Light Induced Frustration of Etching in Fe doped $LiNbO_3$.

Ian E Barry, Robert W Eason

Optoelectronics Research Centre
University of Southampton
Southampton,
SO17 1BJ
U.K.

Gary Cook

Defence Evaluation Research Agency
Malvern
WR14 3PS
U.K.

Abstract

We report the results of light induced frustration of the normal etching behaviour observed when $LiNbO_3$ is immersed in a solution of HF and HNO_3 acids. Light of wavelength 488 nm, from an air-cooled 100 mW Ar ion laser is incident on the rear surface (+z face) of a thin Fe doped $LiNbO_3$ sample, whose front face (-z face) is in contact with the etchant solution. At power densities of >100 Wcm^{-2} etching is suppressed, through light induced charge migration. Below this power density, partial suppression occurs, leading to submicron scale features, whose orientation follows the crystal symmetry.

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There is considerable interest in etching, structuring. and patterning a wide range of insulators, dielectrics, and semiconductors, for microelectronic and microphotonic device applications. The parameters of most importance for such processes are factors such as etch speed and quality, aspect ratios obtainable, and the degree of complexity associated with details such as lithographic patterning that may be a prerequisite for a process such as electrochemical etching. Techniques may be classified into those that require the use of incident ions, electrons, or photons, such as ion-beam, (including reactive etching), electron-beam or ablative etching, and those that involve wet-etching, which may be a direct electrochemical process, with spatial definition achieved using patterning techniques, or photoelectrochemical etching, which has the added advantage of using spatially patternable light to mediate and control the etching process.

Photoelectrochemical and photoassisted wet-etching has been the subject of numerous recent publications, often involving technologically important optoelectronic materials such as GaN, in both bulk, and thin film formats [1-3]. In all cases, the material is immersed in a cell, surrounded by an etchant such as KOH, HCl, or HF, and exposed to combinations of applied electric field, and light. Preferentially enhanced etching of the material occurs in those areas exposed to light, at intensities that can be quite modest (of order mW cm^{-2} to a few W cm^{-2}). Additional aspects such as etch anisotropy and dopant-selective etching, are also important, and add further versatility [4].

In all reports of photoelectrochemical etching we have seen however, the action of light is to enhance or assist the etch process. In this paper, we discuss the opposite effect that we have

observed in $LiNbO_3$ doped with 0.2 molar % Fe. On exposure to light at 488nm, etching of the -z face is suppressed. Material outside the illuminated area is etched at the normal room temperature rate of ~700 nm per hour, whereas at intensities above ~100W cm^{-2}, etching is completely suppressed. This light induced frustrated etching (LIFE) behaviour is novel to our knowledge, and arises due to the light induced carrier generation within the Fe doped material. The electrons liberated through the photorefractive interaction migrate to the -z face, thereby inhibiting the chemical etching process.

The experimental arrangement used is illustrated in figure 1. The cell is constructed from stainless steel, and PTFE, and the etchant is a 1:2 mixture of HF and HNO_3. This is a typical etchant used for $LiNbO_3$, and has the property that etching occurs preferentially on the -z face of the crystal. In studies performed earlier, we have established that this differential etch behaviour is very pronounced: the +z face remains unetched during -z face etching [5]. Light is incident from beneath the $LiNbO_3$ sample, which forms the entrance window of the cell, with the $LiNbO_3$ oriented so that the crystal -z face is uppermost.

This crystal orientation was also necessary due to the phenomenon of photorefractive two-beam coupling [6]. Under the influence of light, charge carriers are preferentially generated at regions of high light intensity, and retrapped at regions of lower intensity. The resulting space charge field modulates the refractive index through the linear electro-optic effect. The laser light used here illuminates the crystal from below, and suffers a Fresnel reflection from the $LiNbO_3$/etchant interface. Although this produces a reflectivity of only~5%, this is sufficient to generate a standing wave intensity pattern within the crystal, and hence a photorefractive grating. The sign

of the electro-optic coefficient determines the coupling direction between the two beams, and occurs in the direction opposite to the incident beam direction if the crystal +z face is uppermost. Light can thereby be very efficiently reflected from this grating, rapidly (within a few ms at the power densities used) experiencing essentially a 100% efficient reflection. This would seriously impede quantitative study of the LIFE results.

The laser used was an air-cooled Ar ion laser operating at 488nm. This wavelength was chosen as it had the highest power available, and Fe:$LiNbO_3$ is known to be very photosensitive in the blue spectral region. We note that an alternative wavelength that might prove more efficient is 482.5 nm. This corresponds to a resonant energy transfer between Fe^{2+}, and Nb^{5+}, yielding a fairly sharp feature (~2 nm FWHM) in the absorption spectrum [7]. At present we have no access to this wavelength, at powers comparable to the 100 mW used in these experiments.There is a line at precisely this wavelength obtainable from Kr ion lasers however, but to date we have not pursued this route.

As shown in figure 1, light from the Ar ion laser was focussed to high intensity using a single plano-convex lens. Image relaying of objects such as test charts is equally easy, using the imaging system also shown above the etching cell. The light is brought to a focus on the top surface of the $LiNbO_3$, and can in principle be constantly refocussed at an arbitrary height as etching progresses. Location of the beam waist at the correct position was achieved by observing the degree of collimation of the weak back reflection from the front surface of the $LiNbO_3$, after passing back through the focussing lens.

From near-field measurements of the Gaussian beam diameter, beam divergence and the focal length of the lens, the focussed spot size was calculated as 50 μm. The laser produced ~90 mW, which after accounting for losses, reflections and transmission through the $LiNbO_3$, yielded a power of ~25 mW at the top face of the crystal. Assuming the lack of any significant aberrations in the focussing lens, this corresponds to a peak power density of ~2.5kW cm^{-2}. After one hour of exposure, the cell was disassembled, and the $LiNbO_3$ crystal examined initially under an optical microscope, and subsequently with an SEM. Figure 2 shows the results from the SEM, overlayed with calculated power densities incident on the crystal, determined from the known spot size. There are three regions which are easily distinguished here. The central area, labelled A, corresponds to a region which has experienced no etching. From the scale, we see that this extends to a diameter of > 200 μm. Outside this, there exists a threshold area, region B, where etching has been reduced, or partially frustrated. The power density at the boundary between these two regions is of order 1 W cm^{-2}. Beyond this again, in region C, etching proceeds as normal over the rest of the crystal face.

Figure 3, which is a surface profile trace across the $LiNbO_3$, confirms these results. The frustrated area is shown as a vertical feature of height ~700nm. The sides of the feature correspond to the region of partial frustration. An SEM picture has also been taken of this area, to examine the structure in more detail. This is shown in figure 4, and provides an intriguing view of the surface that has undergone partial etching. The feature sizes are of order 200 nm, and the convoluted structure is seen to follow the intrinsic crystal symmetry (space group = R3c, hexagonal symmetry as viewed down the c axis). At present this structure is of curiosity value only.

It is clear therefore that the 488 nm light is acting to stop the etch process. This is an unexpected result, as all other references examined indicate that light promotes rather than frustrates etching. We have so far not tried to obtain frustrated etching using imaged objects, but this is our next goal, as the resolution obtainable, under such charge-mediated etch conditions, needs to be evaluated. Further work on the etch concentration, and temperature will be undertaken. We have already established the etch rate for $LiNbO_3$ at elevated temperatures: at T= 110° C, the rate increases to 55 μm per hour [5].

In conclusion therefore, we have observed an unexpected result concerning light induced etching frustration. In common with other literature on this subject, the microscopic details of the etch process, and hence this etch inhibition are unclear. The role of electron generation, transport, and interaction with the etchant needs to be further evaluated.

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References.

1. M.S.Minsky, M.White, E.L.Hu, Appl.Phys.Letts., **68**, 1531, (1996).

2. C.Youtsey, I.Adesida, G.Bulman, Elect.Letts., **33**, 245, (1997).

3. C.Youtsey, I.Adesida, L.T.Romano, G.Bulman, Appl.Phys.Letts., **72**, 560, (1998).

4. C.Youtsey, I.Adesida, G.Bulman, Appl.Phys.Letts., **71**, 2151, (1997).

5. I.E.Barry, G.W.Ross, P.G.R.Smith, R.W.Eason, G.Cook, Mat. Letts., **37**, 246, (1998).

6. L.Solymar, D.J.Webb, A Grunnett-Jepsen, 'The Physics and applications of photorefractive materials' Clarendon Press, (1996)

7. J-P.Huignard, P.Gunter, 'Photorefractive Materials and their Applications I'. Topics in Applied Physics Vol 61. Springer-Verlag. (1989)

Figure Captions.

Figure 1. Cell used for $LiNbO_3$ etching.

Figure 2. Scanning Electron Microscope picture of the etch frustrated region.

Figure 3. Schematic of sample crossection showing masked, etched and etch frustrated areas, with a profilometer scan of etch frustrated area.

Figure 4. Detail of region C, which has undergone only partial frustrated etching. Note the fine structure present at sub-micron scale lengths.

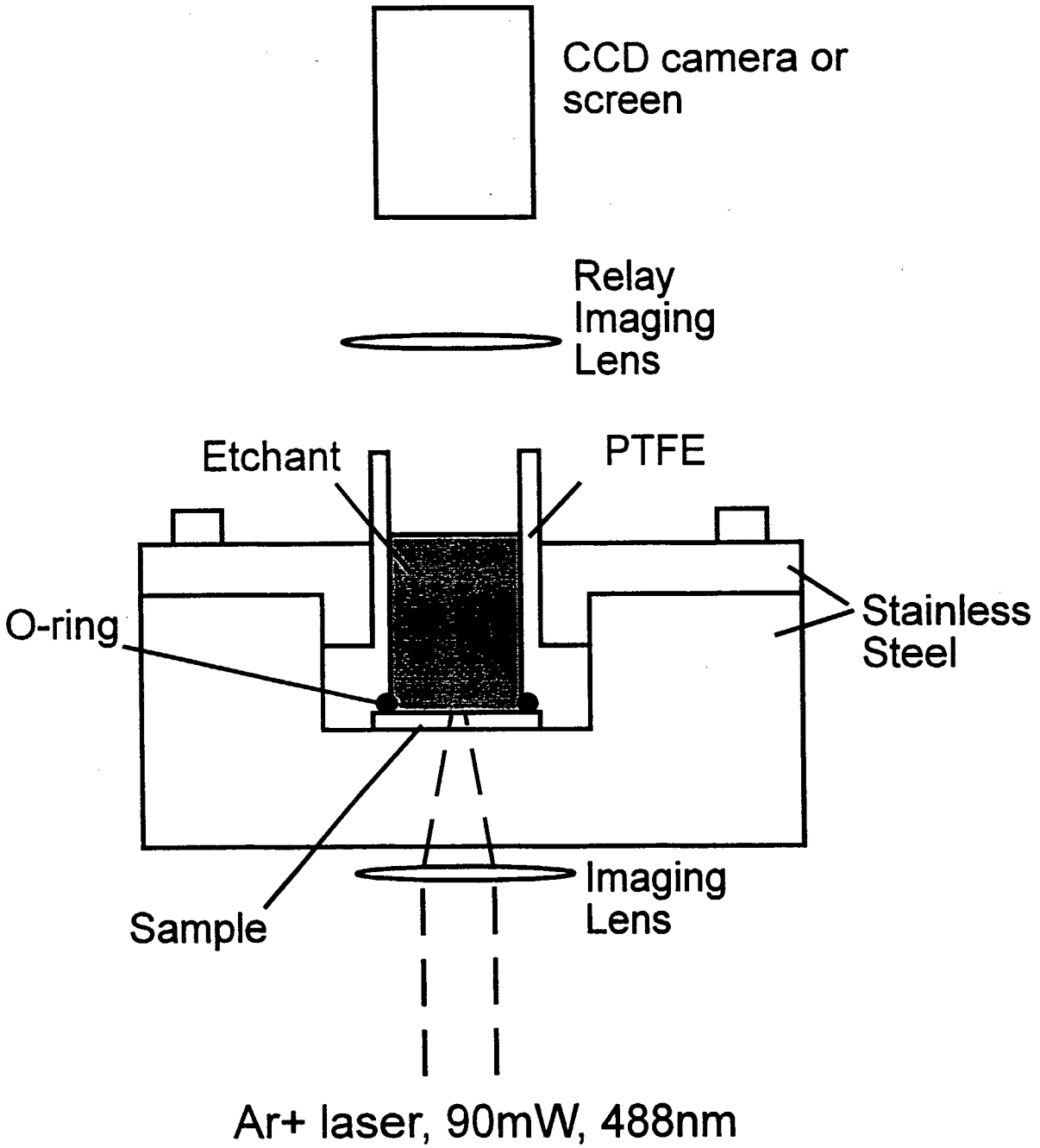

figure 1, BARRY et al., Applied Physics Letters.

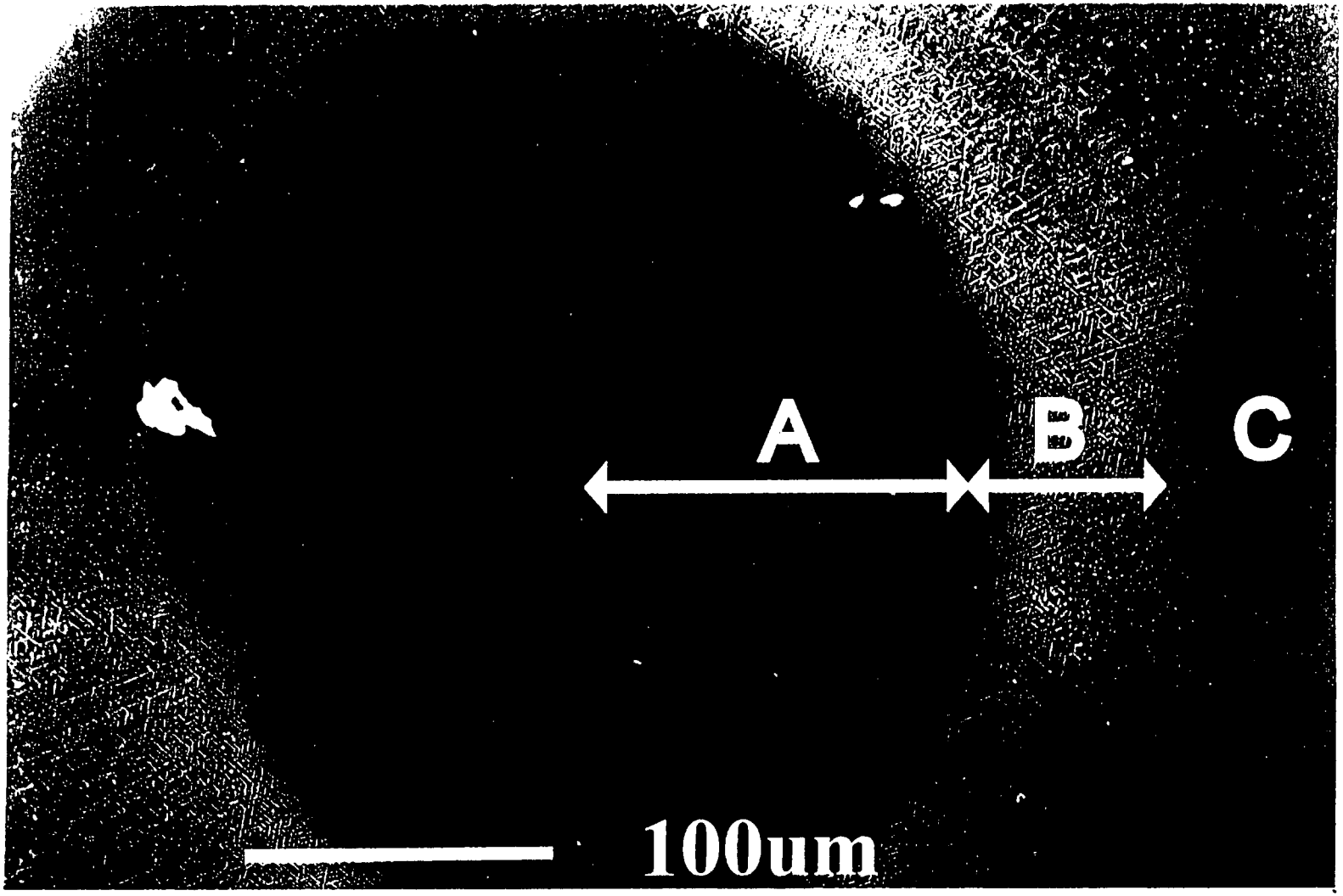

fig 2

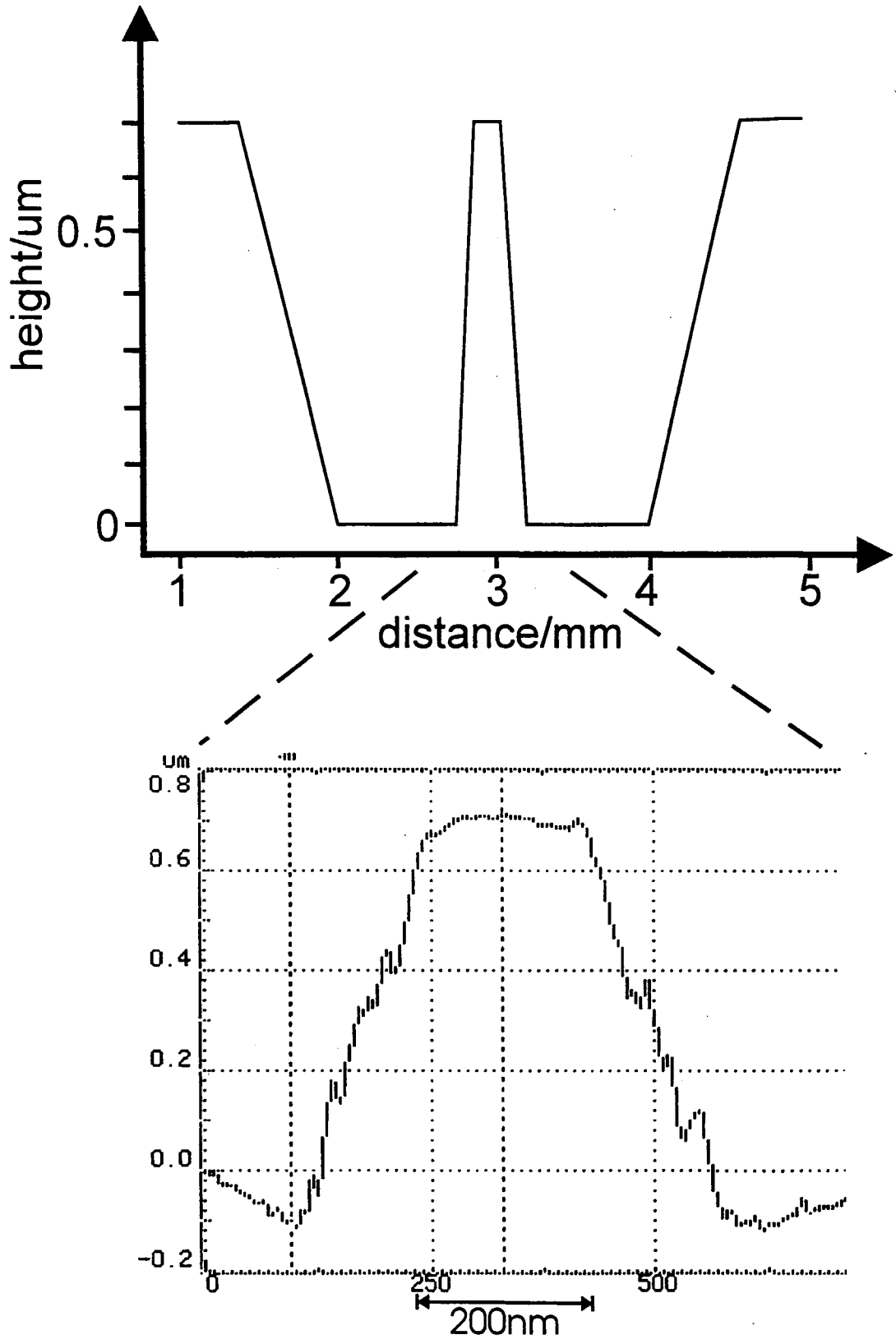

figure 3, IAN BARRY ET AL, APPLIED PHYSICS LETTERS.

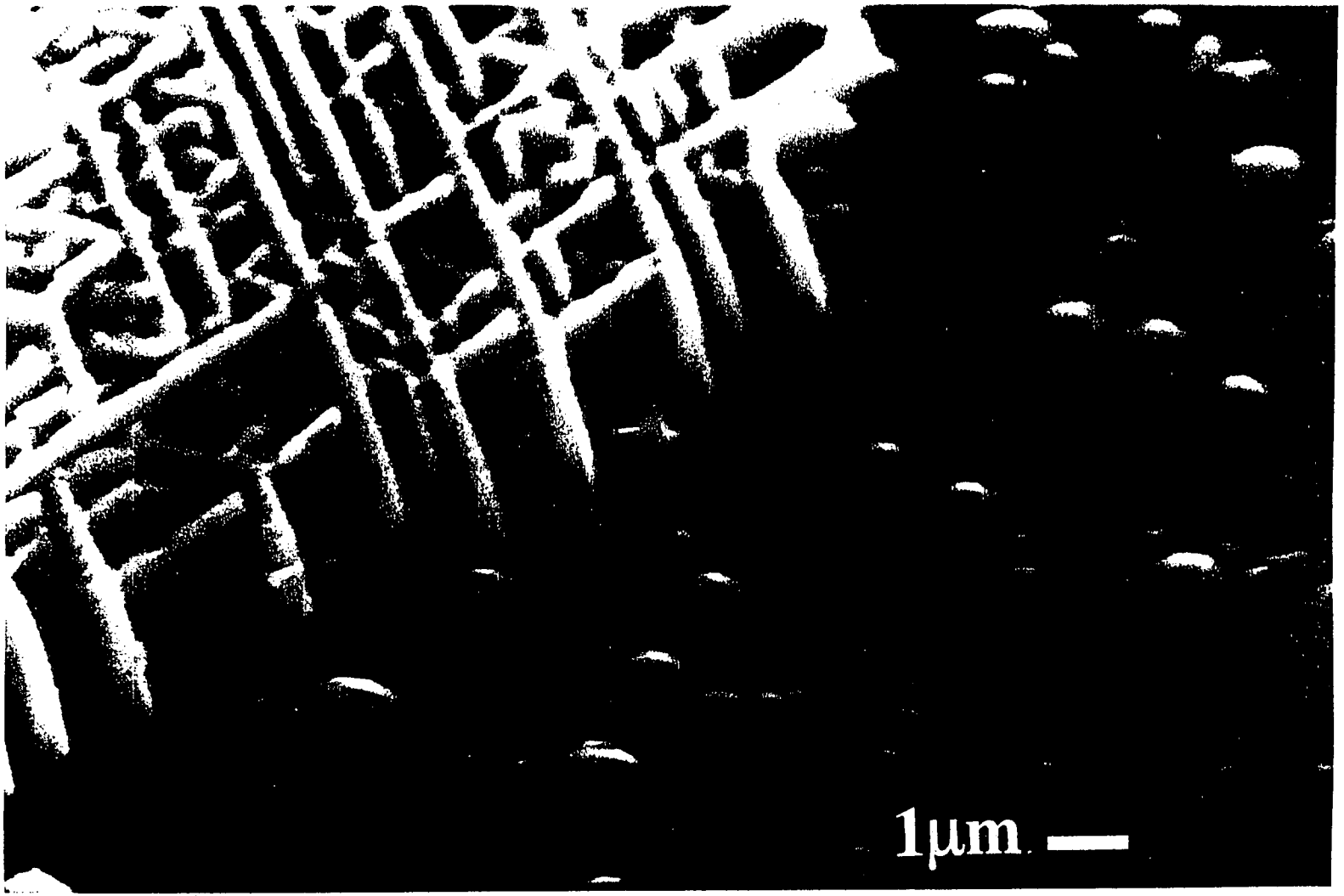

fig 4