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Role of Hydrogen in Dielectrics for Electronics and Optoelectronics Devices

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Silicon dioxide and silicon nitrides are the extensively utilized dielectrics in electronic and oproelectronic devices for various applications. Hydrogen has been used during processing and deposition of SiO_2 and Si_3N_4 to passivate Si dangling bonds at the interface and in the bulk of the dielectric (1, 2). The dangling bonds at the interface of the Si nanocrystals that are embedded in SiO_2 are also passivated with hydrogen (3). Role hydrogen, therefore, continues to be significant for silicon electronic devices in nanometer range even with the introduction of high dielectric constant materials as gate dielectrics. The historical perspective of role of hydrogen in passivation of dangling bonds will be discussed in addition to the current trends.

In the (100) Si-SiO_2 interface, the dangling bonds or the so called P_b centers, distributed in the silicon bandgap, contribute to interface state density, D_{it}, which has detrimental effect on the device characteristics. Hydrogen is regularly used to passivate these interface states through forming gas anneal. Passivation of these centers by hydrogen faced a significant challenge when the device was exposed to harsh environment such as hot electron stress or $\alpha-$ or γ-particle interaction due to radiation. It is because of hydrogen desorption from the passivated site. Incorporation of deuterium, the isotope of hydrogen, at Si-SiO_2 interface improved the hot-carrier & radiation immunity. A reduction in dark current shift in photodiodes, annealed in deuterium was observed when the devices were subjected to radiation.

With the recent introduction of hafnium-based high-k dielectrics the role of hydrogen continued to be significant as Si-HfO_2 interface behaves similar to Si-SiO_2 interface. Hydrogen annealing has been useful to passivate dangling bond defects, the Pb centers, at the interface. Ge as a substrate has also gained recent attention for its high hole-mobility. Efforts are being made to passivate the dangling bonds at Ge-HfO_2 interface. It has been quite unsuccessful because unlike the electronic state Si dangling bonds that are distributed in the Si bandgap, the electronic states associated with the Ge dangling bond lie within the valence band (4). This makes the Ge dangling bonds negatively charged and they become insensitive to electron spin resonance measurement. Therefore, Afanas’ev et al (5) through electron spin resonance measurement found no evidence of Ge dangling bonds at the Ge/HfO_2 interface as electron spin resonance is only sensitive to neutral dangling bonds. In Ge, however, interstitial hydrogen plays a significant role. When these interfaces were subjected to negative bias temperature instability (NBTI) diffusion of hydrogen through the dielectric from the dangling bonds at the Si-HfO_2 interface and interstitial hydrogen from around the Ge-HfO_2 interface respectively degrades the dielectric even further. In silicon devices it is known that during stress Si-H bond breaking occurs at the interface under bias. H-species then diffuse across the bulk HfO_2 at elevated temperature, and thus create defects in the dielectric. In Ge devices no such behavior was noticed (6) even though the samples were subjected to forming gas anneal (Fig. 1). It is because the role of H-species due to Ge-H bond breaking is limited. Any degradation is mainly caused by the interstitial hydrogen. Detailed discussion of hydrogen diffusion through dielectric will also be discussed.

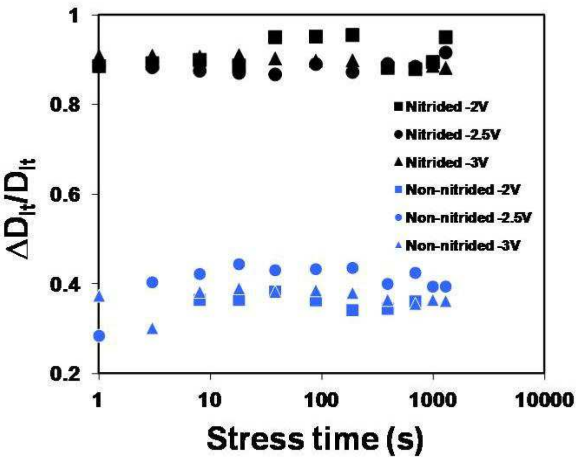

Figure 1 Change in interface trap density, D_{it} for Ge pMOS capacitors for stress bias voltages of −2, −2.5, and −3 v at 125 °C. No Ge-H bond breaking is noticed.

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