Nanocrystals Embedded High-k Nonvolatile Memories – bulk film and nanocrystal material effects

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Metal oxide high-k dielectric thin films have been widely used as the gate dielectric in nano-size MOSFETs and nonvolatile memories (NVMs) (1,2). For the former, the major advantage over the conventional SiO_2 is the low leakage current based on the same EOT. However, it has many disadvantages, such as the low crystallization temperature, the high interface density of states, and the low quality interface layer formation. They can be solved by doping the film with a third element, i.e., to form the mixed oxide, and inserting a monolayer of SiO_2 or SiON before the high-k deposition. For the latter, many different principles have been used. For example, the high-k films have been used as the tunnel or control oxide layers in the ONO or floating-gate structure, the resistive switching layer in the RRAM device, the dielectric in MIM capacitor, etc. (2). Also, there are reports of embedding nanocrystals in the high-k dielectrics for the NVM application (2). The advantages include the low charging voltage, e.g., due to the low electron or hole barrier height with Si, the long charge retention time, e.g., due to the discrete charge trapping media and the relative thick tunnel oxide layer, the good reliability properties, e.g., the large breakdown voltage. The device physics on charge trapping, detrapping, and retention have been studied. This kind of device can be easily fabricated with IC-compatible processes without exotic materials.

In this paper, properties of the composing materials and NVM characteristics of the nanocrystals embedded high-k MOS structure will be reviewed and discussed based on published and new data.

The J-V curve of the Zr-doped HfO_2 (ZrHfO) follows the following Poole-Frenkel (PF) emission mechanism:

$$J = E \cdot \exp\left[\frac{-q(\phi_B - \sqrt{qE/\pi\varepsilon_i})}{kT}\right] \qquad (1)$$

where E is the electric field, q is the electron charge, ϕ_B is the barrier height, ε_i is the insulator permittivity, k is the Boltzmann constant, and T is the temperature. Charges are transferred by the field-assisted tunneling mechanism (3). The inclusion of nanocrystals in the ZrHfO film does not change the charge transfer mechanism, e.g., as shown in Figure 1 for the nc-MoO embedded ZrHfO stack (3,4,5). However, nanocrystals embedded samples show the Coulomb blockade peak in the J-V curve in the low V_g region while the ZrHfO sample does not (4,5). The Coulomb blockade peak disappeared at the high temperature because of the loss of the charge retention capability of the nanocrystal.

The lifetime of the stored charges is dependent on where they are stored. Charges are either loosely or deeply trapped. The former are quickly released upon the removal of the stress voltage. The latter are slowly released subsequently. Figure 2 shows the threshold voltage shift of the nc-RuO embedded ZrHfO MOS capacitor on a p-type substrate after -10V and +10V stresses (6). The loosely trapped holes tunneled back to the Si substrate within a few hundred seconds. The deeply trapped holes were gradually released until after 10 years. Most of the electrons trapped at +10V remained in the high-k stack for a few hundred seconds. Then, they were released at a faster rate. The loosely trapped holes were probably located at the nanocrystal/ZrHfO interface while the deeply trapped holes were within the bulk nanocrystal. The trapped electrons were probably located within the nanoscrytal. After release of the stress voltage, they diffused to the surface and subsequently released to the Si substrate. The nc-RuO in ZrHfO can trap more holes than electrons under the same magnitude of applied gate voltage. However, a portion of the trapped holes were loosely trapped.

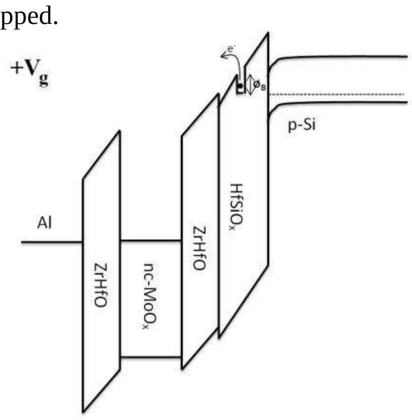

Fig. 1. Field-assisted electron transfer in nc-MoO_x embedded ZrHfO at +V_g condition (4).

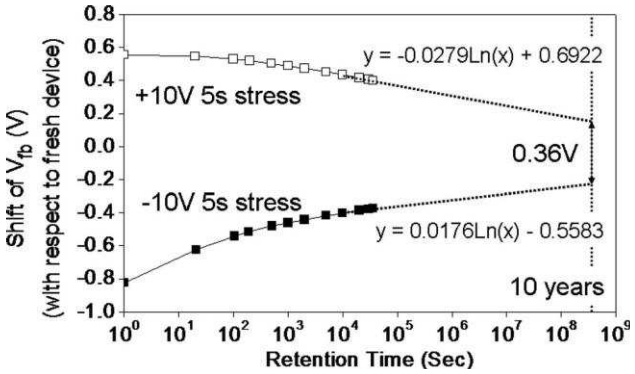

Fig. 2. Hole and electron retention characteristics of the nc-RuO embedded ZrHfO MOS capacitor (6).

Since the ZrHfO high-k film and its HfSiO interface layer with Si trap negligible amount of charges, the embedded nanocrystal determines the preference of charges. For example, most nanocrystals trap both electrons and holes depending on the polarity of the stress voltage (2). The nc-ITO and nc-MoO_x prefer to trap holes instead of electrons (7,8). This phenomenon cannot be explained by the band gap energy or barrier heights. They are related to material properties of the nanocrystal and the interface with ZrHfO, e.g., ITO and MoO_x are n-type semiconductors and the interfaces have different bond structure from the bulk ZrHfO. The charge retention characteristics are also influenced by these properties.

Reliability of the nanocrystals embedded high-k stack, e.g., breakdown induced polarity change, temperature effect on lifetime, and exposure light effects, will be discussed in this talk.

NSF CMMI-0926379 project supported this study.

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