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# New Method for Characterizing Dielectric Properties of High-k Films Using Time-Dependent Open-Circuit Potential Measurement

Koji Kita, Masashi Sasagawa, Kentaro Kyuno, and Akira Toriumi

Department of Materials Science, Graduate School of Engineering, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Phone : +81-3-5841-7161 Fax : +81-3-5841-7161 E-mail: kita@adam.t.u-tokyo.ac.jp

## 1. Introduction

Various materials with higher dielectric constant (high-k) have been studied as possible candidates for the next generation gate dielectric film [1]. The dielectric properties of them often suffer from a depth dependence, due to the formation of interfacial low-k layer. We note that the time-dependent open-circuit potential (t-OCP) measurement during etching in a solution, is expected to clarify the depth-dependent properties, since the measurement surface is continuously moving from top to bottom of the film.

Fig.1 shows the potential diagram, when a silicon top surface covered with a dielectric film is immersed in HF solution. The adsorbed ions on the film form the surface charge  $Q$ , which in turn induces the opposite charge in Si. The t-OCP analysis during etching has been applied for the interface of the chemical oxide [2][3] and ~nm thin  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  [4] on Si. However, bulk properties of those films have never been investigated with the OCP. In this paper, the t-OCP during the during "bulk" etching of "thick" high-k films was examined in order to develop a new characterizing method of high-k films which is extensible to the analysis of depth-dependent dielectric properties.

## 2. Experimental

$\text{HfO}_2$ ,  $\text{Y}_2\text{O}_3$  and  $\text{SiO}_2$  were examined as dielectric films.  $\text{HfO}_2$  (30nm thick) and  $\text{Y}_2\text{O}_3$  (30nm) were sputtered on HF-last  $n^+$ -(100) Si.  $\text{HfO}_2$  film (30nm) was also sputtered on a silicon wafer covered with 2nm-thick chemical oxide formed by SPM ( $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2=4:1$ , 140°C), to examine the effect of interfacial layer on the t-OCP.  $\text{SiO}_2$  (33nm) was thermally grown on the same substrate. The OCP measurements were conducted with the setup shown in Fig.2, using HF 0.5wt% solution. The voltage between the back contact of Si and the reference electrode was measured continuously by a digital voltmeter. H-terminated Si was used as the reference electrode, which was confirmed to show a stable potential of -0.23V vs. Ag/AgCl standard electrode.

## 3. Results and Discussion

The t-OCP of  $\text{HfO}_2$  film on HF-last Si during etching is shown as a solid line in Fig.3-(a). It has three stages, as indicated in the figure. It starts with a rapid increase, which suggests the adsorption of minus ions on the top surface. In the early stage of etching, the potential is not stable, however, it shows a constant gradient in the middle stage. In the final stage it shows a sudden drop similar to the reported result for  $\text{SiO}_2$  film [2], which is explained as starting of mono-oxide etching at oxide/Si interface, followed by a gradual H-termination to reach a constant potential. The t-OCP for  $\text{HfO}_2$  on SPM treated Si is also shown as a dotted line in Fig.3-(a). It shows a relatively small swing, which might be caused by fixed charges in the chemical oxide. In the final stage of the etching, it is similar to the one for the etching of

chemical oxide (Fig.3-(b)), which suggests the etching proceeds by layer-by-layer step.

In a model depicted in Fig.1, the voltage measured between the HF solution and the back side of Si,  $V$ , is determined by solving Poisson equations [2]. If the effect of fixed charge in the film is neglected, it is written as,

$$V = \delta V + Q \left( \frac{d_{ox}}{\epsilon_{ox}} + \frac{W}{\epsilon_{Si}} \right) \approx \delta V + \frac{Q}{\epsilon_{ox}} (d_0 - rt) + \frac{QW}{\epsilon_{Si}}, \quad (1)$$

where  $Q$  is the surface charge density;  $\epsilon_{ox}$  and  $\epsilon_{Si}$  are dielectric constants of the film and Si;  $d_{ox}$  is the dielectric film thickness;  $d_0$  is the initial film thickness;  $W$  is the width of the depletion layer in Si;  $t$ ,  $r$  is the etching time and rate, respectively.  $\delta V$  includes a potential drop in the solution. Note that  $\delta V$  is independent of  $d_{ox}$ , and  $W$  is negligible if the dopant concentration in Si is high enough.  $V$  drops with time as  $d_{ox}$  decreases by etching. The slope of  $V$ - $d_{ox}$  relationship corresponds to  $Q/\epsilon_{ox}$ , assuming both  $\delta V$  and  $Q$  are constant. Such assumption is quite reasonable for stationary "bulk" etching. The t-OCP in "the middle stage" is interesting to analyze since stationary "bulk" etching is supposed to occur.

Figure 4 shows the comparison of t-OCP for  $\text{HfO}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{SiO}_2$ , where the horizontal axis is  $r \times t$ , which is equivalent to the film thickness change,  $\Delta d_{ox}$ . The etching rate,  $r$  was estimated by assuming constant during the whole etching process.  $\text{Y}_2\text{O}_3$  showed an instable behavior, which might be due to its hygroscopic character. It had no sign of etching endpoint, but  $r$  was determined by assuming most of the film except interfacial layer was etched before the OCP became stable. The slopes in Fig.4 correspond to  $Q/\epsilon_{ox}$ . Note that  $Q$  is determined by the amount of ad-ions at the surface, although  $\epsilon_{ox}$  is the mean value of the film. Thus the non-uniformity of the dielectric properties, in principle, can be detected from the non-linear behavior of  $V$ - $d_{ox}$ . With an interfacial layer between Si and high-k film, as depicted in Fig.5, the slope  $Q/\epsilon_{ox}$  will be enlarged as etching proceeds. The precise depth-profile analysis is not discussed here, but such profile will be surely obtained by establishing a more accurate measurement setup.

If uniform  $\epsilon_{ox}$  is assumed,  $Q$  can be estimated from  $Q/\epsilon_{ox}$ . The obtained  $Q$  values by adopting the known  $\epsilon_{ox}$  values, are listed in Table I. In this measurement, the origin of  $Q$  is mainly the adsorbed  $\text{HF}_2^-$  ion. The surface density of ad-ions should have a close relation to the electronegativity of metal atoms emerging at the surface. Taking account that Coulomb potential is proportional to the square of the charge quantity,  $Q$  is plotted as the function of  $\Delta X^2$  in Fig.6, where  $\Delta X$  is the Pauling's electronegativity difference between metal atoms (Hf, Y, Si) and fluorine (=4.0). An almost linear relationship between  $Q$  and  $\Delta X^2$  is clearly shown. It supports our consideration that  $Q$  is determined only by the surface properties. Although the surface density difference of metal

atoms should be taken into account, its contribution is negligible in our argument. The precise analysis of OCP will lead to further understanding of not only the ionic character of surface atoms, but the polarizability of high-k films.

#### 4. Conclusions

The surface charge density obtained from t-OCP analysis was closely related to the electronegativity difference of metal atom and adsorbed ion at the surface, which will give invaluable clues to understand the properties at the dielectric film surface. It was also proposed that t-OCP measurement for thick high-k films enabled to characterize the depth-dependent dielectric properties, by examining the slope of OCP- $d_{ox}$  relationship.

#### Acknowledgement

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#### References

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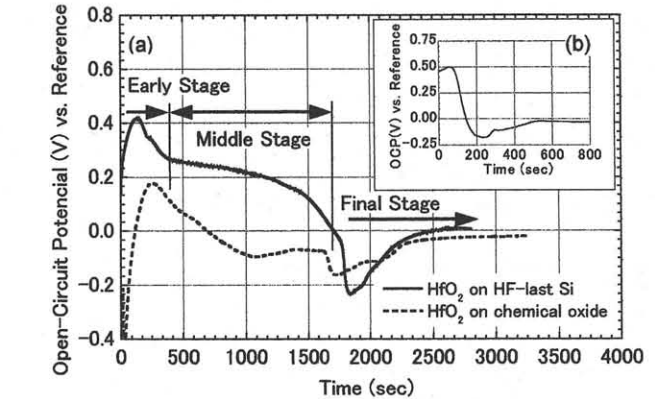


Fig.3 (a) The OCP curves for HfO<sub>2</sub> film on HF-last Si (solid line) and on SPM treated Si (dotted line) in 0.5wt% HF solution. They showed a slope in the middle stage of etching until a sudden potential drop (the end-point of etching). In the final stage of etching, OCP for HfO<sub>2</sub> on chemical oxide (dotted line) was similar to the OCP curve for the chemical oxide shown as (b).

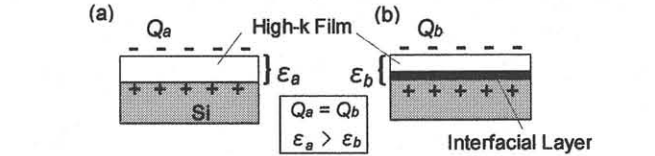


Fig 5 Schematic of the effect of interfacial layer. (a) and (b) show the high-k films with and without interfacial layer, respectively. The surface charge density  $Q$  is coincident, although the mean dielectric constant  $\epsilon_{ox}$  is different. The slope in  $V$ - $d_{ox}$  relationship,  $Q/\epsilon_{ox}$  is larger in case (b).

Table I Comparison of surface charge density  $Q$  obtained from the slope in Fig.4 and the Pauling's Electronegativity  $X_M$ .

Sample	HfO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Dielectric constant $\epsilon_{ox}$	20	15	4
Pauling's Electronegativity $X_M$ (M= Hf, Y, Si)	1.3	1.2	1.9
Estimated surface charge density $Q$ (C/cm <sup>2</sup> )	$1.3 \times 10^{-7}$	$1.6 \times 10^{-7}$	$6.7 \times 10^{-8}$

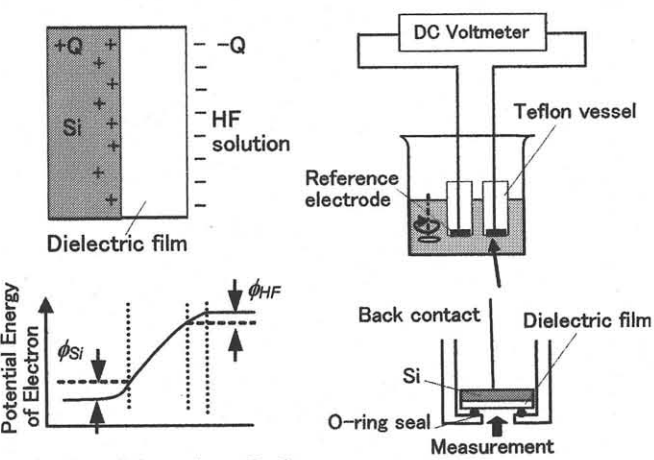


Fig.1 Schematic of the potential diagram when the dielectric film is in contact with HF solution. The total potential drop  $V$  is described as the sum of that in the solution ( $\phi_{HF}$ ), in dielectric film, and in the depletion layer of Si ( $\phi_{Si}$ ).

Fig. 2 Schematic of measurement setup. The sample was sealed with the measurement area 38 mm<sup>2</sup>. The HF solution was kept stirred to fix the etching rate.

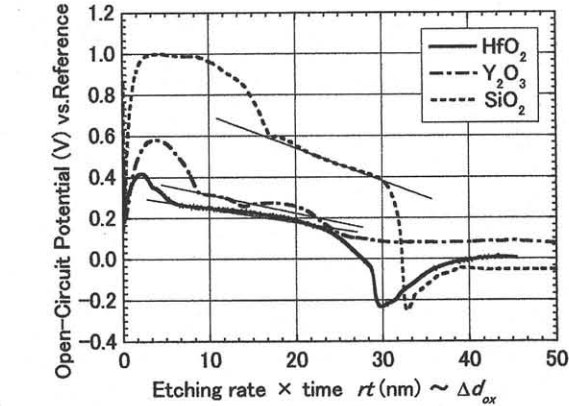


Fig.4 The t-OCP curves for each film measured in 0.5 wt% HF solution. Horizontal axis shows  $r \times t$ , equivalent to the change of oxide thickness  $\Delta d_{ox}$ . The slope in the middle stage corresponds to  $Q/\epsilon_{ox}$ . The data for Y<sub>2</sub>O<sub>3</sub> shows a slightly queer behavior which might be due to its hygroscopic character.

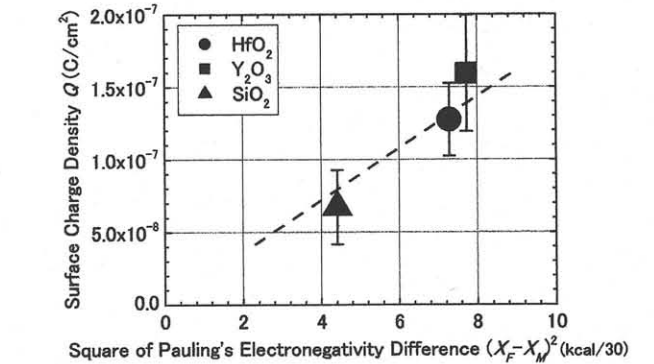


Fig.6 The surface charge density  $Q$  as a function of  $\Delta X^2$ , where  $\Delta X$  ( $X_F - X_M$ ) is the Pauling's electronegativity difference between metal atom (Hf, Y, Si) and fluorine. Almost linear relationship is obtained. The data for Y<sub>2</sub>O<sub>3</sub> has a relatively large estimation error.  $\Delta X^2$  is considered to be related to the Coulomb energy between film surface and ad-ions.