UV laser-induced ordered surface nanostructures in congruent lithium niobate single crystals.

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Abstract

Ultra violet illumination of the -z face of lithium niobate single crystals, under specific conditions, results in an organized arrangement of submicron etch-resistant features that reflect the illuminating intensity distribution. Consequently, spatially resolved illumination can produce periodic structures with submicron periodicity. Furthermore, a size self-adjustment of the submicron etch resistant features was observed which is related to characteristic lengths (e.g. grating period) of the overall structure. The effect occurs for a narrow range of illuminating intensities and is attributed to a photo-induced electrostatic charge distribution which modifies the electrochemical interaction of the acid with the surface. The size and periodicity of the structures which can be achieved with this method are suitable for the fabrication of 2D photonic crystal structures in this electro-optically tunable material.

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1. Introduction

Lithium niobate is among the most important optical materials as it combines a variety of very useful properties. It exhibits significant optical nonlinearity, is electrooptic, photorefractive, pyroelectric, piezoelectric and has extended optical transparency over the infrared and visible spectrum [1], and therefore lithium niobate crystals are extensively used today in the photonics industry for the fabrication of electro-optic modulators and switches [2], acousto-optic devices [3] and nonlinear frequency conversion via quasi-phase-matching in periodically poled material [4]. Furthermore, these properties also show the potential and further application of this material for the fabrication of tunable photonic devices.

However, a very important requirement for the realisation of such devices is the development of micro- and nano-fabrication methods. A very useful property commonly used in microfabrication is differential etching and lithium niobate exhibits extremely strong differential etching behaviour in HF and HF:HNO_3 acid mixtures between ferroelectric domains of opposite orientation. The etch rate of the -z face of the crystal depends on the acid mixture and temperature [5] while the +z face remains unaffected by the etch process in our experience and this property has been used already in conjunction with ferroelectric domain engineering for the fabrication of a range of 2D and 3D microstructures [6,7].

Another method for the modification of the etching characteristics of the -z face of lithium niobate single crystals uses laser-irradiation of the -z face of the crystal prior to acid etching. The interaction of the laser radiation with the crystal surface (under appropriate irradiation conditions) can reduce or even completely stop the etch process locally. This effect has been observed in Fe doped crystals using continuous visible laser irradiation during the etching process [8] and in undoped crystals using UV laser radiation prior to acid etching [9,10].

In this paper we show that spatially resolved pulsed UV laser irradiation of the -z face can act to organize the position and size of etch resistant features enabling the fabrication of submicron periodic structures. The ability for generation of such structures shows great potential for the fabrication of photonic structures with tuning capabilities as the material is both nonlinear and electro-optic.

2. Experimental procedure.

The experimental procedure followed in the present work involved exposure of the -z face of z-cut lithium niobate samples to ultra violet (UV) laser radiation and subsequent chemical etching in HF acid at room temperature. The time interval between exposure and etching varied from minutes to a few hours without any significant change in the results. The laser source which was used for the exposures was a KrF excimer laser emitting pulses of ~20 nsec duration at a wavelength of 248 nm. The samples used were diced from commercial 500 μm thick z-cut congruent lithium niobate wafers, acquired from Crystal technology, USA, with both z faces optically polished.

Spatially resolved illumination of the surface was achieved by using either amplitude masks or phase masks depending on the desired resolution of the illuminating intensity pattern. Transmission Electron Microscopy (TEM) copper grids were used as amplitude masks. These grids were 11 μm thick, having circular shape of ~3 mm diameter and consisting of a two dimensional metallic mesh with openings of either square or hexagonal shape. The widths of the grid openings were: 90 μm, 50 μm and 35 μm.

Initial experiments suggested that the etch frustration results were sensitive to small variations of the illuminating intensity. For this reason the grids were attached to the crystal surface using narrow strips of adhesive tape instead of being pressed against the surface using a UV transparent optical flat, in order to avoid multiple reflections which may well have confused the results. Consequently, the contact between the grid and the crystal surface was imperfect and near-field (Fresnel) diffraction effects were expected to play a significant role in the illumination of the area near the edges of the grid openings.

However, the overall feature size resulting from use of the contact amplitude mask method of illumination will of course be limited to the opening size of the grids and in order to increase the spatial resolution, phase mask illumination was used. The phase mask used in these experiments had a grating period, on the mask, of Λ_m=720 nm and hence was able to produce a near-field periodic intensity pattern with a 360 nm period. The phase mask was optimized for a wavelength of 246 nm. In order to ensure reproducible illumination conditions the spacing between the phase mask and the surface of the sample was kept constant at 125 μm using pieces of standard telecom fibre (with the polymer jacket removed) as spacers. The phase mask was then pressed against the sample in a specially designed holder. The beam profile of the excimer laser was rectangular with dimensions of ~ 30 mm x 15 mm. However, only the central 20 mm x 10 mm portion of the beam was used for spatially resolved exposures in order to obtain improved uniformity of illumination. The quality of excimer laser beams is inherently rather poor, therefore there are always residual irregularities in the intensity profile even in the central portion of the beam. A number of exposures were performed using a portion of the beam with a significant intensity gradient. In this way it was possible to obtain a single spot mapping of the etch frustration behaviour as a function of the local intensity variation.

It is important to note that all the UV exposures were performed using laser fluences below the ablation threshold. The surface of the crystal was examined, after UV exposure, with an optical microscope and surface profilometer measurements but showed no evidence of deformation or damage.

After illumination the samples were etched in HF acid at room temperature and the surface topography was investigated by profilometry and Scanning Electron Microscopy (SEM). All the etching processes took place in a cleanroom environment (class 1000) and the samples were thoroughly cleaned prior to etching using standard sequential solvent procedures at room temperature. However, the UV exposure was performed in a non-cleanroom environment, hence diffraction effects from dust particles located either on the surface of the crystal or on the surface of the phase mask were frequently observed.

3. Results and discussions

Under certain irradiation conditions the UV-illuminated areas of the -z face appeared to totally resist subsequent etching [9,10]. Frustration of etching proved to be very sensitive to small local variations of the laser intensity but rather insensitive to the total exposure (number of pulses). Total frustration of etching was observed for laser energy fluence around 70 mJ/cm^2 and for a number of pulses between 2 and 100.

In order to better visualise the narrow range of intensities which result in etch frustration the following experiment was conducted. The -z face of a lithium niobate sample was illuminated with a portion of the beam having a variable intensity profile, an imprint of which is shown in figure 1(a) as recorded on thermal paper. The energy per pulse used was of order 80 mJ distributed over the area (12.2 mm x 8.4 mm) of the spot. Three different exposures were performed at the same energy per pulse at 25, 50 and 100 pulses on the same sample which exhibited similar surface topography characteristics after 1 hour etching in HF at room temperature.

The imprint was scanned and subsequently encoded in 256 grey levels in a bitmap file. Several cross sections of the digitalized image were obtained by image processing software along the longer dimension of the profile and an average of those cross sections is shown in figure 1(b) showing the intensity variation along the beam profile. However, the imprint on the thermal paper is unlikely to correspond to a strictly linear (intensity→grey levels) process and although it gives an indication of the intensity variation no accurate quantitative results can be obtained in this way. The sample which was illuminated using the portion of the beam shown in figure 1(a) was etched in pure HF for one hour at room temperature revealing etch frustrated patterns along contours corresponding to a restricted range of laser intensity.

Figure 2 shows a profilometer scan revealing the surface topography of the sample after one hour etching in HF acid at room temperature. The scan was performed along the longer dimension of the illuminating profile and shows two sharp etch frustrated areas separated by a flat region of normal etching. The curved baseline of the trace is an artefact of the equipment which becomes more apparent for such long scans. For clarity the surface profilometer scan is superimposed on the cross section of the spot profile. The positioning of the surface profile with respect to the laser spot cross section is based on the hypothesis that the two positions, where etch frustration starts occurring, should correspond to the same intensity level. The dashed lines indicate graphically that the widths of the etch frustrated regions correspond roughly to the same range of intensities according to the profile curve. This experiment also reveals that there is indeed a narrow intensity window of order 10% of the total intensity profile where etch frustration occurs.

Using the TEM grids as amplitude masks a set of exposures at intensity levels which corresponds to the total frustration of etching were performed. Figure 3(a) shows a low magnification view of an array of etch frustrated hexagons corresponding to the openings of the grids as revealed by HF etching. The width of each hexagon is ~50 μm and the hexagons are themselves arranged in a regular hexagonal lattice. Figure 3(b) shows a higher magnification SEM image of a single etch frustrated hexagon. The structure is not solid but consists of an array of submicron features which has resisted etching. The regular structure which can be observed near the edges of the hexagon is attributed to irregular illumination of the surface due to the near-field (Fresnel) diffraction pattern which is the result of the imperfect contact between the grid and the crystal surface. Furthermore, the position of these submicron etch resistant features is not random but they appear, in places, to be arranged in a closed packed hexagonal lattice, as shown in the expanded inset reflecting the symmetry of the structure as a result of the imposed illumination pattern from the near field diffraction near the edges of the grid. In cases where the separation between the grid and the surface is less the regular positioning of these etch resistant features is correspondingly less pronounced, as shown in the SEM image of figure 4, providing a good indication that it is indeed the intensity distribution which is responsible for their regular arrangement. Another interesting feature of the etch resistant features is the size irregularity which they exhibit which seems to be correlated with the characteristic spacing of the diffraction pattern. More evidence for the etch resistant feature size adjustment was provided by the phase mask exposure experiments described next.

The phase mask illumination experiments were performed as described in the previous section, where it was mentioned that the phase mask used was designed to produce a periodic near-field diffraction intensity pattern with a period of 360 nm, optimized for 246 nm illumination. However, it is very often observed that in the reproduced near-field diffraction intensity pattern the bright fringes are not of the same intensity due to small imperfections in the fabrication of the mask. The resultant intensity distribution may look like that shown in figure 5 where two sets of π phase shifted fringes with spacing Λ_m, (Λ_m is the physical period of the grating on the phase mask) are present. These imperfections are usually insignificant for processes where the response of the material depends on exposure rather than intensity, e.g. for direct writing of gratings in photosensitive fibres (where such masks are routinely used) because the intensity non-uniformities will be smoothed out upon saturation. However, in a system where the material response is very sensitive to the illuminating laser intensity, as is the case for lithium niobate, this difference can be very significant as the phase mask illumination results suggests.

Figures 6(a) and 6(b) shows two SEM images of the etched -z face of a lithium niobate sample after exposure through a phase mask, taken from two different areas of the etch frustrated surface which correspond to different laser intensities. The image shown in figure 6(b) corresponds to the border area of the laser spot where there is a gradient of the intensity while figure 6(a) corresponds to the central area of the laser spot where the intensity is relatively uniform. Figure 6(a) shows a periodic pattern with a spacing that matches the period of the phase mask $\Lambda_m \sim 720$ nm.

However, in the etch frustrated structure shown in figure 6(b) it is possible to observe both the Λ_m (in the area enclosed in the square frame) and $\Lambda_m/2$ periods (in the areas enclosed in the circles). The non-uniformity of the etch frustrated pattern is due to intensity variations at the edges of the illuminating spot. The fact that there is a region where both periods are observed confirms both the intensity selectivity of the effect and the hypothesis for imperfections of the phase mask.

A common feature of both SEM images is that the etch frustrated section again consists of submicron features which are ordered in relation to the illuminating intensity pattern. Furthermore, those submicron etch resistant features appear to have a rather uniform size distribution which matches roughly the period of the etch frustrated pattern. This is confirmed also in figure 6(b) where the size of these features is adjusted to match either the $\Lambda_m/2$ or the Λ_m period depending on the characteristic spacing of the periodic pattern.

The observed etch modification effects which were discussed above can be attributed to photo-generated charge. Lithium niobate is an insulator with an energy band gap E_g~3.55 eV, hence the 5 eV energy photons provided by the 248 nm laser source is capable of generating electron-hole pairs in the crystal. Re-trapping of the charge carriers at defect sites near the surface will rearrange the electrostatic map of the surface hence modifying the subsequent interaction of the surface with the acid. The presence of an electrostatic field on the surface of the crystal after the UV illumination was confirmed by the selective attachment of charged micron size particles on the UV illuminated parts of the crystal surface.

Modelling of the process using the assumption of photo-generated positive and negative charges is currently under way and this is expected to improve our understanding of the observed etch behaviour. However, the ability for generating surface relief submicron features with controllable spacing and size has enormous potential for the fabrication of tunable 2D photonic structures in this versatile nonlinear optical ferroelectric material.

4. Conclusions

A method for the fabrication of submicron regularly arranged surface relief features on the -z face of congruent lithium niobate single crystals has been presented. The method combines UV laser illumination followed by wet chemical etching and is able to produce periodic structures with submicron spacing consisting of submicron etch resistant features. The size of these features self-adjusts to match the spacing of the periodic structure providing a tool for the fabrication of tunable photonic structures in this already widely used nonlinear optical ferroelectric material.

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Figure captions

Figure 1. a) Thermal paper recording showing the spatial non-uniformity of the intensity within the laser spot, b) Cross section of the laser spot profile along the 12.2 mm dimension after scanning. The vertical axis corresponds to grey levels after digital encoding of the imprint.

Figure 2. Surface profilometer scan showing the topography of the illuminated and etched surface of the crystal along the 12.2 mm dimension of the spot. The profilometer scan is superimposed on the grey scale encoded cross section of the laser spot intensity profile.

Figure 3. a) SEM image showing an array of etch frustrated hexagons after TEM grid mask illumination and HF etching, b) Detail of a single hexagon showing the effect of the non-uniform illumination due to Fresnel diffraction in the border area and the regular arrangement of the etch resistant features in the circled area.

Figure 4. SEM image of a single etch frustrated hexagon. The Fresnel diffraction effect is less pronounced due to better contact between the TEM grid and the surface and the degree of regularity of the etch frustrated features is reduced.

Figure 5. Schematic of the type of irregularity which can be observed in the intensity distribution produced in the near-field of a phase mask. Λ_m is the spacing of the grating structure on the phase mask.

Figure 6. SEM images of etch frustrated patterns after phase mask illumination taken from two different locations of the illuminated area: a) from the central relatively uniformly exposed area and b) near the edge of the illuminated spot where there is a significant gradient in the illuminating intensity.

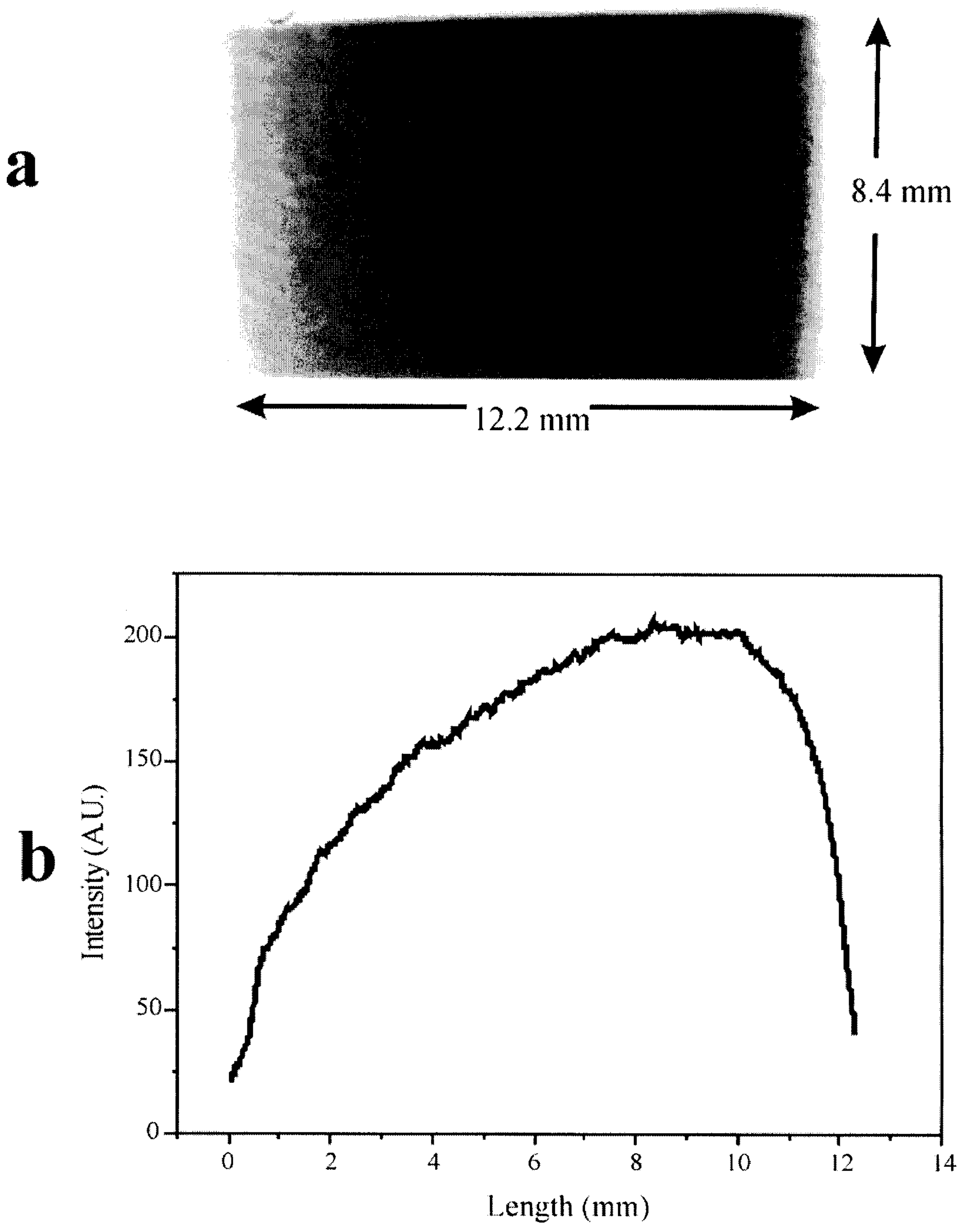

a
8.4 mm
12.2 mm
b
Intensity (AU.)
0
50
100
150
200
0
2
4
6
8
10
12
14
Length (mm)

Figure 1

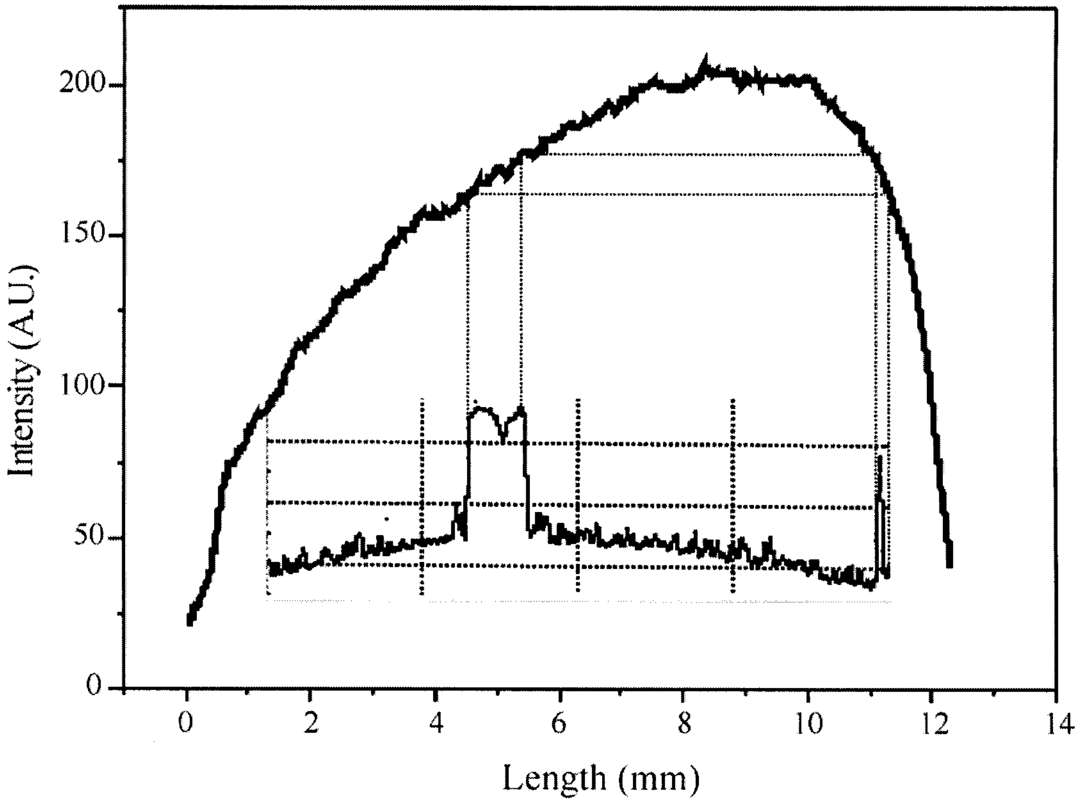


Figure 2

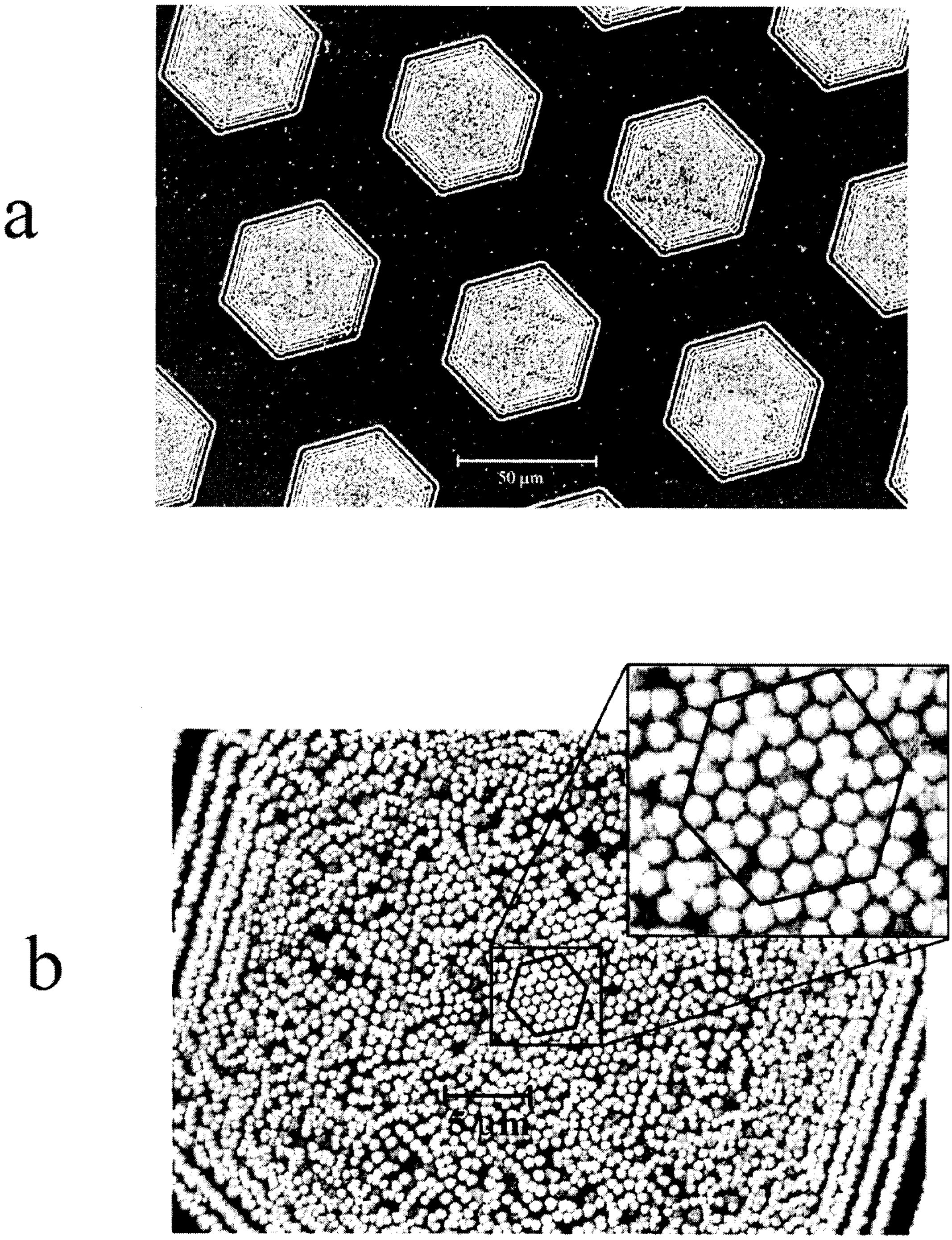


Figure 3

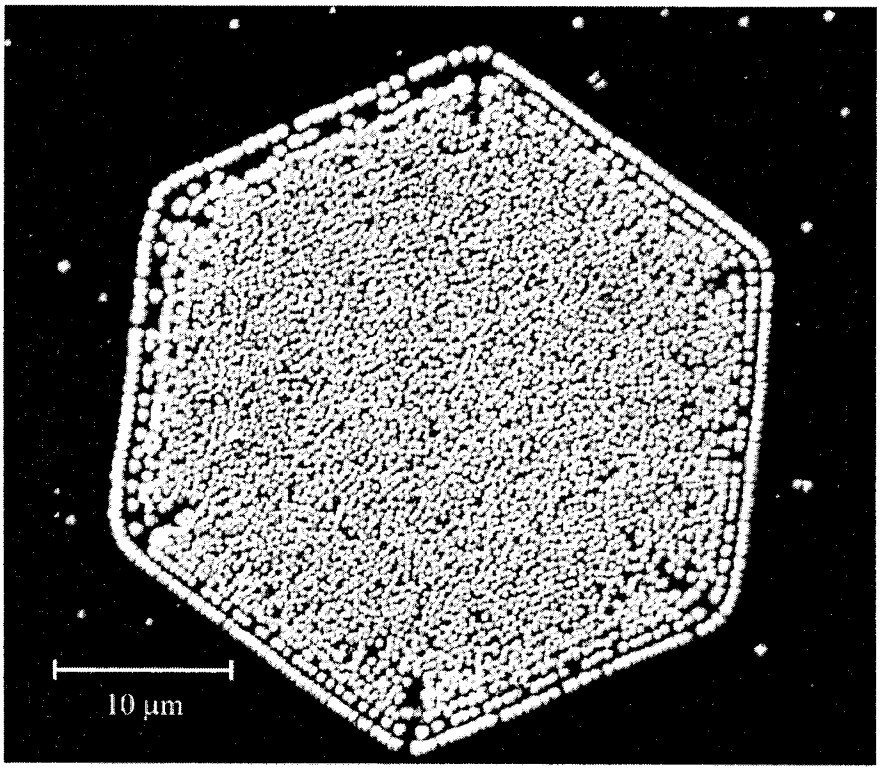
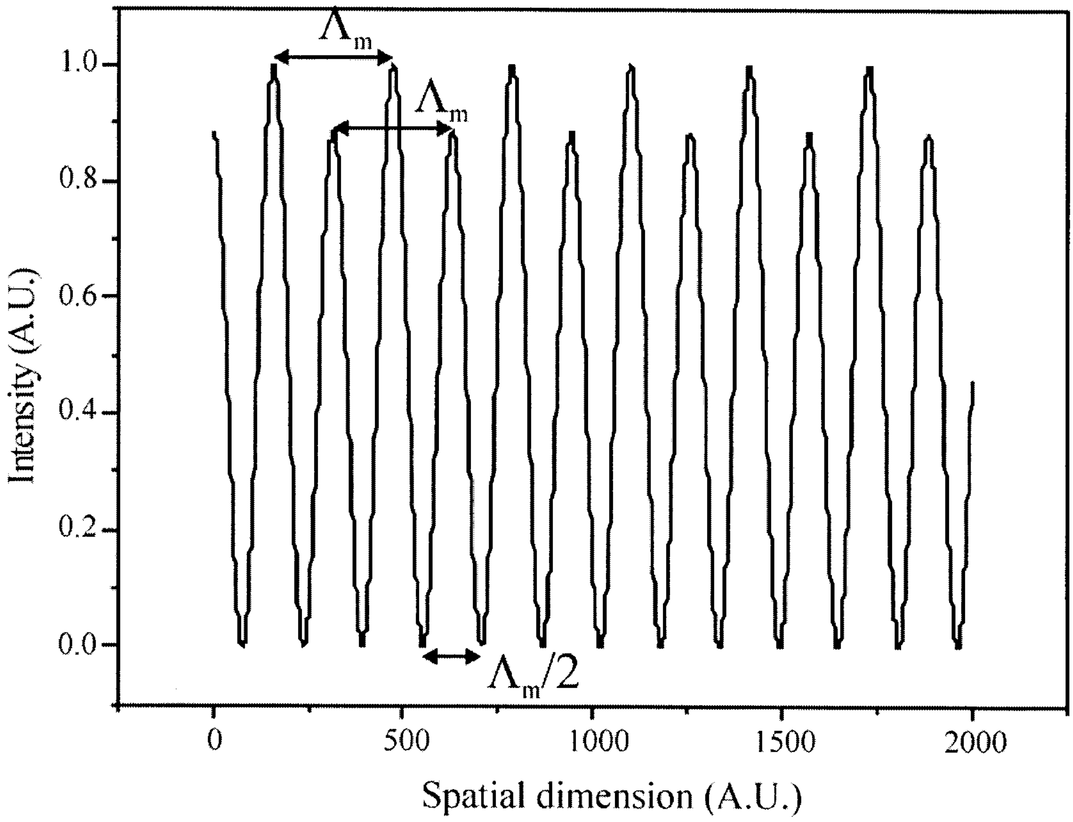


Figure 4



Λ_m
Λ_m
$\Lambda_m/2$
1.0
0.8
0.6
0.4
0.2
0.0
Intensity (A.U.)
0
500
1000
1500
2000
Spatial dimension (A.U.)

Figure 5

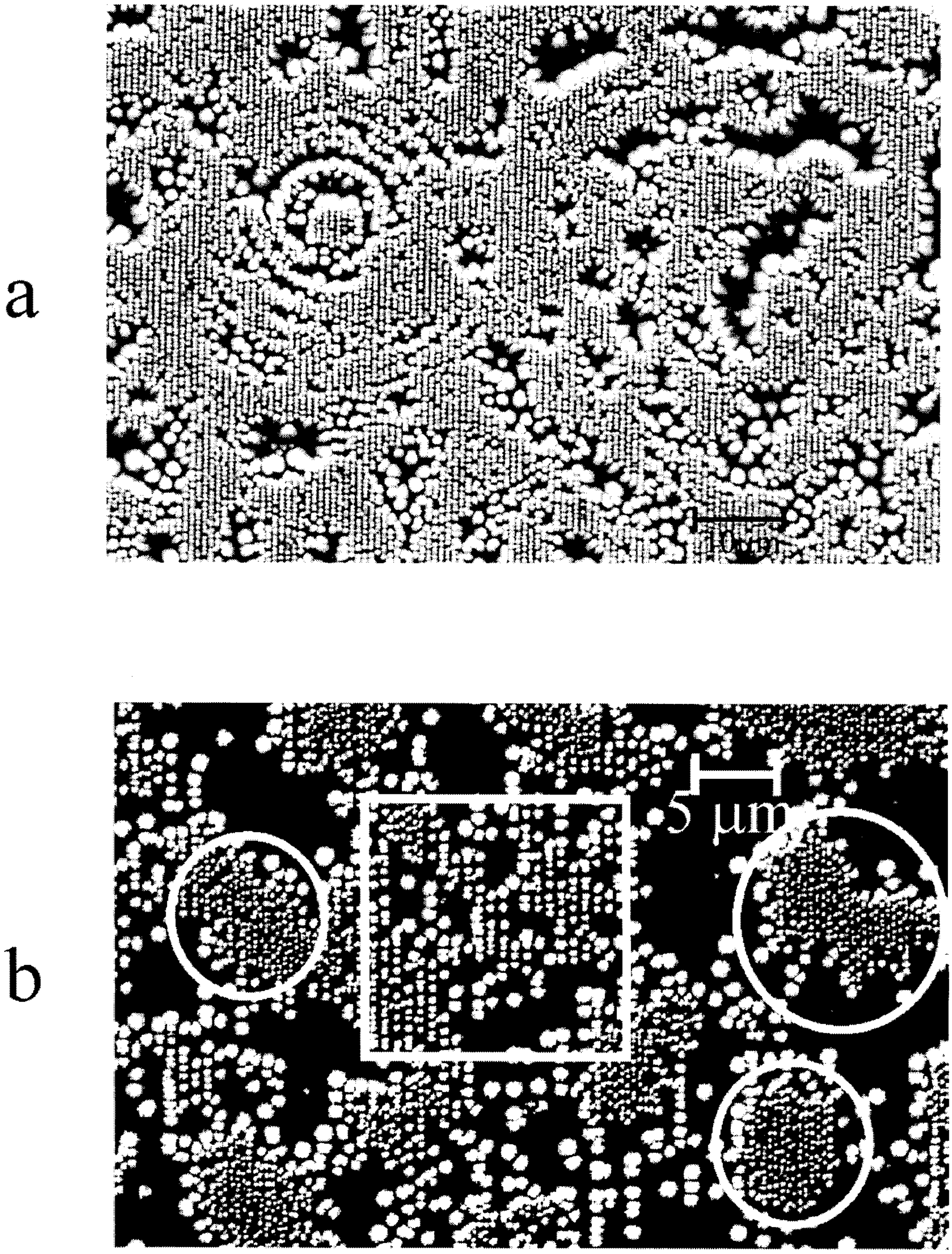


Figure 6