Effects of Ultraviolet Exposure on the current-voltage characteristics of high-$k$ dielectric layers

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ABSTRACT

The effect of ultraviolet (UV) (4.9 eV) exposure on capacitance-voltage (C-V) characteristics of silicon nitride (SiN, $k = 7.9$) and hafnium oxide (HfO$_2$, $k = 20$) was examined. Surface potentials and C-V characteristics were measured to determine the number of trapped charges within the dielectric samples. It is shown that UV exposure cures the processing-induced damage (the dangling bonds) of SiN. Low-dose UV exposure cures the silicon dangling bonds of HfO$_2$, while high-dose UV causes significant damage to HfO$_2$ by introducing oxygen interstitial defects (OIDs).
During plasma processing of microelectronic devices, dielectrics can be damaged by charged particle bombardment and vacuum ultraviolet (VUV) and ultraviolet (UV) radiation.\textsuperscript{1,2,3} In order to cure the damages, many techniques have been developed.\textsuperscript{4,5,6,7} Among these methods, UV-radiation has been applied to many different materials.\textsuperscript{8,9,10} For example, UV exposure has been shown to cure damage caused by VUV photons incident on low-\textit{k} samples by repopulating charge from the defect states.\textsuperscript{11} Capacitance-voltage (C-V) characteristic measurements have been used to obtain the flat-band voltage ($V_{FB}$) shift due to VUV and UV exposure of low-\textit{k} dielectric samples.\textsuperscript{12}

In this Letter, we examine the effects of UV exposure on high-\textit{k} dielectric samples. Two high-\textit{k} dielectric samples were used to test the curing effects of UV. They are: (1) 50 nm silicon nitride (SiN, $k = 7.9$) and (2) 20 nm hafnium oxide (HfO$_2$, $k = 20$). Both of the samples are deposited on a \textit{p}-type silicon substrate. To determine the effects of UV on damage, each sample was exposed to VUV because this has been shown to cause damage due to depopulation of the charges from the defect states.\textsuperscript{13,14,15} VUV exposure was done using the University of Wisconsin Synchrotron while UV exposure was done with a HgAr lamp. The photon energy for VUV exposure was set at 10 eV because this energy is above the bandgap energies of both samples (5.3 eV for SiN,\textsuperscript{16} 5.7 eV for HfO$_2$\textsuperscript{17}), so that all the defect states within the bandgap of the dielectrics can be depopulated. The UV photon energy is 4.9 eV for the HgAr lamp. This photon energy is typically used for UV-curing.\textsuperscript{9,10}

The left-hand side of Figure 1 shows the surface potential of the two samples after VUV
exposure. It is seen from Figure 1 that both the SiN and HfO\textsubscript{2} samples accumulate positive charge during VUV exposure. With a high photon dose, the most of the electrons from the defect states are depleted, so that the charge accumulation reaches a steady state resulting in a constant value of the surface potential. These steady-state values depend on the density of the total trapped charges (or defect-state concentrations) within the dielectrics.

The VUV exposure was followed by UV exposure on both samples. The right-hand side of Figure 1 shows that the surface potential for SiN decreases as the UV photon dose increases. This indicates that UV exposure, when used for curing, can repopulate the electrons in the defect states of SiN. Thus, the damage (accumulation of trapped charges) due to VUV exposure can be cured by UV exposure in SiN.

On the other hand, for the HfO\textsubscript{2} sample, it is seen from Figure 1 that UV does not cure the damage from VUV exposure. From the right-hand side of Figure 1, we see that the surface potential remains constant until the UV photon dose exceeds 4×10\textsuperscript{14} photons/cm\textsuperscript{2}. Then, the surface potential increases with UV photon dose. As a result, more charges are trapped during UV exposure. This indicates that high-dose (above 4×10\textsuperscript{14} photons/cm\textsuperscript{2}) UV exposure introduces different defect states and is not able to cure the HfO\textsubscript{2} sample.

In order to verify this result, the C-V characteristics of both samples were measured using a mercury probe. Typical high-frequency C-V curves for samples deposited on p-type silicon substrates were obtained as shown in Figure 2. Figure 2(a) shows the C-V
characteristics for SiN. Here, it is seen that, due to VUV exposure (photon dose: $5 \times 10^{14}$ photons/cm$^2$) the flat-band voltage shifts from -4.1 V to -7.2 V indicating an increase in the total trapped charge. After UV exposure (photon dose: $5 \times 10^{14}$ photons/cm$^2$), the trapped charges are cured and the flat-band voltage shifts back to -1.0 V. The extra shift of the flat-band voltage compared with the case of no exposure is likely due to the curing of those defects that were formed during the processing of the samples. Increasing the UV photon dose cures more of these defect states until the flat-band voltage reaches the ideal value of zero. Meanwhile, the magnitude of the capacitance changes during UV exposure. We believe it is due to the physical shrinking effects of the UV. Since UV exposure decreases the thickness of the dielectric sample, the porosity as well as the doping density increases, resulting in a change of the capacitance. Thus, it is seen that for a SiN sample, the UV exposure can cure both VUV- and processing-induced damage.

For HfO$_2$, the C-V characteristics are shown in Figure 2(b). We see that, after VUV exposure (photon dose: $1 \times 10^{15}$ photons/cm$^2$), the flat-band voltage shifts from -1.5 V to -4.2 V. Then, after UV exposure (photon dose: $1 \times 10^{15}$ photons/cm$^2$), the flat band shifts even further to -5.5 V. Thus, we find that more trapped charges are accumulated during UV exposure. This result is consistent with the surface-potential measurements that were shown in Figure 1 and shows that UV exposure cannot cure the VUV-induced damage to the HfO$_2$ sample.

The C-V characteristics for the HfO$_2$ sample were then measured after various UV photon doses, as shown in Figure 3. It is shown that with a low UV photon dose ($\sim 1 \times 10^{14}$
photons/cm²), UV exposure can cure some of the trapped charges from the defect states. With a high UV photon dose (above $5 \times 10^{14}$ photons/cm²), the UV-curing effect disappears. Instead, more trapped charges began to accumulate. This can be explained as follows: with a low UV photon dose, UV photons produce primarily photoinjection. That is, electrons are photoinjected from the silicon substrate into the dielectric layer. These electrons are repopulated into the silicon dangling bonds ($P_b$ defect states) at the interfacial layer. This results in a decrease of the trapped charges within the dielectric until the $P_b$ defect states are cured, \textit{i.e.} the flat-band voltage shifts to zero. Then, the UV photon energy goes to the electrons in the vacancies and interstitial defects within the dielectric layer. These “excited” electrons go to the conduction band of the dielectric and recombine with holes. As more electrons are excited into the conduction band, the flat-band voltage shifts to a negative value. This implies that UV is producing damage to the HfO₂ dielectric.

Thus, from the C-V measurements, we find that UV exposure can cure SiN VUV damage, but not cure HfO₂ VUV damage. This can be explained because the two dielectric samples have different defect-state energy levels within the bandgap. The defect states of the SiN sample are the silicon dangling bonds that have energy levels at 2.2 eV below the conduction band of SiN. Thus, they can be cured with photoinjection of electrons from the substrate when the sample is irradiated with 4.9 eV UV photons.

To consider HfO₂, the situation is more complicated. HfO₂ has both silicon dangling bond ($P_b$) states and oxygen interstitial defects (OID). The $P_b$ energy levels are at 1.7
eV below the conduction band and these can be cured by UV exposure. However, the OIDs have energy levels that are 5.3 eV below the conduction band and therefore cannot be cured with UV exposure. With low-dose UV exposure in HfO$_2$, the $P_b$ states are cured resulting in the flat-band voltage going to zero. With a high-dose UV exposure, more electrons go to the OIDs. These defects can easily transfer electrons to the silicon substrate, resulting in damage to the dielectric.

In summary, we find that UV exposure, as a curing method, can be safely used with SiN, but must be used carefully with HfO$_2$. A low-dose UV exposure can cure the silicon dangling bonds in HfO$_2$ while a high-dose UV exposure will cause damage by introducing a number of oxygen interstitial defects. We conclude that investigation of the defect-state types within the dielectric layer is important in order to determine whether UV exposure is beneficial or detrimental.

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References Cited


**Figure Captions**

Figure 1. Surface potential measurements for SiN and HfO$_2$ samples with VUV exposure followed by UV exposure.

Figure 2. High-frequency C-V characteristic for (a) SiN sample ($C_0 = 360$ pF) and (b) HfO$_2$ sample ($C_0 = 842$ pF) on p-type silicon substrate with VUV and UV exposures, the C-V curves represent the average value of ten sets of measurements.

Figure 3. High-frequency C-V characteristic for HfO$_2$ sample ($C_0 = 842$ pF) with different UV photon doses.
Fig 1.
Fig. 2

(a) C-V for 50 nm SiN

(b) C-V for 20 nm HfO₂
Fig 3.

![Graph showing capacitance vs. voltage for UV on HfO\textsubscript{2} with different doses and exposure levels.](image)