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Oxygen vacancy mobility and diffusion coefficient determined from current measurements in SiO_2/HfO_2/TiN stacks

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Abstract: Oxygen vacancy defects play an important role in process dependent threshold voltage variations, interfacial oxide growth, and trap creation in thin (≲4 nm) HfO_2 gate dielectric stacks [1, 2]. Despite their importance, little is know about their properties such as mobility, diffusion and their distribution in thin HfO_2 layers. In this study, transient gate currents are investigated in SiO_2/HfO_2/TiN nFETs with 2, 3 and 4 nm HfO_2 thicknesses. The study shows that the measured gate current is dominated by the oxygen vacancy related ionic current in thicker HfO_2 films, whereas the electronic component dominates in thinner films. In 3 and 4 nm HfO_2 devices, the gate current versus time curves are observed to exhibit transients with peaks. These transients are analyzed and the mobility (μ) and diffusion coefficient (*D*) associated with oxygen vacancies are estimated: $\mu = 4\text{x}10^{-12}$ cm^2/V–s at 125 °C and $D = 2\text{x}10^{-7} \cdot exp\ (-0.49/kT)$ cm^2/s. These results are shown to be consistent with those for positively charged oxygen vacancies in bulk specimens [3, 4]. Hence, the study not only provides experimental evidence for oxygen vacancy related ionic currents but also demonstrates a novel method for measuring oxygen diffusion in thin HfO_2 films where conventional diffusion methods become increasingly inaccurate. Also, the study provides insights into the distribution of oxygen vacancies in SiO_2/HfO_2/metal stacks: oxygen vacancies are gettered at the HfO_2/metal interface in a fresh device and drifts into the HfO_2 layer under the influence of positive gate bias.

Experimental Details: Measurements were performed on nFETs with $Si/SiO_2/HfO_2$/TiN stacks with three different HfO_2 film thicknesses of 4 nm, 3.5 nm and 2.5 nm and the interfacial SiO_2 thickness is 1.5 nm; nFETs were fabricated using standard gate first processing, including high (>1000 °C) temperature anneals. A step voltage is applied at the gate and the gate current is measured as a function of time with a sampling time of 1 ms; source and drain voltages are set at 0.0 V and the substrate is grounded. A new device is used for each current curve.

Results:

***Oxygen vacancy related ionic current and mobility*:** Fig. 1 and 2 show the gate current versus time curves measured at various gate voltages at 125°C for 4 nm HfO_2 devices. Fig.1 shows current measurements at $V_g < 1.0$ V: the current decreases (J) and becomes time independent (J_o) at longer times. The time independent component J_o is associated with the electronic conduction whereas the time independent component $\Delta J_t = (J\text{-}J_o)$ decreases with a power law time dependence as shown in Fig. 1(b) and such dependence is often identified with dielectric relaxation current. Fig. 2 shows current measurements for $V_g > 1.0$ V: the measured current curve becomes dominated by a new current component consisting of a transient with a peak; similar transients have also been observed in bulk titanates [5]. The measured curves with peaks are analyzed by applying the space-charge-limited (SCL) transient current theory [6] that predicts that the peak position (τ) is a measure of the mobility μ of the drifting charges:

$$\tau = 0.78 \cdot d^2 / \mu \cdot V_{hk} \quad \textbf{(1)}$$

where, *d* is the thickness of HfO_2 in cm and V_{hk} is the voltage applied across HfO_2; V_{hk} is iteratively calculated as a function of V_g taking into account the voltage drop across the interfacial SiO_2 and the silicon substrate. The applicability of SCL analysis to the measured data in Fig. 2 is verified by examining the dependence of τ on V_{hk}. Fig. 3 shows that τ has a linear dependence on $1/V_{hk}$ as predicted by eq. 1, and the slope is a measure of the charge mobility $\mu = 4\text{x}10^{-12}$ cm^2/V-s at 125°C. Since this mobility value is similar to those for oxygen vacancies in bulk metal oxides films [3, 5], the observed $\mu = 4\text{x}10^{-12}$ cm^2/V-s is identified with the ionic mobility for positively charged oxygen vacancies in HfO_2 layer.

***Oxygen diffusion coefficient*:** The Nerst-Einstein relation states that if the current is due to ionic charges then mobility (μ) and diffusion coefficient (*D*) are related:

$$D = kT \cdot \mu / q \quad \textbf{(2)}$$

where *k* is Boltzmann constant, *T* is the temperature in Kelvin, and *q* is the charge of an oxygen vacancy; $q = 3.2\text{x}10^{-19}$ Coulombs.

The diffusion coefficient for oxygen vacancies can be determined by measuring the temperature dependent transient currents and equations 1 and 2. Fig. 4 shows the measured transient current curves at various temperatures and $V_g = 1.6$ V for 4 nm HfO_2 nFETs: τ decreases with increasing temperature. Fig. 5 shows the measured results for oxygen vacancy diffusion in 4 nm HfO_2 gate dielectric layer: $D = 2\text{x}10^{-7} \cdot exp\ (-0.49/kT)$ cm^2/s. Similar current transients and diffusion results are also observed for 3 nm HfO_2 devices. However, the electronic conduction mechanism became dominant in thinner 2 nm HfO_2 devices, and consequently ionic current component consisting of transients with peaks could not be observed.

Since oxygen diffusion studies in undoped HfO_2 bulk specimens have not been conducted, the measured diffusion parameters of Fig. 5 are compared with those in similar oxides such as bulk ZrO_2 [3,4]. As summarized in Table I, measured E_o and D_o values are in agreement with those for oxygen vacancies in bulk specimens and also with the first principle calculations [7].

***Oxygen vacancy distribution in HfO_2*:** We would like to point out that the transient currents with peaks as shown in Fig. 2 and Fig. 4 are observed *only* for the positive polarity gate voltages. Since SCL theory predicts that transients with peaks would only be observed if a reservoir of charges exists at the injecting interface, this implies that positively charged oxygen vacancies are not uniformly distributed but are gettered at the HfO_2/metal interface, consistent with first principle calculations [8].

Conclusion: Using transient gate currents, mobility and diffusion coefficient for oxygen vacancies are measured in thin HfO_2 gate dielectric films and shown to be consistent with those for positively charged oxygen vacancies in bulk specimens. Hence, the study provides evidence for ionic current component and demonstrates a novel method for measuring oxygen diffusion. The study also shows that the oxygen vacancies are gettered at the HfO_2/metal interface in a fresh device and that the application of a positive gate bias causes the gettered vacancies to drift towards HfO_2/SiO_2 interface.

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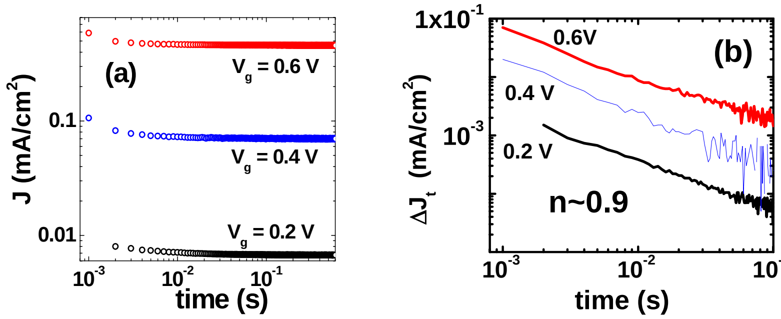

Fig. 1: **(a)** Measured current density (J) versus time curves at $V_g < 1.0$ V and 125°C for 4 nm HfO_2 nFETs; J decreases with time and reaches a steady state value at longer times, thus indicating that measured J has time dependent (ΔJ_t) and time independent (J_o) components. **(b)** $\Delta J_t = (J - J_o)$ is extracted from Fig. 1(a): $\Delta J_t \propto \text{time}^{-0.9}$.

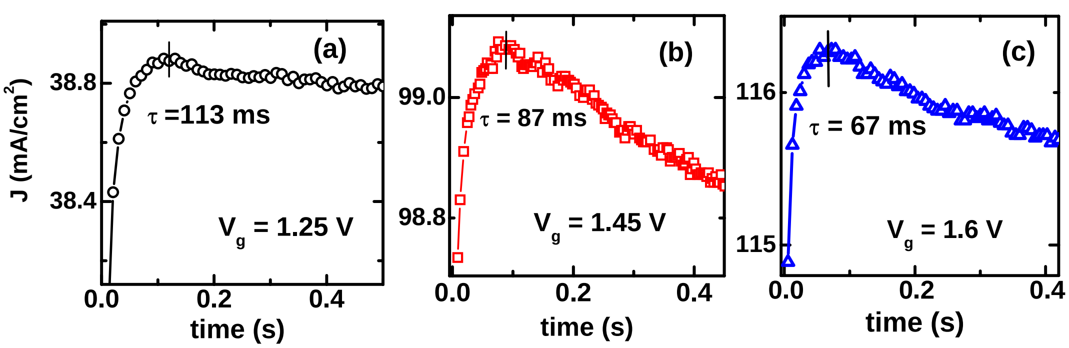

Fig. 2(a) - (c): Measured gate current density versus time curves at $V_g > 1.0$ V and 125 °C for 4 nm HfO_2 nFETs; a new device is used for each curve. For $V_g > 1.0$ V, the measured current is dominated by a new current component that exhibits a transient with a peak that moves towards shorter times with increasing V_g; these transients are analyzed using SCL theory [6], and are identified with positively charged oxygen vacancy diffusion in HfO_2 layer.

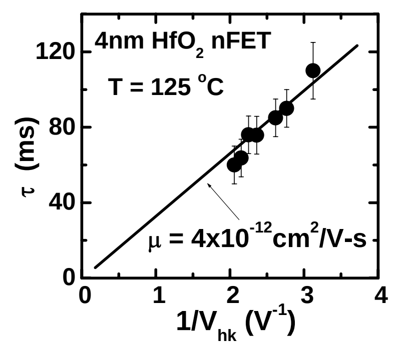

Fig. 3: Dependence of the peak position (τ) on the voltage across HfO_2 layer (V_{hk}); τ is obtained from Fig. 2; the solid line slope is a measure of mobility (μ) as predicted by eq. 1.

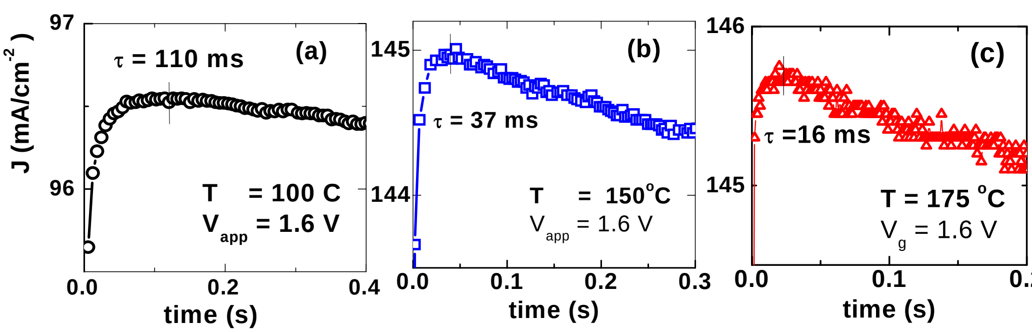

Fig. 4 (a) – (b): Measured gate current transients at three different temperatures and $V_g = 1.6$V for 4nm HfO_2 nFETs; peak position (τ) moves towards shorter times with increasing temperature.

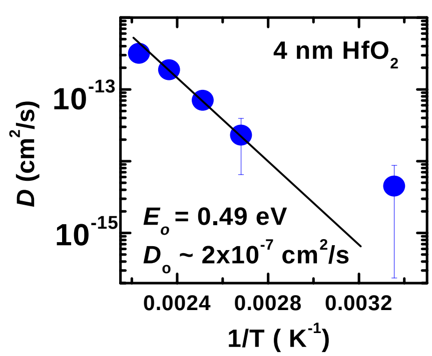

Fig. 5: Measured dependence of the diffusion coefficient (*D*) on temperature; *D* is obtained using τ from Fig. 4 and eq. 1 & 2.

	Fig. 5	Meas. Bulk values	Theoretical
E_o (eV)	0.49	0.59 [3] 0.4 - 0.8 [4]	0.69 [7]
D_0 (cm^2/s)	$2x10^{-7}$	10^{-7} - 10^{-6} [3]	

Table I: Comparison between the measured diffusion coefficient parameters E_o and D_o (Fig. 5) and the literature values. Ref. [3] discusses the result for migration of positively charged oxygen vacancies in bulk ZrO_2; [4] discusses the results for bulk CeO_2; [7] discusses the first principles calculation results for positively charged vacancy migration in thin HfO_2 films. Fig. 5 results for thin HfO_2 devices are in good agreement with both measured (bulk) and first principle calculation results for positively charged oxygen vacancy diffusion.