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Physical Origin of Fast Transient Charging in Hafnium Based Gate Dielectrics

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1. Introduction

Transient charging in high-k dielectrics has been identified as a major issue affecting various characteristics of high-k devices such as threshold voltage (V_{th}) instability [1-3], hot carrier reliability assessments [4-6], constant voltage stress [7-9], and mobility measurements [1,2,10-12]. The origin of transient charging has been often attributed to shallow traps, but the physical origin of these traps has not been fully understood.

This paper examined various factors affecting the transient charging effects in hafnium-based gate dielectrics and speculated on the possible physical origin of fast transient charging (FTC).

2. Experiments and results

In this work, the effects of various factors on the fast transient charging in HfO_2 or HfSiON were examined using ultra-short pulse measurement and charge pumping techniques. Various samples were prepared to properly assess the effect of these parameters. All the samples were subjected to a 1000ºC, 5-sec heat cycle and were processed with TiN electrodes. In addition, some results from the literature are cited.

HfO_2 thickness (T_{phy}=2nm, 3nm, 4nm): As the high-k film becomes thinner, FTC gets smaller, and it is reduced beyond the detection limit in a 2nm HfO_2 sample (Fig.1). This result indicates that FTC originates from a high-k layer rather than an interfacial layer [13]. Even though the properties of the interfacial layer may vary as a function of the thickness of high-k layer [14], these changes can affect the FTC only via the variation of a tunneling barrier, which controls a substrate electron injection into the high-k layer.

Crystalline structures (transmission electron microscopy [TEM] on T_{phy}=2nm, 3nm, 4nm of HfO_2): After a high temperature anneal, 2nm HfO_2 film shows a pattern similar to phase separation observed in Hf-silicate (Fig.2) and, apparently, smaller degree of crystallinity (although, due to resolution limitation, this tentative conclusion is awaiting collaborative evidences from other techniques). While all three samples show some degree of crystalline structure, FTC is not seen in the 2nm HfO_2 sample as shown in Fig.1. Thus, the crystallinity itself may not be a source of FTC.

Defects states at boundary formation: Plan-view TEM of 2nm, 3nm, 4nm of HfO_2 shows that the density of boundary lines decreases as the high-k becomes thinner. For the 2nm sample, it is difficult to see the grain boundary (Fig.2). Thus, the defects responsible for FTC may be associated with the defects at the boundaries, assuming that the coordination of bonds at the interface of crystalline boundaries is different from the surface state of nano-crystallites which may exist at 2nm sample. If FTC is affected by boundary density, a narrow short channel device may fluctuate as the density of boundary defects varies, but no clear evidence has been found yet (data not shown).

Interface passivation (with and without passivation using high pressure (HP) H_2 anneal at 10atm.): Although hydrogen passivation drastically improves the mobility of high-k dielectrics by decreasing interface states density [15] and increases hydrogen density even in the high-k layer [16], no distinct change in FTC has been observed before and after a HP hydrogen anneal (Fig.3). Thus, defects that can be passivated by hydrogen, such as Si dangling bonds, can be excluded from the sources of FTC.

Si content (0%, 30%, 60% silicate formation): Small amount of silicon added into HfO_2 reduces FTC (Fig.5). Adding Si is known to change the crystalline structure of as-deposited high-k film. However, since the spinodal decomposition of Hf-silicate creates nano-crystallites embedded in SiO_2 after a 1000ºC, 5-sec anneal even in a Hf-silicate containing 60% of SiO_2 [17], the nano-crystallite structure should be ruled out from the source of FTC, but boundary formation might be still related to the reduced FTC. Alternative interpretation is that the FTC can be related to the total volume of HfO_2 formed in the silicate film after phase separation after 1000ºC, 5-sec anneal, assuming the FTC is an intrinsic characteristics of HfO_2.

Nitrogen incorporation in 3.5nm Hf-silicate (50% SiO_2): Nitrogen incorporation drastically reduces FTC even in thick Hf-silicates (Fig.6). About 10% of nitrogen can effectively reduce FTC below detection limits. However, when nitrogen concentration is excessive, FTC increases again along with an increase in slow transient charging during CVS (Fig.7). Since nitridation is performed after post-deposition anneal, nitridation-induced amorphization cannot explain this phenomenon. This is very interesting result because it means that FTC is related to the defects which can be passivated by a small amount of nitrogen.

3. Discussions

According to the observations above, FTC appears to be related to very shallow defect states within the high-k dielectric layer. Leading candidate for the source of FTC are oxygen vacancies, which may exist in several charge states and 3 and 4 fold coordinated sites, as well as d-states splited of the conduction band due to Jahn-Teller effect [18,19]. Due to lack of correlation to the grain boundaries density, Jahn Teller states terminated at the boundaries of nano-crystallites are not likely a source of FTC, even though Jahn Teller states can be a source of shallow traps. Recently, it was found that nitrogen could passivate the shallow traps associated with oxygen vacancies [20]. This finding is consistent with our observations of the effects of nitrogen incorporation. On the other hand, effect of extrinsic defects has not been investigated in detail. For example, Zr impurities that are usually present in Hf in the 3-5% may introduce shallow, large size defects [21]. The other extrinsic sources of charge trapping reported in the literature are C and Cl [22]. These impurities appear to affect the result of long-term stress such as time-dependent dielectric breakdown (TDDB) and leakage current, but effect on FTC needs more systematic study.

4. Conclusions

The physical origin of fast transient charging in HfO_2 has been speculated based on results of a controlled experiment and data reported in the literature. Oxygen vacancies within HfO_2 or at the boundary may be the defects contributing to fast transient charging. Since FTC is the primary cause of instabilities in high-k devices, it is very important to find a way to reduce or passivate oxygen vacancies, especially near the interface.

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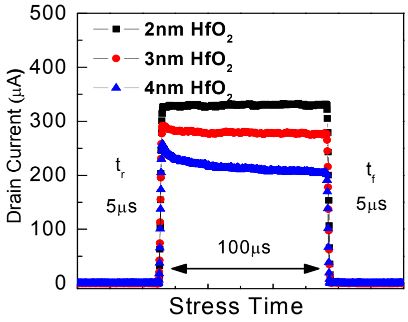

Fig.1 Effect of HfO_2 thickness on transient charge trapping induced Id reduction. Vg = -1 to 1.4 V.

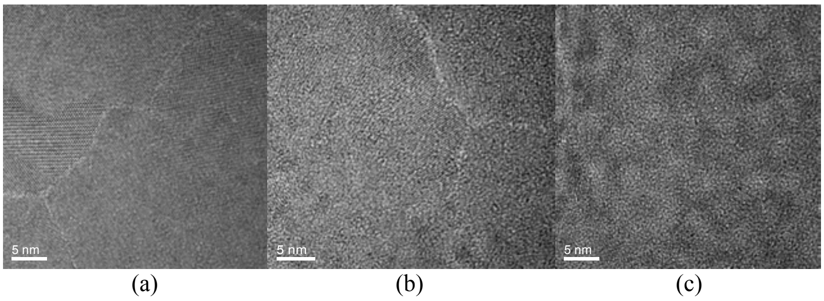

Fig.2 TEM of HfO_2 sample with (a) 4nm, (b) 3nm, (c) 2nm. 4nm sample shows a clear boundary formation while 2nm sample shows structures like phase separation without less distinct boundary formation.

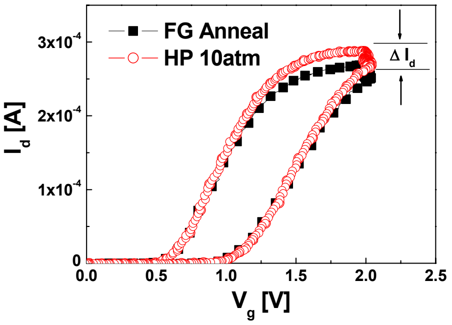

Fig.3 Pulsed Id-Vg measurement showing I-V hysteresis before and after high pressure hydrogen anneal to passivate interface states and Si dangling bonds.

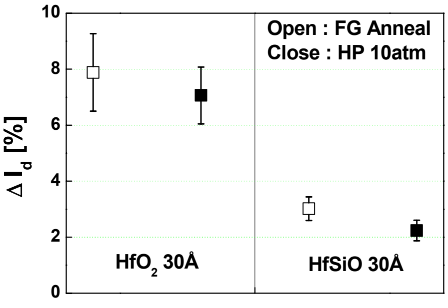

Fig.4 Summary of charge trapping before and after high pressure anneal, indicating hydrogen passivation has a minimal impact on bulk trapping behavior.

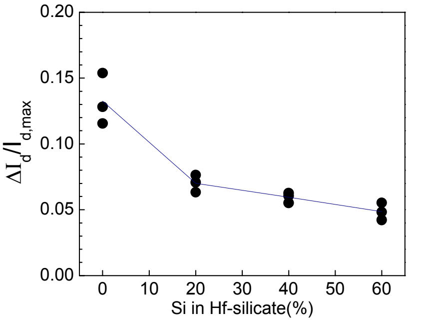

Fig.5 Effect of silicon concentration in Hf-silicate on FTC induced drain current reduction.

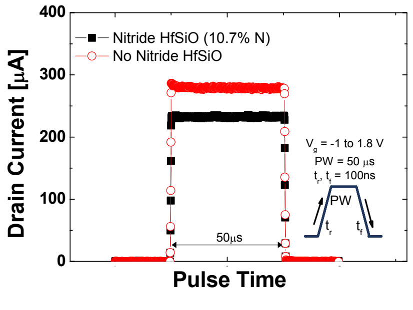

Fig.6 Effect of nitrogen incorporation in 3.5nm Hf-silicate (50% SiO_2). Vg = -1 to 1.8V, PW = ~50μs, tr, tf = 100 ns

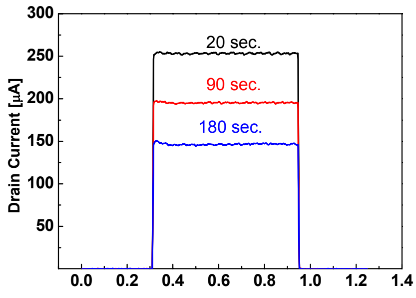

Fig.7 Effect of nitrogen incorporation in 3.5nm Hf-silicate (50% SiO_2). Vg = -1 to 2.5 V, PW = ~500 ms, tr, tf = 100 ns