Dynamic Electrochemical Measurement System “d-EC” for Fundamental CMP Study

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ABSTRACT

In this study, dynamic electrochemical measurement system (d-EC) was developed and applied for a fundamental Cu CMP study. The shape of Tafel plots of Cu obtained by d-EC in static and dynamic conditions with a same slurry were obviously different. We found that corrosion potential of Cu obtained in dynamic condition was shifted toward minus potential compared to the static condition in acidic slurry while the corrosion potential shifted toward plus potential in neutral and alkaline slurry. Furthermore, current density of Cu in Tafel plot in dynamic (CMP) condition with acidic slurry comes higher as polishing pressure comes high while the tendency was not observed with alkaline slurry. These results suggest that Cu passivation layer formed in acidic slurry are removed easier than that in an alkaline slurry.

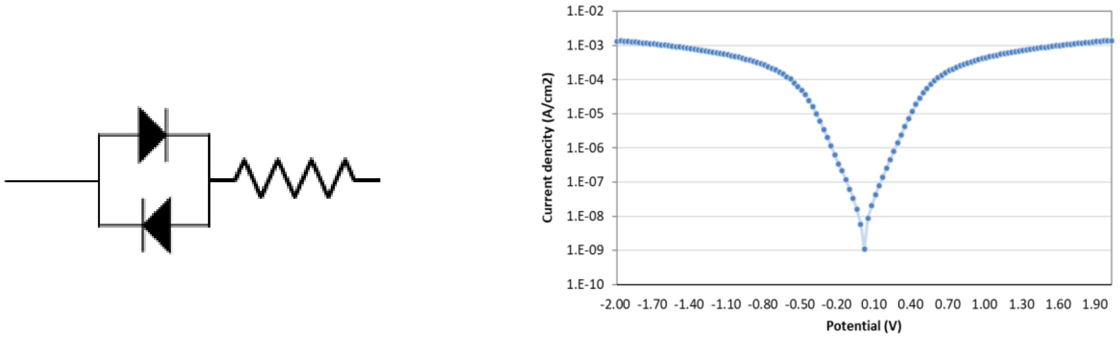
INTRODUCTION

As the structure of large-scale integrated circuit (LSI) comes complicated, various interconnect metal materials has been used in the LSI. Therefore, advanced design on slurries has been required for chemical mechanical polishing (CMP) of metal interconnect. From this background, electrochemical study of metal corrosion comes important. Tafel plot evaluation based on electrochemical measurement using potentiostat system is known as an effective analysis method of metal corrosion [1]. However, the evaluation in the most cases is conducted in static condition because the dynamic measurement requires special electrode like a rotational working electrode. Furthermore, electrochemical measurement itself has been thought to be a difficult system for some engineers because measurement data is easy to affected by environmental noise and contact situation of electrodes. We think that dynamic electrochemical evaluation is necessary because metal surface in dynamic, “during CMP”, should be different from that in static situation, which affects to defect performance of CMP. Shima et al. have been reported significant data about dynamic Tafel in lab-scale [2]. From these reason, development of dynamic electrochemical measurement system that is easy to handle even in the field and facilitates has been desired.

CONFIGURATION OF d-EC SYSTEM

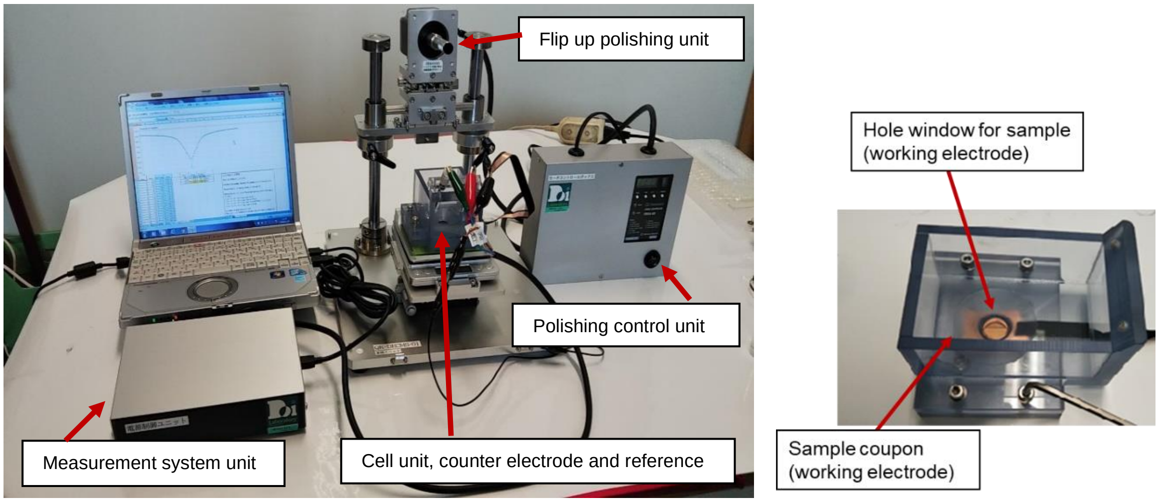
In order to establish a practical development method of a CMP slurry, we developed dynamic electrochemical measurement system (d-EC: Doi Laboratory Inc.,) which have two unique characteristics. One is flip-up polishing unit which can apply wide ranges of rotational speed and down force pressure. The other is “novel test-load circuit (NTLC) which can obtain “Tafel like” plot without connecting any electrode. NTLC is built in the electrically shielded box, and is composed of two diodes and resistor as shown in Fig.1(a). Figure 1(b) is a measurement result of the NTLC. By using NTLC, we can know easily whether electric measurement system works correctly or not and environmental noise effect. As for the polishing unit, we can conduct the dynamic measurement easily without using a special electrode because the polishing head is independent from working electrode in this system.

Figure 2 and 3 show the appearances of “d-EC” system and cell unit. Electric circuits for linear sweep voltammetry (LSV: potentiostat) and NTLC are built in the electrically shielded “measurement system unit”. Cell unit has Φ1.2 cm sized hole window on its bottom, where, rectangular sample of working electrode can be attached to the backside of the cell bottom. The polishing head of flip up polishing system can touch down on sample surface through the window of the cell unit. Polishing pad of Φ1.1 cm size can be mounted on the polishing head, 0 ~ 1000 g/cm^2 of down force pressure and 0 ~1800 rpm of rotational speed can be applied.



(a) Example of NTLC circuit (b) Measurement result of NTLC

Fig.1 NTLC circuit and its measurement result



(a) Whole appearance of d-EC system (b) Cell unit

Fig. 2 Appearance of d-EC system

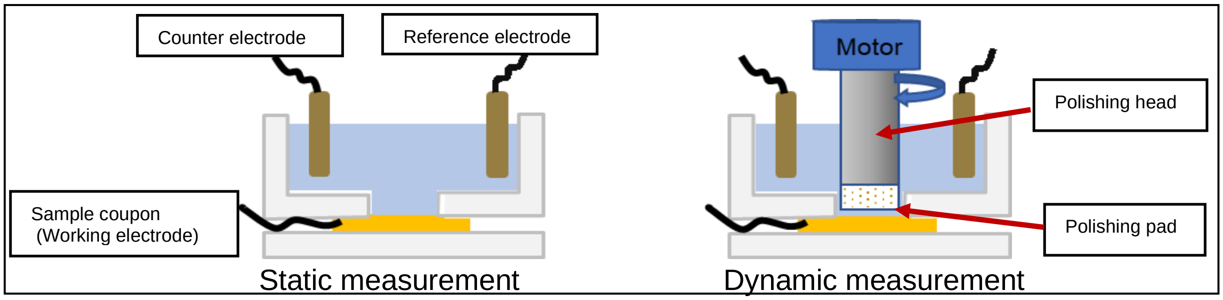


Fig. 3 Schematic diagram of cell unit in “static measurement” and “dynamic measurement”

EXPERIMENTAL PROCEDURE

Tafel plot of a metal obtained under dynamic condition was compared with that obtained under static condition. In this evaluation, 2 cm x 3 cm sized Cu coupons were adopted as a metal because Cu is well known as an interconnect material in LSI. Slurries shown in Table 1 were prepared for the experiments. Where, No. 2 and 3 are the slurries which is prepared by KOH adding to slurry No.1 as pH adjusting. As a pretreatment of Cu coupon, all the coupons were dipped in a citric acid solution to remove the native Cu oxide before each measurement. D-EC measurements for Tafel evaluation were conducted under the condition shown in Table 2. In the dynamic condition, suede type pad with X-Y groove was used as polishing pads. Pt and Ag/AgCl were used as counter electrode and reference electrode, respectively.

Table 1 Slurry composition

Slurry No.	pH	Composition
1	2	Citric acid(6.1wt%) + BTA(0.24wt%)+ colloidal silica (Φ35nm: 1wt%)
2	7	Same as slurry 1(+ KOH as pH adjusting)
3	9.5	Same as slurry 1(+ KOH as pH adjusting)

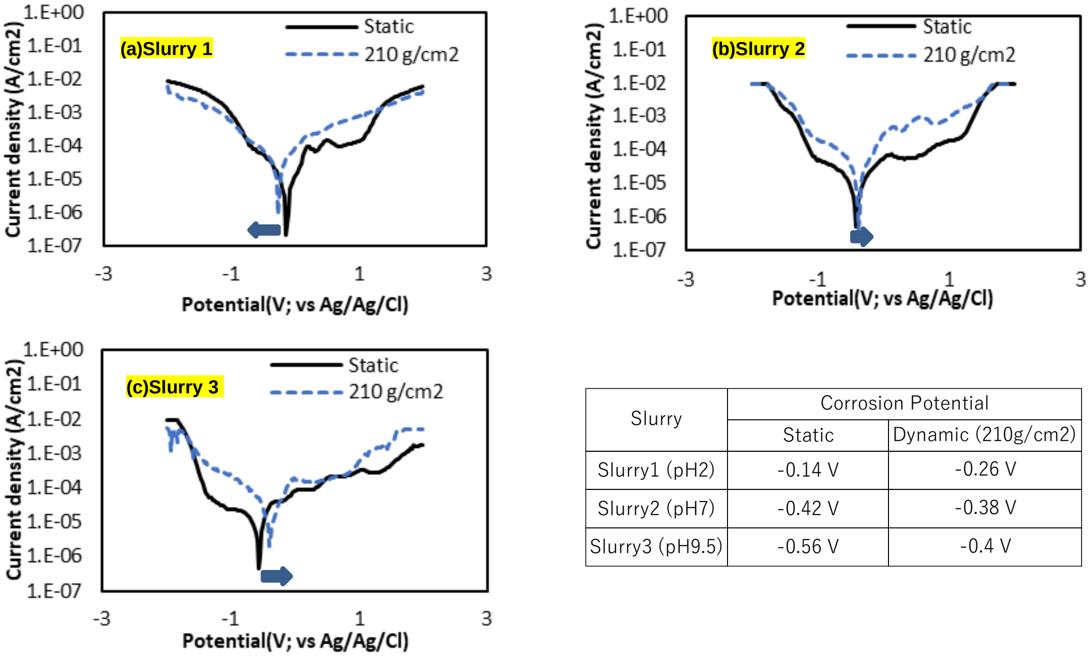
Table 2 Measurement condition by d-EC (LSV)

Condition	Static	Dynamic
Down force pressure (g/cm^2)	0(No touch down)	70 - 350
Rotational speed (rpm)	60	60
Polishing Pad	Suede type	Suede type

RESULT AND DISCUSSION

Dynamic Tafel plots in different pH slurries

Figure 4 shows Tafel plots of Cu in slurry 1 – 3, where, dynamic data with 210 g/cm^2 down force and static data are compared. In all the figures, partially saturated regions of current density are observed in anodic potential under static condition, which mean that passivation layers are formed on Cu surface. On the other hand, this saturation region disappeared in dynamic condition with slurry 1. This means that passivation layer is removed continuously and Cu surface is kept chemically reacting. Furthermore, corrosion potential of Cu in slurry 1 is shifted to minus potential direction under the dynamic condition. It is thought that Cu surface in the acidic slurry is more easily corroded than static surface. On the contrary in slurry 3, corrosion potential under the dynamic condition is shifted to plus potential direction and saturated current region of anodic potential still remained. It means that passivation layer on Cu surface in the alkaline slurry is physically and mechanically strong compare to that in acidic slurry. These results can be explained from the view point of Pourbaix diagram [3].

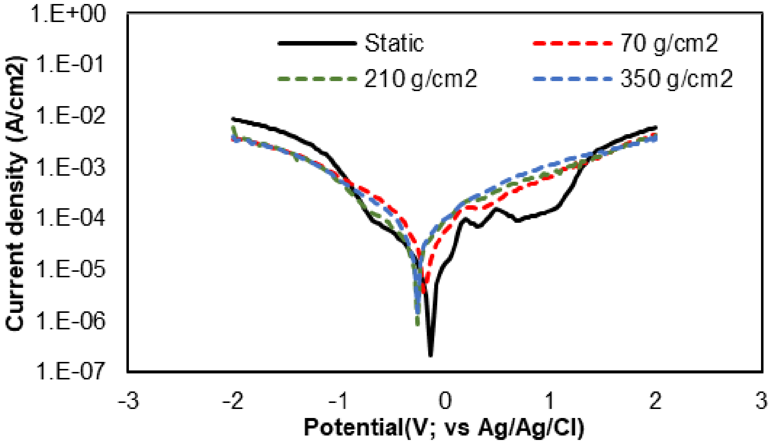


Slurry	Corrosion Potential	
	Static	Dynamic (210g/cm2)
Slurry1 (pH2)	-0.14 V	-0.26 V
Slurry2 (pH7)	-0.42 V	-0.38 V
Slurry3 (pH9.5)	-0.56 V	-0.4 V

Fig.4 Dynamic Tafel plots in different pH slurries

Dynamic Tafel plots at different down force

Figure 5 shows dynamic Tafel plots of Cu at different down force in slurry 1. As shown in this figure, corrosion potential of Cu in the slurry shifted to minus direction of potential as higher down force is applied. Where, potential value at 350 g/cm^2 is same as that at 210 g/cm^2, which is thought to be due to the saturation of removal rate of Cu with slurry 1 over the 210 g/cm^2 down force. Saturated tendency in anodic current is also obviously disappeared and comes higher as higher down force is applied. Where, saturation region slightly remines in 70 g/cm^2 polishing while that is not observed in 210 g/cm^2. It suggested that the threshold downforce to remove passivation layer completely in slurry 1 is during 70 – 210 g/cm^2. These results indicates that dynamic electrochemical study can contribute practical development of metal slurry.



Down force	Corrosion potential
Static (0)	-0.14 V
70g/cm^2	-0.2 V
210g/cm^2	-0.26 V
350g/cm^2	-0.26 V

Fig.5 Dynamic Tafel plots at different down force with slurry 1

CONCLUSIONS

Dynamic electrochemical measurement system (d-EC) was developed and applied for a fundamental Cu CMP study. We found that corrosion potential of Cu obtained under dynamic condition was shifted toward minus potential compared to the static condition in acidic slurry while the corrosion potential shifted toward plus potential in neutral and alkaline slurry. Furthermore, current density of Cu in Tafel plot under dynamic (CMP) condition with acidic slurry comes higher as polishing pressure comes high while the tendency was not observed with alkaline slurry. These results suggest that Cu passivation layer formed in acidic slurry are removed easier than that in an alkaline slurry. We are now evaluating the semiconductor material like GaN by d-EC and the significant data can be obtaining. Our developed d-EC system thought to be useful for a CMP slurry development and understanding the CMP mechanism. (This product “d-EC” is patent pending)

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