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On the variation in the electrical properties and ac conductivity of through-thickness nano-porous anodic alumina with temperature

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ABSTRACT

The electrical response of self-organized through-thickness anodic alumina with hexagonal arrangement of cylindrical pores has been studied as a function of temperature. Mechanically stable thick porous anodic alumina was prepared, by through-thickness anodic oxidation of aluminum sheet in sulfuric acid, with extremely high aspect ratio pores exhibiting fairly uniform diameter and interpore distance. It was observed that the electrical properties of through-thickness anodic alumina are very sensitive to minute changes in temperature and the role of surface conductivity in governing its electrical response cannot be overlooked. At high frequencies, intrinsic dielectric response of anodic alumina was dominant. The frequency-dependent conductivity behavior at low and intermediate frequencies was explained on the basis of correlated barrier hopping (CBH) and quantum mechanical tunneling (QMT) models, respectively. Experimental data was modeled using an equivalent circuit consisting of Debye circuit, for bulk alumina, parallel to surface conduction path. The surface conduction was primarily based on two circuits in series, each with a parallel arrangement of a resistor and a constant phase element. This suggested heterogeneity in alumina pore surface, possibly related with islands of physisorbed water separated by the regions of chemisorbed water. Temperature dependence of some circuit elements has been analyzed to express different charge migration phenomena occurring in nano-porous anodic alumina.

1. Introduction

Owing to high dielectric strength, resistance against hostile environments, mechanical and thermal stability, porous anodic alumina (PAA) has attracted great attention of researchers [1,2]. These characteristics make it a suitable candidate for a variety of applications including fabrication of electronic devices, magnetic storage discs, capacitors with barrier-type dielectric layers, gas sensors, heat sinks in IC's and biological membranes etc. [3–5]. As it is almost transparent to ordinary light [6], its photo- and electro-luminescence properties have been studied for various applications such as photonic crystals (polarizers) [7,8] and host for other fluorescent materials etc. [9,10]. It bears extremely large surface area due to high aspect ratio of ordered nano-channels [11] rendering it novel catalytic, magnetic and electronic properties.

Pore diameter, interpore spacing and mutual arrangement of the pores in PAA can be easily controlled by appropriate choice of anodizing conditions, and pre- and post-treatments [12]. Nano-structured surface obtained by appropriate choice of electropolishing pretreatment as well as suitable anodizing conditions may have excellent hexagonal ordering of the pores with uniform pore diameter and extraordinarily high aspect ratio of straight pores. One of the reasons for widespread use of PAA is ease in its preparation with a variety of architectures [13]. These include, for example, templates with ordered arrangement of tapered nanopores [14], and bi-layer structures in which pores grown from the opposite sides meet at a partially pierced barrier type oxide formed by through-thickness oxidation of alumina sheet [15].

Alumina can host a variety of nanostructures grown in-situ for the formation of electrical, magnetic, optical, catalytic and sensing devices, etc. [16]. Magnetic materials, such as Ni, Co, Fe and CoFe alloy etc., embedded in porous alumina matrix have their applications for the fabrication of high-density magnetic recording media [17,18]. PAA templated ferromagnetic nanowires, Au/Ni wires for example, have been used in the field of biomagnetics, in which these nanowires sense the biomolecules, sort the cells, and perform required biological manipulations [19]. Similarly, the fabrication of electronic devices at nanoscale using PAA templates has

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also been reported [20,21]. Syntheses of one-dimensional semiconductor wires (CdS, $Cd_xZn_{1-x}S$, CdS_xSe_{1-x}, GaAs etc.) and one-dimensional superlattices have been proposed [22,23]. Nanotube arrays of carbon and metals have also been suggested [24,25]. Routkevitch et al. [26] have reported a comprehensive overview of PAA-templated electronic device applications. Alumina itself is extensively used for sensor applications [27,28]. The contribution of electrical and electrochemical response of anodic alumina to the overall response of the devices, in these cases, cannot be ignored. An appropriate understanding of electrical properties of PAA is thus extremely useful for its enhanced use.

Impedance spectroscopy is a very powerful analytical technique used in material research for electrical characterization [29]. It can be used to study the temperature dependence of resistance and capacitance of materials [30]. In this technique, an ac signal is applied to measure the response of the material in terms of a complex electrical quantity as a function of applied frequency. Different complex electrical quantities include electrical impedance (Z^*), dielectric permittivity (ϵ^*), electrical modulus (M^*) and admittance (Y^*). These quantities are interrelated [31]:

$$M^* = 1/\epsilon^* = j\omega C_o Z^* = j\omega C_o(1/Y^*) \tag{1}$$

where C_o is empty cell capacitance, ω is angular frequency and $j^2 = -1$. Dielectric properties have often been represented in terms of complex admittance, which is given by [32]:

$$Y^* = G(\omega, T) + j\omega C(\omega, T) \tag{2}$$

where $G(\omega,T)$ is the conductance and $C(\omega,T)$ is the capacitance, which are functions of frequency and temperature (T). Above relationship can also be expressed as:

$$\sigma^* = \sigma^{/}(\omega, T) + j\sigma^{//}(\omega, T) \tag{3}$$

where $\sigma^*(=Y^*/(S/d)$, where S is the contact area (of the electrode), d is thickness of the sample and their ratio i.e. S/d is the geometric factor) is the complex conductivity and $\sigma^{/}$ $(=G(\omega,T)/(S/d))$ and $\sigma^{//}(=\omega C(\omega,T)/(S/d))$ are its real and imaginary parts.

In this manuscript, we have thoroughly investigated the electrical response of porous anodic alumina by impedance spectroscopy. Extremely thick two-layer anodic alumina has been grown by two-step anodic oxidation of aluminum sheet at 25 V. Effect of temperature on conduction mechanism and charge carrier transport has been studied at different frequencies. The electrical conduction mechanisms have been further explored by analyzing conductivity data and employing different theoretical models, viz. correlated barrier hopping (CBH) and quantum mechanical tunneling (QMT) models, to explain the dependence of electrical response on measurement temperature. An equivalent electrical circuit has also been proposed to interpret and analyze the experimental data.

2. Experimental

Through-thickness anodic alumina structure comprising of porous layers grown from opposite sides and separated from each other at the center by a partially pierced barrier layer containing a very small fraction of residual aluminum pieces was synthesized. The method opted for its preparation was the same as reported in Ref. [15] except 0.3 M sulfuric acid was used and anodizing was performed at 25 V. This resulted in fabrication of bi-layer anodic alumina. The thickness for each layer is approximately ~250 μm.

Scanning electron microscopic images were acquired using SEM (JSM-5910, JEOL) and FESEM (Camscan Apollo 300). Complex impedance spectroscopy was done in the frequency range of 10^{-1}–10^6 Hz using Alpha-N analyzer (Novocontrol, Germany) by applying 0.2 V ac signal. Water permeable thin gold electrodes were deposited on both sides of the sample through sputtering using 99.99% pure gold target. Silver paste was used in a very small quantity to make electrical contacts. The sample was placed inside a homemade sample holder which was connected to a dc power supply in order to control the temperature. The measurements were carried out in the temperature range of 29–70 °C with an accuracy of ±0.5 °C. Temperature was stabilized for about 10 minutes prior to each reading. The absence of any extraneous inductive and/or conductive coupling was ensured in the given frequency range by monitoring the dispersive behavior of the connecting cables using a standard sample. WINDETA software was used for data acquisition while ZView software was used for curve fitting.

3. Results and discussion

Fig. 1(a) and (b) shows typical cross-sectional and top view SEM images, respectively, of the PAA sample prepared by two-step anodizing in 0.3 M H_2SO_4 at 25 V. Cylindrical parallel pores with uniform interpore distance are successfully formed at this voltage. Domains with well-defined hexagonal pore arrangement are seen along with some pentagons (with missing pores at the center) and other irregular arrangements at the domain boundaries (Fig. 1(b)). The average interpore distance is ~62 nm. Apparently, the pores seem to cover about 22% of the surface (Fig. 1b).

In order to view the sandwiched structure between oppositely grown porous oxide layers, cross-sectional views of the middle of typical PAA sample are shown in Fig. 2. The pores are relatively

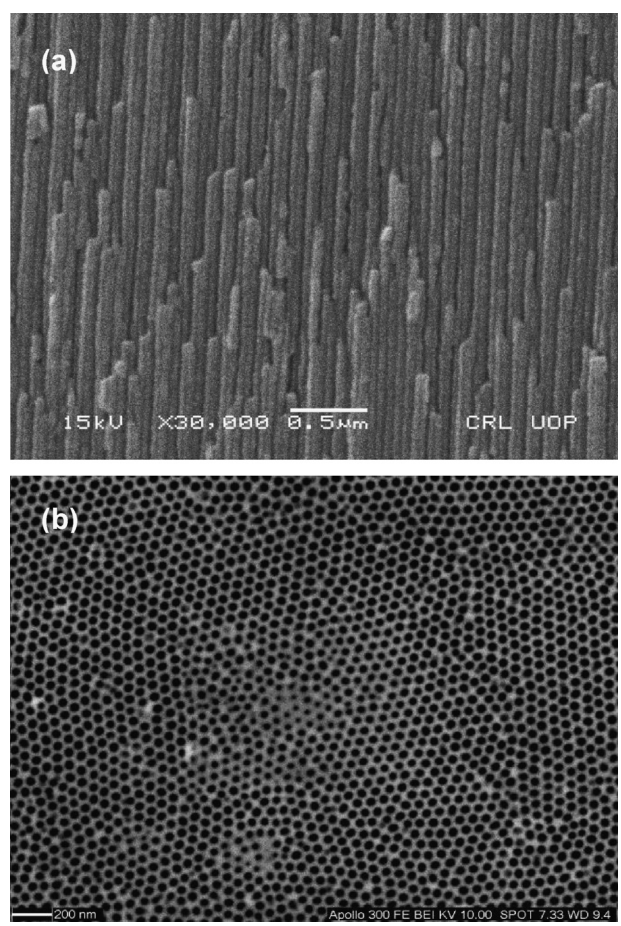

Fig. 1. Typical cross-sectional: (a) and top view (b) SEM images of through-thickness anodic alumina.