Impedance and admittance characteristics of Bi_2S_3 nanowire arrays

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Abstract. Current studies of the electrical impedance and admittance characteristics of the anodised aluminum oxide (AAO) nanoporous arrays and bismuth sulphide (Bi_2S_3) nanowire within AAO membranes are presented. The influence of potential and frequency scan rate effect produced on the real, imaginary and complex electrochemical impedance and double layer capacitance of the AAO nanopore and the Bi_2S_3 nanowire arrays were studied.

1. Introduction

Characterization of conductive properties of Bi_2S_3 nanowire within AAO membranes is important for perspective applications in nanoelectronics, photoelectrochemical solar cells and sensors [1]. Therefore it is important to determine the effects on electrical characteristics of B_2S_3 nanowire after repeated actions of current. It is shown that the resistance of Bi_2S_3 nanowire arrays is instable and varied between 1÷106 Ω cm [2, 3]. The resistance of nanowire arrays depends on method of preparation of nanowires, its size, and applied potential [2, 3].
Electrochemical impedance spectroscopy (EIS) is widely used for characterization of large area electrodes and the electrodes coated with porous layers [2, 5]. Recently EIS was applied for investigation of resistance and impedance of Bi_2S_3 nanowire arrays [4].
Here it is presented the studies of the electrical impedance and admittance characteristics of Bi_2S_3 nanowire arrays and AAO porous membranes. In particular it is addressed the influence of scan rate frequencies on the real, imaginary and complex electrical impedance and double layer capacitance of the AAO nanopores and the Bi_2S_3 nanowire arrays. The AAO membranes and Bi_2S_3 nanowire arrays were investigated applying two different modes of EIS - frequency scan at single potential and potential scan at single frequency.

2. Experimental

Bi_2S_3 nanowire arrays inside the pores of AAO membranes were fabricated by the thermolysis of the single source precursor bismuth bis(diethyldithiocarbamate) [$Bi(S_2CNEt_2)_3$] complex. This complex was prepared by the reaction of Bi_2O_3 with carbon disulfide and diethylamine in methanol and was thoroughly purified by repeated recrystallization as reported previously [6]. Scanning electron microscope Hitachi S4800 was used for visualization of samples (Figure 1 (a) and (b)). Samples containing Bi_2S_3 nanowires were polished mechanically on both sides to open the nanowires and remove reaction products from the surface. Then one side was coated by a 60 nm thick gold layer. For electrical characterization the specific measurement cell was designed in two electrode configuration (Figure 2 (a) and (b)). Deposited Au layer was used as a cathode and a Pt plate for AAO sample and drop of Hg for Bi_2S_3 nanowire arrays sample were used as an anode. Impedance spectra were obtained in potential range from: -0.4 to 0.4 V at scan rate of 10 ÷ 0.1 kHz, scanning number – 40, and measuring amplitude 0.01 V. The air humidity of laboratory was 75 % RH. All measurements were performed with potentiostat “Autolab PGSTA 30”. Results were analyzed by the Frequency Response Analysis (FRA) program for

Windows version 4.9.007. In this report real (Z_r) and imaginary ($-Z_j$) component of impedance, real (Y_r) and imaginary ($-Y_j$) component of admittance is presented.

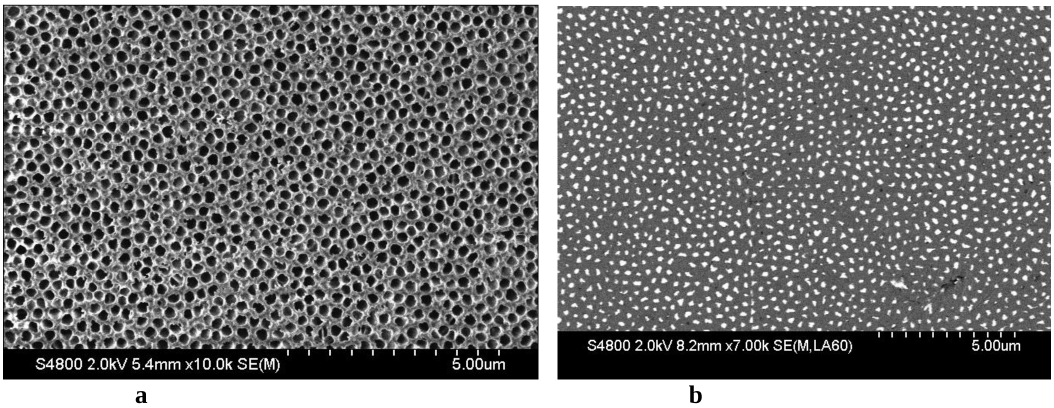

Figure 1 SEM images of AAO nanopore arrays (a) and Bi_2S_3 nanowire arrays (b). All AAO membrane nanopores are packed with Bi_2S_3 substances (b).

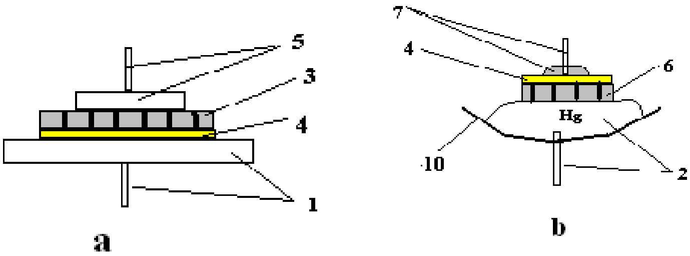

Figure 2 Representation of electrochemical cells for EIS measurement, (a) – electrical impedance spectra measurements for AAO; (b) – electrical impedance measurements for Bi_2S_3 nanowire arrays: 1 – Pt anode; 2 – Hg anode; 3 – the AAO membrane; 4 – the Au layer; 5 – Pt plate (cathode); 6 – Bi_2S_3 nanowire arrays; 7 – the Pt wire on Au layer (cathode); 10 – the small glass cup with Hg droplet.

3. Results and Discussion

The real component of the impedance (Z_r) value for AAO membrane was analyzed at applied current frequency at 10 kHz is insignificant (2÷100 MΩ·cm^2) (Table 1, Figure 3a, 3e). When scanning rate of current frequency was increased from 10 kHz to 1 kHz then the real component of impedance AAO nanopore arrays increased from 2 to 100 MΩ·cm^2. The imaginary component of impedance ($-Z_j$) value at this scanning frequencies increase very fast ($-Zj$ = 2.3 ÷ 7.5 GΩ·cm^2). The real and imaginary

Table 1 AAO nanopore arrays and Bi_2S_3 nanowire arrays impedance and admittance characteristic (in laboratory air, humidity - 75% RH)

Parameters	AAO nanopore arrays, air connect			Bi_2S_3 nanowire arrays, Hg connect, 1-10 kHz		
	-0.3 V	0.0 V	+0.3 V	-0.3 V	0.0 V	+0.3 V
Zr, MΩ cm^2	2-100	2-100	2-100	0.007-0.010	0.010-0.012	0.007-0.008
-Zj, MΩ cm^2	2300-4500	2300-4500	2300-4500	0.002-0.006	0.0034-0.010	0.0031-0.007
/Z/, MΩ cm^2	2300-4550	2300-4550	2300-4550	0.007	0.011	0.008
Yr, µS /cm^2	0.001	0.001	0.001	100	95	120
-Yj, µS /cm^2	0.0003	0.0004	0.0003	130	45	180
/Y/, µS /cm^2	0.001	0.0011	0.001	165	105	216

Table 2 The impedance and admittance characteristics of Al_2O_3 pressed powder and laboratory air at 75% RH humidity

Parameter	Z_r, MΩ cm^2	$-Z_j$, MΩ cm^2	Y_r, nS/cm^2	$-Y_j$, nS/cm^2
Al_2O_3 powder	5	40	200	25
Air layer of laboratory, 75% RH	9	32	10	4
Al_2O_3 powder, 70-80% relative humidity RH	$Z = 5 \cdot 10^6 - 2 \cdot 10^8$ Ω cm		Literature data [7]	
Air layer, absolute dray, 0% RH	$Zeq = 1 \cdot 10^{14}$ Ω cm			

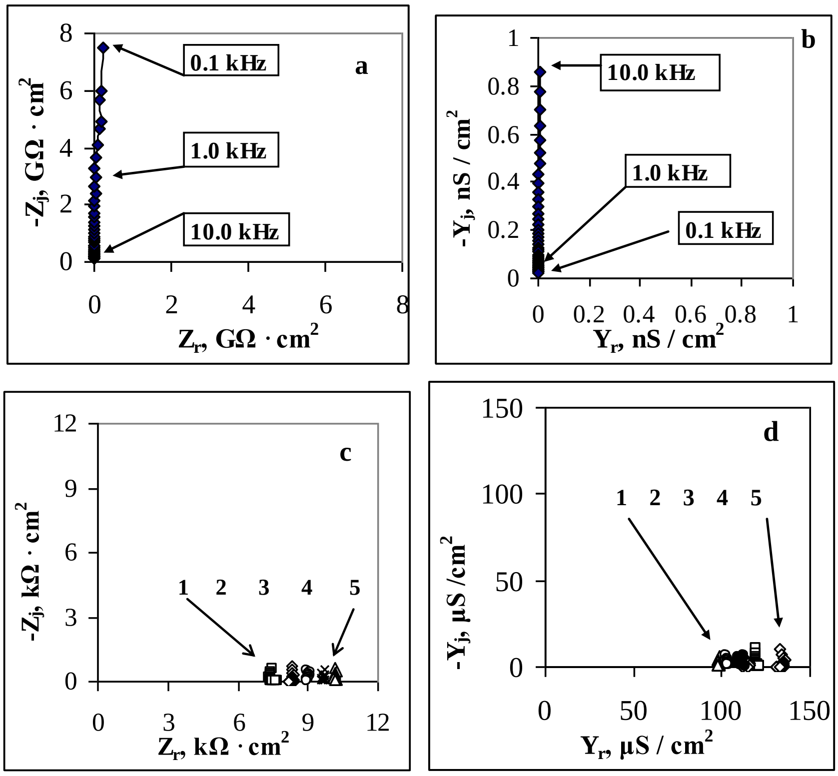

Figure 3 Complex impedance (a, c) and admittance (b, d) diagrams for AAO membrane (a, b) and for Bi_2S_3 nanowire arrays on the mercury droplet (c, d) for different applied potential: 1 -0.00 V; 2 -0.05 V; 3 -0.10 V; 4 -0.15V; 5 -0.20V

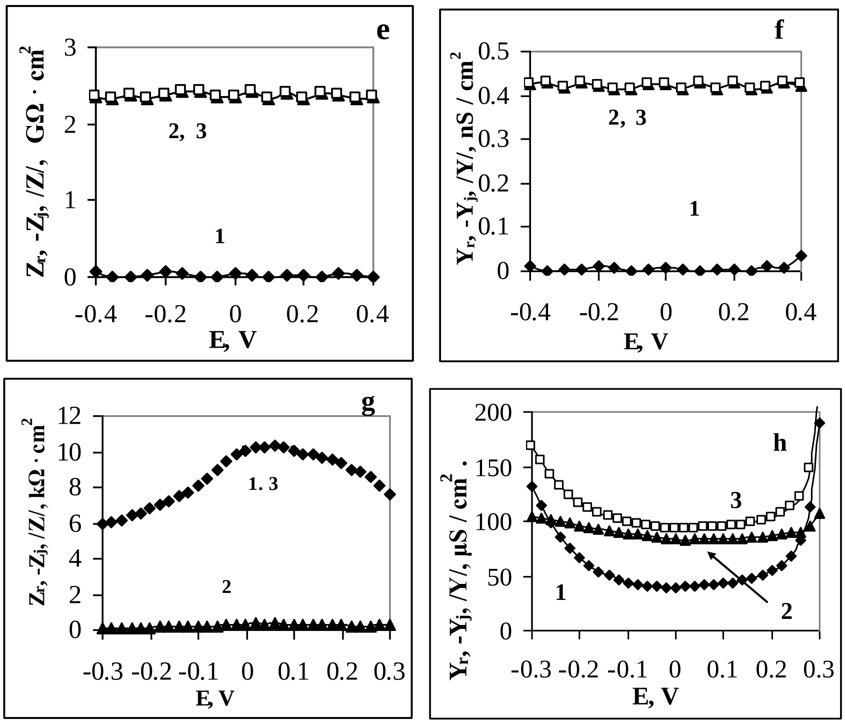

Figure 4 Impedance (e, g) and admittance (f, h) diagrams for AAO nanopore membrane (e, f), and for Bi_2S_3 nanowire arrays on the mercury drop (g, h) in applied potential range from -0.4 V to 0.4 V: 1 – real component of impedance (Z_r) and admittance (Y_r); 2 – imaginary component of impedance ($-Z_j$) and admittance ($-Y_j$); 3 – modulus of impedance (/Z/) and admittance (/Y/).

components of admittance (Table 1, Figure 3b, 4f,) are small – 1.0 nS/cm^2. It is easy to understand, because AAO (that is Al_2O_3) and air is characterized with high electrical resistance (Table 2.) The analysis of impedance spectrum using equivalent electrical circuit show that AAO characterized with one resistance elements (R) and capacitance component is very small, only some pF (Cs = 80 pF/cm^2).
The experiments shows that Bi_2S_3 nanowire arrays real component of impedance (Z_r) and real component of admittance (Y_r) using applied potentials from 0.0 to -0.2 V is rather constant from 7.0 to 10.0 kΩ·cm^2 and from 95 to 120 μS/cm^2, respectively (Table 1, Figure 3c, 3d, 4g, 4h). The both, imaginary component of impedance ($-Z_j$) and imaginary component of admittance ($-Y_j$) are very small at scanning rate of current frequencies below 1 kHz. But applying scan rate at larger frequencies (1.0 - 10 kHz) these components are from 2 to 3.4 kΩ·cm^2 and from 45 to 180 μS/cm^2 respectively. These facts denote that characteristics of Bi_2S_3 nanowire arrays applied at higher frequencies are different than characteristics of Bi_2S_3 nanowire applied at low frequencies.
The equivalent circuit for Bi_2S_3 nanowire arrays is denoted as $R_1(R_2C_1)$, where R_1 is 7.2 kΩ·cm^2, R_2 - 3.0 kΩ·cm^2 and C_1 - 2 nF/cm^2. AAO membrane and Bi_2S_3 nanowire arrays are characterized of two and three parallel positioned impedance elements: $Z_{Al_2O_3}$, Z_{air} and $Z_{Al_2O_3}$, $Z_{Bi_2S_3,bulk}$, Z_{Cs} for AAO membrane and Bi_2S_3 nanowires arrays respectively. For the calculation of impedance components AAO membrane and Bi_2S_3 nanowire arrays formulas **a)** and **b)** are used, respectively**.** Formula **c)** is used for the calculation of capacitance component of impedance**.** Coefficient 0.8 in formula **a)** and **b)** is a fraction of surface area covered by nanopore wall cross section but coefficient 0.2 is relative air double cavity or Bi_2S_3 nanowire area. Z is impedance and Cs is capacitance.

a) $$\frac{1}{Z_{AAO}} = \frac{1}{Z_{Al2O3}} \times 0.8 + \frac{1}{Zair} \times 0.2;$$ **b)** $$\frac{1}{Z_{Bi2S3}} = \frac{1}{Z_{Al2O3}} \times 0.8 + \frac{1}{Z_{Bi2S3,bulk}} \times 0.2 + \frac{1}{Z_{Cs}};$$

c) $$Cs = \frac{1}{2\pi f Z_{Cs}}; \quad (1)$$

The pure real calculated component of impedance ($-Z_{r,Bi_2S_3,\ bulk}$) for Bi_2S_3 nanowire arrays is 50 Ω·cm^2, but imaginary component ($-Z_{j,Bi_2S_3}$) is 2 Ω·cm^2, that is smaller than previously calculated [4].

4. Conclusion

It is experimentally defined that for AAO nanopore membrane the imaginary component of impedance ($-Z_j$) is one order of magnitude higher than the real component of impedance (Z_r), but for Bi_2S_3 nanowire arrays the real component of impedance (Z_r) is order higher than the imaginary component of impedance ($-Z_j$). It is determined that for Bi_2S_3 nanowire array real component of impedance is smaller than it was calculated previously.

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References

[1] A. A. Tahir, M. A. Ehsan, M. Mazhar, K. G. U. Wijayantha, M. Zeller, A. D. Hunter. Chem. Mater., 22: 5984-5092 (2010).
[2] K. A. Z. Syed Abuthahir, R. Jagannathan. Materials Chemistry and Physics, 121 ,184-192 (2010).
[3] P. Birjukovs, N. Petkov, J. Svirksts, J. J. Boland, J. D. Holmes, D. Erts. J. Phys. Chem. C., 112: 19680-19695 (2008).
[4] J. Katkevics, A. Viksna, G. Kunakova, A. Pastare, J. D. Holms, D. Erts. International conference "Functional materials and nanotechnologies 2011", Institute of Solid state physics University of Latvia , April 5 – 8, Riga, p. 186, (2011)
[5] M. E. Orazem, B. Tribollet. ECS-The Electrochemical Society, 159; 533 (2008)
[6] J. Xu, N. Petkov, X. Wu, D. Iacopino, A. J. Quinn, G. Redmond, T. Bein, M. A. Morris, J. D. Holmes. Chem. Phys. Chem., 8, 235-240 (2007)
[7] F. Faver, F. Villieras, Y. Duval, E. McRae, C. J. Rapin. Colloid Interface Sci., Jun 15; 286 (2):615-620 (2005).