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Hydrogen induced positive charge in Hf-based dielectrics

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Abstract

This work investigates the anneal-induced positive charge in Hf-based dielectrics. It is found that anneal in forming gas produces substantially more positive charge than that in N_2 at 500°C, indicating that hydrogen is a reactant for the positive charging. Positive charging is thermally accelerated and can occur in both HfO_2 and Hf-silicates. Nitridation of either interfacial layer or whole dielectric stack enhances the positive charging significantly. These positive charges have a large sample-to-sample variation and are stable. For the first time, both mobile and fixed charges are simultaneously observed for Hf-stacks.

Keywords: Positive charges; Instability; Hydrogenation; HfO_2; Hf-Silicates; High-k dielectrics.

1. Introduction

The commercial application of Hf-based gate dielectric has been delayed by a number of problems, such as process integration, low carrier mobility, and instability. Recently, it has been reported that a substantial amount of positive charge can be formed in high-k stacks by post-deposition annealing [1,2]. There is little information on the properties of this positive charge in high-k stacks, although they were reported for SiO_2 [3,4]. The *objective of current work* is to investigate the features of this positive charge in high-k stacks and explore how it is affected by various factors, including hydrogenation, gate materials, channel polarity, and nitridation.

2. Devices and experiments

The device fabrication starts with an IMEC-clean and a 1nm chemical SiO_2 [5]. For some devices, this interfacial layer was nitrided in NH_3 at 900°C for

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60sec, before depositing HfO_2. Both HfO_2 and Hf-silicates were prepared by ALD with an EOT in the range from 1.13 to 1.8nm. The silicates were nitrided in NH_3 at 800°C for 60sec. The samples were annealed in forming gas (FG) at 520°C for 20min. The temperature used here is higher than the 400°C used for annealing SiON, since it is more difficult for hydrogen to diffuse through the high-k layer [6]. Devices have either poly-Si or TaN gates and both nMOSFETs and pMOSFETs were prepared. The channel length and width is 1μm and 10μm, respectively. Details of the devices used for each test are given in the figure legends.

The test sequence starts with measuring the transfer characteristics (TC) at a drain bias of 0.1V. The device was then exposed to a typical temperature of 500°C for 30min in either FG (10%H_2) again or N_2. After the exposure, TC was measured again and the shift in TC was monitored from the change of gate bias at a constant drain current of 10^{-6}A.

3. Results and discussion

3.1. Features of the anneal-induced positive charge

Fig. 1 shows that TC shifts negatively when temperature is above 400°C, indicating positive charging in HfO_2. It should be pointed out that this positive charging is not caused by electrical stress, but by the anneal process. The positive charging is clearly thermally activated. After annealing at 500°C for 30min, the effective positive charge density can reach $1\times10^{13}cm^{-2}$.

The first feature of the anneal-induced positive charge is a large sample-to-sample variation. Fig. 2a shows the threshold voltage shift, ΔVth, in 10 pMOSFETs after the same anneal. There is a substantial sample-to-sample variation, leading to an uncertainty in V_{th} of ~0.28V. This is unacceptable and could cause yield problem. To confirm that such a large sample-to-sample variation is induced by the anneal process, the pre-anneal sample-to-sample variation was checked. Fig. 2b clearly shows that the variation is indeed caused by the anneal. This behavior is similar to the hydrogen-induced positive charge in some SiO_2 layers [3,4].

The second feature is the simultaneous presence of mobile and fixed positive charges. Fig. 3 clearly shows that there are two components for the anneal-induced positive charge: fixed and mobile. Under Vg>0, mobile charge is pushed towards substrate, resulting in a rise of threshold voltage shift. Under V<0, the opposite happens. A large part of the positive charge is not affected by Vg polarity and is 'fixed'.

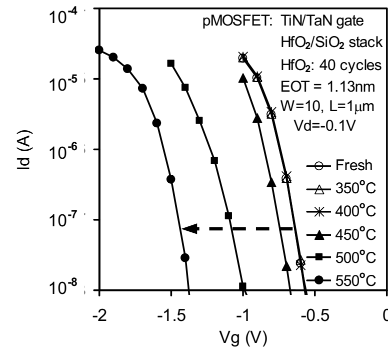

Fig. 1. Hydrogenation induced positive charge formation. The forming gas (FG) anneal is 30min at each temperature. The sample was annealed in NH_3 at 900°C for 60s before depositing HfO_2.

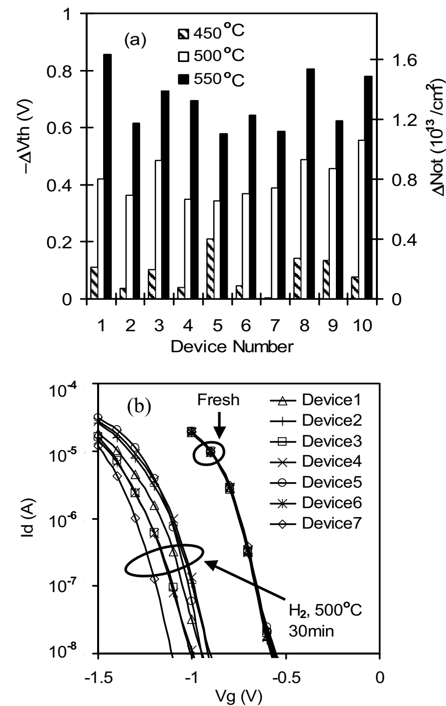

Fig. 2. Sample-to-sample variations. (a) shows the results, after annealed for 30min in FG. The average |ΔVth| for 450, 500, and 550°C is 0.09, 0.42, and 0.70V. The corresponding standard deviation is 0.06, 0.07, and 0.10V. ΔNot is the effective charge density. (b) shows that the variation is negligible for fresh devices.

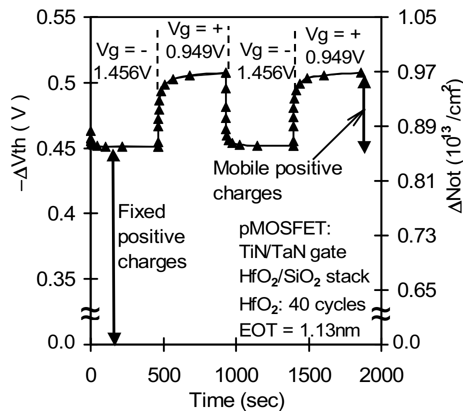

Fig. 3. After a FG anneal at 500°C for 30 min, both mobile and fixed positive charges were observed. Under Vg>0, mobile positive charges were pushed towards the substrate, resulting in a higher |ΔVth|.

The third feature is the stability and non-reactivity of these positive charges. It is well known that the stress-induced positive charge is unstable [7] and the relevant mobile species are highly reactive [8]. When these species arrive at interface, they will be lost [8]. For the anneal-induced positive charge, Fig. 3 shows that the density of mobile charges remains constant, when they were cycled between two interfaces. The fixed charges do not change with Vg polarity and time, either. The different behavior of anneal and stress-induced positive charges indicates that they originate from different defects.

3.2 Influencing factors on positive charging

We now explore how the positive charging is affected by hydrogenation, nitridation, gate materials, and channel polarity. First, the role played by hydrogen is studied. Fig. 4 compares a 500ºC anneal in nitrogen and in hydrogen for the same time. It is clear that hydrogenation substantially enhances positive charging. The relatively low charging after annealing in N_2 is probably caused by the relocation of residual hydrogen in the device. As a result, it is believed that hydrogen is a reactant for the positive charging.

Next, we examine the role played by gate materials, channel polarity and nitridation. The devices used in Figs. 1-4 have a TaN gate and it has been reported that metal gate can substantially enhance the stress-induced positive charging [9]. The question is whether the anneal-induced positive charging is also substantially enhanced by metal gate. The positive charging in TaN and poly-gated devices is compared in Figs. 5a & b. It is clear that the positive charging is negligible in both cases, so that using TaN is not responsible for the positive charge here. Figs. 5a & b also indicate that the positive charge observed in Figs. 1-4 was not caused by any unintended contamination during the anneal, since the same anneal process was used in Fig. 1 and Fig.5. The shift of TC in Fig. 5b is in a direction opposite to the positive charging-induced shift, but in agreement with an increase of the work function of TaN [10].

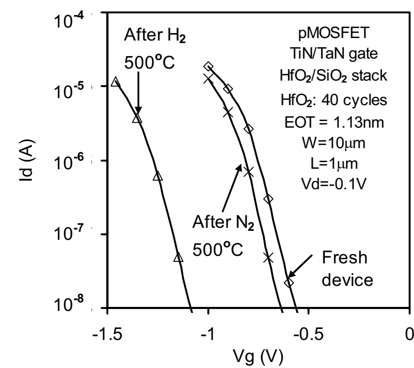

Fig. 4. Two pMOSFETs were annealed for 30 min in FG and N_2, respectively. Positive charging is substantially higher after the FG anneal, suggesting that hydrogen plays an active role in the positive charge formation.

There are two main differences between the samples in Fig. 1 and Fig. 5: channel polarity and nitridation. On channel polarity, it has been reported that negative bias temperature instability (NBTI) requires the presence of holes at the interface [11]. To find if the anneal-induced positive charging can occur in nMOSFETs, an nMOSFET different from that in Fig. 5 was used in Fig. 6. It is clear that positive charging also occurs in nMOSFETs.

The common point between devices used in Fig. 1 and Fig. 6 is nitridation. For Fig. 1, the interfacial layer was nitrided in NH_3 at 900°C for 60sec before depositing HfO_2. For Fig. 6, the Hf-silicate was nitrided in NH_3 at 800°C for 60sec. Nitridation was absent in Figs. 5a and 5b. We speculate that the nitridation of either the interfacial layer or the whole stack enhances the hydrogenation-induced positive charge.

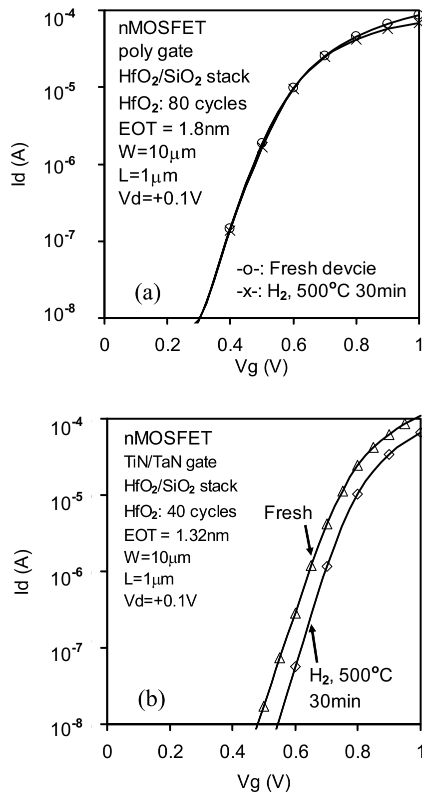

Fig. 5. Without nitridation, the FG anneal has little effect on the poly- (a) and TaN-gated (b) nMOSFETs. The shift in (b) was in a direction opposite to positive charge-induced shift.

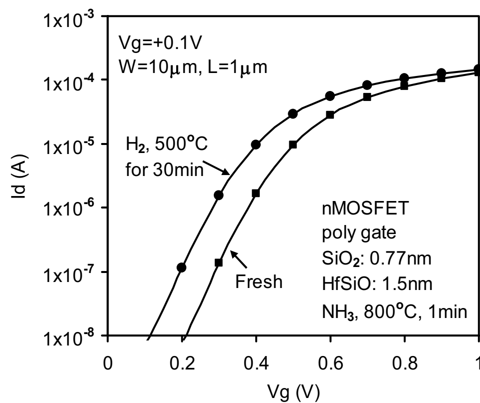

Fig. 6. After nitridation, the FG anneal also results in positive charging in an nMOSFET with poly-gate and Hf-silicate (23%Hf).

4. Conclusions

This work shows that annealing in forming gas at 500°C can induce substantial amount of positive charges in HfO_2 and Hf-silicate stacks. The features of these positive charges include a large sample-to-sample variation, a simultaneous presence of mobile and fixed charges, and their stability and non-reactivity. The positive charging does not originate from the difference in gate materials and channel polarity. Hydrogen is believed to be a reactant for the positive charging and nitridation can substantially enhance it. To suppress this anneal-induced positive charging, process optimization is essential.

Acknowledgements

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