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Citation: Applied Physics Letters **104**, 042901 (2014); doi: 10.1063/1.4862979
View online: http://dx.doi.org/10.1063/1.4862979
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/4?ver=pdfcov
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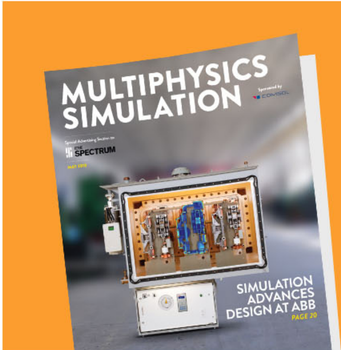

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APPLIED PHYSICS LETTERS **104**, 042901 (2014)

Thermally-driven H interaction with HfO_2 films deposited on Ge(100) and Si(100)

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(Received 19 July 2013; accepted 9 January 2014; published online 27 January 2014)

In the present work, we investigated the thermally-driven H incorporation in HfO_2 films deposited on Si and Ge substrates. Two regimes for deuterium (D) uptake were identified, attributed to D bonded near the HfO_2/substrate interface region (at 300 °C) and through the whole HfO_2 layer (400–600 °C). Films deposited on Si presented higher D amounts for all investigated temperatures, as well as, a higher resistance for D desorption. Moreover, HfO_2 films underwent structural changes during annealings, influencing D incorporation. The semiconductor substrate plays a key role in this process. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4862979]

The continuous downscaling of metal–oxide–semiconductor field effect transistors (MOSFETs) is pushing silicon-based devices to fundamental limits. Thus, there has been significant research on high-mobility semiconductors due to their potential to replace silicon (Si) in future MOSFETs. Although the electron mobility in III-V semiconductors can be several times higher than Si, germanium (Ge) has the highest hole mobility of all semiconductor materials.[1] However, the instability of Ge native oxide (GeO_2), which is also water soluble, has made the goal of a high quality surface passivation a major task. One approach to overcome the above difficulty is to deposit a high-k film on Ge, like HfO_2 or Al_2O_3. However, it has been reported that high-k films on Ge present a high interface state density (D_{it}).[2] In this way, different approaches have been investigated in order to improve the electrical characteristics of the dielectric/Ge interface, such as the use of an interlayer[3] and/or annealings in different atmospheres.[4] Previous theoretical works[5,6] have shown that Ge dangling bonds that may exist at the GeO_2/Ge interface cannot be effectively passivated by forming gas annealing (FGA). On the other hand, a significant reduction in D_{it} figures is observed for gate stacks following FGA.[3,7,8] This apparent contradiction indicates the need for further understanding of the hydrogen (H) role in the electrical and physico-chemical properties of dielectric films on Ge. In view of this scenario, we investigated the thermally-induced interaction of H with HfO_2 films deposited on Ge and Si substrates.

Starting samples were p-type Ge (100) wafers doped with Ga (Umicore), with a resistivity of 0.24–0.47 Ω·cm. They were first cleaned in an ultrasonic acetone bath and then etched in a 40% HF aqueous solution for 1 min. Si (100) samples were cleaned in a mixture of H_2SO_4 and H_2O_2 followed by the same procedure used for Ge substrates. After rinsing the samples in deionized water, they were immediately transferred to load lock chambers which had been pumped down to a base pressure around 10^{-5} millibar. 5 and 100 nm thick HfO_2 films were deposited on both substrates by reactive magnetron sputtering using an Hf target. In order to investigate H incorporation in the as-deposited HfO_2 films, samples were loaded in a static pressure resistively heated quartz furnace, which was pumped down to 2×10^{-7} millibar, before being pressurized with H_2 enriched to 99.8% in the isotope of mass 2 ($^2H = D$), hereafter called D_2 annealing. D_2 annealings were performed in 1000 millibar of D_2, for 1 h, in the 200–600 °C temperature range. The use of D (natural abundance of 0.015%) allows us to distinguish it from H incorporated in the films due to contamination or due to atmospheric air exposure. Annealings under argon atmosphere (Ar) in the same conditions were also employed for comparison. To investigate thermally-driven desorption of D, samples previously annealed in D_2 were submitted to annealing in 1000 millibar of Ar, for 30 min, in the 200–600 °C temperature range. D incorporation was accessed by nuclear reaction analysis (NRA) using the $^3He(D,p)^4He$ nuclear reaction at 700 keV, yielding a sensitivity of $\sim 10^{12}$ D·cm^{-2} and 5% accuracy.[9] The crystalline structure of the films was determined by grazing incidence angle X-ray diffraction (GIAXRD) using a constant incident angle of 1° and a Cu K_α radiation ($\lambda = 1.5418$ Å).

Figure 1 shows D areal densities as a function of D_2 annealing temperature for HfO_2 films deposited on Ge (circles) and Si (squares) substrates. Two HfO_2 thicknesses were employed, namely (a) 5 and (b) 100 nm. At 200 °C (data not shown), D was not detected within the sensitivity of the technique. At 300 °C, we observe a higher D incorporation in samples prepared on Si for both thicknesses. Considering 5 nm thick films (Fig. 1(a)), we observe a D incorporation of 4.5×10^{13} D·cm^{-2} for Ge and 6.0×10^{13} D·cm^{-2} for Si, leading to a 1.5×10^{13} D·cm^{-2} difference (triangles). A similar difference is observed for the 100 nm thick films. Since stoichiometric HfO_2 (as checked by Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS)) was concomitantly deposited on both Ge and Si, one can argue that this difference between Ge and Si arises from the interfacial region. D is incorporated near the HfO_2/Si interface, where P_b-type defects (Si dangling bonds) are

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present[10] and constitute incorporation sites for H. These defects are usually passivated in the SiO_2/Si system using FGA in the 300–500 °C temperature range, incorporating $\sim 4 \times 10^{13}$ D·cm^{-2}.[9] The higher D areal density (6.0×10^{13} D·cm^{-2}) obtained in the present work following annealing at 300 °C can be attributed to a higher defect density in HfO_2/Si in comparison to SiO_2/Si structures. Incorporation in the HfO_2 bulk region could not explain such a difference since a much greater amount of D (around 20 times higher) would be observed in the 100 nm thick samples. The lower D incorporation observed for Ge samples may be related to the theoretically predicted resistance of Ge dangling bonds to H passivation[6] and/or instability of Ge-H bonds.[11] Nevertheless, previous reports showed that the use of FGA in the 300–400 °C temperature range presented a reduction in the D_{it} figures in structures like HfO_2/GeO_xN_y/Ge,[3] Al_2O_3/Ge,[7] and GeO_2/Ge.[8] These results, in conjunction with our observation that most of the D is incorporated near the HfO_2/Ge interface region, point to a H-related passivation effect. Comparing the two HfO_2 thicknesses deposited on the same substrate, we observe a difference of 0.5×10^{13} D·cm^{-2}, which is the same for both substrates, evidencing that D incorporates in the HfO_2 bulk in minor amounts as compared to the interfacial region at this annealing temperature.

At higher annealing temperatures, the previous observed differences in D incorporation become more pronounced. 5 nm HfO_2 samples (Fig. 1(a)) present similar D amounts following annealing in the 400–600 °C range: $\sim 2.0 \times 10^{14}$ D·cm^{-2} and $\sim 3.0 \times 10^{14}$ D·cm^{-2} for Ge and Si samples, respectively. The observed difference in the D concentrations (1.0×10^{14} D·cm^{-2}) is almost one order of magnitude higher than for 300 °C. 100 nm HfO_2 samples do not have the same constant behavior in this temperature range: Higher D concentrations are observed for samples annealed at 500 °C in comparison to their counterparts annealed at 400 °C (a more than twofold increase is observed in both cases). The D incorporation difference between Ge and Si samples is 3.0×10^{14} D·cm^{-2} at 400 °C and almost reaches 1.0×10^{15} D·cm^{-2} at 500 °C. One can conclude that (i) D incorporation in the bulk of HfO_2 is more pronounced at these higher temperatures (since HfO_2 thickness has a stronger influence in contrast to 300 °C) and (ii) the semiconductor substrate plays a role in this process. In the following, the influence of the semiconductor substrate on D incorporation will be showed.

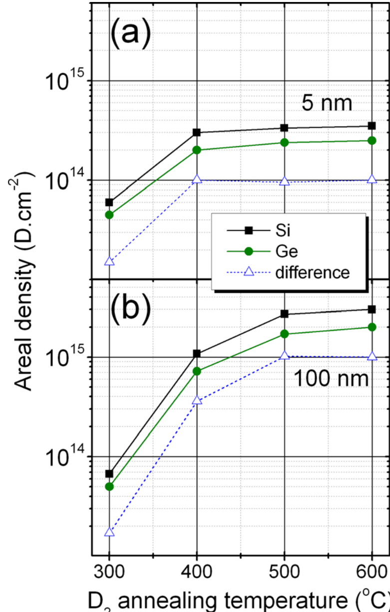

FIG. 1. D areal densities as a function of D_2 annealing temperature for (a) 5 and (b) 100 nm thick HfO_2 films deposited on Ge (circles) and Si (squares). The difference between D areal densities in Si and Ge based samples is represented by triangles. Lines are only to guide the eyes.

Further insights in the D incorporation of HfO_2/Ge structures could be obtained by desorption experiments. Fig. 2 shows D areal densities as a function of Ar annealing temperature for 5 nm thick HfO_2 films on Si (squares) and Ge (circles) previously annealed in D_2 at 300 and 600 °C (interfacial and whole film D incorporation regimes, respectively). At 300 °C, we observe a higher D desorption rate from films deposited on Ge, when compared to their Si counterparts. Following 400 °C Ar annealing, remaining D concentrations are 0.8×10^{13} and 3.0×10^{13} D/cm^2 in Ge and Si samples, respectively. At 600 °C, almost all detectable D are desorbed from samples. Switching to D_2 annealing at 600 °C, one should also expect the influence of D incorporated in the bulk of the HfO_2 film. Fig. 2 shows once again D loss after Ar annealings. Nevertheless, following annealing at 600 °C, we observe a considerable remaining D amount in both Si and Ge samples. This result suggests that D is more tightly bonded in the bulk of the HfO_2 layers than close to the HfO_2/semiconductor interface region. A possible explanation for this behavior is HfO_2 crystallization[12] following annealing in this temperature range. Polycrystalline films present higher diffusion coefficients for H_2, as well as the formation of new interaction sites for D at the grain boundaries. In order to understand the influence of HfO_2 microstructure on D incorporation, GIAXRD was employed.

Fig. 3 shows GIAXRD results for as-deposited HfO_2 films on Ge (left) and on Si (right) and after annealing in D_2 atmosphere. The main HfO_2 monoclinic and cubic diffraction peaks are indicated. As-deposited films and those annealed at 400 °C present only a diffuse halo, commonly attributed to amorphous structures. At 500 °C, we start to

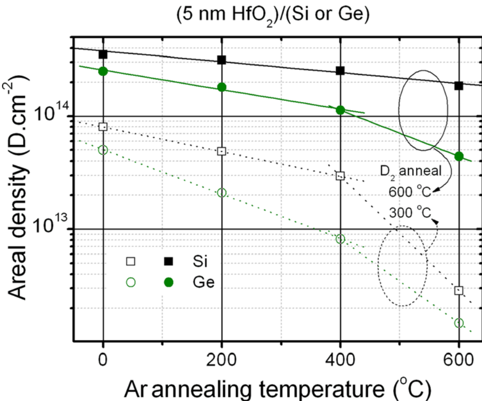

FIG. 2. D areal densities as a function of Ar annealing temperature for 5 nm thick HfO_2 films deposited on Si (squares) and on Ge (circles). Samples were previously annealed in D_2 at 300 (open symbols) and 600 °C (full symbols). Lines are only to guide the eyes.

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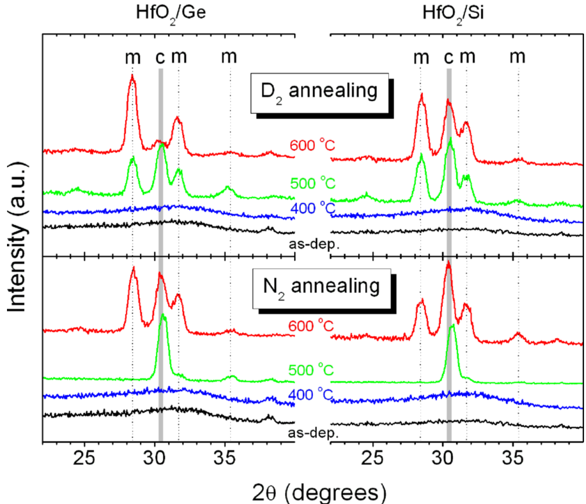

FIG. 3. GIAXRD for HfO_2 films deposited on Ge (left) and on Si (right). Samples were annealed in D_2 (upper part) or in N_2 (lower part). Reflections characteristic of the cubic (c) and monoclinic (m) phases are indicated. a.u. stands for arbitrary units.

observe the formation of monoclinic and cubic phases. Following annealing at 600 °C, crystallization is more pronounced. The major crystalline phase of the Ge sample is the monoclinic while the Si counterpart sample seems to be a mixture of both monoclinic and cubic phases. The higher D amounts incorporated in Si based samples seem to be related to the different crystallization behavior observed here. In order to investigate the crystallization process of HfO_2 without a possible influence of the D_2 atmosphere, we performed the same annealings with N_2. Following annealing at 400 °C, the film is essentially amorphous, but at 500 °C, we observe a pronounced crystallization in the cubic phase for both substrates, in sharp contrast with the results observed using D_2. At 600 °C, the intensities of the monoclinic phase increase, but we still observe comparable portions of cubic phase. These results evidence that in the absence of D_2, the cubic phase is the main crystallization product, which has been also observed for sputtered deposited HfO_2 films annealed in vacuum.[12] The influence of D_2 in the crystallization process is clear.

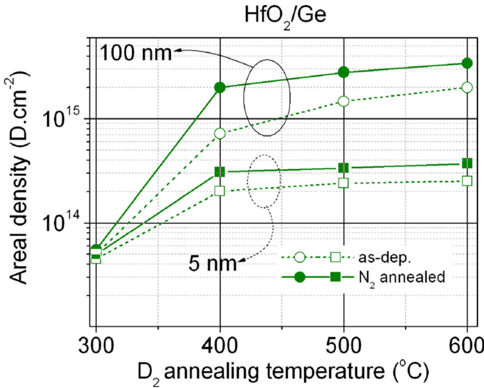

FIG. 4. D areal densities as a function of D_2 annealing temperature for 5 (squares) and 100 nm (circles) thick HfO_2 films deposited on Ge. As-deposited samples (open symbols) and those annealed in N_2 (full symbols) were annealed in D_2 at the indicated temperatures. Lines are only to guide the eyes.

Since HfO_2 films deposited on Si present simultaneously a higher crystallization in the cubic phase and a higher D incorporation, we checked the influence of HfO_2 crystallinity on D incorporation. For that, 5 and 100 nm thick as-deposited amorphous HfO_2 films on Ge underwent a nitrogen (N_2) annealing at 500 °C. According to the results presented in Fig. 3, HfO_2 is mostly crystallized in the cubic phase in these conditions. Sequentially, without atmospheric air exposure, samples were submitted to D_2 annealing. D uptake in these samples are presented in Fig. 4, which shows D areal densities as a function of the D_2 annealing temperature for 5 (squares) and 100 nm (circles) thick HfO_2 films on Ge submitted (full symbols) or not (open symbols) to a previous N_2 annealing. At 300 °C, D incorporation is the same for both thicknesses ($\sim 5 \times 10^{13}$ D·cm^{-2}), indicating that the crystalline structure and/or the thickness of the film play a minor role in D concentration at this temperature. This result corroborates that most of the D is incorporated in the interface region of the HfO_2/Ge. At higher annealing temperatures, a higher D incorporation is observed in films annealed in N_2, as well as in the thicker films. This suggests that (i) D is incorporated in the bulk of the HfO_2 films for temperatures $\geq$400 °C and (ii) HfO_2 cubic phase presents more sites for D incorporation. This second point is probably related to the formation of a higher density of grain boundaries when compared to the amorphous HfO_2, since the films crystallized in the cubic phase also present some portions of the monoclinic phase.

In summary, we investigated the thermally-induced H incorporation in HfO_2 films deposited on Si and Ge. For that, we used D_2 atmospheres to clearly identify H incorporated from the annealing step. D is mainly incorporated near the HfO_2/semiconductor interface region at 300 °C. At this regime, a higher D incorporation is observed for Si based samples, which is probably related to the higher stability of Si-H bonds in comparison to Ge-H. Higher temperatures ($\geq$400 °C) induce D incorporation in the whole HfO_2 film. During D_2 annealing, HfO_2 crystallization takes place forming cubic and monoclinic phases. The cubic phase incorporates higher amounts of D. Both the annealing atmosphere and the semiconductor substrate influence the crystallization process, which explains the observed differences in D uptake. Desorption of D under Ar annealing showed that D in Si based samples is more stable than in Ge counterparts. These results evidence that FGA induces physico-chemical modifications in HfO_2/Ge structures beyond passivation of interfacial defects like in the SiO_2/Si system. The control of such modifications is a key issue for obtaining dielectric/Ge structures with the desired characteristics.

The authors would like to acknowledge support from INCT INES, INCT NAMITEC, MCT/CNPq, CAPES, and FAPERGS.

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