It is shown that the introduction of hydrogen by a dc H plasma treatment leads to the appearance of negatively charged defects in amorphous Al₂O₃ and SiO₂ and positively charged defects in amorphous HfO₂. The concentration of the defects increases with increasing temperature of the dc H plasma treatment between 50 and 100 °C, and the defects appear in all samples independently on their growth conditions and the thickness of the insulators. The origin of the defects is discussed with an emphasis on the existence of interstitial hydrogen in the insulators.

1. Introduction

Hydrogen is an abundant impurity in insulators and it can be easily introduced during the growth and various processing steps in the semiconductor industry. By reacting with different crystal imperfections, H can either passivate them or form novel electrically active H-related complexes. These defects could significantly influence the electrical properties of microelectronic devices and the control over them is an important task in modern microelectronics. The studies devoted to the investigation of the electrical and optical properties of H-related defects in insulators are relatively scarce in the literature. According to theory, isolated interstitial H acting as an amphoteric impurity could also be a source of negative or positive charge in insulators. By using first-principles total-energy calculations, Kilic and Zunger demonstrated that interstitial H should introduce either shallow or deep states depending on the position of the Fermi level in the bandgap of insulators. The authors generalized their results by suggesting the existence of a transition level (+/−) of H which should be located at about 3.0 ± 0.4 eV below the vacuum level. The position of this level defines the charge state of isolated H in insulators. H should be negatively (positively) charged if the Fermi level lies above (below) this level in the bandgap. Shallow hydrogen-like states could also appear in the bandgap of insulators if the transition level is located above the top of the conduction band. The existence of the transition level (+/−) of H was also confirmed by other groups. However, its position was calculated to be significantly deeper at around 4[4] and 4.5 eV[5] below the vacuum level in comparison to that reported in another study.[3]

The behavior of interstitial H was also studied by using hybrid functional[4] and density functional theory[6,7] calculations in some amorphous insulators.[4,6,7] According to these calculations, interstitial hydrogen should also exhibit negative-U properties: positively or negatively charged H should be stable independently on the position of the Fermi level in the band gap of the amorphous insulators, whereas neutral H should be metastable. However, Kaviani et al.[6] also suggested that the metastable atomic H could share its electron with electron-trapping precursor sites in amorphous HfO₂ and the formation energy of this defect could be even lower than that of interstitial H. Similarly, Dicks et al. showed that a H atom could donate an electron into the conduction band and form an OH bond with the nearest-neighbor oxygen in amorphous alumina. This configuration labeled [H+ + e⁻] should be even more stable than interstitial H in this insulator.

Experimental evidence of the presence of isolated H is scarce in the literature. By using muon spin resonance (MSR) measurements, a neutral (paramagnetic) signal of a muonium, which is the light pseudoisotope of hydrogen, was observed even at room temperature in some insulators.[8] Cox et al.[8] also estimated the position of the transition level (+/−) of isolated muonium at around 3.5 eV below the vacuum level and these findings were found to be consistent with the results from theory for interstitial H.

In the present study, we investigate the electrical properties of H-related defects in different amorphous insulators (HfO₂, Al₂O₃, and SiO₂). Hydrogen was introduced into the oxides during growth by the atomic layer deposition technique or using a dc H plasma treatment and annealing in H₂/H₂ atmosphere. We discuss the experimental results with an emphasis on the existence of isolated interstitial H in these insulators.

2. Results

Figure 1 shows C–V curves recorded at 100 kHz in as-grown MOS structures with 30 nm SiO₂ and in samples subjected either to a dc H plasma treatment conducted at 50 and 100 °C or annealing in Ar atmosphere. The dielectric constant of SiO₂ calculated from the accumulation capacitance by considering the simple parallel-plate capacitor model was 3.8 and it was independent of the heat treatments. The flatband voltage determined from the C–V curves in as-grown samples was −0.25 V and a small
negative shift of $V_{FB}$ of around $-0.15$ V was observed after the annealing in Ar atmosphere. In contrast, a dc H plasma treatment leads to the formation of negatively charged defects in these films. The positive shift of the flatband voltage corresponds to the formation of positively charged defects in these films. One should also note that $C-V$ curves recorded after a dc H plasma treatment conducted at $100 \degree C$ and $150 \degree C$ show the increase in the density of interface states in these samples in comparison with that observed in as-deposited SiO$_2$. Table 1 shows the density of the fixed charge calculated from the $C-V$ curves shown in Figure 1.

Figure 2 shows $C-V$ characteristics recorded in MOS structures with 60 nm Al$_2$O$_3$ grown under different conditions by using the atomic layer deposition (ALD) technique and in samples subjected either to annealing in Ar atmosphere or a dc H plasma treatment conducted at $50 \degree C$ and $100 \degree C$. The dielectric constant of the alumina layers calculated from the accumulation capacitance in as-deposited layers was 9.3 (Figure 2a), 9.6 (Figure 2b), and 9 (Figure 2c), and it did not change after annealing in Ar atmosphere or after a dc H plasma treatment. The hydrogenation of the as-deposited structures by using a dc H plasma treatment also results in a shift of the flatband voltage towards higher biases independent on the growth conditions of alumina layers and their thicknesses.

The annealing at $440 \degree C$ in H$_2$/N$_2$ atmosphere also leads to a shift of $V_{FB}$. However, it is significantly smaller in comparison with that observed after a dc H plasma treatment and it depends on the growth conditions. The shift is significantly larger in samples grown with deionized water as a precursor at $150 \degree C$, whereas it is almost negligible in samples grown with ozone as a precursor at $300 \degree C$. The densities of the fixed charge obtained from the shift of $V_{FB}$ in the samples with alumina subjected to different heat treatments are also shown in Table 1.

One should also note that the $C-V$ curves recorded in the annealed samples are not typical for high-frequency measurements and an increase in the capacitance, which is rather a characteristic feature of low frequencies, was observed in the depletion region. This increase might be correlated with the injection of hydrogen into Si and the formation of carbon–oxygen–hydrogen-related defects acting as generation-recombination centers in this semiconductor.$^{[9,10]}$ However, additional studies are necessary to understand this effect in detail.

By XRD measurements, only broad peaks were observed in as-deposited alumina films and in those subjected to heat treatments at $440 \degree C$. The XRD spectra are very similar to those already reported for 100 nm alumina in the study by Kolkovskiy et al.$^{[11]}$ and it shows that alumina layers are amorphous. These findings are also consistent with the low values of the dielectric constant (around 9) obtained from the accumulation region of the $C-V$ curves.

To estimate the H concentration in the alumina layers, we conducted nuclear reaction analysis (NRA) measurements. These measurements determine the total concentration of H and it could differ significantly from that of electrically active H in alumina films. The concentration of H was around $0.5-1$ at % close to the surface of alumina and it reduced significantly toward the interface between Al$_2$O$_3$ and Si. One should also note that the H concentration varies from sample to sample and therefore its comparison in samples grown under different conditions is not feasible.

Figure 3 shows $C-V$ characteristics recorded in as-grown stack structures consisting of hafnia and 60 nm SiO$_2$ and in samples...
subjected either to annealing at 600 °C in Ar atmosphere or a dc H plasma treatment at 100 °C. The dielectric constant of the hafnia layers calculated from the accumulation capacitance was found as 5 and 9 in as-deposited 22 and 35 nm hafnia layers, respectively. However, the values became significantly larger (9 and 14) after annealing at 600 °C in Ar atmosphere. The low dielectric constant in as-deposited films could be explained by the amorphous structure of hafnia, whereas its crystallization is responsible for the larger values obtained in the annealed layers.

A dc H plasma treatment results in the shift of \( V_{FB} \) toward negative bias. The negative shift of the flatband voltage corresponds to the presence of positively charged defects in the stack structure. In contrast, the introduction of negatively charged defects was observed after an annealing of the stack structures at 600 °C in Ar atmosphere. The density of the fixed charge calculated from the \( C-V \) curves in these stack structures is shown in Table 1.

By using XRD measurements, only a broad peak centered at a scattering angle of about 31° was observed in as-deposited hafnia layers. This corresponds to the presence of the amorphous phase of hafnia\[12,13\] and these findings are consistent with the low dielectric constant obtained from the \( C-V \) measurements in as-deposited structures. By using NRA measurements the total H concentration was found to be around 2–3 at% close to the surface in hafnia films and it decreases significantly toward the interface between 35 nm HfO\(_2\) and SiO\(_2\) (around 0.1 at% at 30 nm). These findings were found to be similar to those already reported in the study by Kolkovsky et al.\[14\]

### 3. Discussion

We observed a significant shift of the flatband voltage in all MOS structures subjected to a dc H plasma treatment at 50 and 100 °C (Figure 1–3). Negatively charged defects, which correspond to a positive shift of \( V_{FB} \), were introduced in hydrogenated MOS structures with SiO\(_2\) and Al\(_2\)O\(_3\), whereas positively charged defects, corresponding to a negative shift of \( V_{FB} \), were detected after hydrogenation of the stack structures with HfO\(_2\)/SiO\(_2\). The concentration of the defects increases with increasing temperature of the dc H plasma treatment from 50 to 100 °C. According to the XRD measurements, as-grown layers HfO\(_2\), Al\(_2\)O\(_3\), and SiO\(_2\) are amorphous before and after the dc H plasma treatment at 50 and 100 °C. The MOS structures annealed in Ar atmosphere also exhibit a shift of the flatband voltage which is,
however, significantly smaller in comparison with that observed after a dc H plasma treatment. Therefore, we rule out that the crystallization of the oxides or defects released by annealing at elevated temperatures is responsible for the shift of the flatband voltage in the structures subjected to a dc H plasma treatment. By using deep-level transient spectroscopy measurements, we did not observe any traces of vacancy- and interstitial-related defects with a concentration above $10^{11}$ cm$^{-3}$ in elemental (Si and Ge) and compound semiconductors (ZnO and GaAs) after their hydrogenation with a dc H plasma treatment conducted under similar conditions (accelerating voltage, temperature and pressure). Similarly, we do not expect the presence of high concentrations of these native defects in the oxides hydrogenated by dc H plasma treatments.

By using the muon spin spectroscopy ($\mu$SR) technique, neutral (paramagnetic) muon states were observed in HfO$_2$, Al$_2$O$_3$, and SiO$_2$.[8] The signals corresponding to these states were stable even at room temperature and they disappear in the temperature range of 700–1000 K in HfO$_2$[8] and at around 1200 K in SiO$_2$.[15] The presence of atomic muonium[8,15] in the neutral (paramagnetic) state, which should be generally metastable, could be explained by nonequilibrium conditions of the experiments using radiolytic conditions ($\mu$SR).

Generally, the oxides grown by the ALD technique contain plenty of hydrogen. Kukli et al.[12] demonstrated that H should be a dominant impurity in hafnia layers deposited by ALD and its concentration was a factor of 2–3 higher in comparison with other unintentionally introduced impurities such as carbon and nitrogen. The authors explained these high H concentrations by the use of precursors containing hydrogen during the ALD growth. Similarly, a high concentration of H in as-deposited alumina and hafnia layers was observed by using NRA measurements in the present study. Most of the hydrogen in as-deposited layers is electrically inactive, for example, in the form of H molecules or in other electrically inactive H-related complexes. However, the high concentration of H observed in the insulators, which were grown by the ALD technique, should saturate possible sinks for the H introduced afterward during the dc H plasma treatment. This H cannot freely escape the structures as the insulators are covered with a metal top layer. Therefore, most of it remains confined inside the oxide layers where it should be positively or negatively charged depending on the position of the Fermi level. The presence of negatively or positively charged interstitial H could explain the shift of the flatband voltage observed in samples subjected to a dc H plasma treatment. One can speculate that the larger shift observed at higher temperatures of the treatment corresponds to the larger concentrations of H inside the insulators.

According to theory and muonium studies, the transition level of interstitial H should be located in the upper half of the bandgap or even close to the conduction band in HfO$_2$.[3-5,8] This could explain the existence of the positive fixed charge in these layers. In contrast, the transition level of H is close to the middle of the bandgap of Al$_2$O$_3$ and SiO$_2$ but it is below the midgap of Si.[5] In this case, H could be a source of negative fixed charge in Al$_2$O$_3$ and SiO$_2$ by accepting an electron from the Si channel.

Similarly, we observed a significant increase in the concentration of acceptors in p-type Ge[16] and shallow donors in n-type ZnO[17] after the introduction of H by using a dc H plasma treatment. According to theory,[5] the transition level (+/−) of H should be located above the minimum of the conduction band in ZnO and below the top of the valence band in Ge. In this case, interstitial H should introduce shallow donor states in ZnO, whereas it should be negatively charged independently on the position of the Fermi level in Ge.

We also observed a shift of $V_{FB}$ in samples with alumina and hafnia annealed in H$_2$/He$_2$ or Ar atmosphere. However, this shift was significantly smaller in comparison with that observed after a dc H plasma treatment and it could be attributed to different phenomena. First, a partial crystallization of HfO$_2$ and Al$_2$O$_3$ already occurred at 400–600 °C.[12,13,18] Small crystallites and defects, which appear in the insulators during these heat treatments, could be responsible for the changes observed in the C–V curves in Figure 1–3. Second, complex defects, which were stable at room temperature in amorphous insulators, could be destroyed after annealing at elevated temperatures. In this case, mobile impurities such as H could be released and they

Figure 3. C–V curves recorded in stack structures with 60 nm SiO$_2$ and 22 nm (a) or 35 nm (b) HfO$_2$ before and after the heat treatment at 600 °C in Ar atmosphere (Ar$_{II}$) and after a dc H plasma treatment conducted at 50 and 100 °C. The AC frequency was 100 kHz. The capacitance was normalized to its maximal value $C_{\text{max}}$.© 2021 The Authors. physica status solidi (a) applications and materials science published by Wiley-VCH GmbH
could also influence the electrical properties of the insulators. However, further studies are necessary to understand these processes in details.

4. Conclusion

In the present study, we investigated the influence of the introduction of H by using a dc H plasma treatment on the electrical properties of metal–oxide–semiconductor (M–O–S) structures containing different insulators (Al2O3, SiO2, and HfO2). By analyzing the shift of the flatband voltage, negatively charged defects were detected in hydrogenated amorphous Al2O3 and amorphous SiO2, whereas positively charged defects were responsible for the shift of $V_{FB}$ in hydrogenated MOS structures with amorphous HfO2. In good agreement with theory, these defects were attributed to interstitial H, which should be negatively or positively charged in the insulators depending on the position of the Fermi level.

5. Experimental Section

Samples were 200 mm n- and p-type Si wafers with a resistivity of about 2 $\Omega$cm. 30 nm and 60 nm SiO2 was thermally grown by oxidizing Si wafers at 960 °C. 22 and 35 nm HfO2 was deposited on 60 nm SiO2 by using the ALD technique. Tetrakis(ethylmethylamino)hafnium and ozone were used as precursors for the growth of the hafnia layers. Al2O3 thin films were also deposited by the ALD technique on Si substrates by using different precursors (trimethylaluminum [TMA], ozone, and deionized water) and different temperatures. The thickness of the oxides was determined by ellipsometry measurements. The structural properties of the metal oxide films were investigated by grazing-incidence X-ray diffraction (XRD) measurements. MOS structures were prepared by thermal evaporation of Al on top of insulators with an area of 0.25 cm² at room temperature. A dc H plasma treatment was conducted on square samples with an area of 2 x 2 cm with an accelerating bias of 300 V at 50 and 100 °C. Several samples were annealed at different temperatures in Ar atmosphere. Capacitance–voltage (C–V) measurements were carried out on MOS structures at 100 kHz at room temperature. The flatband voltage was calculated as described in the study by Nicollian et al.[19] Current–voltage (I–V) measurements were carried out at room temperature to control the leakage current in structures used for the C–V measurements. NRA measurements were used for the determination of the H concentration in insulators.

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Conflict of Interest

The author declares no conflict of interest.

Data Availability Statement

Research data are not shared.

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