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Model based precise analysis of the injection currents in $Al/ZrO_2/Al_2O_3/ZrO_2/SiO_2/Si$ structures for use in charge trapping non-volatile memory devices

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ABSTRACT

Metal/insulator/Silicon (MIS) capacitors containing multilayered $ZrO_2/Al_2O_3/ZrO_2/SiO_2$ dielectric were investigated in order to evaluate the possibility of their application in charge trapping non-volatile memory devices. The $ZrO_2/Al_2O_3/ZrO_2$ stacks were deposited by reactive rf magnetron sputtering on 2.4 nm thick SiO_2 thermally grown on p-type Si substrate. *C–V* characteristics at room temperature and *I–V* characteristics recorded at temperatures ranging from 297 K to 393 K were analyzed by a comprehensive model previously developed. It has been found that Poole-Frenkel conduction in ZrO_2 layers occurs via traps energetically located at 0.86 eV and 1.39 eV below the bottom of the conduction band. These levels are identified as the first two oxygen vacancies related levels in ZrO_2, closest to its conduction band edge, whose theoretical values reported in literature are: 0.80 eV, for fourfold, and 1.23 eV, for threefold coordinated oxygen vacancies.

1. Introduction

High permittivity (high-κ) dielectrics have started to attract a lot of attention as materials which might be used in new generations of charge trapping non-volatile memory devices [1–4]. Among them ZrO_2 is is particularly interesting due to its high static permittivity [5]. However it crystallizes at relatively low temperatures of about 400 °C. Some authors report that under specific conditions crystallization can occur even at temperatures as low as 250 °C [6]. It is a problem because crystallization creates conductive channels along the grain boundaries, which might extend through the entire ZrO_2 film thus leading to excessive leakage [7]. Insertion of Al_2O_3 layer in the middle of a high-κ ZrO_2 dielectric ($ZrO_2/Al_2O_3/ZrO_2$ or ZAZ) interrupts these paths and consequently decreases the leakage substantially [8,9], while maintaining high permittivity of the dielectric almost unchanged. In addition, doping of ZrO_2 with small amounts of Al ($<$ 8 at %) increases the temperature of crystallization [10]. It has been shown that boron incorporation also raises the temperature of crystallization [11].

The interfacial SiO_2 layer plays an important role in the manifestation of the dominant conduction mechanism [12]. In order to attain better understanding of conduction and charging/discharging mechanisms in metal/SiO_2/high-κ/SiO_2/silicon (MOHOS) devices of interest, in this work we study simplified metal/high-κ/SiO_2/Si (MHOS) structures containing stacked $ZrO_2/Al_2O_3/ZrO_2$ high permittivity dielectric and Al metal gate ($Al/ZrO_2/Al_2O_3/ZrO_2/SiO_2/Si$). Analysis of the experimental leakage current characteristics is performed by employing a comprehensive model we previously proposed for other high-κ dielectrics [13]. Theoretical and experimental findings on various defects existing in ZrO_2 are taken into account and the results are interpreted in close connection with these findings.

2. Theory

The theoretical analysis in this paper is based on our comprehensive model for metal-Ta_2O_5/SiO_2–Si structures, explained in details in [13]. Here we present shortly the modified model for Al–$ZrO_2/Al_2O_3/ZrO_2/SiO_2$–Si structures.

The band diagram of an Al-ZrO_2/SiO_2-Si structure is given in Fig. 1. This diagram is obtained by upgrading the diagram we used in [13] with the data for ZrO_2/SiO_2 stacks from the work [14].

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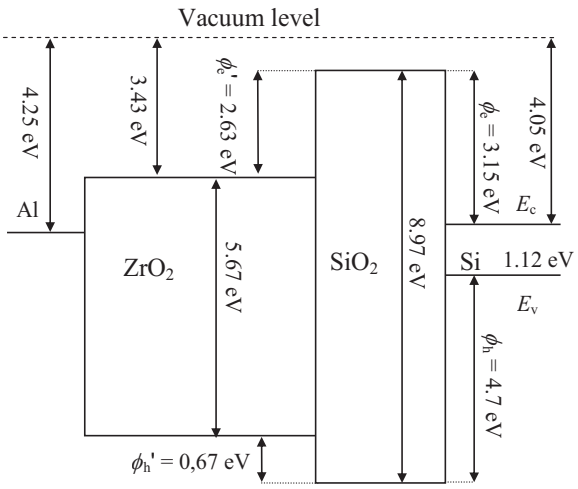

Fig. 1. Band diagram of the Al-ZrO_2/SiO_2-Si structure used in this work.

Somewhat different values of the parameters included in the diagram can be find in the works of other authors obtained either experimentally [15,16] or theoretically by *ab initio* calculations [17], but in principle they are close to the values used in this work and lead practically to the same results. We shall use the same band diagram for the Al–ZrO_2/Al_2O_3/ZrO_2/SiO_2–Si structure since it is expected the extremely thin Al_2O_2 layer inserted between two ZrO_2 layers to modify only some bulk properties such as the effective densities of defects responsible for trapping and conduction, and not the band offsets.

The conduction mechanisms considered as dominant in charge transport through the studied structures are:

1. For the injecting SiO_2 layer, hopping conductivity and direct tunneling through a trapezoidal barrier or Fowler-Nordheim tunneling through a triangular barrier, depending on the electric field in this layer (E_{so}). Tunneling current can be created by electrons or holes. The barrier for the tunneling of holes is substantially higher than the barrier for electrons [18]. Different carriers from the silicon substrate produce this current: electrons in the case of gate positively biased and holes in the case of gate negatively biased [19]. Hence, the current density for the same absolute value of the voltage depends upon the gate polarity.
2. For ZrO_2/Al_2O_3/ZrO_2 stack (ZAZ), hopping conductivity and Poole–Frenkel mechanism, which are both bulk-limited, and hence independent on the polarity.

Considered mechanisms are illustrated in Fig. 2 for positive (a) and negative (b) gate polarity with respect to the substrate (hopping conductivity is not included in this illustration).

At gate positively biased electrons tunnel from the conduction band of Si through the SiO_2 layer to traps in ZrO_2, then they are emitted into the conduction band by Poole-Frenkel mechanism and after multiple trapping and emissions arrive to the interface with Al where they enter into the conduction band of Al. It has been shown that there are oxygen vacancy related defects in ZrO_2 approximately 1 eV below the bottom of the conduction band. In [20] it has been found that there are localized electron energy levels of 0.8 eV and 1.23 eV below the bottom of the conduction band of ZrO_2, both slightly below the bottom of the conduction band in Si. They correspond to the electrons weakly bonded to fourfold and threefold coordinated oxygen vacancies, respectively. In [20] the Poole-Frenkel conduction was attributed to the level corresponding to fourfold coordinated oxygen vacancy; we expect that the threefold oxygen vacancies can also be important under

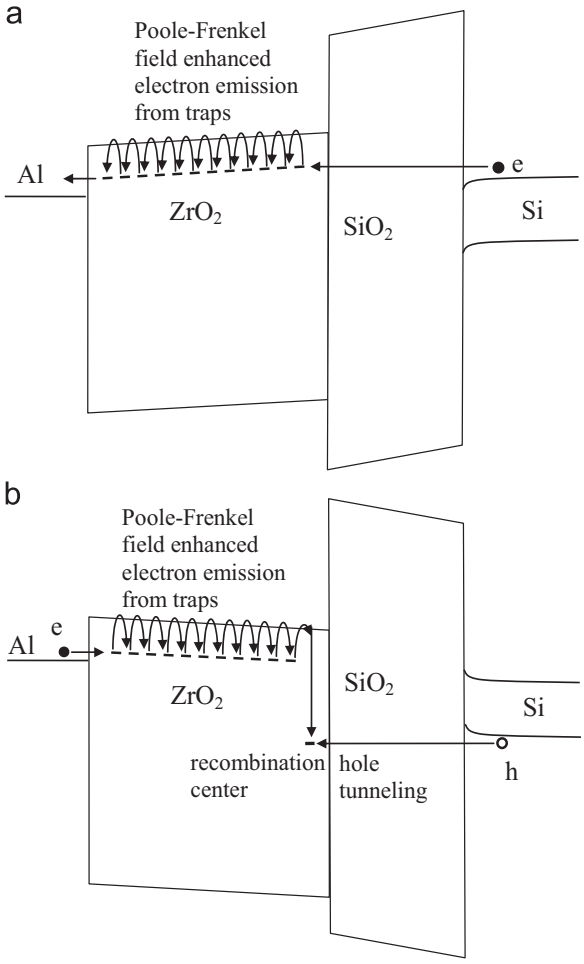

Fig. 2. (a) Charge transport at gate positively biased, excluding hopping conductivity in both layers; electrons tunnel from the conduction band of Si through the SiO_2 layer to traps in ZrO_2, then they are emitted into the conduction band by Poole-Frenkel mechanism and after multiple trappings and emissions arrive to the interface with Al where they enter into the conduction band of Al and (b) charge transport at gate negatively biased, excluding hopping conductivity in both layers; electrons tunnel from the Al conduction band to traps in ZrO_2, then they are emitted into the conduction band by Poole-Frenkel mechanism and after multiple trapping and emissions arrive to the interface with SiO_2 where they recombine with the holes via deep recombination centers.

specific conditions. At low fields conduction by Poole-Frenkel mechanism is expected to be dominant [21], while for higher fields, phonon assisted tunneling takes place [22,23].

At gate negatively biased, electrons tunnel from the Al conduction band to traps in ZrO_2, then they are emitted into the conduction band by Poole-Frenkel mechanism and after multiple trapping and emissions arrive to the interface with SiO_2 where they recombine via deep recombination centers with the holes injected by tunneling from the substrate. It is to be noted that the trap located at 0.8 eV below the conduction band of ZrO_2 is practically on the same energy level as the Fermi level in Al. Thus the probability for electrons to tunnel from Al into ZrO_2 to the closest defect site is extremely high and could not be expected to limit the conduction of the stack [13]. Further, possible recombination centers can be those identified in [24,25] by photoluminescence and attributed to oxygen vacancy distorted ZrO_2 lattice cells. The levels of these centers form a large band within 2.0 eV to 3.2 eV relative to the conduction band edge of ZrO_2. This corresponds to a band extending from the top of the valence band of silicon to about 1 eV down towards the valence band edge of ZrO_2. Therefore, there are states in this band available for tunneling of holes from the valence band of Si into ZrO_2 at various