Research Article

Surface State Capture Cross-Section at the Interface between Silicon and Hafnium Oxide

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The interfacial properties between silicon and hafnium oxide (HfO₂) are explored by the gated-diode method and the subthreshold measurement. The density of interface-trapped charges, the current induced by surface defect centers, the surface recombination velocity, and the surface state capture cross-section are obtained in this work. Among the interfacial properties, the surface state capture cross-section is approximately constant even if the postdeposition annealing condition is changed. This effective capture cross-section of surface states is about $2.4 \times 10^{-15}$ cm², which may be an inherent nature in the HfO₂/Si interface.

1. Introduction

Hafnium oxide (HfO₂) has emerged recently as an essential dielectric material in the semiconductor industry, currently being used in logic gate stacks [1] and considered a promising candidate for resistance switching memory devices [2, 3] as well as surface passivation of advanced Si solar cells [4, 5]. Therefore, the determination of surface state capture cross-section at the interface between silicon and hafnium oxide is of great importance for the semiconductor industry, the photovoltaic industry, and the scientific community. The known characteristics of HfO₂ thin films include a large band gap (~6 eV) [6], a relatively high dielectric constant (>20) [7], an acceptable breakdown strength (>4 MV/cm) [7], excellent thermodynamic stability [8], and an effective mass of carrier transportation [9]. In this work, the interface characteristics of the interface-trapped charge density ($N_a$), the interface-trapped charge density per area and energy ($D_n$), the effective capture cross-section ($\sigma_e$) of surface states, the surface recombination velocity ($S_o$), and the minority carrier lifetime ($\tau_{FIJ}$) are identified. The typically electrical measurements of current-voltage ($I-V$) and capacitance-voltage ($C-V$) characteristics were performed on the Al/HfO₂/p-Si metal-oxide-semiconductor (MOS) capacitors and metal-oxide-semiconductor field-effect transistors (MOSFETs). Both gated-diode method [10, 11] and subthreshold measurement [12] were applied to evaluate the capture cross-section of interface states for the HfO₂-gated MOSFETs. The gated-diode method is a simple way to accurately identify the interfacial characteristics using only a sweeping dc gate voltage, which was introduced in 1966 by Grove and Fitzgerald [10] to determine the surface-state density in MOS structures. According to the gated-diode measurements, the surface recombination velocity and the minority carrier lifetime ($\tau_{FIJ}$) in the field-induced depletion region were extracted. In addition, the interface-trapped charge density per area and energy ($D_n$) was determined by using the device subthreshold measurement. Consequently, the effective capture cross-section of surface states was determined to be about $2.4 \times 10^{-15}$ cm² by the combination of gated-diode and device subthreshold measurements.

2. Experiment

Here, (100) p-type silicon wafers (1–5 Ω-cm) were used as the starting material. Following the standard cleaning procedures, a 500 nm SiO₂ film was grown on silicon wafers by wet oxidation. The source and drain windows were defined by wet etching and doped by phosphorous diffusion. The HfO₂ films were deposited by RF magnetron sputtering in argon ambient at room temperature. The flow rate of argon was 13.5 standard cubic centimeters per minute (sccm). The total pressure during deposition was 20 mtorr. The refractive
index, energy bandgap, and thickness of these thin films were measured by an N&K analyzer. The optical refractive index \((n)\) and energy bandgap \((E_G)\) were around 1.9–2.1 and 5.6–5.8 eV, respectively. The deposited thicknesses of HfO\(_2\) thin films ranged from 12 nm to 47.1 nm. After HfO\(_2\) deposition, the postdeposition anneal (PDA) was performed in either N\(_2\) or N\(_2\)/O\(_2\) (i.e., 50% N\(_2\) and 50% O\(_2\)) with a flow rate of 3 sccm for 60 s at 500°C. All the measurements were performed under dark condition. Based on the high-frequency (1 MHz) C-V measurements for the MOS capacitors, the effective dielectric constant of HfO\(_2\) films annealed at 500°C in N\(_2\) or N\(_2\)/O\(_2\) was evaluated as 18.9 or 19.3, respectively (not shown here). In this work, the relatively large devices were chosen to avoid the short channel effects which may cause the distortion in analysis of surface state capture cross-section.

The channel width \((W)\) is 100 \(\mu\)m and the channel length \((L)\) is 19 \(\mu\)m.

### 3. Results and Discussion

The drastic irregularity of the oxide/Si interface should introduce a large amount of density of states into the forbidden gap near the interface. The interface state may cause the charge trapping and lead to the device instability as well as the degradation of subthreshold swing, off-state current, carrier mobility, and oxide reliability. Charge carriers can be trapped or captured while they come to the physical vicinity of the center of the interface state. The capture cross-section \((\sigma_c)\) of the center is a measure of how close the carrier has come to the center to be captured. In this work, the gated-diode method is used to identify the interface-trapped charge density \((N_{it})\), the surface recombination velocity \((s_r)\), and the minority carrier lifetime \((\tau_{p, MJ})\) in the field-induced depletion region for the nMOSFET devices using HfO\(_2\) gate dielectrics annealed at 500°C. The test structure described by Grove and Fitzgerald to investigate surface properties in MOS structures is identical to a MOSFET without or with an unconnected source region. In this work, the gated-diode measurement was made using a floating source and a grounded substrate on MOSFET structures, as shown in Figure 1(a). The drain is reversely biased with respect to the substrate \((V_R = V_{DB})\). According to the theory of gated-diode method, the reverse current of \(P-N\) junctions \((I_{gen})\) is a function of the gate bias \((V_G)\). The \(I_R-V_G\) characteristics may exhibit three distinct regions [10], as indicated in Figure 1(b). The reverse current of \(P-N\) junctions comes from the generation of electron-hole pairs at generation-recombination centers in the depletion region at room temperature. Hence, the magnitude of reverse current depends on the density of such centers and the volume of the depletion region. As the volume of the depletion region in gated diodes depends on the gate voltage, reverse current also depends on the gate voltage. The HfO\(_2\)/silicon interface is in the accumulation mode when \(V_G\) is less than the flat band voltage \(V_{FB}\), and the reverse diode current originates from the generation-recombination centers in the depletion region of the metallurgical junction \((I_{gen,MJ})\). When \(V_{FB} < V_G < V_T\) (where \(V_T\) is the threshold voltage), the field-induced junction is depleted, and the rapid increase in the reverse diode current is caused by the generation of electron-hole pairs at the generation-combination centers of the surface region \((I_{gen,s})\) and the field-induced junction depletion region \((I_{gen,FIJ})\). At \(V_G > V_T\), the field-induced junction is in the inversion mode and the reverse diode current is reduced by the filling of the interface-trapped charge.

**Figure 1:** (a) Cross-sectional diagram of an HfO\(_2\) gated diode. (b) Effect of the depletion region on the reverse current \(I_R\) of the gated diode at various gate voltages given a fixed reverse drain voltage \(V_R\).
charge states by the minority carriers. The magnitude of the reverse diode current is the sum of the generation currents in the depletion volume of the field-induced junction and in that of the metallurgical junction. Based on the Shockley-Read-Hall theory for the single-level centers [10], the equations for the gated-diode are written as follows [13–15]:

\[ I_{\text{gen,MI}} = qU_{\text{MI}}W_{A_{\text{MI}}}, \]  

\[ I_{\text{gen,DI}} = \frac{qN_{\text{th}}C_{IT}}{2}, \]  

\[ I_{\text{gen,FIJ}} = qU_{\text{FIJ}}A_{\phi}x_{d\max} = \frac{qN_{\text{th}}A_{\phi}x_{d\max}}{2}, \]  

\[ s_{\phi} = \sigma_{\phi}v_{\text{th}}N_{d} = \sigma_{\phi}v_{\text{th}}(n\kappa T)D_{\phi}, \]  

\[ W = \sqrt{2e_{\text{Si}}N_{d}N_{d} / q(N_{A} + N_{d})}, \]  

\[ x_{d\max} = \sqrt{2e_{\text{Si}}N_{d} / qN_{A}}(\phi_{\text{F}} + V_{R}), \]  

where \( n_{d} = 9.65 \times 10^{9} \) cm\(^{-3}\) is the intrinsic carrier concentration in silicon [12]; \( A_{\text{MI}} \) represents the area of the metallurgical junction; \( A_{\phi} = 1.9 \times 10^{-5} \) cm\(^{-2}\) is the gate area; \( s_{\phi} \) is the surface recombination velocity; \( \sigma_{\phi} \) is the effective capture cross-section area; \( v_{\text{th}} = 10^{7} \) cm/s is the thermal velocity; \( V_{\text{bi}} \) is the built-in potential of the \( P-N \) junction; \( \phi_{\text{F}} \) is the quasi-Fermi potential of the majority carriers of the substrate; \( W \) is the width of the depletion region of the metallurgical junction; \( x_{d\max} \) is the maximum width of the surface depletion region; \( \tau_{\text{FIJ}} \) is the minority carrier lifetime in the field-induced depletion region; \( N_{d} \) is the interface-trapped charge density (i.e., density of the single-level surface generation-recombination centers per unit area); \( D_{\phi} \) is the interface-trapped charge density per area and energy (i.e., the density of uniformly distributed surface generation-recombination centers per unit area and energy); and \( U_{\text{MI}}, U_{\phi}, \) and \( U_{\text{FIJ}} \) are the generation and recombination rates of carriers per unit volume in the depletion regions of the metallurgical, the surface region, and field-induced region, respectively.

Figure 2 shows the reverse diode current \( I_{R} \) versus \( V_{G} \) for the HfO\(_{2}\) gated diodes at \( V_{R} = 2 \) V. Through the gated diode method, the surface recombination velocity (\( s_{\phi} \)) and the minority carrier lifetime (\( \tau_{\text{FIJ}} \)) in the field-induced depletion region can be extracted. For HfO\(_{2}\) films annealed in \( N_{2}/O_{2} \), \( s_{\phi} \) and \( \tau_{\text{FIJ}} \) are determined to be \( 4.1 \times 10^{7} \) cm/s and 16 ns. On the other hand, for HfO\(_{2}\) films annealed in \( N_{2} \), \( s_{\phi} \) and \( \tau_{\text{FIJ}} \) are determined to be \( 8.9 \times 10^{7} \) cm/s and 22 ns. Obviously, the reverse diode current of nMOSFETs for HfO\(_{2}\) annealed at 500°C in \( N_{2}/O_{2} \) is smaller than that annealed in \( N_{2} \). The reduction in reverse current may be attributed to the decrease in oxygen vacancy related defects [16–19] in HfO\(_{2}\). The oxygen vacancy is one type of trapping centers and is easily formed in HfO\(_{2}\) due to the transportation of oxygen atoms from HfO\(_{2}\) into Si [18, 19]. During the thermal treatment of PDA in \( N_{2}/O_{2} \) ambient, the oxygen atoms can diffuse into the HfO\(_{2}\) films to partially passivate the existing oxygen vacancies. Hence, the reverse diode current can be reduced by \( N_{2}/O_{2} \) annealing.

Figure 3 shows the \( I_{DS}/V_{GS} \) characteristics. The \( I_{on}/I_{off} \) ratio is larger than \( 10^{6} \) at \( V_{D} = 0.05 \) V, indicating that the nMOSFETs with amorphous HfO\(_{2}\) gate dielectrics have a good current switch capability. The subthreshold swings (\( S_{t} \)) for the HfO\(_{2}\) gate dielectrics annealed at 500°C in \( N_{2} \) and \( N_{2}/O_{2} \) are about 85.1 and 76.4 mV/dec, respectively. According to Figure 3, the density of interface traps per area and energy (\( D_{\phi} \)) can be determined from the subthreshold swing measurement, because \( S_{t} \) is expressed as \( 2.3(kT/q)(1 + C_{D} / C_{IT}) / C_{IT} \) [12], where \( C_{D} \) is the depletion-layer capacitance, \( C_{IT} \) is the capacitance associated with the interface traps,
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Table 1: Capture cross-section of surface states at the oxide/Si interface.

<table>
<thead>
<tr>
<th>Oxide material</th>
<th>Capture cross-section</th>
<th>Deposition method</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1–4 × 10⁻¹⁶ cm²</td>
<td>Thermal oxidation</td>
<td>Charge pumping [22–24]</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>5.8 × 10⁻¹⁶ cm²</td>
<td>rf sputtering</td>
<td>Gated diode [25]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.7 × 10⁻¹⁵ cm²</td>
<td>PECVD</td>
<td>DLTS [26]</td>
</tr>
<tr>
<td>CeO₂</td>
<td>8.7 × 10⁻¹⁵ cm²</td>
<td>rf sputtering</td>
<td>Gated diode [27]</td>
</tr>
<tr>
<td>CeO₂</td>
<td>9.0 × 10⁻¹⁵ cm²</td>
<td>rf sputtering</td>
<td>Charge pumping [28]</td>
</tr>
<tr>
<td>HfO₂</td>
<td>9.4 × 10⁻¹⁵ cm²</td>
<td>ALD</td>
<td>Charge pumping [29]</td>
</tr>
<tr>
<td>HfO₂</td>
<td>2.4 × 10⁻¹⁵ cm²</td>
<td>rf sputtering</td>
<td>Gated diode (this work)</td>
</tr>
</tbody>
</table>

PECVD: plasma-enhanced chemical vapor deposition, DLTS: deep-level transient spectroscopy, and ALD: atomic layer deposition.

Figure 4: Channel electron mobility versus effective surface field for the HfO₂ MOSFETs annealed at 500°C for 60 s in N₂ and N₂/O₂.

and $C_{ox}$ is the dielectric capacitance. The determined $D_{it}$ is about 4.6 × 10¹² and 2.1 × 10¹³ cm⁻²·eV⁻¹ for HfO₂ annealed at 500°C in N₂ and N₂/O₂, respectively. Once $D_{it}$ is determined, $\sigma_i$ and $N_{it}$ can be extracted using (4). For HfO₂ annealed in N₂, $\sigma_i$ and $N_{it}$ are extracted to be about 2.4 × 10⁻¹⁵ cm² and 3.7 × 10⁻¹³ cm⁻², respectively; for HfO₂ annealed in N₂/O₂, $\sigma_i$ and $N_{it}$ are extracted to be 2.4 × 10⁻¹⁵ cm² and 1.7 × 10⁻¹³ cm⁻², respectively. It is worthy of note that the same $\sigma_i$ value is obtained for HfO₂ annealed both in N₂ and in N₂/O₂. This finding may imply that the capture cross-section of surface states is an inherent nature at the HfO₂/Si interface. The universal constant of surface state capture cross-section is around 2.4 × 10⁻¹⁵ cm².

Figure 4 shows the channel electron mobility versus the effective electric field. The effective surface field ($E_{eff}$) and effective channel mobility ($\mu_{eff}$) can be expressed as $E_{eff} = (0.5Q_{inv} + Q_B)/e_S$ and $\mu = (I_{DS}/V_{DS})(L/W)/Q_{inv}$, respectively, where $Q_{inv}$ is the inversion layer charge, $Q_B$ is the bulk depletion layer charge, and $e_S$ is the dielectric constant of Si. The linear approximation of $Q_{inv}$, $Q_{inv} = C_{ox}(V_{GS} - V_T)$, is used in evaluating the mobility. The rest of the symbols have been defined earlier. The maximum channel electron mobility for the HfO₂ annealed in N₂/O₂ and N₂ was determined to be 102 and 43 cm²/V·s, respectively. Evidently the HfO₂ film annealed in N₂ shows lower channel electron mobility than the film annealed in N₂/O₂ condition. In addition, the HfO₂ device has a lowered mobility as compared to a universal mobility curve in SiO₂ MOSFETs [20]. The lowered mobility may come from the larger surface states which cause the increased interface charge scattering [21].

Table 1 lists the capture cross-sections of surface states ($\sigma_i$) at the interface between silicon and oxides, for example, SiO₂, ZrO₂, Al₂O₃, CeO₂, and HfO₂ [22–29]. For SiO₂, the $\sigma_i$ value is 1–4 × 10⁻¹⁶ cm² [22–24] which is smaller than those of high-k dielectrics. For CeO₂, the $\sigma_i$ value is around 9 × 10⁻¹⁵ cm² even if the adopted measurement method is different [27, 28]. In this work, the experimental results show that the HfO₂ films annealed in N₂/O₂ have lower interface state density ($N_{it}$) and higher channel electron mobility ($\mu_i$) compared to the HfO₂ films annealed in N₂. Although the different PDA conditions lead to the different values of $N_{it}$ and $\mu_i$, the same $\sigma_i$ for HfO₂ deposited by rf magnetron sputtering is obtained to be around 2.4 × 10⁻¹⁵ cm². This finding may suggest that the capture cross-section of surface states for some thin film deposition method may be an inherent nature at the interface between silicon and hafnium oxide. It is worthy to note that the capture cross-section of surface states may be influenced by the factors of environment temperature, film thickness, film deposition method, and especially surface preparation of Si substrate prior to HfO₂ deposition.

4. Conclusions

The electrical properties of the HfO₂/Si interface are investigated by the gated-diode method and the subthreshold measurement. Although the HfO₂ films annealed in N₂/O₂ result in lower interface state density and higher channel electron mobility compared to the HfO₂ films annealed in N₂, the determined surface state capture cross-section at the HfO₂/Si interface is the same. This suggests that the surface state capture cross-section may be an inherent nature at the interface between silicon and hafnium oxide.

Conflict of Interests

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