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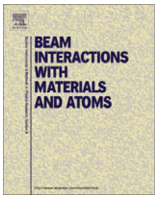

Electrical properties changes induced by electron radiation at TiO_2/Si interface

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ABSTRACT

TiO_2/Si structures were fabricated by electron beam evaporation, and exposed to electron beam irradiation to investigate their electrical properties using the high frequency capacitance–voltage measurements. It was found that samples annealed in oxygen became more radiation resistant than unannealed samples, which can be explained by the Ti valence variations induced by radiation. The samples were characterized by X-ray diffraction to show the Ti_2O_3 crystalline phase transformed to anatase-crystalline phase after oxygen annealing.

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1. Introduction

One of the most challenging problems in the microelectronics industry is looking for an alternative gate dielectric to SiO_2 for very large-scale integrated circuits (VLSI) with sub-100-nm channel length CMOS devices [1–3]. In order to follow VLSI, the gate oxide thickness has been reduced to less than 2 nm, but large leakage currents can arise in these devices due to the direct tunneling from the substrate to the gate electrode. Therefore alternative gate dielectrics, such as Al_2O_3 [4], HfO_2 [5], ZrO_2, Y_2O_3, TiO_2 [6], Ta_2O_5 and the silicates have been studied, focusing on their larger dielectric constants, which can reduce the tunneling leakage current and improve the reliability while scaling the capacitance equivalent oxide thickness (CET) below the direct tunneling limit of SiO_2.

Among these high-*k* materials, titanium dioxide, TiO_2 is a potential candidate because of its high dielectric constant (up to 100) and good thermal stability on silicon [7]. However, studies of the radiation response of these materials are rare. Devices are exposed to various forms of radiation in space, for example, electrons, protons, neutrons, and heavy ions. This radiation affects these devices, causing temporary loss of data to catastrophic failure [8–10], so it is very important to study their radiation response. The effects of ionizing radiation on MOS devices, has been studied extensively since the 1960s, with the aim of developing radiation-hardened MOS devices (primarily silicon dioxide–silicon) [11–14]. A build-up of radiation-induced positive charges in the oxide layer and an increase in the interface traps at the Si–SiO_2 interface can cause serious degradation of the performance of the devices [15–18]. However, little work has been done to study the effects of ionizing radiation on MOS devices based TiO_2 gate dielectric. Zhang et al. selected TiO_2 as a gate dielectric fabricated by DC sputtering [19] and studied the effect of ionizing radiation. He pointed out that Ti ion valence variations induced by electron radiation at the TiO_2/Si interface was beneficial to the stability of TiO_2/Si structure exposed to ionizing radiation. In our work TiO_2 film as a gate dielectric material was fabricated by electron beam evaporation. Meanwhile the radiation effects on the pre-grown TiO_2/Si structures were studied. The radiation effects on the TiO_2/Si structures after annealing in oxygen were also studied.

2. Experimental

The TiO_2 films were fabricated on p-type (1 0 0) silicon substrate by electron beam evaporation, with the substrate temperature at 300 °C, and the film thickness about 10 nm. The pre-grown samples and samples annealed at 500 °C in oxygen for 4 h were exposed to electron radiation with energy 1.5 MeV, with fluences from $1 \times 10^{14}/cm^2$ to $1 \times 10^{15}/cm^2$. Finally, the flat-band voltage shift (ΔV_{FB}) were obtained by HF *C*–*V* measurements; in addition, the synthesized TiO_2 film was characterized by X-ray diffraction (XRD, DX1000, Cu Kα radiation) at grazing incidence.

3. Results and discussion

Fig. 1 shows 1-MHz *C*–*V* curves of the samples, with fluences of $1 \times 10^{14}/cm^2$, $2 \times 10^{14}/cm^2$, $4 \times 10^{14}/cm^2$, $6 \times 10^{14}/cm^2$ and $1 \times 10^{15}/cm^2$. Fig. 1(a) and (b) both show the value of flat-band voltage shift of the first and the fourth measurements. In the inset of Fig. 1(a), the value of flat-band voltage shift is less than 0.4 V with the total fluence below $4 \times 10^{14}/cm^2$. With the fluence more than $6 \times 10^{14}/cm^2$, the value of flat-band voltage shift is high, and the well sidestep can be found in the *C*–*V* curve. The value of

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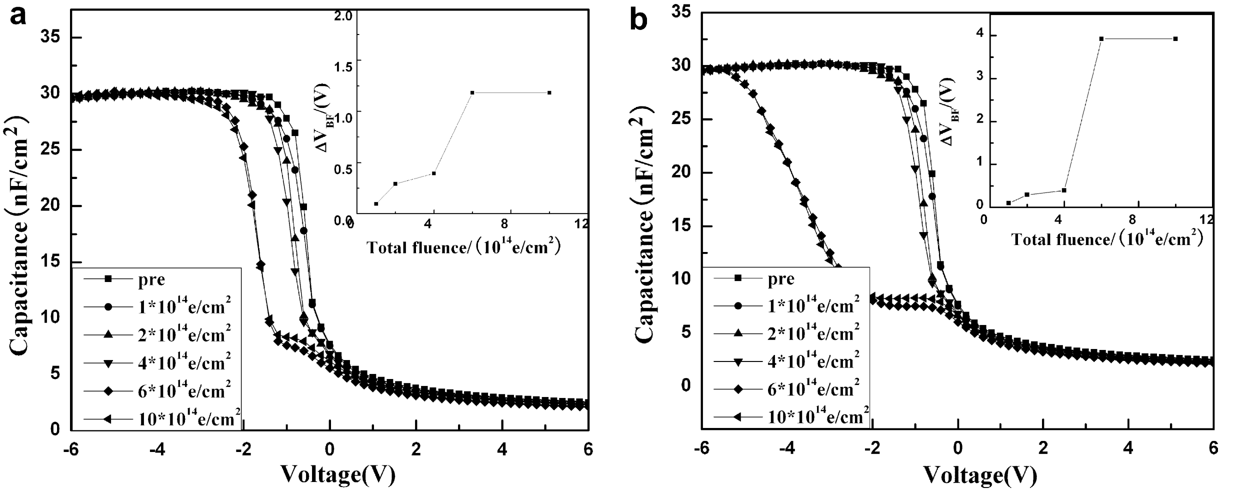

Fig. 1. 1-MHz C–V measurements on pre-grown TiO_2/Si structure and TiO_2/Si structure after electron radiation: (a) the first measurement on samples of different fluence; (b) the fourth measurement on samples of different fluence. The insets show the change of ΔV_{BF} with increase in the total fluence.

ΔV_{BF} increases to 3.92 V with a fluence more than $6 \times 10^{14}/cm^2$, shown in Fig. 1(b), but it is nearly unchanged for a fluence less than $4 \times 10^{14}/cm^2$. The value of ΔV_{BF} increased after a number of measurements.

Fig. 2 shows the number of 1-MHz C–V measurements on TiO_2/Si structure after electron radiation, measured four times per sample. With a fluence of $1 \times 10^{14}/cm^2$, the value of ΔV_{BF} is nearly unchanged with the number of measurements in Fig. 2(a); however, the value of ΔV_{BF} increases with the number of measurements in Fig. 2(b) when the sample was irradiated with a fluence of $1 \times 10^{15}/cm^2$. Thus the measurement process (or gate-voltage) caused effect on ΔV_{FB} with high fluence radiation to certain extent.

Electron irradiation of TiO_2/Si structures mainly results in two processes: radiation-induced electron–hole pairs and radiation-induced chemical composition variation. Chemical composition variation mainly comes from the TiO_2–Si interface, which is a transition layer composed of a non-stoichoimetric oxide TiO_x ($x < 2$), especially in the TiO_2 film by electron beam evaporation. The Ti valence maybe changed by irradiation, via the Ti^{4+} and Ti^{3+} states, however, this transition is different between low fluence and high fluence.

With low fluence radiation, the transition from Ti^{4+} to Ti^{3+} state maybe predominate, and the chemical composition can be prepared by the following reaction:

$$2TiO_2 \rightarrow Ti_2O_3 + O \qquad (1)$$

Thus the excess oxygen forms electron traps in the transition layer and captures the radiation-induced electrons, which has two side-effects: on the one hand, forming negative charges (O^{2-}) to compensate the radiation-induce positive charges, so the flat-band voltage shift ΔV_{FB} is low; on the other hand, fixing the radiation-induced electrons on the trap not to be driven out of the insulator layer by the gate-voltage, so ΔV_{FB} is nearly unchanged after four times with low fluence irradiation.

With high fluence radiation, the energy was enough high to change the valence from the Ti^{3+} into Ti^{4+} state in the transition layer, so Eq. (2) is the dominant process, and the chemical composition could be presented as follows:

$$2Ti_2O_3 \rightarrow 3TiO_2 + Ti \qquad (2)$$

Thus excess titanium can capture radiation-induced holes forming positive charge in the transition layer, which shifts the C–V curve to a very negative gate-voltage, so the value of ΔV_{FB} was high for high fluences. Without negative charge traps, the radiation-induced electrons were only located on neutral traps, and could easily be driven out the insulator layer by a gate-voltage. Therefore, with high fluence radiation, these radiation-induced electrons were droved out the insulator layer by gate-voltage after some time

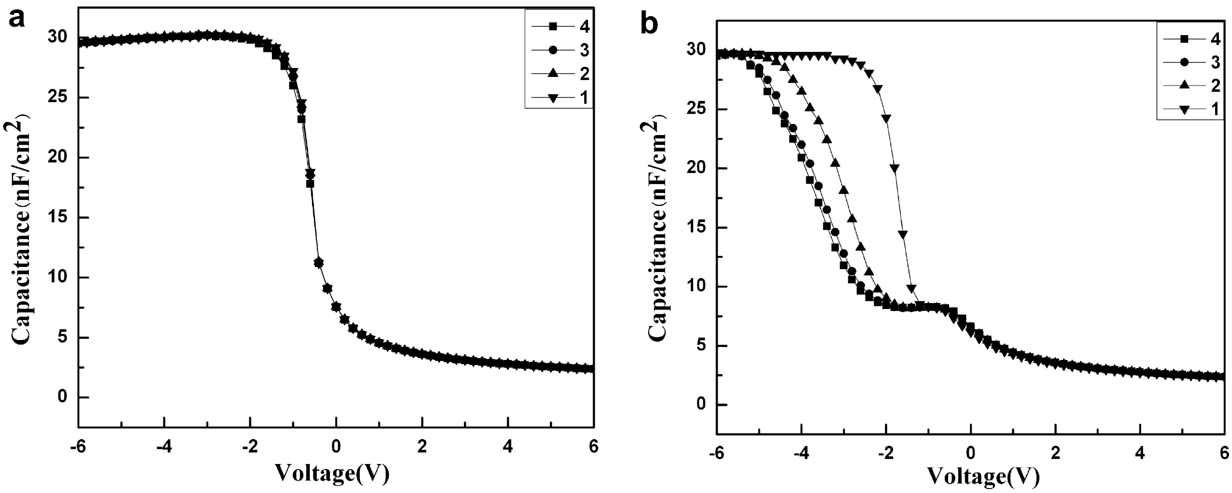

Fig. 2. Number of 1-MHz C–V measurements on TiO_2/Si structure after electron radiation: (a) with fluence of 1×10^{14} e/cm^2, (b) 10×10^{14} e/cm^2.