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Semiconductive Properties of Anodic Niobium Oxides

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Abstract

The semiconductive properties of anodic niobium oxides formed at constant potential and constant current density to different final voltages have been examined by Mott-Schottky analysis.
Thin anodic oxides were formed on sputtered niobium specimens at constant potential in the range of 2.5 to 10 $V_{Ag/AgCl}$ in a borate buffer solution. Thicker oxides were formed, also on sputtered niobium specimens, at a constant current density of 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution to final voltages of 10, 50 and 100 V. Capacitance measurements were performed in a borate buffer solution of pH 8.8, at a frequency range of 200 to 2000 Hz, at a sweep rate of 5 mV s^{-1} from +2.5 to –1 $V_{Ag/AgCl}$. The results obtained show n-type semiconductor behaviour with a carrier density in the range of $8 \times 10^{18} – 6 \times 10^{19}$ cm^{-3} on films formed to 10 V. Thicker films showed lower carrier densities in the range of $1 \times 10^{18} – 2 \times 10^{18}$ cm^{-3} with a calculated charge depletion layer of 33-36 nm.

Keywords: niobium oxides, anodic oxides, Mott-Schottky behaviour.

Introduction

Niobium, together with aluminium and tantalum, belongs to the so-called group of valve-metals. On these materials, an oxide of increasing thickness is formed when a current is passed through a cell containing a suitable electrolyte. The process is possible because the resultant oxide has low electronic conductivity and, when an appropriately high electrical field is applied across the metal/oxide/electrolyte system, ionic transport proceeds [1,2]. The valve-metal oxides can have different ionic conductivities and local structures and they have

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been extensively used as protective coatings against corrosion or as dielectric materials for the electronic industry [3,4].
Niobium oxide is now starting to replace tantalum oxide as a dielectric material in specific capacitors for the electronic industry. However, there are other potential applications for this oxide, including optic-electronic screens and solar energy conversion cells, since the oxide shows electrochromic and photoelectrochemical properties [5,6].
Anodic niobia is usually classified as an n-type semiconductor due to the associated value of the band-gap energy (3.4- 5.3 eV) [7], but factors such as stoichiometry, incorporated foreign species and crystallinity can have an influence on the behaviour of a particular oxide [8,9].
In this paper the semiconducting properties of anodic niobium oxides, formed at constant potential and constant current density with different resultant thicknesses, are analysed from their Mott-Schottky behaviour. The results obtained show n-type semiconductor properties with a carrier density in the range of $8 \times 10^{18} - 6 \times 10^{19}$ cm^{-3} on films formed to 10 V. For films of increased thickness reduced carrier densities, in the range of $1 \times 10^{18} - 2 \times 10^{18}$ cm^{-3}, are calculated.

Experimental

Niobium specimens were deposited by magnetron sputtering using an Atom Tech Ltd system with a target of niobium (99.9%). Sputtering was performed in 5×10^{-1} Pa argon after previous evacuation to 5×10^{-5} Pa. The substrates consisted of high purity aluminium sheet that had been electropolished for 180 s at 20 V in a solution of ethanol and perchloric acid (4:1 by vol.) at 283 K, then anodised to 150 V at 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution at 293 K to provide a flat surface for deposition.
Niobium specimens of working area 2 cm^2, were anodized at 5 mA cm^{-2} to 10, 50 and 100 V, in 0.1 M ammonium pentaborate at 293 K, with recording of the resultant voltage-time behaviours. Selected anodic oxides were also formed on sputtered niobium specimens at constant potential in the range of 2.5 to 10 $V_{Ag/AgCl}$ in a borate buffer solution (0.15 M H_3BO_3 + 0.075 M $Na_2B_4O_7$) of pH 8.8. The potential was applied for 10 minutes.
Capacitance measurements were performed in the borate buffer solution in the frequency range of 200 to 2000 Hz, at a sweep rate of 5 mVs^{-1} from +2.5 to -1 $V_{Ag/AgCl}$, a frequency analyser, model 1250 (Solartron) coupled to an electrochemical interface, model 1280 also from Solartron, controlled by a PC via Zplot software. A three-electrode electrochemical cell was used with an Ag/AgCl reference electrode and a platinum wire (10 cm^2 surface area) as the auxiliary electrode.

Results

The anodising of niobium under the experimental conditions has been examined elsewhere, showing that a linear plot voltage-time response is obtained due to the

formation of anodic niobia. RBS analysis of the oxide showed a uniform composition of Nb_2O_5 within an experimental accuracy of ± 5% [10].
The semiconductor-oxide/electrolyte interface has a characteristic behaviour because a space-charge region can be formed as a result of the electrochemical equilibrium achieved. For an n-type semiconductor a charge depleted layer is usually formed, with a capacitance (C_{SC}) that is related to the applied voltage (U) according to the Mott-Schottky equation:

$$\frac{1}{C_{SC}^2}=\left(\frac{2}{\varepsilon_o \varepsilon_r\, e N_D}\right)\left(U-U_{fb}-\frac{kT}{e}\right) \qquad (1)$$

where ε_r is the relative dielectric constant of the oxide ε_o is the vacuum permittivity, e is the electron charge, N_D is the carrier density, U is the applied potential, U_{fb} is the flat band potential, k is the Boltzmann constant and T is the absolute temperature. The equation is only obeyed in a potential range near the flat-band potential [11]. The value of N_D is obtained from the slope of the plot of C^{-2} against U and corresponds to the delocalised electrons located in the conduction band. Typical values are in the range of 10^{16} to10^{18} cm^{-3}, which is about six orders of magnitude lower than the delocalised electrons in metals [12].

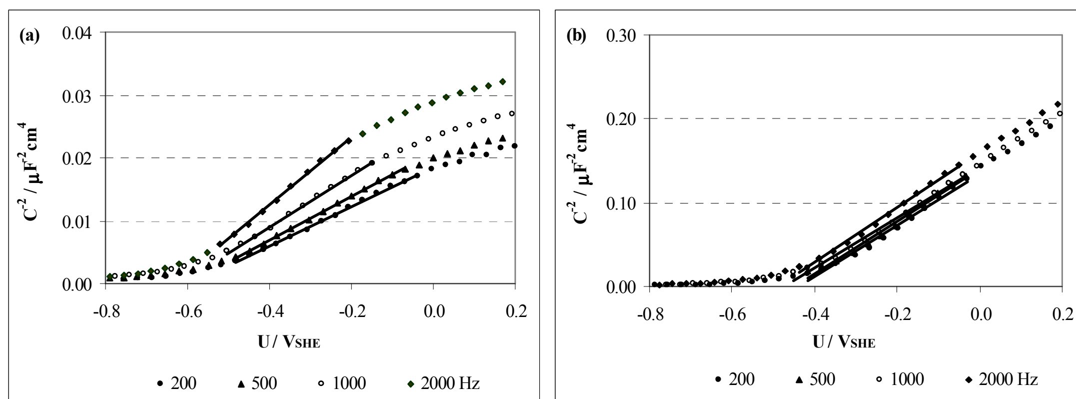

Figure 1. Mott-Schottky plot for anodic niobia formed at constant potential of (a) 2.5 V and (b) 10 V in the borate buffer solution.

The flat band potential can be determined only if the capacitance values are lower than the double layer capacitance (usually in the range 10 to 100 µF cm^{-2}) and assuming that there are no other contributions to the capacitance values [11].
The results, independently of the oxide thickness and oxide forming technique, show Mott-Schottky behaviour in the potential range of -0.2 to -0.6 V_{SHE} (Figs.1 to 3). The plots at different frequencies in the range 200-2000 Hz appear to converge to a common potential value as expected [12]. From this value of potential, the flat band potential is calculated according to (U_{fb}= U – kT/e). The carrier density values obtained are in the range 10^{18}- $10^{19}$$cm^{-3}$ showing that the "doping level" is not too high (Tables 1 and 2). The oxides formed to 10 V at constant potential, show a decrease of the carrier density with increase of oxide thickness. The values calculated for an anodising voltage of 10 V are considered

similar for both anodising methods, suggesting that the oxide thickness is the determining factor for the donor concentration variation in this potential range (Tables 1 and 2).

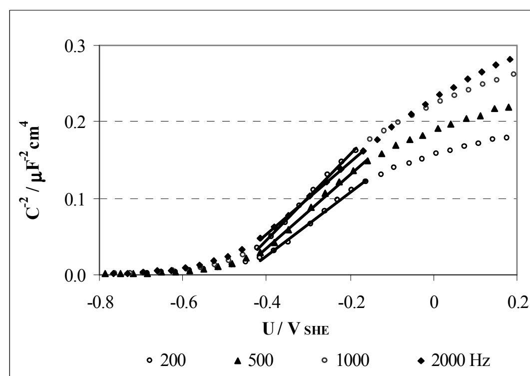

Figure 2. Mott-Schottky plot for anodic niobia formed to 10 V, at constant current density of 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution.

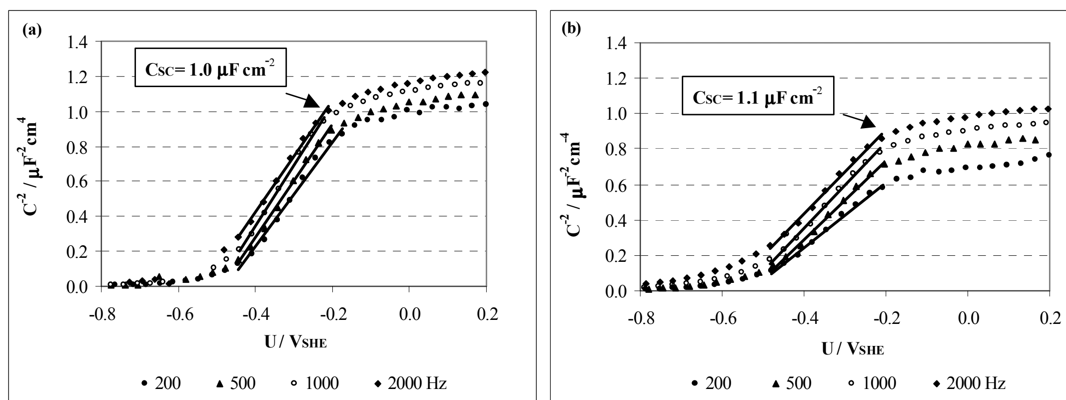

Figure 3. Mott-Schottky plot for anodic niobia formed to (a) 50 and (b) 100 V at constant current density of 5 mA cm^{-2} in 0.1 M ammonium pentaborate solution.

The flat band potential is only calculated for films formed to 50 V and 100V, where the capacitance range is closer or lower than 1 μF cm^{-2}, to assure that the double layer is not affecting the values. The values of flat band potential are, respectively, -0.541 and -0.611 V_{SHE}, in agreement with Biaggio et al. [13], but significantly more negative than values reported by other authors [7, 9,14].

Table 1. Mott-Schottky results obtained at 2000 Hz of the carrier density of the anodic niobia formed at constant potential.

Anodising voltage / V	N_D / cm^{-3}
2.5	6.30×10^{19}
5.0	2.75×10^{19}
7.5	1.70×10^{19}
10	1.06×10^{19}

Table 2. Mott-Schottky results obtained at 2000 Hz of the carrier density and flat band potential of the anodic niobia formed at constant current density.

Anodising voltage / V	N_D / cm^{-3}	E_{fb} (V_{SHE})
10	7.34×10^{18}	---
50	1.11×10^{18}	-0.566
100	1.45×10^{18}	-0.610

Discussion

The experimental results obtained are consistent, certainly associated with the clean and flat sputtered metal surfaces used for anodising, avoiding roughness and foreign surface treatment species that can influence the semiconductor properties.

A power relation ($y = ax^b$) has been observed for the variation of the carrier density with anodising potential for WO_3 [15,16] TiO_2 [17] as well as for anodic niobia [9]. The experimental results of this work confirm this dependence, assuming that only the final voltage is the determining factor (Fig. 4).

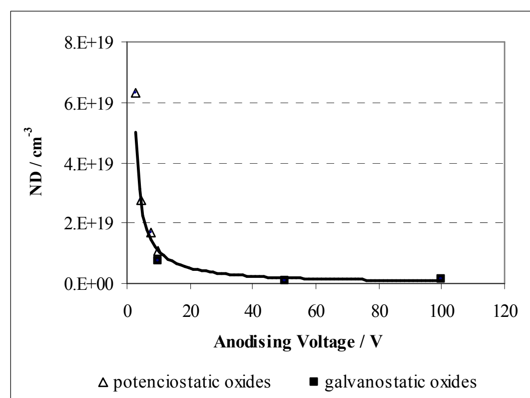

Figure 4. Dependence of carrier density on final anodising voltage for the anodic niobium oxides obtained at constant potential and constant current density.

The Mott-Schottky plots obtained at 2000 Hz for the oxides formed to 50 and 100 V, show an inflection point close to the same values of capacitance and potential (Fig.3). At increased anodic potential, the capacitance still changes with potential, but at a lower rate. A possible interpretation for this feature is to consider that a complete depleted charge carrier layer is achieved at that potential. Modestov et al. have found a similar behaviour on anodic niobia grown to voltages as high as 200 V [18]. The system at this point can be represented by a plane-plate capacitor:

$$C_{SC} = \frac{\varepsilon_r \, \varepsilon_o}{L_{SC}} \tag{2}$$

where -L_{SC}- is the thickness of the depletion layer. The layer thicknesses calculated assuming a conversion factor of 2.3 nm/V [19] have the values of 33 and 36 nm at 100 and 50 V, respectively. The values seem very reasonable as the depletion layer can extend from 10 to 1000 nm. The thickness of the depleted layer corresponds to an anodising voltage of 15.2 V. This value is close to the turning point shown by the power relation fitted to the experimental data (Fig. 4). This suggests that, whenever the depletion layer is thinner than the total oxide layer, the semiconductor/electrolyte interface exhibits a nearly constant carrier density, assuming that the oxide has a constant composition. When the charge depletion layer thickness is similar to the total oxide thickness, the interface metal/oxide has influence on the carrier density (Fig. 5). A possible reason for this effect may be the presence of a non-stoichiometric oxide close to the metal surface and also to the possibility of a decreasing thickness of this thin oxide layer with anodising potential and time.

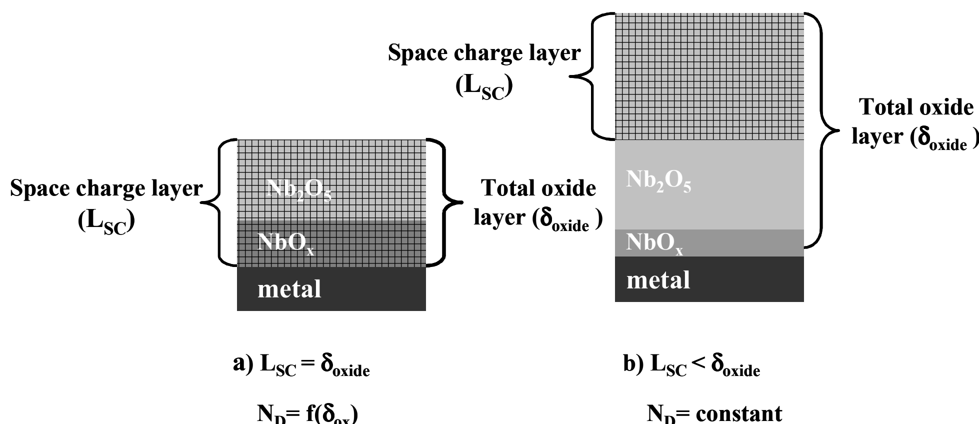

Figure 5. Schematic diagram of the system metal/semiconductor oxide/electrolyte for a charge depletion layer (L_{SC}) formed with a thickness similar to (a) and lower than (b) the total thickness of the oxide layer (δ_{ox}).

Conclusions

- Anodic niobium oxides formed on sputtered niobium show semiconductor behaviour when examined by Mott-Schottky plots.
- N-type semiconductor behaviour is revealed with a carrier density in the range $8 \times 10^{18} – 6 \times 10^{19}$ cm^{-3} for films formed to 10 V. Films of increased thickness show reduced carrier densities in the range $1 \times 10^{18} – 2 \times 10^{18}$ cm^{-3}.
- Anodic oxides formed to voltages of 50 and 100 V show an almost constant carrier density, associated with a charge depletion layer that is thinner than the total oxide thickness.

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