Ta$_2$O$_5$-GATES OF pH-SENSITIVE DEVICES: COMPARATIVE SPECTROSCOPIC AND ELECTRICAL STUDIES

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Abstract

Thin films of tantalum pentoxide (Ta$_2$O$_5$) were prepared on Si/SiO$_2$ substrates by thermal oxidation of tantalum. In systematic oxidation studies we followed the growth of the Ta$_2$O$_5$/SiO$_2$ interface. The oxide layers and their interfaces were characterized by SIMS, SAM, XPS, by comparative $C-V$ measurements and by pH-(ISFET) sensitivities.

Depending on the oxidation procedure, we find non-ideal stoichiometries of the Ta$_2$O$_5$/SiO$_2$ interface, whose widths vary as a function of the oxidation time of the previously evaporated metallic tantalum.

Specific annealing procedures lead to unexpectedly high leakage currents, which correlate with the formation of voids in the oxide layers. Even in the absence of voids, non-ideal interfaces provide high concentrations of electrically-active states in gate oxides of ISFETs, which in turn determine the results of $C-V$ measurements and ISFET characteristics. For ideal stoichiometric and atomically abrupt interfaces, we observe long-term stability and ideal Nernstian behaviour in the pH-(ISFET) sensitivities.

Introduction

The growth mechanism of Ta oxides on SiO$_2$ in the submonolayer and monolayer range gives evidence for the formation of a reactive TaO$_y$/SiO$_x$ ($y < 2.5$, $x < 2$) interface when a thermal oxidation process of metallic tantalum is chosen in the production of gate-oxide structures. Several oxidation states of Ta on SiO$_2$ have been observed during annealing between 600 and 1200 K in UHV [1]. In this paper we study the influence of the Ta oxidation procedure on the spectroscopic and electrical properties of Ta oxide/SiO$_2$/Si structures. The layer thickness of the oxides was comparable to that used in ion-sensitive field-effect transistors (ISFETs).

Experimental

Tantalum was electron-beam evaporated with a thickness of 53 nm onto p-doped silicon wafers Si(001) with a 46 nm thick SiO_2 layer prepared by thermal oxidation. Depending on different oxidation times at $p(O_2) = $ 1000 mbar and temperatures between 800 and 850 K, we obtained samples with incompletely (t_{ox} = 10 min) and completely (t_{ox} = 20 min) oxidized tantalum layers.

For comparative C–V measurements and for the pH-sensitivity measurements, separate test chips made by the same fabrication process with an additional gold or aluminium layer evaporated at the backside were used. To form ohmic contacts [2, 3], we annealed the chips for one hour at temperatures between 700 and 800 K in an N_2 atmosphere.

X-ray photoelectron spectroscopy (XPS) was performed with a double anode set-up with Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) radiation and a hemispherical energy analyser (Vacuum Science Workshop HA 150). Scanning electron microscopy (SEM), scanning Auger microscopy (SAM), and Auger electron spectroscopy (AES) were performed in a Perkin–Elmer PHI-600 system. For secondary-ion mass spectrometry (SIMS) of the layer structures, we used an Atomika Telefocus ion gun and a Balzers QMG 420 quadrupole mass spectrometer. Spectra were usually taken with O_2^+ or Ar^+ primary ions at 10 keV and 45 degrees incidence. For details of the experimental set-up, see ref. 4.

C–V measurements were performed with variable frequencies in a computer-controlled set-up, consisting of a highly stable voltage ramp, Keithley 619 and 610 B electrometers, and an EG&G 5208 two-phase lock-in amplifier. For our studies we chose a frequency of 510 Hz. We used Ag/AgCl as a reference electrode and a standard buffer (pH = 4.01) as an electrolyte.

Results and discussion

As typical examples, Figs. 1(a) and (b) show two SIMS depth profiles of our $Ta_2O_5/SiO_2/Si$ structures, which were prepared by incomplete (Fig. 1(a)) and complete (Fig. 1(b)) oxidation of the samples. Characteristic differences are the presence of the non-stoichiometric region Ta_2O_y with $y < 5$ in the case of partial oxidation (Fig. 1(a)) and of different widths of the tantalum oxide/silicon oxide interfaces, which are not ideal in the sense that there are no atomically-abrupt phase boundaries between stoichiometric Ta_2O_5 and SiO_2.

From the shape of the Ta^+ and the TaO^+ curves in Fig. 1(a), we can distinguish between the Ta_2O_5 and the non-stoichiometric Ta_2O_y region. The surface stoichiometry of the top oxide layer (Ta_2O_5) was determined in XPS by the binding energies of the Ta 4f core levels and the intensity ratio between the Ta 4f and O 1s core levels. As shown in Fig. 1(a), an increase is
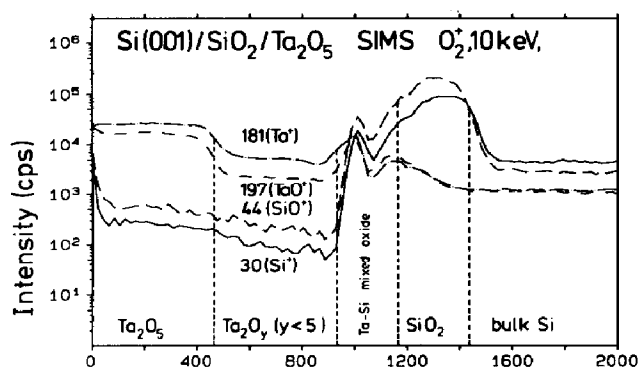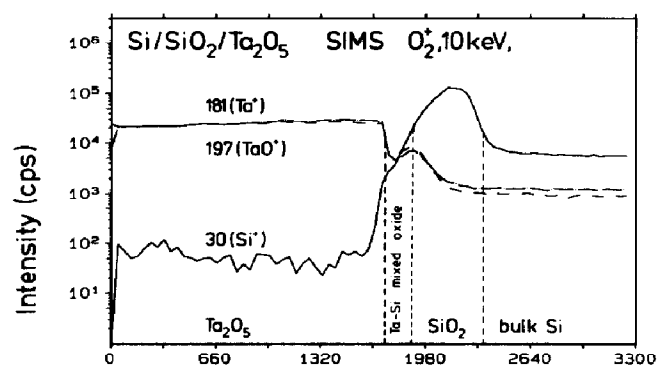
Fig. 1. SIMS depth profile (10 keV, O_2^+, 30 nA) of (a) an incompletely oxidized Ta_2O_5/ SiO_2/Si sample, (b) a completely oxidized Ta_2O_5/SiO_2/Si sample.

observed for the masses 30 (Si^+), 44 (SiO^+), 181 (Ta^+) and 197 (TaO^+) between the non-stoichiometric region and the tantalum oxide/silicon oxide interface due to a sharp increase in oxygen concentration, and hence a higher ionization probability of the sputtered particles [5, 6]. The following sharp decrease of all intensities results from a superposition of a charging effect and the real oxygen deficiency in this region [1].

Even in the case of complete oxidation of the samples (Fig. 1(b)), we find a broadened tantalum oxide/silicon oxide interface region, which is, however, smaller than that in Fig. 1(a). The composition of this region results from a reaction between Ta and SiO_2 during the preparation of the Ta/SiO_2/Si structures, which leads to a time- and temperature-dependent interdiffusion profile.

These interface structures determine sensitively the experimental results of $C-V$ measurements and ISFET characteristics in aqueous solutions. Similar correlations were found earlier in phenomenological studies of the electrical properties of differently prepared tantalum oxide films on silicon or silicon-oxide [7 - 10]. The $C-V$ plot in Fig. 2, curve a, indicates a
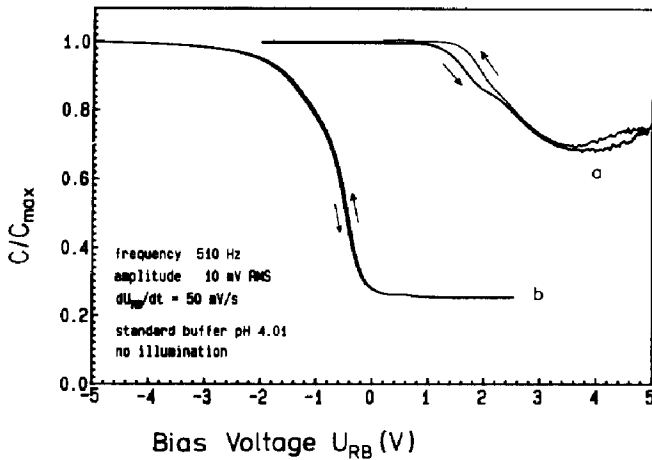
Fig. 2. $C-V$ plot of an incompletely oxidized $Ta_2O_5/SiO_2/Si$ sample (curve a) and of a completely oxidized sample (curve b).

distorted curve, which was found to be typical for partly oxidized layers. In this particular example, contributions from a lateral current flow in the conducting intermediate layers explain the distortions. The $C-V$ plot in Fig. 2, curve b, for the completely oxidized sample shows a nearly ideal shape. The corresponding pH-sensitive ISFET devices with well-defined interfaces show ideal Nerstian behaviour [11], *i.e.*, the slope in a plot of bias voltage *versus* pH value is 59.3 mV/pH at 300 K. Typical results are given in Fig. 3. Non-ideal interfaces lead to non-Nernstian behaviour and drift effects.

SEM pictures of some test chips show voids in the oxide layer with typical diameters of about 10^4 nm (Fig. 4(a)). In SAM elemental maps of Ta (Fig. 4(b)) and Si (Fig. 4(c)), and in AES spectra taken inside the voids, we find that the oxide is removed completely here, and we observe the bare silicon substrate. These samples always show an extremely high leakage current in our $C-V$ measurements.
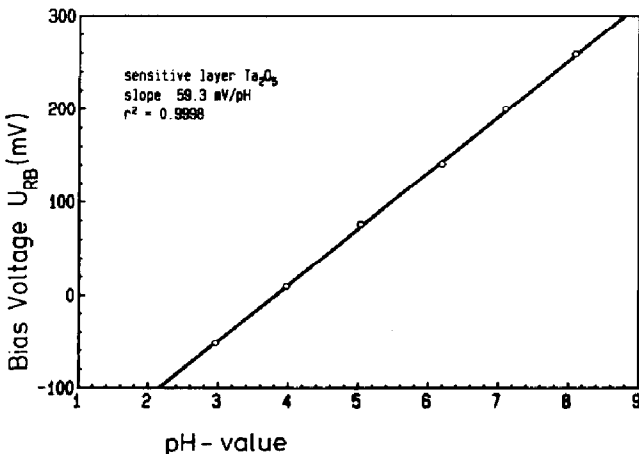

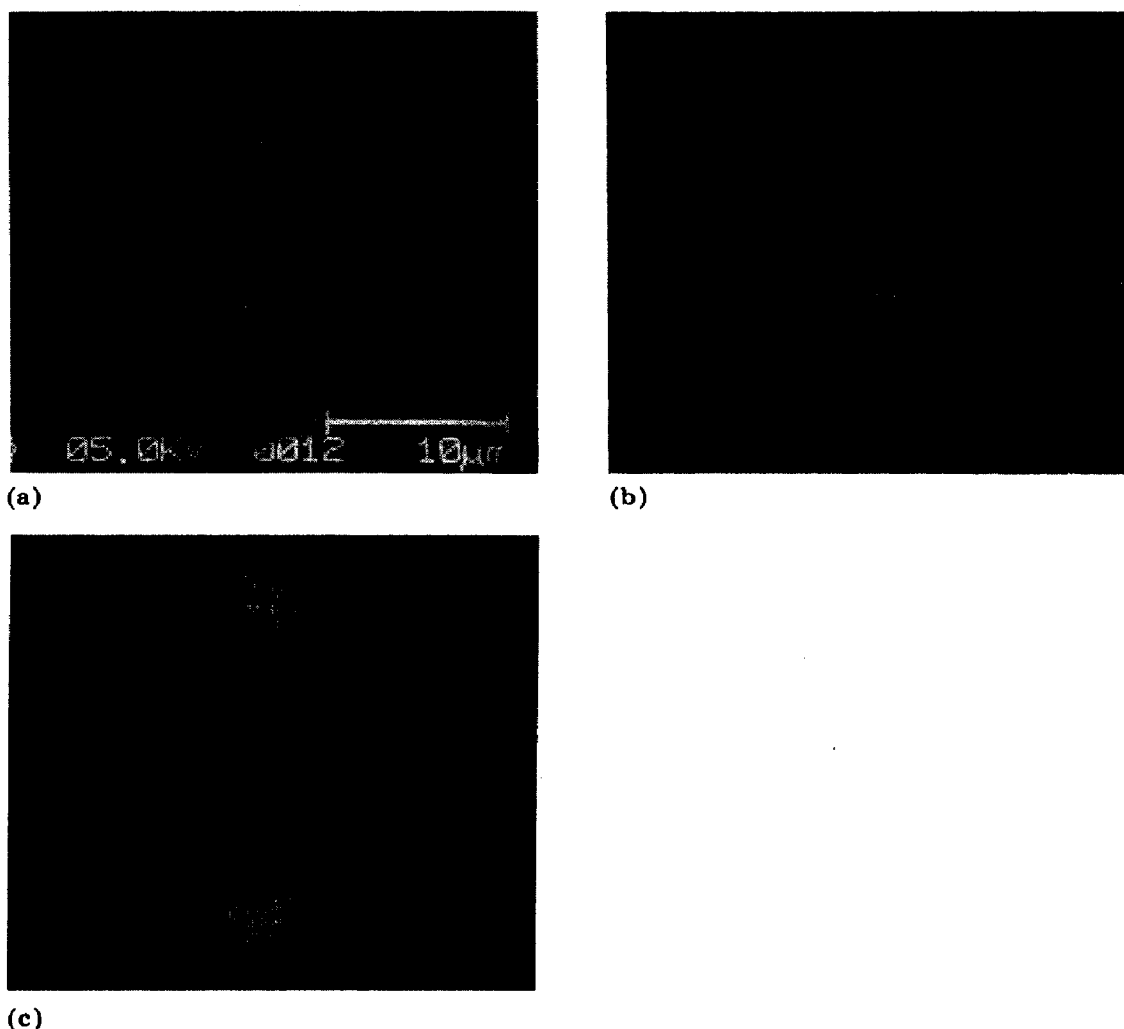Fig. 3. pH-Sensitivity of an ideally processed Ta_2O_5 system measured using the constant capacitance method.

(a)

(b)

(c)

Fig. 4. (a) SEM picture (f = 1650×) of a $Ta_2O_5/SiO_2/Si$ structure showing two voids (dark areas). (b) SAM elemental map of Ta (same sample region as in Fig. 4(a)); bright areas represent high Ta concentrations. (c) SAM elemental map of Si (same sample region as in Fig. 4(a)).

In order to characterize the experimental conditions leading to the formation of voids, we annealed a $Ta/SiO_2/Si(111)$ structure under UHV conditions. Voids with diameters of up to more than 3×10^4 nm and with a higher density are found after heating for longer times (2 h) at higher temperatures (up to 1200 K) (Fig. 5).

For SiO_2/Si structures, a void generation process that is initiated by the reaction

$$SiO_2 + Si \longrightarrow 2 \, SiO_{g\,as}$$
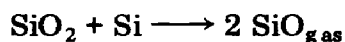
and starts at defects located at the SiO_2/Si interface has been suggested [12 - 16]. Thermodynamic estimations for the gas transport of volatile silicon compounds, formed by the reaction
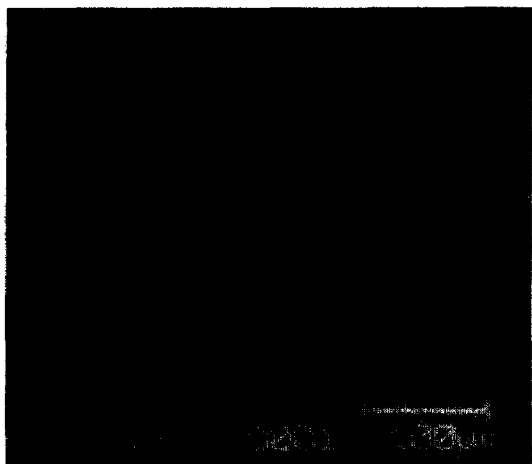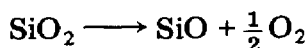
Fig. 5. SEM picture ($f = 112 \times$) of a Ta/SiO$_2$/Si structure after annealing. Several voids of identical diameter can be seen as dark areas.

$$SiO_2 \longrightarrow SiO + \tfrac{1}{2}O_2$$

indicate that sufficient mass transport of gaseous SiO is possible at elevated temperatures of about 1100 K or more [14, 17]. The above-mentioned reaction is the only possible one that may occur under thermodynamically controlled conditions in the system Ta$_2$O$_5$/SiO$_2$/Si at high temperatures and low O$_2$ partial pressures and that takes into account all stable compounds of tantalum, silicon and oxygen.

Summary

Tantalum oxide gates of pH-sensitive devices may be prepared by thermal oxidation of evaporated Ta. If oxidation of the tantalum oxide layer is complete and if long annealing processes at $T > 1100$ K are omitted, we obtain ideal $C-V$/ISFET behaviour.

Acknowledgements

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