P-76: Combined Nanostructured Layers for Display Applications

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Abstract
One-step cost effective process of fabrication of a full inorganic nanostructured transparent conductive electrode and LC alignment layer has been developed. More specifically, the subject comprises a self-organized nanomesh of a valve metal, concomitant porous oxide layer with various functionality and electrochemical method of their fabrication. The nanomesh film is electrically conductive, optically transparent and flexible. It can be fabricated on a variety of substrates, including flexible and rigid substrates. High effective LC alignment layers based of nanostructured alumina can be fabricated at the same anodization process by special electro-chemical technique in sulfuric and oxalic acids to form a self ordered nanoporous structure of alumina which has a "vertical" surface area that prevails over the "horizontal" one even though Al film's thickness is small. The possibility to control distances between pores and their sizes during the process of anodizing/etching enables to optimize alignment surface according to the required LC material.

1. Introduction
Transparent conductive layers coating different dielectric and semiconductor surfaces are widely used as electrodes in flat liquid crystal and OLED displays, touch panels, solar cells, and as antistatic or electromagnetic wave shielding films as well.

Currently, physically or chemically deposited metal oxides, such as indium tin oxide (ITO) or ZnO_x, are the industrial standard materials to provide optical transparency and electrical conductivity. However, metal oxide films are fragile and prone to damage during bending or other physical stresses. They are also requiring of high deposition and/or high annealing temperatures to achieve needed conductivity and better adhesion to a substrate. In addition, the deposition is a costly process demanding complicated equipment.

Conductive polymers have also been used as an optically transparent layer. However, they generally have lower conductivity and higher optical absorption (particularly at visible wavelengths) compared to the metal oxide films, and suffer from lack of chemical and long term stability. Nowadays, transparent metal mesh films also exist, but they are costly and require a high-precision masking. Accordingly, there is a demand to fabricate transparent conductors possessing desirable electrical, optical and mechanical properties, in particular, transparent conductors that are adoptable to any substrates and can be manufactured in a low-cost high-throughput process.

We propose a new technological approach to fabricate a nanostructured transparent conductive electrodes by electrochemical anodization of valve metals (see Figure 1). This technology provides the self organization of a transparent conductive nanomesh of a valve metal and doesn't require any photolithographic process. Moreover, nanoporous oxide layers over a nanomesh can be used either as it is or with filled pores as an alignment, antireflective or optically active (e.g. dyeing) layer as well (Figure 2).

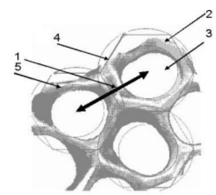

Figure 1. Schematic view of a nanomesh.

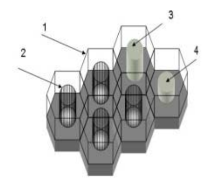

Figure 2. Al nanomesh covered with a porous alumina.

2. Incomplete Electrochemical Anodization
The technology of fabrication of nanostructured transparent conductive layers represents a technology of incomplete electrochemical anodization of valve metals which means that the anodization process is to be either terminated or modified at a moment when the bottoms of pores will reach the bottom of an anodized metal film but the whole metal has not been anodized yet, thus the rest of the metal represents a connected area.

The structure of an Al nanomesh and a nanoporous alumina oxide resembles a cellular structure with hemisphere bottoms of pores. At the definite moment when the anodization front reaches a substrate, the whole metal under the bottom of a hemisphere pore has already been anodized with the metal being left non anodized (Figure 2) on the periphery of hemispheres. Such non planarity of the anodization front allows to produce a nanomesh of a valve metal (Figure 1).

3. Results and Discussion
The geometry of a nanoporous oxide, dimensions of pores and the distance between them in particular (Figure 2), will depend on the anodization mode, applied voltages and choice of electrolyte. Mesh spacing will depend on a pore dimension and wall thickness (the latter is determined by the value of applied voltage). The anodization can be carried out within the range of 5V - 300V in solution of sulfuric, phosphorous, oxalic, citric or tartaric acids corresponding to needed porosity of anodized valve metal. These regimes allow to reach a mesh spacing within the range of 10 -500 nm. As can be seen from Figure 2 the anodization process protects the metal nanomesh with a layer of porous alumina oxide which is obtained due to the same process [1]. SEM photo of the aluminum nanomesh after selectively etching of Al_2O_3 skeleton is presented in Figure 3.

ISSN 0097-966X/11/4203-1385-$1.00 © 2011 SID

In a nanomesh film its transparent and conductive functions are separated in space, but this feature doesn't come out due to a sub wavelength size of the nanomesh pitch. It allows overcoming some fundamental limitations, which are specific to ITO and ultrathin metal films, where conductive electrons works as electric charge carriers and light absorbers simultaneously.

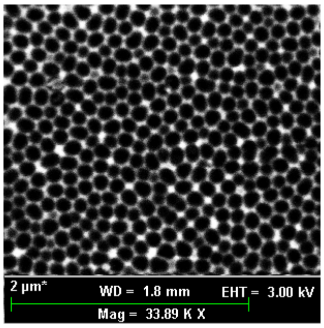

Figure 3. SEM of the aluminum nanomesh.

High effective LC alignment layers based of nanostructured alumina can be fabricated at the same anodization process. To do this a magnetron sputtered 0.5-1 µm Al thin films were anodized by special electrochemical technique in sulfuric and oxalic acids to form a self-ordered nanoporous structure of alumina which has a "vertical" surface area that prevails over the "horizontal" one even though Al film's thickness is small [2]. The possibility to control the changes of distance between pores and their sizes during the process of anodizing/etching enables to optimize alignment surface according to the required LC material.

In addition the described technology has a number of other advantages:

- nanoporous alumina acts as a high quality dielectric and provides additional protection of LC molecules from undesirable chemical reactions near an alignment surface;
- nanoporous alumina is stable and resistant to external actions including heat, UV radiation and mechanical stress, thus prevailing in this respect over commonly used polymers;
- both Al magnetron sputtering and anodizing are low temperature processes compatible with the use of flexible substrates.

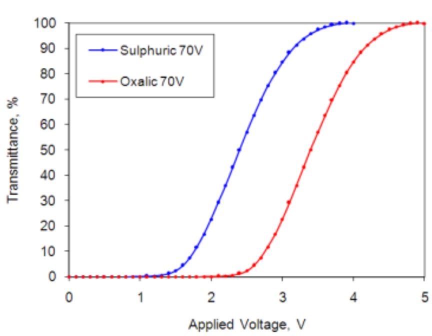

Figure 4. Threshold voltages of LC cells.

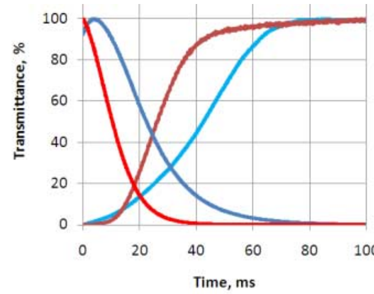

Figure 5. Switching times of LC cells.

Different sizes of pores lead to the change of threshold voltages: lowest voltages are for sulfuric acid (see Figure 4) and switching times: highest times are for sulfuric acid (see Figure 5).

So, we presented quite simple and cost effective technology based on electrochemical method of fabricating of nanostructured alumina which can serve not only as alignment layers but as color RGB-filters or light absorbers as well [3]. Moreover, this technology can be scaled on large-size substrates, including flexible one, i.e compatible with continuous "roll-to-roll" processes.

Test LC cells with Al nanomesh electrodes and nanoporous alumina alignment layers fabricated by one-step anodization process are shown at Figure 6 and Figure 7 [4-6].

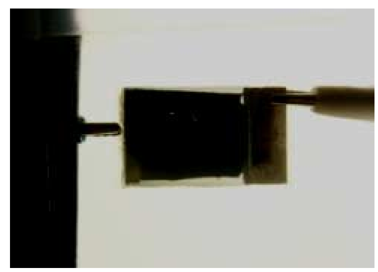

Figure 6. Switch off LC cell with aluminum nanomesh electrodes and nanoporous alumina alignment layers.

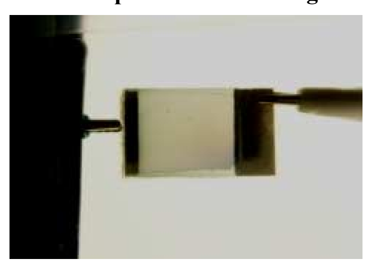

Figure 7. Switch on LC cell with aluminum nanomesh electrodes and nanoporous alumina alignment layers.

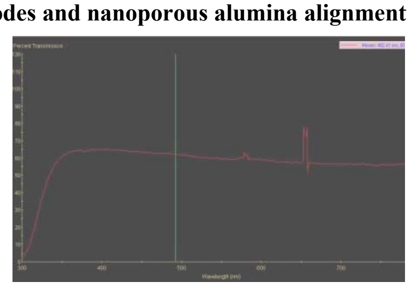

Figure 8. Transparency of nanomesh with alignment layer

The alignment layer produced on Al_2O_3 with Al nanomesh possesses the same transparency as the alignment layer produced on ITO with sub layers (Figure 8) this also makes the manufacturing process easier by reducing the number of operations.

4. Conclusion

One-step cost effective process of fabrication of a full inorganic nanostructured transparent conductive electrode and LC alignment layer has been developed. The nanomesh film is electrically conductive, optically transparent and flexible. It can be fabricated on a variety of substrates, including flexible and rigid substrates. High effective LC alignment layers based of nanostructured alumina can be fabricated at the same anodization process by special electro-chemical technique in sulfuric and oxalic acids to form a self ordered nanoporous structure of alumina. The possibility to control distances between pores and their sizes during the process of anodizing/etching enables to optimize alignment surface according to the required LC material.

5. References

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