



High- k HfO_2 - Ta_2O_5 mixed layers: Electrical characteristics and mechanisms of conductivity

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ABSTRACT

Electrical properties of mixed HfO_2 - Ta_2O_5 films (10;15 nm) deposited by rf sputtering on Si have been studied from the view point of their applications as high- k layers, by standard capacitance–voltage and temperature dependent current–voltage characteristics. The effect of HfO_2 addition to the Ta_2O_5 is thickness dependent and the thicker layers exhibit advantages over the pure Ta_2O_5 (higher dielectric constant, enhanced charge storage density and improved interface quality). The process of HfO_2 and Ta_2O_5 mixing introduces negative oxide charge, tends to create shallow bulk traps and modifies the dominant conduction mechanisms in the stack capacitors as compared to the Ta_2O_5 -based one (a contribution of tunneling processes through traps located below the conduction band of mixed layers to the leakage current in the HfO_2 - Ta_2O_5 stacks is observed). The traps involved in both Poole–Frenkel and tunneling processes are identified.

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1. Introduction

The doped and multicomponent high- k dielectrics based on a variety of metal oxides are a new trend in high- k alternatives engineering. The introduction of a small quantity of a number of elements in high- k films is a way for extending the potential of the pure material and to suppress the negative effect of the lower- k interfacial layer thereby allowing further scaling of the equivalent oxide thickness. To date, Ta_2O_5 has been recognized as one of the best high- k dielectric for storage capacitors of nanoscale dynamic random access memories (DRAMs) [1–6]. The doping-induced variation of its properties depends not only on the type of dopant and its amount but also on the method of doping and the fabrication process of Ta_2O_5 itself [7–14]. Since the structure of Ta_2O_5 does not change significantly after addition of another oxide [15] it is a good base material for doping. We have previously shown that the doping of Ta_2O_5 with Ti (by different doping methods) [10,11] affects the dielectric, electrical and reliability characteristics of the stacks, and the mechanism of the observed current reduction is considered to be due to Ti-induced compensation of existing oxygen vacancies. In the more recent study [16] we have demonstrated the Hf incorporation in sputtered 7–20 nm Ta_2O_5 films is effective in achieving stacks with higher permittivity and lower leakage current compared to the pure Ta_2O_5 stacks. Most of the results available in the literature for the modified Ta_2O_5 -based dielectrics are in fact for doped Ta_2O_5 , and the data on mixed

Ta_2O_5 film with another metal oxide (binary or ternary mixtures) are almost missing.

The purpose of this work is to investigate the electrical characteristics of stack structure composed of HfO_2 - Ta_2O_5 mixed layer on Si, based on our results previously acquired [2,6,12,17–21] on the properties of Ta_2O_5 stacks. The main motivation of the study is to examine how the combination of the two most favorable high- k metal oxides, respectively, for MOSFETs (HfO_2) and for DRAMs (Ta_2O_5) applications, performs as a high- k layer in terms of permittivity, allowable level of leakage current and appropriate oxide and interface properties. Both HfO_2 and Ta_2O_5 sublayers are rf sputtered consecutively one over the other. The more specific aim is to obtain information whether this complex-oxide is better than the pure Ta_2O_5 in the terms of permittivity and leakage current. Capacitance–voltage (C - V) and current–voltage (I - V) measurements are used to characterize electrical behavior of the stacks. A special focus of the study is on the mechanisms of conductivity in the composite stacks.

2. Experimental procedure

Chemically cleaned p-type (100) 15 Ωcm Si wafers were used as substrates (the native oxide was removed by etching in 1% HF solution; no deionized water rinse was performed in an effort to minimize the formation of a new oxide film). The HfO_2 layer with two thicknesses of 5 and 7 nm was deposited by rf sputtering of Hf target in Ar + 10% O_2 atmosphere on the top of rf sputtered Ta_2O_5 with the same thicknesses. In a number of papers [2,17–19] we have shown that high quality Ta_2O_5 layers with a

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dielectric constant, (corresponding to thick films) of about 37 and leakage current below 10^{-8} A/cm² at 1 MV/cm can be obtained by rf sputtering of Ta in Ar + 10% O₂. These optimized conditions were used here for the fabrication of the composite films. The wafer temperature was maintained at 200 °C during the deposition of the two types of films; the working gas pressure was 0.33 Pa and rf power density was 3.6 W/cm²; Ta and Hf targets both with a purity of 99.99 % were used. Before deposition of each film the targets were pre-sputtered in pure Ar atmosphere in order to remove surface target contaminations. Post-deposition annealing was performed in N₂ at 400 °C for 30 min in order to mix both films. It is also expected the passivation of oxygen vacancies in HfO₂ and Ta₂O₅ sublayers by nitrogen which has similar atomic radius as oxygen. The total film thickness, d and the refractive index, n were measured by ellipsometry ($\lambda = 632.8$ nm); the physical thickness of the stacked films was 10 and 15 nm. Relatively large layer thicknesses were intentionally used in order to minimize the very small thickness-related effects and to study the effect of layers intermixing itself. All films have a refractive index ~ 2.1 , i.e. it was not possible to distinguish ellipsometrically the difference in n between Ta₂O₅ and composite HfO₂-Ta₂O₅ layers. According to X-ray diffraction analysis both types of films the pure Ta₂O₅ and the HfO₂-Ta₂O₅ were amorphous. The test structures for electrical measurements were MIS capacitors with a back side electrode of ~ 300 nm evaporated Al. The top electrode was also Al with gate area of 1×10^{-4} cm² defined by photolithography. When it was necessary (mainly for precise study of the film conductivity) the HfO₂-Ta₂O₅-based capacitors were compared to reference MIS structures containing Ta₂O₅ films with the same thickness. A post-metal annealing (PMA) was performed in forming gas (95% N₂ and 5% H₂) at 450 °C for 1 h. The capacitors were electrically characterized by means of C-V and I-V curves. The effective dielectric constant ϵ_{eff} of the films was determined from the capacitance C_0 at an accumulation using ellipsometrically measured values of d . The oxide charge Q_f was evaluated from the C-V curves. The I-V curves were recorded at both polarities with a voltage ramp rate of 0.1 V/s, using Keithley 236 source measurement unit. Temperature dependent (20–100 °C) I-V measurements were performed in order to obtain a deeper insight into the conduction mechanisms governing the current through the structures as well as the energy location of traps participating in these processes. All measurements were carried out in a dark chamber.

3. Results and discussions

3.1. C-V curves and dielectric properties

The C-V curves were obtained by sweeping the applied voltage from accumulation to inversion and back at a ramp rate of 50 mV/s. Fig. 1 shows curves for capacitors with HfO₂-Ta₂O₅ films; the 10 nm pure Ta₂O₅ curve is presented for comparison; the curve corresponding to 15 nm Ta₂O₅ (not shown) is similar. ϵ_{eff} value of pure Ta₂O₅ (determined from C_0 at applied voltage of -2.5 V) is 6.3 and no well pronounced dependence on film thickness was observed. The capacitance at -2.5 V results in the same ϵ_{eff} for 10 nm HfO₂-Ta₂O₅ films and a higher one ($\epsilon_{\text{eff}} = 9.5$) for 15 nm mixed films, i.e. the effect of HfO₂ on the overall dielectric constant is negligible in the former case and is measurable in the latter one. The higher dielectric constant of 15 nm mixed oxides than 10 nm ones reflects generally the known thickness dependence of high- k films permittivity. The decrease of ϵ_{eff} with film thickness refers to slightly lowered density of thinner layer and/or to stronger effect of the interfacial layer. It should be mentioned that the interpretation of C-V curves of dielectric stacks with variable composition is very complicated and requires special attention, but here the C-V

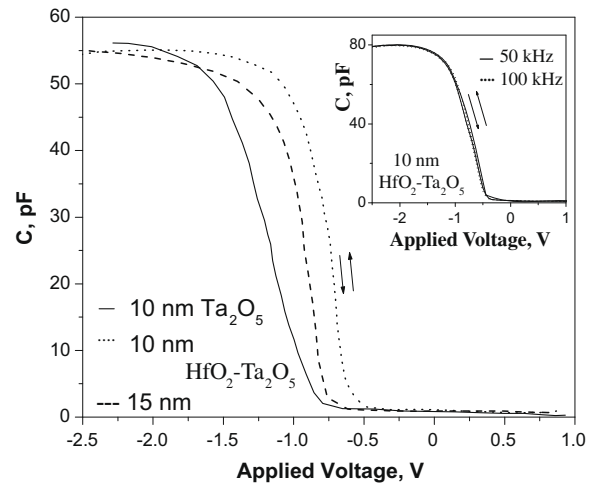


Fig. 1. 1 MHz C-V curves of capacitors with Ta₂O₅ and HfO₂-Ta₂O₅. The inset shows 50 and 100 kHz curves of 10 nm mixed film. The arrows indicate the hysteresis direction.

data will be used to extract only some general parameters of the capacitors. The dielectric constant ϵ_t of the bulk high- k dielectric is evaluated from ϵ_{eff} assuming a stack capacitor (bulk high- k and interfacial layer at Si). According to our earlier investigations of Ta₂O₅ on Si with X-ray photoelectron spectroscopy and transmission electron microscopy analyses [17,22], the interfacial layer is SiO₂-like one ($\epsilon_{\text{int}} = 3.9$), with a thickness $d_{\text{int}} = 1$ nm. Assuming intact by the mixing interfacial layer, the corresponding value ϵ_t of the bulk dielectric constant calculated considering series capacitance model was 6.7 and 10.6 for 10 and 15 nm mixed oxides, respectively. So following the effect of HfO₂ addition to Ta₂O₅ on the ϵ_{eff} values, ϵ_t also increases for thicker and does not change for thinner films; ϵ_t ranges from 6.7 to 9.5 when thickness of pure Ta₂O₅ varies from 10 to 15 nm. The properties of the reference samples and their parameters as evaluated by both C-V and I-V measurements are in accordance with our previous results on Ta₂O₅ stacks and further we will not note this for each individual case. A number of sources of errors in these calculations should be kept in mind but an increase of the permittivity measured at 1 MHz for capacitors with 15 nm HfO₂-Ta₂O₅ films compared to Ta₂O₅ is definitely observed. The films experience some structural modifications during the mixing of Ta₂O₅ with HfO₂ and this results in a change of ϵ_{eff} . These modifications have obviously negligible effect on permittivity of 10 nm films as determined from 1 MHz curves. It was reported [14] that the ϵ_{eff} of Hf-doped Ta₂O₅ is a sensitive function of Hf concentration: ϵ_{eff} decreases in the high Hf concentration range; a non-linear improvement of the dielectric constant in lightly Hf-doped Ta₂O₅ was observed and was attributed to the change of either molar volume or localized bonding order in the bulk high- k layer. The purpose here is not to clarify the mechanism of permittivity variation as a result of mixing and we only acknowledge the contribution of possible effects. In addition, the permittivity values extracted from 1 MHz curves are usually underestimated due to the well-known effect of series resistance on the capacitance at accumulation which is stronger at higher frequencies. Therefore, higher values of permittivity at lower frequencies are expected and ϵ_{eff} extracted from 100 kHz C-V curves of 10 nm mixed films (inset of Fig. 1) is higher indeed: 9 against 6.3 at 1 MHz. Respectively, ϵ_t value at 100 kHz is 10.5 (against 6.8 at 1 MHz). The charge storage density defined by $Q_c = \epsilon_0 \epsilon_t E$, where ϵ_0 is the permittivity of the free space, and E is the applied field across the stack was calculated to be 9.4 fC/ μm^2 for 15 nm HfO₂-Ta₂O₅ layers at $E = 1$ MV/cm. For 10 nm films the value is 5.9 fC/ μm^2 . Q_c for pure Ta₂O₅ do not depend on d and is

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