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C-V Characterization and Electric Parameters of ZrO₂ Received by UV Stimulated Plasma Anodizing

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Abstract. Low temperature technologies creating metals oxides are a promising solution for formation integral circuit elements. In this report the electric properties of zirconia (ZrO₂) received by low temperature (~ 400⁰ C) UV stimulated plasma anodizing have been investigated. Zirconia is a potential high-k dielectric material with potential applications as agate insulator in transistors. This dielectric distinguished by good electric parameters. For this purpose, we 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

Transaction metals oxides are technologically important metal oxides, which are characterized by excellent electrical and optical properties. Zirconia is an insulator at room temperature, at elevated temperatures the vacancies in the anion lattice allow O₂ ions to diffuse and the zirconia becomes a solid electrolyte with applications in oxygen sensors and high-temperature fuel cells [1, 2]. Some stabilized zirconia can be used as resistors or susceptors. They are attractive for applications in the field of electronics and opto-electronics due to their high dielectric constants and wide band gaps [3]. Recently, high dielectric constant (high K) oxides [4], such as ZrO₂ replaces SiO₂ as the gate dielectric in metal-oxide-semiconductor field effect transistors (MOSFETs). One of the main electrical characterizations for MOS structures is C-V characterization [5], because this methodic gives many electric parameters, which define the quality of dielectric layers. The present work is focused on the C-V characterization of ZrO₂ films received by UV stimulated plasma anodizing [6].



2. Experimental

In the experiment were used (100), 10 $\Omega\cdot\text{cm}$, 2 inch, *p*-type silicon wafers as a substrate. Thin films of pure zirconium (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^{-6} torr. All the depositions were carried out at a total pressure of 5×10^{-5} torr. The distance between the target and silicon substrates was kept at 45 mm and the substrate temperature was 400 $^{\circ}$ C.

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

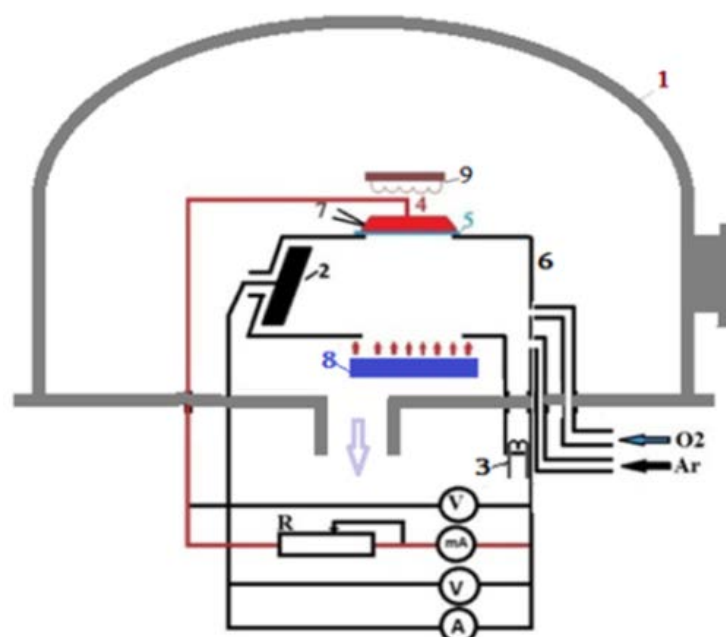


Figure 1. Plasma anodizing system with electrical circuit: 1- vacuum chamber; 2- Anode; 3- Cathode; 4- Contact for sample; 5- Sample; 6- Plasma holder; 7- Thermocouple; 8- Ultraviolet source irradiation

After receiving high vacuum (10^{-6} torr) by diffusion pump in the anodizing chamber, were entered high purity Ar and O₂ gases with ratio 2:8 respectively by needle valves. ZrO₂ samples were performed in different modes (table 1).

Table 1. Different modes of plasma anodizing

ZrO ₂				
Modes	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 was applied voltage 300-400 V between anode and cathode and plasma current were $0.8 \div 1$ A. On structures Si-Zr was applied additional positive voltage base cathode 200-300 V and anodizing current density was $0.5 \div 2$ mA/cm². During metal (Zr) 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 carried at a constant current. In the process of anodizing simultaneously was switched on UV lamp, with wave length 400 nm. It

irradiates the metal surface and thereby stimulates and accelerates the process of oxidation [7]. After plasma anodizing process, the samples were put out from the chamber and by thermal evaporation deposited on both side Aluminum. On the front side was made photolithography for patterning and form metal-oxide-semiconductor (MOS) structure (figure 2). The aluminum top contact area was $6 \cdot 10^{-6} \text{ cm}^2$. In practice, it is usual for $C-V$ measurement that for the back side contact it must be held at ground and the front side contact, to be biased at some potential.

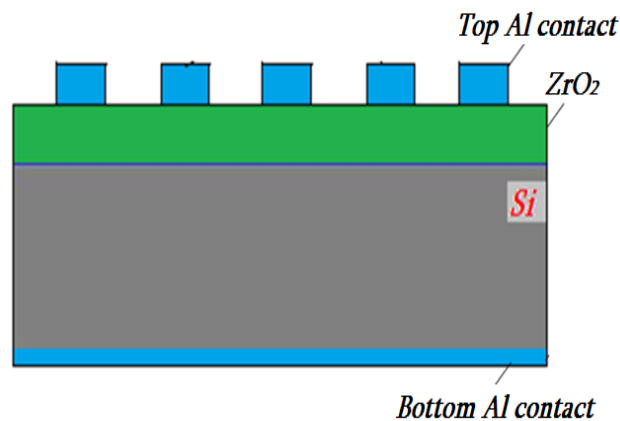


Figure 2. MOS Structure

3. C-V Measurement Results and Discussion

3.1. C-V plots

Capacitance-Voltage ($C-V$) testing is widely used technic for determining semiconductor parameters, particularly in MOSCAP and MOSFET structures. 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. Below we present some research on ZrO_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 the 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.) This behavior for ZrO_2 gate dielectric is shown in figure 3. These $C-V$ curves are made at different frequencies and different anodizing current densities.

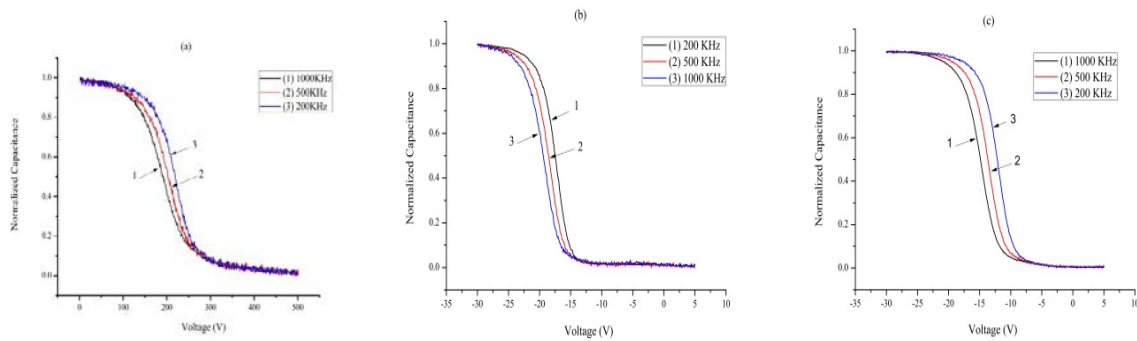


Figure 3. C-V plots at all frequency: a) anodizing current density 0.5 mA/cm², b) anodizing current density 1 mA/cm², c) anodizing current density 2 mA/cm²

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} . In the table 2 is given some calculated data from C-V measurement for ZrO₂ dielectric layer at 1MHz frequency.

Table 2. Calculated parameters from the data analyzed from Figure 3

Anodizing current density, mA/cm ²	C_{FB} , (pF)	V_{FB} , (V)	V_{TH} , (V)	W_{MS} , (V)	Q_{EFF} , (nC)	C_{min} , (pF)	N_{EFF} , ×10 ¹⁰ (cm ⁻²)
0.5	2.67	-13.9	-11.86	-0.595	3.65	1.06	2.3
1	1.78	-25.4	-22.08	-0.599	4.41	0.96	2.8
2	1.4	-21.2	-13.6	-0.626	2.83	0.96	1.8

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. The graphs corresponding to 0.5 mA/cm², 1 mA/cm² and 2 mA/cm² anodizing current densities are shifted towards negative potential; in the dielectric exist positive charge. It is possible for charges to become more or less permanently trapped within the oxide layer or at the Si/ZrO₂ 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 the 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.

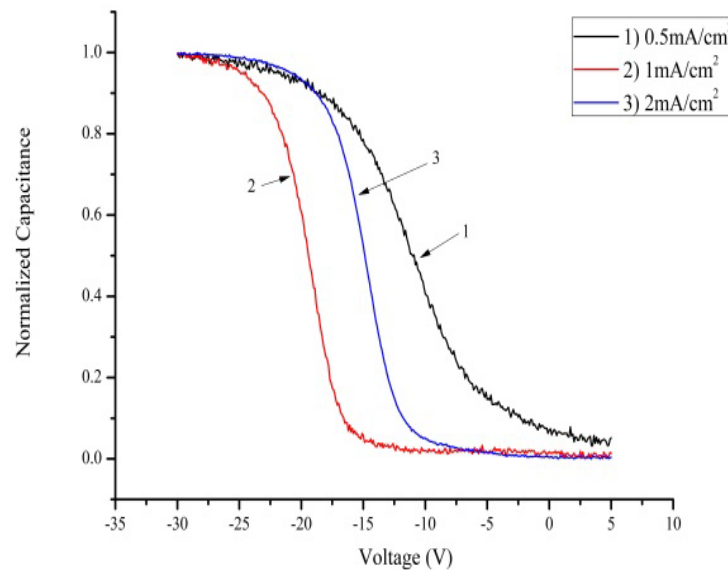


Figure 4. C-V plots at 1MHz frequency and all anodizing current densities

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/ZrO₂ 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 ΔV_{FB} . Clearly, the actual CV plot is shifted by ΔV_{FB} toward more negative bias voltage in comparison to the ideal CV plot. The flat band shift, ΔV_{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 equals to $1.6 \cdot 10^{-19}$ C.

One of the fundamental parameters that can be derived from the C-V accumulation region is the dielectric constant of the dielectric layer, of course, if it is known the thickness of the dielectric layer. In our case, the thickness of the ZrO₂ layer was measured by reflectometer – MprobeVis System, so the dielectric constant can be calculated with the following:

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

Where, A - is the area of the contact, T_{OX} – 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 parameters from data analyzed from Figure 4

Frequency, KHz	200	500	1000	200	500	1000	200	500	1000
Anodizing Current Density, mA/cm ²	2			1			0.5		
Contact Area (A), cm ²	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶	6·10 ⁻⁶
Dielectric Thickness (Tox), nm	45	45	45	52	52	52	30	30	30
Capacitance (C _{ox}), pF	2.69	2.7	2.7	1.8	1.78	1.78	1.43	1.43	1.43
Absolute Permittivity (ε _{ox})×10 ⁻¹⁴ , F/cm	201.8	202.5	202.5	156	154.2	154.2	71.5	71.5	71.5
Dielectric constant (ε _{ox} /ε ₀)	22.8	22.9	22.9	17.6	17.4	17.4	8.1	8.1	8.1

3.2 Dissipation Factor

Figure 5 shows the dependence of dissipation factor (DF) on voltage in different frequencies and different anodizing modes. Dissipation factor is a measure of loss energy in the dielectric, it represents the quality of the dielectric. In a dielectric, only one of either the conduction electrons or the dipole relaxation typically dominates loss of energy. In figures 5a and 5c, the plots are closer and difference between dissipation factors are smaller than in the case 1 mA/cm² anodizing modes.

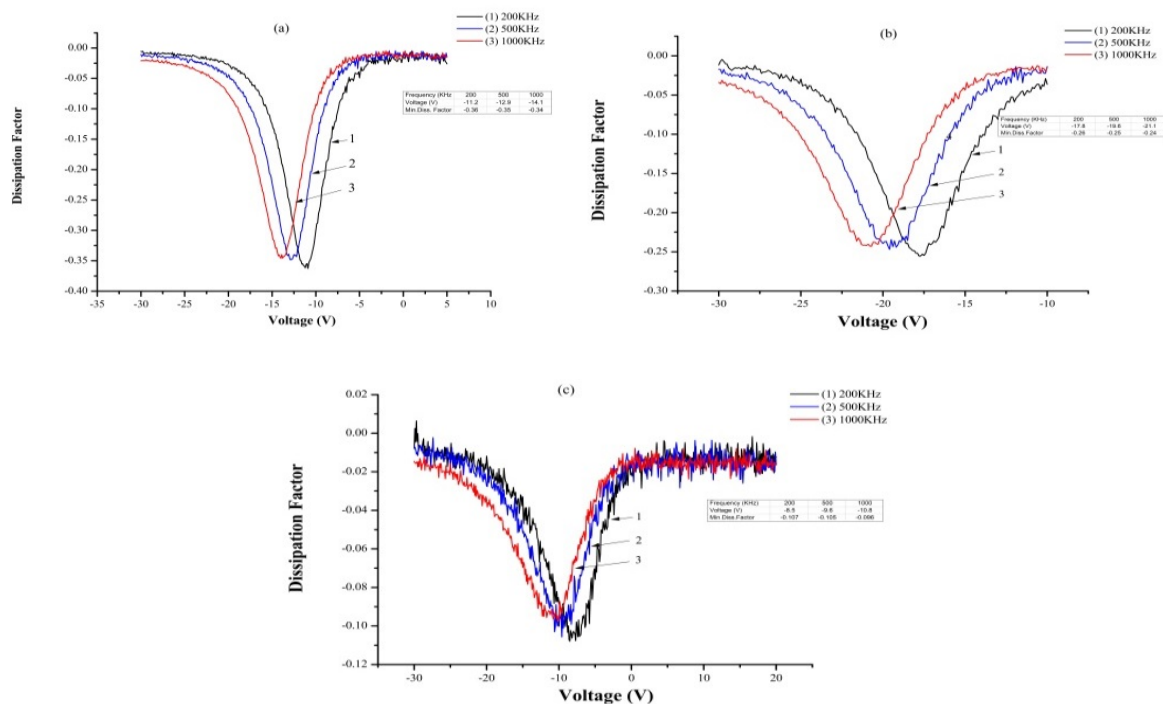


Figure 5. Dissipation Factor vs Voltage: a) anodizing current density 0.5 mA/cm², b) anodizing current density 1 mA/cm², c) anodizing current density 2 mA/cm²

Figure 6 shows the dependence of minimum dissipation factors on frequency for all modes. 2 mA/cm² anodizing mode is better than others and shows relatively small DF. In the I and II modes with anodizing current densities is 0.5 mA/cm² and 1 mA/cm² are relatively small and in the process not every oxygen ions makes bonding with Zr cations. It means that oxygen ions are free and during applied potential, they oscillate and energy loss in the dielectric is higher.

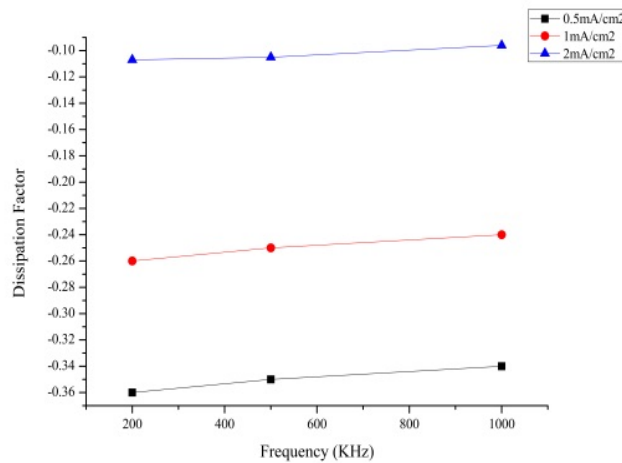


Figure 6. Dissipation factor vs frequency

In the case of III mode with anodizing current density is 2 mA/cm^2 oxygen ions are able to make bonding with Zr cations and dielectric quality is good, which means dissipation factor is low. Anodizing current density 2 mA/cm^2 seems to be the best mode in the anodizing process with small dissipation factor value.

4. Conclusion

The MOS structure was characterized by the C-V characterization. The experiment was carried out in the three modes: 1 mA/cm^2 , 0.5 mA/cm^2 and 2 mA/cm^2 anodizing currents densities in order to define the optimal experimental mode for creating gate dielectric. From the curves (figures 3a, 3c), we can assume that III mode is more optimal. In the process of formation of the dielectric at 2 mA/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 is also small. Moreover, in figure 3(c) the slope of the graph from the vertical axis is smaller, it means that interface state density is less than other modes. The calculated dielectric constant is about 23, which is in good accordance with the dielectric constant of ZrO_2 known in the scientific literature. The main parameter for characterizing the dielectric is a dissipation factor. We can see that from figure 6, the minimum dissipation factor is corresponding to 2 mA/cm^2 anodizing current density.

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