JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 11, No. 10, October 2009, p. 1509 - 1512

Ti doped Ta_2O_5 stacked capacitors♣

E. ATANASSOVA, D. SPASSOV*, A. PASKALEVA, M. GEORGIEVA, J. KOPRINAROVA
Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.

Ti-doped Ta_2O_5 (10; 30 nm) films obtained by rf sputtering are studied with respect to their dielectric and electrical properties. The incorporation of Ti is performed by an original method, (surface doping where a Ti layer is deposited on the top of Ta_2O_5). It is established that the doping is successful for thin-film stacks, (the current is lowered by ~ 1-1.5 orders of magnitude). In the context of advanced high-*k* dielectrics, the surface doped Ta_2O_5 has a potential as an active dielectric in storage capacitors of nanoscale dynamic memories. The incorporation of Ti into Ta_2O_5 causes the generation of negative oxide charge, and the mechanism of current reduction is considered to be due to Ti-induced compensation of existing oxygen vacancies.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: High-*k* stacks, Ti-doped Ta_2O_5, electrical characteristics

---

1. Introduction

High-dielectric constant (high-*k*) materials are being actively researched to enable the continuous down scaling of ultra-large-scale-integrated circuits. Ta_2O_5 has been considered as one of the best active dielectrics in dynamic random access memories, DRAMs [1-3]. The essential parameter which favors Ta_2O_5 in terms of memory applications is its value of stored charge, usually several times higher than the other candidates [1]. Ta_2O_5 has also its challenges typical of the most of the high-*k* dielectrics [1-4], and mixing with another oxide(s) is a way for improving the properties of pure Ta_2O_5. The concept of doping is related to the assumption that the dopants act as network modifiers and therefore quench the dangling bonds of excess oxygen in metal oxides [5], reducing the leakage current and trap density. The dielectric properties of films with the addition of TiO_2, Y_3O_3 or WO_3 to Ta_2O_5 have been found to be improved, and the mechanism of improvement is considered to be compensation of oxygen vacancies by the dopant ions [6,7]. It has been also reported [8] that although the Ti incorporation in Ta_2O_5 results in an increase in the dielectric constant, the amorphous to crystalline transition temperature as well as the leakage current were degraded by the doping. These results imply that the doping-induced variation of the parameters presumably depends not only on the amount of dopant but also on the method of doping, as well as on the fabrication method of Ta_2O_5 itself. The objective of this work is to investigate the variation in the electrical characteristics of stack capacitors, with Al as the top electrode, as different levels of Ti are added into radio-frequency (rf) sputtered Ta_2O_5 (10; 30 nm), by a new, original method of doping.

2. Experimental procedure

The films were deposited on chemically cleaned p-type, 15 Ωcm (100) Si wafers. 10 and 30 nm Ta_2O_5 films were deposited by reactive sputtering of Ta in Ar + 10 % O_2 ambient [3]. The Ti-doped Ta_2O_5 layers were obtained by surface doping of Ta_2O_5, consisting of the deposition of a sputtered Ti layer with two thicknesses 0.7 and 2 nm on top of the Ta_2O_5. Ti was deposited by sputtering of a Ti target in an Ar atmosphere, (gas pressure 0.5 Pa; rf power density 3.9 W/cm^2). Post-deposition annealing was performed in N_2 at 400 ºC for 30 min, in order to mix the films after the doping. The total film thickness, d, and the refractive index, n, were measured by ellipsometry (λ = 632.8 nm). The values of n were ~ 2 for thin and ~ 2.1 for thick pure Ta_2O_5. No variation in n after doping with the smaller Ti content, (0.7 nm Ti layer) was observed. n increased slightly after the higher Ti incorporation, and the values of n were 2.15 for thin and ~ 2.3 for thick films. It was not possible to distinguish ellipsometrically the difference in the thickness of the pure and 0.7 nm Ti doped Ta_2O_5. The thickness of the Ta_2O_5 with a 2 nm Ti layer increased by about 1.5-2 nm. According to X-ray diffraction analysis both the virgin and the doped films were amorphous. The test structures were MIS capacitors with a gate and back side electrode of evaporated Al (gate area, 1x10^{-4} cm^2). The structures were electrically

---

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 characterized by means of high frequency (1 MHz) capacitance-voltage (C-V) and current-voltage curves (I-V). The effective dielectric constant, ε_{eff}, of the films was determined from the capacitance under accumulation, using the ellipsometricaly measured values of d. Leakage currents were measured with a voltage ramp rate of 0.1 V/s, using a Keithley 236 source meter.

3. Results and discussion

The values of ε_{eff} extracted from the C-V curves are presented in Table 1. The higher level of Ti addition results in a higher value of ε_{eff}, as compared to the permittivity of undoped Ta_2O_5. The lower level of Ti addition produces films with a comparable or lower permittivity than that of pure Ta_2O_5. The changes in ε_{eff} as a result of doping are small, i.e. the addition of Ti to Ta_2O_5 does not have a strong impact on the dielectric constant. The tendency of the changes (albeit small), however, varies with the amount of Ti: ε_{eff} is less than that of pure Ta_2O_5 for a 0.7 nm Ti layer, and it is larger for a 2 nm Ti one. A relatively large hysteresis (80-280 mV) is found for both pure and doped Ta_2O_5. During the voltage sweep from accumulation to inversion and back, the curves shift to more positive voltages, indicating negative charge in the slow states. The hysteresis is associated with the existence of traps (poor-oxidation related defects in pure Ta_2O_5) close to the interface with Si, acting as slow states. The density of slow states, Q_{sl}, estimated from the hysteresis is $\sim 1.2 \times 10^{12}$ cm^{-2} for 10 nm and 3.4×10^{11} cm^{-2} for 30 nm pure Ta_2O_5. The doping preserves the sign of the trapped charge in the slow states and slightly changes its density. The doping of 10 nm films lowers Q_{sl} by $\Delta Q_{sl} \sim (5\text{-}8) \times 10^{11}$ cm^{-2}; the effect is stronger for the higher level of Ti. The doping of thicker films causes an increase of Q_{sl} by $\Delta Q_{sl} \sim 1.5\text{-}2 \times 10^{11}$ cm^{-2}, suggesting the generation of additional slow traps. The thinner films of pure Ta_2O_5 show high positive values of the oxide charge $Q_f \sim 3.5 \times 10^{12}$ cm^{-2}; an order of magnitude lower values (2×10^{11} cm^{-2}) 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 [3,9], and is assigned to a poorer quality of thinner films. The doping reduces Q_f for 10 nm films with $(1.8\text{-}2) \times 10^{12}$ cm^{-2}; the effect is slightly stronger for the higher Ti concentration. The oxide charge for 30 nm doped films is negative, suggesting that doping causes the generation of negative charge which completely compensates the existing positive charge in the initial films. So, the final net charge is negative, with a density of $\sim 10^{11}\text{-}10^{12}$ cm^{-2}. The positive value of Q_f is related to oxygen vacancies which are donor-type charged defects and produce positive oxide charge in oxygen deficient films. The oxygen vacancies can be compensated by Ti^{4+} ions, as they are substitutionally incorporated into Ta^{5+} sites in Ta_2O_5 films [7]. Considering this assumption (the Ti^{4+} radius, 0.068 nm, is almost the same as that of the Ta^{5+} ion, 0.07 nm), the observed reduction of the positive charge after Ti addition can be a result of this compensation. With increasing Ti content the negative charge increases, suggesting that this charge is assigned to Ti-related defects rather than to Ta-related ones. In broad terms, part of the negative charge may be due to the OH groups in the films, formed in some way during the doping. The main finding, however, is that the incorporation of Ti in Ta_2O_5 films definitely causes the generation of negative oxide charge. The comparison of the curves to the ideal ones indicates that the midgap interface state density D_{it}^{m} is high ($\sim 10^{12}$ cm^{-2}eV^{-1}) for all samples with the exception of the 30 nm pure Ta_2O_5 stack.

Table 1 Parameters extracted from the C-V curves. The work function difference, φ_{ms} = - 0.7 eV.

sample designation		ε_{eff}	Q_f x10^{11}, cm^{-2}	Q_{sl} x10^{11}, cm^{-2}	D_{it}^{m}x10^{11}, cm^{-2}eV^{-1}
pure Ta_2O_5	10 nm	9.8	34.5	12.5	51
	30 nm	18.3	2	3.4	6
doped Ta_2O_5	0.7 nm Ti/ 10 nm Ta_2O_5	9.2	17	7.6	33.5
	2 nm Ti/ 10 nm Ta_2O_5	10.8	14	5	12
	0.7 nm Ti/ 30 nm Ta_2O_5	15	-14	5.5	40
	2 nm Ti/ 30 nm Ta_2O_5	21	-18	5	45

No systematic trend with regard to Ti concentration and/or total thickness of the films is observed. Although some decrease of D_{it}^{m} of the 10 nm stacks after doping is detected, the density of interface states remains high. The observed high D_{it}^{m} is due to the absence of post-metal annealing of the capacitors. Such annealing was not performed as we aimed at clarifying the net effect of doping. It emerges that the incorporation of Ti in Ta_2O_5 initiates processes and reactions which are a function of the high-*k* layer thickness. What is not in doubt, however, is that: i) Ti incorporation can increase the ε_{eff} of the stack, but only when its amount is high enough; ii) Ti definitely generates negative charge in Ta_2O_5 in the form of oxide charge – when the density of positive oxide charge of pure Ta_2O_5 is too high, (10 nm Ta_2O_5 capacitors), the effect of the induced negative charge manifests itself as a reduction of the initial positive one; when the density of the positive charge is low (30 nm Ta_2O_5 capacitors) the introduced negative charge compensates it and the net effect of doping is an increase in the negative charge with Ti content. Presumably, when the Ti amount is too small it virtually acts as a source of electrically active defects which account for the observed decrease in ε_{eff}. At present, based on these experiments, it is not possible to provide better insights into the specific role of Ti in this process of structural change in Ta_2O_5. The promising result is that generally the Ti doping tends to improve the characteristics, (ε_{eff}, interface and dielectric properties) of the thinner films, which are of practical interest. Fig. 1 illustrates the J-V dependence for the studied capacitors. The leakage current characteristics of pure Ta_2O_5 have been discussed in detail in [3, 9, 10]. The doping of 10 nm Ta_2O_5 reduces the leakage current. The current level slightly depends on the Ti content, and the curves corresponding to 0.7 and 2 nm Ti layers on Ta_2O_5, are similar. The leakage improvement after doping is much more pronounced at high applied voltages: J is more than 10x lower than that of pure Ta_2O_5 at - 1 V applied voltage. The current of the 30 nm films also decreases upon doping. At a positive bias (electron injection from the substrate) current saturation is obtained only for the thin pure Ta_2O_5 films. For thin films, the doping is beneficial for the current, (it is ~ 50x lower than that of pure Ta_2O_5). Compared to that of the 30 nm Ta_2O_5, the doped thick film capacitors have comparable leakages under reverse bias, it seems that the interface region between Si and thick enough Ta_2O_5 does not feel this type of doping.

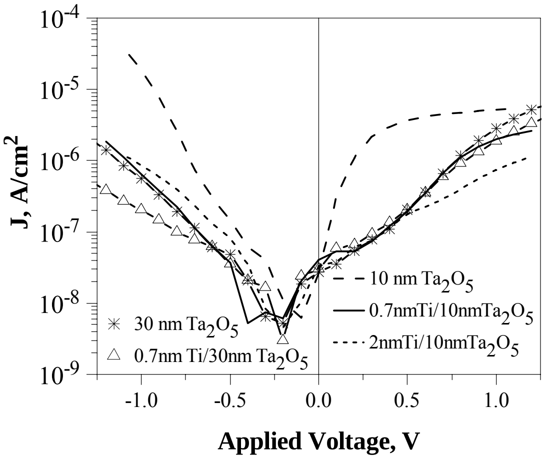

Fig. 1. J-V curves of pure and doped Ta_2O_5.

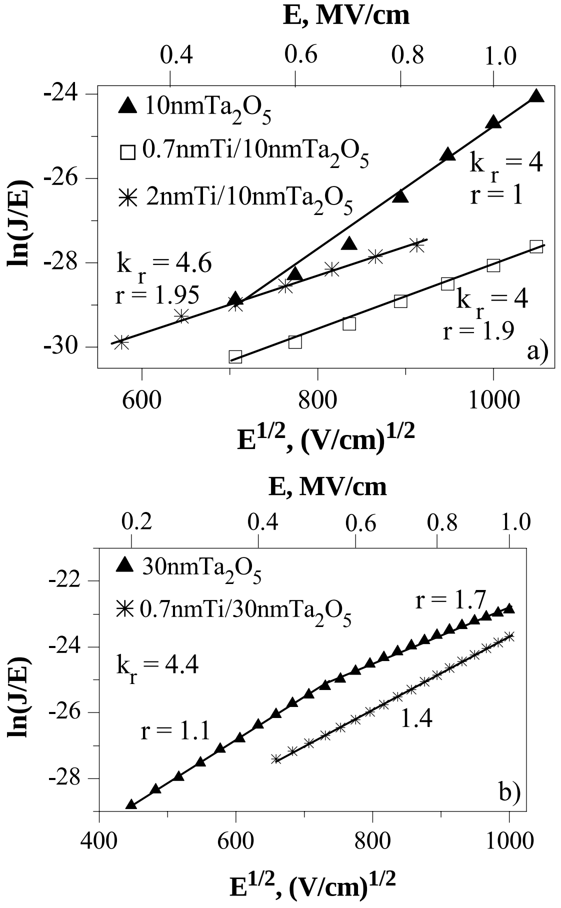

Fig. 2. PF plot of J-V curves of stacks with pure and doped Ta_2O_5: a) d ~ 10 nm, b) ~ 30 nm.

The next point concerns the conduction mechanism in the films. J is almost independent of the applied electric field E in the low field region for the most of the stacks, suggesting the presence of transient currents. Thereupon, the mechanisms of conductivity are discussed at higher fields. The conduction in Ta_2O_5 is usually interpreted with the Poole-Frenkel (PF) effect or by Schottky emission. Plotting ln(J/E) vs. $E^{1/2}$ (PF effect) or lnJ 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. The dominant mechanism is commonly defined by the level of agreement between k_r and n. In the case of modified PF conduction, the effect of compensating traps on the curves is presented by the parameter r, ($1 \leq r \leq 2$). The conduction mechanism in stacks with pure Ta_2O_5 is governed by a normal PF effect in thin film (r = 1 at E ~ 0.5-1.1 MV/cm) and a nearly normal one in thick film capacitors, (r = 1.1; E ~ 0.2-0.5 MV/cm). PF with compensation (r = 1.7) controls the current in thick pure Ta_2O_5 at higher applied fields, ~ 0.5-1 MV/cm (Fig. 2). The PF process also governs the current in the doped samples. In the case of thin films, however, this is conduction with a higher extent of compensation. r is close to its maximum (r = 2) value, suggesting a high density of bulk traps. An opposite trend is observed in thick film devices, (Ti incorporation resulted in films with a smaller r). The slopes of the Schottky plots for all stacks showing operation of the PF mechanism are not consistent with the Schottky effect - the extracted k_r is not consistent with the corresponding value of n, which rules out the Schottky mechanism. Therefore, the results suggest that the doping affects the type and density of bulk traps (the details of this change depend on d) causing the variation in the degree of compensation. Ti incorporation, however, does not change the dominant mechanism of conduction. It should be emphasized that the conduction mechanism in a mixed stack depends not only on the applied voltage across the total dielectric but also on the thickness and dielectric constant of the interfacial layer with the Si. More detailed interpretation of the J-V curves is hampered by the lack of the data for the chemical and structural composition throughout the depth of the stacks. For example, the presence of a concentration gradient of Ti throughout the films seems quite possible. The well pronounced tendency of a change from normal in pure Ta_2O_5 to modified PF mechanism in doped films (Fig. 2a) indicates that Ti occasions a build-up of compensating centers in these films. Virtually, the existence of these centers in doped stacks is a reason for the doping-induced alteration of the conduction mechanism.

4. Conclusion

In exploring the concept of doping, the results indicate that *Ti doping is a way to extend the potential of pure* Ta_2O_5 and the technology can be optimized to achieve a satisfactory value of leakage current. Surface doping is effective in lowering the leakage current (10-50x), and in slightly increasing the permittivity of thin (10 nm) film capacitors. While showing some degree of change, the permittivity of the stacks is virtually not sufficiently sensitive to the Ti amounts used. It emerges that the incorporation of Ti into Ta_2O_5 initiates processes which are a function of film microstructural status defined generally by the film thickness, and there is a critical value of the Ti amount required to cause the expected permittivity enhancement.

Acknowledgements

The work was supported by Bulgarian National Science Foundation under contract F1508.

References

[1] The Intern. Techn. Roadmap for Semicond., (ITRS) 2006, http://public.itrs.net
[2] M. Houssa, High-*k* gate dielectrics, Institute of Physics Publishing, Bristol (2004).
[3] E. Atanassova, T. Dimitrova, in: Handbook of Surfaces and Interfaces of Materials, ed. H. S. Nalwa, Academic Press, San Diego (2001), Vol. 4, p. 439.
[4] E. Atanassova, A. Paskaleva, Microelectron. Reliab. **47**, 913 (2007).
[5] L. Manchanda, M. D. Morris, M. L. Green, R. B. van Dover, F. Klemens, T. W. Sorsch, P. J. Silverman, G. Wilk, B. Busch, S. Aravamudhan, Microelectron. Eng. **59**, 351 (2001).
[6] D. H. Triyoso, R. I. Hegde, S. Zollner, M. E. Ramon, S. Kalpat, R. Gregory, X. D. Wang, J. Jiang, M. Raymond, R. Rai, D. Werho, D. Roan, B. E. White, Jr., P. J. Tobin, J. Appl. Phys. **98**, 054104 (2005).
[7] K. M. A. Salam, H. Fukuda, S. Nomura, J. Appl. Phys. **93,** 1169 (2003).
[8] R. J. Cava, W. F. Peck, Jr., J. J. Krajewski, Nature **377**, 215 (1995).
[9] D. Spassov, E. Atanassova, D. Virovska, Appl. Phys. A **82**, 55 (2006).
[10] E. Atanassova, A. Paskaleva in: Thin Films and Coatings New Research, ed. B. Caruta, Nova Sci. Publ. Inc. New York (2005), p. 27.

---

*Corresponding author: d_spassov@abv.bg