

# Role of hydrogen in Ge/HfO<sub>2</sub>/Al gate stacks subjected to negative bias temperature instability

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This work investigates the role of hydrogen and nitrogen in a Ge/HfO<sub>2</sub>/Al gate stack by comparing the negative bias temperature instability (NBTI) characteristics with and without the surface nitridation of Ge surface prior to HfO<sub>2</sub> deposition. Flatband voltage shift, change in interface state density, and stress induced leakage current were also monitored as a function of stress time. Virtually unchanged interface state density as a function of NBTI indicates no atomic hydrogen release from the dangling bond sites. However, the low  $n$  value in power law dependence of flatband voltage shift suggests diffusion of molecular hydrogen absorbed at the interface. © 2008 American Institute of Physics. [DOI: 10.1063/1.2827567]

Recently, HfO<sub>2</sub> as gate dielectric on Ge substrate has gained significant attention in complementary metal oxide semiconductor (MOS) technologies to compensate mobility degradation as Ge has higher hole and electron mobilities.<sup>1,2</sup> HfO<sub>2</sub>/Ge interface properties seem to limit the performance of Ge transistors because of the formation of a poor quality interfacial layer constituting GeO<sub>x</sub>.<sup>3</sup> In Si/HfO<sub>2</sub> interface, dangling bond defects, the  $P_b$  centers, at the interface play a significant role in the device reliability. It was, however, observed by Afanas'ev *et al.*<sup>1</sup> that no such Ge dangling bonds at the Ge/HfO<sub>2</sub> interface were present when an electron spin resonance was used. The role of hydrogen seems to be minimal and the dominant contributors to interface traps are the defect centers in dielectric layer close to the interface. It is, therefore, possible that the quality of the interface and the interfacial layer have significant impact on the interface state density and amount of hydrogen at the interface of the device. Interface treatments such as surface nitridation of Ge surface have been applied to improve the reliability of Ge/HfO<sub>2</sub>/Al MOS gate stack interface characteristics.<sup>2,3</sup>

Reaction-diffusion model of negative bias temperature instability (NBTI) suggests that the net positive increment of interface states  $D_{it}$  is due to two competing processes of hydrogen-passivated dangling bond breaking and annealing occurring simultaneously.<sup>4</sup> The process depends on H-species density at interface and the energy of hole plays a role in bond breaking and poststress bond annealing.<sup>5</sup> It is known that with H-species diffusion into the oxide dominates as  $D_{it}$  increases by  $t^n$  and as the bonds are broken,  $\Delta D_{it}$  increases with a power-law exponent,  $n \approx 0.2$ . On the other hand, a kinetic model of for silicon based high- $\kappa$  (HfO<sub>2</sub>) gate stacks proposed by Houssa *et al.*,<sup>6</sup> shows that when a negative voltage is applied to the gate, interstitial hydrogen atoms present close to the interface donate their electrons to the substrate, forming protons (H<sup>+</sup>). These protons will then be transported (dispersively) toward the gate, which is negatively biased. These protons can be subsequently trapped at bridging oxygen centers in the bulk high  $\kappa$ , forming over-coordinated positively charged centers.

To further understand the role of hydrogen, nitrogen, and interface quality, this work investigates the effect of surface nitridation on NBTI by comparing the device characteristics with and without the surface nitridation of Ge surface prior to HfO<sub>2</sub> deposition. By evaluating the flatband voltage shift, stress induced leakage current (SILC), and change in the interface state density as a function of stress time, we were able to elucidate the role of hydrogen as well as nitrogen in the reliability of Ge/HfO<sub>2</sub>/Al gate stack.

Ge (100  $n$ -type) wafers with 0.1  $\Omega$  cm resistivity were cleaned using a cyclical rinse of H<sub>2</sub>O<sub>2</sub>, HCl/H<sub>2</sub>O, and de-ionized water.<sup>7</sup> By immersing in a solution of NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O, an initial oxide layer of Ge oxide was formed. This oxide was then removed by thermal adsorption in an ultrahigh vacuum. Following oxide removal, 3.3 nm of HfO<sub>2</sub> films with 0.6 nm of Al<sub>2</sub>O<sub>3</sub> were deposited on the Ge surface (the deposition process is described in Ref. 2). For nitrided Ge, *in situ* surface-nitridation of the Ge substrate at 350–600 °C by exposure to an atomic N beam from a remote rf source at 350 W for 30 s was carried out in some devices. The nitridation was done before HfO<sub>2</sub> deposition. These samples were then cleaned using standard  $m$ -pyrrol before annealing at 450 °C in a forming gas (FGA: N<sub>2</sub>/H<sub>2</sub> 5%). Metal gate, Al, was deposited by e-beam evaporation. Al gate electrodes of various sizes (from  $2 \times 10^{-5}$  to  $2 \times 10^{-3}$  cm<sup>2</sup>) were patterned by photolithography. For back side metal, Al was deposited and subjected to 350 °C forming gas anneal (FGA: N<sub>2</sub>/H<sub>2</sub> 5%). For NBTI study, electrical measurements were performed at 125 °C using HP 4284 LCR meter and HP 4145 semiconductor parameter analyzer.  $D_{it}$  was extracted using the conductance method from the peak of a  $G/\omega$  vs. frequency plot.

Capacitance-voltage ( $C$ - $V$ ) characteristics for different splits are shown in Fig. 1. Significant performance improvement is seen for nitrided devices as the hysteresis and equivalent oxide thickness (EOT) are reduced. It is apparent that surface nitridation played a role in modifying the interface or reduced the interfacial layer. It was observed that an intermixing of HfO<sub>2</sub> with that of interfacial GeO<sub>x</sub> creates more electrically active defects (slow states) near the interface between GeO<sub>x</sub> and HfO<sub>2</sub> leading to larger  $C$ - $V$  hysteresis.<sup>8</sup> Surface nitridation, therefore, suppressed the for-

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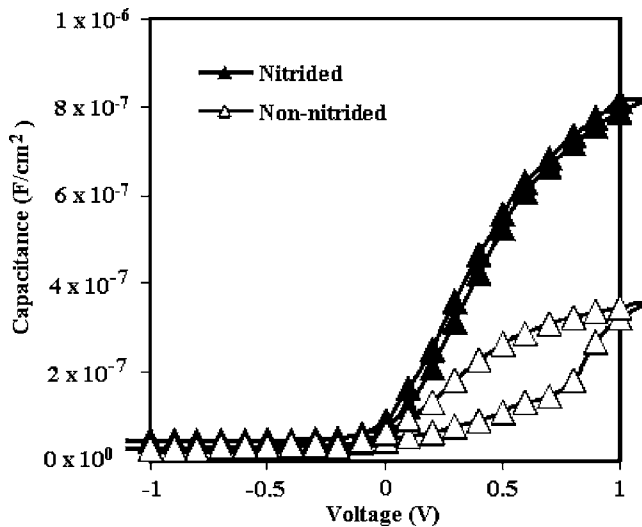


FIG. 1.  $C$ - $V$  characteristics of nitrided and non-nitrided Ge/HfO<sub>2</sub>/Al MOS gate stacks. nitrided devices showed improvements over non-nitrided devices as hysteresis reduced to 0.03 V as compared to 0.5 V.

mation of GeO<sub>x</sub> and at the same time allowing the interaction of HfO<sub>2</sub> with that of Ge substrate.

As negative voltage was applied at room and high temperatures on both nitrided and non-nitrided Ge  $p$ MOS gate stacks, significant shift in flatband voltage was observed. Figure 2 shows the power-law dependence of flatband voltage change,  $\Delta V_{FB}$  at 125 °C with an exponent of  $n \sim 0.12$  for nitrided Ge/HfO<sub>2</sub>/Al gate stack and  $n \sim 0.10$  for non-nitrided gate stacks. Nitrided Ge devices show more  $\Delta V_{FB}$  shift indicating bulk trap creation due to enhanced hydrogen diffusion. The low value of  $n$  suggests an initial large trap concentration in bulk oxides for both devices and possible trap creation due to molecular hydrogen diffusion rather than atomic hydrogen<sup>9</sup> during stress. Additionally, Ge-N bonds created due to surface nitridation<sup>10</sup> may disintegrate at high temperature constant voltage stress and create traps in the bulk oxide or excess nitrogen may diffuse into the bulk oxide and creates oxide traps, which give rise to higher negative flatband voltage shift.

Interface trap density  $\Delta D_{it}$  does not change with stress time and bias voltage for surface nitrided Ge devices and is shown in Fig. 3. Higher initial interface trap density was observed for nitrided devices compared to non-nitrided ones.

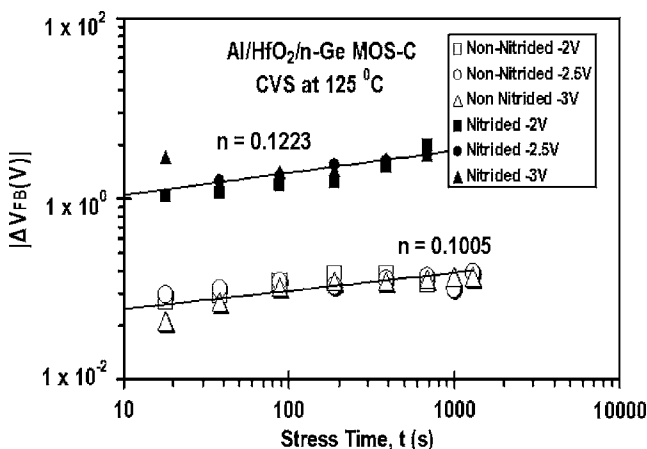


FIG. 2.  $\Delta V_{FB}$  vs stress time for both nitrided and non-nitrided germanium capacitors at different bias voltages.

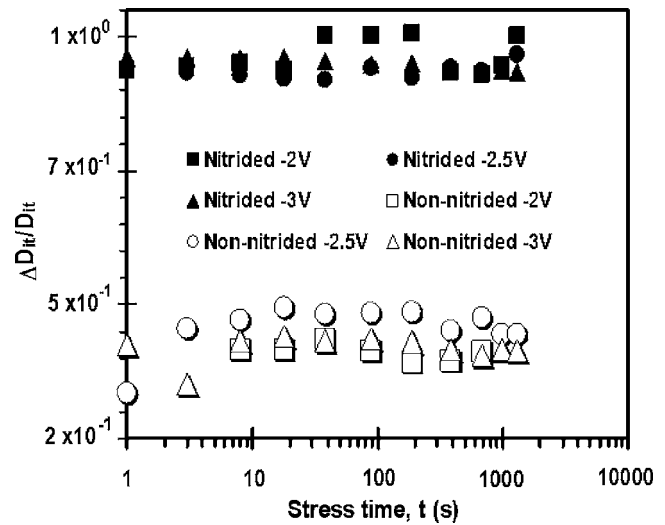


FIG. 3. Change in interface trap density  $D_{it}$  for both nitrided and non-nitrided Ge  $p$ MOS capacitors for stress bias voltages of -2, -2.5, and -3 V at 125 °C.

It is possibly due to the presence of nitrogen at the interface that suppresses the interfacial layer growth. At the same time, it facilitated the formation of Ge-Hf bonds<sup>11</sup> that further degraded the interfacial properties. As mentioned earlier, no measurable density of dangling bonds of the germanium surface atoms is found in Ge/high- $\kappa$  structure.<sup>1</sup> Release of atomic hydrogen from the dangling bond sites is, therefore, minimal. Therefore, we can infer that with increase in stress time, no significant changes in interface state density ( $\Delta D_{it}$ ) was observed for nitrided devices. Nitrogen at the interface seems to play a minimal role in  $D_{it}$  formation during stress. For non-nitrided devices, on the other hand,  $D_{it}$  generation increases linearly initially with stress time (10 s). This initial increase of  $D_{it}$  was also observed in silicon devices<sup>12,13</sup> because increase in stress temperature increases  $D_{it}$  generation at early stress time. It can, therefore, be assumed that only molecular hydrogen absorbed near the interface diffuses during stress rather than atomic hydrogen from the dangling bond sites.

As we compared the stress induced leakage current density (Fig. 4) at high temperature (125 °C) a lower value is observed for nitrided devices as compared to non-nitrided samples. This is in agreement with that of the  $C$ - $V$  measurements (Fig. 1). Surface nitridation definitely shows initial improvement in the device characteristics. HfO<sub>2</sub> with surface nitridation can suppress the interfacial growth and further achieve a small EOT and low leakage current at the same time.<sup>14</sup> Also, nitrogen-incorporated devices are believed to have thinner interface thickness and lower energy band offset,<sup>15</sup> which gives lower leakage current. However, when the devices were subjected to constant voltage stress at high temperatures SILC is higher for low gate voltage (-1-1 V) regime for nitrided devices compared to non-nitrided devices. This also indicates defects generation in the bulk oxide due to possible diffusion of nitrogen or Ge-Hf bond breaking at the interface during stress, which also explains the behavior of flatband voltage shift in nitrided devices during NBTI.

In the kinetic model, described earlier, it is to be noted that broken dangling bonds are not the source of H<sup>+</sup> rather the protons. With the picture inferred from our NBTI experiments and  $D_{it}$  measurements for both nitrided and non-

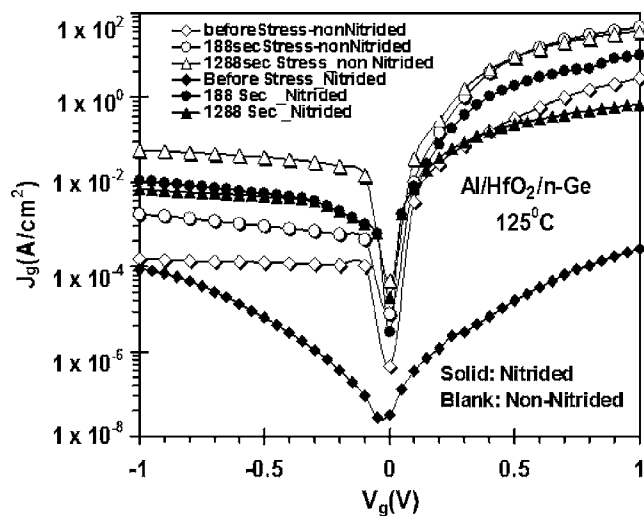


FIG. 4. Effect of constant voltage stress at 125 °C on leakage current density for nitrided and non-nitrided Ge devices after 188 and 1288 s stress time.

nitrided devices we have clearly observed that the interface state generation and  $\Delta V_{FB}$  are not correlated and a minimal increase in  $D_{it}$  was observed. In addition, the value of  $n$  is found to be less than 0.2, which is a signature of  $H_2/H^0/H^+$  diffusion. We may, therefore, tentatively propose that occurrence of dispersive transport of  $H_2/H^0/H^+$  from the absorbed hydrogen and subsequent trapping in  $HfO_2$  gives rise to the observed  $\Delta V_{FB}$  shift related to defects within the bulk high  $\kappa$ . The stress induced leakage current behavior also outlines the possible role of nitrogen in bulk trap creation.

In summary, comparison of NBTI characteristics in Al/ $HfO_2$ /Ge with nitrided and non-nitrided Ge surface at high temperatures (125 °C) reveals that nitridation creates additional bulk traps even though the device shows initial improvements. We, therefore, noticed that nitrided Ge has higher  $\Delta V_{FB}$  shift and stress induced leakage current than

non-nitrided samples. Possible dispersive transport of  $H_2/H^0/H^+$  from the absorbed hydrogen and subsequent trapping at  $HfO_2$ , gives rise to the observed  $\Delta V_{FB}$  shift while explaining the virtually unchanged interface state density during NBTI. The degradation of nitrided germanium surface is also consistent with literature regarding NBTI on nitrided Si devices.

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