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The influence of composition on band gap and dielectric constant of anodic Al-Ta mixed oxides

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ABSTRACT

Al-Ta mixed oxides were grown by anodizing sputter-deposited Al-Ta alloys of different composition. Photocurrent spectra revealed a band gap, E_g, slightly independent on Ta content and very close to that of anodic Ta_2O_5 (~4.3 eV) with the exception of the anodic film on Al-10at% Ta, which resulted to be not photoactive under strong anodic polarization. The photoelectrochemical characterization allowed to estimate also the oxides flat band potential and to get the necessary information to sketch the energetic of the metal/oxide/electrolyte interfaces. Impedance measurements allowed to confirm the formation of insulating material and to estimate the dielectric constant of the oxides, which resulted to be monotonically increasing with increasing Ta content (from 9 for pure Al_2O_3 to 30 for pure Ta_2O_5).

1. Introduction

Investigation of high-κ materials as alternative gate dielectrics for the technology advancement of complementary metal oxide semiconductor (CMOS) applications has started gradually to shift its focus from single metal oxides (HfO_2, Ta_2O_5, ZrO_2, TiO_2 or Al_2O_3) to doped or mixed oxides [1–4]. The idea behind this choice is that by mixing of high-κ dielectrics or by their doping with appropriate elements it would be possible to engineer the electrical properties of the materials, combining the favourable properties of the starting dielectrics while suppressing their individual disadvantages. Since a large number of such materials are valve metals oxides, anodizing has been proposed as a simple and low cost process for preparing both single metal and mixed oxides, whose structure, thickness, composition and morphology can be efficiently and easily tailored controlling the metal or alloy composition and the oxidation conditions [5–14].

One of the most promising candidates for storage capacitors in nanoscale dynamic random access memories (DRAMs) [15–17] is Ta_2O_5 due to its high storage ability and low leakage current. One of the main drawback of this oxide is its band gap which is reported to be low with respect to the value necessary to assure good performances of the devices.

In previous works [18–20] it was demonstrated that mixing WO_3, HfO_2 or TiO_2 to Ta_2O_5 improved the dielectric and insulating properties of thin tantalum oxide films. A promising oxide partner for Ta_2O_5 is Al_2O_3, not only due to its very high band gap, but also due its glass former character [21], which reduces the possibility of crystallization. Moreover, Al can be incorporated as substitutional atoms into Ta_2O_5, acting as acceptor and compensating oxygen vacancies with consequent minimization of leakage current. In spite of this very encouraging perspectives, previous study on Al doped Ta_2O_5 prepared by radio frequency reactive sputtering and subsequent high temperature annealing has shown that permittivity of the doped tantalum oxide is lower with respect to the corresponding pure oxide, and that some caution must be used in the selection of the metal gate, which can react with Al doped oxide, building up other oxide layers between metal and dielectric with detrimental effect on the performance of CMOS devices [22].

Nevertheless, the variation of electrical properties of mixed oxides strongly depends on the amount of added partner oxide, on the method of incorporation and on the structure of the films, thus, in this work we focused on the preparation and characterization of Al-Ta mixed oxides by anodizing in aqueous solutions sputter-deposited Al-Ta alloys. Photoelectrochemical measurements were carried out in order to estimate the band gap and flat band potential as a function of the oxide composition. Impedance measurements were performed in order to study the electrical properties of the oxides and to estimate the permittivity as a function of their composition. The experimental findings were

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used to sketch the energetics of the metal/oxide interface and thus to estimate the band offset.

2. Experimental

Aluminium, tantalum and Al-Ta alloys (10, 18, 20, 30, 42, 62, 81, 91 at% Ta) were deposited by dc magnetron sputtering on glass substrates. The deposition was carried out in a Shimadzu, SP-2C system, at a rate of 0.11 nm s^{-1}, by using targets of 99.99wt% Al and 99.9wt% Ta; the chamber was initially evacuated to 5×10^{-5} Pa with subsequent sputtering using Ar at 3×10^{-1} Pa.

Anodizing was performed potentiodynamically at 10 mV s^{-1} at room temperature in a borate buffer (0.42 M H_3BO_3, 0.08 M $Na_2B_4O_7$) (pH = 8), in which both Al_2O_3 and Ta_2O_5 are thermodynamically stable, according to Pourbaix's diagrams relative to Al-H_2O and Ta-H_2O at room temperature [23]. Alloys were anodized to

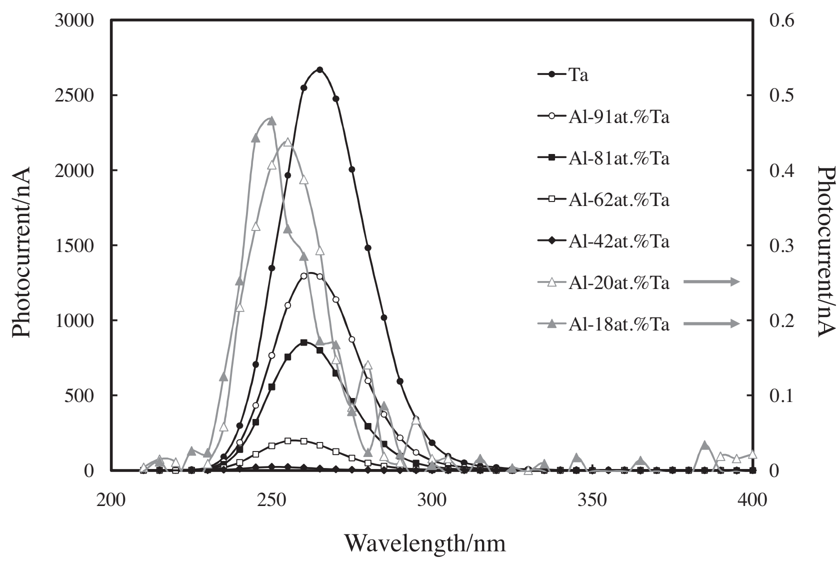

Fig. 1. Raw photocurrent spectra relating to anodic films grown up to 10 V vs Hg/HgO on Al-18at% Ta, Al-20at% Ta, Al-42at% Ta, Al-62at% Ta, Al-81at% Ta, Al-91at% Ta alloys and on pure Ta, recorded by polarizing the electrodes at 5 V in 0.1 M ABE.

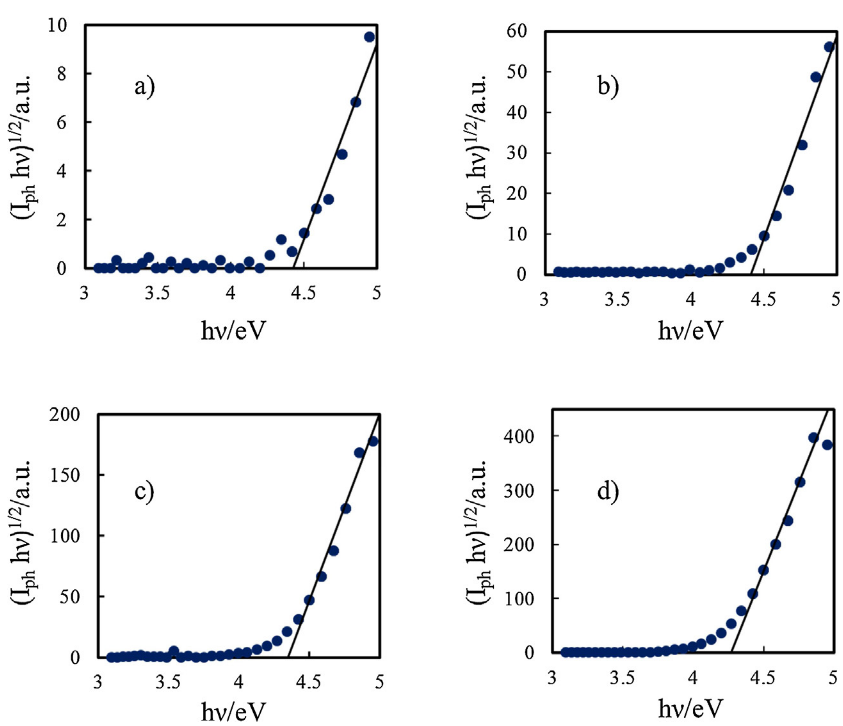

Fig. 2. Band gap estimate by assuming non direct optical transitions relating to anodic films grown to 10 V on (a) Al-18at% Ta, (b) Al-42at% Ta, (c) Al-62at% Ta, and (d) Al-91at% Ta alloys, recorded by polarizing the electrodes at 5 V vs Hg/HgO in 0.1 M ABE.