Copper electroless plating in weakly alkaline electrolytes using DMAB as a reducing agent for metallization on polymer films

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ABSTRACT

Copper electroless plating at low pH (7–9) using dimethylamine borane complex as a reducing agent is studied electrochemically by linear sweep voltammetry, cyclic voltammetry and chronopotentiometry in full electrolytes. We find that the mixed potential theory is not applicable to the described system. We show that both the working potential and the rate-controlling mechanism are dependent on the pH of the solution. The effects of altering the mechanism on the resulting film conductivity, morphology and adhesion are studied on copper films deposited onto a polyimide (PI) substrate.

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1. Introduction

Copper electroless plating (ELP) has been a hot topic in the electronics industry for decades. It enables large-scale highly conductive copper deposition on insulating substrates and on patterns of complex geometry [1]. It is a wet process that does not require any vacuum-assisted equipment. Metal plating on polymer substrates is particularly interesting because it directly relates to flexible and transparent device applications.

Common copper ELP solutions use formaldehyde as a reducing agent [2–5]. They show higher deposition rates compared to other copper electroless baths, long electrolyte stability and good film conductivity and mechanical characteristics. However, formaldehyde has a number of disadvantages, such as volatility, toxicity and instability. The greatest disadvantage faced when applying formaldehyde-based electrolytes for metallization on polymer surfaces is the high pH required, which can ruin the polymer surface and thus greatly reduce the metal film adhesion. Glyoxylic acid [6] and hypophosphite [7–9] are less common reducing agents for copper ELP. Glyoxylic-acid-based electrolytes also operate at high pH and are therefore unattractive for metallization on polymer surfaces. A hypophosphite-based copper ELP bath is very stable, does not give off dangerous fumes and can be used at lower pH (9). However, because the deposited copper cannot catalyze the oxidation of hypophosphite, a suitable amount of nickel ions must exist in the hypophosphite-based bath to enable continuous plating [7–9]. As a result, nickel ions are co-deposited onto the copper film, decreasing its conductivity.

Electroless copper plating has been performed on polymer substrates with different electrolytes, including ones based on formaldehyde [10–12] and hypophosphite [13]. In most cases, to overcome the degradation effects caused by the high pH used, which leads to the poor adhesion of copper to the substrate, substrates are pre-treated by plasma surface modification or dry etching. We propose the use of a low-pH electrolyte that does not hinder film adhesion during deposition and decreases the number of steps required.

One of the reducing agents that functions at lower pH levels is dimethylamine borane (DMAB), which was first suggested by Jagannathan [14]. Amine borane reducing agents and ligands based on neutral tetradeatate nitrogen donors were used. The authors developed a completely new electrolyte suitable for low-pH (<9) copper deposition. It was stated that the copper obtained was of superior quality, having a higher conductivity and low roughness compared to the film deposited with hypophosphite. The high bath stability (a few days) was achieved by simultaneously using a strong chelating agent (ethylenediamine tetraacetic acid, EDTA) and a strong buffer (triethanolamine, TEA). The strength of the tested chelating agents was shown to increase as follows – triethylene tetraamine, 1,5,8,12 tetraazadodecane, 1,4,8,12 tetraazacyclopentadecane and 1,4,8,11 tetraazadodecane. The use of the bath to form interconnects of sub-micron dimensions was also successfully performed using the new electrolyte.

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However, the mechanism of copper ELP from weakly alkaline electrolytes using DMAB as a reducing agent has not been studied in detail. The activity of DMAB on gold changes with changing pH because each step of the oxidation reaction involves an OH⁻ ion as was shown in Ref. [15]. Assuming that the reaction goes similar way on Cu electrodes, the plating rate and the deposited film characteristics should also change with pH. A detailed study on the rate-controlling mechanisms is needed to better understand the process and optimization of the plating conditions.

In this work, we electrochemically study copper ELP solutions employing DMAB as a reducing agent for copper metallization on polyimide (PI) films. The applicability of the mixed potential theory is investigated and found to be inadequate. We find that the anodic and cathodic polarization curves almost never intersect, and if they do, the current density is extremely low, significantly lower than that corresponding to the observed deposition rate. The working potential is then measured by two methods: cyclic voltammetry in full electrolytes and direct chronopotentiometric measurement. A drastic change in the working potential and corresponding rate-controlling mechanism is observed with changing pH.

Finally, we investigate the deposition of copper films (growth rate, adhesion, resistivity) onto PI substrates depending on the solutions’ pH. We find that a low pH (7.5) is highly advantageous for PI substrate metallization, both for the high adhesion and low resistivity of the copper deposits.

2. Experimental

All solutions were prepared from distilled and deionized water (DI water). The partial reactions, studied by linear sweep voltammetry (LSV) in incomplete ELP solutions and the cyclic voltammetric (CV) measurements performed in complete ELP solutions were both carried out in a standard three-electrode cell using an electrochemical workstation (Zahnier Elektrik IM6ex). The working potential of copper ELP was measured by taking CV measurements in the three-electrode cell and by taking chronopotentiometric (CP) measurements in a two-electrode cell. The reference and counter electrodes used were Hg/HgO and a Pt plate, respectively. All potentials mentioned in the manuscript are given with respect to the Hg/HgO reference electrode (0.098 V vs. Standard Hydrogen Electrode). The working electrode was a 2-mm-diameter copper wire (Sigma–Aldrich, 99.999% purity) sealed in a glass tube. The electrode was successively polished to a mirror-like surface with 1.0 and 0.05 μm Al₂O₃ slurries on a wet pad, washed in a stream of DI water, dried with a flow of N₂ gas and immediately transferred to the activation solution. The electrode was then activated by cycling in 0.1 mol dm⁻³ NaOH for 5 cycles in the potential range of −1.3 to +0.8 V at a scan rate of 50 mV/s (the starting and ending potentials were both −1.3 V), rinsed in DI water again and immediately used for the electrochemical measurements. For reproducibility, the polishing and activation procedure was performed prior to every measurement.

Polyimide (PI, SKC Kolon PI, Korea) films were used as substrates for copper ELP. The films were pre-cut into pieces 2 cm by 5 cm in size and etched in 30 wt% HCl (Duksan Reagents & Chemicals, Korea) water solution for 30 min to roughen the surface. Then, the samples were rinsed well in DI water, dried with N₂ gas and placed in a drying oven at 70 °C for at least 2 h. A silica-like layer was formed on the surface by dip-coating the samples in 3:10 solution of 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich) in anhydrous benzene (Sigma Aldrich) and drying them on a hot plate heated to 135°C for 30 min. Then, the film was annealed by UV light for 30 min. For a more detailed explanation of the procedure, see Ref. [16].

Pd activation was applied to the silica-like layer by immersing the substrates into a water bath containing 1.1 mmol dm⁻³ PdCl₂ (Sigma–Aldrich) and 0.15 mol dm⁻³ HCl for 20 s.

Copper ELP deposition was performed in solutions containing 0.03 mol dm⁻³ CuSO₄•5H₂O, 0.035 mol dm⁻³ EDTA, 0.1 mol dm⁻³ DMAB and 0.38 mol dm⁻³ TEA. The pH was adjusted by the addition of small amounts of tetramethylammonium hydroxide (TMAH, Sigma Aldrich) and phosphoric acid (Sigma Aldrich).

The adhesion of the copper films to the PI substrates was measured by a 4000PT Peel Tester (DAGE) with a 90° peeling angle and a peel speed of 100 μm/s. For this measurement, glass substrates were first covered with epoxy resin; then, PI–Cu samples with a Cu thickness greater than 100 nm and less than 200 nm were placed on the epoxy-covered glass so that the Cu would be in contact with the epoxy resin. The samples were left overnight at room temperature to cure such that the Cu film would fix to the epoxy resin layer and the PI film would be detachable. Finally, by peeling off the PI film, the adhesion strength between the PI and Cu film was measured.

The sheet resistance of the Cu films was measured by the 4-point probe method using a CMT-Series 4-Point Probe Meter (Chang Min Co. Ltd., Korea). At least 5 measurements were taken for each sample, and then the resistance value was averaged. The standard deviation was calculated and multiplied by the film thickness to produce error bars.

Scanning electron microscopy (SEM) images were taken by a field-emission scanning electron microscope (FE-SEM) (JEOL JSM-7000F) and were used to study the morphology of the resulting Cu films.

3. Results and discussion

The ELP reaction can be described as at least two partial reactions, one cathodic and the other anodic, which take place

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Fig. 1. Polarization curves for (a) anodic and (b) cathodic partial reactions taken at activated Cu disk electrode in solutions containing (a) 0.1 mol dm⁻³ DMAB and 0.38 mol dm⁻³ TEA and (b) 0.03 mol dm⁻³ CuSO₄•5H₂O, 0.035 mol dm⁻³ EDTA and 0.38 mol dm⁻³ TEA. The scan rate was 50 mV/s; the starting potential was (a) −1.8 V for anodic scans and (b) −0.2 V for cathodic scans. The holding time was 30 s for anodic scans and 0 s for cathodic scans. The pH of the solutions is indicated. (c) Summary of anodic and inverted cathodic polarization curves for solutions with pH = 7.5.
on the same electrode [17]. According to mixed potential theory (MPT), if the reactions are assumed to be independent of each other, the electrode reaches a stable potential at which the partial reactions compensate each other. The stable potential is referred to as the mixed potential. It can be measured directly on a conductive substrate or calculated from cathodic and anodic polarization curves taken in solutions where metal salt and reducing agent are missing, respectively, assuming that the two reactions are independent of each other. Comparing the two methods can provide information about how the partial reactions affect each other.

In an attempt to analyze the partial reactions in our electrolyte, the polarization curves corresponding to DMAB oxidation and Cu–EDTA complex reduction were measured (Fig. 1a and b, respectively). The peaks observed in the cathodic polarization curves in the range of −0.4 to −0.2 V are due to residual oxide reduction on the surface of the electrode formed during exposure to air and at the open-circuit potential in the electrolyte (the peak height was dependent on the preparation procedure, i.e., longer air exposure led to a higher peak current). In general, the current density values for the Cu–EDTA complex reduction only slightly depend on the solution pH value.

Unlike the cathodic current, the anodic current due to DMAB oxidation strongly depends on the pH value and decreases monotonically as pH is decreased. This is expected because the known DMAB oxidation reaction involves OH⁻ ions (studied on gold electrodes in [18]):

\[
\text{BH}_3(\text{OH})^- + 6\text{OH}^- = \text{B(OH)}_4^- + 3\text{H}_2\text{O} + 6\text{e}^-.
\]

\[\text{(1)}\]

According to MPT, ELP should occur at potentials where the anodic and inverted cathodic polarization curves intersect. In our measurements, the curves only intersected when the electrolyte pH was 7.5 (Fig. 1c). For all other pH levels applied, the anodic and cathodic curves never intersected within the measured range (the original plots of anodic and uninverted cathodic curves are shown in Fig. 1a and b, respectively; the corresponding plots other than for pH = 7.5 in Fig. 1c are omitted for clarity). It is observed that at pH = 7.5 the intersection point is near a potential of −0.75 V, where the corresponding current density is 0.17 mA/cm². Assuming the

Fig. 2. CV curves taken in full solutions containing 0.03 mol dm⁻³ CuSO₄ 5H₂O, 0.035 mol dm⁻³ EDTA, 0.1 mol dm⁻³ DMAB and 0.38 mol dm⁻³ TEA at scan rate 50 mV/s. The pH of each solution is indicated in the graphs.
coloumbic efficiency to be 1, the deposition rate corresponding to this current would be

\[
\frac{dh}{dt} = \frac{jM}{FZ\rho},
\]

where \( j \) is the current density, \( F = 96,485 \text{ C/mol} \) is the Faraday constant and \( M = 63.5 \text{ g/mol} \), \( \rho = 8.92 \text{ g/cm}^3 \) and \( Z = 2 \) are the molecular weight and density of copper, and stoichiometric coefficient of the metal ion, respectively. Substituting the parameters for copper and the obtained current density, we obtain 238 nm/h. Later, we will show that both the potential and deposition rate do not correspond to those actually obtained in a full electrolyte.

To gain a better understanding of the partial reactions occurring in the same solution, CV scans were taken over a range of pH values in full solutions containing both a reduction agent and Cu–EDTA complex. The results are shown in Fig. 2. The potentials at which the CV curve crosses the x-axis correspond to the expected deposition potential. The two directions of the scan indicate two possible potentials that can be interpreted as the mixed potential. As we will show later, in the real deposition process, the electrode potential shifts from more positive to more negative values over the deposition time. Hence, we use the cathodic scan to define the mixed potential. It is clear that at pH = 7.5 and pH = 8, the zero–current density potential is approximately −0.3 V, and at higher pH values, it jumps to the low overpotential region for DMAB oxidation, −0.6 V. A summary of the dependence of the zero–current density potential on the pH is provided in Fig. 3b, grey circles.

The same trend is observed for the chronopotentiometric (CP) measurements in solutions containing both DMAB and Cu–EDTA in a two-electrode cell. The pH values ranged from 7.5 to 9 when a zero current was applied (see Section 2). The CP curves are shown in Fig. 3a and the corresponding dependence of the mixed potential (averaged with time) on pH is shown in Fig. 3b (black squares). A drastic change in the mixed potential is observed when the pH value changes between 8 and 8.5. We believe that the mechanism that causes the mixed potential change is related to the change in the rate-determining step of the electrodeless plating reaction. At lower pH, the limiting step of the reaction is DMAB oxidation, and the mixed potential is in the region of high overpotential for DMAB oxidation and low overpotential for Cu–EDTA reduction (around −0.3 V). Vice versa, at higher pH, the mixed potential (−0.6 V) corresponds to a low overpotential for DMAB oxidation and high overpotential for Cu–EDTA reduction; correspondingly, the rate-limiting step is the cathodic reaction. Such a switch in the rate-controlling mechanism has been observed in a formaldehyde-based electrolyte when changing the reducing agent and copper–EDTA complex concentrations [19]. Here, in the DMAB-based electrolyte, however, the switch is due to a change in the concentration of OH− ions, which are involved in the DMAB oxidation reaction [15], and not the concentration of the reducing agent and the Cu–EDTA complex in the solution.

Summarizing the polarization curve measurements and the measurement of the working potential both by CV and CP in full solutions, we can say that the partial reactions in our system are not independent of each other. Moreover, both cathodic and anodic reactions are catalyzed by each other, and the real deposition rate must be higher than that predicted by cathodic LSP. This phenomenon was observed recently in a similar system [20] of copper ELP at pH = 11.6 from Cu–1,5,8,12-tetraazaadecane complex with DMAB as a reducing agent. By separating partial reactions in a double galvanic cell, the authors showed a 40% decrease in the overall deposition rate. A possible explanation for this effect is that the reduction agent oxidation is enhanced on freshly deposited Cu and an intermediate or product of its oxidation might be a catalyst for Cu–EDTA complex reduction. This theory was proposed by Weber et al. in [21] for a formaldehyde-reduced electrolyte containing Cu–EDTA complex and was supported by Vaskelis et al. [22].

To study the effect of the pH and the corresponding rate-controlling mechanism on the film quality, we deposited copper on PI substrates activated with Pd as described in Section 2. Pd is known to catalyze DMAB oxidation [17], making it suitable for the initiation of copper ELP. A silica-like layer prepared on the surface prior to Pd activation served as an adhesion layer [16]. The reason to apply this method is a lack of chemical bonds formed directly between Pd molecules and Cu film. Another method to overcome the problem is to modify the substrate surface with plasma-assisted treatment as described in Refs. [10,23–26]. In this work an all-wet method was chosen to form the adhesion layer to avoid using vacuum-assisted technologies.

Typical SEM images of the copper films deposited from ELP electrolytes with pH ranging from 7.5 to 9 are shown in Fig. 4. The deposition time for each electrolyte was chosen in order to produce similar film thicknesses (200–300 nm). Low-pH electrolytes produced smooth, small-grain deposits, whereas high-pH electrolytes led to rougher surfaces and larger grain sizes.

The dependence of the observed growth rates of copper films on the pH of the deposition solutions is illustrated in Fig. 5. Note that the values shown are only approximate because the growth
rate is time-dependent, i.e., the rate changes over time and with film thickness. We did not observe growth rate saturation, even for thick films. The values shown were calculated from weight-gain measurement for films with thicknesses between 100 and 300 nm. The points corresponding to pH between 7.4 and 8 do not fit the linear trend for deposition rates at other pH values. We believe that this is related to the switch in the growth rate control mechanism observed in the mixed potential measurements.

Typical photographs of the deposited films are shown in Fig. 6. One can see that copper films deposited in low pH solutions (7.5 and 8) are shiny and uniform; the films of similar thickness but deposited at higher pH levels (8.3–9) have a rough surface and often have large defects (on millimeter scale). We believe the defects are due to the high deposition rate, the short initiation time and the high rate of hydrogen evolution during the higher-pH ELP process. The general trend of microscale morphology reduces the grain size with the decreasing pH level of the electrolyte. The uniformity and microscale morphology of the films must affect their electrical resistance. It is known that small-grain films usually exhibit higher resistivity than those composed of larger grains. On the other hand, the large defects observed in the images of rough films obviously reduce the total resistivity of the film.

The sheet resistance of large samples (2 cm by 5 cm) was measured at different locations on each sample, and the thickness of each film was calculated from weight-gain measurements. The error bars are based on the standard deviation of the various sheet resistance measurements. In Fig. 7, the resistivity of films with thickness ranging from 70 nm to 90 nm is shown. The film with the lowest resistivity, 159 Ω nm (one order of magnitude higher than the bulk value for copper), was deposited at pH = 7.5. Measurements of this film also yielded the smallest error bar. Note that at pH = 7.5, we observed the slowest deposition rate, lowest initiation time, smallest grains and the least defects in comparison to films deposited at other pH values. The films deposited at pH = 8, 8.5 and 9 show much higher resistivity, and the films deposited at pH = 8.5 and 9 show large deviations in resistivity. We found that at pH = 8.3, at the point or very close to the point at which the mechanism of the deposition undergoes the change from anodic to cathodic (see Fig. 3), the deposition rate was unstable and the measured resistivity was high and irreproducible (up to 9000 Ω nm with standard deviation as large as 200Ω). The trend observed for the thin films was that lower pH values led to lower resistivity values, likely due to fewer voids and general improved film uniformity.

Fig. 8 shows the resistivity measurement results for thicker films (thickness ranging from 250 nm to 300 nm), which were obtained by increasing the deposition time. Here, the films deposited at pH = 7.5, 8 and 8.5 show higher resistivity than the thin films deposited at the corresponding pH values (Fig. 7). However, thick films deposited at pH = 9 shown lower resistivity than their thin counterparts. It may be expected because the thick films deposited at pH = 9 have very few if any voids on the micron scale and appeared shiny (smooth), leading to more efficient electronic transport. Nevertheless, the overall quality of these films was low, as macro-sized voids were formed in the films. We believe that the macro voids are due to an adhesion layer and/or seed layer distraction in high-pH electrolytes. The larger error bars for films deposited at pH = 8 and 8.5 may be due to the non-uniform nature of the deposition.

**Fig. 4.** SEM images of Cu films deposited in DMAB-based electrolytes with (a) pH = 7.5, (b) pH = 8, (c) pH = 8.3, (d) pH = 9. The thickness of the films is in the range of 200–300 nm.

**Fig. 5.** Growth rate of copper films in DMAB-based electrolyte at different pH values.
of the films, which led to largely differing sheet resistance values over the various measured regions of the samples.

To summarize, the resistivity measurement shows that at low pH (7.5), Cu ELP is highly advantageous on polymer substrates if a thin, smooth and uniform copper film is desired. The only drawback for this deposition condition is the very low growth rate (105 nm/h for pH = 7.5 compared to 1850 nm/h for pH = 9). To obtain thicker copper films, a high pH (9) seems more advantageous. However, although relatively undetectable by resistivity measurements, the films have poor adhesion and large defects that can be seen by the naked eye. Moreover, the high-pH electrolytes are less stable than the lower-pH solutions. An electrolyte with pH = 7.5 is stable for weeks, whereas an electrolyte with pH = 9 precipitates within 2 or 3 h.

Another property of metal deposits crucial for interconnect applications is adhesion of the films to the substrate. In our copper films, the adhesion is provided by chemical bonds between the silica-like layer and the PI substrate and between the Pd seed layer and copper films and the silica-like layer. It is known that
high-pH electrolytes tend to break these bonds, thus reducing the films’ connection to substrates. Therefore, we investigated film adhesion by performing peel-off adhesion tests. The adhesion strength was averaged over the sample length. Cu film adhesion is highest for thin films deposited at pH = 7.5 and 8, as can be seen in Fig. 9. The actual adhesion of the films deposited at pH = 7.5 is underestimated because the copper film did not detach during the measurement, with all of the Cu film remaining on the PI substrate. We believe that the poor adhesion of these Cu films to the epoxy resin is due to the highly smooth surface of the Cu. The adhesion of copper films to PI substrates has been investigated in only a few studies. To our knowledge, the highest values demonstrated are up to 7 N/cm after various plasma-assisted pretreatments of PI films [27–31]. The adhesion values obtained in our study are comparable to those reported previously.

4. Conclusions

A Cu ELP process employing DMAB as a reducing agent and EDTA as a complexer is studied. A detailed study on the rate-controlling mechanism is carried out. The mixed potential theory is found inapplicable for this system because the partial reactions are interdependent and catalyzed by each other. The working electroless potential is measured directly and compared with that calculated from LCV measurements as well as with the working potential measured by CV in full electrolytes. A drastic change in the deposition mechanism is observed in the electrolyte when the pH value changes between 8 and 9, likely at 8.3. Only measurements taken in full electrolytes (CV and working potential measurement) coincide and show a trend that indicates the working potential’s dependence on the pH value.

To investigate the application of the DMAB-based Cu ELP solution, copper films are deposited on a polymer substrate (PI) in the pH range from 7.5 to 9. Low-pH (7.5 and 8) copper films show the strongest adhesion to the PI substrate, comparable to the highest values obtained so far on polymer substrates with plasma-modified surface [32]. Thin films deposited at pH = 7.5 and thick films deposited at pH = 9 show the highest conductivity. Overall, low-pH deposition, despite the low deposition rate, seems to be the most advantageous because it leads to the lowest resistivity, best adhesion, and fewest defects in the resulting film.

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