Research on the Wake-up Effect of Ferroelectric HfO2-ZrO2 Thin Films

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ABSTRACT: The appearance of ferroelectric (FE) and anti-ferroelectric (AFE) properties in HfO2-based thin films is highly intriguing in terms of both the scientific context and practical application in various electronic and energy-related devices. Interestingly, these materials showed a “wake-up effect”, which refers to the increase in remanent polarization with increasing electric field cycling number before the occurrence of the fatigue effect. The appearance of ferroelectric (FE) and anti-ferroelectric (AFE) properties in HfO2-based thin films is highly intriguing in terms of both the scientific context and practical application in various electronic and energy. In this paper, we have conducted an in-depth study on the relationship between the Wake-up effect in HfO2-based films and oxygen vacancies.

1. Introduction
In recent years, as representative high-k dielectrics, HfO2 have been extensively implemented in microelectronics industry. Recently, HfO2-ZrO2 thin films were discovered to exhibit pronounced ferroelectricity[1]. Due to its superior compatibility to silicon-CMOS integration technology, HfO2 can improve traditional ferroelectrics in electronic devices, including Si-based complementary metal oxide semiconductor-compatibility, matured deposition techniques, a low dielectric constant and the resulting decreased depolarization field, and stronger resistance to hydrogen annealing. New type of FRAM——HZO (HfZrO) FRAM, has received widespread attention, but this kind of FRAM has obvious Wake-up effect, which limits its application. Wake-up effect was first studied by Zhou et al[2]. At present, the research on the generation mechanism of the Wake-up effect of HZO ferroelectric thin films is no clear conclusion, and this effect is related to the fatigue problem during the application of the films, which shortens the service life of the device[3][4]. Mechanisms, influencing factor and suppressing this effect are the major issues in current research.

To prepare the samples in the experiment, 9 nm of Hf0.4Zr0.6O2 films were sputtered on the Si substrate by ALD, and the top and bottom electrodes were both 10 nm TiN electrode. In order to prevent the top electrode from being exposed to air and oxidized, a 75 nm W electrode was sputtered on the TiN top electrode by DC sputtering. The crystal structure of the film was characterized by X-ray diffraction (XRD) spectroscopy (Lab XRD-6000, SHIMADZU) using a Cu kα source. Polarization–electrical field (P–E) hysteresis loops were measured using a Radiant Precision workstation. Capacitance-voltage (C–V) curves were measured using a semiconductor parameter analyzer (B1500A, Agilent Technologies, USA). For temperature test and For C–V measurements, a small alternating signal of 200 mV amplitude and 1 MHz frequency was applied across the sample.
2. Wake-up behaviors of HZO thin films

Figure 1(a). The P–V hysteresis loops
Figure 1(b). Pr-Cycles

Figure 1(a) The P–V hysteresis loops of W/HZO/TiN structure. The hysteresis loop measured in the initial state (0 cycle) was a double hysteresis loop with an antiferroelectric phase. When the number of voltage turns was 10^3 cycles, it became a ferroelectric hysteresis loop.

(b). values of the positive and negative remnant polarization on the same coordinate axis to get the graph (b). We found that when the voltage reached 10^3~10^4 cycles, the remnant polarization of the sample increased by about 90% compared with the original state.

3. Study on the mechanism of Wake-up effect

The C–V loops were measured for the thin film. With the increase of voltage cycles, a more and more asymmetric C-V loop can be observed as shown in figure 2. Pintilie et al. proposed that the C–V curve of a ferroelectric material can be expressed by the following equation[5]:

\[ C = \frac{q\varepsilon_0\varepsilon_s N_{eff}}{2(V + V_{bi} \pm \frac{p}{\varepsilon_0 \varepsilon_s \delta})} \]  

\( N_{eff} \) is the effective charge density in the space charge region of the Schottky diode, \( V_{bi} \) is the built-in potential in the absence of polarization, and \( \delta \) is the distance between the polarization sheet of charge and the physical metal–ferroelectric interface. The \( \pm \) sign indicates the two possible polarization orientations.
Figure 2. C-V loop, as the number of cyclic electric field increases, the peak capacitance is decreasing. According to the theory of semiconductor physics, since the depletion is approximated in the reverse bias voltage region, the capacitance measurement will be more accurate. The HZO ferroelectric thin film (capacitor) is similar to a PN junction[6]. When the reverse voltage is applied to the upper electrode, that is, the reverse bias region of the upper electrode, Vbi can be ignored. When the reverse bias voltage increases, the internal depletion region widens to reach the consumption to reduce the barrier capacitance and make the measured capacitance more accurate. Therefore, we performed data on the reverse bias voltage of the top and bottom electrodes of the sample under different cycle voltage cycles during the Wake-up effect Extraction, so for the top electrode, we select (-1 ~ 0V) this region to fit the data. and the corresponding slope of 1/C2–V (figure 3) was fitted to extract Neff of the W/HZO interface under reverse bias.

Figure 3(a). Variation curve of the number of Neff in the reverse bias region of the top electrode with the number of voltage cycles.
Figure 3 (b). Variation curve of the number of Neff in the reverse bias region of the bottom electrode with the number of voltage cycles

4. Conclusions

Through the fatigue test of the film samples, it was found that as the number of fatigue cycles increased, the HfO2-ZrO2 film had an obvious Wake-up effect, that was, the film changed from the antiferroelectricity to ferroelectricity, and the remnant polarization significant increased. During the process of the Wake-up effect, the C-V curve of the film was measured, and then the change of the Neff concentration was calculated. It was found that the Neff had an overall increasing trend. Since the oxygen vacancy concentration and Neff have a complementary relationship, it is speculated that the movement of oxygen vacancies will cause the Wake-up effect of the HfO2-ZrO2 thin film.

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