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R. P. Pezzi, M. Copel, M. Gordon, E. Cartier, and I. J. R. Baumvol

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R. P. Pezzi[a)]
Instituto de Física, UFRGS, Avenida Bento Gonçalves 9500, Porto Alegre, RS 91509-900, Brazil

M. Copel, M. Gordon, and E. Cartier
IBM Research Division, T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

I. J. R. Baumvol
Centro de Ciências Exatas e Tecnologia, UCS, Caxias do Sul, RS 95070-560, Brazil and Instituto de Física, UFRGS, Avenida Bento Gonçalves 9500, Porto Alegre, RS 91509-900, Brazil

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Oxygen transport and incorporation were investigated following postdeposition annealing of metal-oxide-semiconductor structures having ultrathin rhenium films as metal electrode and HfO_2 films as dielectric on Si(001). Isotopic tracing, nuclear reaction analysis, narrow resonant nuclear reaction profiling, and x-ray photoelectron spectroscopy were used to pursue this investigation. For annealing temperatures below 400 °C, oxygen from the gas phase incorporates mainly in near-surface regions of the overlying Re cap. Significant oxygen incorporation into the HfO_2 films is observed only after annealing at 500 °C. The present results are discussed considering that supplying oxygen to the metal/dielectric interface can cause device threshold voltage shifts. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2209720]

The search for alternative materials to be used in future generations of Si-based metal-oxide-semiconductor field-effect transistor (MOSFET) devices is a lively research area.[1–8] Device downscaling based on standard materials, such as heavily doped polycrystalline Si (poly-Si) gate contacts and SiO_2 gate dielectric materials, is reaching its physical limit due to excessively high gate leakage current as well as threshold voltage shifts because of undesired boron diffusion through the gate dielectric. The use of alternative gate dielectric (high κ)[1–4] and metal contact materials[5–8] is proposed to overcome these limitations.

One of the issues concerning metal gates is precise control of threshold voltages.[5–7] It is commonly observed that the effective work function of each metal depends on the underlying gate dielectric material. This is partially explained by a metal induced gap state (MIGS) model,[9] while pronounced alterations of the threshold voltage can be attributed to either oxygen vacancies[10] or dangling bonds[11] near this interface. Surprisingly, noble metals such as platinum and rhenium that are nominally inert are strongly affected.[12,13] The effective work function of both Pt (Refs. 12 and 13) and Re (Refs. 8 and 13) gate contacts on hafnium oxide is altered by the density of oxygen vacancies present at the metal/HfO_2 interface, which in their turn are particularly sensitive to residual oxygen during postgate metallization annealing. This may lead to instabilities in the stack during processing or over time, since it is highly sensitive to the presence of oxygen.

The oxygen transport mechanism in Pt electrodes is well known. Previous investigations[14] reported that platinum does not form an oxide at temperatures up to 500 °C, while oxygen diffuses through thin Pt films even at much lower temperatures. Thus, the ease of oxygen transport favors oxygen delivery (removal) to (from) the metal/dielectric interface, keeping the electrode intact. On the other hand, although the electrical behavior of Re contacts on HfO_2 is similar to Pt,[13] the nature as well as the mechanisms of oxygen diffusion and reaction in Re gate contacts remain unclear. We report here on investigations of atomic transport of oxygen and chemical reaction investigations in ultrathin Re/HfO_2/Si(001) structures after thermal annealing in low oxygen partial pressure atmospheres.

The Re/HfO_2/Si structures were obtained by chemical vapor deposition (CVD) of 3.5 nm HfO_2 films on a clean Si(100) substrate followed by deposition of a 7 nm thick Re layer, resulting in crystalline HfO_2 films, as verified by x-ray diffraction (not shown).[15] Samples were cleaved and annealed for 2 h at temperatures ranging from 300 to 500 °C in 1 torr of $^{18}O_2$, i.e., O_2 enriched to 97% in the rare isotope of atomic mass of 18. Uncapped, 3.5 nm thick, HfO_2 films on Si were also loaded in the furnace for comparison. Nuclear reaction analysis (NRA) and resonant nuclear reaction profiling[16,17] (NRP) were then used for ^{18}O quantification (with 5% accuracy) and profiling (~1 nm depth resolution), respectively. Elemental chemical information was accessed using x-ray photoelectron spectroscopy (XPS).

Figure 1 shows the ^{18}O amounts versus annealing temperature in Re/HfO_2/Si (circles) and HfO_2/Si (squares) as determined by NRA using the $^{18}O(p,\alpha)\,^{15}N$ nuclear reaction induced by 800 keV protons, which corresponds to a plateau region of the nuclear reaction cross-section curve. Incorporation of ^{18}O in the range of $(1-10)\times10^{15}/cm^2$ is observed in the HfO_2/Si structures, according to the annealing temperature. It is also seen that oxygen incorporation from the gas phase is reduced by a rough factor of 2 when the Re electrode is deposited on the HfO_2 surface, revealing that either Re acts as an oxygen diffusion barrier or it inhibits oxygen migration and/or fixation in some other way.

In order to investigate in further detail if oxygen atoms were able to diffuse through the metal and reach the hafnium

[a)]Electronic mail: pezzi@if.ufrgs.br

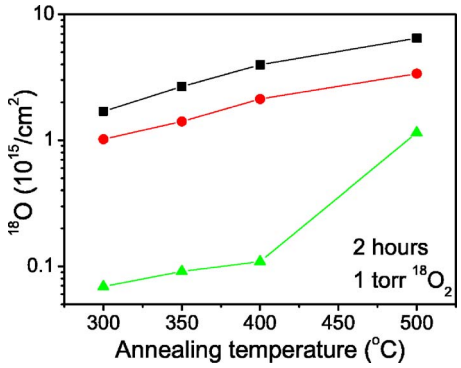

FIG. 1. (Color online) Total ^{18}O amounts vs $^{18}O_2$ annealing temperature in $Re/HfO_2/Si$ structures before (circles) and after (triangles) Re removal by a H_2O_2 etch as well as from the reference, uncapped HfO_2/Si (squares) as determined by nuclear reaction analysis using the $^{18}O(p,\alpha)\,^{15}N$ nuclear reaction as a function of annealing temperature.

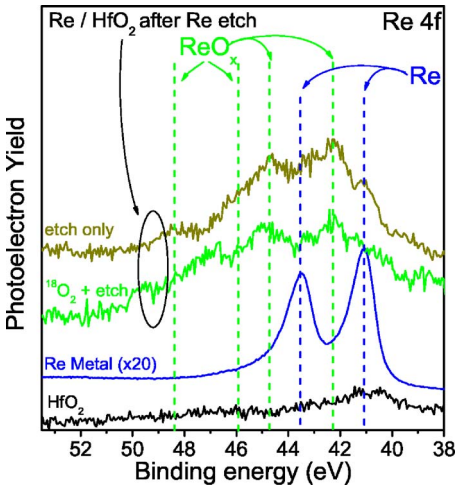

FIG. 2. (Color online) Re $4f$ x-ray photoelectron regions from the $Re/HfO_2/Si$ structures after Re removal by a 4 min H_2O_2 etch, metallic Re, as well as from the monitor HfO_2/Si sample.

oxide films during annealing, the Re (or, eventually, ReO_x) cap was removed after thermal annealing in ^{18}O-enriched O_2 atmosphere, by performing a 4 min etch in H_2O_2 at room temperature (Fig. 1, triangles). In this case, NRA quantification shows that for temperatures below 400 °C, ^{18}O incorporates mainly within the overlying Re cap since most of ^{18}O was removed during the H_2O_2 etch, while significant ^{18}O incorporation in the HfO_2 films is observed only after annealing at 500 °C. There is a smaller but detectable ^{18}O signal within the HfO_2 dielectric film at temperatures lower than 400 °C. This suggests that some oxygen can diffuse through the metal layer without being fixed therein, reaching the metal/dielectric interface and thus confirming the oxygen supply to this interface, which can be the cause of device threshold voltage shifts.[8]

The above presented results indicate that, in contrast to platinum that is known to oxidize only above 500 °C,[14] Re oxidation owing to oxygen transport and reactive incorporation from the gas phase takes place even at temperatures as low as 300 °C. However, it is noteworthy that the formation of rhenium oxide in the gate contact is only of secondary concern. Indeed, since rhenium oxide is a conductor rather than an insulator, one should be mainly concerned with the contribution of oxygen incorporation to the effective gate work function and sheet resistance.

To ensure the effectiveness of the H_2O_2 etching step, we compared the Re $4f$ x-ray photoelectron regions induced by Mg $K\alpha$ radiation ($h\nu$=1253.6 eV) in UHV conditions from as-deposited and $^{18}O_2$-annealed Re/HfO_2 structures after etching as well as from metallic Re and the control HfO_2 sample, as shown in Fig. 2. One can identify one photoelectron doublet assigned to metallic Re and at least two others assigned to Re in several different oxidation states.[18,19] By inspecting the Re $4f$ photoelectron spectra, one can see that there is still rhenium (metallic and/or oxidized) left on the samples after H_2O_2 etch—notice that the signal from Re metal is not in scale.

One further aspect to be considered is that substrates were kept at high temperature during Re deposition by CVD, raising the possibility of partial Re and HfO_2 intermixing during Re deposition that could result in the observed residual Re after H_2O_2 etch. However, we were able to exclude the possibility of thermally activated Re/HfO_2 intermixing by depositing Re by e-beam evaporation in an identical HfO_2/Si substrate kept at room temperature, and then subsequent H_2O_2 etch and XPS analysis. The corresponding Re $4f$ XPS region (not shown) presented peaks with similar components and intensity, as those shown in Fig. 2.

In order to clarify how diffusion and reaction of oxygen from the gas phase ($^{18}O_2$) takes place in Re/HfO_2 structures, one can use the narrow and isolated resonance at 151 keV in the cross-section curve of the $^{18}O(p,\alpha)\,^{15}N$ reaction to determine the ^{18}O concentration depth distribution. By scanning the energy of incident protons around the nuclear reaction resonance energy and measuring the reaction yield, one can build an excitation curve that contains detailed information regarding elemental concentration profile with a depth resolution of 1 nm or less.[16,17] Figure 3 shows the excitation curves corresponding to samples annealed in 1 torr of $^{18}O_2$ at 500 °C before (a) and after (b) Re (and ReO_x) removal. Figure 3(a) shows two isolated oxygen peaks. One corresponding to ^{18}O atoms fixed near the sample surface, forming ReO_x therein, and a second one at higher proton energy cor-

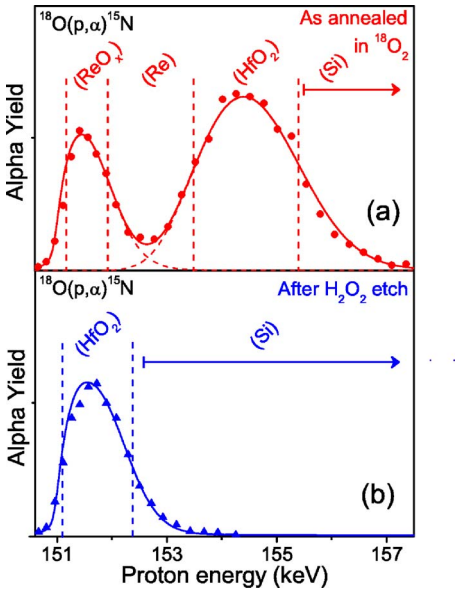

FIG. 3. (Color online) Excitation curves of the $^{18}O(p,\alpha)\,^{15}N$ nuclear reaction around the resonance at 151 keV corresponding to the ^{18}O concentration profiles from the $Re/HfO_2/Si$ samples annealed in 1 torr of $^{18}O_2$ for 2 h at 500 °C (a) before and (b) after H_2O_2 etch.

responding to diffusive oxygen that is incorporated uniformly in the HfO_2 layer without reacting with bulk Re. One notices from Fig. 3(a) that between these two characteristic ^{18}O distributions there is a marked region of the metallic Re film where there is no visible incorporation of ^{18}O. Figure 3(b), on the other hand, shows the same uniform ^{18}O distribution through the HfO_2 layer after removal of the Re (and ReO_x) cap by a H_2O_2 etch. Thus, the experimental evidence indicates that in the $Re/HfO_2/Si$ structures, part of the propagating oxygen front from the gas phase is fixed in near-surface regions of the Re layer, forming ReO_x, whereas the rest of it migrates across this layer, without reacting with it, to be fixed within the HfO_2 film.

The absence of ^{18}O in the bulk of the Re film suggests that surface defects may turn near-surface Re more prone to oxidation than the film bulk. On the other hand, migrating oxygen that reach the HfO_2 dielectric can fill oxygen vacancies at the metal/dielectric interface, causing the reported Fermi level instability. This mobile oxygen may also incorporate into the crystalline HfO_2 film following an oxygen isotopic exchange reaction mechanism characteristic of HfO_2 (Ref. 20) or ZrO_2 (Ref. 21) films on Si. These previous investigations indicated significant differences in the amounts of incorporated ^{18}O in amorphous HfO_2 and ZrO_2 films on Si with respect to crystalline ones, both occuring mostly by isotopic exchange for ^{16}O atoms previously existing in the films, which can be attributed to the higher oxygen defect concentration (and consequently mobility and $^{18}O/^{16}O$ exchange rate) in the amorphous films. The effect of annealing temperature in $^{18}O_2$ was dominant in the present work since the starting structures were already crystalline $Re/HfO_2/Si$. However, qualitative differences in ^{18}O incorporation versus annealing temperature are expected for amorphous HfO_2 films given that the healing of structural defects following annealing at increasing temperatures moderates this incorporation in the same way as for amourphous ZrO_2.[21] Finally, one should not disregard the effect of a thermally grown interfacial SiO_2, since devices annealed at 500 °C showed a marked decrease of the overall effective capacitance.[8] Nevertheless, recall that any possible SiO_2 interfacial layer thermally grown at 500 °C by the arrival of oxygen from the gas phase will be extremely thin,[17] most likely of the order of 0.5 nm ($\sim 2\times 10^{15}$ oxygen/cm^2) or less.

In summary, we investigated the transport and incorporation of oxygen in ultrathin $Re/HfO_2/Si(100)$ structures during postdeposition annealing in oxygen-containing atmospheres at low partial pressures. The present results show that although Re and Pt gate electrodes present similar electrical behavior, Re electrodes incorporate oxygen at temperatures much lower than Pt. Here, oxygen from the gas phase is seen to be incorporated in the topmost Re films at temperatures as low as 300 °C, forming rhenium oxides with various stoichiometries. This picture changes after annealing at 500 °C, as oxygen from the gas phase is found to form rhenium oxides not only in near-surface regions of the electrode but also in the underlying HfO_2 film, eventually reaching the dielectric/Si interface. In the whole temperature range studied here, oxygen from the gas phase is absent from the bulk of the Re films. Therefore, besides incorporation within the HfO_2 film, part of the oxygen from the gas phase that diffuses across the Re layer without reacting with the Re metal network can fulfill oxygen vacancies at the metal/dielectric interface or at the dielectric layer. All these findings may have direct consequences on the effective gate work function and sheet resistance. In addition, the presence of oxidized Re at top gate regions may raise some device reliability issues since little is known about the stability of Re oxides and its long term implication on device performance. While Re oxide is a conductor, it can act as a source of oxygen that may reach the metal/dielectric interface, indirectly modifying device electrical characteristics during regular operation. This issue remains open, deserving further investigation.

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