Microwave Irradiation Effect on Ti-Doped Ta_2O_5 Stacked Capacitors

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Abstract: The effect of short time (up to 15 s) microwave irradiation at room temperature on the electrical characteristics of Ti-doped Ta_2O_5 (8-30 nm) stacks with Al and W gates has been investigated. The irradiation has major impact on the leakage current and can strongly reduce it up to 4 orders of magnitude (current level below ~ 10^{-7} A/cm^2 is easily obtained). The current reduction and a tendency of conduction mechanism changing upon irradiation is considered to be due to irradiation induced annealing of electrically active defects generated during Ta_2O_5 deposition, during doping and/or by a high damage gate deposition process as rf sputtering. The results are compared with those for pure Ta_2O_5 and are discussed in terms of relative influence of the initial parameters of the stack, and the role of incorporated Ti on the oxygen-vacancy related defects. The current reduction is not accompanied by either interface layer thickness increase or film crystallization. As easily applicable method microwave irradiation can be used as alternative to high temperature annealing process for leakage current characteristics improving of high-*k* Ti-doped Ta_2O_5 capacitors. The review covers important Patents which are useful in this field.

Keywords: Top-down microelectronics, (nanoelectronics), high-*k* dielectrics, storage capacitors, dynamic memories, electrical characteristics, AFM, annealing approach, microwave irradiation.

1. INTRODUCTION

At present, Ta_2O_5 is considered as the strongest high-*k* candidate as an active dielectric in storage capacitor of dynamic memories [1-6]. The essential parameter which favors Ta_2O_5 in terms of memory applications is its value of stored charge (i.e. the combination of permittivity and breakdown field), usually several times higher than the other candidates [1]. At the same time, Ta_2O_5 has typical of high-*k* alternatives disadvantages and challenges, (unstable interface with Si resulting to formation of SiO_2-like interfacial layer at Si; relatively low, ~ 600º C, crystallization temperature). The lower-*k* interfacial layer preserves the good quality of the Si interface but it compromises the equivalent oxide thickness, (EOT). The doping of Ta_2O_5 with a small quantity of proper elements, (Ti, Hf, Al, N, C, Zr) or mixing of Ta_2O_5 with another high-*k* oxide is a promising way for improving the insulating properties of pure Ta_2O_5 and suppressing the negative effect of SiO_2-like layer [7-14]. The fabrication of mixed high-*k* layers based on Ta_2O_5 is also a way to extend the potential of pure Ta_2O_5 as a high-*k* material, (higher *k* value of the stack while maintaining the favorable properties of Ta_2O_5 such as low leakage current and high breakdown fields). Adding of third element into the Ta_2O_5 can change (it is desirable to increase) the crystallization temperature. Since the crystal structure and grain size are affected by the dopant concentration, the doping changes actually the crystallization mechanism of the films and by this way, affects the dielectric and electrical properties of the films. The density of interface states and charge trapping can be also significantly suppressed by incorporating of a proper dopant; the films show good electrical characteristics allowing further EOT scaling [15,16].

To improve the electrical performance of the Ta_2O_5-based film/Si system various temperature annealing steps are usually necessary [17-20]. As a rule the high temperature treatments result in a partial crystallization of the films which is unacceptable for high density devices [15,17,18, 21,22] and/or lead to undesirable change of parameters of interfacial lower-*k* layer [1-3,17-20], both effects compromise the benefit of Ta_2O_5 as a high-*k* alternative. The change of the interface parameters may have a large impact on the current through the capacitors resulting in unpredictable leakage current characteristics. A possible way to avoid problems with high temperature annealing is to find alternative low temperature annealing processes [23]. Recently, [24,25] we have shown that seconds of microwave irradiation at room temperature could be successfully used as a method for improving the electrical properties of Ta_2O_5 on Si, (a reduction of leakage current and an increase of *k* have been established; the process preserves the amorphous status of the films). The big advantage of this method is the strongly reduced thermal budget, (room temperature, extremely short exposure times). The results implied that most likely the effect is universal and will be valid for other high-*k* dielectrics. Its specific manifestation, however, is a function of the initial parameters of the stacked capacitors and their technological history.

The purpose of this paper is to study the effect of the microwave irradiation as eventual annealing process for capacitors with Ti-doped Ta_2O_5 on Si obtained by rf sputtering. The duration of microwave treatment is optimized for a certain stack (considering high-*k* film thickness, Ti content

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and the method of doping) in terms of improving the leakage current and enhancement of the permittivity. No appearance of irradiation-induced crystal phase(s) is expected. Since the type of metal electrode can have strong influence on the leakage current [26,27] and respectively on the mechanisms of conductivity, we will also trace the effect of the microwave irradiation on the capacitors with two different top electrodes, (Al, W) as well as whether or not this treatment anneals the gate-induced damage in the Ti doped Ta_2O_5 stacked capacitors as it does that in capacitors with pure Ta_2O_5 [25]. It is known, that the conventional poly-Si gate is not the right solution for high-*k* alternatives and respectively new electrode materials (metals or metal-systems) have been investigated to replace poly-Si gate. The suitable metal electrode is not specified yet [1,4,5,12], because the effective work function of the metal/high-*k* stack can be controlled by many factors, and it is best to consider the gate and given high-*k* dielectric as a separate system that requires simultaneous optimization. In this study, evaporated Al and sputtered W layers were used as top electrodes to the doped films. A combination of capacitance-voltage (C-V) and current voltage (I-V) curves of the formed MOS capacitors are used to characterize the impact of microwave treatment on the stack parameters in dependence on the level of Ti addition, method of doping and exposure time. The relationship between electrical properties and the uniformity (as evaluated by atomic force microscopy) of the doped films is also discussed.

2. EXPERIMENTAL PROCEDURE

The films were deposited on chemically cleaned p-Si 15 Ωcm, (100) wafers, (after HF last pre-clean to remove the native oxide layer). No deionized water rinse was used in an effort to minimize the formation of a new oxide layer. The Ti doped Ta_2O_5 layers were prepared by using two methods of doping: i) “surface doping” of Ta_2O_5 by deposition of rf sputtered Ti layer with two thicknesses, 0.7 and 2 nm, on the top of ~ 8-10; 20; 30 nm Ta_2O_5 (these samples will be referred to as samples type A), and ii) “bulk doping” of Ta_2O_5 - in this case the film has layered structure consisting of 0.7 or 2 nm sputtered Ti film sandwiched between two Ta_2O_5 films with equal thicknesses, ~ 5; ~ 10 and 15 nm; (these samples will be referred to as samples type B). The stacked films in MOS configuration containing Ti-doped Ta_2O_5 are compared with reference samples, (devices with undoped Ta_2O_5). Tantalum pentoxide was deposited by reactive sputtering of Ta (99.9 % purity) in Ar+10% O_2 gas mixture; the working gas pressure during the process was 0.33 Pa. Details on the deposition conditions are given elsewhere [2,28,29]. In a number of papers [2,21,22,28, 30,31] we have shown that high quality layers, with dielectric constant of the bulk Ta_2O_5, (corresponding to relatively thick films) of about 37 and leakage current density below 10^{-9} A/cm^2 at 1 MV/cm, can be obtained by rf sputtering. These optimized fabrication conditions were used here for deposition of Ta_2O_5 to be subjected of doping. Ti was deposited by sputtering of Ti target (99.9 % purity) in Ar atmosphere, (gas pressure, 0.5 Pa; rf power density was 3.9 W/cm^2). The wafer temperature was maintained at 200-220ºC during deposition of all the films. Post-deposition annealing was performed in N_2 at 400ºC for 30 min in order to stimulate mixing of the films after the doping. The total film thickness, *d*, and the refractive index, *n*, were measured by ellipsometry, (λ = 632.8 nm). *d* of the doped stacks is ~ 8-10; 20 and 30 nm. The test structures for electrical measurements were MOS capacitors with a bottom electrode of ~ 300 nm evaporated Al. The top electrodes (evaporated Al and sputtered W) with gate areas, A (1;2.25;6.25;25x10^{-4} cm^2) were defined by photolithography. The capacitors were electrically characterized by means of high frequency capacitance-voltage (C-V) and current-voltage (I-V) curves, measured respectively before and after microwave irradiation. The effective dielectric constant of the films ε_{eff}, was determined from the capacitance C_0 at an accumulation using the ellipsometrically measured values of *d*. The oxide charge Q_f was evaluated form 1 MHz C-V curves. Leakage currents were measured with a voltage ramp rate of 0.1 V/s. All electrical measurements were carried out in a dark chamber at room temperature. The stacked capacitors (test structures for electrical measurements) and the structures Si/Ta_2O_5-based layer without metallization, were exposed to microwave irradiation in a magnetron (*f* = 2.45 GHz, power density of 1.5 W/cm^2) at irradiation times of t_i = 1-15 s. During the exposure the temperature of the samples is close to room one. The distribution of micro-non-uniformity in the non-metallized films before and after irradiation was studied with atomic force microscopy, (AFM).

3. RESULTS AND DISCUSSION

3.1. C-V Curves and Charges in the Stacks

The microwave irradiation affects neither the physical thickness nor the refractive index of all the films, (undoped and doped ones), implying at a first approximation that the film density remains unchanged during the exposure. The ellipsometer measurements yielded refractive index of *n* ~ 2-2.15 for the doped films. The values of n for as-deposited layers are as follows: i) for the low level Ti doping independently of the method of dopant introduction, *n* = 2 for 8-10 nm and 2.1 for 20 and 30 nm film thickness; ii) *n* = 2.15 for the higher Ti amount for all film thickness studied; *n* is ~ 1.9 for the thinnest (8 nm) and 2.1 for the thickest (30 nm) pure Ta_2O_5. The measured dielectric constant ε_{eff} of the pure Ta_2O_5 stack is 7, 12 and 14 for 8, 20 and 30 nm films, respectively in a good accordance with our previous results especially for W-gated capacitors [30]. The thickness of the interfacial SiO_2-like layer for the pure Ta_2O_5 stacks is ~ 1 nm, as determined earlier by X-ray photoelectron spectroscopy (XPS) and transition electron microscopy (TEM) [2,22,28,31]. This layer, at the technological conditions used here, is SiO_2-like one with a small quantity of Si_2O. Since its permittivity is lower than that of the bulk Ta_2O_5, the interfacial layer dominates ε_{eff} of the thin film stacks causing it to decrease, and the effect is more pronounced for the thinner films. Respectively, the dielectric constant, ε_t, of the bulk Ta_2O_5, for the capacitors with pure Ta_2O_5 assuming 1 nm SiO_2-like interfacial layer with permittivity ε_s = 3.9, (at a first approximation equals to that of SiO_2) is: ε_t = 8 for *d* = 8 nm, ε_t = 13.5 for *d* = 20 nm and ε_t = 15.5 for *d* = 30 nm. Preliminary results of XPS and TEM analyses of Ti-doped Ta_2O_5 showed that both the thickness and the composition of the interfacial region are a function of Ti content and the method of its introduction. The interfacial layer is a mixed one of Ta-, Si- and Ti-oxides with various concentrations, and the evaluation of the dielectric constant of this layer is a non-trivial task; the approximation of SiO_2-like layer with its value of dielectric constant is unsound, quite rough approximation, and the correct calculation of ε_t of the bulk dielectric of Ti-doped stacks is not possible. Presumably, the situation is additionally complicated under the microwave exposure of the capacitors keeping in mind the possible effect of the irradiation on the interface at Si. With this in mind, we will compare only the values of ε_{eff} for doped Ta_2O_5, respectively before and after microwave exposure. Generally, the changes of ε_{eff} as a result of doping are small, i.e. the addition of Ti to Ta_2O_5 in our cases has not essential impact on the measured dielectric constant. The tendency of the changes (although small) varies with the amount of Ti: compared to pure Ta_2O_5, ε_{eff} is less or comparable after the lower level of doping (0.7 nm Ti), and it is higher after doping with 2 nm Ti layer. No well pronounced effect of the method of Ti incorporation on the values of the permittivity is observed. The dielectric constant corresponding to as-deposited doped Ta_2O_5 is between 10 and 21 in dependence on the film thickness and the method of doping. The variation of ε_{eff} with the doping method is out of interest here and we focus only on the effect of irradiation on C_0 and ε_{eff}. Figure (**1**) exhibits the representative C-V curves for Ti-doped Ta_2O_5 before and after irradiation. The curves are obtained by sweeping the gate voltage from accumulation to inversion and back at a sweep rate of 50 mV/s. For thin film B type doped samples, (4 nm Ta_2O_5/0.7 or 2 nm Ti/4 nm Ta_2O_5) the values of C_0 remains intact over the time exposure of 1 to ~ 15 s, (only the curve after t_i = 2 s is shown, Fig. (**1a**)) implying that the irradiation is not accompanied by any structural modifications in this kind of stacks, affecting permittivity, (e.g. a change of the interfacial region thickness; measurable variation of the chemical composition of both the bulk dielectric and the interface layer). All other structures, (thin and thick surface-doped films and thick films B type samples) exhibit different C_0 when they were exposed at different t_i; the effect of irradiation on C_0 does not depend on the type of the gate. The short exposure time (1~5 s) leads to lower C_0 than that of the reference samples; the drop in capacitance at accumulation is ~ 30-50% and ε_{eff} lowers up to 2 times, indicating that the stacked films undergo structural modifications. As t_i increases to ~ 7 s, C_0 and respectively ε_{eff} increases to the values typical of the initial non-exposed samples - it is difficult to identify the difference between C_0 value of the irradiated and the unirradiated stacks. The values of C_0 and ε_{eff} show no further variation any more with increasing of t_i up to 15 s. This is illustrated in Figs. (**1b,c**) for two different stack capacitors. Note that measurements on all gate areas used produce similar and consistent results. At present we have not clear explanation of the observed variation of the permittivity with t_i, and only register the obvious relation between t_i and some structural modifications in doped Ta_2O_5. Since XRD analysis indicated that the films are amorphous before and after microwave irradiation, these structural modifications could not be attributed to a polycrystalline nature of the films. So far the results suggest that microwave irradiation has different effect on Ti-doped Ta_2O_5 as compared to pure

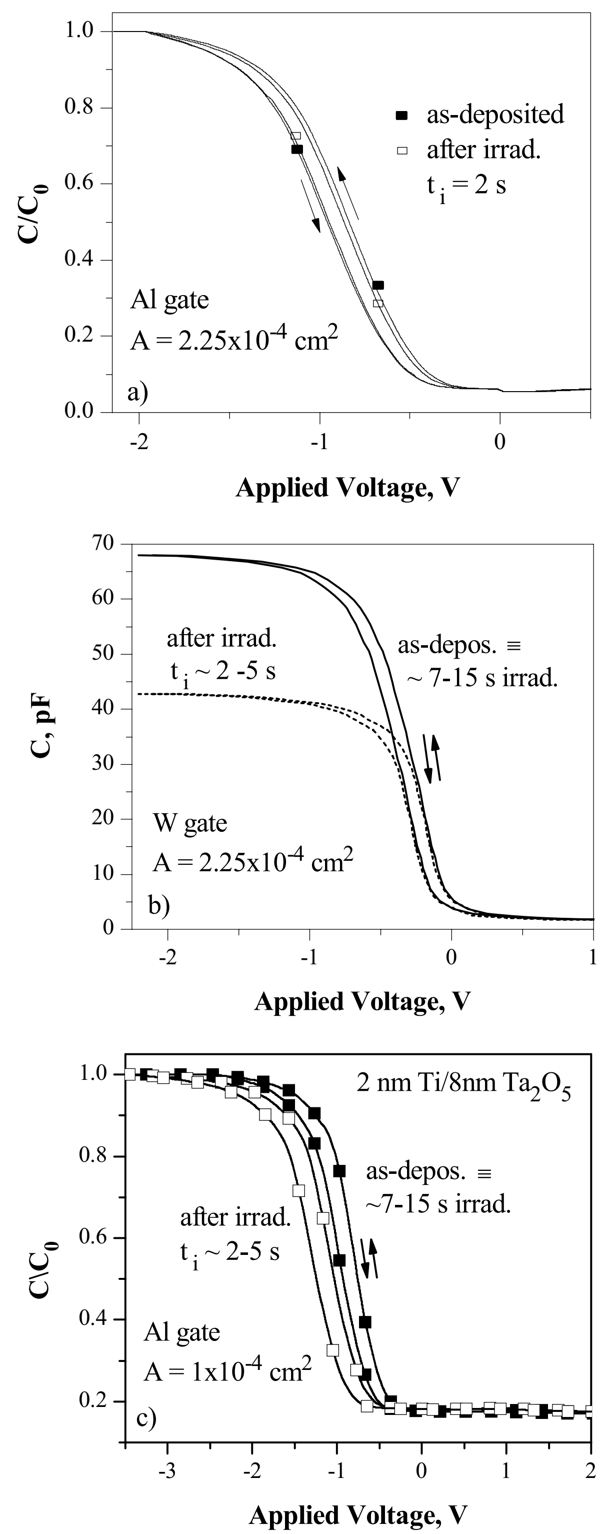

Fig. (1). HF C-V curves of capacitors with different Ti-doped layers before and after microwave irradiation: a) Al-gated 4 nm Ta_2O_5/2 nm Ti/4 nm Ta_2O_5 stack; b) W-gated 15 nm Ta_2O_5/0.7 nm Ti/ 15 nm Ta_2O_5 stack; c) Al-gated 2 nm Ti/8 nm Ta_2O_5 stack. The arrows indicate the hysteresis direction; a) and c) normalized C-V curves.

Ta_2O_5 films, for which we have found consistently an increase of the measured dielectric constant with t_i, [24,25]. For Ti-doped Ta_2O_5 the irradiation either does not affect C_0 at all or after initial drop of both C_0 and ε_{eff} for small t_i, the following irradiation with longer exposure times returns these parameters to their initial values. Since the purpose here is to establish the presence of an eventual annealing effect of the microwave irradiation, the long time irradiation treatment which at least does not cause permittivity degradation is of more interest. The negative flat band voltage, V_{fb}, indicates the presence of positive oxide charge Q_f in the most of the films. Q_f is high for the initial samples ($2x10^{11}$-10^{12} cm^{-2}) which is typical of high-*k* alternatives without appropriate annealing, including post-metallization annealing. The gate-deposition-induced defects (for example, radiation defects during sputtering of W or damaged layer at Al gate due to reaction between high-*k* and Al) can account for a part of Q_f as we have established recently [26,27,30]. The capacitors with thin (8-10 nm) films of pure Ta_2O_5 show high positive values of the oxide charge, $Q_f \sim 3x10^{12}$ cm^{-2}; an order of magnitude lower values are found for thicker films. The thickness dependence of Q_f is well known for high-*k* materials and for Ta_2O_5 in particular [2,5,18,28,30], and is addressed to the poor quality of the thinner films. Q_f of the doped films, independently of the method of doping, does not show well pronounced thickness dependence. The oxide charge is positive for the most of the stacks with exception of sandwich type 30 nm films, (15 nm Ta_2O_5/0.7 or 2 nm Ti/15 nm Ta_2O_5) for which negative oxide charge ($Q_f = -2.5x10^{11}$ cm^{-2}) is observed. These properties of the doped Ta_2O_5, generally different from these of pure Ta_2O_5, are a result of the compensation effect of Ti in the matrix of Ta_2O_5, and its complex dependence on both Ta_2O_5 thickness and the doping conditions [12,29]. Generally, for the capacitors with a domination of negative oxide charge, Q_f is assigned to Ti-related defects rather than to Ta-related ones. The last case (typically observed in pure Ta_2O_5) as a rule leads to positive oxide charge originating from the oxygen vacancies. Here we will not discuss any more the initial parameters of the films and will only trace their variation with microwave irradiation. The lowest Q_f value ($1.8x10^{11}$ cm^{-2}) is observed for thick film bulk doped samples (10 nm Ta_2O_5/2 nm Ti/10 nm Ta_2O_5). After a short time exposure Q_f decreases weakly for all capacitors, and in fact the final Q_f value of the irradiated samples depends on the initial ones - respectively, the lowest density of the oxide charge, $7x10^{10}$ cm^{-2}, is detected for the stacks with the lowest Q_f initial value. Unlike the pure Ta_2O_5 [24,25], Q_f does not change any more with further increase of t_i up to 15 s.

During the voltage sweep from accumulation to inversion and back the C-V curves shift to more positive voltages indicating negative charge in the slow states, Fig. (**1**). The hysteresis is addressed to the existence of traps close to the Si interface acting as slow states. When considering C-V hysteresis it should be mentioned that the correct investigation of this parameter requires detailed study of its dependence on the voltage sweep rate, the waiting time at inversion, and the bias range. Here we use the hystersis only as a qualitative characteristic of stacked films. One observes relatively large C-V hystersis (100-150 mV) for the initial films and the estimated from the hysteresis density of slow states Q_{sl} is 2-$6x10^{11}$ cm^{-2}. The irradiation preserves the sign of the trapped charge in the slow states and affects its density. Q_{sl} lowers by ~ $2x10^{11}$ cm^{-2} after short 2~5 s exposure time without noticeable dependence on the technological history of the sample. Q_{sl} does not change any more when the stack undergoes longer t_i up to 15 s. In broad terms this means that the irradiation has weak effect on trapping/detrapping processes during the sweep. The comparison of the C-V curves to the ideal ones indicates that the density of the interface states at midgap, D_{it}^{m} is not affected by the irradiation over the exposure times used; there is not visible change of the slope of the curves (Fig. (**1**)), i.e. obviously the density of interface states in the whole Si band gap is not also influenced by the irradiation, indicating that the interface at Si is not sensitive to microwave treatment with duration 1-15 s. Comparing these results with our previous ones for pure Ta_2O_5 [24,25] we may conclude that the microwave radiation affects C-V characteristics of the doped and undoped Ta_2O_5 differently: the exposure to radiation leads to a real annealing effect (increase of ε_{eff} and decrease of density of oxide charges) whereas it weakly affects the interface and near interfacial region in the stacks with pure Ta_2O_5. The microwave treatment does not improve the permittivity of Ti-doped Ta_2O_5 stacks (depending on t_i, the permittivity either degrades or remains unchanged); a reduction of both Q_f and Q_{sl}, however, occurs upon irradiation.

3.2. Current-Voltage Characteristics and Mechanisms of Conductivity

Typical room temperature I-V curves of different stacks before and after microwave irradiation are shown in Figs. (**2** and **3**). There is no contribution due to a ramp voltage induced displacement current in the figures. The leakage current density *J* of the as-deposited films depends on doping conditions and thickness of the layers. It is generally attributed to poor-oxidation related defects and defects due to Ti incorporation. Gate-deposition-induced defects and/or reaction product between dielectric and the gate may also contribute to the leakage of the initial films [26,27,30]. We will trace the effect of irradiation on the curves, and the technological aspects of the films will be considered wherever they define the irradiation response of the stacks. Note the comparable leakage current (before as well as after irradiation independently of t_i) for all type of capacitors with different gate areas. Actually both C-V and I-V curves do not exhibit well pronounced dependence on the gate area for all samples studied, indicating an uniform quality of the films within the regions defined by the gate area. The curves presented in this section usually correspond to the smallest area. The leakage current density after irradiation showed a dependence on the parameters of the initial stacks. All films undergoing surface doping Fig. (**2**) provide lower leakage current after irradiation and the current is virtually independent of Ti content. Almost no variation in J-V curves after short time (1~5 s) exposure is observed for 2 nm Ti/8 nm Ta_2O_5 capacitors. The current density at accumulation mode (negative bias, injection of electrons from the gate) after t_i ~ 7-15 s is found to be ~ 3-4 orders of magnitude lower than that of the initial stack. It is below about 10^{-7} A/cm^2 at a bias voltage of -2 V, (E ~ 2 MV/cm) which is strongly improved as compared with both the initial and short time irradiated capacitors. The current for 0.7 nm Ti/8 nm Ta_2O_5 films after long time irradiation (not shown) is comparable to that shown in Fig. (**2a**). A similar tendency of current decrease is seen with thicker (20, 30 nm) films but the extent of the leakage improvement is weaker especially at greater applied voltages, (as illustration, the structure 0.7 nm Ti/20 nm Ta_2O_5 is shown in Fig. (**2b**)). So very low leakage current at two polarities in longer time irradiated stacks is obtained, and the best are the characteristics of the thinnest films (~ 8-9 nm): the current as low as 10^{-7} A/cm^2 is detected at a voltage region (-2, +2) V; for the thicker films this region is (-1.5, +1) V. The current density at these bias regions is attributed to a transient conduction which has weak field dependence [27,30,31]; the current is small and can be detected only when the steady state conduction is negligible. In the stacks showing current higher than ~ 10^{-7} A/cm^2 the larger steady state currents prevent observation of the transient current. As is seen a transient conductivity for all A-type samples is consistently observed after long time irradiation, and only the voltage region upon which it exists exhibits thickness dependence. The as-deposited bulk-doped

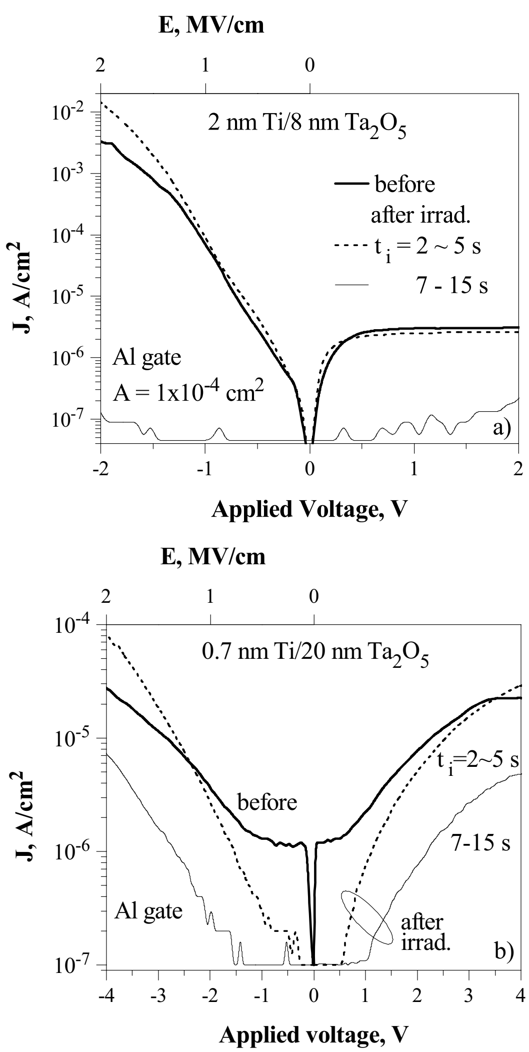

Fig. (2). Effect of microwave irradiation on the current-voltage characteristics of Al-electroded capacitors with surface doped 8 nm (a) and 20 nm (b) Ta_2O_5 films. The gate area is $1x10^{-4}$ cm^2.

films have different current behavior; the shape of the curves varies in dependence on the thickness of the film and the type of the gate. As we have already discussed in our recent paper [29], the behavior of J-V curves of Ti doped Ta_2O_5 is assigned to the combined impact of various electrically active centers. Possible reasons for their creation are: i) poor-oxidation; ii) Ti incorporation, and iii) gate-deposition process. The later results either in gate-deposition induced defects, (a case typical of W-gated stacks) or in damaged region at the gate due to an undesirable gate-high-*k* reaction, (process scenario for Al-gated capacitors), [26,27,30]. The introduction of Ti leads to compensation (partially or completely) of the positive charge which is inherent for pure Ta_2O_5 [32]. It is no purpose here to assess which of these processes dominates for each stack type. We will consider them generally as a technological history of the samples that constitutes the initial parameters of the capacitors. With this in mind, we will trace how the irradiation effect depends on the initial parameters of the stacks. The capacitors from B-type group exhibit response to irradiation which depends on both the layer thickness and the type of the gate but this response is not sensitive to Ti content. The most striking feature of the J-V curves of the sandwich type films is that the irradiation affects only the thickest (~ 30 nm) films with W gate independently of the Ti amount, 0.7 or 2 nm embedded Ti layer. Fig. (**3a**) shows the curves of 15 nm Ta_2O_5/0.7nm Ti/15 nm Ta_2O_5 before and after irradiation. The current lowers about 3 decades for two bias polarities in the whole applied voltage range used, and the shape of the current changes after a short time exposure. Thereafter, a little longer, ~ 7 s time is enough to achieve an additional reduction of the current to the level typical of the transient current and no bias dependence can be detected. The increase of t_i up to 15 s has no further measurable effect on the curves. For all of the rest capacitors with bulk-doped Ta_2O_5 the irradiation over the exposure time interval used does not show noticeable effect on the leakage curves, as it is illustrated in Fig. (**3b,c**) for two of the capacitors, (10 nm Ta_2O_5/ 2nm Ti/ 10 nm Ta_2O_5 and 4nm Ta_2O_5/2 nm Ti/ 4nm Ta_2O_5) with different gates. The curves of sandwich type capacitors with the thinner Ta_2O_5, (10, 20 nm) do not feel the irradiation and the curves before and after microwave process are almost the same. No effect of Ti amount is also observed. The current at applied voltage region (-1, +1) V is low enough and gradually enhances with applied voltage, Fig. (**3b**) illustrates the case of 20 nm film capacitor). Comparing the curves of the thick and the thinner film capacitors with an equal technological history Figs. (**3a,b**) one observes that the impact of microwave treatment depends as if on the microstructural status, electrical activity of the defect centers and the leakage current of the as-deposited films: if the initial samples are defective (high leakage current) the irradiation acts as an annealing process and can reduce the current; if the initial samples are good enough, (relatively low leakage current) the microwave treatment does not affect the curves at all. It emerges that if the capacitors exhibit poor leakage characteristics, the microwave irradiation is beneficial in terms of leakage current. It undoubtedly anneals defects responsible for high leakage current and thereby provide films with the overall greatly reduced currents. In opposite, if the current of the

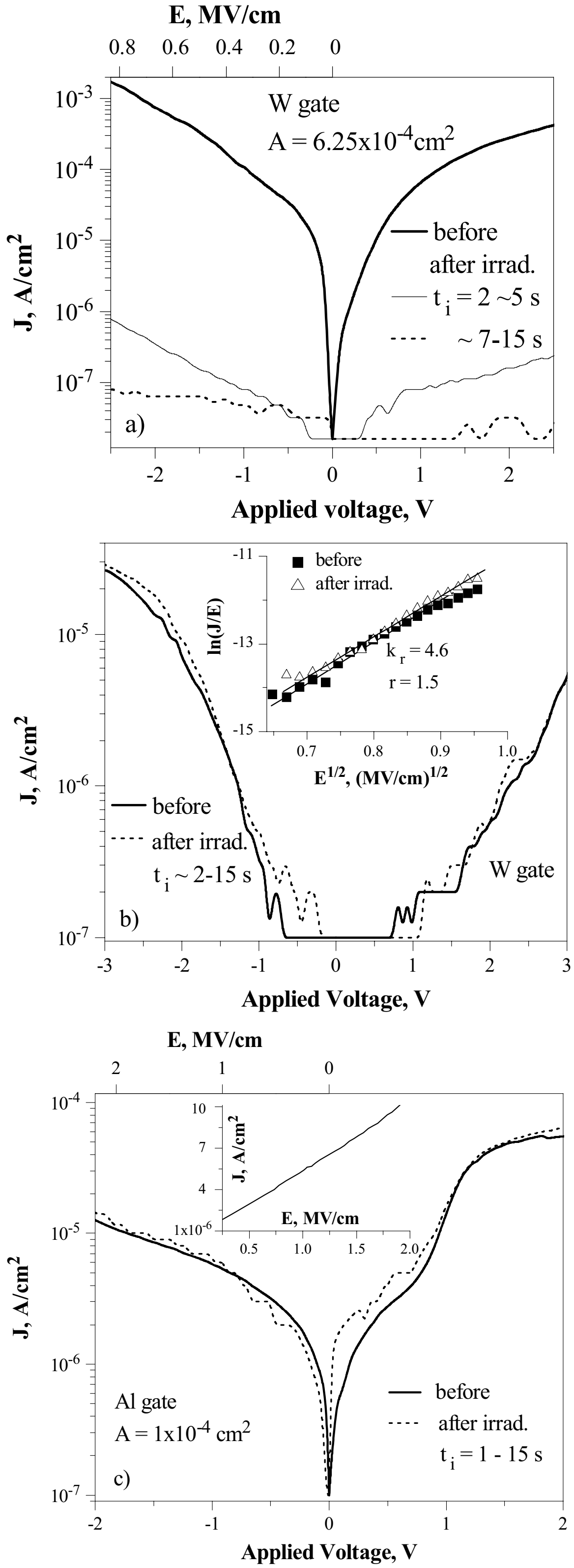

Fig. (3). J-V curves of bulk doped Ta_2O_5 (with different film thickness, Ti amount and metal electrode) before and after microwave treatment: a) W gate, 15 nm Ta_2O_5/0.7 nm Ti/15 nm Ta_2O_5 stack; b) W gate, A = $1x10^{-4}$ cm^2, 10 nm Ta_2O_5/2 nm Ti/10 nm Ta_2O_5 stack; inset, J-E dependence in PF plot of the initial and irradiated samples; c) Al gate, 4 nm Ta_2O_5/2 nm Ti/ 4 nm Ta_2O_5 stack; the linear behavior of the J-E characteristics is shown in the inset.

initial capacitors are low enough (acceptably low), the capacitors do not feel the action of microwave irradiation at all, and the curves before and after irradiation are nearly identical, Figs. (**3b,c**). The high leakage current of the initial samples as displayed in Fig. (**3a**) might be originated from both film-fabrication related defects, (poor oxidation and doping-induced defects) and the gate deposition-induced defects. The last ones, for W-gated capacitors, are in the form of radiation defects introduced during sputtering of W electrode. Then, the strong leakage reduction (more than 4 decades) after microwave treatment could be caused by annealing of these radiation defects. Since a strong effect of irradiation is observed only for the thickest films with W gate, we speculate that the improvement of the leakage current is addressed to the annealing of W-deposition-induced defects rather than to other defects which are generally attributed to the fabrication process of the dielectric.

For conciseness, the capacitors presented in Figs. (**2** and **3**) were chosen for a detail discussion of the mechanism(s) of conductivity and whether it changes upon irradiation. These stacks are representative for the radiation response of the samples with various initial parameters to the radiation and the tendencies observed are typical of a certain set of samples defined by the film thickness, method of Ti incorporation and type of the gate. The leakage current density of the thin film surface-doped samples undergoing long time exposure is independent of the applied voltages suggesting a presence of transient current. (This is illustrated for Al-gated 2 nm Ti/8 nm Ta_2O_5 stacks). Thereupon, the mechanisms of conductivity in the surface-doped devices are only discussed for the initial and short-time-exposed stacks. The current increases rapidly at low voltages (forward bias) and enhances gradually at higher voltages. At very low applied voltages (up to ~ -100 mV), the current increases approximately linearly with the electric field displaying nearly Ohmic behavior, Fig. (**4a**). A plot of J vs. E indicates that for electric fields up to ~ 0.2 MV/cm the relation is Ohmic indeed, before and after 2~5 s irradiation. The conduction mechanisms in Ta_2O_5 at relatively high applied fields are usually interpreted with Poole-Frenkel (PF) effect and Schottky emission. In order to verify whether any of these mechanisms is present, the curves of Al-gated 2 nm Ti/8 nm Ta_2O_5 stacks at negative applied voltages (ensuring the p-Si wafer is in accumulation and the electric field is applied across the dielectric) have been drawn in PF and Schottky plot, Figs. (**4b,c**). Plotting ln(J/E) vs. $E^{1/2}$, (PF effect) 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, ($k_r = n^2$) can be derived. In the case of modified PF conduction, the impact of compensating traps on the curves is presented by the parameter, r, ($1 \leq r \leq 2$). Poole-Frenkel emission is expressed by the equation:

$$J = C_t E \exp[-q(\phi-(qE/\pi\varepsilon_0 k_r)^{1/2})/kT]$$

where J is the current density, C_t is a trap density related constant, E is the electric field, q is the charge of electron, ϕ is the barrier height, ε_0 is the permittivity of the free space, k is the Boltzmann constant and T is the absolute temperature. The current governed by the Schottky emission is expressed by:

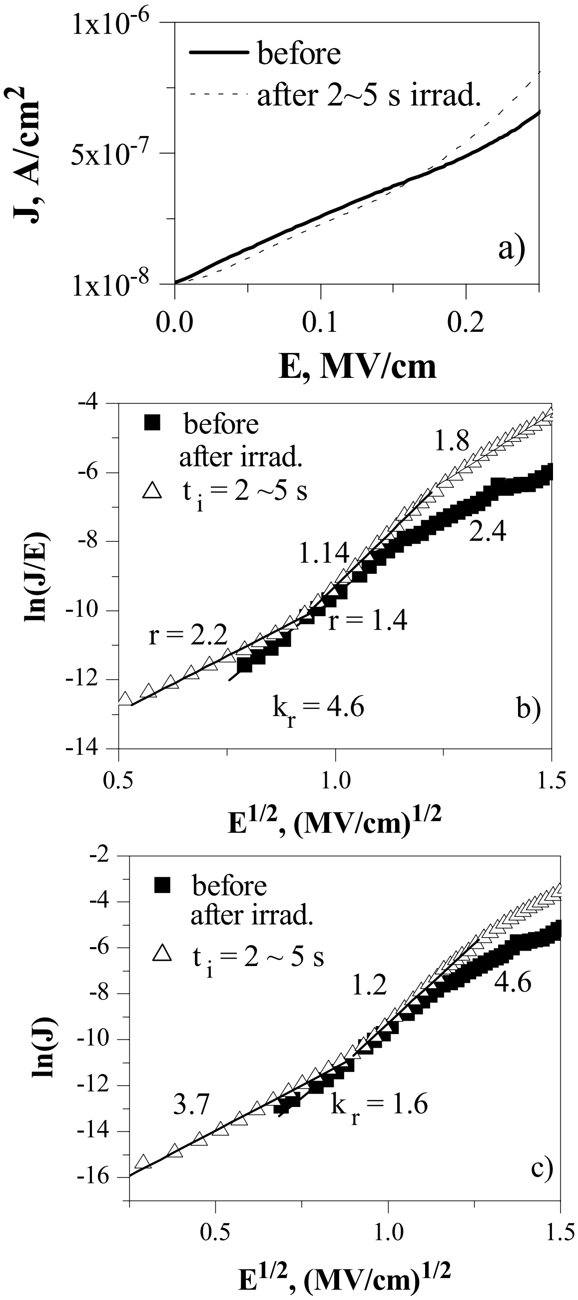

Fig. (4). Leakage current density of Al-gated capacitors with surface doped 2 nm Ti/8 nm Ta_2O_5 stacked films, before and after microwave treatment in a linear scale for low field region (a); at higher electric fields in PF plot (b) and in Schottky plot (c).

$$J = AT^2\exp[(q^3E/4\pi\varepsilon_0 k_r)^{1/2}/kT]$$

$$A = C_{RD}\exp(-\phi_b/kT)$$

(C_{RD} is Richardson constant, ϕ_b is the Schottky barrier height). Having in mind the value of n, (n = 2.15) for the devices presented in Fig. (**2a**), k_r = 4.6 is a value in accordance with PF effect, (Fig. **4b**) for both the as-deposited and the irradiated films. The conduction mechanism in the initial capacitors is governed by PF effect with compensation, (r = 1.4) at E ~ 0.6-1.3 MV/cm. At higher applied fields the value of compensation factor is too high, (r = 2.4) and is not consistent with PF transport. Schottky emission controls the current in this case, Fig. (**4c**), and the agreement of the extracted value of k_r, (4.6) from the Schottky plot and the refractive index is accurate. A nearly normal PF effect (r = 1.14) is operating in the field region of 0.9~1.5 MV/cm of irradiated stacks; PF emission with high compensation, r = 1.8, controls the leakage current at higher (~1.5~2.2 MV/cm) fields. As is known, PF emission is a major conduction process in insulators with a high impact of bulk traps and the conductivity is through the mediation of these traps. If there are many traps in the films studied the dominant contributor in the current should be PF emission. The obtained value of r close to ~ 2 is in fact a characteristic of trap-limited PF effect. The slopes of the Schottky plot at medium and high fields for irradiated stacks in Fig. (**2a**) are not consistent with Schottky effect. Although the curves are actually fitted with straight lines in the Schottky scale, the extracted dynamic dielectric constant, (the slope of the fit) are not in accordance with the corresponding values of refractive index - the values of k_r (1.2-3.7) are lower than 4.6 which rules out the domination of Schottky mechanism. Then at medium fields E = 0.3-0.9 MV/cm, neither PF nor Schottky mechanism governs the current in these stacks after irradiation. Space-charge-limited current mechanism (J vs. V^2) does not also control the current. Obviously another mechanism contributes to the current. Clarifying the exact conduction in such kind of mixed high-k stacks is very difficult due to the complex impact of trap-rich bulk high-k and low-k interface layer. Depending on the voltage range, injection polarity and physical thickness the conduction mechanism is in fact a contribution of different mechanisms including tunneling through the interface layer. A lack of domination of PF and Schottky emission in the discussed capacitors means that due to the simultaneous effect of several conduction mechanisms it is impossible to interpret I-V curves without the help of simulations and knowledge of the exact defect structure of the doped films. Additional extended examination of the stacks, (including I-V-T measurements) have to be performed to separate the effect of every mechanism, which is out of the scope of this work.

There is only slight difference between the current at positive and negative polarities of surface-doped thick (20, 30 nm) films before as well as after irradiation (Fig. (**2b**)) indicating domination of bulk type conductivity and suggesting that the transport under both gate polarities may be limited by similar activation energies. The shape of the curves changes after irradiation but does not depend on t_i - the curves corresponding to various exposure times are parallel to each other and the lowest current level (in fact transient current, ~ 10^{-7} A/cm^2, in the voltage range -1.5 V, +1 V) belongs to longer (7-15 s) t_i. The short irradiation also leads to a reduction of the current (~ 1 order of magnitude) but only at low applied voltages. It emerges that long time exposure stabilizes the films, keeping relatively low current at high applied voltages. The high field data in Fig. (**2b**), (E > 0.5-1 MV/cm) is analyzed in terms of Poole-Frenkel, Schottky and space-charge-limited process to establish the mode of conduction in these films. No one of the three mechanisms govern the current in these films indicating again that a combination of several mechanisms account for the conduction. Both the Schottky and PF plots show a linear relationships but the extracted values of the dynamic dielectric constant and/or compenstation factor, *r*, are not consistent with the corresponding value of the refractive index. Considering the observed change of the shape of J-V curves after irradiation, at present we can say only that irradiation provokes a modification of the mechanism of conductivity of surface doped thick Ta_2O_5.

Plotting the data of Fig. (**3a**) in Schottky and PF plots, one can see that the conduction mechanism is via Schottky emission for both the initial and the irradiated bulk doped capacitors (in the range of applied field $E \sim 0.3$-1 MV/cm): the values of k_r (~ 4-4.5) are consistent with the values of refractive index. The curves presented in Fig. (**3b**) are almost symmetrical suggesting enhanced influence of bulk limited conduction mechanism. The current at forward bias is indeed well fitted by $\ln(J/E)$ vs. $E^{1/2}$ relation; modified PF emission with compensation factor $r = 1.5$ and $k_r = 4.6$ in the medium and high field regime, ($E = 0.4$ to 1 MV/cm) controls the current, inset of Fig. (**3b**). Although the curves are fitted with straight lines in the Schottky scale, the extracted values of k_r are quite low (~ 1.5) which rules out the Schottky mechanism in both the initial and the irradiated devices. We speculate that titanium compensates trap sites in Ta_2O_5 and therefore accounts for the observed bulk limited conduction mechanism. Whatever is the reason for the bulk conductivity, the findings here is that microwave irradiation does not change either the current level or the dominant conduction mechanism in thin film bulk doped stacks with W gate; the conduction is modified PF type at medium and high field and it remains intact after the treatment.

The I-V curves of all Al-gated B type capacitors remain virtually unchanged upon irradiation independently of t_i. Neither Poole-Frenkel nor Schottky emission can be invoked to explain the conductivity for these type of capacitors. The J-V dependence is linear at low and high fields (from 0.1 to 2 MV/cm) indicating electron-hopping-conductivity, as it is shown in the inset of Fig. (**3c**). This mechanism is also bulk limited and the current is described by $J \sim E\exp(-E_a/kT)$, i.e. thermal excitation of the trapped electrons from one isolated site to other dominates the transport in the film. (E_a is the activation energy of hopping electrons and can be obtained from I-V-T measurements). So the data show that bulk-limited conduction mechanisms happen more oftenly in the capacitors (both initial and irradiated) but a combination of several mechanisms has to be considered in some cases too. Note also that clarifying the exact influence of the interface layer on the overall conduction of the structures is behind the interest of this work. That is why the electric field distribution within the double-layered dielectric (high-*k*/interface layer) does not consider when discussing the mechanisms controlling the current in capacitors. The curves at reverse bias (positive voltage at the gate, electron injection from the substrate) are actually an electrical manifestation of the properties of the interface layer at Si. For the non-irradiated samples, the curves are generally characterized by a rapid increase of the current at very small voltages Figs. (**2**,**3**) with a tendency of saturation at higher voltages. The saturation level is influenced by the electrode material and high-*k* film thicknesses [26,27]. The irradiation provides lower leakage current at reverse bias for all surface-doped devices. After 7~15 s exposure the current level below ~ 10^{-7} A/cm^2 is easily achieved for this set of capacitors. In dependence on the film thickness and Ti amount (Fig. (**2**)) some features in the curves are observed: saturation level disappears and the current becomes independent of the gate voltage for thin film capacitors; the tendency of current saturation is interrupted for thick film capacitors by the start of soft breakdown events in the interface layer (the current starts to enhance) at increasing voltages. Some kind of soft breakdown events also accounts for the observed current jumps at a reverse bias for thin film sandwich type samples with W gate, Fig. (**3b**). These effects and their origin are out of the purpose here, and the essential information is that the irradiation does not affect the I-V dependence for these devices at positive bias. The same can be concluded for the stacks of this group but with Al gate, i.e. all thin film bulk doped capacitors do not feel the irradiation in terms of leakage current. The microwave treatment, however, definitely improves the leakage current at positive biases of thick bulk-doped film devices with W gate, and a well pronounced current reduction with increasing t_i is detected, (Fig. (**3a**)); current lowers with more than four decades after ~ 7 s irradiation. Natural explanation of this is the microwave irradiation-induced annealing of the interface region at Si. If one compares the data for the two gate polarities it is seen that the character of microwave effect on the leakage current is the same for negative and positive biases. In other words, there is not a case when the irradiation affects the current at forward and does not at reverse bias and vice versa. This suggests that if interaction between irradiation and a certain stack occurs, it happens in the bulk of the film as well as at both interfaces with the gate and with the Si.

3.3. Surface Roughness Parameters

As emphasized in the preceding sections a scenario emerges for structural changes in the films as a result of irradiation. To examine the variation of surface morphology under the irradiation the atomic force microscope images were analysed and two roughness parameters were derived: the Z_{range} (peak-to-valley in the scan range 1x1 μm and RMS (root-mean-square) surface roughness values. It was not possible to distinguish any difference between pure and bulk doped Ta_2O_5 for a certain film thickness in terms of surface morphology. That is why we will focus only on the effect of irradiation on both pure and surface-doped Ta_2O_5. Three dimensional AFM images of the initial non-irradiated films, (pure and surface doped Ta_2O_5 with three various thicknesses) are shown in Fig. (**5**). The two surface roughness parameters in dependence on the film thickness and doping conditions, before and after 5 s microwave irradiation are summarized in Table **1**. It can be seen that the layers with a thickness of Ta_2O_5 of 5 and 10 nm are with reasonably smooth surface with nearly constant RMS and Z_{range} values: the RMS value is about 0.08 nm for pure as well as doped Ta_2O_5 independently of the level of Ti doping; Z_{range} value is ~ 0.7 nm with a very weak tendency to decrease at higher amount of Ti. Thus, no substantial change in the doped Ta_2O_5 surface micro roughness values was observed. The average surface roughness slightly increases with increasing *d* to 20 nm. The doped Ta_2O_5 surface also gets a little rougher for thicker films; the effect seems to be stronger for

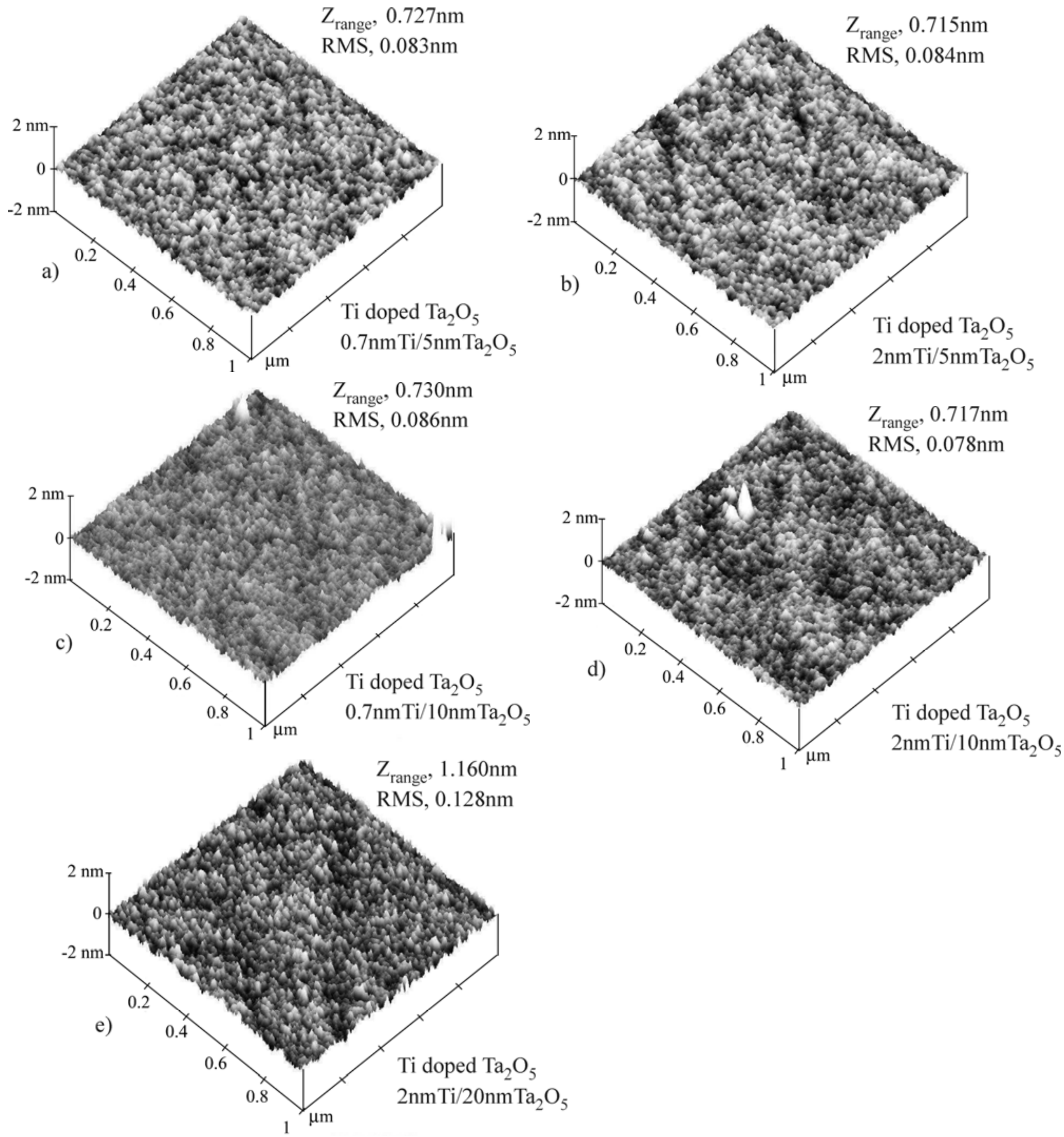

Fig. (5). AFM 3D topography of as-deposited pure and surface-doped Ta_2O_5 with various film thickness and two levels of Ti doping: a) 0.7 nm Ti/5 nm Ta_2O_5; b) 2 nm Ti/5nm Ta_2O_5; c) 0.7 nm Ti/10 nm Ta_2O_5; d) 2 nm Ti/10 nm Ta_2O_5; e) 2nm Ti/20 nm Ta_2O_5.

higher level of doping, (2 nm Ti vs. 0.7 nm Ti). These films indicate a little more rugged surface with Z_{range} = 1.08; 1.16 nm and RMS = 0.105; 0.128 nm for the two types of doping, respectively. We have established a similar film-thickness-dependent surface roughness for pure Ta_2O_5 on Si [24]. That is why the results observed here are presumably a phenomenon rather to film thickness than to doping. In all cases, however, the roughness is around 0.1 nm which is a very good value for RMS and the doping does not modify the roughness of the top surface, (for thinner films which are of practical interest, RMS is even below 0.1 nm). The effect of 5 s irradiation depends again on *d* rather than on the doping: a negligible variation in the values of both RMS and Z_{range} is observed upon irradiation. As illustration, Fig. (**6**) shows the micrographics of the doped Ta_2O_5 with different thicknesses after 5 s microwave irradiation. It emerges that if the surface is very smooth, (RMS < 0.1 nm; Z_{range} < 1nm), 5s

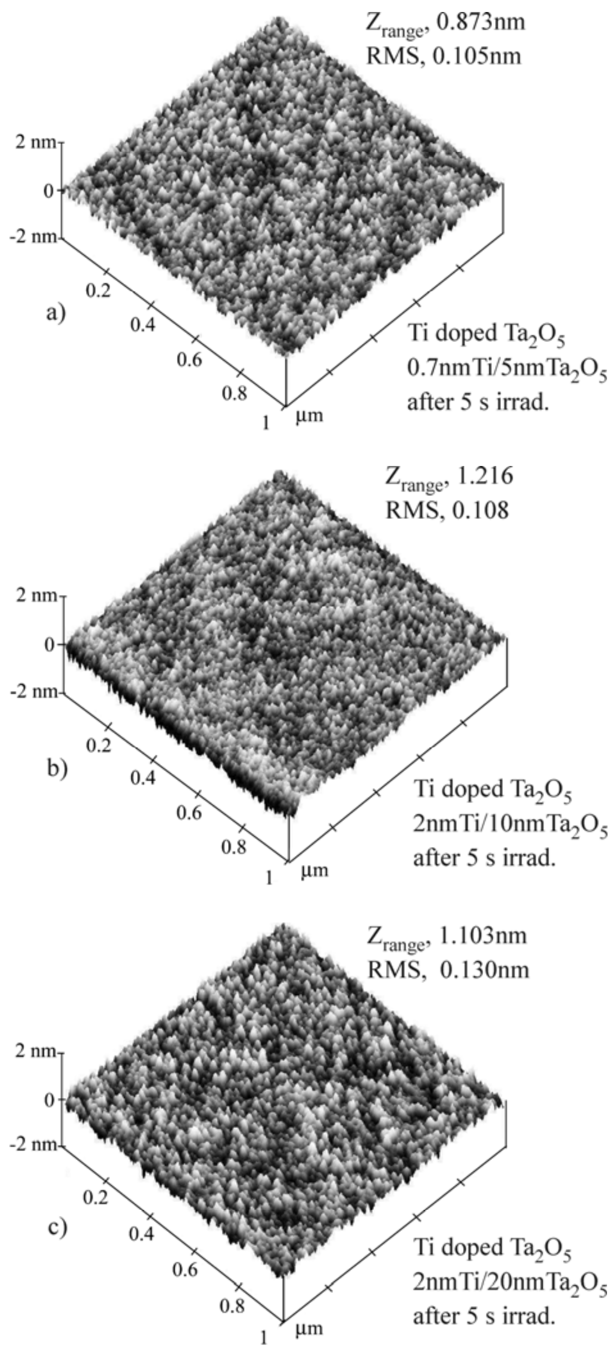

Fig. (6). AFM images of 5s irradiated surface-doped Ta_2O_5, with different film thickness and Ti content: a) 0.7 nm Ti/5 nm Ta_2O_5; b) 2 nm Ti/10 nm Ta_2O_5; c) 2 nm Ti/20 nm Ta_2O_5.

exposure increases slightly the roughness independently of the exact chemical composition of the films, (pure or doped Ta_2O_5), Table 1. When the surface has some level of roughness (RMS above 0.1 nm, $Z_{range} \geq 1$ nm), 5 s irradiation has actually no effect on the surface morphology, (thicker doped Ta_2O_5). Generally, every enhancement of the film roughness can lead to a decrease of contact area in comparison with patterned geometrical value as the inner surface of deposited metallic layer is contacted only on the tops of the roughs of the films. Note, however, that for all samples studied the change of the surface roughness parameters are very, very small and, it was not identified that the surface morphology could be degraded by 5 s microwave exposure. The surface morphology of all the films upon shorter irradiation time than 5 s is not changed at all. The longer t_i (10, 15 s) tends to increase Z_{range}; the effect on the RMS is nearly the same as after t_i = 5 s. This is illustrated in Fig. (**7**) where the surface morphology of the thinnest doped Ta_2O_5 after 10 s irradiation is presented. Hence, based on the results in this section it can be concluded that in terms of surface morphology there is actually no difference between the effect of shortest t_i used (2 s) and the longest one, (15 s). Thus AFM results reveal that the surface structure of the films before and after microwave radiation is smooth enough

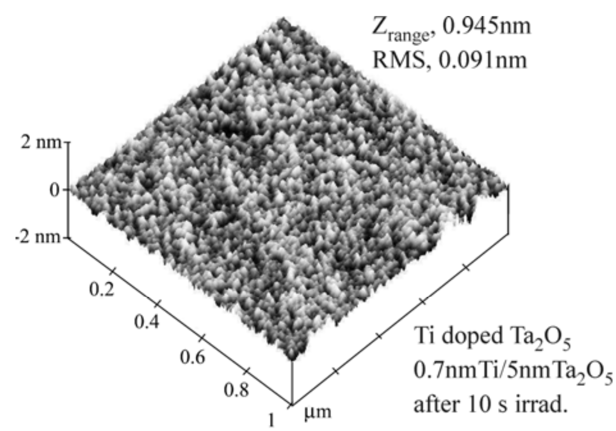

Fig. (7). AFM image of the surface of 0.7 nm Ti/5 nm Ta_2O_5 stack after 10 s microwave treatment.

with no cracks and defects, and with negligible surface roughness. From this, we additionally conclude that an eventual mismatch stress developed during Ti doping of Ta_2O_5 is not significant and does not reflect on the surface morphology. Note also that the layers are amorphous before and after irradiation and consequently the surface morphology observed does not reflect crystallization processes either during deposition or during irradiation. Films on Si are used for AFM evaluation, and respectively the microwave treatment acts directly on the films surface in contrast to irradiation of the test structures for electrical measurements (MOS configuration, metal gate on Ta_2O_5). This peculiarity should be taken into account when comparing and combining the data of AFM with these of electrical measurements. While the topography of the as deposited samples does not differ significantly from that of the irradiated samples, the I-V and C-V curves show changes after irradiation. Since RMS roughness of all samples studied does not exceed about 0.5-2.2 % relative to the film thickness then thin spots in the films can not affect the capacitance and leakage current.

Table 1. Roughness Parameters of 1×1 µm^2 Area of the Surface of Pure and Surface Doped Ta_2O_5 Films, Before and After 5 s Microwave Irradiation

samples	RMS (nm); Z_{range} (nm)	
	as-deposited film	after irradiation
pure Ta_2O_5, d (nm)		
5	0.084;0.720	0.109;0.913
10	0.085;0.725	0.093;0.784
20	0.098;0.987	0.116;1.020
Ti doped Ta_2O_5		
0.7 nm Ti/5 nm Ta_2O_5	0.083;0.727	0.105;0.873
2 nm Ti/5 nmTa_2O_5	0.084;0.715	0.129;1.196
0.7 nm Ti/10 nm Ta_2O_5	0.086;0.730	0.090;0.768
2 nm Ti/10 nm Ta_2O_5	0.078;0.717	0.108;1.216
0.7 nm Ti/20 nm Ta_2O_5	0.105;1.080	0.110;0.090
2 nm Ti/20 nm Ta_2O_5	0.128;1.160	0.130;1.103

4. CURRENT & FUTURE DEVELOPMENTS

In this report we show that short time (up to ~15 s) microwave irradiation is worthy for significant reduction of leakage current (up to 4 decades) in Ti-doped Ta_2O_5 stack capacitors. Generally, the effect of radiation depends on the initial parameters of the stacks defined by the thickness of the doped film (~8-30 nm), method of Ti incorporation in the matrix of Ta_2O_5, and the type of the gate, including the technique of gate deposition. The most sensitive parameter to the irradiation is the leakage current, i.e. the impact of microwave treatment is related with the electrical activity of the defect centers. If the leakage current of the initial stack is high the irradiation acts as annealing process, strongly reduces the current and tends to modify the conduction mechanism; if the initial stack is good enough (relatively low leakage current) the microwave treatment does not affect the current at all. The irradiation undoubtedly anneals defects responsible for high leakage current (by any means these defects are introduced - by doping or during gate deposition), and the poorer the leakage characteristics the more susceptible the capacitor is to the treatment. The irradiation stabilizes the films keeping low current at two gate polarities, (the current level below 10^{-7} A/cm^2 is easily obtained) implying that the irradiation affects not only the bulk traps but also both interfaces at Si and at the gate. Unlike the case of pure Ta_2O_5, however, the microwave irradiation weakly affects the permittivity of Ti-doped Ta_2O_5 indicating that the process of exposure of doped layers is not accompanied by any structural modifications in the stacks affecting strongly enough the permittivity (change of the stoichiometry of the layers, crystallization effects etc.) Presumably this phenomenon seems to result from a compensation effect of incorporating Ti on O-vacancy related defects with subsequent reduction of Ta-suboxides in the doped films, i.e. the smaller density of oxygen vacancies in the initial doped films as compared with the pure Ta_2O_5 could account for the absence of a remarkable change of permittivity upon microwave exposure. Since there is no evidence for a change of the interface layer thickness and surface roughness upon irradiation, we suggest that the current reduction and the modification of mechanism of conductivity are probably due to neither structural and surface morphology change nor to change in the stoichiometry of the film. It emerges that a strong current reduction is caused by an annealing of charged defects which is supported by the observed decrease of the density of both the oxide and the slow states. This means that microwave irradiation has a potential to anneal bulk traps and slow states in Ti-doped Ta_2O_5. Based on these results and on our previous data for the effect of microwave treatment on pure Ta_2O_5, obtained by different methods and with various thickness, we speculate that by using appropriate exposure times the microwave irradiation could be effective in leakage current reduction in another type of high-*k* dielectric-based capacitors too. It should be mentioned, however, that since the electrical characteristics of a certain high-*k* stack are affected by both the type of the gate and the method of its deposition, it is difficult to generalize the conclusion on the effect of microwave irradiation from the high-*k* fundamental parameters point of view.

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