Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, Hamamatsu, 1997, pp. 34-35 **B-1-5**

# The Effect of Capacitor Electrode Contaminant on High Density DRAM's Device Characteristics

Y.Kawai, E.Uchida, M.Itoh, M.Yoshimaru and J.Ida

Oki Electric Industry Co.,Ltd. VLSI R&D Center, 550-1 Higashiasakawa, Hachioji, Tokyo 193, Japan
·Phone: +81-426-62-6104, Fax: +81-426-8367, E-mail: paexl@lken.ed.oki.co.jp

## 1. Introduction

Metal-Insulator-Metal structure for possible application as DRAM cell capacitor has been widely investigated. The availability of the metals such as Ruthenium(Ru), Ruthenium oxide, Iridium and Platinum has been reported for the capacitor electrodes[1,2]. Low resistivity characteristic are required for the metals even if the metals are oxidized in the capacitor fabrication process, for example post annealing process or post oxidation process. Ruthenium oxide has the characteristics of conductor, therefore Ru can be useful for the total device processing. It is a new material for ULSI processing. Therefore, the effect of Ru contaminant on processing is very important for practical usage of it. However, there are few data about it on literatures. This paper presents the first reports on the effect of Ru contaminant on Device characteristics, especially on gate oxide film.

## 2. Experimental

The intentional contamination of Ru was carried out, as follow. The surface of p-type Si treated with RCA cleaning was contaminated with ruthenium chloride solution. The contamination method was spinning coat with the solution. The Ru concentration on the Si surface was measured by total reflection X-ray fluorescence(TRXRF) as shown Fig.1. Detection limit of TRXRF was indicated as D.L.line in this figure. Good linearity was obtained above 0.1vol%. We used this line as the know concentration of the contaminated in this experiments.

## 3. Diffusion in Si substrate and thermal $SiO_2$

There are no data of Ru diffusion characteristics in Si or $SiO_2$ in literature. Therefore, it was analyzed with SIMS analysis. Si surface and thermal $SiO_2$ film surface, that of the thickness of 300nm, were contaminated with the solution of the concentration of $1.5x10^{14}$atoms/cm$^2$ and annealed in Ar ambient at the temperature from 750℃ to 950℃ for 60min. Fig.2 shows the profiles of Ru in Si substrate and thermal $SiO_2$. The diffusions of Ru in the both substrates were independent on anneal temperatures. Furthermore, the profiles compared with anneal and non-anneal condition were almost the same. These results show that Ru diffuses hardly into Si and $SiO_2$ film. This means that Ru dose not diffuse into substrate after Ru electrode formation for DRAM cell capacitor. Next, Ru concentration of these surfaces were measured by TRXRF. Fig.3 shows the dependence of the concentration on the anneal temperature about (a) Si surface and (b) $SiO_2$ film surface. There were no dependence of the concentration on the anneal temperature. Furthermore, the concentration on these surface were decreased at any temperature compared with that of non-anneal sample.

These results shows that Ru has the characteristics of outside-diffusion from Si surface and thermal oxide film surface. This means that a production system such as furnace system, resist removal system or cleaning system is contaminated from a contaminated wafer. We defined maximum permissible Ru concentration to affect device characteristics, especially gate oxide film.

## 4. Characteristics of Contaminated Gate Oxide Film

The characteristics of gate oxide film contaminated with Ru were investigated. Fig.4 shows the fabrication flow to contaminate gate oxide film. Fig.4(a) and Fig.4(b) show the intentional contamination flow on Si surface and on gate oxide film. The thickness of these oxide film was 7nm. The concentration of Ru was varied from $5x10^{10}$atoms/cm$^2$ to $5x10^{12}$atoms/cm$^2$. The characteristics of the gate oxide film were evaluated by breakdown field intensity measured by Hg probe (SSM-600), interface charge density (Qox) and interface state density(Dit) measured by surface charge analyzer. Fig.5 shows the dependence of breakdown yield of gate oxide film on the concentration. The breakdown field up to 10MV/cm was counted in having good characteristics. The both of the films was started to degrade in the concentration of about $5x10^{11}$atoms/cm$^2$. Especially, the degradation was remarkable about the contaminated on the oxide film. Fig.6 shows the dependence of the interface charge density (Qox) (a) and the interface state density (Dit) (b) on the concentration. Qox and Dit were degraded up to the concentration of $5x10^{11}$atoms/cm$^2$. Furthermore, the degradation was remarkable for the contaminated on the gate oxide film. These results show that the maximum permissible Ru concentration to affect the characteristics of gate oxide film is $5x10^{11}$atoms/cm$^2$.

## 5. Conclusion

The characteristics of Ru on Si and $SiO_2$ film and the effect of Ru contaminant on gate oxide film were reported for the first time and concluded, as follow. 1) Ru dose not diffuse into substrate after Ru electrode formation for DRAM cell capacitor 2) Ru has the characteristics of outside-diffusion from Si and $SiO_2$ surface at the temperature from 750℃ to 950℃. 3) Maximum permissible concentration to affect the gate oxide integrity is $5x10^{11}$atoms/$cm^2$.

These mean that a production system is contaminated from a contaminated wafer, and when a wafer in the process of gate formation is introduced into the contaminated system, the characteristics of gate oxide film degrades. Ru contamination must be controlled based on the new insight on this study, although further studies are necessary.

## References


1) S.Yamauchi and M.Yoshimal:Integrated Ferroelectrics. vol.14(1997)159

2) S.Takehiro,S.Yamauchi and M.Yoshimaru:Proc.Electrical Society.vol.97-3(1997)263


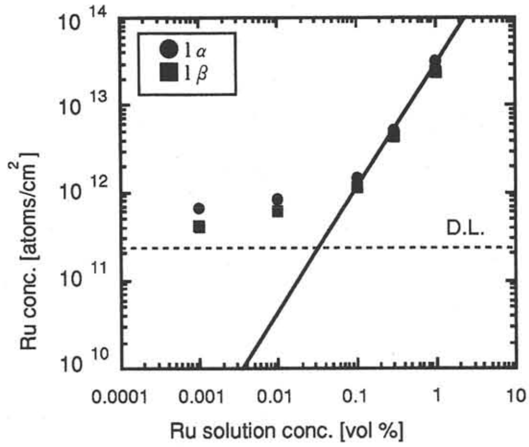


Fig.1 Dependence of Ru concentration on Ru solusion measured by TRXRF.

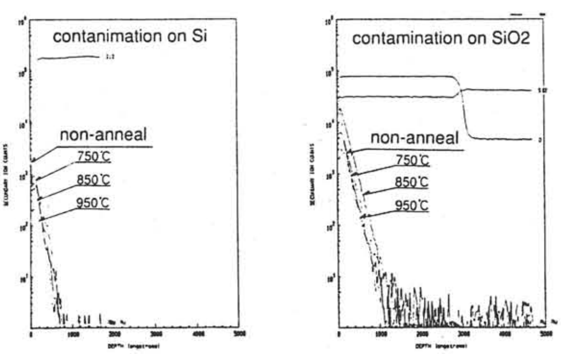


Fig.2 SIMS analysis of Ru diffusion in Si substrate and thermal $SiO_2$

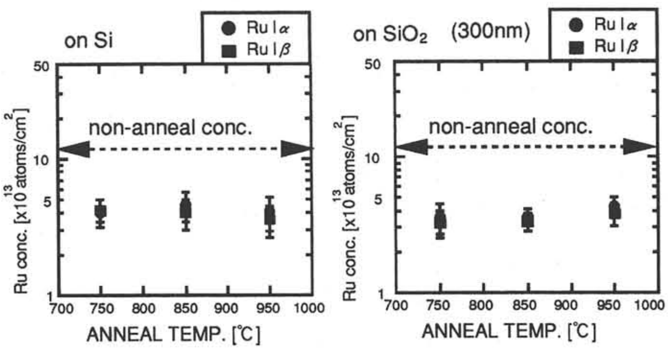


Fig.3 Dependence of Ru concentration on (a)Si surface and (b)$SiO_2$film surface.

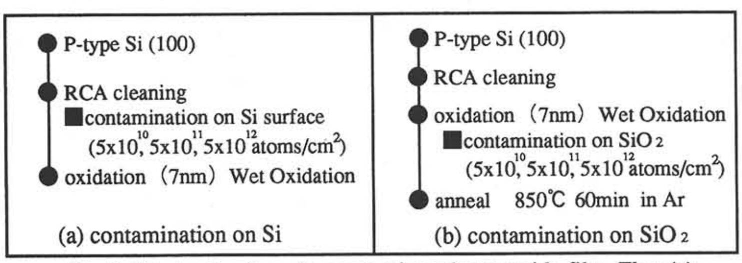


Fig.4 Fabrication flow for contaminated gate oxide film. Flow(a) is contamination on Si surface and flow(b) is contamination on $SiO_2$ film surface.

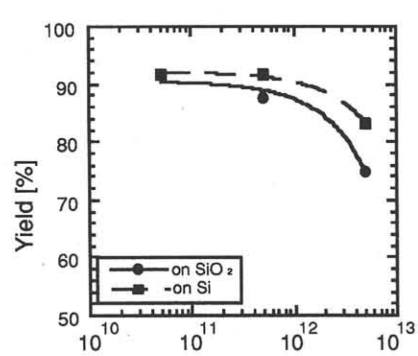


Fig.5 Dependence of breakdown yiels of gate oxide film on Ru concentration. The films are contaminated on gate oxide film and Si surface and oxidation.

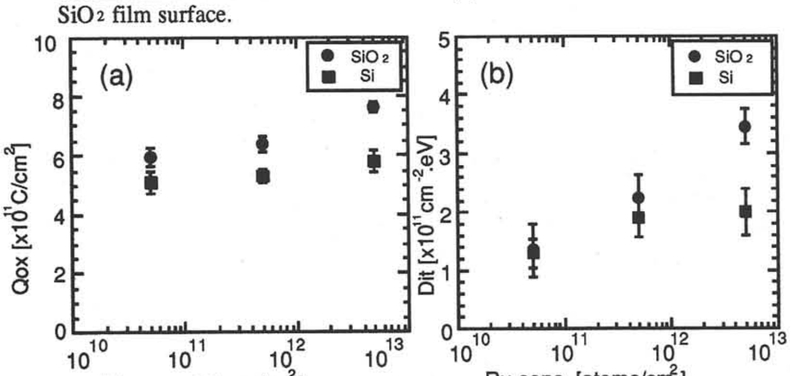


Fig.6 Dependence of interface charge density (Qox)(a) and intaerace state dencity (Dit)(b) of gate oxide film on Ru concentration.