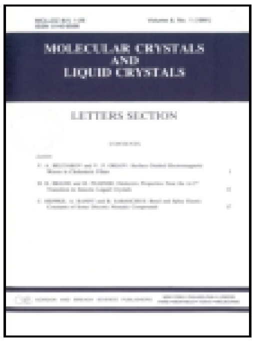

Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Design and Application of Anisotropic Nanostructured Conductive and Alignment Coatings

V. Zhylinski, V. Bagamazava, A. Chernik, V. Bezborodov & I. Zharski

Mol. Cryst. Liq. Cryst., Vol. 612: pp. 129–134, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1030970

Design and Application of Anisotropic Nanostructured Conductive and Alignment Coatings

V. ZHYLINSKI,* V. BAGAMAZAVA, A. CHERNIK,
V. BEZBORODOV, AND I. ZHARSKI

Faculty of Organic Substances Technology, Belarusian State Technological University, Minsk, Belarus

The paper describes the investigations of electrochemical preparation of self-organized aluminum mesh for display applications. This new technology can be used for the production of optically transparent electrodes for display devices without indium-tin oxide films. The aluminum meshes on glass surface were obtained by anodizing of thin Al films sputtered on sodium glass in oxalic acid solution at voltage of 50 V and chemical etching of porous alumina. It has been shown that the maximum Al meshes conductivity can be prepared by anodizing of thin Al films in acid solutions at a higher temperature.

Keywords: self-organized aluminum mesh; anodizing; porous alumina; optically transparent electrodes; display devices

1. Introduction

Transparent conductive layers coating with different dielectric and semiconductor surfaces are widely used in liquid crystal displays, touch panels, solar cells [1–5]. Currently, physically or chemically deposited metal oxides, such as indium-tin oxide (ITO) or ZnO_x, are the industrial standard materials with a good optical transparency and electrical conductivity [1]. However, metal oxide films are broken by bending or other physical stresses. And, unfortunately, they are requiring of a high deposition and/or high annealing temperatures to achieve necessary conductivity and better adhesion with a substrate, and for their production is needed complicated equipment [1–5].

As to concern the transparent metal mesh films, the cost and a request to fabricate desirable electrical, optical and mechanical properties of transparent conductors don't allow widely using them for the displays production.

It should be noted, that the adoptable transparent conductors on different substrates can be manufactured by low cost high-throughput process [1]. One of these processes is electrochemical anodization of thin (50-1000 nm) Al layer sputtered on sodium glass [1, 5]. In this process, Al anodization is accompanied by the formation of porous alumina layer on metal surface [1].

Typically, self-organized alumina porous layer is formed in acidic electrolytes like sulphuric acid [6, 7], oxalic acid [6–9], and phosphoric acid [6, 7, 10–12]. It was found that

*Address correspondence to V. Zhylinski, Belarusian State Technological University, Sverdlova Str., 13, 220006, Minsk, Belarus; E-mail: zhilinski@yandex.ru

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

structural features of anodic aluminum oxide (AAO), such as pore diameter and interpore distance, are depended by operating conditions: a type of electrolyte, an anodizing potential, a temperature and duration of the anodizing step. Both, the pore diameter and the interpore distance of AAO are increased linearly with the anodizing potential [6, 7]. Moreover, the anodizing temperature influences on pore diameter and, sometimes, interpore distance, and the porosity of AAO [7].

In this paper we report the temperature and concentration influence on the conductivity of invisible Al meshes on the sodium glass obtained by anodization in oxalic acid of thin Al film sputtered on sodium glass.

2. Materials and Methods

Thin Al layers (thickness of 1000 nm) were sputtered on sodium glass by using magnetrons spraying. The specimens with dimensions of 5 × 1.5 cm were degreased in acetone and ethanol, and then the working surface area of 3.0 cm^2 was insulated from the rest of the sample using an acid resistant paint.

Nanoporous alumina layers were prepared by an anodization of the specimens at voltage of 50 V in oxalic acid solution. The duration of anodization was determinated by the current drop (multimeter APPA 107). Oxide films were removed by chemical etching in a mixture of 5 wt.% H_3PO_4 and 2 wt.% H_2CrO_4 at 30°C for 0.2 h. The acid resistant paint was washed off after the anodization by acetone [7].

Experiments were performed at various temperatures (20, 35, 40, 45, 50 and 60°C) and concentrations of oxalic acid (0.15, 0.3, 0.6 and 1.7 M) in order to investigate the temperature effect on the conductivity of invisible Al meshes. The solutions of oxalic acid were prepared by dissolving the calculated sample of dihydrate oxalic acid in 500 ml of water.

The conductivity of the prepared samples was measured by multimeter APPA 107. The optical transmittance of Al meshes on glass was detected in the range from 350 to 600 nm using the spectrophotometer SF-26. The chemical energy-dispersion X-ray analysis of the samples was carried out by the system EDX JED-2201 JEOL. The structural features of nanoporous alumina layers were estimated using scanning electron microscope LEO-1455VP (SEM images).

3. Results and Discussion

Typical SEM image of invisible Al meshes after anodization of thin Al film and chemical etching are shown in Figure 1. It should be noted, that the morphology of metal mesh is formed during the anodization when self-organized vertical pores germinate through metal layer (Figure 2) [1].

Defects in hexagonal arrangement of mesh were caused by deference in rates of the formation of self-organized pores. According to the energy-dispersion X-ray analysis (Table 1), the rest and a mass fraction of aluminium on glass was 3.23 wt.%. Unfortunately, this parameter doesn't ensure the required conductivity of display electrode.

For the investigation of the influence of oxalic acid concentration on the surface conductivity of invisible Al meshes the specimens anodization and the nanomesh formation have been done in 0.15, 0.3, 0.6 and 1.7 M oxalic acid at voltage of 50 V (Figure 3a). One prepared sample with technical aluminium contacts is presented on Figure 3b.

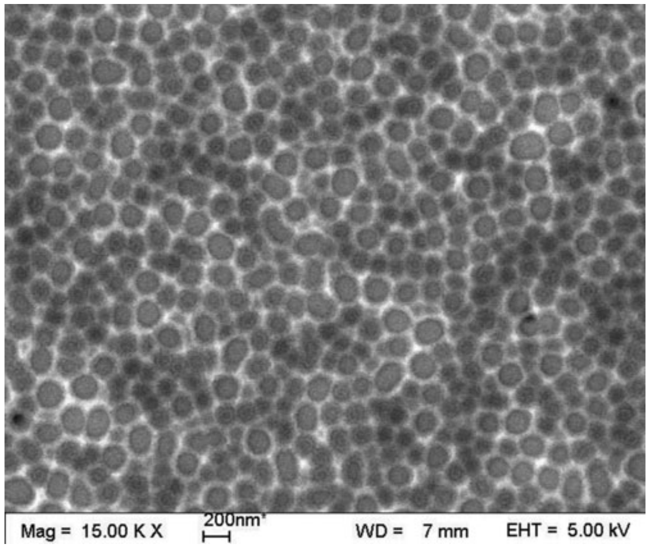

Figure 1. SEM image of invisible Al meshes after anodization of thin Al film in 0.3 M oxalic acid and chemical etching.

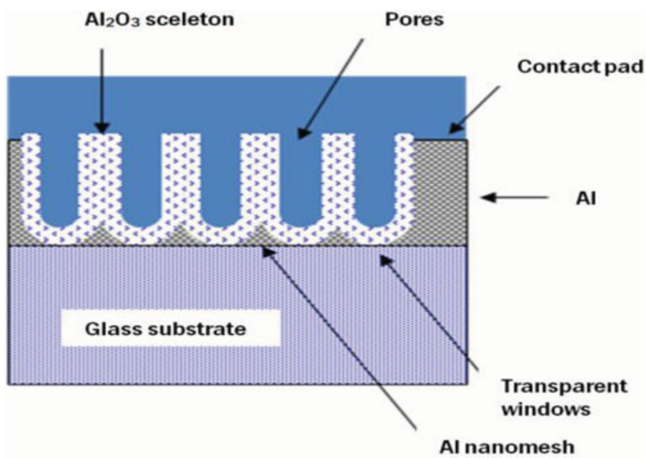

Figure 2. Scheme of Al nanomesh formation on glass.

Table 1. Results of chemical energy-dispersion X-ray analysis of invisible Al mesh on the glass after anodization in 0.3 M oxalic acid and chemical etching

Element	Energy (keV)	W (wt.%)
O	0.525	34.76 ± 0.40
Na	1.041	9.97 ± 0.18
Mg	1.253	2.01 ± 0.13
Al	1.486	3.23 ± 0.12
Si	1.739	42.01 ± 0.11
Ca	3.690	8.03 ± 0.17

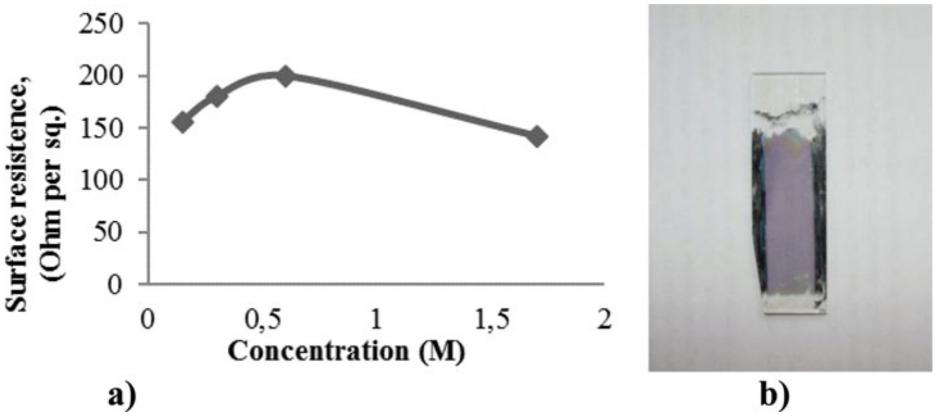

Figure 3. The influence of oxalic acid concentration on the surface conductivity of invisible Al meshes (a) and prepared sample with technical aluminium contacts (b).

The increase of acid concentration initiates the growth of the surface conductivity. The minimal surface resistance is obtained by the anodization of the specimens in 1.7 M oxalic acid. Perhaps, it is caused by an increase of the pore diameter and the size of remanding Al mesh too.

The influence of temperature on the surface resistance of mesh layers is shown on Figure 4a. As can be seen from Figure 4a, the surface resistance decreases with the growing of anodizing temperature till 45°C. This tendency can be explained by the enhanced dissolution of aluminum oxide at the oxide/electrolyte interface and the pore diameter increase [7]. But the higher temperature leads to an increase of the surface resistance. It may be interpreted by local dissolution of aluminum and alumina at the bottom of pore in the hot acidic electrolyte during the anodization.

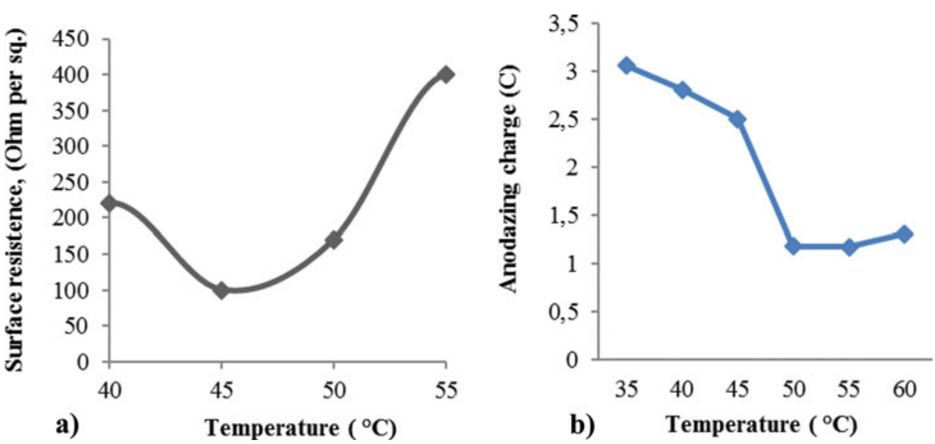

Figure 4. The influence of temperature on the surface resistance of mesh layers (a) and anodizing charge required for electrochemical oxidation of Al layer in 1.7 M oxalic acid (b).

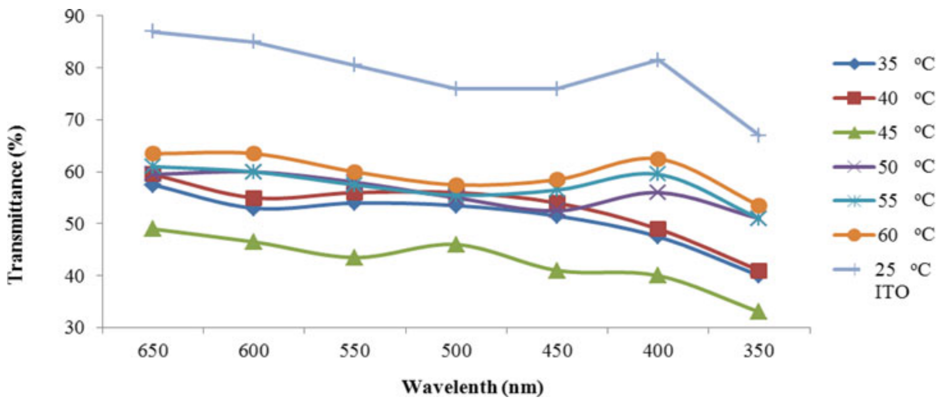

Figure 5. The transmittance spectra of display electrodes obtained at different temperatures of the anodization in 1.7 M oxalic acid.

Analysis of the obtained spectra of optical transmittance (Figure 5) shows that the type of the spectra of display electrodes with Al mesh is not different from the spectrum of glass with ITO film (thickness of 150 nm).

The transmittance value of display electrodes obtained in 1.7 M oxalic acid is lower on 20-30% then the same value of ITO film.

4. Conclusions

Thus, the self-organized formation of porous alumina can be used for the production of optically transparent electrodes for display devices without using ITO technology. Aluminum meshes on glass surface obtained by anodization of thin Al films sputtered on sodium glass are acceptable for the display production. The maximum conductivity was observed for the samples prepared in concentrated acid solutions at a higher temperature. It can be explained by the enhanced dissolution of aluminum oxide at the oxide/electrolyte interface which leads to the increase of the pore diameter in alumina and size of the remaining invisible mesh of aluminum.

References

[1] Jaguiro, P., Stsiapanau, A., Hubarevich, A., Mukha, Y., & Smirnov, A. (2010). *Semiconductor Physics, Quantum Electronics & Optoelectronics*, *13*, 305.
[2] Maeda, T., & Hiroshima, K. (2004). *Jpn. J. Appl. Phys.*, *43*(8A), 1004.
[3] Wang, Q., Li, Ch., Yuan, G., & Gu, Ch-Zh. (2009). *Chinese Phys. Lett.*, *26*, 86.
[4] Sai, H., Fujii, H., Arafune, K., Ohshita, Y., & Yamaguchi, M. (2006). *Appl. Phys. Lett.*, *88*, 201116.
[5] Park, S., Lee, H., Cho, J., & Lee, K. (2005). *Electrochem. & Solid-state Lett.*, *8*, 5.
[6] Ono, S., & Masuko, N. (2003). *Surf. Coat. Technol.*, *139*, 169.
[7] Zaraska, L., Stępniowski, W. J., Ciepiela, E., & Sulka, G. D. (2013). *Thin Solid Films*, *534*, 155.
[8] Lillo, M., & Losic, D. (2009). *Mater. Lett.*, *457*, 63.
[9] Romero, V., Vega, V., Garcia, J., Prida, V. M., Hernando, B., & Benavente, J. (2012). *J. Colloid Interface Sci.*, *40*, 376.
[10] Choi, D. H., Lee, P. S., Hwang, W., Lee, K. H., & Park, H. C. (2006). *Curr. Appl. Phys.*, *e125*, 681.

[11] Brevnov, D. A., Barela, M. J., Brooks, M. J., Lopez, G. P., & Atanassov, P. B. (2004). *J. Electrochem. Soc.*, *B484*, 151.
[12] Zhang, R., Jiang, K., & Ding, G. (2010). *Thin Solid Films*, *3797*, 518.
[13] Stępniowski, W. J., & Bojar, Z. (2011). *Surface & Coatings Technology*, *206*, 265.