Electron trapping properties at HfO_2/SiO_2 interface, studied by Kelvin probe force microscopy and theoretical analysis*

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Electron trapping properties at the HfO_2/SiO_2 interface have been measured through Kelvin Probe force microscopy, between room temperature and 90 °C. The electron diffusion in HfO_2 shows a multiple-step process. After injection, electrons diffuse quickly toward the HfO_2/SiO_2 interface and then diffuse laterally near the interface in two sub-steps: The first is a fast diffusion through shallow trap centers and the second is a slow diffusion through deep trap centers. Evolution of contact potential difference profile in the fast lateral diffusion sub-step was simulated by solving a diffusion equation with a term describing the charge loss. In this way, the diffusion coefficient and the average life time at different temperatures were extracted. A value of 0.57 eV was calculated for the activation energy of the shallow trap centers in HfO_2.

Keywords: Kelvin probe force microscopy, traps, diffusion coefficient, activation energy

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1. Introduction

Ongoing miniaturization of semiconductor logic devices calls for high-κ (HK) gate dielectrics with ultrathin equivalent oxide thickness in order to improve the driving current and gate-channel coupling capacitance.[1] Hafnium-based oxides, such as HfO_2, are the most investigated HK materials for the gate dielectrics in metal–oxide semiconductor (MOS) transistors. However, the performance and reliability of these HK-based gate stacks is strongly affected by the high density of as-grown or process-induced bulk defects.[2,3] On the other hand, the existence of a lot of traps makes HfO_2 suitable for the trapping layer in the charge-trapping memory devices.[4] Thus, it is important to characterize these traps so as to know properties such as the activation energy and density. A lot of methods have been proposed to realize this goal. Theoretically, one can use *ab initio* density functional theory to calculate the trap formation energy and the transition energy between different charged states.[5,6] For fully fabricated devices, one can use electrical methods to charge and discharge the traps in order to observe the response of different traps.[7] To investigate as-grown traps in HfO_2 thin film materials, one can use Kelvin probe force microscopy (KPFM).[8,9]

Tzeng *et al.* have used variable-temperature KPFM to study trapping properties in the Si_3N_4/SiO_2 interface[8] In their experiment they used a large injection area of 2 μm×2 μm and extracted the charge retention time by fitting the evolution of the contact potential difference (CPD) at the central point to an exponential decay function. For such a large injection area, the decrease of the CPD at the central point is due mainly to the charge loss through SiO_2. They also theoretically analyzed how to relate the measured CPD value to the surface density of traps, obtaining activation energy values of 1.52 eV for electron traps and 1.01 eV for hole traps in Si_3N_4. Han *et al.* used the same technique and analysis method to investigate charge trapping in HfO_2 with an injection area of 1 μm×1 μm.[9] They obtained trap energy values between 0.5 eV and 0.7 eV depending on the thickness of HfO_2. As the injection was small, diffusion behavior was clearly observed. So the lower CPD at the central point is not only from the charge loss through SiO_2 but also from the lateral diffusion. This indicates the activation energy data may not be very accurate.

In the present paper, we directly consider lateral diffusion and charge loss in order to extract the lateral diffusion coefficient and then draw its Arrhenius plot with the absolute temperature to derive values for electron trap energy.

2. Experiment and model

The gate stack HfO_2(8 nm)/SiO_2(8 nm) was fabricated on 8 Ω·cm ∼ 12 Ω·cm p-type Si (100) substrate. After a standard cleaning, an 8 nm SiO_2 layer was thermally grown at 900 °C in dry O_2 ambience. The HfO_2 film was subsequently grown by atomic layer deposition at 250 °C. The wafers were then subjected to a post-deposition anneal at 700 °C for 30 s in N_2. Charge injection was done with a tip-to-substrate voltage of −13 V by a Bruker scanning probe microscopy system (Multimode 8) between room temperature (RT at 27 °C) and 90 °C. Before measurement, all samples were prebaked at 150 °C for more than 30 min to remove humidity. Electrons are injected into an area of 0.5 μm×0.5 μm, and then CPD profiles are

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scanned and saved in consecutive mode with alternating up-down and down-up scan images. From the total scanning time of each image and its file generation time we can calculate the scanning time for each scanning line in all image files.

Next we describe how to build a model for the evolution of CPD profiles. The injected electrons first transport to the HfO_2/SiO_2 interface, and then accumulate there and diffuse laterally. Some electrons may leak away through the SiO_2 layer. For a thick Al_2O_3 layer with deep traps, we observed the peak value of CPD first increasing and then decreasing. We believe this phenomenon is a clear indication of a two-step diffusion process. For the 8nm-HfO_2 layer used in this experiment, after injection, electrons diffuse toward the HfO_2/SiO_2 interface very quickly, as can be seen from the monotonic decrease of the CPD peak. Electrons in HfO_2 are trapped in defect centers and need some activation energy to diffuse.

Based on the analysis of Tzeng *et al.*, the CPD measured by KFM is not proportional to the trapped charge density in general.[8,10,11] However, for electron injection into HfO_2 with a p-type Si substrate, the Si surface is an accumulation region, so the surface potential is negligibly small. If we assume that electrons in HfO_2 are near the HfO_2/SiO_2 interface, we can show that the CPD value is proportional to the trapped charge surface density: $C(x,y,t) = CPD \times \varepsilon_{ox}/(qt_{ox})$.[8] Here q is the charge of an electron; ε_{ox} and t_{ox} are the dielectric constant and thickness of the SiO_2 layer, respectively. For convenience, the absolute value of CPD signals is used in this paper.

It is still difficult to numerically solve the two-dimensional diffusion equation even when we want to model the lateral diffusion step. In the horizontal cross-section through the central point of the injection square, the vertical distance between the top and bottom boundaries of the CPD profile is the largest, so we make an approximation by ignoring the effect of vertical diffusion. Increasing the injection range in the vertical direction can remove the effect of diffusion in this direction, but the time to record one image also increases several times. Thus, we have a longer time interval between the two consecutive records of the CPD profile along the same horizontal scanning line. It is not good to capture the information of the fast lateral diffusion at high temperature. This is the reason we choose the injection area of 0.5 μm×0.5 μm. Following an initial transient stage, only the lateral diffusion in HfO_2 along the horizontal direction will be considered for the evolution of the CPD profile in the central horizontal cross-section. The reasonability of such an approximation is supported by the good quality of data fitting. This approximation also simplifies the initial condition for the diffusion equation, because the CPD profile is recorded at a different time in each horizontal scanning line.

The CPD value is proportional to the trapped electron surface density $C(x,y,t)$ for our bias condition. When focusing on the central horizontal scanning line with $y=0$, $C(x,y=0,t)$ is written as $C(x,t)$, and its evolution fulfills the following diffusion equation:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} - \frac{C(x,t)}{\tau(t)}. \tag{1}$$

Here D is the lateral diffusion coefficient and $\tau(t)$ is the time-dependent life time.

Integrating over x in two sides of Eq. (1), and defining $C_{tot}(t)$ as

$$C_{tot}(t) \equiv \int_{-\infty}^{+\infty} C(x,t)\,\mathrm{d}x. \tag{2}$$

we get

$$\frac{\mathrm{d}C_{tot}(t)}{\mathrm{d}t} = -\frac{C_{tot}(t)}{\tau(t)}. \tag{3}$$

With $C_{tot}(t)$ at moment t and $C_{tot}(t+\Delta t)$ at moment $t+\Delta t$ and assuming that $\tau(t)$ is approximately a constant between t and $t+\Delta t$, we have

$$\tau(t) = \Delta t \ln\left(\frac{C_{tot}(t+\Delta t)}{C_{tot}(t)}\right). \tag{4}$$

In practice, equation (4) is not fully valid, so we can only take the CPD profile in each image from approximately the same horizontal cross-section. Other factors such as fluctuation and coupling between two lateral directions in longer time may also have effects. To calculate $\tau(t)$, we first smooth the measured CPD profile in the horizontal cross-section to remove noise and then do the numerical integration to obtain $C_{tot}(t)$. If $C_{tot}(t+\Delta t) < C_{tot}(t)$, we can calculate the value of $\tau(t)$ between t and $t+\Delta t$. This is the case for most data points. Otherwise, we can set $\tau(t)$ to the value from the neighboring time segments. Then we take that CPD profile as the initial $C(x,t)$ to solve Eq. (1) to fit the diffusion coefficient D. Except for the possible existence of an initial transient process, $\tau(t)$ does not change very much and can be set to a constant.

The diffusion coefficient is assumed to have the following dependence on the absolute temperature[12]

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right). \tag{5}$$

Here k_B is the Boltzmann constant and D_0 is a constant. Fitting through an Arrhenius plot gives the value of activation energy E_a.

3. Results and analysis

After electron injection, a waiting time is needed to adjust and stabilize the CPD measurement temperature. It is generally less than 5 min and is slightly different for each set of CPD data. During this time, the main physical process is the diffusion of injected electrons from the surface toward the HfO_2/SiO_2 interface. This first diffusion process is very complicated and its modeling is not attempted in this paper. So in

the following we consider only the lateral diffusion near the HfO_2/SiO_2 interface, and the zero-time for each set of CPD evolution is just an early time point in the lateral diffusion step. In the following the labeled time during the CPD evolution is relative to this zero-time.

Normalized $C_{tot}(t)$ versus relative time is shown in Fig. 1. Except for curve RT2 and 90 °C, the electron injection and CPD measurement were performed at the same temperature. The curve RT2 is the data with electrons injected at 70 °C and CPD measured at RT. The idea for this is to accelerate the electron vertical diffusion so the electrons can quickly arrive at the HfO_2/SiO_2 interface. The curve at 90 °C is the data with electrons injected at 70 °C and CPD measured at 90 °C. If both the electron injection and the CPD measurement are performed at 90 °C, the CPD signal is only about 30 mV, too small and too noisy. It can be seen that even for the lateral diffusion step there are still two evolutionary sub-steps for the CPD profile: 1) an initial sub-step wherein the integrated CPD value decreases monotonically with increasing time and electrons are trapped and detrapped at shallow centers, and 2) a plateau sub-step in which the CPD profile changes very slowly and electrons may get trapped at deep centers. In this paper we focus on the first sub-step of lateral diffusion.

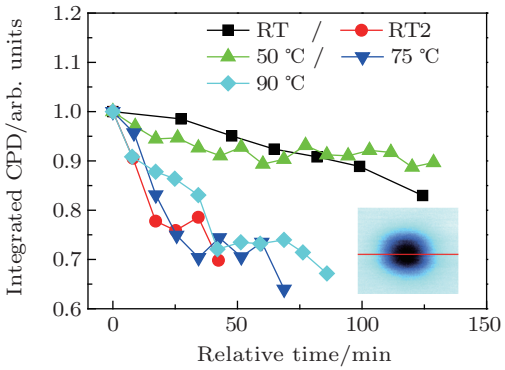


Fig. 1. (color online) Time dependence of normalized integrated CPD measured at different temperatures. The inset shows the horizontal cross-section through the central point of the injection square. For both curves RT and RT2, CPD signals are measured at 27 °C. Other conditions are given in the text.

Figure 2(a) shows measured and fitted CPD profiles for the case of both electrons injection and CPD measurement being done at RT. We take the first measured CPD profile as the initial condition for Eq. (1) and then integrate the differential equation by the Crank-Nicolson method. The average value of $\langle\tau(t)\rangle$ is 5.7×10^4 s and the diffusion constant D is 2.5×10^{-14} cm^2/s. We also checked our results by choosing another curve of measured CPD profiles as the initial conditions and fitting CPD profiles at later moments with the same set of $\langle\tau(t)\rangle$ and D. The two approaches agree very well. We also observed that near the CPD plateau sub-step, the difference between the calculated and measured CPD becomes slightly larger. Figure 2(b) shows measured and fitted CPD profiles for electrons injected at 70 °C and CPD profiles measured at RT (corresponding to curve RT2 in Fig. 1). The profiles enter the flat region very quickly. Our fitting gives a diffusion constant D of 2.5×10^{-14} cm^2/s and an average value of $\langle\tau(t)\rangle$ is 5.4×10^3 s.

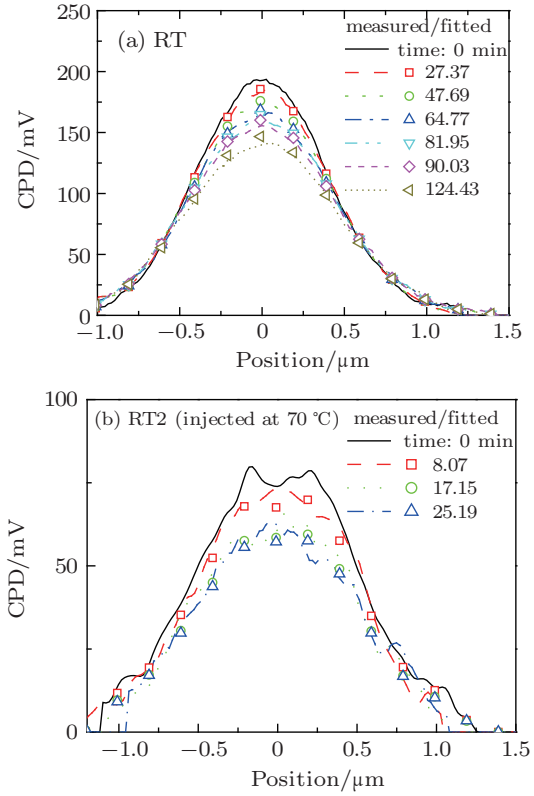


Fig. 2. (color online) Measured (solid lines) and fitted (symbols) CPD profiles at RT: (a) injection at RT, (b) injection at 70 °C.

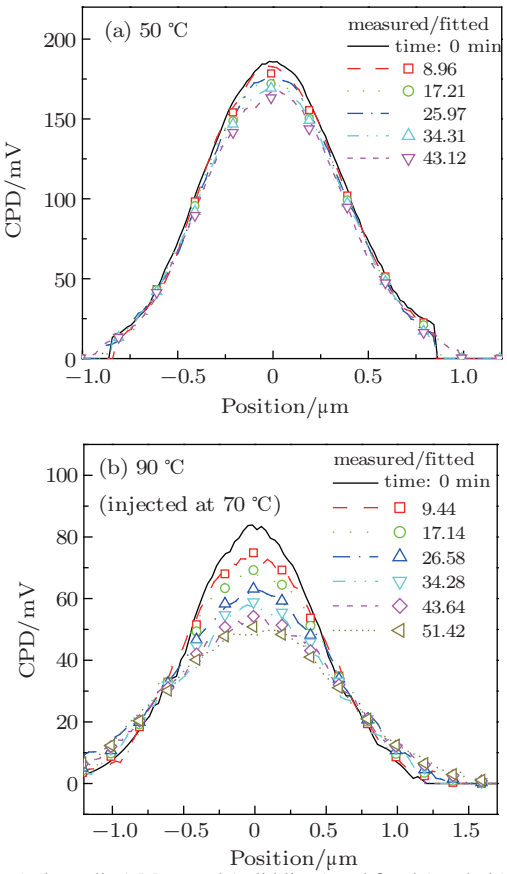


Fig. 3. (color online) Measured (solid lines) and fitted (symbols) CPD profiles: (a) 50 °C, (b) 90 °C.

The electron injection at 70 °C should reduce the average distance from trapped electrons to the HfO_2/SiO_2 interface and thus increase the probability of escape through SiO_2 and reduce the value of $\langle\tau(t)\rangle$.

Figures 3(a) and 3(b) show both measured and fitted CPD profiles for 50 °C and 90 °C, respectively. For 50 °C data, the integrated CPD at 17.21 min and 26.97 min are almost the same, so we take both the first (0 min) and the fourth (26.97 min) measured CPD profiles as the initial conditions to solve Eq. (1). The fitted diffusion constant D of and the average value of $\langle\tau(t)\rangle$ are 2.5×10^{-14} cm^2/s and 1.8×10^4 s, respectively. For 90 °C data, the value of $\tau(t)$ shows an initial transient of 480 s between the first two moments and is $\langle\tau(t)\rangle = 1.5\times10^4$ s, on average, for later moments.

Table 1 summaries the extracted D and the average value $\langle\tau(t)\rangle$ of the lifetime. Notations "a" and "b" emphasize that the electron injection and CPD measurements are performed at different temperatures. Figure 4 shows the extraction of activation energy from the values of D at 50, 75, and 90 °C. For shallow traps in HfO_2, we get $E_a = 0.57$ eV, which is very near the values obtained by Han *et al.*[9] These authors used Tzeng's method[8] to extract E_a.

Table 1. Extracted diffusion coefficient D and the average lifetime $\langle\tau(t)\rangle$ for different measurements. Notation (a) is for injecting at 70 °C and measuring at RT, and notation (b) is for injecting at 70 °C and measuring at 90 °C.

Temperature/°C	27 (RT)	50	75	90
D/(cm^2/s)	2.5×10^{-14}	2.5×10^{-14}	1.0×10^{-13}	2.5×10^{-13}
τ/s	5.7×10^4 5.4×10^3(a)	1.8×10^4	6.0×10^3	1.5×10^4(b)

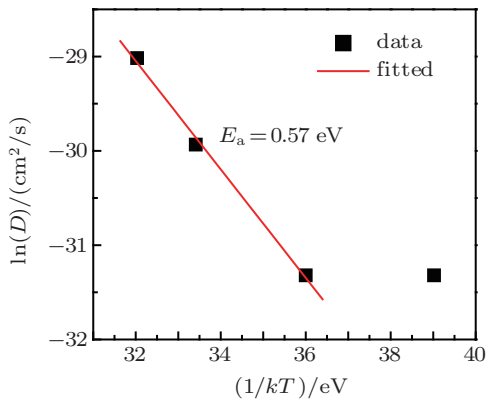


Fig. 4. (color online) Activation energy, extracted through the Arrhenius plot of D at 50, 75, and 90 °C.

For both RT and 50 °C, the same value of diffusion constant D is extracted. The reason may be related to the dispersive transport of electrons in HfO_2.[12–14] There should be a range of trap depths. The electrons in deep traps have larger emission time constants than those in shallow traps. With increasing time, more electrons get trapped in deeper taps. The result is that the diffusion constant depends on time in a long time scale,[12,14] as is also very clear from Fig. 1. Our model can be considered to be a short-time approximation. Further refining the model is necessary.

4. Conclusion and perspectives

In summary, we measured electron trapping properties at the HfO_2/SiO_2 interface by Kelvin probe force microscopy between room temperature and 90 °C. Electron diffusion in HfO_2 is a multiple-step process. In the first step, after injection, electrons diffuse quickly toward the HfO_2/SiO_2 interface. In the second step, electrons diffuse laterally near the HfO_2/SiO_2 interface. From the change of integrated CPD profiles through the central horizontal cross section of the injection region, it is concluded that the lateral diffusion step includes two substeps of evolution: a fast diffusion through shallow trap centers and a slow diffusion through deep trap centers. The fast lateral diffusion sub-step was simulated by solving the diffusion equation with a charge loss term. The diffusion coefficient and the average life time at different temperatures were extracted. Activation energy of 0.57 eV was calculated by drawing the Arrhenius plot of the diffusion coefficients with the absolute temperature. Such a value corresponds to a kind of shallow traps in HfO_2near the HfO_2/SiO_2 interface.

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