

# C-V Measurement of HfO<sub>2</sub> Dielectric Layer Received by UV Stimulated Plasma Anodizing

Amiran Bibilashvili<sup>1</sup>, Zurab Kushitashvili<sup>2</sup>

<sup>1</sup> Ivane Javakhishvili Tbilisi State University, LEPL Institute of Micro and Nanoelectronics, Chavchavadze ave.13, 0179 Tbilisi, Georgia

<sup>2</sup> Ivane Javakhishvili Tbilisi State University, LEPL Institute of Micro and Nanoelectronics Chavchavadze ave.13, 0179 Tbilisi, Georgia

E-mail address: amiran.bibilashvili@tsu.ge

**Abstract.** In this report we consider HfO<sub>2</sub> dielectric layer received by UV stimulated plasma anodizing. This dielectric is distinguished by good electric parameters. For this purpose, it was used C-V characterization technic and calculate dielectric constant, flatband voltage, threshold voltage, bulk potential, work function, oxide effective charge, charge concentration. The C-V measurement was carried out on Keithley Instrument – Semiconductor Parameter Analyzer 4200, oxide thickness was measured by reflectometer – MprobeVis System.

## 1. Introduction

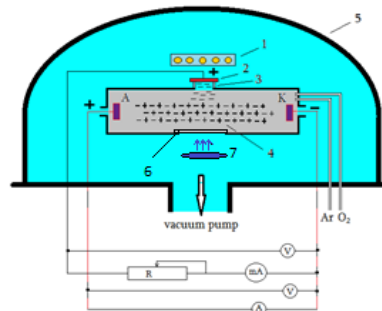
Transition metals oxides are technologically important metal oxides [1], which are characterized by excellent electrical and optical properties. They are attractive for applications in the field of electronics and opto-electronics [2-9] due to their high dielectric constants and wide band gaps. Recently, high dielectric constant (high K) oxides, such as HfO<sub>2</sub> replaces SiO<sub>2</sub> as the gate dielectric in metal-oxide-semiconductor field effect transistors (MOSFETs) [10, 11]. One of the main electrical characterizations for MOS structures is C-V characterization, because this method gives many electric parameters, which define the quality of dielectric layers. The present work is focused towards C-V characterization of HfO<sub>2</sub> films received by UV stimulated plasma anodizing.

## 2. Experimental

In the experiment were used (100), 10 Ω·cm, 2 inch, *p*-type silicon wafers as a substrate. Thin films of pure Hafnium (99.9%) were deposited by e-beam evaporation. Rotary and turbo pump combination was used to get the desired vacuum. The base pressure of the system was less than 10<sup>-6</sup> torr. All the depositions were carried out at a total pressure of 5x10<sup>-5</sup> torr. The distance between the target and silicon substrates was kept at 45 mm and the substrate temperature was 473K.

In the experiment were planned to use several samples for using them in the several anodizing process for forming dielectric layers. After deposition of pure Hf, each sample was placed in plasma anodizing vacuum chamber (Figure 1.) to proceed the anodizing.





**Figure 1.** Plasma anodizing system with electrical circuit; 1. heater; 2. substrate; 3. isolators; 4. local plasma area; 5. vacuum chamber; 6. Quarts plate; 7. UV lamp

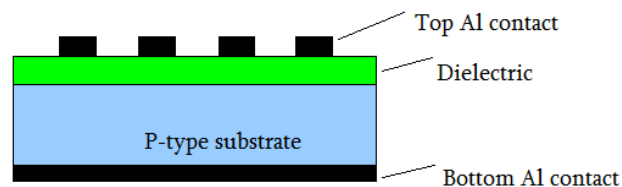
After receiving high vacuum ( $10^{-6}$  torr) by diffusion pump in the anodizing chamber, were entered high purity Ar and  $O_2$  gases with ratio 2:8 respectively by needle valves.  $HfO_2$  samples were performed in the different modes (Table I).

**Table 1.** Different modes of Hf plasma anodizing

Modes	$HfO_2$		
	I	II	III
Temperature ( $^{\circ}C$ )	400	400	400
Anodizing current density ( $mA/cm^2$ )	0.5	1	2

At a set pressure  $10^{-2}$  torr between anode and cathode was applied voltage 300-400v and plasma current was  $0.8 \div 1A$ . On structures Si-Hf were applied additional positive voltage base cathode 200-300v and anodizing current density was  $0.5 \div 2mA/cm^2$ . During metal (Hf) oxidation oxide resistivity is increased and anodizing current must be dropped, therefore we had increased the voltage step by step so, that hold the anodizing current constant and process curies at a constant current.

In the process of anodizing simultaneously was switched on UV lamp (Figure 1), with wavelength 400nm. It irradiates metal surface and thereby stimulates and accelerates the process of oxidation. After plasma anodizing process the samples were put out from the vacuum chamber and by thermal evaporation was deposited Al on the both side. On the front side was made photolithography for patterning and create metal-oxide- semiconductor (MOS) structure (Figure 2). The Al top contact area was  $3 \cdot 10^{-5}cm^2$ . In practice, it is usual for C-V measurement that for the backside contact it must be held at ground and the front side contact, to be biased at some potential.



**Figure 2.** MOS structure

### 3. C-V Measurement results and Discussion

#### 3.1 C-V plots

Capacitance-Voltage (C-V) testing is widely used technic for determine semiconductor parameters, particularly in MOSCAP and MOSFET structures (Lee 2009). From C-V measurement can be derived

many parameters including dielectric constant, flatband voltage, threshold voltage, bulk potential, work function, oxide effective charge, charge concentration, doping profile, depletion depth. Below we present some research on  $\text{HfO}_2$  dielectric films received by UV plasma anodizing. The testing was carried out at Keithley Instrument – Semiconductor Parameter Analyzer 4200.

As from the theory of C-V measurement known the C-V curve has three regions: accumulation, depletion and inversion regions. For high frequency measurement on the MOS structure is applied small sinusoidal oscillating (AC) signal on the voltage sweep. This is because equilibrium conditions imply that there is sufficient time for the inversion layer carrier concentration to respond to any changes in applied field. Any inversion layer must be formed from minority carriers generated in the depletion region and swept to the surface by the electric field. If the material quality of the silicon is good, carrier generation - recombination processes occur very slowly, with a time constant on the order of milliseconds. Therefore, for an applied AC voltage in the megahertz range, the response of the inversion layer is simply too slow to follow the signal and similar to ionized dopant impurity atoms, the inversion layer appears fixed with respect to the AC component of the bias (Of course, the inversion layer does respond to the primary voltage sweep.) C-V characterization of  $\text{HfO}_2$  gate dielectric is shown in the Figure 3. These C-V curves are made at a different frequencies and different anodizing current densities.

For high frequency conditions, the capacitance measured in inversion is the series combination of oxide capacitance and capacitance of the depletion region. Furthermore, since, the depletion width reaches a maximum value, the combined capacitance saturates at  $C_{\min}$ . Some calculated data from C-V measurement for  $\text{HfO}_2$  dielectric layer at 1MHz frequency are shown in Table 2.

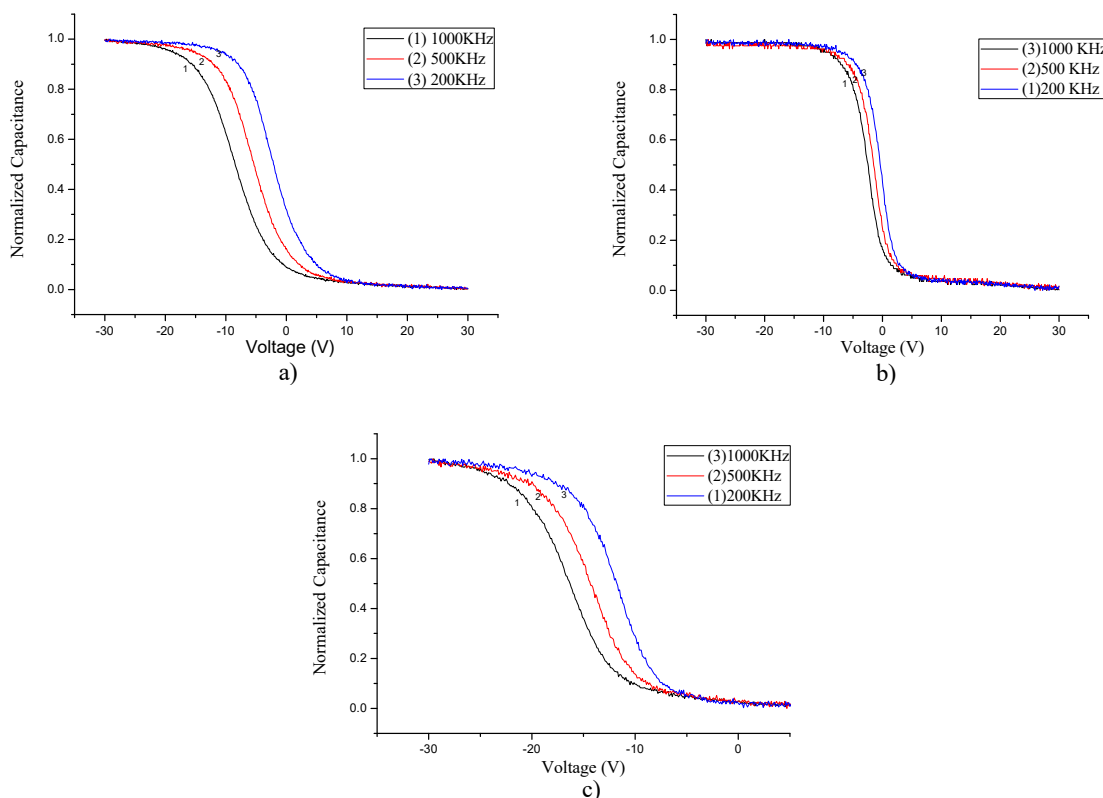


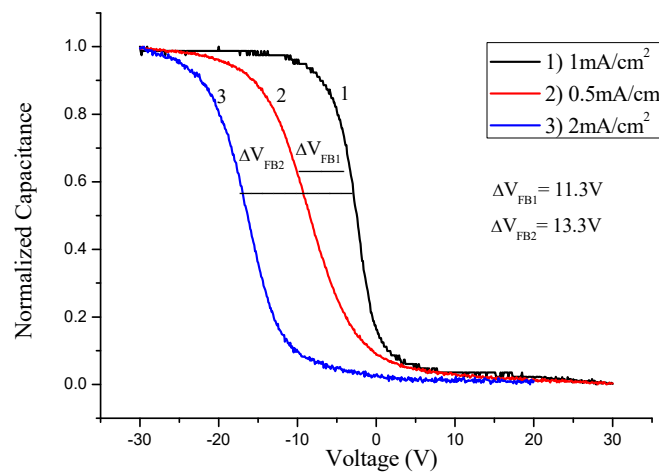
Figure 3. C-V characterization of  $\text{HfO}_2$  at different anodizing current densities: a)  $0.5\text{mA}/\text{cm}^2$ , b)  $1\text{mA}/\text{cm}^2$ , c)  $2\text{mA}/\text{cm}^2$

**Table 2.** Table of parameters calculated from the C-V measurement

Anodizing current density, mA/cm <sup>2</sup>	$C_{FB}$ , (pF)	$V_{FB}$ , (V)	$V_{TH}$ , (V)	$W_{MS}$ , (V)	$Q_{EFF}$ , (nC)	$C_{min}$ , (pF)	$N_{EFF}, \times 10^{10}$ (cm <sup>-2</sup> )
0.5	2.16	-24.9	-2.24	-0.696	4.1	0.98	2.5
1	1.75	-13.6	6.92	-0.682	2.2	0.98	1.4
2	1.61	-26.9	-9.61	-0.670	5.0	0.96	3.1

Where,  $C_{FB}$  – is a flatband capacitance,  $V_{FB}$  – flatband voltage,  $V_{TH}$  – threshold voltage,  $W_{MS}$  – work function difference metal-semiconductor,  $Q_{EFF}$  – effective oxide charge.

Figure 4. shows the comparison of the different anodizing modes in the same frequency (1MHz). As from the graph seems in the dielectric exist positive charge.

**Figure 4.** C-V characterization of HfO<sub>2</sub> at 1MHz

The graphs corresponding to 0.5 mA/cm<sup>2</sup> and 2 mA/cm<sup>2</sup> anodizing current densities are shifted towards negative potential, in the dielectric exist positive charge larger than in the case 1 mA/cm<sup>2</sup> anodizing mode. It is possible for charges to become more or less permanently trapped within the oxide layer or at the Si/HfO<sub>2</sub> interface. Furthermore, in many cases these charges behave as if they are fixed. Therefore, in analogy to ionized impurity atoms in the substrate, such fixed oxide charges do not participate in nor are changed by charging the MOS capacitor. However, the existence of extraneous fixed charges does cause an overall shift in the position of the depletion region with respect to applied bias voltage. This is easily understood in elementary terms, since if one solves Poisson's equation, one finds that a layer of fixed charge inside the oxide layer just results in a constant potential offset. This is most conveniently analyzed by considering the capacitance and voltage for which the semiconductor is in a flat band condition. The flat band voltage should correspond just to the effective work function difference between the metal contact and the doped silicon substrate. However, if charges are present within the oxide layer, then the flat band voltage corresponds to the expression:

$$V_{FB} = W_{MS} - \frac{Q_{EFF}}{C_{OX}} \quad (1)$$

Where  $W_{MS}$ -is work function difference between the metal contact and the doped silicon substrate,  $Q_{EFF}$  – fixed charge,  $C_{ox}$  – is the capacitance in the accumulation region.

$Q_{EFF}$  is found to be positive, in which case  $V_{FB}$  is more negative than the work function difference. Hence, if positive fixed charges are present near the Si/HfO<sub>2</sub> interface, then the CV plot is translated to more negative values of bias voltage. This translation from the ideal flat band voltage corresponding to the simple work function difference, to flat band voltage experimentally observed in a CV plot is called flat band shift  $\Delta V_{FB}$ . Clearly, the actual CV plot is shifted by  $\Delta V_{FB}$  toward more negative bias voltage in comparison to the ideal CV plot. The flat band shift,  $\Delta V_{FB}$ , has a magnitude of  $\frac{Q_{EFF}}{C_{OX}}$  and, therefore, is a direct measure of fixed charge density  $N_{EFF}$  by this formula:

$$N_{EFF} = \frac{Q_{EFF}}{q} \quad (2)$$

$q$  is an elemental charge, which equal to  $1.6 \cdot 10^{-19}$  C.

One of the fundamental parameter that can be derived from C-V accumulation region is the dielectric constant of dielectric layer, of course if it is known the thickness of the dielectric layer. In our case the thickness of HfO<sub>2</sub> layer was measured by reflectometer – MprobeVis System, so dielectric constant can be calculated with following:

$$\epsilon_{ox} = \frac{Tox \cdot C_{ox}}{A} \cdot 10^{-7} \quad (3)$$

Where,  $A$ - is the area of the contact,  $Tox$  – is the thickness of the dielectric,  $C_{ox}$  – is the capacitance in the accumulation region,  $10^{-7}$  is a proportion coefficient (cm→nm). Below is given Table 3 which shows some data analyzed from Figure 4.

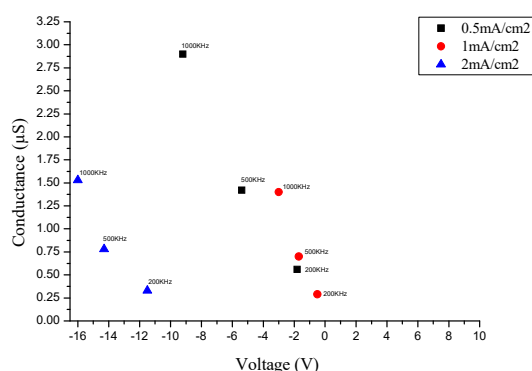
**Table 3.** Calculated dielectric constant

Frequency, [kHz]	200	500	1000	200	500	1000	200	500	1000
Anodizing Current Density, mA/cm <sup>2</sup>	0.5			1			2		
Contact Area ( $A$ ), cm <sup>2</sup>	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
Dielectric Thickness ( $Tox$ ), nm	45	45	45	52	52	52	15	15	15
Capacitance ( $C_{ox}$ ), pF	2.18	2.17	1.73	1.76	1.76	1.76	1.64	1.63	1.63
Dielectric Constant ( $\epsilon_{ox}$ ), F/cm	32.7	32.6	25.9	30.5	30.5	30.5	8.2	8.2	8.2

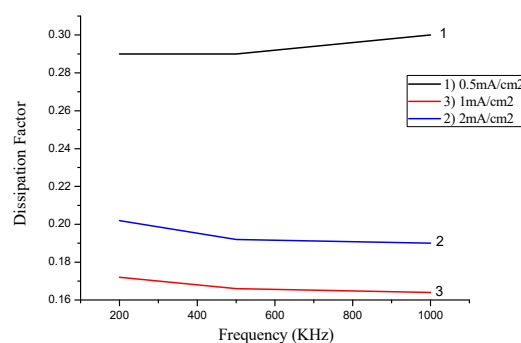
### 3.2 Conductance and Dissipation Factor

In all experiments conductance increases with increasing AC signal frequency. Figure 5. shows dependence of conductance on frequency. In the all modes the behaviour of the graphs are the same – increasing frequency causes increase of conductance, but it must be said, that in the 1mA/cm<sup>2</sup> anodizing mode the graphs are narrower and are characterized with good dependence between conductance and applied voltage.

Figure 6. shows dependence of minimum dissipation factors on frequency for all modes. 1mA/cm<sup>2</sup> anodizing mode is a better than others and shows relatively small DF. In the I mode anodizing current density is 0.5mA/cm<sup>2</sup>, it is relatively small and in the process not every oxygen ions makes bonding with Hf cations. It means that oxygen ions are free and during applied potential they oscillate and energy loss in the dielectric is a bit higher. In the case of III mode anodizing current density is 2mA/cm<sup>2</sup> and at these currents oxygen ions not able to make bonding with Hf cations due to their high speed and dielectric quality is not good, which means dissipation factor is high. In the II mode the dissipation factor is an optimal value comparing with modes I and III. Anodizing current density is 1mA/cm<sup>2</sup> and it seems to be best mode in the anodizing process with small dissipation factor value.



**Figure 5.** Conductance vs Voltage



**Figure 6.** Dissipation Factor vs Frequency

#### 4. Conclusion

The MOS structure was characterized with C-V characterization. The experiment was carried out in the 3 modes:  $1\text{mA}/\text{cm}^2$ ,  $0.5\text{mA}/\text{cm}^2$  and  $2\text{mA}/\text{cm}^2$  anodizing currents densities in order to define the optimal experimental mode for creating gate dielectric. From the curves (Figure 3) we can assume that II mode is more optimal. In the process of formation of dielectric at  $1\text{mA}/\text{cm}^2$  anodizing current, the structure of the dielectric is better in quality. It means that created dipoles in the anodizing process are less and surface charge also is small (twice less than other modes). Moreover, in the Figure 3 (b) the slope of the graph from vertical axis is less, it means that interface state density is less than other modes. Calculated dielectric constant is about  $30.5\text{F}/\text{cm}$ , which is intermediate value between I and III anodizing modes. Because of less dipoles inside the dielectric the resistance caused by dipoles also small and with several voltages the conductance reaches only  $1.4\mu\text{S}$ . The main parameter for characterizing the dielectric is a dissipation factor. We can see that from the Figure 6. the minimum dissipation factor is corresponding to  $1\text{mA}/\text{cm}^2$  anodizing current density.

#### Acknowledgments

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