Using Anodic Aluminum Oxide Film and Nanoimprint to Produce Polymer Anti-counterfeit Labels

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ABSTRACT

An anodic aluminum oxide (AAO) film fabrication process and photolithography were combined to produce a patterned array of nano-hemispheres. This barrier was then used as the substrate on which conductive metals were vapor-deposited to produce electrodes. Nano electroforming was then utilized to deposit nickel on the surface of the array of nano-hemispheres. Finally, the technique of nanoimprinting was used to transfer the unique structure of the barrier to a polymer. Scanning electron microscopy (SEM) was used to explore the effects of different voltages on the fabrication process and of phosphoric acid etching time on the shape of the barrier. An atomic force microscope (AFM) was used to verify that the nano-array structure of the aluminum oxide film had been completely replicated on the polymer. The regular arrangement of nano-hemispheres refract light and also cause interference, such an array is referred to as a photonic crystal. This type of special structure can be used in counterfeit protection and in many other optical applications.

1. Introduction

Since the discovery of carbon nanotubes, by Sumio Iijima, the field of nanomaterials has rapidly expanded to include various materials such as nano granules, lines, porous nanofilm, and nanoarrays [1–8]. Once a material enters the ‘nano size’ realm the range of its physical and chemical characteristics expands to include some which were previously irrelevant at the macro level. Traditional theories no longer fit and new ones are needed. One example is the Van der Waal’s force; normally regarded as negligible, this force becomes quite significant in nano-sized materials. The unique structure and nature of one-dimensional nanomaterial has great potential for development in the optics, electrical, and mechanical structure fields. Of these, metal nanoarrays possess unique electronic, optical, and chemical properties, and are currently an important topic of study.

As regularly arranged 3D nanostructures have a broad range of applications, and a lot of recent research has been focused on their fabrication. Methods such as
electron-beam lithography [9,10], focused ion-beam etching [11,12], bottom up approaches, and scanning-probe-based writing [13,14] have all been used. Anodic aluminum oxide (AAO) is a 3D nanomaterial that has the ability to self-assemble, it has regularly arranged hemispheres on the surface and can cause the diffraction and interference of light. The structure is that of a photonic crystal, many of which exist in nature, and their development is simply an attempt to mimic natural structures [15–20]. However, most biological nanostructures are very fragile and most attempts to physically replicate them fail short. Consequently, many different processes for making nanostructured photonic crystals have been devised. The earnest development of structure color technology began in 2014, and is based mainly on the photonic scattering effect of cyclical metal nanostructures. Montelongo et al. proposed using this to produce multi-color holograms with silver nanoparticles via scattering and refraction [21]. Olson et al. developed a pixel-based full color imaging device in which a cyclically arranged aluminum nanostructure is produced for each pixel. The height and spacing of the aluminum nanostructure is used to control the scattering of visible light [22]. Tan et al. used a similar method, and utilized electron-beam lithography and electron-beam vapor deposition to produce a 0.3×0.3 mm nano oil painting [23].

However, producing photonic crystal structure by electron-beam lithography takes a long time and requires very expensive equipment. Much cheaper methods have been devised. Hu et al. used magnetically induced self-assembly to produce anti-counterfeit labels. The refraction color of the label in a superparamagnetic nano-colloid can be controlled by magnetically induced self-assembly [24]. Bai et al. used inkjet printing to deposit silica nanoparticles on a pre-designed pattern. This formed a colloid photonic crystal structure the color of which could be controlled by the silica size and spacing. Steam injected into the porous colloid photonic crystal will change both the structure and color, and a dual color structure is developed, while alcohol steam can render hidden colors visible. However, steam injection to change structure color is impractical for anti-counterfeit applications [25]. Xu et al. analyzed the optical characteristics of AAO film and its reflected light color producing mechanism. The results showed that phosphoric acid etched AAO has superior color saturation. The main reason for this is that the nanoholes in phosphoric acid etched AAO are not very regular, and can easily scatter light reflected from an oxidized aluminum or pure aluminum interface [26]. Xu et al. filled the AAO nanoholes with carbon nanotubes to form a CNT@AAO composite thin film. The color of this composite depends on the thickness of the AAO. If an area different from the original AAO film is wet-etched, to produce holes of different depth which are then filled with carbon, the color displayed will be controllable by different thickness of nanotubes on the CNT@AAO composite thin film, and can be used for anti-counterfeit applications. However, the same thin film process has to be repeated for each label and in any case the AAO is a fragile ceramic material, and not appropriate for practical application [27]. In another study, Kang et al. developed a high optical haze film composed of self-aggregated alumina nanowire arrays [28]. The total and diffuse transmittance, and haze value of these photonic films were found to be controllable by the packing density of the alumina nanowires produced by etching AAO in phosphoric acid for times ranging from 43 to 45 min. The photonic films were integrated with a PTB7:PC70BM-based organic photovoltaic solar cell. The power conversion efficiency (PCE) was enhanced as compared to the bare device and a direct dependence between the features of the haze film and the PCE feature was established. Binary composite heterostructures based on nanopillars of titanium dioxide (TiO2) and cuprous oxide (Cu2O) were produced by a selective etching of AAO thin films used as templates [29]. Homogeneously distributed arrays of TiO2 (photoanode) and Cu2O (photocathode) were demonstrated as electrode platforms for artificial photosynthesis using two different reaction centers with an appropriate electron transport chain. In another interesting study, Ashley et al. used AAO films as templates to produce semiconducting metal halide perovskites structures based on nanowires with controlled diameter (50–200 nm) [30]. Nanostructured thin films based on CH3NH3PbI3, CH3NH3PbBr3, and Cs2SnI6 were produced using this approach. The chemical, structural, crystallographic, and photoluminescence properties of these structures were characterized to demonstrate the feasibility of this fabrication method to generate electrodes for solar cell and photodetection applications. Waleed et al. used a similar approach to produce photoelectrodes based on CH2NH2SnI3 nanowires [31]. This study established that nanostructuring can lead to a dramatic enhancement of the stability of the photoelectrodes. This phenomenon was attributed to the effective blockage of the diffusion of water and oxygen within the photoelectrode structure.

Current photonic crystal development and applications have been hindered by overly complex fabrication technique, expensive equipment that must be operated by specially trained personnel, and excessive manufacturing cost. We propose using AAO technology, semiconductor photolithography, nano/micro electroforming mold fabrication, and nanoimprint technology to prepare a nano nickel mold. Nanoimprinting can then be used to mass produce low cost polymer anti-counterfeit labels.
2. Principle, Materials, and Method

2.1. AAO Back Barrier Layer Forming Mechanism
When an acidic solution is used for anodic treatment of pure aluminum, the electrolyte will decompose the aluminum surface and an oxide layer will begin to grow. Tiny holes will form on the surface of the aluminum and the bottom of the holes will form a barrier separating the layer of oxide from the metal. When the hole formation stabilizes, they will begin to grow at a fixed rate, to form an oxidized aluminum layer with a beehive structure.

2.2. Structural Color Formation
Figure 1 is a diagram illustrating the reflected spectrum from incident light impinging on an array of nano-hemispheres. According to the grating principle, when incident light enters a cyclical structure, its amplitude and phase is regulated by the spacing, this causes interference in the diffracted light to produce spectral changes. The nano-hemisphere structure produced for this study can be treated as a reflective grating. When incident light enters the structure surface, its size and arrangement causes the reflected light to produce spectral changes. The resulting diffraction spectrum is related to the size of the nanostructure and the angle of incidence. The grating formula (1) can be used to elucidate the relationship between incident angle, diffraction wavelength, and the structure.

\[
\Lambda \sin \theta_i + \sin \theta_m = m \lambda
\]  
(1)

\(\Lambda, \lambda, \theta_i, \text{ and } \theta_m\) are the spherical spacing, diffraction wavelength, incident angle, and the mth diffraction angle.

2.3. Polymer Anti-counterfeit Labels
Figure 2 shows the polymer anti-counterfeit label manufacturing process, this includes the AAO film fabrication, semiconductor lithography, nano/micro electroforming, and nanoimprinting. Details of the process are as follows.

2.3.1. The AAO Film
(i) Pure aluminum specimen preparation: a piece of pure aluminum (99.999%) was placed in an oven and annealed at 400 °C for four hours. It was then washed sequentially in acetone, alcohol, and water, and dried before use.
(ii) Electrolytic polishing: the specimen was immersed in a 1:3 mixture of perchloric acid in absolute alcohol. A biased electric current of 20 V was applied for two minutes to polish the specimen.
(iii) Anodic treatment: the polished specimen was immersed in a 5wt% phosphoric acid solution held at 0°C and anodized using 160–180 V for 3–6 h.
(iv) Removal of the aluminum substrate: a solution of CuCl₂ in HCl was used to remove the remaining aluminum material to leave the back barrier layer with nano-hemisphere structure, see Figure 2(A).

2.3.2. Semiconductor Lithography
The back barrier layer was spin coated with 1μL of AZ 1518 positive photoresist (Figure 2(B)) and then soft baked
at 100°C. The piece was then exposed and developed in 2.38% TMAH developer. This produces a patterned micro structure on the AAO film back barrier layer.

2.3.3. Nano/micro Electroforming
An electrochemical process was used to reduce the metal and transfer the desired pattern to an electroforming mold. A 10 nm gold film was deposited as a conductive layer onto the AAO surface before electroforming in nickel aminosulfonate (Ni(NH₂SO₃)₂ 4H₂O) was carried out. A positive voltage with a setting of 10 mA/cm² to the anode was optimal for deposition of nickel into the nano holes and good electroforming results. Sodium hydroxide (1.0 M) was used to etch the AAO to produce the nano/ micro nickel mold (Figure 2(C)).

2.3.4. Nano/micro Structure Imprint
UV-curing resin was used to make the actual anti-counterfeit labels. The resin was evenly distributed on the surface of the nickel mold, which was then exposed to UV for 45 s to solidify the resin (Figure 2(D)). The mold was then removed to obtain the anti-counterfeit label (Figure 2(E) and (F)).

3. Result and Discussion
Figure 3((A)–(F)) shows SEM images of AAO barrier films formed at different voltages. From the figure it can be seen that the size of the nano-hemispheres and regularity of their arrangement is proportional to the voltage used. Highly regular arrangements of hemispheres can be achieved using phosphoric acid for electrolysis, and the SEM images show the diameter of nano-hemispheres formed with 180 V is about 400–450 nm. Figure 4 shows the result of etching the barrier with 1.0 M phosphoric acid and it can be seen that as the etching time increases, the original hemisphere structure gradually becomes flatter. The figure also shows that the etching speed is uneven, the surface of the spheres etch faster than the material in the gaps between them. This is because the aluminum metal is mainly situated in the gaps while the oxide is on the spheres themselves [32]. To further confirm that nanostructures can be completely transferred to the nickel mold, we used an Atomic Force Microscope (AFM) to inspect and analyze the nanostructural size changes in the different materials, as shown in Figure 5. The structure size changes in Table 1 show that the AAO mold structure roughness was 30 ± 1.1 nm. This roughness is greater than that of the resin (28.9 ± 0.9 nm) possibly because residual air was trapped during mold replication onto the resin. The structure of nanophotonic crystals is generally ordered to a substantial degree and can diffract light over
reflects a different wavelength of light; the result is a dramatic shift in color.

4. Conclusions

Nanophotonic crystals with different structural size and arrangement can cause light scattering that shows different colors. The fabrication of photonic crystal structure is usually complex and expensive and this limits mass production and commercialization. However, the nanophotonic crystal structure transfer process described here could be very valuable for the fabrication of anti-counterfeit labels and is comparable to existing applications that use dyes. This simple method involves the use of a nickel mold and easily prepared nanophotonic crystals. An AAO film back barrier layer with nanophotonic structure is used as a master and electroforming is used to prepare a nickel mold. These reusable molds can be used to make impressions on a polymer to produce low-cost anti-counterfeiting labels with photonic crystal structure. The results show that this process can effectively imprint nano/micro structure without affecting the final color changes.
Future work will include the integration of fluorescent patterns with both structure and fluorescent colors.

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