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Current transients in solution-derived amorphous Ta_2O_5-based thin-film capacitors

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Abstract: Ta_2O_5-based thin films were prepared by Chemical Solution Deposition at temperatures not exceeding 400 °C. Amorphous Ta_2O_5 and Ta_2O_5–Al_2O_3–SiO_2 (Ta:Al:Si = 8:1:1 atomic ratio) films on platinized Si-substrates were investigated. The Ta_2O_5 film heated at 400°C exhibited the highest relative dielectric permittivity, ε_r (27±3). The ε_r decreased with a lowering of the processing temperature, and showed lower values for the Ta_2O_5–Al_2O_3–SiO_2 samples. However, the mixed-composition thin films exhibited less leakage and thus had improved current-voltage characteristics, compared to those of the pure Ta_2O_5 thin films.

Current vs. time (*I–t*) measurements were performed for the investigated Ta_2O_5-based capacitors in the metal-insulator-metal geometry. The drop in the current depended on both the composition and the thermal budget of the insulator. The recorded current transients are considered to be due to the trapping of the injected carriers in the dielectric film. The charging process proved to follow an exponential law.

This work is dedicated to the late Professor Marija Kosec

Keywords: leakage current, high-*K* dielectrics, amorphous materials, sol-gel chemistry

Prehodni tok v tankoplastnih kondenzatorjih na osnovi Ta_2O_5, pripravljenih s sintezo iz raztopine

Izvleček: S sintezo iz raztopine, nanašanjem z vrtenjem in s segrevanjem pri temperaturah do 400 °C smo pripravili amorfne tanke plasti na osnovi Ta_2O_5 in Ta_2O_5 – Al_2O_3–SiO_2 (molsko razmerje Ta: Al: Si = 8:1:1) na platiniziranih silicijevih podlagah. Plasti Ta_2O_5 izkazujejo najvišjo dielektričnost ε_r (27±3) po segrevanju pri 400°C, medtem ko je dielektričnost plasti, pripravljenih pri nižjih temperaturah nižja. Dielektričnost plasti na osnovi Ta_2O_5 – Al_2O_3–SiO_2 je prav tako nižja od dielektričnosti plasti samega Ta_2O_5, vendar plasti na osnovi mešanice oksidov izkazujejo boljše tokovno-napetostne karakteristike. Izmerili smo prehodne toke *I–t* tankoplastnih kondenzatorjev s strukturo kovina-dielektrik-kovina. Upadanje toka s časom ob konstantni napetosti izkazuje nepričakovano dolge časovne konstante. Hitrost upadanja toka s časom je odvisen tako od temperature segrevanja plasti kot tudi od kemijske sestave plasti. Razloge za opisani potek *I–t* pripisujemo procesu ujetja nosilcev naboja v dielektriku. Dejstvo, da lahko časovno odvisnost tokov v plasteh dielektrikov matematično opišemo z vsoto dveh ali treh eksponentnih funkcij nakazuje na to, da je v materialu prisotnih več različnih defektov z različnimi časovnimi konstantami procesa ujetja in sprostitve naboja.

Ključne besede: uhajalni tok, dielektriki z veliko dielektričnostjo, amorfni materiali, sol-gel

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1 Introduction

Transparent electronics has attracted much interest in the past years since it is considered to have the potential to be the next generation of optoelectronic devices [1]. It aims at the realization of fully transparent, lightweight and reliable electronics for everyday applications, *e.g.,* flexible displays. Thin-film transistors (TFTs) are important electronic devices that are mainly used as *on-off* switches in the active-matrix backplanes of

flat-panel displays. A lot of effort has been put into the research and development of transparent TFTs [2]. The requirements to be fulfilled include: low-cost deposition, low-temperature processing, suitable properties of the thin films both from the performance point of view and device downscaling. The first devices were reported about a decade ago [3,4,5], and have attracted considerable attention with respect to display applications. The transition from the a-Si:H TFTs to the transparent ones was conditioned by the use of materials with a higher dielectric permittivity (ε_r or *K*) than SiO_2. Therefore, the so-called high-*K* dielectrics should have an ε_r over 10, and preferably higher than 20 [6].

Ta_2O_5 thin films have attracted a lot of attention as insulating materials for metal–oxide–semiconductor field-effect transistors (MOSFETs) and high-density memory cells [7,8] due to their high dielectric constant [6], high refractive index and their chemical and thermal stability [9]. In past years the use of Ta_2O_5 as a gate dielectric in transparent TFTs has also been proposed. Thin films deposited by rf magnetron sputtering [10], and e-beam evaporation [11] showed promising performance in the new generation of oxide TFTs. To the best of our knowledge, little work has been reported on the sol-gel processing of such thin films, although it is an economic, versatile and effective method. In this work an investigation of the conduction mechanisms and the charging effects in Ta_2O_5-rich thin films in view of their application as gate dielectrics in TFTs is presented. Thin films of both the ternary composition Ta_2O_5–Al_2O_3–SiO_2 with the Ta:Al:Si = 8:1:1 atomic ratio (further denoted as 8:1:1) and pure Ta_2O_5 (further denoted as Ta) prepared by Chemical Solution Deposition (CSD) were investigated. The samples were processed at low temperatures, *i.e.,* not exceeding 400 °C, in order to check their suitability for gate-dielectric applications, and also to ensure their amorphous structure, which is generally preferred in TFTs [10]. As a typical high-*K* material, tantalum pentoxide begins to crystallize at 600 °C and it is crystalline above 700 °C [12]. Moreover, it is expected for Al_2O_3 and SiO_2 to stabilize the amorphous phase in multicomponent dielectrics based on Ta_2O_5, hindering crystallization up to about 1000 °C [13].

2 Methods

Alkoxide-based precursor solutions were synthesized at room temperature in a nitrogen atmosphere. The sol-gel synthesis of the precursors has been described elsewhere [14].

The Ta_2O_5-rich thin films were deposited on platinized silicon ($Pt/TiO_2/SiO_2/Si$, further denoted as Pt/Si) substrates purchased from aixACCT Laboratories (Institut für Werkstoffe der Elektrotechnik, Aachen, Germany) by spin coating for 30 s at a controlled speed of 3000 rpm. After each deposition, the films were heated in air on hot plates at 150 °C for 2 minutes and at 250 °C, 300 °C, 350 °C or 400 °C for an additional 2 minutes. The process was then repeated several times in order to achieve the film thickness of 100–200 nm.

All the films were amorphous, as determined by X-ray diffraction (XRD, PANalytical X'Pert PRO diffractometer) with Cu Kα1 radiation [15].

A JEOL Ltd. JSM–7600F Field Emission Scanning Electron Microscope (FE-SEM) was used to investigate the fracture surfaces of the films on the Pt/Si and to determine the film thickness.

The electrical characterization was performed on metal-insulator-metal (MIM) capacitors fabricated by sputtering Au/Cr top electrodes with a diameter of 0.4 mm using shadow masks.

The capacitance and loss factor, tan δ, were measured at room temperature with a driving signal of 50 mV using a HP 4284A impedance analyzer. The relative permittivity values, ε_r, were determined at a frequency of 100 kHz.

The current–voltage (*J*–*V*) characteristics were measured using a Keithley 238 Source Measurement Unit with down to 10 fA of current-measurement resolution.

3 Results and Discussion

The fracture surfaces of the thin films deposited on Pt/Si were checked by FE-SEM. The analysis of the cross-section images revealed no microstructural features, in agreement with the amorphous state of the films, as determined by XRD [15]. The thickness of around 200 nm was determined for the samples heated at 250 °C, and it decreased considerably with the thermal budget. The densification was enhanced by the higher heating temperatures, leading to a thickness of about 115 nm for the samples heated at 400 °C. The results are listed in Table 1.

The dielectric properties of the films, in terms of capacitance and loss factor, were checked with little change in the frequency range from 10 kHz to 1 MHz. The ε_r values determined at 100 kHz are listed in Table 1.

For amorphous Ta_2O_5 thin films, relative dielectric permittivities in the range 20–28 are generally reported [6,16,17]. Among the samples investigated in the present study, the Ta film heated at 400 °C exhibited the

Table 1: Thickness values as determined from the FE-SEM cross-section images, and room-temperature dielectric permittivity and the loss factor of the investigated thin films, measured at 100 kHz. The values were estimated with an uncertainty of 10%.

T (°C)	Thickness (nm)		εr		tan δ	
	Ta	8:1:1	Ta	8:1:1	Ta	8:1:1
250	190 ±19	210 ±20	10 ±1	9 ±0.9	0.032	0.029
300	187 ±18	181 ±18	17 ±1.7	18 ±1.8	0.027	0.025
350	150 ±15	134 ±13	25 ±2.5	19 ±1.9	0.055	0.040
400	115±11	118 ±12	27 ±2.7	22 ±2.2	0.044	0.028

highest ε_r, a value of 27± 3. The 8:1:1 sample heated at the same temperature exhibited a lower permittivity of about 22± 2. The difference in ε_r between the two compositions also persisted for the heating temperature of 350 °C. The samples heated at 300 °C and 250 °C showed similar permittivity values for both compositions, with an important decrease for the lowest heating temperature as compared to the rest. The samples exhibited dielectric losses from 2.5% up to 5.5% at 100 kHz.

It is known that compared to Ta_2O_5, Al_2O_3 and SiO_2 have a lower ε_r, being respectively 9 and 3.9 [6]. Since the relative permittivity value roughly follows a linear rule of mixtures with composition [13], the multicomponent dielectrics containing alumina and/or silica would exhibit decreased permittivity as compared to the pure oxides. The ratio 8:1:1 was considered in order to have acceptable permittivity values. According to Robertson an ε_r value higher than 20 is expected to fulfil the requirements of further downscaling in the development of microelectronics and integrated micro-technology devices [18]; therefore, the thin films heated above 300 °C are suitable for further applications.

For good performance in passive and active electronic devices, *i.e.,* capacitors and TFTs, the dielectric layer should exhibit both high permittivity and high resistivity, and thus a low leakage current.

In our previous study, the current-voltage measurements revealed considerably improved characteristics for the 8:1:1 samples within the investigated heating temperature range, with a significant overall decrease of the leakage currents in contrast to that of the Ta_2O_5 thin films [15]. The *J–V* characteristics were also dependent on the thermal budget of the samples, *i.e.,* the leakage currents for the investigated samples increased with the processing temperature (Fig.1 a). The current-voltage characteristics were ohmic at low applied electric fields (E < 100 kV/cm) and exhibited a Poole-Frenkel-like behaviour at higher applied fields. The Ta samples heated at 350 °C and 400 °C exhibited highly nonlinear behaviour at E > 100 kV/cm [15].

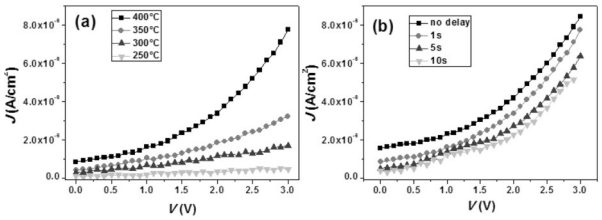

Figure 1: (a) Current density versus applied voltage characteristics of the 8:1:1 thin films recorded after a delay time of 1 s at each measurement point. (b) *J-V* characteristics recorded with different delay times for the 8:1:1 thin film processed at 400 °C.

We noticed a significant dependence of the *I–V* curves if measured at different scan times. In order to understand the charge transport in solution-derived Ta_2O_5-based thin films further investigations were performed. Fig. 1 b shows the leakage current densities of the 8:1:1 sample processed at 400 °C obtained with the fastest scan-rate or after a certain delay between the voltage set and the current measurement for each point. A decrease in the leakage current at longer step delay times was observed. Similar results were obtained for the Ta sample. The *J–V* characteristics recorded for the thin films heated at lower temperatures proved to be less influenced by the step delay time chosen for the measurements.

The time-dependent decrease of the current in the Ta_2O_5 films with the applied d.c. voltage, also known as the current transient, has been previously reported [19,20,21]. To obtain an insight into the time scale of this effect, we performed additional current *vs.* time (*I–t*) measurements at a constant applied voltage of 1 V (Fig. 2) for 1 min. The samples processed at higher temperatures showed more pronounced current drops, which is in agreement with the larger differences in the *J–V* characteristics when recorded after longer delay times. The 8:1:1 samples had a lower drop of the current as compared to the Ta ones, which is in accordance with the difference in the capacitance between the two series.

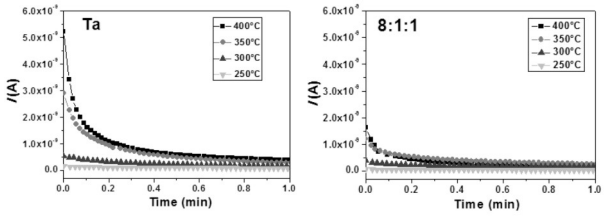

Figure 2: Room-temperature current transients measured under a constant applied voltage of 1V.

The time-dependent current variation in the Ta_2O_5 thin films was reported to occur as an initially high drop of the current followed by a gradual decrease after a certain relaxation time [20]. In this study, the Ta sample heated at 400 °C reached the steady-state after about 10 min (Fig. 3a). For the rest of the samples the measurements were performed for longer times. As the relative change of the current depends on its absolute value [20], the films having larger initial currents when the voltage was applied reached their steady-state currents much faster. Therefore, the Ta thin films heated at lower temperatures required much longer times to reach their steady-state current values. Moreover, the 8:1:1 samples reached the steady-state currents only after several hours (Fig. 3b).

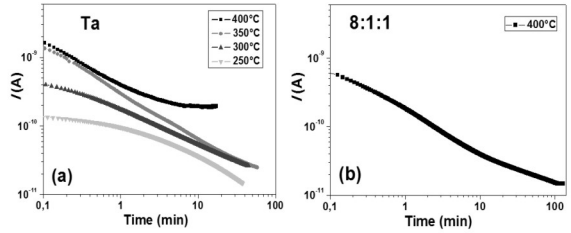

Figure 3: *I–t* characteristics of the Ta thin films series (a) and the 8:1:1 sample processed at 400 °C (b), measured under the applied voltage of 1V.

It is clear that such current transients cannot occur due to the intrinsic capacitance of the sample only, but they might originate from the dielectric absorption and mostly from an additional bulk charge-trapping mechanism since high-*K* dielectrics contain a large bulk density of defects and trapped charges [6]. Therefore, we checked to see how the conductivity is dependent on the voltage polarity. The current was recorded as the voltage was swept from the negative to the positive bias and back. Besides the initial build-up, also the current hysteresis width proved to be dependent both on the composition (Fig. 4 a) and the heating temperature of the samples (Fig. 4 b). This suggests that charge trapping occurs when the voltage is applied. The clockwise hysteresis proves that charges are trapped when going positively and released when going back. The process is more pronounced for the Ta sample or for a larger thermal budget. Charge trapping can be reduced by different heat treatments, or by changing the composition. It was reported that $HfSiO_x$ exhibits a lower hysteresis than HfO_2 [6], which is consistent with our results. The delay time played little role, as the hysteresis width was only slightly reduced for the step delay times of up to 10 s.

At first, the current transients were believed to be an intrinsic characteristic of the Ta_2O_5 and to be due to charge-trapping (or emission) in the dielectric film [19].

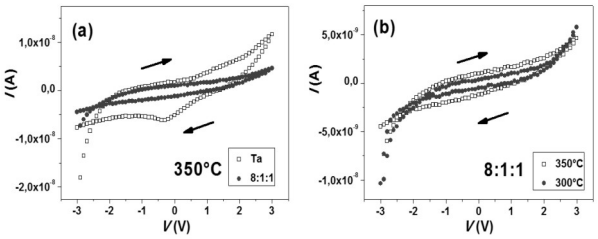

Figure 4: *I–V* curves of Ta_2O_5-based thin films measured with the minimum delay time. The voltage was swept from the negative to positive values and back as indicated by the arrows in the figures.

Later, other explanations for the current-transients in the metal-insulator-semiconductor (MIS) capacitors were given [20,21]. More recent papers of A. Persano et al. (2010) reported the room-temperature current-voltage characteristics of amorphous Ta_2O_5 thin films measured in the MIM configuration and proposed the temporal variation of the polarization to be the cause of the transient currents. Their proposed explanation is that the charge carriers injected by applying an electric field are trapped in the defects of the dielectric film, thus changing the polarization [22]. We assume a similar effect in the case of our Ta_2O_5-based thin films.

For the investigated samples, the current transients were modelled as the exponential decay given by Eq. (1) with correlation coefficients higher than 0.99.

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) + y_o \quad (1)$$

where t is time, A_1, A_2, and A_3 are process pre-factors, τ_1, τ_2, and τ_3 are process time constants, and y_0 is the steady-state current due to ohmic resistivity.

Fig. 5 shows the current transients of the thin films heated at 400 °C fitted with Eq. (1). The parameter values used for excellent agreement are listed in Table 2. The fact that the relaxation process is determined by three time constants shows that the charge-trapping occurs at different rates, indicating that different kinds of bulk defects are involved in the process. Similar results were obtained for the thin films heated at 350 °C and 300 °C. For the samples heated at 250 °C (Fig. 5b), the current transients were fitted with a second-order exponential decay, *i.e.*, A_3=0. These results are in agreement with our previous results, which proved that the 250 °C thin films exhibited only ohmic behaviour, even at an applied electric field higher than 100 kV/cm, whereas in the case of the thin films heated at higher temperatures, the Poole-Frenkel conduction mechanism was dominant.

Table 2: The steady-state current due to ohmic resistivity (y_0), the process prefactors (A), and the process time constants (τ) used for fitting the current transients depicted in Fig. 5, which were modelled as third- and second-order exponential decays for the samples heated at 400 °C and 250 °C, respectively.

T (°C)	Sample	y_0 (A)	A_1 (A)	τ_1 (s)	A_2 (A)	τ_2 (s)	A_3 (A)	τ3 (s)
400	Ta	1.92 x10-10	1.65 x10-9	0.19	3.17 x10-9	0.03	3.83 x10-10	1.49
	8:1:1	3.16 x10-11	1.52 x10-10	2.68	4.83 x10-10	0.36	1.02 x10-9	0.04
250	Ta	1.38 x10-11	5.95 x10-11	10.53	6.67 x10-11	1.19		
	8:1:1	2.00 x10-11	1.54 x10-11	1.70	2.41 x10-11	13.20		

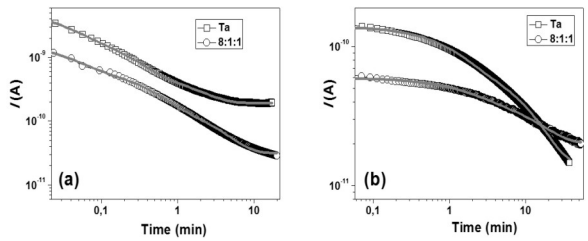

Figure 5: Current transients of the Ta and 8:1:1 thin films heated at 400 °C (a) and 250 °C (b), upon applying a constant voltage of 1 V. The solid lines are the fits to the current data with the third- (a) and the second-order (b) exponential decay, respectively.

4 Conclussions

Solution-derived Ta_2O_5 and Ta_2O_5–Al_2O_3–SiO_2 (Ta:Al:Si = 8:1:1 atomic ratio) thin films were processed in the temperature range from 250 °C to 400 °C. The amorphous thin films exhibited ε_r values up to 27± 3 for the Ta sample processed at 400 °C. The dielectric permittivity depended both on the composition and the heating temperature, showing lower values for the 8:1:1 samples and an important decrease for the sample heated at 250 °C.

The dc electrical conduction in the Ta_2O_5-based dielectric films was described in terms of bulk-limited processes, with Poole-Frenkel becoming the dominant mechanism for applied fields E > 100 kV/cm. Long-lasting current transients were recorded in the investigated samples at a constant applied electric field. The room temperature *I–t* measurements proved to be dependent on the thermal budget of the samples, rendering smoother transients and lower overall current values for the samples processed at lower temperatures. Moreover, the drop of the measured current was higher for the single-oxide samples than for the Ta_2O_5–Al_2O_3–SiO_2 films, in agreement with the dielectric permittivity results. The charging process has been investigated, finding that it follows an exponential law that can be fitted with two to three different time constants, indicating that different kinds of defects are involved in the charge-trapping process.

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