High-\(k\) HfTaO stacks in response to microwave irradiation

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Abstract. The effect of microwave treatment (6-15 s) at room temperature on the leakage current and mechanisms of conductivity in mixed HfTaO (10 nm) stacks has been studied by temperature dependent (20-100°C) current-voltage characteristics. It was established that the short 6 s irradiation affects the electrically active centers in the stack, provokes modification of the dominant conduction mechanism and improves the temperature stability of capacitors manifesting as low level of current at high temperatures (current decrease up to 4 orders of magnitude at 100°C after the treatment is detected). The traps involved in the conduction process in pre- and post-irradiated capacitors are identified.

1. Introduction

The doped high-\(k\) materials and the composite films of two or more high-\(k\) films were recognized as the next step in the way of extending the potential of pure high-\(k\) dielectrics [1]. A doping or mixing-induced improvement of these insulators, allowing further scaling of equivalent oxide thickness, was observed and the mechanism of improvement was considered to be oxygen vacancy compensation by the ions of dopant. The focus on Ta\(_2\)O\(_5\) (the most attractive high-\(k\) alternative for nanoscale dynamic random access memories) is currently shifted on Ta\(_2\)O\(_5\) doped with different elements or mixed with other high-\(k\) films [2,3]. Recently, [4] we have reported that mixing of Ta\(_2\)O\(_5\) with HfO\(_2\) modifies the traps resulting in a change of the dominant conduction mechanism in comparison to pure Ta\(_2\)O\(_5\) stack. We have also shown that seconds of microwave irradiation of pure Ta\(_2\)O\(_5\) [5] at room temperature could be successfully used as an alternative to high temperature annealing steps, and this is a way to avoid some high-temperature processes obstacles as partial crystallization of the films. The big advantage of this treatment is the strongly reduced thermal budget (room temperature, extremely short exposure times). The results imply that the specific manifestation of the effect of microwave treatment is a function of the initial parameters of high-\(k\) stack, and hence we are motivated here to study the impact of this irradiation on the trap parameters and conduction mechanism in the composite HfTaO films.

2. Experimental procedure

Chemically cleaned p-type (100) 15 \(\Omega\)cm Si wafers were used as substrates. The HfTaO mixed layers were obtained by consecutive deposition of 5 nm HfO\(_2\) film on the top of 5 nm Ta\(_2\)O\(_5\) film. The HfO\(_2\) and Ta\(_2\)O\(_5\) films were deposited by rf sputtering of Hf and Ta targets, respectively, in Ar +10\% O\(_2\) atmosphere. Ta and Hf targets with purity of 99.99\% were used. Optimized conditions [6] guaranteeing Ta\(_2\)O\(_5\) with high dielectric constant (up to 37) and low leakage currents (< \(10^{-9}\) A/cm\(^2\) at
1 MV/cm) were used for the fabrication of the composite films. The wafer temperature during the deposition of both films was 200°C; the working gas pressure was 0.33 Pa and rf power density was 3.6 W/cm². Details on the deposition conditions are presented in [4]. Post-deposition annealing in N₂ at 400 °C for 30 min was performed, in order to mix the two layers. The total film thickness d and the refractive index n were measured by ellipsometry, \( d = 10 \text{ nm}, \ n = 2.1 \). MIS capacitors with Al gate (area of \( 1 \times 10^{-4} \text{ cm}^2 \)) were used as test structures. A post-metal annealing was performed in a forming gas at 450 °C for 1 h. The capacitors were exposed to microwave irradiation in a magnetron (2.45 GHz, power density of 1.5 W/cm²) at irradiation time of \( t_i = 6-15 \text{ s} \). The temperature of the samples during the exposure was close to the room one. The heating due to the irradiation itself does not exceed ~ 50 °C, and consequently does not lead to some annealing effect. This heating is considered as a feature of the irradiation effect. The irradiation affects neither \( d \) nor the refractive index of the films. According to X-ray diffraction analysis pre- and post- irradiated films are amorphous. Temperature dependent (20-100°C) current-voltage (J-V) curves were recorded before and after irradiation with a ramp rate of 0.1 V/s using Keithley 236 source meter unit in a dark chamber.

3. Results and discussion

Figure 1 compares the J-V curves at room temperature before and after microwave treatment. There is no measurable effect of 6 s exposure on the curves. J reduces with increasing \( t_i \) from 6 to 10 s for the whole applied field range and further the current does not longer change with increasing \( t_i \), i.e. ~ 10 s irradiation is effective enough for the current reduction to the constant value below \( 10^{-7} \text{ A/cm}^2 \). This confirms our previous results [5] indicating the presence of optimal exposure time to improve the current; the exact value of this optimal time depends on the composition of high-\( k \) film and \( d \), but in all cases \( t_i \) is of the order of seconds. The behavior of the curves for 10-15 s treated stacks (the current is nearly constant up to the appearance of breakdown events) does not enable to invoke any of the commonly observed in high-\( k \) layers conduction mechanisms. With increasing the temperature the shape of the curves is preserved, only the start of the breakdown events moves to lower applied voltage reaching about -1 V at \( T \approx 90-100^\circ \text{ C} \). With this in mind we will focus on the J-V characteristics of the initial and 6 s irradiated capacitors (figure 2). The asymmetry of the curves observed between forward (negative voltage) and reverse bias (positive voltage) is mainly due to the difference in the barrier heights at Al and Si interfaces, and the saturation of J at reverse biases is assigned to the limited amount of available minority carriers in the space charge region of the substrate. The curves at positive applied voltage are actually an electrical manifestation of the properties of the interfacial layer at Si. The differences in the shape of the right part of the curves in figure 2 suggest a measurable effect of the microwave treatment on the interface layer at Si, which manifests itself as low level of current at high temperatures. The current as low as \( 10^{-7} \text{ A/cm}^2 \) is

![Figure 1](image-url)
detected in the very low voltage region around zero bias; this current and the observed current fluctuations are attributed to a transient conductivity which has weak field dependence and can be detected only when the steady state conduction is negligible [7]. So the treatment provides lower $J$ at high temperatures for reversely biased electrode and changes the shape of curves: the saturation level of the current at 100°C is two orders of magnitude lower than the corresponding level of non-irradiated samples. Improved temperature stability after irradiation is also observed at forward biases. The current strongly increases (~ 6 orders of magnitude) in the non-irradiated capacitors as $T$ changes from 20 to ~ 40°C; further the current rise with increasing $T$ to 100°C is negligible. The increase of $J$ is due to temperature stimulated detrapping of electrons and as is seen a thermal activation takes place even at 40°C. The shape of the curves measured at different $T$ is significantly changed after the treatment, indicating radiation-induced modification of the mechanism of conductivity. The change of $T$ from 20 to 100°C increases by an order of magnitude the current of irradiated capacitors but finally $J$ at 100°C is more than $10^2$ smaller than $J$ of the initial samples. Two regions in the curves of irradiated stack can be identified: a gradual increase of the current with the temperature in the low voltage region; when the applied voltage becomes more negative the leakage current is not affected by the temperature in the interval of 20-80°C, and further at $T$ ~ 90-100°C it increases almost $10^3$. The irradiation lowers the current at high (~80-100°C) temperatures ~ 3 orders of magnitude at -0.5 V applied voltage and keeps a constant current at fields of ~ 2 MV/cm in the temperature interval 20-80°C. The improved temperature stability is generally assigned to the irradiation-induced annealing of both the damaged interface at Al gate (as a result of reaction between Al and the mixed film, quite possible scenario for layer containing Ta$_2$O$_5$) [7] and the oxygen vacancies in the bulk of high-$k$ layer. The conduction in Ta$_2$O$_5$ is usually interpreted with Poole-Frenkel (PF) effect, Schottky emission and trap-assisted-tunneling (TAT). To verify the presence of any of these mechanisms, the curves at forward biases for all temperatures have been plotted in PF ($\ln J/E^{1/2}$) and Schottky ($\ln J$ vs. $E^{1/2}$) scales, where $E$ is the applied field. The electric field in the layer is assumed to be homogeneous and is determined by dividing the applied voltage on the stack by the thickness. $E$ is described in an assumption of absence of trapped charge at the border between high-$k$ layer and interfacial layer at the substrate. PF emission is expressed by the equation:

$$J = C_i E \exp[-q(\phi_t - (qE/\pi\varepsilon_0 kr_k)^{1/2})/kT],$$

where $q$ is the charge of electron; $C_i$ is a trap density related constant; $\phi_t$ is the trap barrier height; $\varepsilon_0$ is the free space permittivity; $k$ is the dynamic dielectric constant; $r$ is the compensation factor; $k$ is Boltzmann constant and $T$ is the absolute temperature. The current governed by Schottky process is:
\[ J = AT^2 \exp\left(\frac{q^2 E}{4 \pi \varepsilon_0 k_r} \right)^{1/2}/kT, \]

\[ A = C_{RD} \exp(-\phi_b/kT), \] (\( C_{RD} \) is Richardson constant and \( \phi_b \) is the Schottky barrier height). Plotting \( \ln(J/E) \) vs. \( E^{1/2} \) (PF) and \( \ln J \) vs. \( E^{1/2} \) (Schottky emission) should lead to a straight line, from the slope of which the value of the dynamic dielectric constant, \( k_r \) (\( k_r = n^2 \)) is derived. Since \( n \sim 2.1 \) before as well as after irradiation, \( k_r \) should be \( ~4.4 \). In the case of modified PF conduction, the effect of compensating traps on the curves is presented by the compensation factor, \( r \) (\( 1 \leq r \leq 2 \)). As far as the precise modelling of the PF and Schottky conduction is beyond the aim of this work, the standard formulas were used having in mind that the charging effects can modify slightly the values of \( r \) and \( k_r \). The conduction mechanisms was also investigated by plotting the data in TAT process scale, \( J \sim \exp(V) \). This equation describes two-step tunneling of injected electrons via trap. The mechanisms of conductivity of the initial films were discussed in [4]. At room temperature, the TAT process dominates at low applied fields, and at \( E > 1 \) MV/cm the experimental results are fitted very well by both PF emission with compensation (\( r = 1.9 \)) and TAT, and it is not possible to give preference to one of them. With the increase of \( T \) the contribution of PF mechanism (\( r = 1.6 \)) to the conductivity increases and at high temperatures it fully governs the current at \( E \) of 0.7-1.3 MV/cm; at lower fields TAT dominates. The results for irradiated capacitors are as follows: the modified PF process controls the leakage current at fields of \( \sim1-2.8 \) MV/cm of all the curves of irradiated capacitors, but contrary to the fresh stack, with temperature-dependent compensation factor: \( r = 1.8 \) at 20°C and further it decreases to 1.45 with increasing \( T \) to 100°C (figure 3a). The irradiation does not influence the mechanism of conductivity at \( E \geq 1 \) MV/cm – it is PF emission with compensation. As a result of the treatment, however, the proportion between the density of compensation and donor centers

**Figure 3.** PF plots (a) and TAT plots (b) of \( J-V \) curves at different \( T \) of post-irradiated stacks, \( t_i = 6 \) s.
participating in PF process changes with the temperature. The modification of the mechanism towards weak compensation with increasing $T$ means a decrease of the part of acceptors available for compensation, i.e. the microwave treatment affects the electrically active defects in the composite films, and the high temperature facilitates the manifestation of this irradiation-induced trap modification. The slopes of the Schottky plot (not shown) of irradiated capacitors for all $T$ are not consistent with Schottky effect since the values of $k_t$ do not agree with $n$. TAT, however, describes also very well all curves in the interval from 20 to 100°C, (figure 3b). So, two mechanisms of conductivity can be identified for irradiated samples: TAT at a wide field range (0.4-2.5 MV/cm) and PF with compensation at fields of 1-2.8 MV/cm. In the range of $E \sim 1-2.5$ MV/cm the current fits well PF as well as TAT mechanisms and it is no possible to detect transition from one to another mechanism, suggesting a regime PF+TAT exists. The energy location $\phi_t$ of traps for PF emission and activation energies $E_a$ for TAT were obtained from the Arrhenius plots of $J$ (figure 4) at different applied voltages across the stack, $V_{\text{stack}}$. $\phi_t$ of traps accounting for PF emission is $\sim 0.32$ eV for both the initial and the irradiated films, implying that the same traps are involved in the conduction. The trap energy shows, however, field dependence and the value of 0.31 eV is obtained at $V_{\text{stack}} = -1.5$ V after irradiation. This correlates with irradiation provoked modification of the transport mechanism at -1.5 V from the conductivity implying contribution of different mechanisms before irradiation to PF effect with compensation after microwave exposure. At $V_{\text{stack}} = -0.9$ V the PF conductivity with compensation for non-irradiated samples turns into TAT for the irradiated ones. TAT operates for fresh and irradiated samples at $E$ up to 0.7 $\sim$ 1 MV/cm, with $E_a$ which is field dependent. Deep traps, $E_a = 0.32, 0.33$ eV define the conductivity before and after irradiation at very low applied voltages (0.2 V). The conductivity is via the traps with $E_a = 0.13$ eV and with 0.32 eV in the initial and irradiated stacks, respectively at $V_{\text{stack}} = -0.5$ V, i.e. irradiation tends to create deeper traps. In some cases the trap energy level obtained for PF emission ($\sim 0.3$ eV) is comparable to the activation energy of TAT. This means that the same bulk traps which govern the current through PF effect at high fields above 1 MV/cm participate also in the lower field conductivity but through TAT, as is illustrated in the inset of figure 4. The activation energy of 0.32; 0.33 eV is very close to the energy of the localized Ta-d state acting as an electron trap at $\sim 0.3$ eV above the Si conduction band edge of Ta-aluminates [8]. The assignment of the activation energy of $\sim 0.3$ eV to trapping into Ta d-states, however, works only if one assumes that the energies of Ta-introduced localized d-states are independent of the specific dielectric composition (HfO$_2$-Ta$_2$O$_5$ mixed layer in our case instead of Ta-aluminates in [8]).

Figure 4. Arrhenius plots for initial and irradiated capacitors. Solid symbols represent data before and open symbols after microwave irradiation. The energy depth of electron traps and the activation energies from experimental fits are given.
The traps with $\phi_t \sim 0.3$ eV could be also Si/O vacancy complex single donor [9]. The irradiation initiates a change of the conduction at fields about and above 1 MV/cm ($V_{\text{stack}} = -0.9$ and -1.5 V): it modifies the PF mechanism into TAT with $E_a = 0.1$ eV in the former case ($E \sim 1$ MV/cm) and the fairly temperature insensitive current into the PF effect controlled current in the last case ($E > 1$ MV/cm). The constant current region ($T \sim 35-100^\circ$C) means field ionization of electrons (process is essentially independent of the temperature) into the conduction band presumably from the same centers as for Poole-Fenkel conduction (field-enhanced thermal excitation). Therefore, the 6 s irradiation suppresses PF emission at low fields and stimulates the tunneling process; most likely the same traps participate in both processes. There is not evidence, however, for irradiation-induced traps annealing leading to current reduction (figure 1) unlike the case of longer treatment (10-15 s). Most likely 6 s treatment provokes changes of the local environment of defects manifesting as electron traps and this results in a change in their energy position. Since the current reflects mainly the changes in the cathode electric field it seems that the traps responsible for conductivity are localized in the dielectric near the Al-gate interface. Previously [7,10] we have reported that these defects can seriously compromise leakage and reliability characteristics of Ta$_2$O$_5$ and Ti-doped Ta$_2$O$_5$ capacitors. Generally, the microstructural nature of the defects is weak and strained Ta-, Si- and Hf-related bonds; the presence of gate-induced defects as a result of reaction between Al and high-$k$ layer [6] is also possible. The complementary information here is that these defects are affected by microwave treatment, and the strongly reduced leakage after 15 s exposure could be addressed to their annealing.

4. Conclusion
The short term (~ 6 s) microwave treatment at room temperature changes the dominant conduction mechanism(s) in HfTaO based capacitors: PF conduction turns into TAT at fields < 1 MV/cm and modifies towards weaker compensation at higher fields. The radiation-modified conductivity is accompanied by better stability of the irradiated capacitors at elevated temperatures. Therefore, a short term microwave irradiation may potentially serve as an engineering solution to current stability at high temperatures in these high-$k$ stacks. Although, the exact mechanism of microwave treatment effect on the electrically active centers is not addressed in this work it can be assigned to some kind of reconstruction of the defects in both the bulk of high-$k$ layer and the interfacial region during the exposure. Longer treatment (10-15 s) strongly reduces the current down to 3-4 orders of magnitude indicating that by using an appropriate exposure time the leakage current in the stacks could be kept low enough.

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