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Spatially-microstructured topology of chalcogenide glasses by a combination of electrothermal process and selective etching for functional infrared media

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Abstract: Chalcogenide glasses exhibit a wide transparency domain spanning from near infrared (IR) to mid-IR and thus, have become highly attractive optical materials in a range of applications. Controlling the topology of these glasses can be seen as a key aspect for the design of optical elements such as gratings, metasurfaces, waveguides, and other diverse refractive and diffractive optical components. Here, we demonstrate the structuring of large, millimeter square areas that have been structured at the micrometer scale employing an easy two-step process, incorporating a micro-poling step followed by immersion in an amine solvent. Ge-Sb-S-Na glasses have been investigated, and the influence of the sulphur and sodium content on the pre- and post-poling material dissolution response has been discussed. Three compositions of varying sulphur and sodium content were selected to study the influence of thermal poling using either a homogeneous or a structured electrode. It was found that either a large difference in dissolution rates of poled and unmodified regions or a large poled layer thickness leads to the generation of significant topological contrast. The origin of the poled region's selective etching has been explained on the basis of a poling-induced density decrease. Finally, it was demonstrated that when the targeted resolution is micrometric, this rather easy process could be employed as an alternative to classical lithography techniques.

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1. Introduction

The control of a material's surface topology is a key aspect of its design and potential use in optical applications. In particular, a wavelength length-scale (nano- or micrometer length-scale) control is necessary to produce diffractive optical elements, [1] antireflective surfaces, [2] waveguides, [3] plasmonic surfaces [4] or metasurfaces. [5,6] Multiple processes have been shown to be suitable to structure surfaces, including lithographic techniques, which are limited to the wavelength of the tool. These methods, inherited from the microelectronic domain are among the most common and have been recently applied to low loss hybrid (diffractive/refractive) optical elements and metastructures based on chalcogenide phase change alloys. [7–9] Lithography is a cumbersome method employing multi-step processes including deposition and patterning of a photosensitive sacrificial layer, which subsequently allows the selective destruction of the material of interest's surface to realize the target structure. In each case, material-specific protocols are required, while the determination of such

45 a 'recipe' is time consuming, and requires compatibility between resist, etchant, and writing
46 wavelengths for each desired composition and element's design.

47 In the 1990's, nanoimprint lithographic techniques were developed, [10] allowing generation
48 of low-cost, sub-25 nm structures over large areas ($15 \times 18 \text{ mm}^2$). These techniques differ from
49 classical lithography since a mold is employed to directly structure the desired material
50 (generally polymeric resins). The mold, pressed against the sample (under load at temperature),
51 generates a thickness contrast, and the compressed zones are preferentially etched or displaced
52 for subsequent etching using either a wet or dry reactive ion etch step. Employing this
53 technique, Kohoutek *et al.* managed to periodically structure the surface of an arsenic selenium
54 chalcogenide glass resulting in an effective diffraction grating. [11] Here, the authors had to
55 heat up their system to 5 °C below the glass' transition temperature (T_g) (i.e., 225 °C) in order
56 to imprint the pattern. However, for glasses exhibiting higher T_g , the required pressure and
57 temperature to imprint the patterns increase and can cause several problems, including higher
58 processing costs, difficulty to realize the process over large areas, material volatilization, and
59 reduced life expectancy of the molds. [12–14] To circumvent this difficulty, Takagi *et al.*
60 applied an electric field and used their mold as an anode. [12] While the applied voltage in this
61 case was only of about a hundred of volts, and the pressure was one of the driving force, the
62 nanoimprint process employed by the authors is similar to thermal micro-poling. The thermal
63 poling method consists of heating an amorphous material below its T_g while applying a strong
64 electric field (several kilovolts per millimeter) with a structured electrode. [15] The sample is
65 then brought back to room temperature before removal of the electric field. Brunkov *et al.* and
66 Lipovskii *et al.* demonstrated a control of silicate and nano-composite glasses' surface
67 topologies using this process. [14,16,17] However, the reliefs obtained are only (typically) tens
68 of nanometers high which is insufficient to consider the fabrication of efficient gratings for
69 instance. Ikutame *et al.* suggested augmenting the poling treatment with one inducing chemical
70 attack. Here, they obtained relief heights higher with subsequent chemical attack than with
71 poling alone. [18]

72 The first studies regarding chemical attacks of poled glasses date back to the early days of
73 thermal poling. In 1974, Carlson noticed that the poled surface (hence depleted from its alkali
74 cations) of a silicate glass was shown to be more resistant to molten alkali salts attack than the
75 untreated surface. [19] Others relied on the difference in etching rate difference of the poled
76 and unpoled zones to measure the poled thickness in fused silica and silicate glasses. [20,21] It
77 is only more recently that authors started focusing on post-poling chemical attack in the optic
78 of realizing devices such as diffraction gratings employing structured electrodes. [22] Poled
79 silicate glasses are selectively dissolved by acidic attack, [23,24] but authors also demonstrated
80 a dry etching route by plasma or reactive ion etching where preferential removal rates differ
81 between poled and unpoled regions. [24,25] These two possibilities allow one to preferentially
82 etch either the unpoled or the poled zones. It follows that the electrode's pattern can be either
83 directly transferred on the glass' surface or negatively transferred. The step's heights obtained
84 by these techniques on the (to-date) studied oxide glasses' family (silicate glasses) are measured
85 to be between 0.5 and 1.2 μm .

86 Dissolution of chalcogenide glasses (ChGs) has been the subject of many studies since the
87 1980's. Numerous works focus on thin films synthesis by dissolution of bulk glasses followed
88 by spin coating. [26–29] It was demonstrated in the last decade that sulfur glasses were
89 effectively dissolved in amine solvents such as ethylene diamine (EDA). Furthermore, our
90 previous works on G-Sb-S-Na glasses have shown the efficiency of micro-poling on these
91 glassy compositions. Indeed, after the treatment, the sodium repartition, the structural
92 modifications, the index variations, and the second harmonic optical response follow the pattern
93 of the structured electrode. [30–32] In the present work, our aim has been to transfer the know-
94 how realized in post-poled selective dissolution of silicate [22–24] to this chalcogenide glass

95 system while identifying and quantifying the key parameters that can control the topologies of
96 the resulting surfaces.
97

98 2. Experimental method

99 2.1 Glass synthesis

100 Glasses were prepared using high purity elemental Ge, Sb, and S (Alfa Aesar 99.999%).
101 Anhydrous sodium sulfide (Na_2S – purity unspecified) was used to incorporate sodium in the
102 glass matrix. The nominal composition of the glasses can be written as: $(100-x)(\text{Ge}_{25-y}\text{Sb}_{10}\text{S}_{65+y})$
103 $+ x\text{Na}$ with $x = 0, 2, 5.5$ and $y = 0, 2.5, 5, 7.5$. Two series of compositions were selected. (1)
104 The first one with varying S to Ge ratio (i.e., increasing amount of sulphur) and fixed sodium
105 content: A- Na_2 , B- Na_2 , C- Na_2 , D- Na_2 where $x = 2$ and $y = 0, 2.5, 5, 7.5$, respectively. (2) The
106 second one, with varying sodium content and fixed S to Ge ratio: C- Na_0 , C- Na_2 , C- $\text{Na}_{5.5}$ where
107 $x = 0, 2, 5.5$, and $y = 5$, respectively. These different parameters are summarized in the Table 1.
108

109 **Table 1. The S/Ge ratio, the sodium content, the densities, and the glass transition temperatures of the
synthesized glasses as well as the name they are referred to.**

Sample	S/Ge ratio	Na content (at.%)	Density (g/cm^3)	T_g ($^\circ\text{C}$)
A- Na_2	2.6	2	3.163 ± 0.006	313 ± 2
B- Na_2	3.0	2	3.099 ± 0.006	270 ± 2
C- Na_2	3.5	2	3.057 ± 0.012	241 ± 2
D- Na_2	4.1	2	2.982 ± 0.006	-
C- Na_0	3.5	0	3.06 ± 0.01	274 ± 2
C- $\text{Na}_{5.5}$	3.5	5.5	3.05 ± 0.01	250 ± 5

110

111 Raw materials for 15 g batches were weighed out in a glove box under nitrogen atmosphere
112 and inserted in a quartz ampule. The system was put under vacuum (10^{-2} mbar) and sealed using
113 an oxygen-methane torch. The sample was placed in a rocking furnace heated at a rate of
114 $1^\circ\text{C}/\text{min}$ up to 850°C for 12 h. After this time period, rocking was stopped, and the
115 temperature decreased to 750°C before quenching in water. The sample was then placed into
116 an annealing furnace for 6 h at 40°C below its glass transition temperature (T_g). Finally, glasses
117 were cut and polished to obtain 1 mm thick disks of 1 cm diameter. The glass transition
118 temperatures were determined by differential scanning calorimetry (Netzsch DSC 204 F1
119 Phoenix) using aluminum pans and a heating rate of $10^\circ\text{C}/\text{min}$ up to 550°C . Glass densities
120 were determined using the Archimedes method by immersing the samples in diethyl phthalate
121 at room temperature. The measured T_g and densities are reported in the Table 1.

122 2.2 Vibrational spectroscopy

123 Raman spectroscopy to assess structural changes was carried out and two-dimensional spatial
124 Raman intensity maps were acquired using a LabRAM HR Evolution (Horiba) spectrometer
125 with a laser source at 785 nm and a $100\times$ (N.A.= 0.9) objective with a one micron resolution.

126 2.3 Thermal poling

127 Thermal poling was performed under flowing nitrogen. The 1 cm diameter glass slides were
128 heated up to 170°C at a $15^\circ\text{C}/\text{min}$ rate (temperature fixed for all samples). A DC voltage of
129 3 kV was then applied (at a 320 V/min rate) by a $5 \times 5 \text{ mm}^2$ electrode placed at the center of
130 the glass disk and left on for 30 min. The samples were then brought back to room temperature
131 before removal of the DC field. Two types of anodes were employed in this work. They
132 consisted of a 100 nm platinum film deposited on a glass slide ($5 \times 5 \times 1 \text{ mm}^3$) and were either
133 (1) left as such (homogeneous electrodes that are everywhere conductive) or (2)
134 lithographically structured to form ($40 \times 40 \mu\text{m}^2$) non-conductive squared patterns delimited
135 by $10 \mu\text{m}$ large conductive platinum grid. On the cathode side, a piece of silicon wafer was

136 used, and a microscope coverslip was placed between the silicon and the sample to preserve
137 the optical quality of the sample on this side.

138 2.4 Dissolution

139 Throughout this work, the solvent where the dissolution was carried out was EDA mixed at
140 15 volume % in dimethyl sulfoxide (DMSO). The dissolution of samples (i) prior to poling, (ii)
141 after a homogenous poling, and (iii) after a structured poling were studied. For these three
142 situations, different methods had to be developed to follow the dissolution rate. Specifically,
143 (i) In order to track the dissolution rate of virgin glasses, we chose to look at the dissolved mass
144 of the different samples with respect to the immersed time in the solvent. The one-centimeter
145 square and 1 mm thick glass samples were weighted out with a 0.01 mg precision scale. They
146 were immersed in the solvent and placed in an ultrasound bath for a given time. They were then
147 rinsed with distilled water and dried before being weighted again and placed back to the
148 ultrasound bath. (ii) To track the dissolution of the poled layer, weighting the samples is not
149 adapted anymore as this layer is only several micrometer thick. Drawing on the methodology
150 adopted by Reduto *et al.*, [23] we chose to protect a part of the surface with a metallic (gold)
151 thin film (Q300TD, Quorum Technologies) and to measure the step height between the metallic
152 film (not affected by the solvent) and the poled glass' surface with respect to the immersed time
153 in the solvent. These measurements were also performed on virgin (non-poled) gold-protected
154 samples for reference. The height step was measured with a Bruker's Dektak 6M stylus profiler.
155 The measured height corresponded to the mean value of at least four measurements at each
156 immersion time. Unlike the dissolution of the virgin glasses, the ultrasound bath was not used
157 here to prevent the deterioration of the gold thin film. (iii) The samples poled with the structured
158 electrode were immersed in the solvent in an ultrasound bath for different times. They were
159 rinsed with distilled water, and dried. The topological profiles around the imprinted structures
160 were then measured by atomic force microscopy (AFM) on an AFM Dimensions Icon Bruker
161 instrument in PF-QNM mode. The topographic images were acquired using a ZYGO 6300
162 white-light interferometer.

163 3. Results

164 3.1 Dissolution of the virgin glasses

165 We first discuss the effect of the glasses' compositions on the dissolution rate of the samples
166 prior to poling. In Fig. 1 are presented the dissolved masses with respect to the immersed time
167 in the solvent. Fig. 1a illustrates the effect of varying sulphur content (for a fixed sodium
168 content) while in Fig. 1b, the effect of the sodium content is investigated. On the first hand,
169 from Fig. 1a, one can clearly observe that the higher the sulphur content is, the higher the
170 dissolution rate is. The glass D-Na₂ is dissolved about four times faster than the stoichiometric
171 glass (A-Na₂). On the other hand, the effect of the sodium content (Fig. 1b) is less pronounced.
172 Taking into account the error bars, we can consider that, in the sodium concentration range
173 evaluated in this study, the effect on the dissolution rate is negligible.

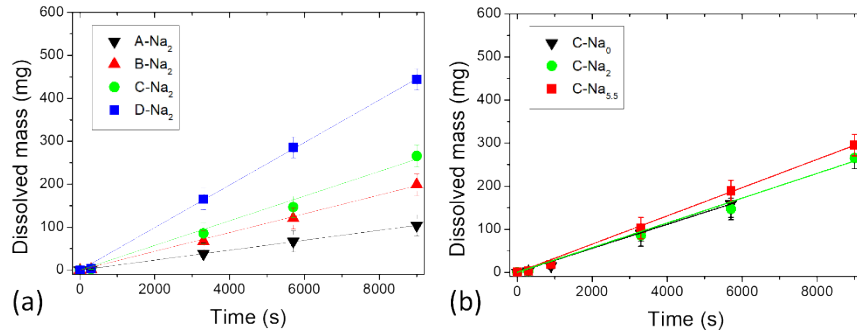


Fig. 1. Virgin glasses' dissolved mass with respect to time as a function of (a) the S/Ge ratio and of (b) the sodium content for 1 cm² area samples. The error was estimated to 25 mg to account for the experimental error coming from the weighting and the sample's area estimation, the lines correspond to linear regressions.

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179 3.2 Dissolution of homogeneously poled glasses

180 To highlight the effect of poling and the resulting imparted change in the glass on the
 181 dissolution rate, the adopted methodology, as described in the experimental section, was to
 182 protect a part of the sample with a gold film and to measure the step height between this film
 183 and the glass as a function of the immersed time. Three compositions possessing two different
 184 S/Ge ratio and two different sodium contents – namely A-Na₂, C-Na₂ and C-Na_{5.5} – were
 185 selected for evaluation. The results of this set of experiments are presented in Fig. 2. One can
 186 first notice a linear increase in the step height for the virgin glasses that enables the dissolution
 187 rate (v_{UP}) of virgin-like (unpoled) glass regions to be estimated. These values are gathered in
 188 the Table 2. From this table, it appears that C-Na_{5.5} has the fastest dissolution rate, followed by
 189 C-Na₂ and A-Na₂. These observations are consistent with the dissolved mass evolutions seen
 190 in Fig. 1. In the poled samples, one can clearly identify two dissolution rates. First, the glass
 191 dissolves quicker than the virgin glass, and after a given time, the dissolution rate reaches that
 192 of the virgin glass. Here, the slope inflection point corresponds to the thickness of the poled
 193 layer, L_{poled} . For each sample, its value as well as the dissolution rate of the poled region (v_p)
 194 are reported in the Table 2.

195 In order to generate structures with a maximum contrast, it is crucial to consider Δh_{max} , the
 196 maximum gap between the poled and the unpoled zones. This parameter is illustrated by the
 197 schematic in Fig. 2d. It is formulated as Eq. (1):

$$\begin{aligned}
 \Delta h_{max} &= L_{poled} - L_1 = L_{poled} - t_1 v_{UP} = L_{poled} - L_{poled} \frac{v_{UP}}{v_p} \\
 &= L_{poled} \left(1 - \frac{v_{UP}}{v_p} \right) \#(1)
 \end{aligned}$$

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199 From Eq.(1) and Fig. 2d, it follows that there are two methods to maximize Δh_{max} : having a
 200 sample exhibiting either a thick poled layer, or a large difference in dissolution rates of the
 201 poled and unpoled regions. In the selected compositions, two good candidates stand out: C-Na₂
 202 with its eight microns-thick poled layer and C-Na_{5.5} with a significant difference in dissolution
 203 rates of the poled and unpoled regions (lowest ratio v_{UP}/v_p , see Table 2).

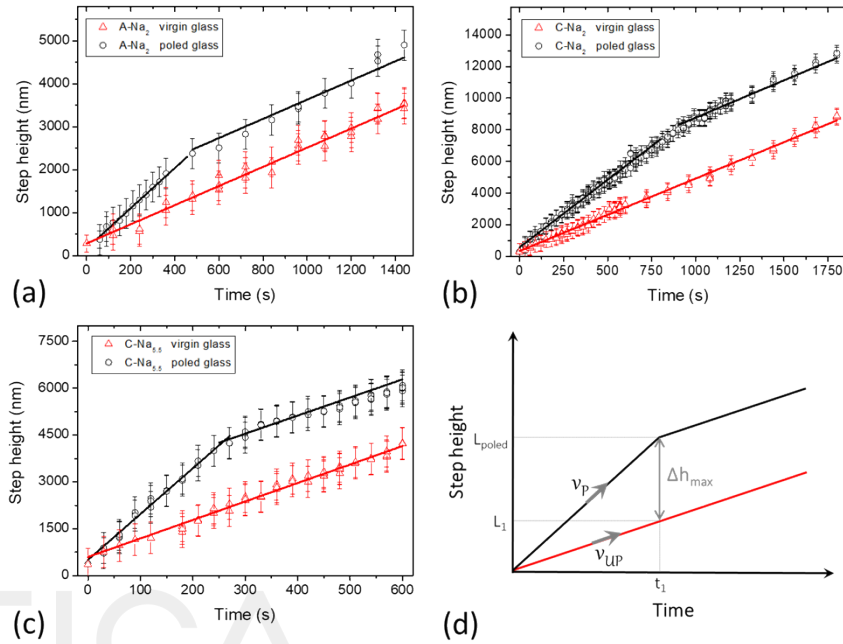


Fig. 2. Step heights measured between the protective gold film and the glass' surface as a function of the immersion time in the solvent for the compositions (a) A-Na₂, (b) C-Na₂, and (c) C-Na_{5.5}. The dots and lines correspond to the measured points and linear regressions, respectively. The error is mainly linked to the use of the profilometer and was estimated to be between 300 and 500 nm. The red lines and points correspond to the virgin glasses while the black ones correspond to the homogeneously poled samples. A schematic (d) illustrates the key parameters namely: L_{poled} , the poled layer thickness, v_p and v_{UP} the poled and unpoled dissolution speeds, and Δh_{max} , the maximum height that can be reached between the poled and the unpoled zones.

Table 2. Key parameters extracted from Fig. 2: poled zone's thickness, poled and unpoled regions' dissolution speeds, and their ratio as well as the theoretical maximal height that can be reached for each sample calculated from Eq. (1).

Sample	L_{poled} (μm)	v_p (nm/s)	v_{UP} (nm/s)	v_{UP} / v_p	Δh_{max} (μm)
A-Na ₂	2.4 ± 0.3	4.7 ± 0.5	2.2 ± 0.2	0.47	1.3 ± 0.2
C-Na ₂	8.0 ± 0.8	8.5 ± 0.9	4.7 ± 0.5	0.55	3.6 ± 0.4
C-Na _{5.5}	4.3 ± 0.4	14.7 ± 1.5	5.8 ± 0.6	0.39	2.6 ± 0.3

3.3 Dissolution of the micro-poled glasses

In this section, we no longer use a homogenous, two dimensional conductive electrode but an electrode that has been structured such that it allows for the micro-scale control of the poling process and opens the way for the design of surfaces for specific applications such as gratings. [22,24] As shown in prior work on this particular glassy system, the size and shape of the electrode influences the spatial extent of the electric field that serves to cause migration of the charged alkali ion (here sodium). [30,32] An optical image of the structured electrode used in this study is presented in Fig. 3a. It consists of a ten micron wide metallic grid separated by $40 \times 40 \mu\text{m}^2$ squares that are not conductive. Here, we define two regions on the micro-poled sample: the region in contact (IC) with the metallic grid during the process and the region not in contact (NIC) with the grid.

228 Following the methodology adopted in our previous works, [31,33] the effect of micro-poling
229 (prior to any dissolution) on the glass' structure can be readily investigated by Raman
230 microscopy. These results are presented for the C-Na_{5.5} sample throughout Fig. 3. The Raman
231 spectra extracted from the NIC and IC with the grid regions and are presented in the top part of
232 Fig. 3b. Since only slight differences between these two spectra can be observed, the Raman
233 difference spectrum (IC minus NIC) is also presented in Fig. 3b. The spatial evolution of the
234 Raman response is illustrated by the cartographies of the five bands selected on the Raman
235 difference spectrum.

236 In our previous work, a complete attribution of these bands is presented relying mainly on the
237 works of Ward, [34] Lucovsky *et al.* [35] and Koudelka *et al.* [36] Specifically, in these glasses,
238 antimony and sulphur form SbS_{3/2} pyramids, while germanium is organized as GeS_{4/2}
239 tetrahedra. In glasses without sodium, the Sb-S stretching modes appear at 302 cm⁻¹ [band (ii)].
240 When sodium is added, they shift to lower wavenumbers [band (i)]. The GeS_{4/2} tetrahedra are
241 mainly organized as corner sharing (CS) configuration [band (iii)] but also in edge sharing (ES)
242 configuration [band (iv)]. Sodium-rich glasses present more ES units than sodium poor glasses,
243 the opposite goes for CS units. As for the band (v), it is attributed to S-S homopolar bonds in
244 S_n chains or S₈ rings.

245 In the present work, similar patterns are observed for all Raman intensity maps. In particular,
246 sodium-rich glassy structures exhibit bands such as (i) and (iv) which are negative in the IC
247 zones and positive in the NIC regions. The opposite behavior is seen for the sodium-poor glassy
248 structures related bands such as bands (ii) and (iii). This conclusive variation in network
249 configuration confirms the effectiveness of the micro-poling process that results in the micro-
250 scale control of the structural variations as well as the observed sodium content distribution
251 within that network.

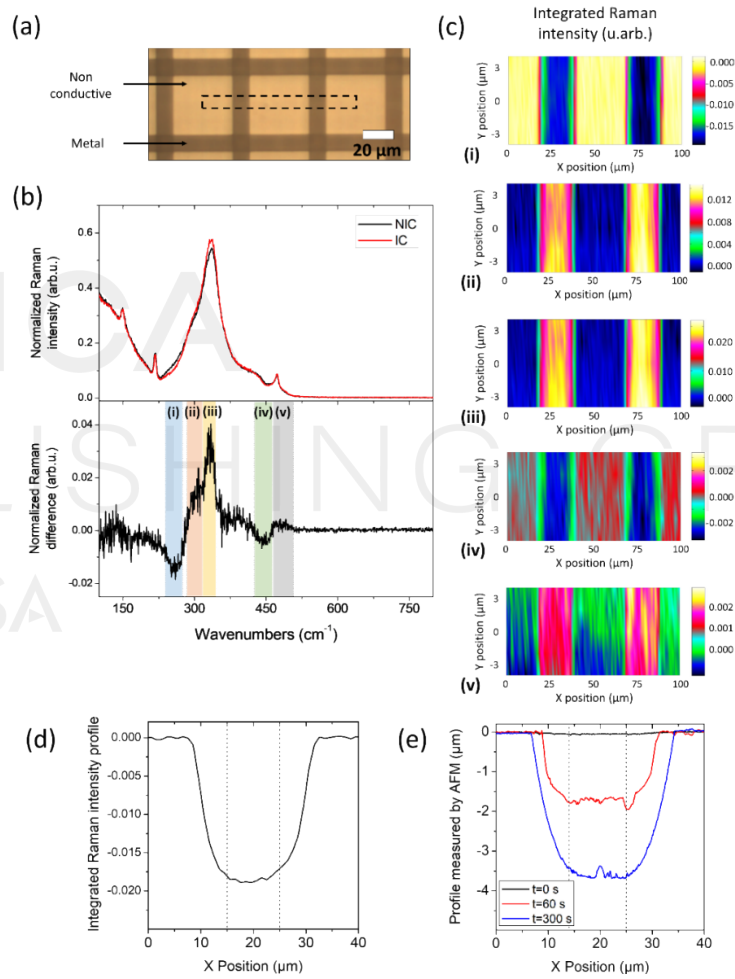
252 The spatial intensity profile of the band (i) is shown in Fig. 3d. On this graph, the region
253 between the dotted lines corresponds to the region IC defined by the metallic grid. As
254 previously stated, this band is negative in this region but one can also notice a gradient in the
255 intensity profile. The structural modifications are thus not only effective where the metallic
256 electrode is in contact with the glass surface but they also extend to adjacent regions to
257 about five microns on each sides of the grid. In other words, there is not a perfect overlap
258 between the IC and poled zones as well as between the NIC and unpoled regions: the poled
259 zone extends beyond the IC zone. This is the result of an in-plane poling similar to that observed
260 in other systems. [15,31,37,38] We have shown that it is possible to take advantage of this
261 gradient in our previous work where we specifically aimed to design flat micro lenses through
262 inducing a gradient in refractive index within this glassy system. [30]

263 Now that the microscale patterning of the structural variations generated by the micro-poling
264 is confirmed, we now focus on the dissolution behavior of this sample. The topology profiles
265 measured by AFM at different dissolution times are presented on the Fig. 3e. Immediately after
266 poling (at $t = 0$ s), the sample's surface is flat. After immersion in the solvent, the IC zone can
267 be seen to be selectively etched. This is consistent with the results from Fig. 2 where the poled
268 samples exhibited more rapid dissolution than the virgin glasses. After 60 s of immersion, the
269 glass surface forms a 1.7 μm high step; after 300 s, it reaches 3.7 μm . Comparing the AFM
270 profiles with the Raman intensity profile from Fig. 3d, it appears that the shape of the etched
271 structures reproduces exactly the structural modification gradient.

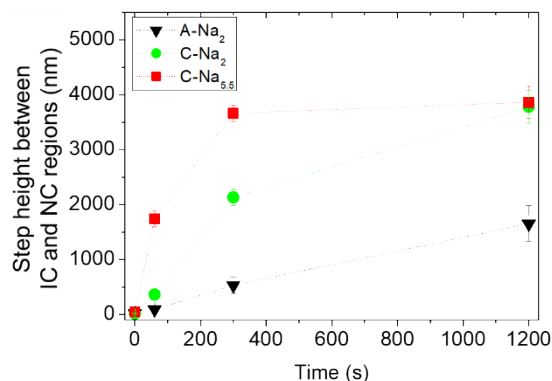
272 At longer dissolution times (at $t = 1200$ s), the structure's height reaches a plateau as shown in
273 Fig. 4. This demonstrates that after this time, the whole poled layer thickness of the C-Na_{5.5}
274 sample was dissolved, and no further contrast between IC and NIC zones can be achieved. On
275 this graph is also shown the maximal height measured by AFM as a function of the dissolution
276 times for the two other selected samples, namely A-Na₂ and C-Na₂. It appears that for short

277 dissolution times (under 300 s), the generated structures are rather small (about 500 nm) for the
 278 A-Na₂ sample, bigger for C-Na₂ (2.1 μm), and the biggest for C-Na_{5.5} (3.7 μm). If the later
 279 reached a plateau after 300 s, it is not the case of the other two samples. The step height
 280 continues increasing for C-Na₂ and A-Na₂, and respectively reaches 3.8 and 1.6 μm after
 281 1200 s.

282 As predicted, in order to generate large topological contrasts, two parameters must be taken
 283 into account: (a) a significant difference in dissolution speeds of poled and unpoled regions and
 284 (b) a thick poled layer. From Fig. 3, it appears that the difference in dissolution speeds plays a
 285 major role during short dissolution times (C-Na_{5.5} exhibits the biggest structures) while the
 286 thickness of the poled layer is a key parameter at longer dissolution times (C-Na₂ and C-Na_{5.5}
 287 exhibit similar structure heights after 1200 s).



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 289 Fig. 3. (a) Optical image of the electrode employed for micro-poling with conductive and non-
 290 conductive zones highlighted. (b) Normalized Raman spectra extracted from the regions of the
 291 poled C-Na_{5.5} glass that were in contact (IC) – in red – and non in contact (NIC) – in black –
 292 with the conductive zones of the electrode during the poling process and the Raman difference
 293 spectrum (spectrum IC minus NIC). (c) Spatial evolution of the selected bands from the
 294 Raman difference spectrum. (d) Intensity profile along the X position of the band (i)'s Raman
 295 intensity. (e) Topology of the sample measured by AFM in the same region upon dissolution
 296 for different times. The dotted lines in the two last graphs correspond to the metallic grid
 297 position during the poling treatment.



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Fig. 4: Height of the step measured between the region in contact (IC) with the metallic part of the electrode during micro-poling and the one non in contact (NC) for the selected micro-poled samples as a function of the dissolution time. The dotted lines are guides for the eye, the experimental error is estimated to be of 10 %.

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4. Discussion

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Throughout the present work, we have demonstrated that in the glassy Ge-Sb-S-Na system, micro-poling followed by immersion in an amine solvent yields a structured topology of these glasses. A topological contrast as large as about four microns was obtained and is at least four times bigger than anything obtained by this process on silicate glasses. [22–25] Here we discuss the different parameters associated with the origin of this selective etching to shine the light on the different levers that one can have access to in order to control these structures.

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Previous structural studies of this exact system [31,36] or related glassy systems [34,35] relying on Raman spectroscopy have shown that the higher the sulphur content, the more numerous the S-S homopolar bonds were. There are no S-S bonds in the stoichiometric glass (A-Na₂) since only one sulphur atom connects the different glass entities, forming SbS_{3/2} pyramids and GeS_{4/2} tetrahedra. [36] When sulphur is added, the interconnections between the different entities are made with more sulphur atoms. Sulphur atoms also form polymeric S_n chains as well as S₈ rings for high sulphur containing compositions.

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As mentioned earlier, chalcogenide thin film synthesis via spin coating of dissolved glass solution has been the object of many studies with the objective of fabricating new planar photonic components. Dissolution mechanisms of these glasses in amine solvent were therefore at the center of interest of some of these studies. [39,40] They revealed that S-S homopolar bond are preferentially attacked by amine solvents, whereas heteropolar bonds are less reactive. These findings are also confirmed by studies focusing on sulfur-amine chemistry. [41] It follows then that the dissolution rate of glasses exhibiting a high S-S bonds content would be higher, consistent with what we observe with a slower dissolution rate of the stoichiometric glass (A-Na₂) as compared to that of the sulphur-rich glass (D-Na₂).

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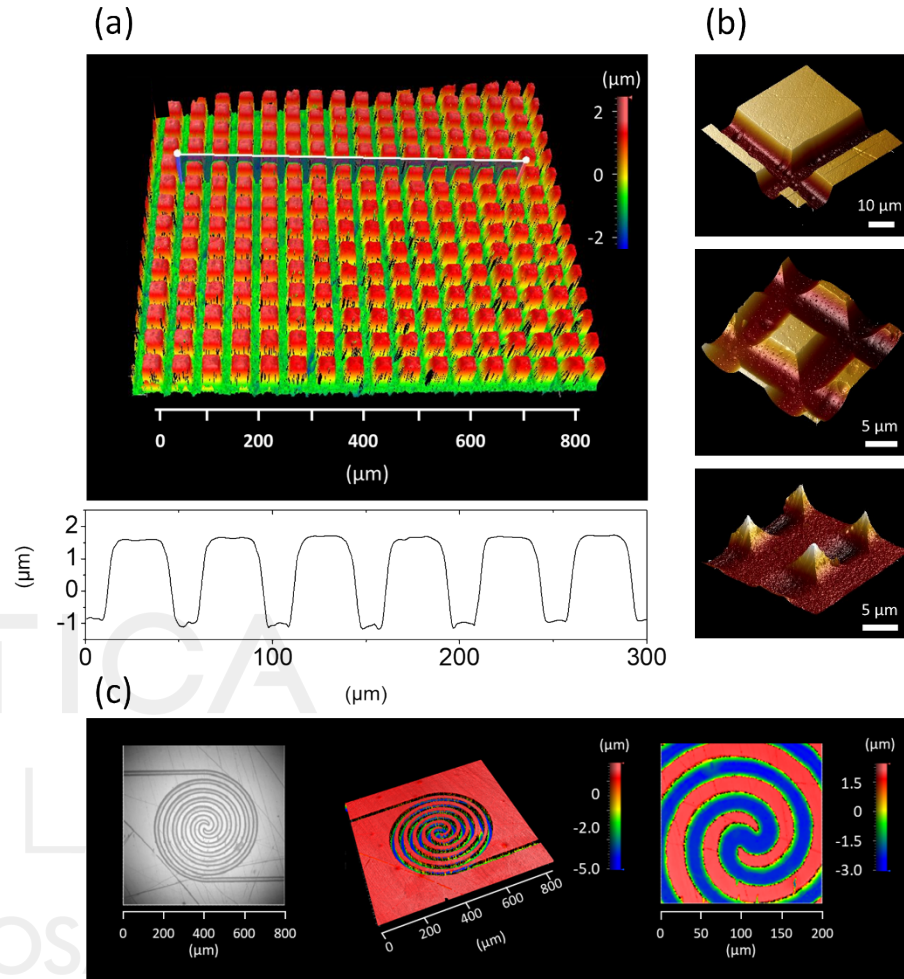
332

The comparison of the poled and virgin glasses' dissolution rates (Fig. 2) has revealed that in EDA, the poled zone was dissolved more rapidly than the unmodified one. One must note that this is not always the general behavior; for instance, acidic etching of poled silicate results in a faster dissolution rate of the unmodified region compared to the poled one. [22] In our previous work, the Raman study of these glasses (i) as a function of the sodium content and (ii) before and after poling has shown that the structural organization of a poled glass was similar to that of the glass without sodium. [31] In other words, the glass matrix was flexible enough to rearrange itself under the electric field and temperature combination to exhibit the composition

333 and structure of a glass without sodium. However, the dissolution of virgin glasses with
334 different sodium contents (Fig. 1b) has shown that the influence of the sodium content on the
335 dissolution rate was negligible. Therefore, the poled region's selective etching cannot be
336 explained by an effect of the structure nor composition.

337 A previous work on these glassy systems has demonstrated a control of the index variation by
338 micro-poling. [30] A decrease in refractive index was observed in the poled regions (therefore,
339 in the IC zones of the present work). Furthermore, on other glass systems, [33] we have
340 demonstrated that this decrease in refractive index was linked to a decrease in the glass
341 network's density upon poling. The higher the initial sodium content was, the larger the density
342 decrease was. Recall, the difference in dissolution rates of poled and unmodified regions is
343 larger for the sample C-Na_{5.5} than for C-Na₂; that is, for a same S/Ge ratio, the difference is
344 larger for higher initial sodium content. It follows that the selective etching of the poled region
345 could be explained by this decrease in density that would facilitate the dissolution

346 One of the major advantages of this technique is illustrated in Fig. 5a: large areas can be
347 structured at once. So far, only millimeter square surfaces were tested but as thermal poling can
348 be readily scaled up to larger sizes in an efficient manner, it should also be extendable toward
349 centimeter square areas. In Fig. 5b and Fig. 5c, one can see different kind of shapes that can be
350 obtained by micro-poling and subsequent dissolution. This clearly demonstrates the versatility
351 of this process with an accurate spatial control of the structures shapes that can be tuned easily
352 by a control of the immersion time.



353
 354
 355 Fig. 5: (a) (top) Topography of a glass sample after micro-poling and dissolution measured by an optical profilometer
 356 giving evidence of the possibility to control the topology of large surfaces and (bottom) profile extracted from this
 357 image showing the regularity of the process. (b) AFM measured topographies of poled glasses at different dissolution
 358 times illustrating the different surface morphologies that can be obtained by this process. (c) Optical image (left) and
 359 topography (center and right) measured by an optical profilometer of a poled glass after dissolution. The structured
 360 electrode employed here consisted of lithographically made gold spiral. As opposed to previous patterns, here the
 361 conductive part is small (only the spiral). This kind of designs open possibilities in the domain of microfluidics for
 362 instance.
 363
 364

365 5. Conclusion

366 Throughout this work, we demonstrate a control of the topology of chalcogenide glasses by the
 367 combination of an electrothermal process and a chemical attack. The origin of the selective
 368 etching of the poled glasses was discussed: a decrease in the density upon poling is most likely
 369 at its origin. The influence of the composition (sulphur and sodium contents) was also
 370 evidenced. Significant (up to 4 μm) topological contrasts were achieved, and large (millimeter
 371 square) areas were structured. We have shown that a control of the spatial variations in size
 372 and shape (in 3-dimensions) was possible by tailoring the glass type, the electrode feature and
 373 the experimental conditions (of the poling and of the chemical attack). This process could be
 374 seen as an alternative to classical lithography techniques.

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386 **Disclosures**

387 The authors declare no conflict of interest.

388 **Data availability**

389 Data underlying the results presented in this paper are not publicly available at this time but may be obtained from
390 the authors upon reasonable request.

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