Aluminium pre-patterning for highly ordered nanoporous anodized alumina

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Self-organized porous anodic alumina (PAA) nanostructures have attracted considerable attention in both scientific and commercial fields as an indispensable part of nanotechnology. Porous anodic alumina films provide templates for growing one dimensional nanostructures such as nano-tubes and nano-wires of suitable material [I]. Porous anodic alumina with parallel nano-pores is also interesting for its optical properties as an homogeneous material (with an equivalent refractive index) [ii] or as a 2D-photonic crystal [iii]. Aluminium porous anodization is usually performed in acid solutions, such as sulphuric, oxalic and phosphoric acids [iv]. When the anodization voltage lies with a small range, the channels can self-organize into domains of hexagonally closed-packed (HCP) array. Typical dimensions of this naturally ordered domains are in the microns range. To achieve a highly ordered pore arrangement over larger areas, many pre-treatments or pre-patterning techniques have been studied. Masuda and Fukuda [v] first proposed a two-step anodization. Subsequently Masuda and co-workers also presented a mechanical pre-texturing process [vi]. Recently, some modified pre-texturing methods, such as pre-patterning on aluminium by optical diffraction grating, atomic force microscope, focused-ion beam polystyrene beads, have been also attempted.

In this work a pre-patterning method based on direct writing laser (DWL) lithography process is presented. A film of positive photoresist is deposited by spin-coating on the aluminium substrate and a hexagonally closed packed array layout is then impressed. By tuning the pattern parameters, the 2D lattice impressed on the resist can exactly match the constraints deriving from the anodization conditions, leading to a more regular ordered pattern of pores. In particular, the dimensions of the pores obtained are compatible with PAA behaving as a PBG structure in the infrared range. Also, in principle any pore pattern can be reproduced on the resist by lithography, for instance allowing the introduction of defects into the 2D lattices. By subsequent etching process, shallow etching pits are produced on aluminium surface. These pits induce the pore initiation during the anodization and led to an ideally ordered pore arrangement within the stamped area. The final anodization step demonstrates the ordering capability of such pre-patterning technique.

Our DWL system consists of a stationary focused writing laser beam (266nm solid state laser), and a high-precision translation stage (6” area, 8nm resolution). A 350nm layer of UV6 photoresist is spun onto a polished Al substrate at (50s at 6000rpm) and softbaked (60s at 130°C). By DWL technique HCP arrays are exposed on an area of 20x50\(\mu\)m\(^2\) with pores diameter of \(d=300\)nm and interspace distance of \(s=2d\). After post exposure bake (90s at 132.5°C) and development (45s in TMAH 2.38%), the array pattern on resist (figure 1) is transferred on the Al by wet etching in a chrome etchant (Shipley Chrome Etch18). The obtained hollows well fit the typical concave holes of the anodization process (figure 2).

In order to demonstrate the effectiveness of the process, an anodization step has been performed with phosphoric acid 0,5Mol in ethanol (30’ at -10°C at 195V); figure 3 shows the preliminary SEM images of the achieved large ordered area (tens of microns) and the transition with the unpatterned one.

The developed process demonstrates the capability of pre-patterning large areas of aluminium forcing the order and protecting alumina 2D lattice structures from the influence of the grain boundaries of the aluminium substrate. In such way it is possible to obtain highly ordered nanoporous anodized alumina.
Figure 1. SEM image of the resist mask wrote with DWL technique.

Figure 2. AFM images of DWL pre-patterned Al after wet etching.

Figure 3. SEM images of pre-patterned area (left) and transition to unpatterned one (right).


