Electrochimica Acta 59 (2012) 382–386

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The influence of nitrogen incorporation on the optical properties of anodic Ta_2O_5

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ARTICLE INFO

Article history:
Received 11 August 2011
Received in revised form 25 October 2011
Accepted 26 October 2011
Available online 3 November 2011

Keywords:
Nitrogen incorporation
Anodic Ta_2O_5
Band gap
XPS
GDOES

ABSTRACT

Anodic oxides were grown on sputter-deposited Ta in different aqueous solutions. A photoelectrochemical investigation was performed in order to estimate the band gap of the films as a function of the anodizing bath composition and formation voltage, i.e. thickness. Photoelectrochemical results provided evidence of sub-band gap photocurrent for films formed in a bath containing ammonium ions at pH 9. Elemental depth profiles obtained by glow discharge optical emission spectroscopy revealed the presence of nitrogen species in the outer part of the anodic films, which is bonded to Ta according to XPS analysis. A mechanism of nitrogen incorporation is proposed in order to account for the pH dependence of film composition.

1. Introduction

Transitional metal nitrides and oxy-nitrides show great hardness, high melting points, high abrasion and corrosion resistance, interesting electrical and optical properties. Concerning these last aspects, tantalum based oxynitrides have been proposed as non-toxic pigments [1] and more recently as photoelectrodes for water splitting processes. H_2O cleavage is favoured by their band gap values usually lower than that of the corresponding oxide. The narrowing of the band gap is caused by a shift of the valence band edge toward higher potential energy caused by N 2p and O 2p orbital hybridization involved in the oxynitride formation. The possibility to tailor the band gap of such compounds in a rather large range of energy values makes this class of materials an appealing candidate to work as photocatalysts and photoelectrodes under visible light illumination [2].

As far as we know, according to the literature [2–4] the insertion of nitrogen atoms into Ta_2O_5 oxide is restricted to the use of high temperature reaction (>1100 K) in reducing N_2 and/or NH_3 containing atmosphere.

In a recent paper [5], it has been reported that by anodizing Nb in ammonium hydroxide containing electrolytes, it is possible to incorporate nitrogen into the anodic film with a marked change in the dielectric properties of the oxide. Starting from these experimental findings, in this work we propose a fully electrochemical procedure to prepare N-doped tantalum oxide consisting in a room temperature anodizing process of tantalum in an ammonium containing aqueous solution. The influence of anodizing parameters (bath composition, pH and final formation voltage) on the photoelectrochemical behaviour of anodic oxide films on Ta is discussed. The results are interpreted by taking into account the occurrence of N incorporation into the anodic layers.

2. Experimental

Ta samples were prepared by dc magnetron sputtering using a 99.9% tantalum disk of 100 mm in diameter. Substrates were glass plates. Thickness of metallic layer was 300 nm. According to X-ray diffraction (XRD) analysis, the deposited films had β-Ta phase with a tetragonal structure [6].

All the electrochemical and photoelectrochemical experiments were performed in a three electrode cell: a saturated silver/silver chloride electrode (0 V vs Ag/AgCl = 0.197 V vs SHE) was employed as reference electrode, while a Pt net was used as counter electrode.

The anodizing was undertaken in 0.1 M NaOH, in 0.1 M ammonium biborate (ABE) (pH 9) and in 0.1 M $(NH_4)_2SO_4/H_2SO_4$ (AMS, pH 0.3).at 298 K potentiodynamically at 10 mV s^{-1}.

The photoelectrochemical experiments were carried out in 0.5 M H_2SO_4 aqueous solution (pH 0.3). The experimental set-up employed for the photoelectrochemical investigations is described elsewhere [7]: it consists of a 450W UV–VIS xenon lamp coupled with a monochromator (Kratos), which allows monochromatic irradiation of the specimen surface through electrochemical cell quartz windows. A two-phase lock-in amplifier (EG&G) was used in connection with a mechanical chopper (frequency: 13 Hz) in order to separate the photocurrent from the total current circulating in the

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doi:10.1016/j.electacta.2011.10.086

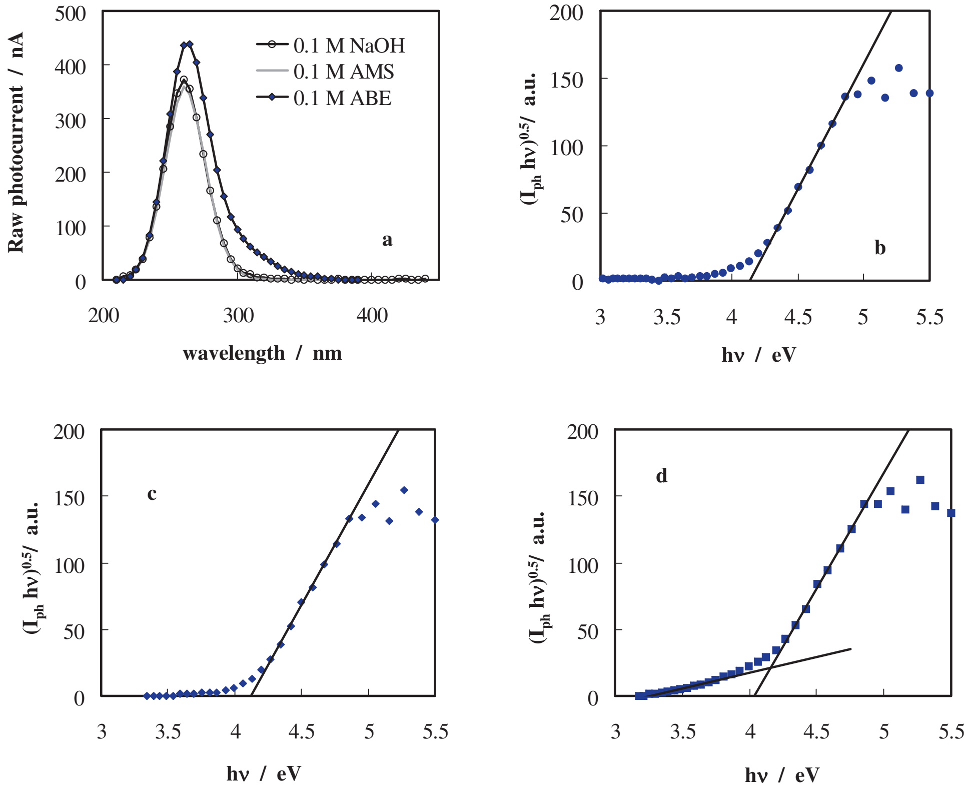

Fig. 1. (a) Raw photocurrent spectra relating to anodic films grown on Ta to 5 V (Ag/AgCl), recorded at 2 V (Ag/AgCl) in 0.5 M H_2SO_4. $(I_{ph}h\nu)^{0.5}$ vs $h\nu$ plots relating to the oxides grown in (b) 0.1 M NaOH, (c) 0.1 M AMS and (d) 0.1 M ABE.

cell due to the potentiostatic control. The raw photocurrent was corrected for the relative photon flux of the light source at each wavelength in order to allow to estimate the band gap of the investigated films.

Elemental depth profile analysis was conducted by glow discharge optical emission spectroscopy (GDOES) using a Jobin-Ybon 5000 instrument in an argon atmosphere of 600 Pa by applying RF of 13.56 MHz and power of 35 W with a pulse mode of 100 Hz and a duty cycle of 0.1. The wavelengths of the spectral lines used were 302.017, 149.262, 249.678 and 130.217 nm for tantalum, nitrogen, boron and oxygen respectively.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a JEOL JPS-9200 spectrometer with a hemispherical energy analyser and Mg Kα excitation (1253.6 eV). The pressure in the analysis chamber during the XPS measurements was 1.0×10^{-7} Pa. The spectra were recorded at a 90° take-off angle with 0.1 eV step and 10 eV pass energy. The binding energy was calibrated by using the C1s peak at 285.0 eV as the reference.

3. Results

In Fig. 1a we report the raw photocurrent spectrum relating to the anodic layer grown to 5 V (Ag/AgCl) (~11 nm thick) in 0.1 M NaOH, recorded by polarizing the electrodes at 2 V (Ag/AgCl) in 0.5 M H_2SO_4. By assuming indirect (non direct for amorphous materials) optical transitions, the following equation holds [7]:

$$(I_{ph}h\nu)^{0.5} \propto (h\nu - E_g) \tag{1}$$

where I_{ph} is the photocurrent corrected for the relative photon efficiency of the light source at each wavelength and E_g is the optical band gap. For amorphous material E_g, is a measure of the mobility gap, E_{gm}, in the Tauc's approximation [8]. By extrapolating to zero the $(I_{ph}h\nu)^{0.5}$ vs $h\nu$ plot a mobility gap of 4.13 eV has been estimated for the film formed in NaOH solution (see Fig. 1b), and in good in agreement with the band gap values reported in the literature for anodic oxide on Ta metal [9] and quite close to the value of crystalline Ta_2O_5 oxide (~3.9 eV). As previously suggested [7,8] the difference (~0.2 eV) in the optical band gap value of amorphous and crystalline tantalum oxide can be attributed to the effect of lattice disorder in amorphous oxide which affect both the DOS distribution in the vicinity of band edges and the intensity of optical transition between localized states [8]. The small tailing at lower energy observed in Fig. 1b agrees with the model of DOS suggested in [7,8].

Photocurrent spectra (see Fig. 1a) very similar to those relating to films grown in NaOH solution were recorded for anodic films similarly grown in 0.1 M $(NH_4)_2SO_4$ (pH corrected to 0.3 by the addition of H_2SO_4), for which a band gap value of 4.1 eV was estimated according to Eq. (1) (Fig. 1c).

A different photoelectrochemical behaviour was displayed by the anodic layer grown in 0.1 M ABE (see Fig. 1), due to the presence of a consistent red-shift in the optical absorption extending well below the band gap of Ta_2O_5 reported above. In this last case, apart from the band gap value (4.04 eV) very close to that estimated for anodic films grown in the other investigated electrolytes (see Fig. 1d), it was possible to derive from the longer wavelength region of photocurrent tail a second lower threshold at around 3.25 eV.

The presence of sub-band gap photocurrent is more evident for thicker films formed in 0.1 M ABE. In Fig. 2a we compare the photocurrent spectra relating to anodic films grown on tantalum to 50 V in AMS, NaOH and ABE solutions. By assuming non direct optical transitions, according to Eq. (1), two linear regions are present in the $(I_{ph}h\nu)^{0.5}$ vs hν plots for the anodic film grown in ABE, corresponding to optical transitions at 3.25 and 4.05 eV (see Fig. 2b),