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Selective electric field assisted dissolution as a technique for micro and nano structuring of metal thin films

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A technique for patterning compact thin metal layers is presented. The technique is based on a successive application of well known, cost-effective, and simple methods of glass poling and electric field assisted dissolution. A microstructure from the patterned anode was copied onto a thin silver layer on a glass substrate. It is demonstrated that electric field assisted dissolution can be used for selective dissolution of compact metal layers. Nanostructuring of compact metal layers is interesting as it can be used in the production of metamaterials, metasurfaces, and optical circuits. The proposed two-step technique does not involve expensive equipment, and the duration of the structuring process is independent of the size of the required structured surface. *Published by AIP Publishing.* https://doi.org/10.1063/1.5042037

Micro- and nano-structured conductive layers are fabricated using engraving techniques, photolithography, X-ray lithography, or electron beam lithography, depending on the required scale of the structure.[1–4] Some of these techniques involve expensive equipment. Moreover, the structuring process may be time-consuming, especially in the case when a large area with a high resolution structure is demanded. In this paper, we demonstrate an alternative technique for conductive layer patterning, based on the processes of thermal glass poling[5] and electric field assisted dissolution (EFAD) of metal.[6–8]

In the process of glass poling, an internal electric field forms in the glass upon application of an external electric field and increased temperature.[9] Alkali ions contained in the glass are driven by an external electric field and drift towards the cathode. Na^+ ions, having the highest mobility, dominantly contribute to the ionic current. The mobility of ions increases with the rise in temperature. As a result, the region below the cathode is depleted by ions and the internal electric field is formed due to the ion redistribution. The region remains depleted even after turning off the external electric field and cooling. It is possible to obtain a selective depletion in the glass structure by applying a patterned anode: the depletion occurs only in the regions beneath the contacts with the electrode. Since the depleted regions have a lower molar volume, poling with the patterned anode also results in the relief structuring of the glass surface itself.[5,10]

Similar to glass poling, the EFAD process involves the application of an external electric field and increased temperature. Upon application of the external electric field to a glass containing metal nanoparticles, the electrons from metal atoms embedded in the glass matrix are stripped away and metal ions start drifting, similar to alkali ions.[7] The application of a patterned anode to a metal island film (MIF)[11] results in the patterning of the film: metal nanoparticles beneath the anode contacts are dissolved, but elsewhere they remain on the glass surface. In fact, EFAD and glass poling in this case take place simultaneously. Besides the process of metal nanoparticle dissolving, the glass surface region beneath the anode depletes with Na^+ ions, resulting in a patterned surface if a structured anode is applied.[12]

EFAD enables the dissolution of metal nanoparticles embedded in a glass matrix, located on a glass surface as a MIF, embedded in a thin dielectric film,[13] or from a compact metal thin film.[14] However, all the attempts to make a selective EFAD of a compact metal thin film thus far were unsuccessful. The problem is that even if the contact with the anode is realized in only one point, the whole metal layer sets at the same potential and the dissolution unselectively starts throughout the whole layer. At this point, it is important to highlight that compact metal layers are of special interest for nano- and micro-structuring, as they could be used for metamaterials, metasurfaces, and optical circuits.

We propose an alternative approach for obtaining structured metal layers involving glass poling and EFAD. The scheme of the proposed process is presented in Fig. 1. The first step is glass poling with a patterned anode [Fig. 1(a)]. In the second step, the glass surface that was facing the anode in the first step is coated with a metal layer [Fig. 1(b)]. The final step is EFAD of the metal layer, applying non-patterned electrodes [Fig. 1(c)]. A structured metal thin film is obtained as a result of the completed process [Fig. 1(d)].

The depleted glass regions obtained by poling with a patterned electrode (first step) behave as insulation regions, and therefore, they prevent charge transfer. Although these regions can be partially refilled by hydrogenated species,[5] the mobility of these species is several orders of magnitudes lower than that of alkali cations and the depleted regions do not recover conductivity. As a consequence, metal ions from the metal layer right above the depleted region cannot pass into the glass matrix when potential is applied (third step). As a result, these parts of the layer remain complete, i.e., conductive, while the layer parts right above the non-depleted regions (i.e., the regions that were not in contact with the patterned electrode during poling) dissolve.

A standard 1 mm thick microscope slide glass is used in the experiment as the sample. The patterned anodic electrode surface had different parts: (i) a 500 nm thick chromium

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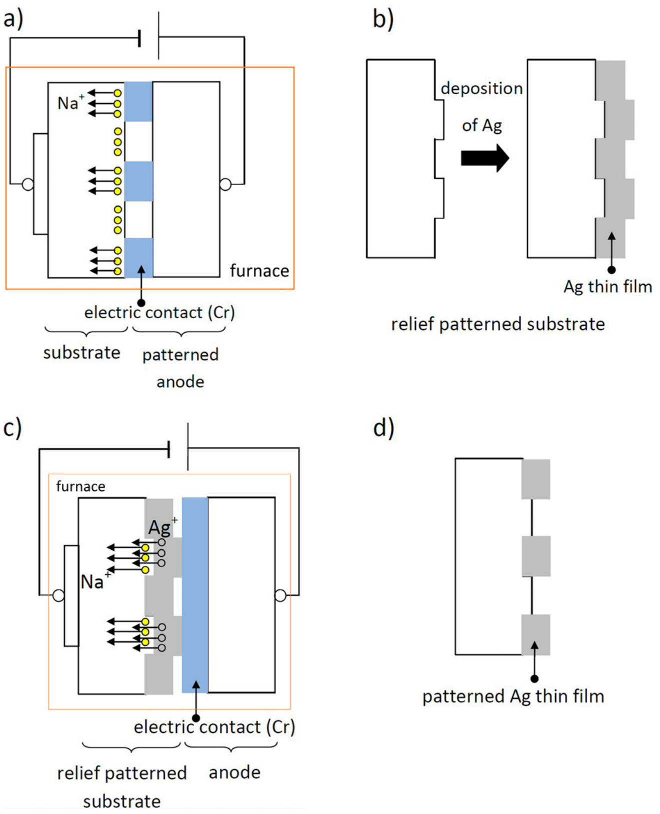

FIG. 1. Schematic presentation of the selective EFAD for structuring the metal layer: (a) poling of the glass substrate with a patterned anode. (b) Coating of the obtained relief structure with a thin metal film. (c) Application of a non-patterned anode to the metal film and selective dissolution of the film. (d) The final structured Ag thin film—the direct copy of the anode pattern in the metal layer.

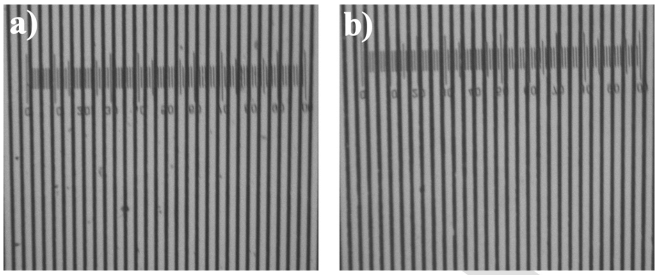

FIG. 2. Optical microscopy images of the (a) patterned anode and its (b) copy in the metal layer of the sample. The distance between lines on the rule is 10 μm.

layer, (ii) a part of the Cr layer etched into a pattern of 25 μm wide chromium stripes separated by 10 μm wide and 500 nm deep grooves having bare glass bottoms, and (iii) an uncoated part-bare BK7 substrate. A smooth aluminum plate was used as the cathode. Poling was performed in air at 200 °C, with an applied voltage of 900 V, for 2 h. After poling, a 70 nm thick silver layer was deposited onto the sample surface that was facing the anode during poling. Ag was deposited by electron beam evaporation onto a microscope slide without substrate pre-heating. After this, the sample was once more placed between the electrodes for EFAD. This time the anode was a non-patterned smooth chromium layer on BK7 [Fig. 1(c)]. The sample was treated in air at 150 °C, with an applied voltage of 300 V for 2 h. As a result of the selective EFAD process, a direct copy of the anode pattern was obtained in the conductive silver layer. Optical microscopy images of the patterned anode and the sample are presented in Fig. 2. On this scale, it is not possible to distinguish between the original pattern and the pattern obtained by selective EFAD of the deposited compact metal layer.

The bare substrate-like zone obtained on the sample is denoted as zone A. It corresponds to the bare BK7 substrate on the anode used in the first step. Figure 3(a) presents transmittance (T) measurements of zone A together with the data of an untreated microscopic glass. The part where the silver-like layer remained on the substrate is denoted as zone B. It corresponds to the part completely covered with chromium on the first anode. Figure 3(b) presents transmittance measurements of zone B together with the simulated transmittance of a silver layer, using optical constants from WVASE software. The correspondence of bare substrate data and zone A [Fig. 3(a)] and silver layer simulated data and zone B (presenting a typical metal behavior: low transmittance throughout visible and near-infrared part of the spectrum) [Fig. 3(b)] confirms that the anode pattern was copied onto a compact silver layer, resulting in compact metal and dielectric parts. Note that the non-compact metal film would show increased transmittance in the infrared part of the spectra since absorption would be primarily related to the surface plasmon resonance of isolated particles, as previously reported.[11]

In order to get a better comparison of the patterned anode and its copy (Fig. 2), the samples were subject to SEM. It was found that Cr stripes of the anode are 10 μm wide with 25 μm separations and Ag stripes are 13 μm wide with 22 μm separations. SEM images (Fig. 4) illustrate the resemblance of the patterned anode [Fig. 4(a)] and its copy in the metal layer [Fig. 4(b)] on a smaller scale than the optical microscopy ones (Fig. 2). Here, it is possible to clearly distinguish the differences between the two: the edges of Cr stripes are better defined than the Ag ones. By analyzing Ag

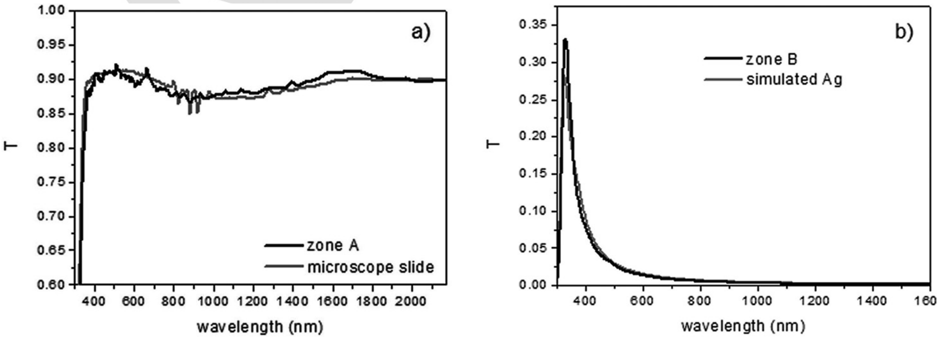

FIG. 3. Zone A (a) and zone B (b) transmittance measurements (black), together with the experimental data of the bare substrate (a) and the simulated transmittance of a 55 nm silver layer (b) (gray).

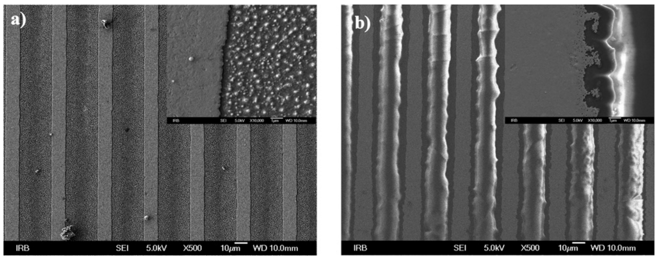

FIG. 4. SEM micrographs of the patterned anode (a) and its copy in the Ag layer (b). Metal stripes are uniformly light grey.

stripe edges (inset), it is possible to notice holes in the metal layer positioned within approx. 1.5 μm from the edge. The shapes and the holes of the edge irregularities, together with the holes on the stripe surface, suggest that the Ag dissolution process was not completed. Having in mind that the width of the area containing holes on the stripes surface is approx. 3 μm (1.5 μm from each edge) and that Ag stripes are approx. 3 μm wider than Cr stripes, it is possible to conclude that prolonged time of EFAD would result in completely dissolved Ag in edge areas containing holes, resulting in better defined stripes and a copy with a better resolution.

The sample was investigated by atomic force microscopy (AFM) in order to check the profile of the final structure. The profile of the transition between the stripes is presented in Fig. 5. The lower part (zone A) corresponds to the bare substrate bottom obtained after selective dissolution of silver. The higher part (zone B) corresponds to the preserved compact metal stripes. The step height is around 45 nm, which is less than the thickness of the deposited silver layer (70 nm). One has to keep in mind that the coating was deposited onto the surface relief with pattern consisting of glass grooves and glass tops. The depleted regions beneath the grooves of the poled glass surface were blocking EFAD, and so, the silver layer above the glass grooves was preserved. In this way, the metal stripes of the final surface relief pattern are formed at the positions of the former grooves. In other words, the metal layer is partially buried under the level of the final sample glass grooves. It has to be mentioned that as glass poling is taking place simultaneously with the EFAD process, it is to be expected that the glass tops obtained by poling were partially decreased during the subsequent EFAD. The result of all the applied processes is that the final relief corresponds to the one schematically presented in Fig. 1(d), having 45 nm steps (Fig. 5).

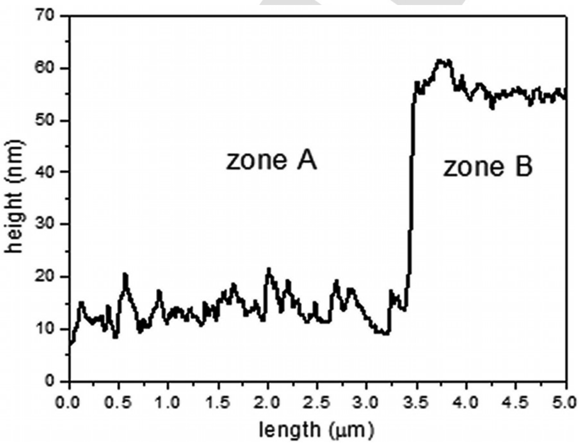

FIG. 5. AFM profile of the transition between the final pattern stripes: zone A corresponds to the bare substrate bottom (where silver was dissolved) and zone B to the compact silver layer.

The steepness of the ramp between the bare substrate and the silver stripe top is around 50%. This steepness depends on the ions' lateral drift, limiting the resolution[5] that can be achieved by the proposed two-step process. Namely, the occurrence of the transition region around the edges of anode contacts due to the lateral drift of ions can be expected. Although lateral drifts cannot be avoided, it can be moderately controlled by the process conditions (potential, temperature, and duration of the process), the ions' concentration, and their kind. The lateral resolution of the fabricated structure will depend on the surface relief and alkali ion distribution profile upon glass poling and EFAD of the metal layer. The resolution limit is yet to be determined through optimization of the mentioned process conditions. We expect that this technique is suitable to obtain structures of all the metals to which EFAD can be applied, such as noble[6–8,11,13] and transition metals.[14]

In this work, it is demonstrated that the combination of glass poling and EFAD enables selective dissolution on conductive metal layers and that it can be used as a simple, alternative method for micro- and nano-structuring of compact metal films. The main strength of the demonstrated technique is that it does not require a complex setup with expensive devices. Moreover, glass poling and EFAD processes use the same setup. Once a patterned anode for the first step is provided, a furnace together with a high voltage power supply and a device for metallization are sufficient. A properly prepared patterned anode can be used tens of times.[15] It must be emphasized that the processing time is independent of the size of the required patterned surface, in contrast to other structuring techniques. Indeed, the structuring process takes place simultaneously over the whole sample where the electric field is applied and the structured surface area is only limited by the electrode size. We expect that the use of EFAD as a selective process for structuring of metal thin films can contribute to broadening the production and general use of devices based on metal micro- and nanostructures.

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