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Original scientific paper

A MODEL BASED METHOD FOR COMPARING THE PROPERTIES OF SOME METAL-Ta_2O_5/SiO_2-Si STRUCTURES

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Oxygen annealed radio frequency (RF) reactively sputtered and thermally grown (thermal) Ta_2O_5 films on silicon were comparatively studied by using combination of *C-V* and *I-V* measurements and the previously developed comprehensive model for the metal-Ta_2O_5/SiO_2-Si structures. Dielectric properties of separate layers were extracted by comparing the experimental and the theoretical results. It is found that the net leakage properties of the Ta_2O_5 layer are significantly better in the case of RF than thermal, particularly in the case of the Au gate. Excessive growth of the SiO_2 layer of about 0.3 nm in the case of RF films leads to an unwanted increase of the equivalent oxide thickness. Appropriate interface engineering is required in order to prevent the SiO_2 excessive growth during the oxygen annealing. Such a growth can reduce the beneficial effects of the annealing on the net properties of Ta_2O_5 films obtained by RF.

Key words: high permittivity dielectrics; conduction in dielectrics; leakage currents model

INTRODUCTION

Ta_2O_5 films are nowadays extensively investigated for various applications, such as coatings for gravitational-wave detectors [1], multilayer stacked electrode in organic light-emitting diodes [2], resistive switching memories [3], gapless-type atomic switches [4], photocatalysts [5] etc. Ultrathin Ta_2O_5 films are particularly important as a new dielectric material for DRAM capacitors, because of their outstanding properties [6–9], such as high dielectric permittivity, high breakdown fields and low leakage current densities. The oxygen anneal of RF sputtered Ta_2O_5 films at high temperatures is found to be highly beneficial for their insulating properties [10, 11]. It significantly increases the dielectric constant, reduces the fixed charge Q_f (as low as 10^{10} cm^{-2}), reduces the leakage currents, and increases the breakdown field [8]. Pure oxygen ion assisted deposition provides similar improvements [12]. The fabrication of the insulating layer in the case of thermal growth [9] and RF-sputtering followed by oxygen anneal [8] is accompanied by unintentional formation of a silicon dioxide layer, and hence the insulating film has to be treated as a stacked layer. In [13, 14] we proposed and used a comprehensive model describing the leakage currents of thus obtained Ta_2O_5/SiO_2 stacked layers. It has been later generalized for different similar structures [15].

In the present work we study comparatively the RF-sputtered and thermally grown tantalum pentoxide films on silicon by using the model described in [14], in order to compare the impact of the discussed technologies on the properties of separate layers.

EXPERIMENTAL

Chemically cleaned p-type (100) 15 Ω·cm Si wafers were used as substrates. Some of the Ta_2O_5films were deposited at 220 °C by radio frequency (RF) reactive sputtering of 99.99 % pure Ta in a gas mixture of Ar and O_2. Other films were obtained by RF-sputtering of a Ta target in Ar atmosphere followed by thermal oxidation in dry O_2 at 600°C (thermal). All the films were subsequently annealed in dry oxygen at 900 °C for 30 min. The thickness of Ta_2O_5 and the refractive index were measured by ellipsometry (λ = 632.8 nm). The obtained thickness was $d_{tp} = 50$ nm. The refractive index was typically 2.1, approximately equal to the generally adopted value 2.2.

Metal-Insulator-Semiconductor (MIS) capacitors with two different gate electrodes (Al and Au) were formed. Al and Au electrodes were deposited by thermal evaporation. Au electrodes were deposited onto the Ta_2O_5 film using shadow mask technique. The corresponding gate electrode area is 1.96×10^{-3} cm^2. The MIS capacitors for the Al top electrodes were defined using photolithography and have the active areas of 2.5×10^{-3} cm^2.

High frequency (1 MHz) *C-V* characteristics were measured by a HP 3284 A LCR-meter. For the quasi-static measurements a HP 4140 B picoammeter/voltage source was used, at a voltage ramp rate of 0.1V/s.

I–V characteristics were measured by a HP 4140 A picoammeter DC voltage source. Current was measured in steps of 0.1V, with a hold time of 5 s, allowing for the obtainment of negligible displacement current, as it was confirmed by reversing the voltage range of the measurement. Repeated measurements in the ranges used in this work gave practically the same results, proving that the charge trapping during these measurements does not affect significantly the film properties.

THEORY (SECTION III)

The conduction mechanisms that are considered are:

1. For the SiO_2 layer, hopping conduction along with direct tunneling through a trapezoidal barrier or Fowler-Nordheim tunneling through a triangular barrier, depending on the electric field in the layer (E_{so}). Tunneling current can be created by the electrons or the holes. The barrier for the tunneling of holes is substantially higher than the barrier for electrons. Different carriers from the silicon substrate produce this current: electrons in the case of gate positively biased and holes in the case of gate negatively biased. Hence, the current depends upon the gate polarity.

2. For tantalum pentoxide, Poole–Frenkel mechanism, that is bulk-limited, thus independent on the polarity.

Direct tunneling current density through the SiO_2 layer (J_{DT}) is given by the following expression:

$$J_{DT} = \frac{q^2}{8\pi h\Phi} E_{so}^2 \exp\left(-\frac{8\pi\sqrt{2m^* q\Phi^3}}{3hE_{so}} \left(1 - \left(1 - \frac{d_{so}}{\Phi} E_{so} \right)^{3/2} \right) \right) \tag{1}$$

and Fowler-Nordheim tunneling current density by

$$J_{FN} = \frac{q^2}{8\pi h\Phi} E_{so}^2 \exp\left(-\frac{8\pi\sqrt{2m^* q\Phi^3}}{3hE_{so}} \right), \tag{2}$$

where q is the electron charge, h is the Planck's constant, m^* is the effective tunneling mass of carriers in SiO_2, d_{so} is the thickness of SiO_2 layer, Φ is the tunneling barrier height, and E_{so} is the electric filed in SiO_2 layer.

Total leakage current density through the SiO_2 layer (J_{so}) is given by

$$J_{so} = \sigma_{hc} E_{so} + \begin{cases} J_{DT} & E_{so} < \dfrac{d_{so}}{\Phi} \\ J_{FN} & E_{so} > \dfrac{d_{so}}{\Phi} \end{cases}, \tag{3}$$

where σ_{hc} is the hopping conductivity in the SiO_2 layer.

The voltage drop on the SiO_2 layer (V_{so}) is:

$$V_{so} = E_{so} d_{so}. \tag{4}$$

Leakage current density due to the Poole-Frenkel mechanism in the Ta_2O_5layer (J_{tp}) is given by the following expression:

$$J_{tp} = \sigma_{tp} E_{tp} \exp\left(\frac{1}{kT} \sqrt{\frac{q^3}{\pi\varepsilon_0 K_T}} \sqrt{E_{tp}} \right), \tag{5}$$

where E_{tp} is the electric field in the Ta_2O_5 layer, σ_{tp} is temperature-dependent defect-related constant having dimensions of conductivity, k is the Boltzmann constant, ε_0 is the dielectric constant of vacuum and $K_T = n^2$ is the optical frequency dielectric constant (n is the refractive index) of Ta_2O_5.

The voltage drop on the Ta_2O_5layer (V_{tp}) is given by:

$$V_{tp} = E_{tp} d_{tp}, \quad (6)$$

where d_{tp} is the thickness of the Ta_2O_5 layer.

The two quantities that are computed simultaneously here are the oxide voltage:

$$V_{ox} = V_{tp} + V_{so} = d_{tp} E_{tp} + d_{so} E_{so}, \quad (7)$$

and the current density in steady state

$$J = J_{tp} = J_{so}. \quad (8)$$

Current density $J = J_{so}$ was computed for given field E_{so} in the silicon dioxide, then the field in Ta_2O_5 layer was computed as inverse function of current of $J_{tp} = J$ and the oxide voltage determined with the use of the expression (6). Following typical values were used in computations: $m_e^* = 0.61$ m_0– effective electron mass in SiO_2 (m_0 denotes the mass of free electron), $m_h^* = 0.51$ m_0 – effective hole mass in SiO_2 and $K_T = 4.84$.

The voltage on the insulating stacked layer (V_{ox}) was calculated by using relations involving the flatband voltage (V_{fb}),the gate voltage (V_g) and voltage drop in the semiconductor (φ_s) [16]

$$V_{ox} = V_g - V_{fb} - \varphi_s. \quad (9)$$

The voltage drop in the semiconductor (φ_s) has been computed solving numerically the following equation [15]:

$$E_{so} = \pm \frac{\varepsilon_s}{\varepsilon_{so}} \sqrt{\frac{2kTp_0}{\varepsilon_s \varepsilon_0} \left[\left(\exp\left(-\frac{q\varphi_s}{kT} \right) + \frac{q\varphi_s}{kT} - 1 \right) + \frac{n_i^2}{p_0^2} \left(\exp\left(\frac{q\varphi_s}{kT} \right) - \frac{q\varphi_s}{kT} - 1 \right) \right]}, \quad (10)$$

where ε_s is the relative permittivity of Si (11.9), ε_{so} is the relative permittivity of SiO_2 (3.9), ε_0 is the permittivity of vacuum, n_i is the intrinsic concentration of carriers in Si (1.45×10^{10} cm^{-3}) and p_0 is the steady state majority carrier (holes) concentration in p-type Si.

RESULTS AND DISCUSSION

The high-frequency (1 MHz) *C-V* characteristics for all the considered samples are shown in Figure 1. It is visible that the capacitances in accumulation for RF samples are lower than those for thermal ones. The entire characteristics for RF are shifted towards the right compared to the thermal. Applying the standard procedures used for MOS structures, the equivalent oxide thickness (d_{eq}) [17], the fixed charge density (Q_f) [18] and the interface state density at midgap (D_{itm}) [19]were computed. The results are shown in Table 1. Equivalent thicknesses of the RF films are significantly higher than those of the thermal ones. Fixed charge is positive in the case of the thermal films and negative in the case of RF. The interface state densities are of order of 10^{12} eV^{-1}cm^{-2} and are significantly lower in the case of RF than thermal. Fixed charges of thermal films are about 4×10^{11} cm^{-2}, that is less positive than the value obtained for the films without oxygen anneal, 1.2×10^{12} cm^{-2} [15]. RF films with the fixed charge of about -1.5×10^{12} cm^{-2} manifest similar shift toward the negative values compared to the unanealed RF films ($Q_f = 6 \times 10^{11}$ cm^{-2}) [15]. The oxygen annealing leads in some cases to negative values of Q_f. It is certain that not only positively charged defects are reduced, but an important amount of negatively charged defects is created. This can be explained by the crystallization of the Ta_2O_5 layer, leading to broken bonds at the Ta_2O_5/SiO_2 interface [20]. We have shown that the oxygen anneal at lower temperatures (600 ÷ 850 °C) leads to very low fixed charges (as low as 10^{11} cm^{-2}) [8]. Therefore, increasing the annealing temperature to 900 °C or above can have harmful effects on the fixed charge.

Table 1. Parameters extracted from the *C-V* characteristics

Growth	Gate	d_{eq} (nm)	Q_{ox} (cm^{-2})	D_{itm} (eV^{-1}cm^{-2})
RF-sputtered	Al	8.7	-1.4×10^{12}	1.2×10^{12}
	Au	9.2	-1.6×10^{12}	2.0×10^{12}
Thermal	Al	8.3	4×10^{11}	4.0×10^{12}
	Au	8.4	6×10^{11}	3.0×10^{12}

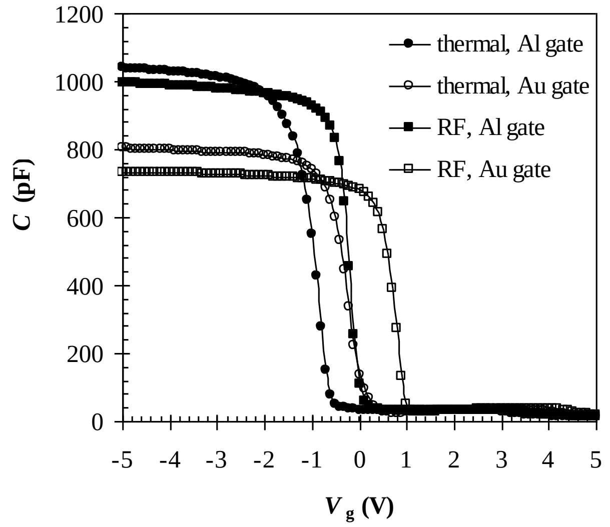

Figure 1. *C-V* characteristics of the MOS capacitors with areas of 0.0025 cm^2 (Al gates) and 0.00196 cm^2 (Au gates) containing thermally grown and RF-sputtered Ta_2O_5 films

The leakage current characteristics shown in Figures 2 and 3 were analyzed by using the model described in the Section III. Few of the parameters were fitted to obtain the matching between the theoretical and experimental results. These are the parameters influenced by the technological processes and not those that are accurately determined in the literature, listed in Section III. The parameters extracted by fitting the theoretical to the experimental results are given in Table 2.

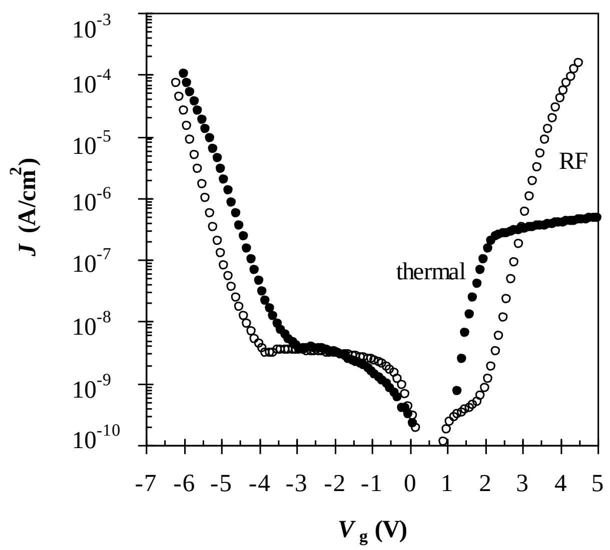

Figure 2. Leakage currents for MOS capacitors with Al gate containing thermally grown and RF-sputtered Ta_2O_5 films

Very good agreement between the theoretical and experimental results in the entire measurement region is obtained (Figure 4), justifying the use of the proposed model in the analysis. Saturated part for the positive gate is due to the strong inversion and is not described by this model.

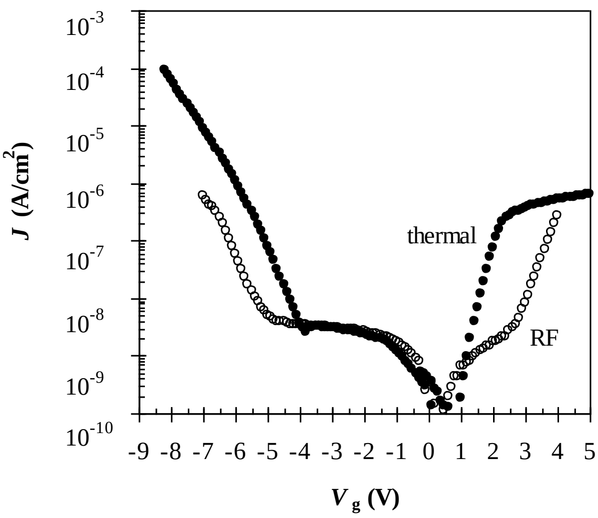

Figure 3. Leakage currents for MOS capacitors with Au gate containing thermally grown and RF-sputtered Ta_2O_5 films

The interfacial SiO_2 layer thickness for thermal films is about 2.7 nm, while for RF it is from 0.3 nm to 0.5 nm higher. Compared to the total thickness (50 nm) it is a very small value, but its contribution to the equivalent oxide thickness is significant. Barriers are practically equal to those for SiO_2 films from literature [13]. There are some differences between the values of the SiO_2 layer hopping conductivity for different samples, but they are comparable to the measurement error and can be disregarded. Thus, we can conclude that the quality of the SiO_2 layer is practically the same for both processes and both gate materials.

The parameter σ_{tp} is the most influenced by the technology and the gate material, which describes the net leakage properties of the Ta_2O_5 layer. In the case of Al gate, σ_{tp} is 3 times lower for RF than thermal films, while for Au gate, it is 10 times lower for RF than thermal. In [13] we explained the difference between Al and Au gates by the creation of defects due to the reactivity of Al with Ta_2O_5. In the case of non-reactive Au gate, the obtained value of σ_{tp} can be considered as intrinsic for the insulating material. Thus, the leakage factor for RF films is an order of magnitude lower than for thermal. In the case of Al gate, the difference between the RF and thermal films is less marked, because the majority of the defects responsible for the leakage are created by the reaction of the Al gate with the film and not during the growth of the insulating layer.

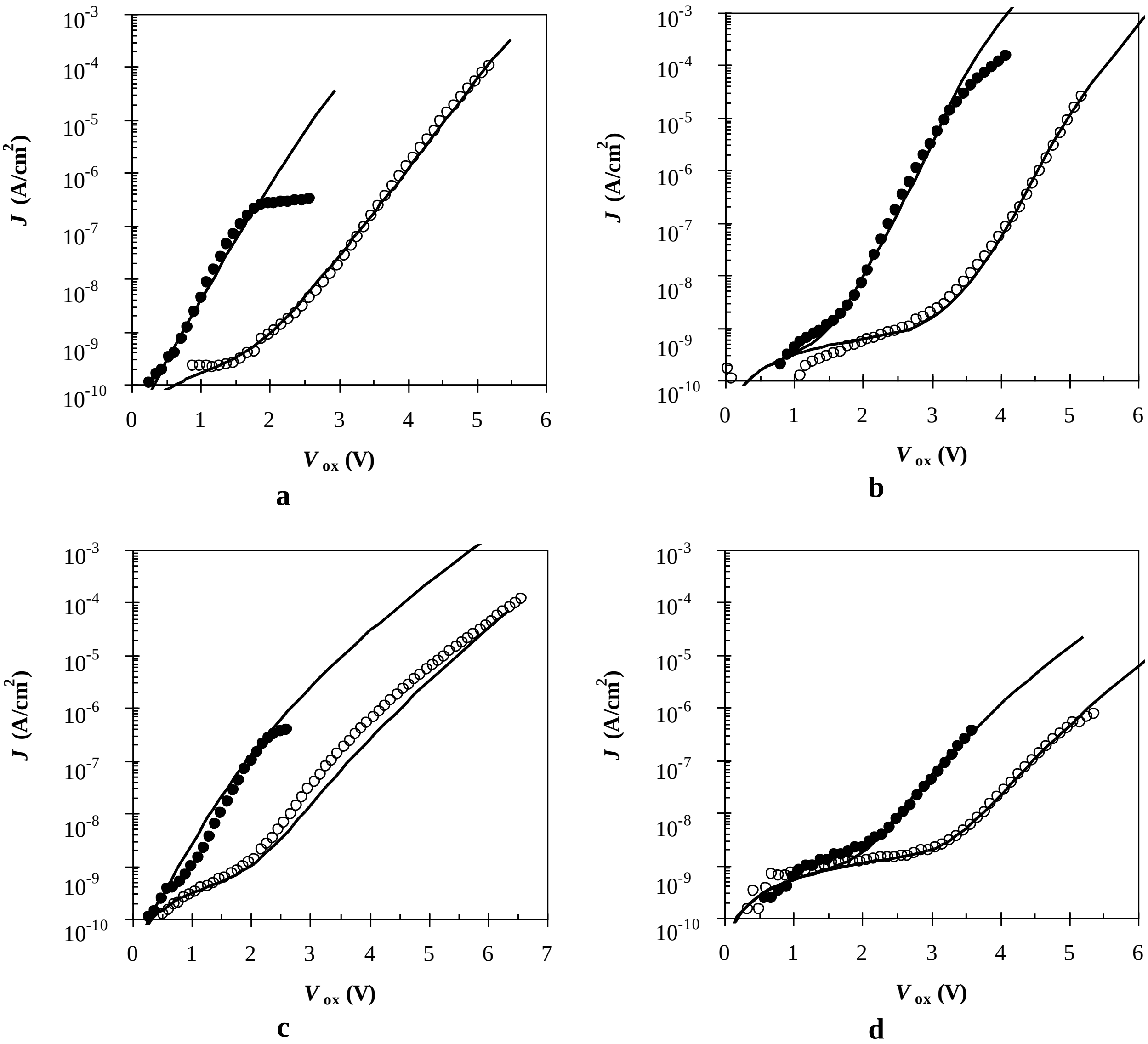

Figure 4. Experimentally obtained leakage currents versus oxide voltage for positive (closed circles) and negative gate (open circles) compared to the theoretical computations: **a)** thermally grown, Al gate, **b)** RF-sputtered, Al gate, **c)** thermally grown, Au gate, **d)** RF-sputtered, Au gate

Table 2. Parameters extracted from the *I-V* characteristics

Growth	Gate	d_{so} (nm)	σ_{hc} ($\Omega^{-1}cm^{-1}$)	σ_{tp} ($\Omega^{-1}cm^{-1}$)	Φ_e (eV)	Φ_h (eV)
RF-sputtered	Al	3.02	9.0×10^{-17}	2.5×10^{-11}	3.15	4.70
	Au	3.20	1.8×10^{-16}	5.9×10^{-15}	3.15	4.30
Thermal	Al	2.70	6.0×10^{-17}	8.2×10^{-11}	3.15	4.70
	Au	2.75	6.0×10^{-17}	6.6×10^{-14}	3.15	4.70

Using the measured total thickness values (d) and the obtained values for the SiO_2 layer thickness (d_{so}) and the equivalent oxide thickness (d_{eq}), the effective oxide dielectric constant (ε_{ef}) and the net dielectric constant of the Ta_2O_5 layer (σ_{tp}) were computed. Their values are given in Table 3. All the values are close to these reported in literature [15]. The values obtained for Al gate are slightly higher than these for Au gate, for both RF and thermal.

Table 3. Effective dielectric constant of the stack (ε_{ef}) and net dielectric constant of the tantalum pentoxide layer (σ_{tp}).

Growth	Gate	ε_{ef}	σ_{tp}
RF-sputtered	Al	22.5	34.8
	Au	21.1	32.3
Thermal	Al	23.5	34.8
	Au	23.2	34.4

CONCLUSIONS

Based on the use of a comprehensive model for leakage current in metal-Ta_2O_5/SiO_2-Si structures it has been found thatthe oxygen anneal of RF-sputtered films leads to significantly better net leakage properties of the Ta_2O_5 layer, compared to the thermally grown. However, the thickness of the interfacial SiO_2 layer for RF films is about 0.4 nm higher than this for thermal. Therefore, appropriate interface engineering in required in order to benefit from the outstanding net Ta_2O_5 layer without compromising the equivalent oxide thickness.

The use of the model of comparative analysis in description of the properties of separate layers, as is demonstrated in this work, provides in deep insight into the properties of the materials with reduced number of technological experiments compared to direct approach. Therefore, it is to be used in directed search of the technological solutions for materials with required properties.

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МОДЕЛЕН МЕТОД ЗА СПОРЕДБА НА СВОЈСТВАТА НА СТРУКТУРИ ОД ТИПОТ МЕТАЛ-Ta_2O_5/SiO_2-Si

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Филмови од Ta_2O_5 врз силициум добиени со високофреквенциско реактивно распрашување и термички третирани во кислород (РФ) и филмови од Ta_2O_5термички израснати (thermal) се проучувани компаративно со употреба на *C-V* and *I-V* и претходно развиениот сеопфатен модел за структури метал-Ta_2O_5/SiO_2-Si. Преку споредба на експерименталните со теориските резултати сеопределени диелектричните својства на одделните слоеви. Најдено е дека чистите својства за протекување низ слоевите од Ta_2O_5се значајно подобри во случајот на РФ отколку кај термички израснатите филмови, особено во случајот на горната електрода од Au. Додатниот пораст на слојот од SiO_2за околу 0,3 nm во случај на РФ-филмовите води до несакан раст на еквивалентната дебелина на оксидот. Потребно е да се направи соодветно нагодување на интерфејсот со цел да се избегне претеранпораст на SiO_2,едновремено користејќи ги подобрените чисти својства на филмовите од Ta_2O_5 добиени со РФ.

Клучни зборови: диелектрици со висока пермитивност; спроводливост низ диелектрици; модел за струите на протекување