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Analysis of the improvement of Al–Ta_2O_5/SiO_2–Si structures reliability by Si substrate plasma nitridation in N_2O

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ABSTRACT

Reliability properties of 30-nm thick insulating films grown by thermal oxydation of Ta deposited on plasma nitrided Si for times varying from 5 to 15 s were studied for the case of constant current stresses. Stress-induced leakage currents of thus obtained Ta_2O_5/SiO_xN_y stacked layers with the stress were monitored by the evolution of the parameters extracted with the use of our recently developed comprehensive model for leakage currents. It is concluded that the nitridation of the substrate prior to the Ta_2O_5 formation, simultaneously with the increase of the dielectric constant of the stack and the decrease of the leakage currents in fresh samples, improves the reliability properties against constant current stress. The increased charges to breakdown and the decreased trapping in the insulating film were explained by the improved resistance of the interface with substrate to the stress due to the incorporation of a small amount of nitrogen atoms. Since the N atoms are much stronger bonded to the Si substrate, the nitrided interface becomes more resistant to the stress. The optimum observed for nitridation times of about 10 s was explained by the strengthening of the interface with N-atoms without excessive growth of the SiO_xN_y–Si interfacial layer and without excessive lowering of its injection barriers.

1. Introduction

High permittivity (high-*k*) dielectric materials are nowadays extensively studied as a replacement of the silicon dioxide in various microelectronic applications [1–3]. Specifically, tantalum pentoxide was found to be exceptionally convenient for the use as a dielectric in dynamic random access memories (DRAM) [4]. Effects of various technological processes aimed at further improvement of its dielectric and reliability properties are studied [5–6] for the applications in nanoscale DRAMs [7]. Between them the nitridation of tantalum pentoxide layers attracts particular interest [8]. Reliability properties of such dielectrics are studied by various stress tests [9].

Due to the thermodynamical instability of the Ta_2O_5/Si interface, an unavoidable interfacial layer formation occurs. Therefore, thus obtained dielectric has to be studied as a non-uniform or a stacked layer. In numerous important cases, the insulating film can be considered to be composed of two homogeneous parts: a Ta_2O_5 and an SiO_2-like interfacial layer. Previously we have developed and used a model for description of the electrical properties of metal-Ta_2O_5/SiO_2–Si structures [10,11]. The above model was applied to the analysis of the stress-induced leakage currents in these structures [12], as well as to the combined conduction and charge analysis [13]. This model is based on the method used much earlier by Frohman–Bentchkowsky and Lenzlinger for describing leakage currents in metal–nitride–oxide–silicon structures [14]. Chanelliere et al. applied a similar method to study various types of Ta_2O_5/SiO_2 and Ta_2O_5/Si_3N_4 stacked strucuttres on Si, but only in the case of positive gate polarity, where electrons are injected from the substrate [15]. As we found in [10], in the case of negative gate, an injection of holes from the substrate occurs, since there are almost no free carriers in Ta_2O_5 layer to be injected into the SiO_2 interfacial layer. In the case of SiO_2 interfacial layers, values of band offsets for electrons and holes obtained by our model precisely agree with the best known literature data from independent experiments, while for films grown on nitrided substrates they provide good agreement with the known SiO_xN_y bandgaps.

It is known that the nitridation of the substrate in N_2O or NH_3 improves the dielectric and leakage properties of the films [16]. Our study on the electrical and dielectric properties of rf-sputtered Ta_2O_5 films on rapid thermally nitrided substrates in N_2O or NH_3 showed that the improvement is due to the increased permittivity of the interfacial layer with nitrogen incorporation, without substantial decrease of the injection barrier heights [17]. Substrate nitridation in soft plasma before Ta_2O_5 growth substantially improves the dielectric and electrical properties of the insulating film [18].

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Reliability properties of ultrathin insulating films attract particular attention, since these films are subject to violent electric field/current stresses. The well known destructive dielectric breakdown being the most important reliability property for thicker films also applies for ultrathin films [19,20], but as the thickness of the insulating film decreases, the so called progressive breakdown, manifested by appearance of increased fluctuations of the applied voltage at a constant current stress, comes out to be more important [20]. Some authors use the term progressive wear-out [21], since quite often the electrical properties degrade continuously with the stress time. Besides charge trapping [22,23] and trap generation [24], stress-induced leakage current is an important measure of the degradation [25]. Even without manifested breakdown event of various types (hard destructive breakdown, soft breakdown or progressive breakdown), the reliability of the insulating films and devices that include them is limited by the increase of the leakage up to unacceptably high values.

There are few studies of the breakdown of tantalum oxide films [26]. In [27] we observed an improvement of the reliability properties with nitridation in soft plasma, as manifested by increased charges to breakdown and lowered trapping. In [28] we reported stress-induced leakage current analysis for one particular case. In this work we present the detailed analysis of the effect of soft plasma substrate nitridation on the reliability properties of Ta_2O_5 films obtained by thermal oxidation of Ta and discuss the origin of this improvement. The contributions of the Ta_2O_5 bulk, the interfacial layer and interface with substrate were separately studied, since the nitridation influences simultaneously the interfacial layer thickness and its properties, as well as the structure and properties of the interface with substrate that is known to play important role in the reliability properties of ultrathin insulating films on silicon [29]. As obtained from the above analyses, the contribution of the Ta_2O_5 bulk is not significantly affected with the nitridation, and hence it will not be discussed later.

2. Experiment

Chemically cleaned p-type (100) 15 Ω cm Si wafers were nitrided at room temperature for 5, 10 and 15 s in N_2O soft plasma. Tantalum films were deposited on thus nitrided substrates by rf sputtering of a Ta target in Ar atmosphere. Subsequently, Ta films were oxidized in dry O_2 at 600 °C. The oxidation temperature was chosen to be low enough to minimize the substrate oxidation and to prevent the formation of tantalum silicide. The thickness d and the refractive index of the insulating films were measured by ellipsometry ($\lambda = 832.8$ nm). The refractive index n was typically 2.1 and the thickness $d = 30$ nm. Al films for top electrodes were deposited by evaporation. Square gates for metal-insulator-Si capacitors with an active area of 2.5×10^{-3} cm^2 were defined by photolithography. The fabrication sequence was finalized by a conventional MOS technology post-metallization annealing in H_2 at 450 °C for 1 h.

I-V (current-voltage) characteristics as well as the high frequency (50; 100 kHz and 1 MHz) *C-V* (capacitance-voltage) characteristics were measured on Al gate MOS capacitors with areas 2.5×10^{-3} cm^2, both for fresh and for stressed samples at constant current density $J = 10$ mA/cm^2, and different stress times t, ranging from about 10 s to 1000 s. *C-V* characteristics were measured with the use of a HP 4284A LCR meter. *I-V* characteristics were obtained by using a HP 4140 A picoampermeter/DC voltage source, for both positive and negative gate polarity, in the voltage range from −3 to 3 V, where no visible wearout or charge trapping occurs during the measurement. Current was measured in steps of 0.1 V, with a hold time of 5 s, allowing obtaining negligible displacement currents. Constant current was generated with a HP 3245 A universal source and the gate voltage evolution during the stress followed by a HP 3458 A system multimeter. Both the uninterrupted and the interrupted stress gate voltage variations were recorded.

3. Theory

The theoretical analysis is based on our comprehensive model for Ta_2O_5/SiO_2 structures, explained in details in [11]. Here we present shortly the modified model for Ta_2O_5/SiO_xN_y structures.

The conduction mechanisms considered in this study to be the most important are:

1. For the interfacial SiO_xN_y layer, direct tunneling through a trapezoidal barrier or Fowler–Nordheim tunneling trough a triangular barrier, depending on the electric field in the layer (E_{IL}). Tunneling current can be created by the electrons or the holes. The barrier for the tunneling of holes is substantially higher then the barrier for electrons. 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 [10]. Hence, the current density for the same absolute value of the voltage depends upon the gate polarity.
2. For tantalum pentoxide, Poole–Frenkel mechanism, that is bulk-limited, thus independent on the polarity. The above assumption has been confirmed experimentally on metal-Ta_2O_5-metal structures [30].

Direct tunneling current density through the interfacial SiO_xN_y layer (J_{IL}) is given by the following expression:

$$J_{IL} = \frac{q^2}{8\pi h\Phi}E_{IL}^2 \times \exp\left(-\frac{8\pi\sqrt{2m^* q\Phi^3}}{3hE_{IL}}\left(1-\left(1-\frac{d_{IL}}{\Phi}E_{IL}\right)^{3/2}\right)\right). \tag{1}$$

and Fowler-Nordheim tunneling by:

$$J_{IL} = \frac{q^2}{8\pi h\Phi}E_{IL}^2 \exp\left(-\frac{8\pi\sqrt{2m^* q\Phi^3}}{3hE_{IL}}\right) \tag{2}$$

where q is the electron charge, h is the Planck's constant, m^* is the effective tunneling mass of carriers in SiO_xN_y, d_{IL} is the thickness of SiO_xN_y layer, Φ is the tunneling barrier height, and E_{IL} is the electric filed in the SiO_xN_y layer.

The voltage drop on the SiO_xN_y layer (V_{IL}) is:

$$V_{IL} = E_{IL}d_{IL}. \tag{3}$$

The current density due to the Poole–Frenkel effect in the Ta_2O_5 layer (J_{TP}) is given by the following expression:

$$J_{TP} = \sigma_{TP}E_{TP}exp\left(\frac{1}{kT}\sqrt{\frac{q^3}{\pi\varepsilon_0 K_T}}\sqrt{E_{TP}}\right). \tag{4}$$

where E_{TP} is the electric field in the Ta_2O_5 layer, σ_{TP} is temperature-dependent defect-related constant having dimensions of conductivity, k is the Boltzmann constant, ε_0 is the dielectric constant of vacuum and $K_T = n^2$ is the optical frequency dielectric constant (n is the refractive index) of Ta_2O_5.

The voltage drop on the Ta_2O_5 layer (V_{TP}) is given by:

$$V_{TP} = E_{TP}d_{TP}. \tag{5}$$

where d_{TP} is the thickness of the Ta_2O_5 layer. The two quantities that are computed simultaneously here are the oxide voltage:

$$V_{ox} = V_{TP} + V_{IL} = d_{TP}E_{TP} + d_{IL}E_{IL}. \tag{6}$$

and the current density in steady state (Kirchhoff's laws)

$$J = J_{TP} = J_{IL}. \tag{7}$$