

Amorphous Semiconductor-Electrolyte Junction revisited. a-WO₃-Aqueous Electrolyte: a case study.

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One the most versatile methods used by electrochemists to study the oxide-electrolyte interface is based on the EIS technique. This technique can provide numerous information both on the kinetics of charge transfer at the metal/oxide/electrolyte interfaces as well as on the solid state properties of the passive layers grown on metals.

The study of such properties has received a large interest owing to the wide range of application of thin oxides in different technologically important fields like: catalysis, microelectronics, sensors and last but not least corrosion and passivity. In this last case the study of the electronic properties of passive films is aimed to understand the kinetics of charge transfer at the metal/oxide and oxide/electrolyte interfaces.

The electronic properties are frequently investigated by measuring the capacitance of the junction as a function of electrode potential and frequency of ac superimposed signal. A complete frequency study is preferable for getting a reliable equivalent circuit able to interpret the impedance data of the passive film/electrolyte junction.

However in many cases the study of electronic properties of passive films is performed by using only one frequency whilst the analysis of the impedance behavior of anodic oxide films-electrolyte junction is very often based on the use of the Mott-Schottky analysis of capacitance data valid for crystalline materials. The use of this last assumption for interpreting the impedance behavior of amorphous semiconductor-electrolyte junction has been questioned by the present authors by reinterpreting the impedance results of different oxide-electrolyte junctions showing semiconducting behavior typical of amorphous materials (1 and ref. therein).

In the case of anodic oxides grown on tungsten it is very well known that the passive films, formed in a large range of current density and in different electrolytic solutions, are amorphous and display a semiconducting behavior typical of n-type semiconducting material (2). The amorphous nature of anodic oxide films (a-WO₃), grown in phosphoric acid solutions and in a wide range of concentration (0.1 M -14.7 M H₃PO₄), has been recently confirmed in an elegant work reported in ref. (3). It is interesting to note that in such a work it was evidenced a very negligible amount of phosphate anions incorporation, into the external part of the film, at variance with a previous suggestion (4) based on capacitance data. Moreover these authors reported a value of anodizing ratio, directly measured by transmission electron microscopy on ultramicrotomed sections of anodic oxide, in agreement with the results of previous kinetic growth studies (4) based on the use the high field model (HFM). The validity of HFM for the kinetic of growth of anodic WO₃ film was still recently confirmed by an EQM and EIS study performed on films grown up to 8 V (5).

These results and interpretations have been recently challenged by different authors (6-10) on the basis of impedance studies and a model of growth of anodic oxides which rely on the validity of Point Defect Model suggested by D.D. Macdonald years ago (11). According to these studies anodic films grown on tungsten present an

impedance behavior typical of a metal-semiconductor-insulating duplex layer (inverted MIS, ref. 8) or of a n-i-p structure (9, 10) in agreement with the theoretical expectations of growth of anodic oxides based on PDM. Moreover in ref (8) the nonlinear behavior of the M-S plots was assumed as incompatible with any model of semiconductor-electrolyte junction previously reported in the literature.

In this work we report the results of a preliminary study on the impedance behavior of anodic passive films grown on W in 1M H₃PO₄ in a wide range of frequencies (3 Hz -10 KHz) and for film thickness in the order of 25 nm obtained after different stabilization times (1 hour to 21 hour) in the same anodizing solution. It will be shown that the impedance behavior of a-WO₃-aqueous electrolyte junction is in agreement with the impedance behavior of thicker ($D_{ox} > 50$ nm) a-WO₃ oxide films, previously investigated in organic solution (12), and explained on the basis of the impedance behavior of amorphous semiconductor-electrolyte junctions (12). The n-type semiconducting behavior as well as the difficulty to hypothesize the presence of any duplex structure (like p-i-n or inverse metal-semiconductor-insulator) will be discussed on the basis of impedance and photoelectrochemical data.

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