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Microelectronics Journal 32 (2001) 553–562

Microelectronics Journal

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Influence of γ radiation on thin Ta_2O_5–Si structures

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Received 18 January 2001; revised 26 February 2001; accepted 19 March 2001

Abstract

The effect of γ irradiation (10^6–5×10^7 rad) on the electrical and dielectric properties of thin tantalum pentoxide layers obtained by two methods (rf sputtering and thermal oxidation) have been investigated. It is established that the irradiation degrades the characteristics of the layers in terms of dielectric constant, oxide charge and leakage current. At the same time the irradiation does not affect the breakdown fields significantly. The influence of radiation depends on both the dose and the initial quality of the layers including their thickness: the degradation is more severe for the higher dose and the thinner layers; the as-fabricated, non-annealed films show poor immunity to radiation damage. The main source of electrically active defects in irradiated films is associated with the oxygen vacancies and the broken Ta–O and Si–O bonds. It was established that the higher temperature oxidation or annealing in O_2 are more beneficial for the radiation hardness of Ta_2O_5, which seems to be due to more a perfect layer structure obtained at high temperature oxygen treatment.

Keywords: High-k dielectrics; Radiation damage; MOS structure

1. Introduction

Further progressing in Dynamic Random Access Memories (DRAM) requires more reduction of memory cell area. The conventional films based on SiO_2 have reached their physical limits in terms of thinning for the needs of high density DRAMs. To overcome this problem, the use of high dielectric constant insulators has been suggested. As a result, the most obvious application of these materials in microelectronics at present is for memory cell dielectrics in DRAMs. Ta_2O_5 is one of the strongest candidates to replace SiO_2 based insulators in the high density dynamic memories such as 256 Mbit and beyond [1–11]. Accordingly the parameters of tantalum oxide films prepared by various techniques have been extensively investigated in terms of microstructure, stoichiometry, electrical and dielectric properties. Since so much work has been done on Ta_2O_5, it is now in the closest position to practical application among the other metal oxides. Usually as-deposited or as-grown Ta_2O_5 has amorphous structure due to low temperature fabrication [12,13] and the films may crystallize during the high temperature post-formation processes [12–16]. Recently [4,7–11], we have reported the results on highly reliable Ta_2O_5 films with superior leakage characteristics applicable to sub-half micron memory devices. The layers have been obtained by two methods — rf sputtering and thermal oxidation of tantalum layer on Si. MOS capacitors with Ta_2O_5 layers exhibit excellent dielectric and electrical characteristics: dielectric constant of 37, oxide trap density $\sim10^{10}$ cm^{-2} and leakage current density less than 10^{-8} A cm^{-2} at approximately 1 MV cm^{-1} applied field. The conclusion made was that amorphous and stoichiometric Ta_2O_5 thin films can be successfully obtained by these two methods and the films are suitable for 64 and 256 Mbit DRAM applications.

An important factor on which the electrical parameters of thin layers depend and which in many cases causes electrical conduction in the microstructures is their radiation hardness. Since the tantalum pentoxide could be potentially used in radiation rich conditions, it is critical to have a knowledge of the radiation effects in MOS devices with Ta_2O_5. These effects in MOS capacitors with Ta_2O_5 as an insulator are very poorly studied [6]. It is found that, in general, the trapped positive oxide charge, the interface state density and the leakage current density have increased after irradiation. The conditions, however, under which the change in the leakage currents and in both the electrical and dielectric properties occurs in close relation with the parameters of the irradiation have not yet been clarified. The

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0026-2692/01/$ - see front matter
PII: S0026-2692(01)00043-X

purpose of this paper is to study the effect of γ irradiation on the properties of thin Ta_2O_5 layers (rf sputtered and thermally grown) in dependence on the technological conditions for films preparation.

2. Experimental procedure

p-type (100) Si wafers with the resistivity of 13–17 Ω cm, cleaned with a standard for submicron technology process were used as substrates in this study. Two sets of samples were formed: (i) After the chemical cleaning of the substrates, Ta film was deposited on Si by rf sputtering of a tantalum target in ambient Ar. The process parameters were as follows: base pressure — 6×10^{-4} Pa; Ar pressure — 3 Pa; rf power density — 2.2 W cm^{-2} and a deposition rate of 9.3 nm min^{-1}. The substrates were not intentionally heated during the Ta deposition and presumably remained at temperature close to the room. Subsequently the Ta films were oxidized in dry oxygen at atmospheric pressure at two temperatures, 823 and 873 K and the O_2 flow rate was 5 l min^{-1}. It is proposed that the oxidation temperatures T_{ox} are low enough so that the formation of tantalum silicide is prevented. After oxidation, capacitors were defined by evaporation of Al (thickness of 500 nm) through a shadow mask; capacitor area is in the range $0.1–2.5\times10^{-3}$ cm^2. Postmetallization annealing (PMA) was carried out in H_2 at 723 K for 1 h. (ii) Tantalum pentoxide layers were deposited on Si by rf reactive sputtering of a tantalum target in an Ar + O_2 mixture: oxygen content 10%, working gas pressure 3.3 Pa, rf power density 3.6 W cm^{-2}, deposition rate 5 nm min^{-1}, substrate temperature $T_s = 293$, 493 K. After deposition, the samples were annealed at 873 and 1123 K for 30 min in dry O_2.

All the samples were treated with γ radiation (1.25 MeV, ^{60}Co) with intensity 120 Rö s^{-1}. The temperature in the irradiation zone was under 313 K. Irradiation doses of 10^6, 10^7 and 5×10^7 rad were used. The thickness d of Ta_2O_5 and the refractive index n_{eff} were determined by ellipsometry ($\lambda = 632.8$ nm). Samples with d in the range from 25 to 90 nm were studied. The dielectric and electrical characteristics of the Ta_2O_5 structures were studied using HF (1 MHz) capacitance–voltage ($C–V$), current–voltage ($I–V$) and oxide breakdown voltage V_{bd} histogram measurements. The static dielectric constant ε_{eff} of the Ta_2O_5 layers was determined from the capacitance value C_0 in strong accumulation. V_{bd} of approximately 60 capacitors were measured on each wafer (2 inch in diameter). During the stress, the gate electrode was negatively biased so that the p-type silicon surface was in accumulation and the entire applied electric field appeared across the oxide. Ramp $I–V$ characteristics were used to investigate the leakage current through Ta_2O_5 at low voltages. The data were acquired by a microcomputer through IEEE interface bus. All electrical measurements were carried out in a screened dark chamber at room temperature.

3. Experimental results and discussions

3.1. Dielectric parameters

n_{eff} of the both types of as-prepared Ta_2O_5 (rf sputtered as well as thermally oxidized) was found to be in the range of 1.95–2.3 in dependence on the specific fabrication conditions of the layers [7,8]. The radiation did not change neither the thickness of the layers nor the values of n_{eff} as indicated by ellipsometry. Here we examine the changes of the effective dielectric constant and the oxide charge as a result of irradiation.

3.1.1. rf Sputtered Ta_2O_5

The effective dielectric constant of the layers with thickness of 25 nm is 12–14 and 15–16 for the as-deposited and the annealed layers respectively. After irradiation, ε_{eff} decreases to the values of 5–6 independently of the radiation dose as well as of the initial values of ε_{eff}. The fixed oxide charge density Q_f has changed from 2×10^{11} cm^{-2} for the as-deposited films to 3×10^{12} cm^{-2} after irradiation. The shift of the $C–V$ curves has indicated positive charge build-up as a result of exposure to ionizing radiation only for the as-deposited layers. For illustration, Fig. 1 presents HF $C–V$ curves before and after exposure to a dose of 10^7 rad for the samples obtained at $T_s = 293$ K. One can see that C_0 of the irradiated layer is lower as compared to the initial one, which is due to the radiation induced decrease of ε_{eff}. The flat band voltage shift ΔV_{fb} is negative in all cases indicating a net positive charge trapping in the films. The radiation induced oxide charge (without gate bias during irradiation) ΔQ_f is about 5×10^{11}, 2×10^{12} and 3×10^{12} cm^{-2} for doses 10^6, 10^7 and 5×10^7 rad, respectively. After radiation the

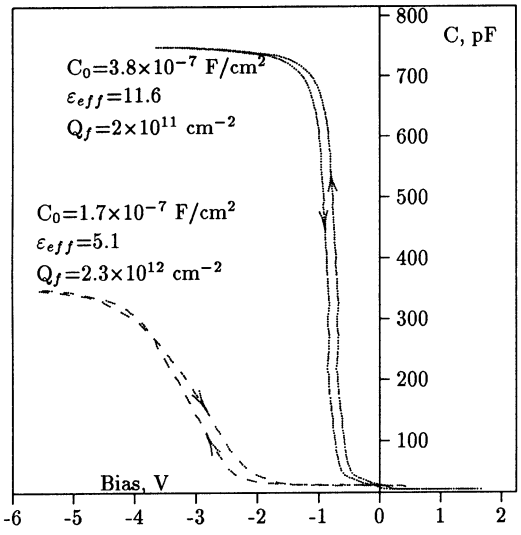


Fig. 1. Typical 1 MHz capacitance–voltage curves with a ramp rate of 100 mV s^{-1}, for as-deposited 293 K sputtered 25 nm Ta_2O_5 MOS capacitor (4 nm thickness of SiO_2) before (-) and after (- -) 10^7 rad γ irradiation; the dielectric constants are 11.6 and 5.1, respectively; the direction of voltage sweep is indicated by arrow.

C–V curves are stretched out along the voltage axis. This voltage stretch out can be caused either by an increase of charge nonuniformity or by an increase of interface trap density. Even a dose of 5×10^7 rad does not cause a generation of oxide charge in the oxygen annealed samples (873 or 1123 K) and the density of oxide charge in these layers remains about 10^{10} cm^{-2} before as well as after the radiation. Hysteresis effects are observed in the bidirectional scans of C–V curves in Fig.1. The hysteresis of the curves for the as-deposited layers is positive and respectively the density of slow states is determined to be $\sim 3 \times 10^{10}$ cm^{-2}. After irradiation the hysteresis is negative indicating an additional $\sim 2 \times 10^{11}$ cm^{-2} positive charge build-up. No C–V hysteresis was observed for annealed layers before as well as after the irradiation. Since the slow states (which are also called border traps) are usually related with the presence of oxygen vacancies in the Ta_2O_5–Si system, the results provide evidence for the negligible amount of the oxygen vacancies in the annealed layers before as well as after the γ irradiation. The as-deposited, non-annealed films, however, are not radiation hard enough and the exposure generates oxygen vacancies in the form of slow states with significant density, which is practically independent of the dose.

3.1.2. Thermal Ta_2O_5

The values of ε_{eff} of the thinner layers decrease slightly after exposure (Fig. 2) with a tendency to saturate at 10^7 rad. The radiation does not influence ε_{eff} for thicker layers ($\sim$90 nm) at all. (As we have reported recently [9,10], the dielectric constant of the thicker layers as a rule is larger than that of the thinner ones). So, the results imply that the irradiation has not a significant effect on ε_{eff} values up to doses of 5×10^7 rad. Very well-defined HF C–V curves together with a strong accumulation effect were obtained

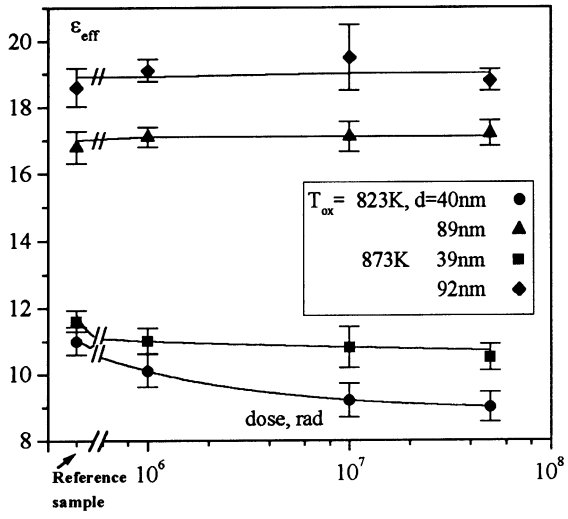


Fig. 2. Radiation dose dependence of the measured dielectric constant for thermal Ta_2O_5 obtained at two oxidation temperatures to thickness $d \sim 40$ and $\sim$90 nm.

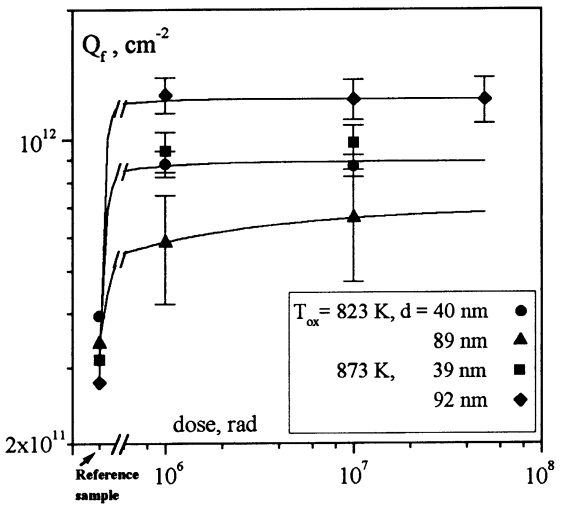


Fig. 3. Q_f vs radiation dose for the same Ta_2O_5 layers presented in Fig. 2.

for the as-grown Ta_2O_5 [9,10]. The variation of Q_f as a function of the dose is shown in Fig. 3 for the layers obtained at the two temperatures of oxidation. For the reference samples, Q_f is $\sim 3 \times 10^{11}$ cm^{-2} without a clear dependence on d and T_{ox}. After radiation with 10^6 rad, Q_f increases 2–4 times and after that it does not change with dose. The temperature of oxidation does not influence Q_f values for the thinner oxides. For thicker oxides, the radiation induced fixed oxide charge is lower for the oxides obtained at lower oxidation temperature (823 K). In general, the irradiation does not degrade the radiation hardness of the layers significantly. As far as ΔQ_f is found to depend slightly on the oxidation temperature, it can be concluded that the oxides grown at different temperatures show no apparent difference in radiation hardness. However, it is hard to say if the oxidation temperature of 823 K is better than 873 K since ΔQ_f is dependent not only on T_{ox} but also on the thickness. In general it seems that the increase of growth temperature above 823 K degrades the radiation hardness.

The hysteresis of the C–V curves of the samples before as well as after the radiation was negligible (the flat band voltage shift arising from the hysteresis effects is around 0.1–0.2 V for all curves, after sweeping from accumulation to inversion and back) and the curves were steep, indicating no generation of some kinds of traps (most likely slow states) located in the Ta_2O_5 very close to the interface with silicon. No change in the sharpness of the C–V curves after radiation was observed, i.e. in a first approximation, the radiation did not affect the density of fast surface states. The presence of extremely thin SiO_2 layer between Ta_2O_5 and Si detected by us previously [8] may be responsible for the formation of a high quality interface at Si.

3.2. Leakage current characteristics

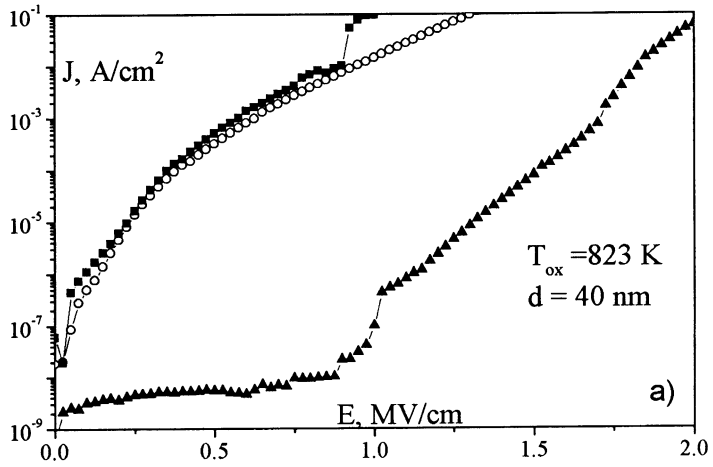
To clarify the effect of radiation on the conduction

properties of Ta_2O_5 films, leakage current characteristics of the irradiated capacitors were examined.

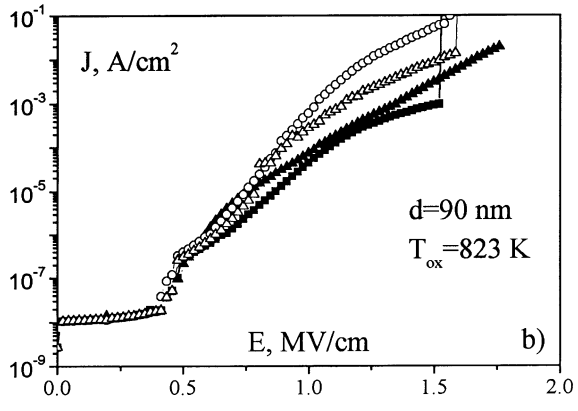
3.2.1. Thermal Ta_2O_5

Fig. 4 shows the leakage current density vs electric field characteristics for the MOS capacitors with Ta_2O_5 layers grown at 823 K. The as-grown Ta_2O_5 shows a low leakage current, $J \leq 10^{-8}$ A cm^2 up to 4 V applied voltage. Above 4 V, the leakage increases monotonically. After irradiation J is higher than that of the as-grown layers and the extent of the current increase depends on the layer thickness and the applied voltage. (The I–V characteristics of the initial samples as well as their change after irradiation for Ta_2O_5 obtained at 873 K are almost the same and they are not shown in the figure). The larger is the increase for the thinner layers (Fig. 4a) and for low applied fields ($\leq$0.7 MV cm^{-1}), it is 4–6 orders of magnitude higher than the current of the as-grown samples. At higher fields, the current increases monotonically with the applied voltage. The leakage current increase for 40 nm layers is the same for radiation doses in the range of 10^6–5×10^7 rad, i.e. no obvious radiation dose dependence in the behaviour and in the values of the current was observed. No deterioration of the leakage current was found for samples with thicker Ta_2O_5 (90 nm) irradiated at 10^6 rad (Fig. 4b). The radiation only reduced the catastrophic (hard) breakdown fields, (from 3 MV cm^{-1} before to 1.6 MV cm^{-1} after irradiation). The catastrophic breakdown field or the breakdown strength is defined as a field at which a sudden and an irreversible increase in leakage current occur. The layers irradiated with doses of 10^7–5×10^7 rad have inferior leakage current characteristics for fields greater than 1 MV cm^{-1} as compared to the pre-irradiated ones — the leakage is increased by 1–2 orders of magnitude, leading quickly to an early breakdown (Fig. 4b).

Generally, the results show that γ irradiation will be a problem for the Ta_2O_5–Si structures and the capacitors with irradiated films have deteriorated leakage characteristics compared to the initial ones. This effect is most probably due to the radiation generated defects in the Ta_2O_5 and at the



(a)



(b)

Fig. 4. Leakage current density on the applied field, E, for the thermal Ta_2O_5 MOS capacitors, before -▲- and after γ radiation: -■- 10^6 rad; -○- 10^7, 5×10^7 rad; (a) $d = 40$ nm; (b) $d = 90$ nm.

interface with Si, which leads to an increase of the leakage current. On the other hand, at least two other factors could contribute to the increased leakage and they cannot be neglected: the radiation induced change of the thickness of the interfacial SiO_2 (most likely increase of the thickness as indicated by the decrease of the global dielectric constant of the thinner layers, Fig. 2), which is inevitably formed during the fabrication of Ta_2O_5. Recently, our X-ray photoelectron spectroscopy investigations [9] clearly revealed the formation of interfacial SiO_2 layer (of about 2–3 nm) under all technological regimes used. The thickness and the quality of this layer depend on the oxidation temperature. As far as the total thickness of the layer as measured by ellipsometry is almost completely independent of the radiation, the deterioration of the current may be due to the increase of SiO_2 thickness as a result of the reduced thickness of the outer Ta_2O_5. (The growth of SiO_2 layer at the interface leads to an increase of the equivalent oxide thickness of the layer. The change of the thickness of SiO_2 leads also to a redistribution of the electric field). The second phenomenon can be correlated with an eventual radiation induced crystallization effects in the initial layers, which have been found to be amorphous [8–11] after the growth. A deterioration of the leakage current is usually observed when the layers are crystallized [2,17]. The current increase is thought to be caused by the grain boundaries which serve as current paths resulting in poor leakage current characteristics. The relationship between the leakage current properties and the crystalline structure of the tantalum oxide has not yet been clarified. Eventual radiation induced crystallization effects in Ta_2O_5 are not understood at all, and further investigations are mandatory to explain the above observations.

3.2.2. rf Sputtered Ta_2O_5

Fig. 5a shows current density J vs applied voltage for the as-deposited at 293 and 493 K 25 nm Ta_2O_5 before and after oxygen annealing (the leakage current characteristics did not show a difference from capacitor to capacitor on one and the same wafer). For the as-deposited films, leakage current about and below 10^{-8} A cm^{-2} at 0.5 MV cm^{-1} can be achieved without annealing steps. The films fabricated at 493 K have a little better leakage current characteristics at low applied fields. The annealed films show improved characteristics, $J \sim 10^{-8}$ A cm^{-2} for applied voltages up to ~6 V. As is seen, after oxygen annealing (OA), there is a general shift of the curves to higher voltages, indicating an increase of breakdown fields and dielectric strength. The effect seems to result from the repairing of oxygen vacancies in Ta_2O_5 and densification of the layers as a whole. The comparison of Fig. 5a and b shows that 10^6 rad dose has negligible influence on the leakage current up to voltages which are actual from a practical point of view and are close to the breakdown voltages. The effect of radiation is well pronounced for 10^7 rad — J increases by 1–3 orders of magnitude when the applied voltage increases up to 5 V. The radiation does not alter the I–V characteristics up to fields of ~0.5 MV cm^{-1}. For simplicity, the effect of dose on the I–V curves is presented in Fig. 5c only for one of the layers (annealed at 873 K). In the case of 5×10^7 rad, the leakage current is nearly equally deteriorated as that for 10^7 rad dose. So, the results indicate that the layers are stable to γ irradiation up to the dose of 10^6 rad, i.e. this dose does not change the quality of the capacitors in terms of leakage current. Relatively severe degradation of the leakage current can be observed after exposure to 10^7–5×10^7 rad. The reason for the worsening of the electrical properties in this case is that the layers are damaged by introduction of radiation defects in the form of broken Ta–O and/or Si–O bonds. The radiation induced crystallization of these films also cannot be ruled out. From the analysis of Fig. 5 it is clear that the initial quality of starting oxide influences the magnitude of the leakage current after radiation: the irradiated annealed films have lower current in comparison with the irradiated as-deposited ones. This means that the annealed in O_2 layers have higher γ radiation hardness. It emerges that for higher voltages the relative change of the leakage current after irradiation as compared to the initial current value is nearly the same (Fig. 5c), i.e. the relative change depends on the average electric field in the oxide rather than on the absolute current level. As is seen, the curve corresponding to 10^7, 5×10^7 rad shifts parallel to lower voltages with respect to the curve of the non-irradiated oxide. This implies that most probably the radiation induced damage is uniformly distributed throughout the Ta_2O_5.

In general, three possible explanations [6,18] exist for the observed increase of the leakage current after γ radiation: (i) lowering of the barrier height at Al/Ta_2O_5 interface because the building up of a charge in Ta_2O_5 near this contact seems possible, (ii) reduction of Ta_2O_5 to tantalum suboxides and hence an increase of the conductivity of the layers (the oxygen deficiency in Ta_2O_5 is one of the reasons for the leakage current through the films [19,20]) and (iii) modification of Si–Ta_2O_5 interface as a result of reduction of Ta_2O_5 and oxidation of Si substrate during radiation, leading to enlargement of the mixed transition layer consisting generally of both tantalum and silicon suboxides. The possibility for such modification is supported by the observed changes in Q_f. So, we have obtained that the irradiated films have leakage current larger than the starting ones. Recently [21], we have shown by X-ray diffraction (XRD) that the sputtered as-deposited as well as annealed at 873 K layers are amorphous, whereas crystalline Ta_2O_5 (orthorombic β-Ta_2O_5 phase) was obtained after OA at 1123 K. It should be kept in mind, however, that in order to detect crystallinity with XRD methods, a certain size of crystallites is required. The absence of diffraction peaks provide only an upper limit of the volume fraction of the crystalline phase. For XRD the lower limit of detection is approximately a volume fraction of the crystalline phase of 0.001 [22]. That is why XRD data have to be considered only in terms of the sensitivity of this method. A combination of

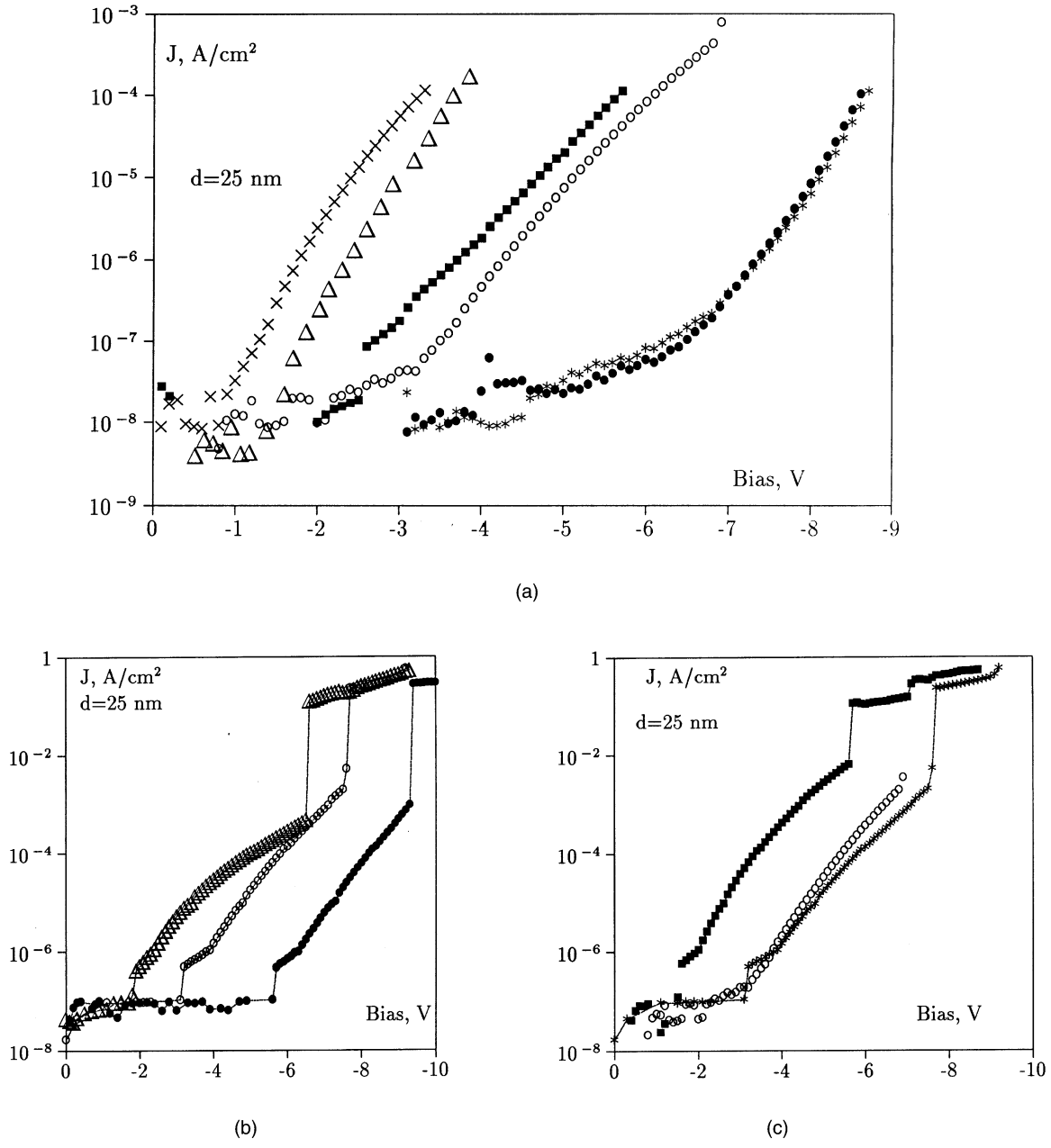


Fig. 5. (a) Current density–voltage curves for rf sputtered Ta_2O_5 MOS capacitors: $T_s = 293$ K, × as-deposited, ○ OA, 873 K; ● OA, 1173 K; $T_s = 493$ K, △ as-deposited; ■ OA, 873 K; ∗ OA, 1123 K, (b) J–V curves of rf sputtered Ta_2O_5 MOS capacitors after 10^6 rad γ radiation; $T_s = 493$ K, △ as-deposited; ○ OA, 873 K; ● OA, 1173 K, (c) J–V curves of MOS capacitors with rf sputtered oxygen annealed at 873 K Ta_2O_5 layers before ○ and after γ irradiation (∗ 10^6 rad, ■ 10^7, 5×10^7 rad).

XRD data and the present leakage current and Q_f data suggests and reveals that the crystalline Ta_2O_5 (obtained after heating at 1123 K) shows better leakage current properties. The I–V data for the rf sputtered layers strongly suggest also that the radiation hardness is completely independent of the crystal (amorphous) status of the layers — the relative increase of the leakage current is practically the same for the amorphous and the crystalline Ta_2O_5. The absolute value of the current after irradiation depends on the initial value before the exposure — the annealed layers have better leakage current characteristics before as well as after irradiation. Having in mind also the dielectric constant data it is seen that for the amorphous (as-deposited and annealed at 873 K) films the intrinsic dielectric constant of Ta_2O_5 is 23–27 and for the 1123 K annealed when a crystalline phase appeared it is significantly higher (32–37), i.e. the crystalline Ta_2O_5 shows larger values of dielectric constant. The deviation of the measured dielectric constant

ε_{eff} from the values of the relative dielectric constant of the bulk Ta_2O_5 is due to the presence of the ultrathin SiO_2 at the interface with Si. Usually, Ta_2O_5 leakage current increases with its crystallization [2,17]. In contrast, we obtain that for the crystalline 1123 K annealed layers the leakage current is smaller. On the other hand, the leakage current degradation after radiation can be correlated with eventual critically high level of radiation induced crystallization of the films, leading actually to the increase of the current. No one, however, of the presented possible explanations for the current degradation could be ruled out at this stage of our investigations. The exact clarification of this fact requires further detailed study of an eventual crystallization of the irradiated layers.

3.3. Breakdown fields

Breakdown characteristics of the layers before and after irradiation are discussed in this section. Breakdown field E_{bd} is detected when the leakage current is larger than 10^{-6} A. As is seen in Fig. 6, the breakdown characteristics of the annealed rf sputtered Ta_2O_5 layers are better than that of the as-deposited one. Since no obvious dependence of E_{bd} histograms on the substrate temperature is observed, for simplicity only the data for $T_s = 493$ K are given in the figure. The oxide equivalent breakdown field E_{eq} of the annealed layer is as high as 20 MV cm^{-1}. E_{eq} is the breakdown field obtained using the "equivalent SiO_2 film thickness", which is defined by assuming that the films consist of a single layer having a dielectric constant of SiO_2. In general, OA improves the breakdown characteristics of Ta_2O_5 obtained at both deposition temperatures used — the effect is stronger for the higher temperature of annealing, Fig. 6a. These phenomena indicate that most of the fabrication induced defects were passivated during the anneal process. We correlate the improvement in E_{bd} with a reduction in oxygen vacancies and the non-perfect Ta–O bonds in the initial layers as well as with the general densification of the layers. The as-deposited layers exhibit a distribution of the measured breakdown fields in the range 3.5–5.5 MV cm^{-1} with a main peak at ~4.2 MV cm^{-1}. These parameters for the 1123 K annealed samples are 5–7 MV cm^{-1} and ~6.6 MV cm^{-1}, respectively. The results are consistent with the leakage current reduction after OA and the higher annealing temperature is more effective in

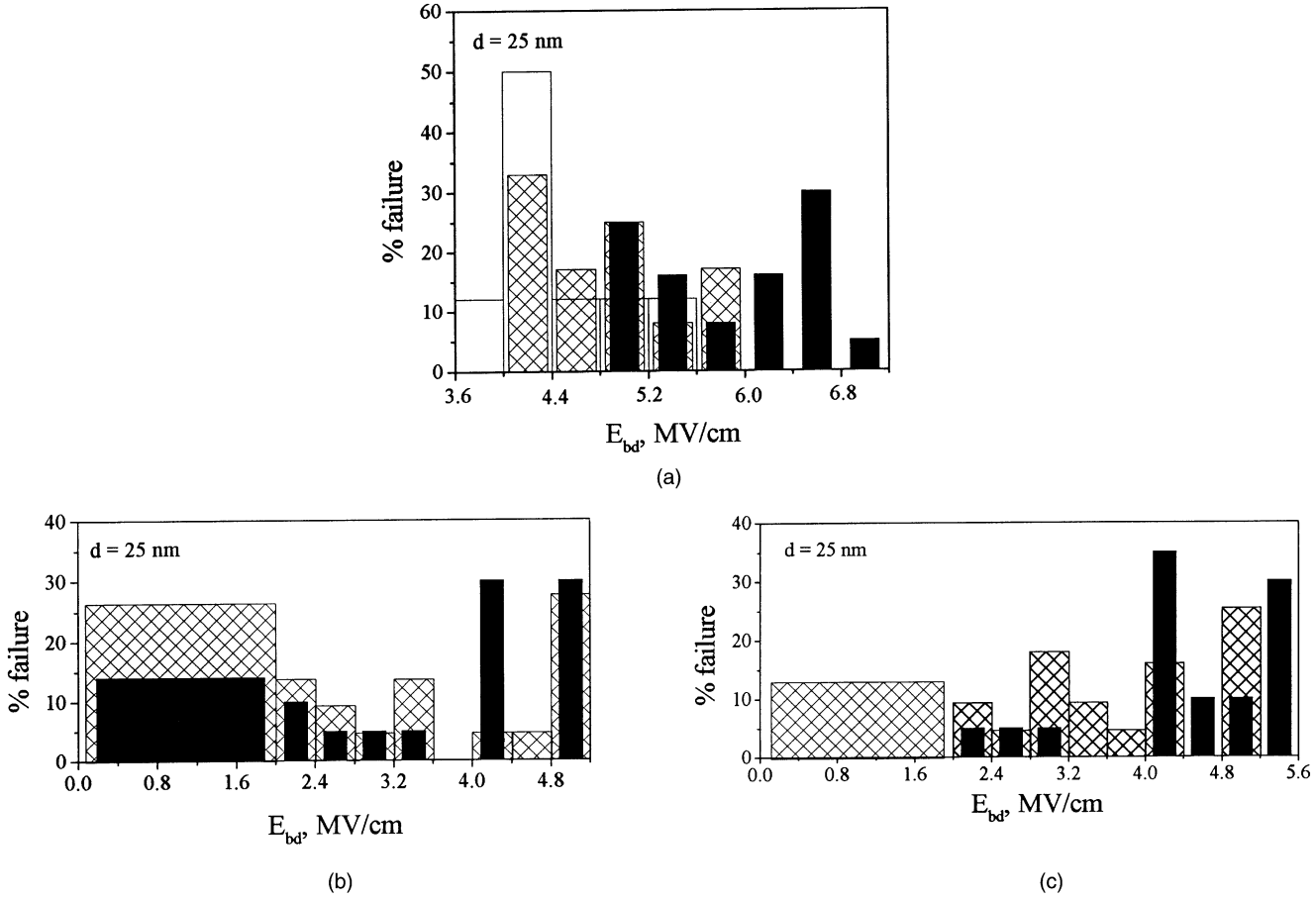


Fig. 6. (a) Breakdown histograms of 25 nm rf sputtered Ta_2O_5 before □ and after oxygen annealing at 873 K -##, 1123 K ■, (b) Breakdown histograms of 25 nm, 493 K as-deposited Ta_2O_5 after γ irradiation, ■ 10^6 rad; ## 10^7 rad, (c) Breakdown histograms of 25 nm, 493 K, oxygen annealed at 1123 K Ta_2O_5 after γ irradiation, ■ 10^6 rad; ## 10^7 rad.

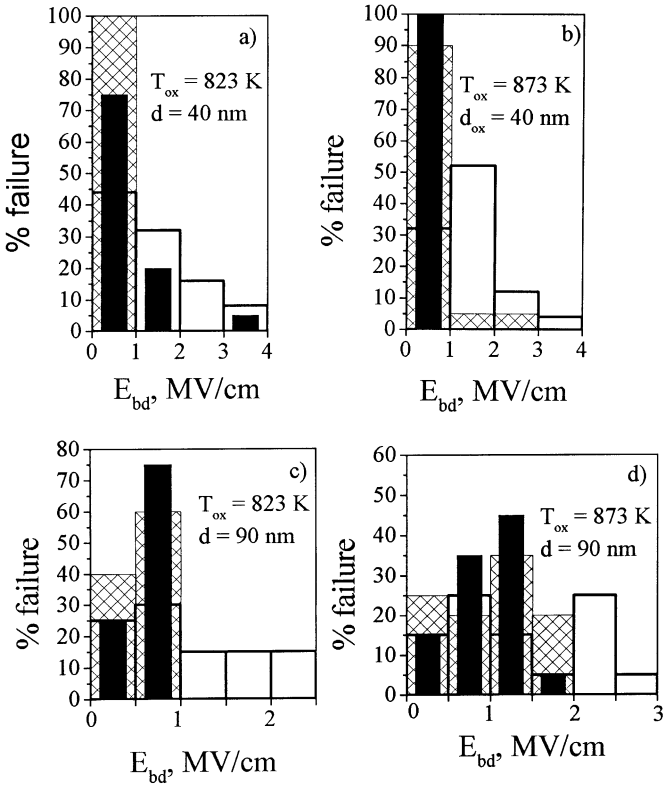


Fig. 7. Breakdown histograms of thermal Ta_2O_5 with two thicknesses obtained at two oxidation temperatures, before □ and after ## 10^6, ■ 10^7 rad, γ irradiation.

reducing the leakage. In general, all the irradiated samples with rf sputtered Ta_2O_5 exhibit not very strong deterioration of the breakdown field distribution. The influence of the radiation on the gate oxide breakdown frequency depends on both the dose and the initial quality of the layers. The as-deposited films are damaged more severely by irradiation: after 10^6 rad treatment, a low breakdown appears in the range 0.2–2 MV cm^{-1} with a peak intensity of ~15%; the high breakdown field peak shifts to the left at 4–5 MV cm^{-1} without intensity reduction. The higher dose irradiation (Fig. 6b) produces additional degradation — a main fraction of capacitors (~27%) break at 0.1–2.2 MV cm^{-1}; the high field breakdown localizes at about 5 MV cm^{-1} with an intensity of ~30%. The irradiation slightly affects the annealed samples — the degradation after the higher dose is more pronounced. The distribution for 10^6 rad dose is characterized with two main peaks at ~4 and 5.5 MV cm^{-1} with 30% intensity, and peaks with low intensity (≤10%) in the ranges 2–3 and 4.5–5 MV cm^{-1} (Fig. 6c). The higher dose leads to more random distribution of the breakdown fields: low and medium breakdowns appear in the ranges 0.2–2 and 2.2–4 MV cm^{-1}, respectively; the maximum E_{bd} is at 5 MV cm^{-1} with a slight reduction of the intensity.

The breakdown field of the thermal Ta_2O_5 slightly increases with increasing the growth temperature implying that the higher oxidation temperature is beneficial in terms of breakdown characteristics. The breakdown fields are practically the same for the two thicknesses used (Fig. 7) suggesting that the composition and the microscopic structure of the thermal oxides do not change significantly when varying the thickness from 40 to 90 nm. There is a weak tendency for slight increase of high field breakdowns for the thinner oxides — a peak with a small intensity (<10%) at 3–4 MV cm^{-1} appears. The intensity of high field breakdowns, however, remains low for all samples. After radiation the breakdown field characteristics worsen (the low and the medium field breakdowns increase and the effect is stronger for the higher dose) with slight dependence on d and T_{ox}. Fig. 7 shows the radiation induced breakdown histogram changes. All irradiated thermal Ta_2O_5 films break down at an electric field of about 0.5–1 MV cm^{-1} for 823 K and ~0.5–2 MV cm^{-1} for 873 K formed layers respectively, indicating that the higher oxidation temperature is more beneficial for radiation hardness of Ta_2O_5 in terms of breakdown. (For non-irradiated samples the breakdown frequencies have also a more random distribution). The damage of devices exposed to 5×10^7 rad is not more than that of devices with 10^7 and it is higher than 10^6 rad irradiated oxide. The breakdown of 90 nm Ta_2O_5 does not critically depend on dose in the range used. For the thinner (40 nm) films, however, the radiation damage is a severe problem — the main fraction of capacitors break down in the field range 0.2–1 MV cm^{-1} after exposure to 10^6 as well

as to 10^7 rad. Based on these results, one would tend to conclude that the radiation induced breakdown depends on the thickness of the oxide rather than on the radiation dose. It means also that the radiation induced damage (in the form of interface states and bulk traps) is relatively heavy and affects the breakdown characteristics. It can be concluded also that the tantalum oxides with a thickness above ~40 nm prepared at relatively high oxidation temperatures (like these used here) have good radiation hardness. The breakdown data for both types Ta_2O_5 (rf sputtered and thermal) are consistent with the results deduced from the I–V and C–V measurements. To understand and control the degradation of the electrical characteristics of the irradiated layers it is desirable to relate them to the composition and microscopic structure of the film and its interface. Usually the breakdown is manifested by the formation of a conductive path through the oxide, initiated by the presence of weak spots. It is related in this way to the microscopic properties of the layers and interface with Si and is basically associated with defects induced by the technological process (intrinsic defects like oxygen vacancies) as well as defects generated by the radiation. Although the true mechanism of the radiation induced breakdown in Ta_2O_5 is unclear, it is probably associated with broken bonds (Ta–O and/or Si–O). The exact answer of this question is related to the more general question concerning the mechanism of breakdown in Ta_2O_5 and particularly to the presence of ultrathin SiO_2 at the interface with Si. At present these questions remain open. We cannot eliminate a priori the possibility for the radiation induced crystallization effects in Ta_2O_5 — the issue that is not studied at all.

4. Conclusion

In this work we have examined the γ irradiation (10^6–5×10^7 rad) effect on the dielectric and electrical parameters of rf sputtered and thermal (25–90 nm) Ta_2O_5 layers on Si. The results presented allow to draw the following conclusions:

4.1. rf Sputtered Ta_2O_5

The radiation causes higher leakage current and lower dielectric constant, which decreases to values of 5–6 independently of its initial value as well as of the dose. The lower dielectric constant value confirms that the film structure is modified by the radiation. The as-deposited films are not radiation hard enough and the exposure generates significant defects in the form of positive oxide charge (5×10^{11}–3×10^{12} cm^{-2}) and slow states with a density of about 2×10^{11} cm^{-2}. The effect seems to result from some kind of oxygen vacancies generation related reaction. The formation of oxygen vacancies in the as-fabricated oxides results mainly from non-perfect oxidation. The results provide evidence, however, for the negligible amount of oxygen vacancies in the annealed layers. Even the highest dose used does not cause a generation of oxide charge in the OA samples.

The leakage current of the as-fabricated layers is larger after irradiation with a different value of increase in dependence on the dose. A relatively severe degradation is detected after 10^7–5×10^7 rad. The increase in the leakage current density most likely is attributed to broken Ta–O and/or Si–O bonds. The radiation induced crystallization of the as-deposited films also cannot be ruled out, and the leakage current degradation can be related with an eventual critically high level of radiation induced crystallization of the films leading actually to an increase of the current. The irradiated annealed films have lower current in comparison with the irradiated as-deposited ones, i.e. the oxygen annealed layers have higher radiation hardness. In this context, it can be concluded that the initial quality of starting oxide influences the magnitude of the leakage current after radiation and OA is beneficial for radiation hardness. These phenomena indicate that most of the irradiation induced defects are oxygen vacancies and/or some kind of degradation in the stoichiometry of the layers. They also support the argument that the latent defects, which are activated during irradiation, are in the form of oxide traps and are responsible also for the deterioration of breakdown characteristics. Since the radiation induced decrease of breakdown field is relatively weak, it can be concluded that the irradiation does not worsen the interface and the bulk to an extent at which the radiation induced catastrophic breakdown occurs and in fact the oxide is only slightly weakened.

4.2. Thermal Ta_2O_5

The radiation does not degrade the dielectric properties of the layers significantly: the dielectric constant decreases slightly for thinner layers and does not change for thicker ones at all; the density of oxide charge increases 2–4 times for 10^6 rad and saturates above a dose of 10^7 rad; no generation of slow states is observed — the presence of extremely thin SiO_2 layer between Ta_2O_5 and Si, may be responsible for the formation of high quality interface transition region. The results show, however, that the γ irradiation will be a problem in terms of leakage current — the extent of the current increase after irradiation depends on the layer thickness and the applied voltage; the effect of radiation is stronger for the thinner layers and higher doses — the current increase is 4–6 orders of magnitude at low applied fields $\leq$0.7 MV cm^{-1}. This result is attributed to the generation of electrically active defects in Ta_2O_5 and at the interface as well as to the radiation induced increase of interfacial SiO_2 layer as indicated by the decrease of the global dielectric constant after γ radiation for the thinner oxides.

The higher oxidation temperature is more beneficial for the radiation hardness of Ta_2O_5 in terms of breakdown, which is consistent with the data for the dielectric and electrical parameters of the layers. The results give evidence that a suitable choice of the oxidation temperature can

improve the radiation hardness. The radiation induced breakdown depends rather on the thickness of the oxide than on the radiation dose — the data clearly show that Ta_2O_5 with a thickness above about 40 nm prepared at a relatively high oxidation temperature has a good radiation hardness.

In summary, we have shown that γ irradiation can increase leakage current and oxide charges significantly. In fact, the presence of radiation induced traps in the system Ta_2O_5–Si is expected. The results prove the introduction of damage by radiation and the high level of leakage current is attributed to the presence of these traps. Although the true mechanism of radiation induced breakdown in Ta_2O_5 is unclear yet, it is most likely associated with broken and non-perfect Ta–O and Si–O bonds with a key influence of the interface transition region where SiO_2 and the intermediate oxidation states of Si coexists. Additional support of this suggestion is the good correspondence between the breakdown data and the results deduced from I–V and C–V measurements. In the context of advanced MOS technologies it is clear that the irradiation will give rise to reliability problems, which may be related to oxide failures, i.e. radiation induced damage remains a major concern for Ta_2O_5 reliability. Based on the results, however, one would tend to conclude that γ irradiation induced damage will have less impact on devices with thicker Ta_2O_5 and obtained or annealed at relatively high temperatures.

Acknowledgements

This work has been supported by Bulgarian National Science Foundation at Ministry of Education and Science under contract Physics 901.

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