Interface studies of tungsten gate metal–oxide–silicon capacitors

Huiling Shang a) and Marvin H. White
Sherman Fairchild Lab, EECS Department, Lehigh University, Bethlehem, Pennsylvania 18015

Kathryn W. Guarini, Paul Solomon, Eduard Cartier, Fenton R. McFeely, John J. Yurkas, and Wen-Chin Lee b)
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

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The Si/SiO 2 interface in 100-nm-thick chemical vapor deposition (CVD) tungsten gate metal–oxide–semiconductor (MOS) structures exhibits high interface state densities \( D_{it0} > 5 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1} \) after conventional forming gas anneals over varying temperatures and times. In this letter, we show this is a consequence of the low diffusivity and solubility of molecular hydrogen in tungsten and the high temperature CVD process. We have discovered that atomic hydrogen is more effective in passivating tungsten gate MOS interfaces because of its higher diffusivity in tungsten. Atomic hydrogen can be produced (1) by the reaction of aluminum with water vapor when aluminum is evaporated on the top of tungsten, (2) by hydrogen implantation, and (3) by hydrogen plasma. These techniques can passivate the Si/SiO 2 interface effectively in MOS structures \( D_{it0} < 5 \times 10^{10} \text{cm}^{-2} \text{eV}^{-1} \) with 100-nm thick CVD tungsten gates. © 2001 American Institute of Physics.

With the continued scaling of the gate length to the tens of nanometers regime, metal gate electrodes 1–3 have been studied extensively to eliminate polysilicon gate depletion and to reduce gate resistance. For devices well below 0.1 \( \mu \text{m} \), a gate material with a midgap work function is desirable to permit the use of lightly doped channels in fully depleted, ultrathin complementary metal–oxide–semiconductor (CMOS) silicon-on-insulator devices. This approach (1) minimizes threshold voltage variations from fluctuations in local dopant concentration and film thickness from device to device 7 and (2) increases the carrier mobility from reduced impurity scattering and normal electric fields. 5

Tungsten is one of the most promising candidates for metal gate CMOS technology because of its low resistivity and near ideal midgap work function. The refractivity of tungsten permits process integration in the very early stages of the standard CMOS technology. For ultrathin dielectrics, tungsten permits process integration in the very early stages and near ideal midgap work function. The refractivity of tungsten is the preferred method to produce low resistivity thin tungsten films. 6 Although there have been studies on the performance of tungsten gate MOS field effect transistors, 7–9 the CVD tungsten gate MOS interface has not been examined in great detail.

Historically, heating of MOS capacitors with aluminum electrodes between 350 and 500 °C in either nitrogen or hydrogen ambient reduces interface states to very low levels. The effectiveness of aluminum has been attributed to atomic hydrogen produced by the reaction of aluminum with water vapor adsorbed at the Al–SiO 2 interface. 10 Interface states in polysilicon gate MOS devices can be passivated with forming gas anneals (10%H 2, 90%N 2 ) at temperatures around 400–550 °C. 11

In our studies, we have found that standard forming gas anneal (FGA) treatments provide very little passivation of the Si/SiO 2 interface (the midgap interface trap density \( D_{it0} > 5 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1} \) when applied to MOS capacitors with 100-nm-thick CVD tungsten gate electrodes. One possible explanation is our hydrogen-free CVD process, which effectively eliminates any internal source of hydrogen. Another possibility might lie in the low solubility and diffusivity of H 2 in tungsten, which prevents hydrogen from outside. 12

In our experiments, tungsten is deposited at 680 °C in high vacuum using the W(CO) 6 method. 5 Two different tungsten thicknesses (100 and 20 nm) are deposited directly on n-type silicon test wafers (resistivity around 1–2 \( \Omega \text{cm} \), with thermally grown silicon dioxide layer of 20 nm thickness. In the case of the thicker 100 nm tungsten we have two sets of tungsten gate capacitors: (1) capacitors defined with conventional photolithography (structure A) and (2) capacitors defined with a hard etch mask formed by shadow-evaporated aluminum, where the aluminum remains on the top of the tungsten (structure B). A combination of quasi-static (45 mV/s) and high frequency (10 kHz) capacitance–voltage (C–V) curves have been taken to extract the interface trap density with the high-low method. 13 Results on various size capacitors (10–4–10–2 \( \text{cm}^2 \)) did not show size dependence.

The passivation of structures A and B is completely different. Both high frequency C – V and quasi-static C – V, after a 30 min FGA at 350°C, are shown for each structure in Figs. 1(a) and 1(b). Samples with structure B are very well annealed: \( D_{it0} \) is in the low \( 10^{10} \text{cm}^{-2} \text{eV} \) range after FGA. In contrast, interface states in structure A are hardly passivated after the same FGA, with \( D_{it0} \) in the mid \( 10^{11} \text{cm}^{-2} \text{eV} \) range, similar to as deposited case. Subsequent long-time and higher temperature FGAs are not effective and only increase the interface trap density. In an attempt to passivate structure A samples, we employed various anneal methods with nitrogen, oxygen and water vapor ambient; however, none of these treatments passivated the Si/SiO 2 interface (\( D_{it0} > 5 \times 10^{11} \text{cm}^{-2} \text{eV}^{-1} \)).

\( ^a \)Electronic mail: hus2@lehigh.edu

\( ^b \)Also at: EECS Dept., University of California at Berkeley, CA 94720.
The excellent passivation shown in structure B can be also obtained by annealing in an inert ambient, such as nitrogen ambient, which strongly suggests there are passivating elements already in the MOS system of structure B and these elements can diffuse through the 100 nm tungsten gate electrode to the Si/SiO₂ interface. Since aluminum is known to be a source of atomic hydrogen by reacting with a monolayer of water vapor, we believe the passivating element in structure B is atomic hydrogen. Pursuing this hypothesis we annealed the tungsten gate capacitors in structure A with known sources of atomic H: an implanted H and hydrogen plasma, and studied the passivation of the Si/SiO₂ interface with C–V characteristics.

In our studies with hydrogen implantation, two different implant energies were selected to set the implant ranges: (1) 10 keV with range in tungsten of 535 Å and straggle of 300 Å, and (2) 5 keV with range in tungsten of 300 Å and straggle of 156 Å. Implant range and straggle were determined using TRIM. In addition, two different doses (1 × 10¹³/cm², 1 × 10¹⁴/cm²) accompany each implantation energy. The quasistatic and high frequency C–V characteristics for each sample measured as-implanted are severely stretched out in all samples, especially for the heavier dose deep implant, likely due to implant damage. The interface state density is reduced after a postmetal anneal (PMA) at 350 °C in nitrogen for 30 min as shown in Fig. 2. The interface state density D₀, in the sample implanted at 5 keV with dose 1 × 10¹⁴/cm², is lowered to 1 × 10¹¹/cm² eV. This experiment demonstrates clearly that atomic H can act as the passivating species. We believe the interface trap density can be even lower if the implant energy and dose are optimized.

Atomic hydrogen was also generated by creating hydrogen plasma. In this experiment, the plasma is created using a single frequency microwave cavity and brought directly to the sample in a load-lock chamber. Room temperature hydrogen plasma treatment plus a post anneal at 350 °C was not sufficient to introduce atomic H to the interface. Another set of experiments was conducted with the samples maintained at 350 °C during the hydrogen plasma. In this case, the efficiency of H introduction to the Si/SiO₂ interface is greatly improved with the interface trap density reduced to 3.5 × 10¹⁰/cm² eV. However, further postanneals at a higher temperature, such as 400 °C, deteriorate the passivation as shown in Fig. 3(a). We have also found the quality of passivation is very sensitive to the plasma anneal temperature and the H₂ flow pressure. Figure 3(b) indicates that either a lower temperature (300 °C) or a lower H₂ flow pressure (100 mTorr) leads to less passivation. In our experiment, hydrogen plasma with 200 mTorr H₂ flow pressure at 350 °C for 10 min shows the best passivation.

To answer the question whether the role of tungsten in preventing passivation by a standard FGA is simply a diffusion barrier for molecular hydrogen, we fabricated capacitors with much thinner (20 nm) tungsten electrodes. Figure 4 shows the C–V of samples receiving both 30 min and 150 min FGA treatment at 350 °C. Clearly, the samples receiving the longer time FGA received the better passivation. The interface trap density D₀ measured on the sample annealed for 150 min is lowered to 9.5 × 10¹⁰/cm² eV. In contrast with the thick (100 nm) tungsten case, the improved passivation of the 20 nm tungsten samples with the long and low temperature FGA suggests the diffusion of hydrogen through thin tungsten is possible. The enhanced diffusion might be related to the microstructure of thin tungsten.

In summary, our experiments demonstrate that a thick
(100 nm) tungsten electrode prevents passivation, in forming gas, of the underlying Si/SiO₂ interface because it is relatively impermeable to molecular hydrogen. In contrast, thin (20 nm) tungsten may be so passivated. Passivation is achieved for thick tungsten when hydrogen is introduced by implantation into tungsten or from a source of atomic hydrogen such as Al electrodes or hydrogen plasma. Further experiments are needed to optimize the annealing process and study the reaction kinetics in more detail to fully understand the complex interplay between the diffusivity of different species of hydrogen and surface reaction rates. Nevertheless, our experiments show that passivation may be achieved given the arrival of hydrogen at Si/SiO₂ interface in any form, and the relative advantage of atomic hydrogen may be due to better permeability of tungsten for atomic H than molecular H.

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