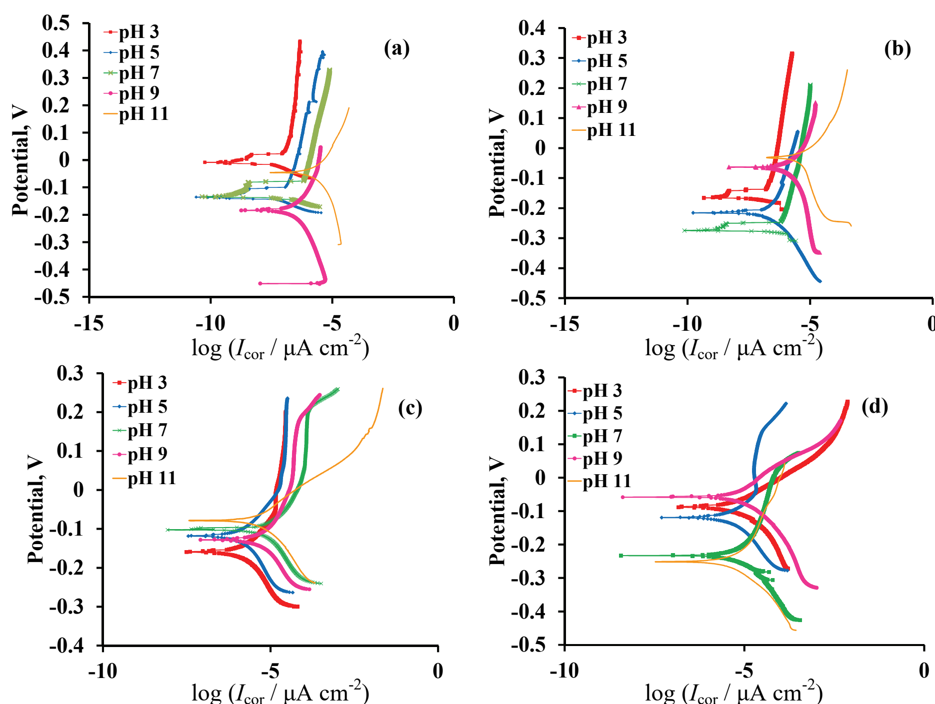

Fig. 4. Potentiodynamic polarization curves of Ta and Cu in the presence of 1 wt. % Na_2CO_3 at various pH values: a) Ta without urea, b) Ta with 0.1 wt. % urea, c) Cu without urea and d) Cu with 0.1 wt. % urea.

On extrapolation of the anodic and cathodic branches, I_{corr} values are obtained for without and with urea and the values are presented in Table I. In the absence of urea, I_{corr} values of tantalum increased from 0.059 to 1.78 μA cm^{-2} with increasing pH value from 3 to 11. After the addition of urea, an increase in I_{corr} value of Ta from 0.07 μA cm^{-2} at pH 3 to 2.84 μA cm^{-2} at pH 11 was observed. This could be due to the adsorption of urea in the Ta surface. The Tafel plot for Cu with the same composition of electrolyte as reported earlier without and with 0.1 wt.% urea are depicted in Fig. 4c and d, respectively.

TABLE I. Tafel parameters for Ta in the presence of 1 wt. % Na_2CO_3 with and without urea at various pH values

pH	Without urea		With urea	
	E_{corr} / mV *vs.* Ag/AgCl	I_{corr} / μA cm^{-2}	E_{corr} / mV *vs.* Ag/AgCl	I_{corr} / μA cm^{-2}
3	–3.13	0.059	–169.71	0.07
5	–128.58	0.07	–211.83	0.156
7	–139.17	0.202	–265.28	0.321
9	–187.17	0.232	–70.73	1.14
11	–48.78	1.78	–37.15	2.84

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The I_{corr} values obtained from extrapolating the anodic and cathodic branches without urea and with urea for both the metals are given in Table II. In the absence of urea, the I_{corr} value decreases from 2.34 to 1.14 μA cm^{-2} with increasing pH value from 3 to 11. However, in the presence of urea, the I_{corr} value decreases from 1.66 μA cm^{-2} at pH 3 to 0.988 μA cm^{-2} at pH 11. With the addition of urea, an inhibition mechanism occurs which causes a reduction in the I_{corr} value over the entire pH range, which corroborates with the CMP results. Galvanic corrosion arises when different electrochemical materials come into electrical contact after they are immersed in an electrolyte. Further optimization of the slurry is required based on the galvanic corrosion potential difference, which could be considered as future plan of this work.

TABLE II. Tafel parameters for Cu in the presence of 1 wt. % Na_2CO_3 with and without urea at various pH values

pH	Without urea		With urea	
	E_{corr} / mV *vs.* Ag/AgCl	I_{corr} / μA cm^{-2}	E_{corr} / mV *vs.* Ag/AgCl	I_{corr} / μA cm^{-2}
3	–162.948	2.342	–89.331	1.633
5	–121.284	2.009	–115.205	1.375
7	–101.106	1.614	–226.11	1.216
9	–126.762	1.369	–53.003	1.142
11	–84.603	1.142	–252.897	0.988

Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy results of Ta and Cu metal coupons performed in the sodium carbonate solution with and without urea at different pH values are shown in Fig. 5a–d.

EIS results were modelled using Zsimpwin software and the best fit is shown in Fig. 5a–d. Each trend shows a solid line and marker. The solid line refers to the modelled data while the marker show the corresponding experimental data.

As shown in Fig. 6, a combination of three resistance (R) and two constant phase element (CPE), electrical equivalent circuit (EEC) was employed. R_{sol}, R_{film} and CPE_{film} signifies electrolyte solution resistance, the oxide layer pseudo--resistance and its corresponding constant phase element, respectively. R_{ct} and CPE_{dl} signifies the charge transfer resistance and the constant phase element of electrical double layer, respectively.[22,23]

The shaped semicircles are due to the formation of a thin oxide film after the adsorption of sodium carbonate on the metal surface. As an outcome of this conduct, the above stated both *CPEs* are assimilated in the EEC. The *CPE* arises from the distribution in the current density along the electrode surface because of surface heterogeneity and surface roughness of the electrode.[24]

EEC fit parameters for Ta and Cu in the presence of 2 wt. % alumina, 1 wt. % Na_2CO_3 with and without 0.1 wt. % urea at various pH are given in Table III.

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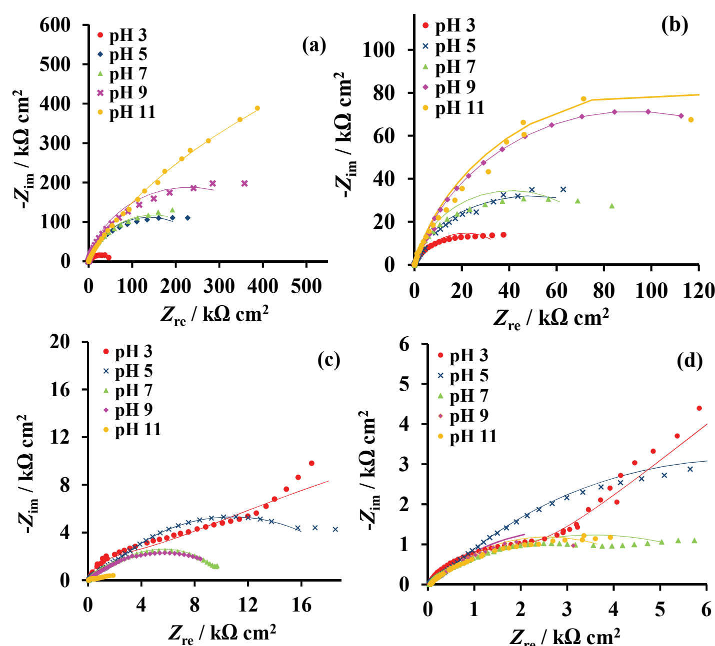

Fig. 5. EIS spectra of Ta and Cu in the presence of 1 wt. % Na_2CO_3 at various pH: a) Ta without urea, b) Ta with 0.1 wt. % urea, c) Cu without urea and d) Cu with 0.1 wt. % urea.

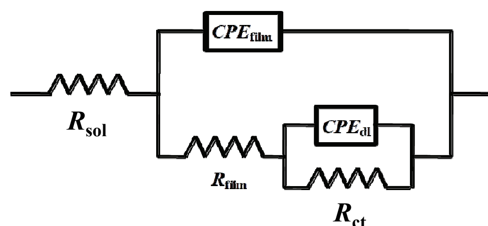

Fig. 6. Electrical equivalent circuit to analyze the experimental data.

As shown in Table III, the values of R_{sol} and R_{film} for Ta decrease as the pH changes from the acidic to the alkaline range. With the addition of urea, a declination in both the resistances is observed for all the pH range, caused by the adsorption of urea on the Ta surface. The variation in resistance is perchance associated with the change in the passive film thickness. R_{sol} and R_{film} for Cu increases with increasing pH, having minimum resistance at pH 3, as shown in Table IV. After addition of urea, the value increases for all the pH range. The pattern obtained in resistance variation matches well with the MRR resulting from the CMP experiments.

The Kramers–Kronig transformation (KKT) was employed to check the electrochemical impedance data for stability, linearity and causality[25] and the equations are reported elsewhere.[26]

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TABLE III. EEC fit parameters for Ta in the presence of 2 wt. % alumina, 1 wt. % Na_2CO_3 with and without 0.1 wt. % urea at various pH values

Parameter	pH									
	Without urea					With urea				
	3	5	7	9	11	3	5	7	9	11
R_{sol} / Ω cm^2	29.4	29.3	28.9	27.2	26.5	18.7	16.7	15.7	15.5	14.3
Y_{film}×10^5 Ω^{-1} s^n cm^{-2}	0.6	2.1	0.4	0.7	1.6	5.9	2	5.2	2.8	2.5
n_{film}	0.8	0.8	1	0.9	0.9	0.9	0.8	0.8	0.8	0.9
R_{film} / Ω cm^2	29090	20080	253.2	71.9	22.9	184700	68450	20810	1847	634.6
Y_{dl}×10^5 Ω^{-1} s^n cm^{-2}	0.5	4.6	2.3	1.7	0.2	51.2	0.2	10.1	0	0.8
n_{dl}	0.8	1	0.8	0.8	1	1	1	0.8	0.8	0.9
R_{ct} / kΩ cm^2	3007.0	461.00	295.30	279.30	18.30	208.5	82.16	21.78	20.05	4.512

TABLE IV. EEC fit parameters for Cu in the presence of 2 wt. % alumina, 1 wt. % Na_2CO_3 with and without 0.1 wt. % urea at various pH values

Parameter	pH									
	Without urea					With urea				
	3	5	7	9	11	3	5	7	9	11
R_{sol}, / Ω cm^2	49.6	59.0	67.5	73.8	76.8	46.3	51.9	26.9	27.6	26.2
Y_{dl}×10^5 Ω^{-1} s^n cm^{-2}	12.5	1.5	1.5	0.2	1.5	0.4	0.0	15.9	248.8	1.6
n_{film}	0.6	0.8	0.8	0.8	0.8	0.5	0.8	0.8	0.8	0.8
R_{film} / Ω cm^2	419.3	778.2	17280	1540	1875	300.5	309.1	1994	5060	5913
Y_{dl}×10^5 Ω^{-1} s^n cm^{-2}	185.5	9.1	11.5	7.5	0.1	429.6	305.0	22.2	20.9	31.8
n_{dl}	0.7	0.8	0.8	0.8	0.8	0.2	0.8	0.4	0.8	0.5
R_{ct} / Ω cm^2	134100	10380	18720	8486	11590	1008	20200	6870	13240	18520

The recorded experimental data were used to calculate the value of $Z(\omega)$ for a finite frequency range from ω_{min} to ω_{max} using the equations. This ensures adequate integration accuracy with small integration steps dx on interpolation.[27] Once the imaginary part is known for entire frequency range the real part is assessed using KKT. The KKT plots for Ta and Cu in 1 wt. % Na_2CO_3 with 0.1 wt. % urea, Z_{re} *vs.* frequency and $-Z_{im}$ *vs.* frequency are shown in Fig. 7. The electrochemical system is found to be stable and linear, as the experimental and fitted data matched well.

Proposed Ta and Cu removal mechanism

In order to explain Ta and Cu removal mechanism using sodium carbonate as oxidizer and urea as complexing agent, the following chemical reactions are proposed at alkaline pH values. Initially, the Na_2CO_3 present in the slurry reacts with water and dissociates into sodium hydroxide (NaOH) and carbon dioxide as given in Eq. (1).[28] Ta has a tendency to cover itself with an oxide layer of tanta-

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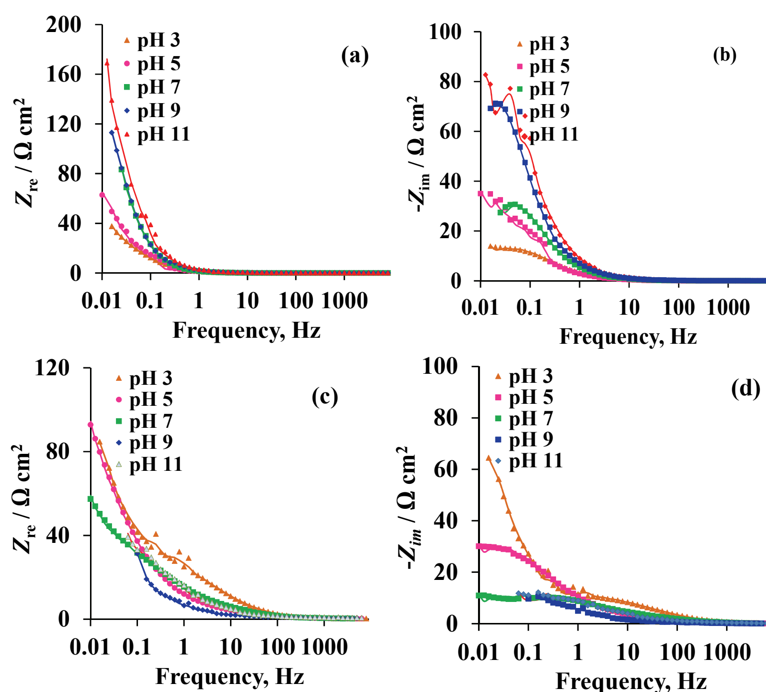
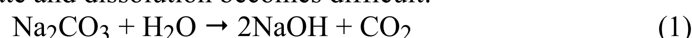
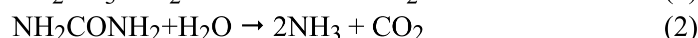


Fig.7. KKT fits for Ta: a) Z_{re} *vs*. frequency, b) $-Z_{im}$ *vs*. frequency, and for Cu: c) Z_{re} *vs*. frequency and d) Z_{im} *vs*. frequency, in 1 wt. % Na_2CO_3 with 0.1 wt. % urea.

lum pentoxide (Ta_2O_5). Ta_2O_5 is the only formed hard stable oxide, due to which the material removal rate and dissolution becomes difficult:[29]

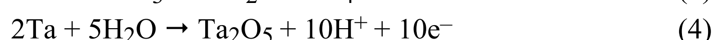


$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \quad (1)$$

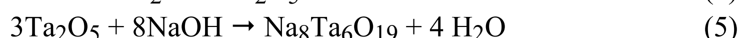


$$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2 \quad (2)$$

$$2NH_3 \leftrightarrows NH_2^- + NH_4^+ \quad (3)$$



$$2Ta + 5H_2O \rightarrow Ta_2O_5 + 10H^+ + 10e^- \quad (4)$$



$$3Ta_2O_5 + 8NaOH \rightarrow Na_8Ta_6O_{19} + 4\ H_2O \quad (5)$$

Urea reacts with water and produces ammonia and carbon dioxide (Eq. (2)), further NH_3 molecule encounters self-dissociation when comes in contact with water. It dissociates into its conjugate acid and conjugate base which are NH_4^+ and NH_2^-, shown in Eq. (3). In the next step (Eq. (4)), Ta undergoes oxidation, *i.e.*, reacts with atmospheric water molecules and Ta_2O_5 is formed at all pH and concentrations.[30] The formed Ta_2O_5 reacts with NaOH at alkaline pH,[28] which results in a polytantalate compound $Na_8Ta_6O_{19}$, depicted in Eq. (5), which is less stable[31] and easy to remove. The formed ammonium ions form a complex with the polytantalate compound, which is perhaps unstable and easier to abrade, hence an enhanced removal rate is observed.

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Cu metal reacts with the O_2 present in the atmosphere/aqueous environment and becomes oxidized into cupric oxide, as shown in Eq. (6). Formation of cupric oxide is confirmed from the presence of blue color on the metal surface during Cu CMP:[32]

$$2Cu + O_2 \rightarrow 2CuO \quad (6)$$

$$CuO + 2NaOH + H_2O \rightarrow Na_2[Cu(OH)_4] \quad (7)$$

The formed cupric oxide further reacts with the formed sodium hydroxide (Eq. (1)) and produces sodium tetrahydroxocuprate, a more stable compound, as shown in Eq. (7). The ammonium ions from Eq. (3) along with the formed oxide compound, further form a complex due to which the material removal rate is suppressed.

CONCLUSIONS

Urea was confirmed as a complexing agent for Ta and Cu CMP in a sodium carbonate based alumina slurry. Metal removal rates of Ta and Cu were measured with different urea concentrations, at varying pH, increasing applied pressure and increasing the rotating speed of platen. The Ta removal rate increases as the pH increases from 3 to 11, having a maximum removal rate at pH 11 without urea. Whereas, a reduction in Cu RR was observed with increasing hydrogen ion concentration from pH 3 to 11, having a maximum removal rate at pH 3. With the addition of urea, the Ta removal rate was enhanced and suppression in Cu removal rate was seen, which gives desired nearly 1:1 polishing selectivity. Urea enhances the Ta RR at the same time suppresses the Cu RR, which results in the desired selectivity. The trend obtained in the I_{corr} values from Tafel plots for both the metals resembles well the results obtained from the CMP experiments for both the metals. The variation in both R_{sol} and R_{film} with pH shows an alteration in the passive film thickness and variation in dissolution rate, which enhances the removal for Ta and at same time, suppresses the Cu RR.

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И З В О Д

УРЕА КАО КОМПЛЕКСИРАЈУЋЕ СРЕДСТВО ЗА СЕЛЕКТИВНО УКЛАЊАЊЕ Ta И Cu У БИКАРБОНАТНОЈ СУСПЕНЗИЈИ ГЛИНИЦЕ ЗА ХЕМИЈСКО–МЕХАНИЧКУ ПЛАНАРИЗАЦИЈУ

ARPITA SHUKLA, NOYEL VICTORIA SELVAM и MANIVANNAN RAMACHANDRAN

Department of Chemical Engineering, National Institute of Technology Raipur, Chhattisgarh-492010, India

Овај рад приказује улогу урее као комплексирајућег средства у бикарбонатној суспензији глинице која се користи за хемијско–механичку планаризацију тантала и бакра. Ta и Cu су полирани коришћењем суспензије глинице (2 мас. %) и Na_2CO_3 (1 мас. %) са и без додатка урее. Разматрани су ефекти pH вредности суспензије, концентрације

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урее, примењеног притиска и брзине ротирања цилиндричне плоче. Без додатка урее је запажено да брзина уклањања Ta расте са променом pH суспензије од киселе ка алкалној уз постизање максимума на pH 11, док брзина уклањања Cu опада са повећањем pH са минимумом на pH 11. Међутим, у присуству урее брзине уклањања Cu и Ta су биле једнаке на pH 11. Додатак урее је повећао брзину уклањања Ta и истовремено смањио брзину уклањања Cu на pH 11, јер се уреа адсорбовала на површини метала. За одређивање корозионе струје и корозионог потенцијала примењена је потенциодинамичка поларизација. Урађена је и спектроскопија електрохемијске импеданције оба метала у суспензији предложеног састава и дискутовани су добијени резултати.

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