# Emerging Stress-Free Ruthenium Removal Study in Advanced Node Interconnect Structure

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## 1 Abstract

Ruthenium exhibits significant potential as a contact, liner or interconnect material in advanced semiconductor technologies; however, its high hardness and chemical inertness present considerable challenges for its removal and planarization via conventional chemical mechanical polishing (CMP). In this work, an integrated stress-free polishing (SFP) and wet etching process was developed as a novel solution for efficient ruthenium removal. Based on an electrochemical reaction mechanism, the SFP step modifies the ruthenium surface to form a thin ruthenium oxide layer. This oxide layer can be readily etched by hydrofluoric acid (HF) solution, whereas metallic ruthenium shows negligible reactivity with HF. By optimizing the process parameters, a rapid removal rate exceeding 1800 Å within 120 seconds was achieved. Furthermore, fine-tuning the dilute HF (DHF) concentration enabled a high removal selectivity between ruthenium and $SiO_2$. The proposed SFP–wet etch integration demonstrates strong potential as a replacement for conventional CMP in advanced-node ruthenium interconnect fabrication.

## 2 Introduction

Driven by the rapid development of the electronic industry, the demand on mini-size, low power consumption and high reliability becomes inevitable to electronic products. Emerging materials, such as cobalt and ruthenium are introduced into the middle-end of line (MEOL) for sub-7nm technology nodes[1]. Especially for sub-3nm technology nodes, ruthenium, deposited by chemical vapor deposition (CVD), is replacing the conventional copper as the contact material on metal nitride (e.g., TiN, TaN) barrier layers[2]. In traditional process flow, ruthenium films are removed by chemical mechanical planarization (CMP). However, the removal of ruthenium presents significant challenges, including a low removal rate and poor selectivity between ruthenium and metal nitride barrier layer, due to ruthenium's high hardness and chemical inertness.

In this study, based on electrochemical reaction mechanism, a stress-free polish (SFP) technology is applied to treat ruthenium surface and form a ruthenium oxide film. The ruthenium oxide film could be etched by hydrofluoric acid (HF) solution while the metallic ruthenium film is barely reacted with hydrofluoric acid. Hence, through controlling the ruthenium oxide film thickness, the ruthenium film removal thickness could be precisely determined by the integrated process which contains SFP and HF etch (refer to Figure 1). As presented in Figure 2, in the SFP process, the wafer is fixed on a chuck, which carry the wafer to do horizontal, vertical and rotational movement. The ruthenium oxide film thickness is dominated by the electrolyte property, process current, wafer rotation speed, horizontal movement speed, electrolyte flow rate etc. The integrated process solution could overcome the limitation of the low removal rate in CMP for ruthenium interconnection structures. Moreover, the absence of mechanical stress, abrasive particles, and chemical components from CMP slurry during the process is expected to significantly minimize associated defects.

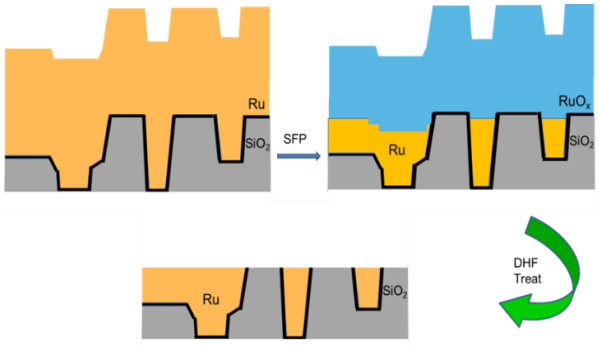


**Figure 1** Stress-Free Polish and HF Etch Process Flow

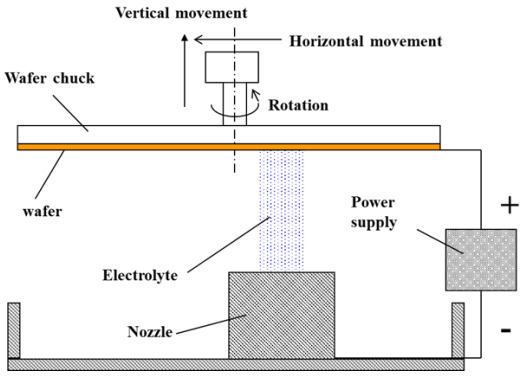


**Figure 2** Stress-Free Polish Mechanism

# 3 Experimental

Two kinds of samples were prepared for the experiments. Silicon wafers with 200 nm ruthenium layer were diced into pieces of approximately 4 cm × 4 cm for the preliminary tests. Each piece was affixed to a 300 mm blanket copper wafer at a radial position of 75 mm from the wafer center using conductive copper tape. The samples were subjected to sequential SFP and Diluted HF (DHF) cleaning processes. To create a reference surface, the left half of each Ru piece was masked with a rectangle tape to prevent polishing. In the formal experiments, the whole ruthenium wafers were directly used, also with a tape covering a small part of the surface also at the radial position of 75 mm. After the processes, a step height was formed between the masked and unmasked regions. The step height was measured by a stylus profilometer, and the Ru removal rate was calculated accordingly.

The ESP9000 developed by our company was used as the polishing electrolyte with a flow rate of 32 LMP from the main nozzle in Figure 2. The wafer rotated at a speed of 100 RPM. The varying constant voltage of 0, 50, 100 and 200 V was applied respectively for four samples with a polishing time of 60 s. The following DHF cleaning process adopted a solution with 3 wt% DHF at a flow rate of 1.5 L/min and lasted 120 s.

# 4 Results and Discussion

## 4.1 Ru removal rate analyses

In the preliminary experiments, a variety of four different voltage conditions as listed in table 1 were adopted: no SPF power output, 50V, 100V and 150V constant voltage, respectively. After the polishing and HF etching, the rectangle tape covering the Ru blanket wafer surface to form the reference area which could not be polished was removed. The profile of the corresponding samples was presented in Figure 3 and the result of the removal thickness was listed in Table 1.

In the first condition without SFP, the removal thickness of sample #1 was just around 99 Å, mainly determined by the DHF etching process. Since Ru is relatively stable, the DHF has no significant chemical reaction with Ru. When the SFP process was conducted with a constant voltage of 50 V, the inert Ru surface still could not be oxidized by the electrochemical reaction, as suggested by the result of sample #2. When the constant voltage was increased to 100 V and 150 V for sample #3 and #4, the removal thickness reached a high level of 959.2 Å and 1336.2 Å, respectively. This suggested that the Ru film was effectively oxidized and the oxidized Ru film--$RuO_x$

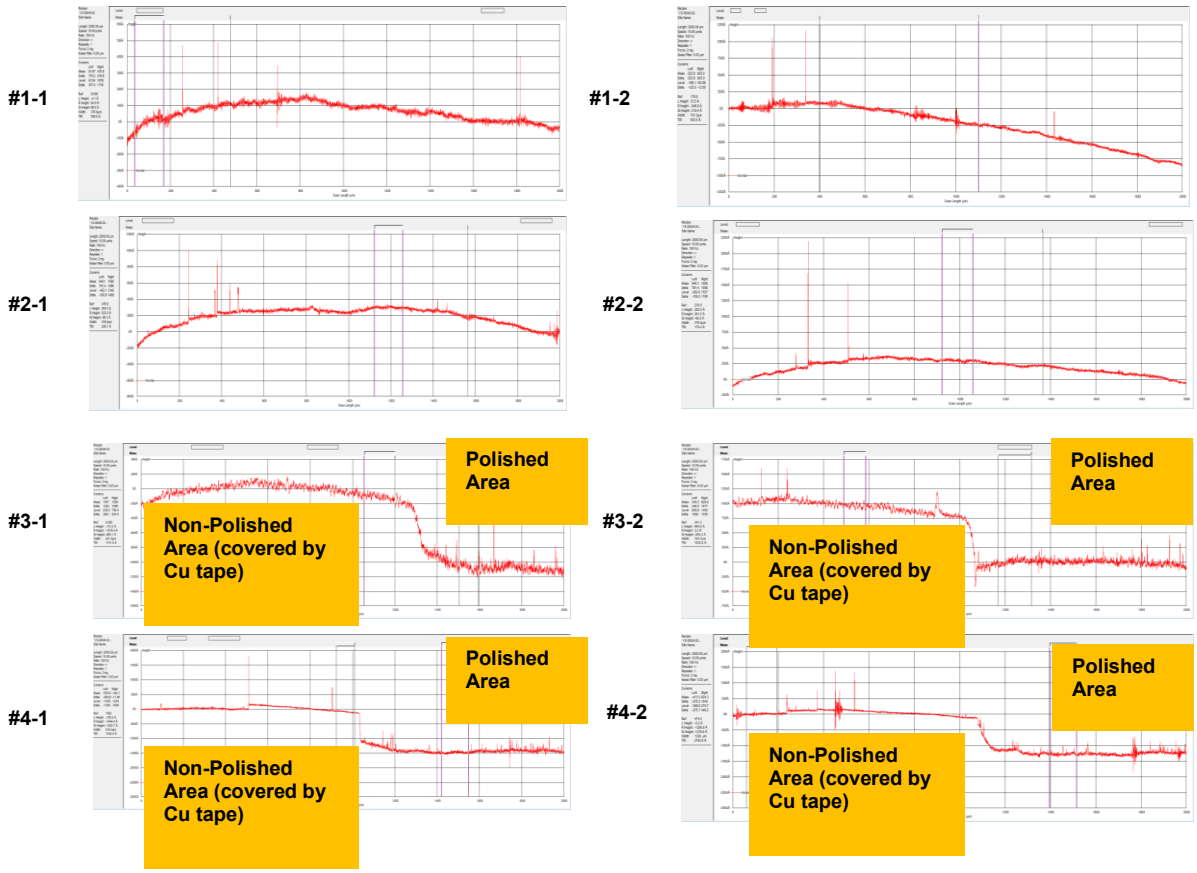


**Figure 3** Removal Thickness vs. SFP Process Voltage

reacted with dilute HF. As Ru barely reacted with DHF, the results indicates that the etch stop layer is the interface between Ru and $RuO_x$. Hence, the final Ru removal thickness is equal to the oxidized Ru thickness during the SFP process.

Table 1. Removal Thickness under Different SFP conditions

| No. | Process Condition | Removal Thickness (Angstrom) |
|---|---|---|
| 1 | No SFP | 99 |
| 2 | SFP 50V | 90.4 |
| 3 | SFP 100V | 959.2 |
| 4 | SFP 150V | 1336.2 |

In the formal experiment with the whole Ru wafers, the constant voltage was further increased to 200 V to maintain a high level of current density, considering the large area to be polished. After 120 s, the obvious step height (SH) of 1820.9 Å and 1814.8 Å between the polished and unpolished areas was observed in Figure 4.

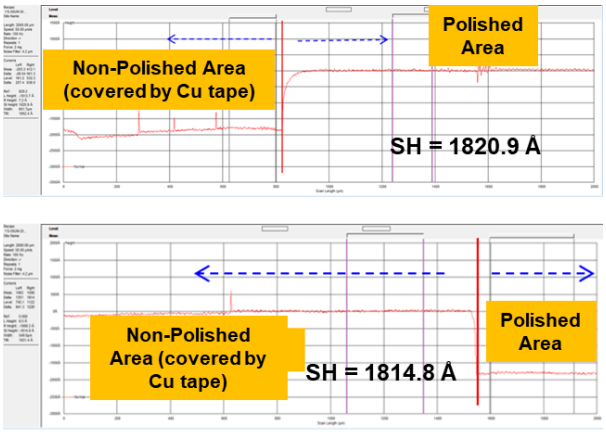


**Figure 4** Removal Thickness for the Whole Ru Wafer

## 4.2 Ru/$SiO_2$ removal selectivity

For the actual Ru interconnection structure, there is $SiO_2$ under the Ru layer. The selectivity between Ru and $SiO_2$ in no-pattern area is another critical process request. An experiment is designed for different HF concentration on $RuO_x$ and $SiO_2$. And the SFP process is using the same condition. The $SiO_2$'s removal rate is much higher than Ru in higher concentration HF, hence lower concentration of dilute HF is recommended for this Ru removal application.

Table 2. Removal Rate Selectivity ($SiO_2$/Ru)

| No. | Condition | Removal Rate Selectivity ($SiO_2$/Ru) |
|---|---|---|
| 1 | Ra (SFP + $SiO_2$ 1% DHF 20s)/Ra(SFP + Ru 1%DHF 20s) | 1.64 |
| 2 | Ra (SFP + $SiO_2$ 3% DHF 20s)/Ra(SFP + Ru 3%DHF 20s) | 3.31 |

## 4.3 Mechanism analysis

Figure 5 shows the Pourbaix (E–pH) diagrams for Cu and Ru in aqueous solution, illustrating how their existing form varies with pH and electrode potential. In contrast to copper—which readily forms oxides or dissolves to ionic species over a wide pH range even at relatively low potentials—ruthenium is markedly inert: oxide formation requires much higher potentials, and direct dissolution (in the form of $RuO_4^-$) occurs only under restricted conditions. Common oxidizers in CMP slurries therefore struggle to oxidize Ru, highlighting the advantage of applying an external bias with SFP to deliberately regulate Ru-oxide formation. After SFP, the obtained Ru(III), Ru(IV), or Ru(V) oxides and hydroxides react with DHF to form soluble species, $H_n[RuF_6]$, through the following reactions (1) - (5), and are carried away by the solution flow, enabling efficient material removal. Meanwhile, the underlying metallic Ru(0) remains intact because DHF alone cannot oxidize and react with this inert metal, allowing the Ru film removal thickness to be precisely controlled within the integrated process parameter.

$$Ru(OH)_3 + 6HF \rightarrow H_3[RuF_6] + 3H_2O \quad (1)$$
$$Ru_2O_3 + 12HF \rightarrow 2H_3[RuF_6] + 3H_2O \quad (2)$$
$$RuO_2 + 6HF \rightarrow H_2[RuF_6] + 2H_2O \quad (3)$$
$$RuO(OH)_3 + 6HF \rightarrow H_2[RuF_6] + 2H_2O \quad (4)$$
$$Ru_2O_5 + 12HF \rightarrow 2H[RuF_6] + 5H_2O \quad (5)$$

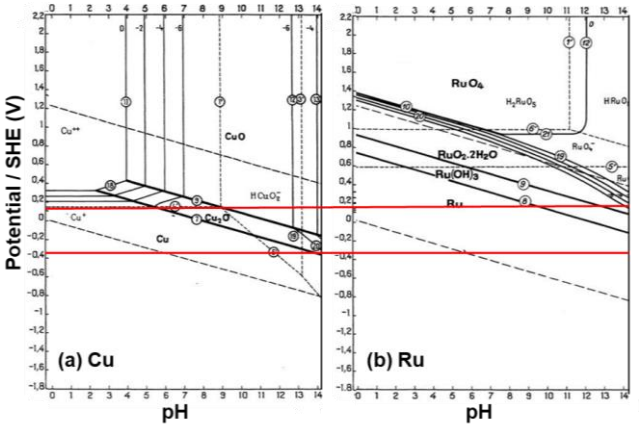


**Figure 5** Potential-pH equilibrium diagram for Cu-$H_2O$ and Ru-$H_2O$ systems at 25 ºC (obtained from the website of National Materials Corrosion and Protection Data Center of China)

# 5 Conclusion

In this work, an integrated process of SFP and wet etch was developed as an emerging stress-free ruthenium removal solution. Through the optimization of process parameters, rapid removal of ruthenium wafers by more than 1800 Å within 120 s was achieved. Furthermore, by fine-tuning the DHF concentration, a high removal selectivity between Ru and $SiO_2$ was also realized. The process flow of SFP and wet etch

demonstrates high potential for replacing the conventional CMP process in advanced node ruthenium interconnection structure.

# 6 Literature


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