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Study of the interface stability of the metal (Mo, Ni, Pd)/HfO_2/AlN/InGaAs MOS devices

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The degeneration of the metal/HfO_2 interfaces for Mo, Ni, and Pd gate metals was studied in this paper. An unstable PdO_x interfacial layer formed at the Pd/HfO_2 interface, inducing the oxygen segregation for the Pd/HfO_2/InGaAs metal oxide capacitor (MOSCAP). The low dissociation energy for the Pd-O bond was the reason for oxygen segregation. The PdO_x layer contains O^{2-} and OH^- ions which are mobile during thermal annealing and electrical stress test. The phenomenon was not observed for the (Mo, Ni)/HfO_2/InGaAs MOSCAPs. The results provide the guidance for choosing the proper metal electrode for the InGaAs based MOSFET. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4986147]

Hafnium-based oxides are recently considered as promising candidates as the high-k dielectric for III-V channel devices.[1–6] The HfO_2/InGaAs interface, which affects the power consumption of complementary metal-oxide-semiconductor (CMOS), has been greatly improved recently.[7,8] The reactions between the metal electrode and the oxide layer may lead to the degeneration of the oxide layer. To prevent these interface reactions, the multilayer metal alloy of TiNi was used as the gate electrode for the HfO_2/InGaAs metal oxide semiconductor capacitor (MOSCAP).[9] Also, a thin AlN layer was inserted between the metal electrode and the HfO_2 layer to suppress this interface reactions.[10] Yoshida et al.[11] recently reported that the reactions between the high-k material and InGaAs were due to the interaction at the metal/oxide interface. Their study indicated that the metal electrode affects not only on the metal/HfO_2 interface but also on the HfO_2/InGaAs interface. To suppress this interfacial interaction, the passivation of HfO_2/InGaAs interface using AlN layer was reported.[7,12] Therefore, the mechanism suggested by Yoshida et al. should be complemented when a non-oxide layer is used to passivate the HfO_2/InGaAs interface. Additionally, the oxide degeneration depends not only on the electrode-high-k reaction but also on the inter diffusion between the oxide layer and the metal electrode after post metal-deposition annealing (PMA). In this study, the oxygen segregation at the (Mo, Ni, Pd)/HfO_2 interfaces of the HfO_2/AlN/InGaAs MOSCAP is investigated. Mo was chosen due to its low work function applicable for NMOS InGaAs devices, while Ni and Pd were chosen because of their high work function suitable for PMOS InGaAs devices.

The MOSCAP was fabricated on the 100-nm epitaxial $In_{0.53}Ga_{0.47}As$ layer ($5 \times 10^{17}/cm^3$ Si-doped n-type wafer) which was grown on the n+-InP substrate (using molecular beam epitaxial (MBE) growth technique). First, the wafer went through an HCl:H_2O (3.8%) solution treatment for 2 minutes before it was loaded into the ALD chamber. Then, 0.8-nm AlN layer and 50 cycles HfO_2 were deposited on the InGaAs layer.[13] The AlN layer serves as the passivation layer to prevent the

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reaction between oxygen atoms in HfO_2 and In, Ga, and As atoms in the InGaAs channel.[7] After that, the samples were annealed in forming gas (FG) at 450 °C for 5 minutes using rapid thermal annealing (RTA). Three types of metal including Mo, Ni, and Pd (with the same thickness of 50 nm) were studied as the gate metals on the HfO_2 layer. The gate metals were deposited through E-gun evaporation with the based pressure about 3×10^{-7} torr. The deposition rate was controlled by quartz crystals (gold, 6 MHz) and kept to be 1 Å/s. The AuGeNiAu was deposited on the backside of the wafer to form the ohmic contact. Finally, the MOSCAPs were annealed in three different ambiences including FG, nitrogen (N) and oxygen (O) at 350 °C for 30s using RTA for comparison. The metal/HfO_2 interfaces were characterized by using a Field Emission High-resolution transmission electron microscopy (HRTEM) JEM-2100F, while the thickness of HfO_2 was determined by using a SOPRA GES5 Ellipsometer and confirmed by HRTEM measurement. The capacitance-voltage (C-V) and current-voltage (J-V) were performed by using an HP4284A LCR meter. The X-ray photoelectron spectroscopic (XPS) were measured in a commercial Microlab 350 XPS system with Al $K\alpha$ source. The core levels were determined by using XPSPEAK (version 4.1) with Gaussian-Lorentz line shape and a Shirley background. Sample charging effects were corrected by placing the Au $4f_{7/2}$ peak at binding energy of 84.0 eV and shifting the rest of the regions accordingly. The uncertainty of the core position was 0.05 eV.

Figure 1(a) shows the capacitance-voltage hysteresis (ΔV_{FB}) of the (Mo, Ni, Pd)/HfO_2/AlN/InGaAs MOSCAPs. The flat band voltage (V_{FB}) was determined from the comparative method.[14] The fact that the ΔV_{FB} of the Pd MOSCAP is very large (~ 1V), while the ΔV_{FB} of the Mo MOSCAP is very small (~ 0.11 V) indicates that a large number of bulk oxide traps was created after Pd was deposited on HfO_2 and annealed in FG. The large ΔV_{FB} was due to the interaction of Pd atoms and O atoms at the Pd/HfO_2 interface, which creates oxygen vacancies inside the HfO_2 layer. This reaction leads to the increase of the oxide thickness and reduces the accumulation capacitance (C_{acc}) of the Pd MOSCAP as shown in Fig. 1(b). Based on the thermodynamics, the ΔC_{acc} of the Mo MOSCAP should be larger than the ΔC_{acc} of the Pd MOSCAP because the Mo-O reaction (oxidation formation enthalpy $\Delta H \sim -178$ kCal/mol) is more exothermal than the Pd-O reaction (ΔH – 49.9 kCal/mol).[15] However, the opposite results were observed in Fig. 1(b), indicating that the oxidation at the Pd/HfO_2 interface is not the only reason for the oxide degeneration for the Pd/HfO_2/AlN/InGaAs MOSCAP. Instead, an unstable IL PdO_x at the Pd/HfO_2 interface should attribute to the oxygen segregation at the Pd/HfO_2 gate stack. Fig. 1(c) and 1(d) show the leakage currents and the D_{it}, respectively, for the three MOSCAPs. The leakage currents of the three MOSCAPs were in the range of 2×10^{-8} A/cm^2 ~ 6×10^{-8} A/cm^2, indicating that the HfO_2/InGaAs interface was totally passivated by AlN IL layer.[6,7]

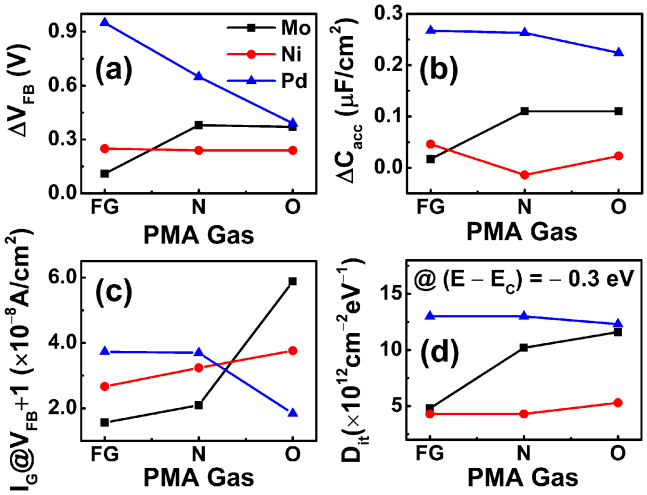

FIG. 1. The electrical characteristics of (Mo, Ni, Pd)/HfO_2/AlN/InGaAs MOSCAPs after PMA in FG, N and O ambient gases at 350 °C for 30s, (a) the hysteresis at V_{FB} of the C-V curves after PMA, (b) the C_{acc} variation of the MOSCAPs after PMA measured at +2 V and 1MHz, (c) the leakage currents at V_{FB} + 1 (V) after PMA, and (d) the D_{it} at $E - E_C = -0.3$ eV from the conduction band edge after PMA.

The low D_{it} values ($\sim 4 \times 10^{12}$ $cm^{-2}eV^{-1}$ determined from Terman method[16]) of the Ni MOSCAP and the Mo MOSCAP, shown in Fig. 1(d), are in agreement with the previous reports.[6,7,10] Note that Terman method gives both slow and fast traps and provides a reliable value for Dit at mid-gap.[16] The In out-diffusion[9,17–20] from InGaAs substrate to the oxide layer (Al_2O_3 or HfO_2) was also reported to affect the quality of the oxide layer. The D_{it} values of Pd MOSCAPs are much higher than those of Ni and Mo MOSCAPs as shown in Fig. 1(d), indicating that the PdO_x layer at Pd/HfO_2 interface reduces the passivation effects of AlN layer. The increase of oxygen vacancies inside HfO_2 due to the reaction of Pd and HfO_2 may facilitate the out-diffusion of In atoms from InGaAs substrate to HfO_2 layer, leading to the increase of D_{it} for the Pd MOSCAPs. Fig. 1 also shows that the PMA process has little effect on the electrical characteristics of the Ni MOSCAP; thus, Ni is a more suitable gate metal for the InGaAs based p-MOSFET.[7]

The dissociation energies (D_S) of the metal-oxygen bonds for the metals used in this study are Mo-O bond (119.9 kCal/mol), Ni-O bond (87.42 kCal/mol), and Pd-O bond (53.87 kCal/mol).[21] It can be seen that PdO_x is easier to decompose during the PMA process compared to other oxides in this study following the equation:

$$PdO_x \rightarrow Pd^{2+} + xO^{2-}. \quad (1)$$

The O^{2-} ions can easily diffuse into the Pd layer, leading to the formation of a thick PdO_x IL at the Pd/HfO_2 interface as shown in Fig. 2(a). This IL was not found at the Ni/HfO_2 interface as shown in Fig. 2(b). Fig. 2(c) shows the Energy-dispersive X-ray spectroscopy (EDS) spot profile of the PdO_x IL. An oxygen percent of ~ 24 % was found in the PdO_x layer, indicating a significant internal diffusion of the O^{2-} ions from the HfO_2 layer into the Pd layer. Fig. 2(d) and (e) show the scanning electron microscope (SEM) images of the Pd MOSCAP and the Ni MOSCAP, respectively, after RTA in FG at 400 °C for 5 minutes. Some bubbles occurred at the surface of the Pd MOSCAP, indicating that the Pd MOSCAP was destroyed due to the diffusion of O^{2-} ions from the HfO_2 layer into the Pd layer.

To investigate the stability of the PdO_x IL due to the oxygen segregation at the HfO_2 layer, the XPS analysis was conducted on the clean HfO_2 surface, the (2-nm) Mo/HfO_2 interface, and the (2-nm) Pd/HfO_2 interface; the results are shown in Fig. 3. For the clean HfO_2 surface, the XPS data is shown in Fig. 3(a). The strongest peak O^I (530.57 eV) is attributed to the oxygen in a metal-oxygen bond without oxygen vacancy; the peak O^{II} (532.54 eV) and the peak O^{III} (533.83 eV) are attributed to the oxygen in the metal-oxygen bond with oxygen vacancy and the OH group attached to Hf $^{2+}$ ions, respectively.[22] The O 1s peak of the Mo/HfO_2 interface after PMA in FG at 350 °C for 30s is same as the O 1s peak of the clean HfO_2 surface, indicating that the Mo/HfO_2 interface is quite stable due to the large dissociation energy of the Mo-O bond. For the Pd/HfO_2 interface, due to the overlap of the Pd $3p_{3/2}$ peak with the O 1s peaks, the Pd $3p_{1/2}$ peak was firstly set at 562.20 eV[23] as a standard for the Pd $3p_{3/2}$, O^I, O^{II}, and O^{III} peaks fitting. The spin-orbit splitting of the Pd 3p peak was chosen at 27.8 eV, which was in agreement with the previous report.[24] It was found that the O^I intensity decreased from 85.4 % for the clean HfO_2 surface to 33 % for the Pd/HfO_2 interface as shown in Table I. The considerable increase of the intensities of the O^{II} and O^{III} peaks at the Pd/HfO_2 interface indicates a significant increase of the oxygen vacancies in HfO_2, due to the diffusion of O^{2-} ions from the HfO_2 layer to the Pd layer. The same phenomenon was observed in Fig. 3(b). The intensity of the Pd 4d peak (~ 1.4 eV) clearly decreased after the Pd/HfO_2 interface was annealed in FG at 350 °C for 30s, while the intensity of O 2p peak (~ 7eV) increased after the sample was annealed. The Hf 4f peaks shifted after Pd deposition on the HfO_2 surface; this shift was due to the metal induced gap state phenomenon[25] at the Pd/HfO_2 interface. After the Pd MOSCAP was annealed, the increases of the O^{2-} and OH^- ion densities, as can be seen in Fig. 3(a), induced a dipole at the Pd/HfO_2 interface which increased the binding energy of Hf 4f peak as shown in Fig. 3(b).

Figures 4(a) and (b) show the C-V characteristics of the Pd MOSCAP and the Mo MOSCAP, respectively, with the gate stress at − 2 V and + 2 V for 1800s; the C-V behavior can be used to investigate the effects of the O^{2-} and OH^- ions diffusion on the oxide film. To track the degeneration of the oxide layer due to a movement of the O^{2-} and OH^- ions, the C-V measurements were suddenly conducted during the constant-voltage-stress.[26,27] For the Pd MOSCAP, the C-V curve was found to have negative shift, and the C_{acc} was found to increase after it went through the negative stress

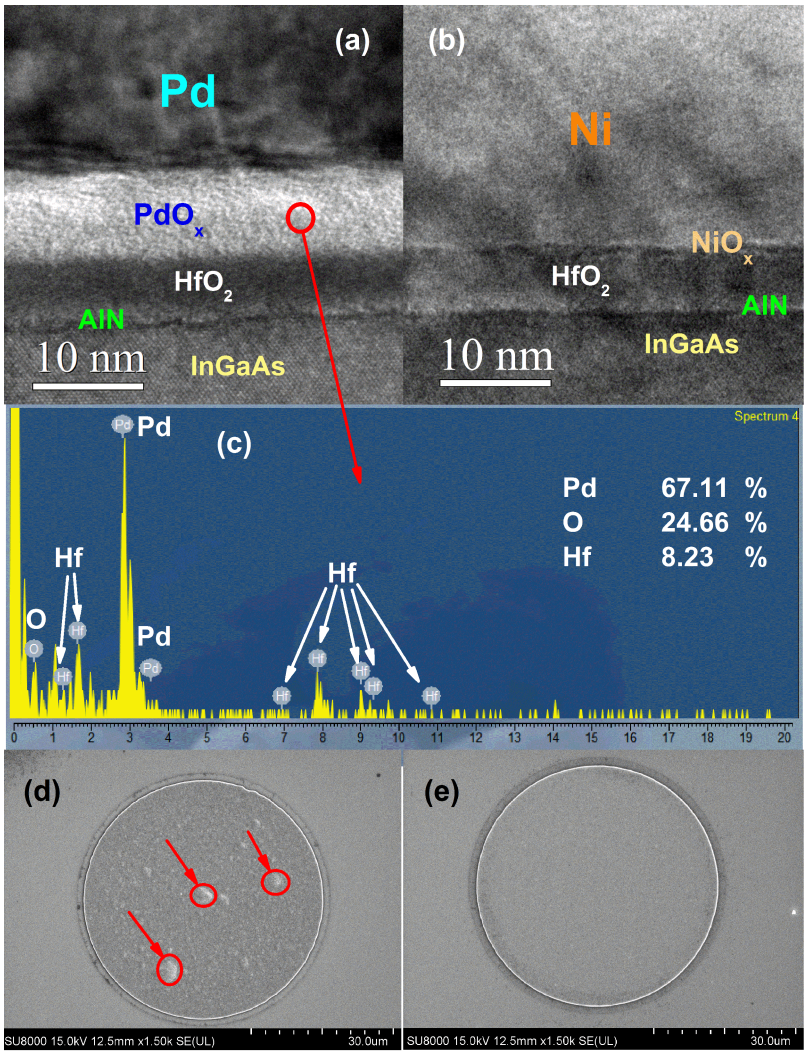

FIG. 2. (a) and (b) TEM cross sections of Pd/HfO_2/AlN/InGaAs and Ni/HfO_2/AlN/InGaAs structures after RTA in FG at 350 ^oC for 30s, respectively, (c) the EDS spot profile of the interfacial layer PdO_x at the Pd/HfO_2 interface, (d) and (e) SEM images of the patterns of Pd/HfO_2 and Ni/HfO_2 MOSCAPs, respectively, after RTA in FG at 400 ^oC for 5 minutes.

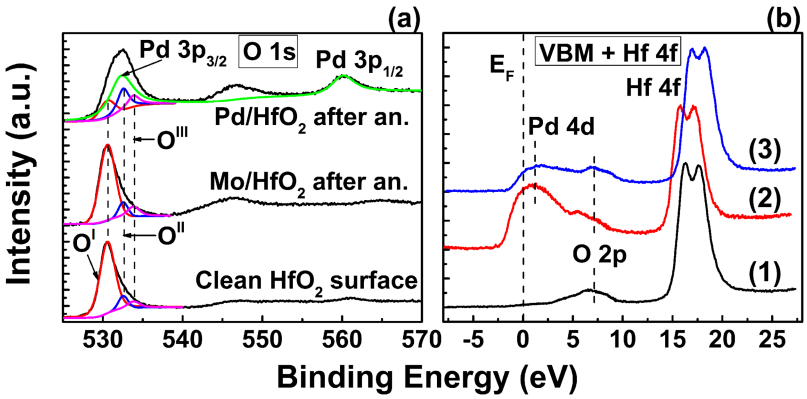

FIG. 3. XPS spectra of (a) O 1s peaks of clean HfO_2 surface, Mo/HfO_2 and Pd/HfO_2 interfaces after PMA in FG at 350 ^oC for 30s, (b) valance band maximum (VBM) and Hf 4f peaks of (1) clean HfO_2 surface, (2) Pd/HfO_2 interface as deposited and (3) Pd/HfO_2 interface after PMA in FG at 350 ^oC for 30s.

TABLE I. The area percent (%) of O^I, O^{II}, and O^{III} peaks of clean HfO_2 surface, Mo/HfO_2 interface and Pd/HfO_2 interface.

$O^i/(O^I+O^{II}+O^{III})$	Clean HfO_2	Mo/HfO_2	Pd/HfO_2
O^I	85.4	79.8	33.0
O^{II}	8.5	9.5	41.7
O^{III}	6.1	10.7	25.3

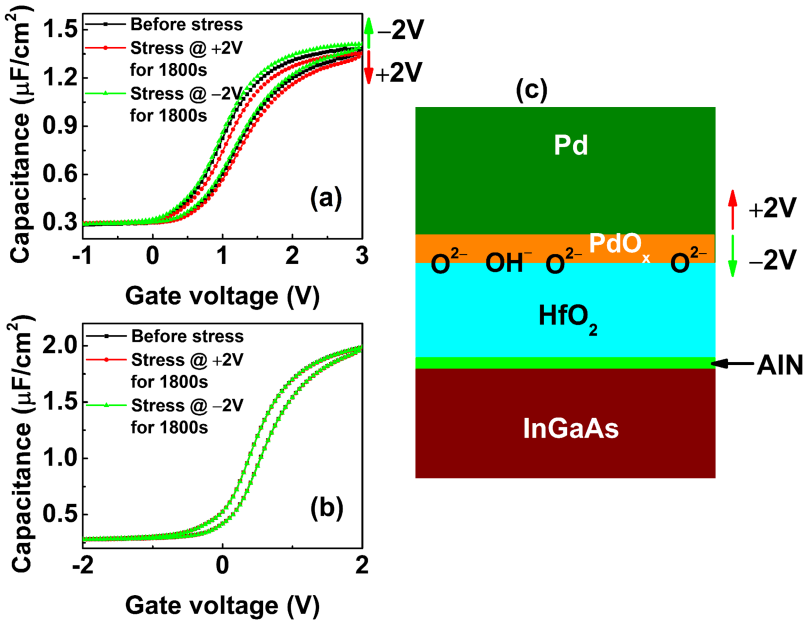

FIG. 4. The effects of O^{2-} and OH^- ions on the C-V behaviors of Pd MOSCAP and Mo MOSCAP, (a) and (b) the C-V characteristics of Pd MOSCAP and Mo MOSCAP, respectively, after gate stressed at – 2 V and + 2 V for 1800s; (c) the schematic PdO_x interfacial layer after gate stressed at – 2 V and + 2 V for 1800s.

(at – 2 V). The negative stress reduced the densities of the O^{-2} and OH^- ions, leading to the reduction of the PdO_x thickness and the negative shift of the C-V curve. After the positive stress (at + 2 V), the opposite phenomenon appeared with the positive shift of the C-V curves and the reduction of C_{acc}. The effect of the voltage stress on the PdO_x layer is illustrated in Fig. 4(c). For the Mo MOSCAP, the C-V curve shift and the C_{acc} reduction were not found, as shown in Fig. 4(b). The results indicate that the stable Mo-O and Ni-O bonds can prevent the oxygen segregation at the (Mo, Ni)/HfO_2 interfaces. However, for the Pd/HfO_2 case, the unstable Pd-O bond (with very low D_S) favors the oxygen segregation at the Pd/HfO_2 interface, leading to the increase of the thickness of the PdO_x layer as shown in Fig. 2(a) and the oxygen vacancies in the HfO_2 film as shown in Fig. 3(a).

The stability of the (Mo, Ni, Pd)/HfO_2 interfaces is investigated for low power consumption InGaAs based MOS device applications in this study. The oxidations at the Mo/HfO_2 and the Ni/HfO_2 interfaces were found to have no effect on the quality of the gate stack; however, the formation of the interfacial layer PdO_x at the Pd/HfO_2 interface considerably increased the oxygen vacancies in the HfO_2 film. The unstable PdO_x layer contains the O^{2-} and OH^- ions, which are mobile during annealing and the electrical stress test. The results demonstrate that the dissociation energy of the metal-oxygen bond and the enthalpy of formation of the metal oxide should be considered when choosing the right gate metal for the InGaAs MOSFET devices.

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