# Ultra-smooth lithium niobate photonic micro-structures by surface tension reshaping

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**Abstract:** Annealing of micro-structured lithium niobate substrates at temperatures close to, but below the melting point, allows surface tension to reshape preferentially melted surface zones of the crystal. The reshaped surface re-crystallizes upon cooling to form a single crystal again as it is seeded by the bulk which remains solid throughout the process. This procedure yields ultra-smooth single crystal superstructures suitable for the fabrication of photonic micro-components with low scattering loss.



**OCIS codes:** (130.3730) Lithium niobate; (130.2260) Ferroelectrics; (130.3990) Micro-optical devices; (350.3850) Materials processing.

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## 1. Introduction

Dense integration of optical waveguide circuits requires large dielectric contrast between the waveguide core and the cladding material which is typically achieved by fabricating devices which consist of super-structures (e.g. ridge waveguides and whispering gallery mode (WGM) resonators) where the optical confinement is high due to the high refractive index contrast between the optical material and the surrounding air. However, one of the sources of optical power loss and performance degradation in such photonic structures is surface imperfections such as residual surface roughness which introduces scattering loss. These fabrication imperfections can be corrected by thermal treatment i.e. using laser annealing methods to locally melt the surface allowing for the surface tension to reshape the relevant structure to

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form an extremely smooth perfect globule. WGM resonators which are fabricated in this way usually exhibit very low scattering loss and hence high Q factors [1,2].

Although such a method can be applied to glass, which is an amorphous material, without undue problems it is rather different if applied to single crystal materials mainly because the single crystal properties are not generally preserved after the melting and cooling cycles [3]. Light propagating in such a poly-crystalline material will experience scattering at the boundaries between adjacent crystallites introducing significant optical loss. Furthermore the macroscopic physical and optical properties of the single crystal will be compromised due to the random orientation of the crystallites hence such a material will not be suitable for electro-optic and non-linear optical applications.

Here we present a method for the surface reshaping of micro-structured crystalline substrates which can produce smooth surfaces while maintaining the useful crystalline properties of the original material. The method is based on the observation that annealing of a crystal at temperatures close to, but lower than, the melting point induces preferential melting of a surface layer [4]. Upon cooling the melted surface layer re-crystallizes, seeded by the bulk that remains solid during the process, and is reshaped by the surface tension to form ultra-smooth single crystal superstructures. In order to demonstrate the potential of this method for the fabrication of photonic structures we have applied it to surface micro-structured lithium niobate, a nonlinear optical ferroelectric crystal which is widely used in the photonics industry.

## 2. Experiments and results

The melting temperature for congruently melting lithium niobate crystals is 1257°C (provided by Crystal technology, Inc.) and the Curie temperature which marks the ferroelectric to paraelectric phase transition is 1142°C, however this value does depend on the exact composition of the crystal and changes substantially with the lithium content.

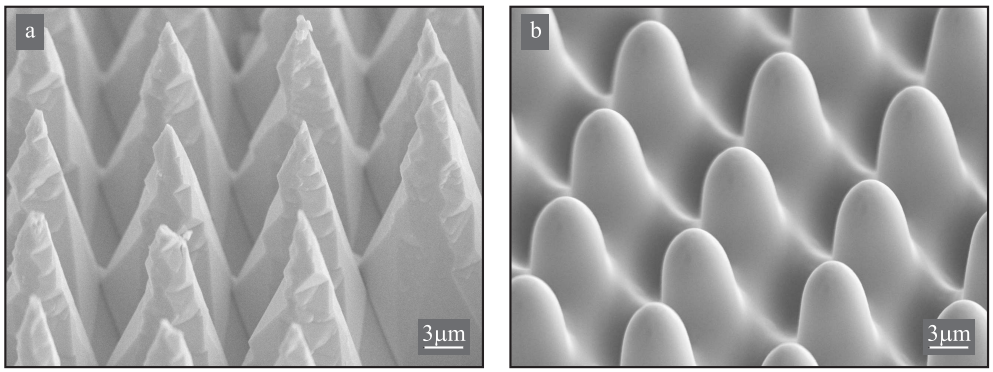


Fig. 1. SEM images of the micro-structured lithium niobate crystal surface (45° tilted) a) after deep etching of a 2D lattice of inverted ferroelectric domains and b) after thermal treatment.

We have prepared a micro-structured z-cut crystal surface by HF etching of a ferroelectric domain-engineered substrate [5]. The micro-structured crystal surface, which is shown in the scanning electron microscopy (SEM) image of Fig. 1a, consists of a 2D array of micro-pyramids which exhibit a rough side surface and a sharp tip. The initial ferroelectric domain inverted lattice in this particular sample consisted of an array of circularly shaped + z polar surfaces and was achieved by UV laser induced poling inhibition [6]. A + z face is not affected by the HF acid, however as the pillar structure develops due to the preferential etching of the crystal surface that surrounds the circular + z domains, the revealed side surface of the pillars is now subject to sideways etching along the three y-directions of the crystal. Hence, after prolonged etching the pole-inhibited domain etches away to produce a single point (as observed in Fig. 1a). The sideways etching is also responsible for the conical shape of the features which are shown in Fig. 1a. The sample was then subjected to thermal

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annealing to a temperature of 1130°C for 50 hrs in a continuous flow of oxygen gas in order to suppress lithium out-diffusion. The temperature was ramped up at a rate of 5 degrees per minute and after the required dwell time it was ramped down also at a rate of 5 degrees per minute. The surface topography after annealing is shown in the SEM image of Fig. 1b. It is obvious that all the sharp features have been smoothed out as the micro-structures have been reshaped by the surface tension.

These surface tension reshaped structures can be defined, to some extent, by the initial shape of the crystal microstructure. Figure 2a shows a lithium niobate microstructured pillar with an undercut top section as a result of HF etching of an isolated surface domain produced by inhibition of poling [6]. After thermal annealing for 50 hrs at 1120°C the pillar is reshaped by the surface tension to form a quasi-oblate spheroid structure as shown in Fig. 2b. Such a structure is suitable for supporting WGMs while the smooth side surface guarantees low scattering loss. Its small dimensions can reduce dramatically the number of supported WGMs and increase the device free spectral range. Both features are beneficial in a number of advanced optical applications such as optical filters and lasers.

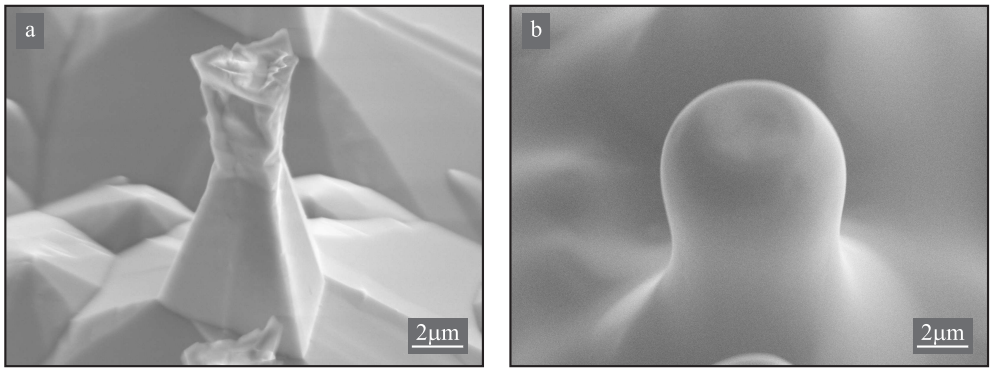


Fig. 2. SEM images of a) the initial structure, comprising an undercut, produced by inhibition of poling followed by deep chemical etching using HF acid, b) corresponding annealed structure showing a quasi-oblate spheroid top. In both images the sample is tilted by 45°.

Although the range of temperatures that the lithium niobate crystals experienced during the thermal treatment were kept below the Curie point and hence well below the melting point, it is evident that, at some point during the process, the surface was in the liquid phase in both examples shown in Figs. 1b and 2b. However, preferential melting of the surface is possible at temperatures lower than the bulk melting temperature, with the thickness of the melted zone being a function of the temperature [4].

In the cases which were presented so far the temperature was kept just below the Curie point. Hence it is expected that the bulk of the processed material is still single crystal and ferroelectric throughout the thermal processing, while the surface undergoes melting to the liquid phase. However even when the crystal was treated at temperatures higher than the Curie temperature we found that there is always a substantially deep layer of the crystal that maintains a single polarization state. Although similar observations have been made in thermally-treated $LiTaO_3$ crystals at temperatures exceeding the Curie temperature [7], we are not aware of any such reports on $LiNbO_3$. Such prolonged thermal treatment can lead to lithium out-diffusion which may be substantial and which consequently leads to domain inversion on the + z face of the crystal. As a result a uniform domain-inverted layer is formed with a depth which depends on the duration of the thermal treatment. We have observed that in extreme cases where a crystal slab is annealed at temperatures exceeding the Curie point the depth of the domain-inverted layer can reach half the slab thickness. Interestingly though both of the two sections of the slab remain single domain.

Etching in HF acid is routinely used to reveal the presence of inverted ferroelectric domains in lithium niobate as the two opposite z faces of the crystal etch at different rates (actually the + z face remains totally unaffected by the acid) [8]. However, differential etching

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can also be observed between opposite y-faces of the crystal. The topography of the etched y-face can reveal the domain structure of a multi-domain lithium niobate crystal because, as has been shown in [9], domain inversion corresponds to a 180° rotation of the z axis around the x axis of the crystal. Consequently the y axis is also rotated by 180° and hence opposite ferroelectric domains present opposite y-faces on the same y surface.

The etched y-face of the crystal slab which was annealed at a temperature exceeding the Curie temperature is shown in the SEM image of Fig. 3 where the two single domain regions are clearly visible due to the differential etching of the opposite y-faces which are presented on the same y-surface as indicated in the figure. The top edge of the image corresponds to the original -z face of the sample while the bottom edge corresponds to the original + z face which has now been domain-inverted, as a consequence of thermal annealing, to form a -z face. Consequently, after annealing the crystal presents a -z face on both z-surfaces.

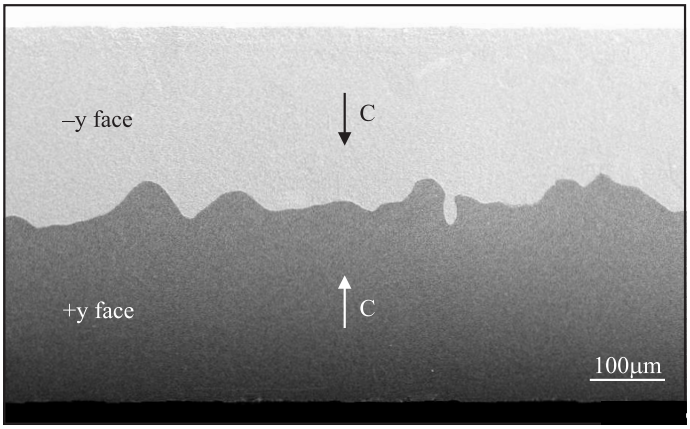


Fig. 3. Etching of the y-face of a z-cut crystal slab annealed at T = 1200°C (above the Curie temperature) for 10 hrs revealing the ferroelectric domain structure.

In order to assess the quality of the crystal after the thermal process the annealed crystal surface was investigated using piezoresponse force microscopy (PFM) [10], Raman spectroscopy and finally chemical etching.

A series of small area PFM scans was performed on various locations of the annealed microstructured substrate. All PFM images obtained in these scans showed the very same uniform grey-level, and thus the same piezoresponse, indicating that the melted and re-solidified surface is single domain and piezoelectric. In order to quantify the piezoresponse obtained on the annealed substrate, we performed a comparative measurement on an untreated multi-domain single crystal (PPLN). We could thereby show, that the amplitude of the PFM signal measured on the microstructured substrate is identical to the one on the -z – face of the untreated sample. In addition, we also observed strong surface charging on the re-solidified material [11]. Based on those evidences we concluded that the annealed microstructured substrate is both single crystal and ferroelectric. Micro-Raman spectroscopy and chemical etching corroborated the PFM results.

A set of spatially-selective Raman spectra has been acquired from different positions on the annealed micro-structured substrate shown in Fig. 1b. The micro-Raman spectrometer which was used to acquire the spectra employed a × 50 microscope objective to both focus the probe laser beam and collect the Raman signal. The depth resolution of the system is limited by the depth of focus of the objective which is less than 1 μm.

Figure 4 shows a set of Raman spectra which were acquired from a single reshaped tip. These Raman spectra were taken at different focusing conditions and can be compared to a reference spectrum (solid line) taken from an unstructured and untreated z-cut substrate in the z(yy)z configuration [12]. The dashed line spectrum corresponds to a well-focused acquisition from a spot on the summit of a single tip, while the dotted line corresponds to a slightly

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defocused acquisition on the same spot. Finally the dash-dotted line corresponds to a spot between two adjacent tips (focused acquisition).

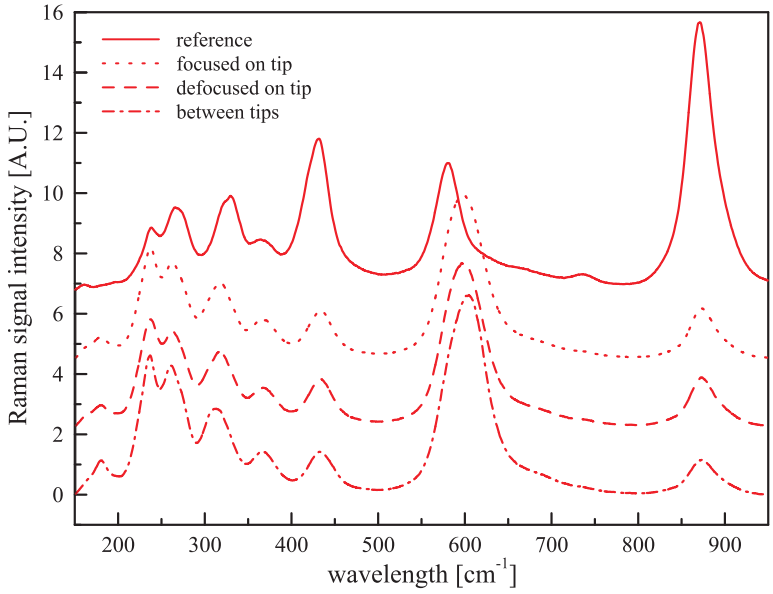


Fig. 4. Raman spectra acquired from different points on the annealed microstructured sample shown in Fig. 1b and with different focusing conditions as indicated in the legend. The solid line corresponds to a spectrum that was taken from a virgin z-cut sample in the z(yy)z configuration. An offset was introduced between spectra for clarity.

The acquisition of spectra under different focusing conditions was performed in order to collect signals from the surface layers of the structure, which had experienced melting, in order to detect any possible structural changes after the process. However, there was no obvious difference between these spectra (dashed line and dotted line in Fig. 4).

Further observation of the spectra reveals that some Raman lines corresponding to the reshaped tips appear to be shifted with respect to the corresponding peaks in the reference spectrum (the 582 $cm^{-1}$ peak in particular) while others (like the 432 $cm^{-1}$ and 873 $cm^{-1}$ peaks) exhibit a relative intensity change as compared to the reference spectrum. Raman spectra of crystalline materials however are subject to selection rules which depend on the specifics of the crystal face and polarization mode of the exciting beam and the detection channel. Since the annealed structure is curved it does not present a pure z-face to the direction of incidence of the interrogating laser beam the entrance/exit faces are in general different compared to the reference z-cut substrate. Additionally, the curved interfaces can alter the polarization state of both the exciting beam and of the collected signal. These factors which influence both the position and intensity of the Raman peaks are likely to be responsible for the differences which are observed between the various Raman spectra taken from the reshaped surface and the reference spectrum taken from the pure z-cut crystal.

The lateral differential etching between opposite y-faces was used earlier for the visualization of the ferroelectric domain structure of the crystal. However, as a consequence of the threefold symmetry of the lithium niobate crystal structure there are three indistinguishable pairs of y-faces corresponding to three y-axes which are rotated by 120° with respect to each other. This threefold symmetry can be readily identified in the x-y cross-section of etched isolated inverted domains. Here we have used HF acid etching to look for this characteristic threefold symmetry on the re-solidified crystal features in order to assess the quality of the thermally treated crystal.

Figure 5a shows an SEM image of a smoothed feature as a result of the surface tension reshaping that took place during the annealing process. After brief etching in HF acid

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characteristic facets (due to differential etching between opposite y-faces) start to emerge revealing the characteristic threefold symmetry of lithium niobate as shown in the SEM image of Fig. 5b.

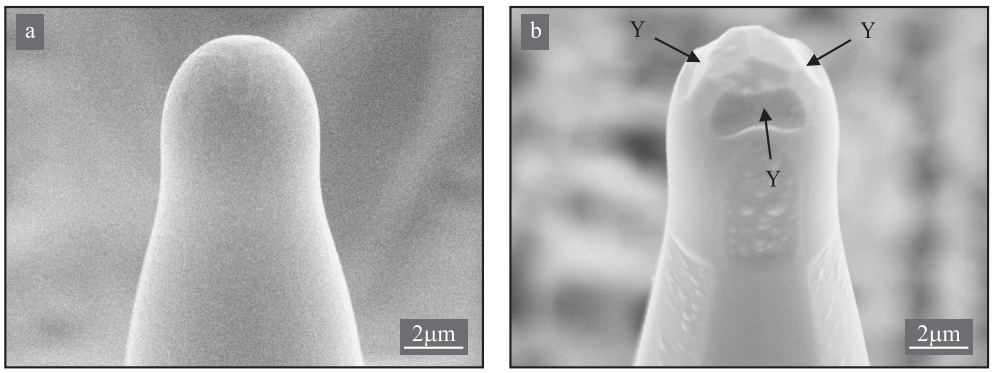


Fig. 5. a) SEM image of a surface tension reshaped feature, b) SEM image of a feature briefly etched in HF showing characteristic y-face differential etching as indicated by the arrows.

## 3. Conclusions

In summary, we have demonstrated a method for achieving ultra-smooth single crystal lithium niobate structures. The method is based on selective surface melting at temperatures below the Curie point, followed by seeded re-crystallization. The single crystal nature of the re-crystallized surface layer was confirmed experimentally by piezoresponse force microscopy, Raman scattering and chemical etching. Elimination of the residual surface roughness promises a significant reduction of the propagation losses in any micro-structured photonic structure such as ridge waveguides, ring waveguide resonators and lasers enabling the miniaturization of photonic circuits without sacrificing the device performance. Hence, the method is expected to increase dramatically the optical performance of $LiNbO_3$-based crystalline waveguide structures, 1-D and 2-D surface relief gratings and WGM micro-resonators. We further anticipate that this method could also be extended to other crystalline materials.


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