Methodological Consideration on the Prediction of Electrochemical Mechanical Polishing Process Parameters by Monitoring of Electrochemical Characteristics of Copper Surface

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ABSTRACT
The removal characteristics of copper (Cu) from electrochemical surface by voltage-activated reaction were reviewed to assess the applicability of electrochemical-mechanical polishing (ECMP) process in three types of electrolytes, such as HNO\(_3\), KNO\(_3\), and NaNO\(_3\). Electrochemical surface conditions such as active, passive, transient and trans-passive states were monitored from its current-voltage (I-V) characteristic curves obtained by linear sweep voltammetry (LSV) method. In addition, the oxidation and reduction process of the Cu surface by repetitive input of positive and negative voltages were evaluated from the I-V curve obtained using the cyclic voltammetry (CV) method. Finally, the X-ray diffraction (XRD) patterns and energy dispersive spectroscopy (EDS) analyses were used to observe the structural surface states of a Cu electrode. The electrochemical analyses proposed in this study will help to accurately control the material removal rate (MRR) from the actual ECMP process because they are a good methodology for predicting optimal electrochemical process parameters such as current density, operating voltage, and operating time before performing the ECMP process.

Keywords : Electrolyte, Electrochemical Removal, Electrochemical-Mechanical Polishing (ECMP), Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV)

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1. Introduction

Chemical-mechanical polishing (CMP) is the most widely used planarization technique in the semiconductor integrated circuit fabrication process [1-5]. This application of CMP technology has been most useful in the manufacture of Cu damascene structures, especially in multilevel interconnection process [6-8]. However, a material with low dielectric constant (low-k) in a device structure of 65 nm or less requires low down-force mechanical polishing to maintain an integrated structure at the bottom during the subsequent polishing process because of its fragile feature [9]. To overcome these problems, a new planarization technology was developed that uses chemical electrolytes instead of abrasive slurry to compensate for reduced mechanical down force [9-12]. This new attempt is called electrochemical mechanical polishing (ECMP), and this ECMP process can be used as a technology to replace or supplement the current CMP technology. The most important thing in this ECMP process is that a proper balance between electrochemical surface conditions and mechanical removal rate is needed to achieve optimal electrochemical results.

In this paper, the mechanism by which Cu material is removed during the Cu-ECMP process is based on the voltage-activated electrochemical reactions [13-15]. This voltage is designed to control the anodic decomposition that forms Cu\(^{2+}\) or Cu\(^{+}\) ions on the working electrode surface within three types of electrolytes, such as KNO\(_3\) [16], NaNO\(_3\) [17], and HNO\(_3\) [18], used in this paper. First, I-V curves obtained from linear sweep voltammetry (LSV) and cyclic voltammetry (CV) methods were used to monitor the effect of electrolyte concentration on the electrochemical surface reaction of Cu electrode. From these curves, it was possible to characterize the elec-
trochemical states such as active, passive, transient
and trans-passive. Second, the oxidation and reduc-
tion process of the Cu surface was monitored by
repeated scans of anodic and cathodic potential in
different electrolytes. From these monitoring meth-
ods, it is very important to understand the electro-
chemical characteristics for determining the optimum
ECMP process parameters, such as electrolyte con-
centration, operating voltage and current density,
before performing the ECMP process. Finally, using
x-ray diffraction (XRD) pattern and energy disper-
sive spectroscopy (EDS) analysis, the chemical state
and element composition of Cu surface were investi-
gated according to electrolyte concentration and
operating voltage variations.

2. Experimental

The voltage-activated electrochemical reactions
were investigated in order to evaluate the possibility
of Cu-ECMP process in the acid-based HNO\textsubscript{3}, alkali-
based KNO\textsubscript{3} and NaNO\textsubscript{3} electrolytes. Pure Cu sam-
ple of 99.99% with 2 cm×2 cm size was used as an
experimental species in a standard two-electrode
glass cell containing a platinum (Pt) counter elec-
trode (CE) and a Cu working electrode (WE) as
shown in our previous reports [16-18]. All experi-
ments were performed at room temperature in the
absence of the mechanical polishing. De-ionized
water and reagent graded chemicals were used to pre-
pare the electrolyte of HNO\textsubscript{3}, KNO\textsubscript{3}, and NaNO\textsubscript{3}
with different concentration level as follows; 1, 5, 10,
and 20 wt% (weight percent), respectively.

The I-V measurement system of Keithley 236
Model was used to analyze the electrochemical sur-
face states of Cu electrode at various electrolyte con-
centrations. Electrochemical states, such as active,
 passive, transient and trans-passive from the I-V
curve by LSV method, have been characterized to
determine the range of the applied voltage before the
subsequent quantitative tests. The voltage scanning
rate was 8 mV/s because it was measured 1,000 times
at a 0.5 s interval from -2.0V to +2.0V.

In quantitative tests, the voltage-activation process
was performed to identify the relationship between
weight loss and current density that was decomposed
by electrochemical reactions. The weight of the sam-
ple before and after the quantitative test was mea-
sured on precision electronic scale, and the polishing
removal rate of Cu was calculated. The composition
of elements on Cu surface according to the applied
voltage was confirmed through XRD pattern and
EDS analysis.

The methodological approaches of three-step dis-
cussed in this study are summarized as follows.
Step 1: Determine the range of voltages from the I-
V curve obtained by the LSV method to point out the
active, passive, transient and trans-passive states.
Step 2: After observing the Cu removal thickness
according to voltage application time at different
electrolyte concentration, calculate the equations
such as linear and polynomial fits, and predict the
quantity of Cu removal according to operation time
in advance to determine the range of appropriate volt-
age application time.
Step 3: Monitor the adsorption (oxidation) and
desorption (reduction) behavior of Cu ions in the cur-
rent density curve according to the applied voltage
obtained by CV method in electrolyte with different
concentrations, predicts the optimal voltage condi-
tions applicable to the subsequent ECMP process.

3. Results and Discussion

Fig. 1 shows the current density as a function of
applied voltage variation within the HNO\textsubscript{3}, KNO\textsubscript{3}
and NaNO\textsubscript{3} electrolytes with different concentration.
When the anode potential is at the active region (I) of
Fig. 1, the initial potential of the anode means the
beginning of electrochemical reactions, and the
anode starts the normal dissolution reaction, which is
called active state. And then, the passive region (II)
begins to form as voltage increases gradually. In gen-
eral, the passive film consists of a metallic hydroxide
compound. However, after the formation of the pas-
seeive film, the passive state remains as the voltage
increase, unable to overcome this passive barrier (so-
called plateau region). Therefore, the passive film
starts to peel off until it reaches the transient potential
region (III). From hereafter, it enters the trans-passive
region (IV) of Fig. 1, and its reaction became very
active. Also, two notable ohmic drops were observed
in Fig. 1, the first voltage (V=IR) drop means the
beginning of an active state, and the second IR drop
indicates the beginning of a trans-passive state [17].
That is, such a voltage drop implies the abrupt
increase of resistance. In other words, the increased
resistance indicates that a passive oxide, such as CuO
or Cu₂O, was formed on Cu surface [18]. As mentioned above result of Fig. 1, it is important to understand the various electrochemical behaviors such as active, passive, transient, and trans-passive states from the I-V curve in order to choose the optimal process parameters prior to the ECMP process.

Fig. 2 shows the comparison of the Cu removal thickness as a function of voltage application time at the voltage of trans-passive state in three electrolytes with different concentrations. The removal amounts were obtained by calculating the weight loss before and after the voltage-controlled electrochemical reaction. The measured experimental data are presented separately by different symbols as shown in Fig. 2(a, b, and c). The solid lines in Fig. 2(a, b) represent linear fit corresponding to 1 wt% and 10 wt% concentration, and the solid line in Fig. 2(c) shows polynomial fit for electrolyte with a concentration of 20 wt%. For 1 wt% and 10 wt% of these three electrolytes, linear dependences of removal rate on voltage application time were predicted as shown in Fig. 2(a, b). However, for the case of 20 wt% electrolyte, the dependence of polynomial was obtained as shown in Fig. 2(c). That is, the composite data of a polynomial fit with two steep slopes were presented. The data for 20 wt% HNO₃ and 20 wt% NaN₃ electrolytes in Fig. 2(c) represent a composite data set that fit satisfactorily to two straight lines by polynomial fit with two steep slopes. The respective dependence equations were written in the graph.

The slopes in Fig. 2 show the global averages of Cu removal rates after voltage-activated electrochemical treatment, while each data represents the
local mean value of Cu removal thickness at a given voltage application time. The characteristics of instantaneous removal thickness shown in Fig. 2 are due to changes of the potential profile at the electrochemical interface caused by accumulation of Cu\(^+\) and Cu\(^{2+}\) ions on the surface of the Cu electrode. These changes in the interfacial potential mainly affect the rate constants of electrochemical reactions, thus also affects the Cu dissolution rate in the short-time voltage activation processing. However, in the case of long-time voltage processing time, the surfactant concentration of the Cu\(^+\) and Cu\(^{2+}\) ions reaches steady state where the Cu dissolution rate is no longer affected by the individual voltage processing time [9]. The remarkable features of Fig. 2 are that the Cu removal thicknesses are decreased and then increased at the application time of 60 s, this is a critical point that imply any meaningful discussion. In addition, the Cu removal thickness of NaNO\(_3\) electrolyte at the voltage operating time of 60s represents the minus value. That is, the minus(−) value refers to an increase in the weight due to the adsorption (deposition) of various reactants, metallic ions, and metallic hydroxides after the electrochemical reaction by voltage-activation process, while the plus(+) value indicates that the Cu weight decreased due to the desorption (stripping) of the Cu ions after voltage-activated treatments[17]. In addition, the relatively flat curve in Fig. 2 means that the Cu decomposition is inhibited in the KNO\(_3\) and NaNO\(_3\) electrolytes. Therefore, we were able to predict the deposition and stripping status of Cu\(^+\) and Cu\(^{2+}\) ions due to the changes in surfactant potential from the results of Fig. 2. These adsorption (oxidation process: Cu→Cu\(^{2+}\)+2e\(^-\)) and desorption (reduction process: Cu←Cu\(^{2+}\)+2e\(^-\)) mechanisms of Cu ions were confirmed by changes in the cathodic and anodic current peak values of I-V curves obtained using the CV method shown in Fig. 3.

Fig. 3(a), (b), and (c) show typical I-V plots of Cu samples obtained by CV method in three types of electrolyte with different concentration. CV method has become a very popular technique for initial electrochemical studies of new systems and has proven very useful in obtaining information about fairly complicated electrode reactions. When the voltage is scanned in a positive direction from −2,000 mV to +2,000 mV, these electrochemical reactions correspond to oxidation (R → O + ne\(^-\); Cu→Cu\(^{2+}\)+2e\(^-\)) step. On the other hand, when the negative voltage is scanned from +2,000 mV to −2,000 mV, these electrochemical reactions correspond to the reduction (R ← O+ne\(^-\); Cu←Cu\(^{2+}\)+2e\(^-\)) step. Distinctly differ-
ent signs of distinguishing the adsorption and deposition of Cu were observed in Fig. 3. The cathodic current peaks correspond to bulk deposition (BD) and under-potential deposition (UPD) of Cu$^{2+}$ on Cu surface, whereas the anodic peaks represent stripping of bulk and under-potentially deposited copper [9,13,14,18]. Meanwhile, the two anodic peaks suggest that two structurally different crystal surfaces exist in the UPD layer, which is probably due to two dominant crystal faces on the surface of the polycrystalline Cu [18-20]. Fig. 3(a, b, and c) showed that the electrical behavior of the Cu electrode between –2,000 mV and +2,000 mV were non-faradaic current due almost entirely to double-layer charging. In summary, the voltage scans in the positive direction correspond to adsorption of Cu ions during oxidation of electrochemical reactions, while the voltage scans in the negative direction involve desorption of Cu during the process of reduction step. These distinct features were confirmed by the predominant XRD pattern of Cu (200) and Cu (220) shown in Fig. 4.

Fig. 4 compares the XRD patterns of the Cu electrodes before and after the electrochemical process by voltage-activation at different applied voltages. In the case of the original Cu electrode before applying voltage, a strong peak of Cu (220) was observed at 20=75°. At the same time, the three relatively weak peak values of Cu (111), Cu (200), and Cu (311) were generated at 0=42°, 20=50°, and 20=90°, respectively. However, the dominant peak of Cu (220) decreased dramatically after the active state voltage of –1.0 V was applied as shown in Fig. 4(a). This means that the chemical state of the Cu surface has changed with a voltage of –1.0 V corresponding to the voltage of the active state. In other words, this indicates that Cu ions such as Cu$^{+}$ and Cu$^{2+}$ are starting to peel-off. On the other hand, the peak of Cu (220) was increased again in the trans-passive state as shown in Fig. 4(c). This indicates the re-adsorption of the Cu ions. It is assumed that the Cu ions produced by the decomposition of Cu in the electrolyte have electrochemically reactivated during the voltage-activation, repeating the process of adsorption and desorption. These observations were confirmed by positive and negative directional voltage scans on the CV curves shown in Fig. 3. In addition, the two anodic current peaks shown in Fig. 3 are derived from the two structurally dominant crystal faces (200) and (220) on the underlying polycrystalline Cu surface [18-20].

Fig. 5 shows a comparison of the contents of copper and oxygen obtained from metallurgical components of the Cu electrode using EDS analysis when different active, passive, and trans-passive voltages are applied. The copper content was the lowest in the passive state, while the oxygen content was the high-
4. Conclusions

The removal characteristics of Cu from the surface with various electrochemical reactions by voltage-activation were reviewed to assess the possibility of ECMP application in three types of electrolytes, such as HNO$_3$, KNO$_3$, and NaNO$_3$. From the I-V curve obtained by LSV and CV method, the optimal process parameter such as the applied voltage, operating times and concentration of electrolyte were determined before the subsequent ECMP process. The adsorption (deposition) and desorption (stripping) mechanism of Cu electrode by DC voltage-activation was also investigated. Distinctly different sign of deposition (adsorption) and stripping (desorption) of Cu are observed. The cathodic current peaks correspond to adsorption of Cu$^{2+}$, whereas the anodic peaks correspond to desorption of bulk and under-potentially deposited copper. Electrochemical mechanisms in active, passive, and trans-passive states were observed and confirmed by XRD and EDS analyses. Because the characteristics and analyses of electrochemical Cu surfaces proposed in this study are a good methodology for finding optimal electrochemical process parameter, the above mentioned results will provide an accurate control of material removal rates (MRR) in ECMP applications.

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Fig. 5. Oxygen and copper contents obtained from metallurgical compositions of Cu by energy dispersive spectroscopy (EDS) analysis in the HNO$_3$, KNO$_3$ and NaNO$_3$ electrolytes with different concentration.