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Effects of neutron irradiation of ultra-thin HfO_2 films

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Neutron irradiation at low fluence decreases the Pb-type and E′ defect levels in ultra-thin hafnium dioxide films because electrons can fill existing states. These electrons come from electron-hole pairs generated by neutron interactions with silicon and oxygen. Thus, a low fluence of neutrons "anneals" the sample. However, when neutron fluence increases, more neutrons collide with oxygen atoms and cause them to leave the lattice or to transmute into different atoms. This causes the E′ states to increase. As defect-state concentrations increase, leakage currents increase, but since the E′ is much lower than the Pb concentration, this is not a dominant factor.
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Continued exposure to cosmic ray irradiation can cause single event upsets (SEU),[1] can contribute to time dependent dielectric breakdown (TDDB)[2] and also can decrease reliability of devices. In the past, radiation hardening of devices was one of the principal drivers for damage measurements as a function of fluence (dose) for military and space applications. Initially, radiation hardening was investigated for basic devices utilizing SiO_2 on Si.[3] Following this, studies were undertaken to investigate SEUs to understand "random" malfunctions of DRAM and later static random-access memory (SRAM). SEUs are typically produced by two mechanisms: (1) energetic charged particles, such as alpha particles and protons, produced by radioactive metallic impurities[4] and (2) charged particles produced by neutron recoil.[5] The former can be prevented with a relatively thick polymer coating, such as polyimide, of the Si chip after removing radioactive impurities in the metal interconnects, while the latter can be reduced with careful design for devices and the introduction of parity bits for memory.

However, despite the above attempts to minimize SEUs, based on the fact, for example, that (1) critical dimensions are continuously decreasing and (2) single-electron transistors have the potential to be used in microelectronic devices SEU upsets will become serious in the future. Of primary concern in this Letter is the concentration density of defect states in high-k dielectrics used for resistive random-access memory (RRAM) is subjected to irradiation by neutrons with energies above 1 MeV. Hafnium dioxide (HfO_2) is one of the most popular RRAM materials.[6] Changes in the defect-state concentrations of HfO_2 can lead to changes in the resistive-switching mechanism which has the potential to convert a "0" into a "1" in RRAM or vice versa.

In this work, blanket films of HfO_2 deposited on Si were irradiated with neutrons of various fluence at the University of Wisconsin Max Carbon Radiation Science Center. Electron-spin resonance (ESR) was used to detect defect states that have paramagnetic electrons.[7,8] Previous work using ESR shows that HfO_2 has numerous defect states.[9] The most common are Pb-type (Pb0 and Pb1), E′, etc.[9] The Pb-type states are silicon dangling bonds. The two Pb-type on (100) silicon wafers are defined as Pb0 and Pb1.[10] The E′ states are positively charged oxygen vacancies in the Si/HfO_2 interfacial layer.[11] Recent studies indicate that HfO_2 deposition generates a very thin (∼1 nm) SiO_2 interfacial layer on silicon.[12]

The HfO_2 films were 20-nm thick room-temperature atomic-layer-deposited on (100) Si. The resistivity of the silicon substrate was 4000 Ω/cm. This resistivity is needed to obtain adequate ESR measurements.[13] Two sets of HfO_2 samples were irradiated with neutron fluence, which are shown in Table I.

Multiple samples (25) irradiated with the same neutron fluence were used for the ESR measurements. The ESR measurements were performed at room temperature, using a Bruker EleXsys E500 spectrometer working at a frequency of 9.8418 GHz in the first-derivative mode. The ESR data were obtained at a modulation magnetic-field frequency of 100 kHz, a modulation amplitude of 6 G, and, to avoid saturation, a microwave power of 10.02 mW.

The averaged ESR signals are represented by black lines and can be decomposed into the three defect states as shown in Figure 1. Each type of defect has a different g-factor[14] that depends on the microwave frequency and the magnetic field strength as

$$g = \frac{h\nu}{\mu_B B_0},$$

where h is Planck's constant, μ_B is the Bohr magneton $eh/(4\pi m_e)$, ν is the microwave frequency, and B_0 is the magnetic field strength at the peak of ESR absorption for each

TABLE I. Neutron fluence levels irradiated on the two samples.

	Fluence		
Neutron type	Thermal	Epithermal	Fast
Sample 1 (neutrons/cm^2)	1.33×10^{14}	3.84×10^{12}	1.76×10^{13}
Sample 2 (neutrons/cm^2)	1.33×10^{15}	3.84×10^{13}	1.76×10^{14}

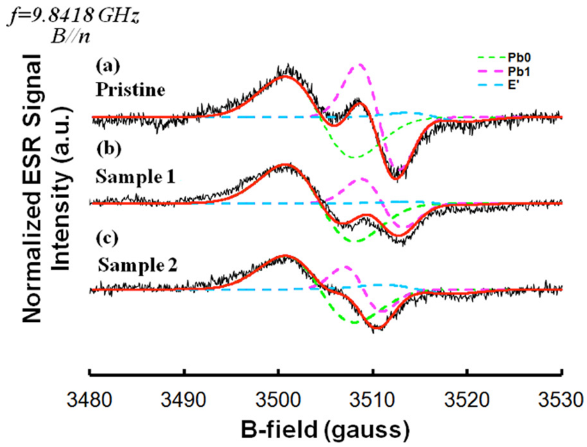

FIG. 1. ESR signals and defect-state fitting curves.

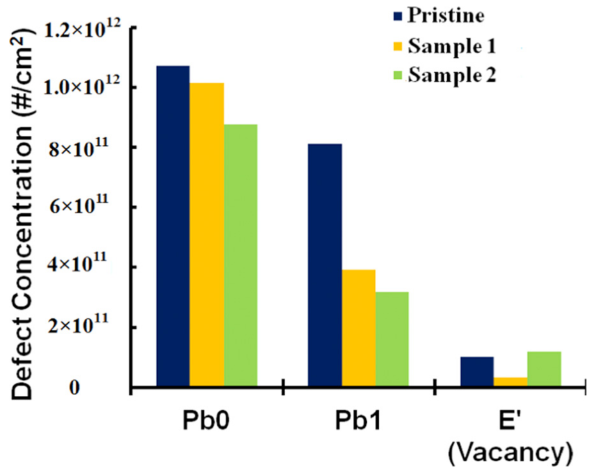

FIG. 2. Absolute values of the defect-state concentrations.

defect. Each defect can also be represented as a Gaussian derivative. The integral of the Gaussian distribution is used to determine the relative concentration of the defects. They can be easily expressed as

$$\mathrm{f}'_{\mathrm{Gauss}}(\mathrm{B}) = -\frac{2A(B-B_0)}{\sigma^2} e^{-\left(\frac{B-B_0}{\sigma}\right)^2}$$

and

$$\mathrm{C}_{\mathrm{Gauss}} = \int_{B-low}^{B-high} f_{Guass}(B)dB \cong \sqrt{\pi}A\sigma,$$

where A, B_0, and σ are found using a least-squares fitting process. A is the amplitude, σ is the B-field-width of the defect state. B_0 allows us to determine the g value of the defect state.[13]

To identify the Pb0, Pb1, and E′ states, ESR measurements were made on unexposed samples as a function of magnetic-field orientation.[15] At $\Theta = 0$ (B-field parallel to the sample normal), the Pb0, Pb1, and E′ states were found to have g values of 2.0062, 2.0037, and 2.0002 respectively, which are typical values.[13]

Next, the HfO_2 samples were irradiated with neutrons. ESR measurements were again made with the B-field parallel to the surface normal of the sample. Using the same least-squares fitting process, the ESR signal was again decomposed into the three defect states.

The measured and fit ESR data for the irradiated samples are shown in Figures 1(b) and 1(c). The corresponding defect states concentrations are shown in Figure 2. The concentration is obtained by comparing the detected signals with that from a 0.0003% KCl weak-pitch sample (3.7×10^{13} spins/cm). In addition, the concentration of E′ centers obtained in this way is consistent with the previous work.[16] Figure 2 shows that the concentration of the Pb0 and Pb1 states decreases after neutron irradiation. The defect concentrations decrease as fluence increases. However, E′, which is the oxygen-vacancy defect, first decreases when fluence increases, but it is followed by a bounce-back upwards in the sample at the highest radiation dose.

There is a large body of literature showing that neutrons can interact with semiconductor material and release a cascade of electron/hole pairs.[17,18] The reaction cross section for reactions decreases rapidly with increasing neutron energy. The decrease generally follows an $1/E$ dependence. Since the HfO_2 in this work was irradiated in a light-water-moderated nuclear reactor where a continuous neutron spectrum is present including thermal, epithermal, and fast ($>$1 MeV) neutrons, it is very likely that electron-hole pairs are generated during irradiation. These electrons can then fill existing Pb and E′ states. Hence, the number of defect states decreases first. However, as the neutron fluence increases, an increasing number of oxygen atoms are knocked out of the lattice structure that then leads to the formation of a greater number of oxygen vacancies.[1]

In the previous studies of high-k gate materials, the leakage current through HfO_2 was usually attributed to Poole-Frenkel emission.[19] The Poole-Frenkel mechanism generates conduction through defect states.[20] Therefore, it is likely that leakage currents in HfO_2 will be influenced by neutron radiation.

The leakage currents of the pristine samples and samples irradiated by three different neutron fluences are shown in Figure 3. Each leakage-current measurement was repeated 5 times for each neutron fluence, and the results shown in Figure 3 are the averages of the data. It is clear that the leakage currents decrease when the radiation fluence increases. This is believed to be due to the decrease in the number of

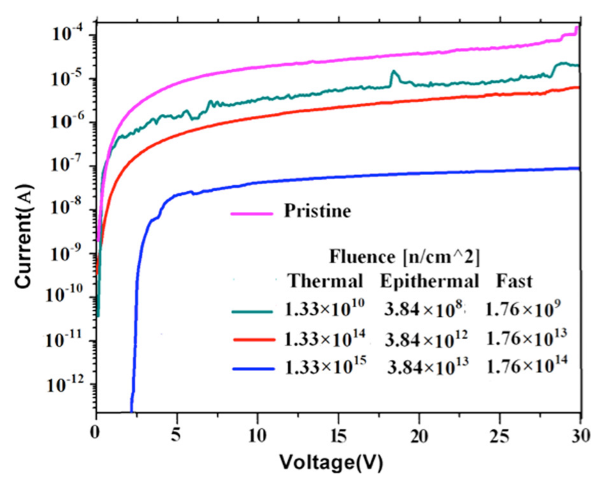

FIG. 3. I-V characteristics of pristine and neutron irradiated HfO_2.

Pb-type defect states as was also shown in the ESR measurements. For pristine samples, the Pb-type defect states that are very near the Si/HfO_2 interface reduce the barrier at the surface of HfO_2, which enhances Poole-Frenkel conduction.[21] However, after neutron irradiation, the number of Pb-type defect states decreases with a concomitant reduction in leakage current. It should be noted that in this experiment, although the E′ state concentration increases at high neutron fluence, this defect has a negligible effect on the leakage current, since the number of E′ states is very small compared with the number of Pb-type states.

In conclusion, we find that neutron radiation decreases the Pb-type defects levels in ultra-thin HfO_2 from electrons filling existing defect states. These electrons come from electron-hole pairs generated by neutron interactions with silicon and oxygen atoms. Thus, we may say that lower doses of neutrons "anneal" the sample. However, when the neutron radiation dose increases, more and more neutrons collide with oxygen atoms and cause them to leave the lattice or to transmute into different atoms. This step then causes the number of E′ states to increase. These defect states are related to the electron transport in HfO_2. Thus, the leakage current of HfO_2 can be modified as the defect concentrations are changed.

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