Self ordered sub-micron structures in Fe-doped $LiNbO_3$ formed by light-induced frustration of etching (LIFE)

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Abstract

We have produced millimetre-sized areas of self-ordered, sub-micron scale, complex structures in iron-doped single crystal lithium niobate, using the combined interaction of laser light and etching with acid. We report here the factors that influence the formation of the structures, and illustrate the types of structure that may be formed, using images taken by a Scanning Electron Microscope (SEM) and subsequent Fourier Transform analysis of those images. We also consider the physical processes which initiate and control the growth of the structures.

Introduction

Lithium niobate continues to be the material of choice in many spheres of optical and nonlinear-optical research and development. It has found widespread applications in areas of scientific and technological interest such as modulators, frequency conversion and second harmonic generation, surface acoustic wave and electro-optic devices, as well as in optical waveguide devices. The ability to easily create relatively large areas of sub-micron sized structures on lithium niobate could allow the production of many more useful devices, including Bragg gratings and photonic crystals, and also encourage the development of microoptoelectromechanical systems (MOEMS).

The existence of a differential etch behaviour of lithium niobate, when immersed in a suitable etchant, has been known for many years [1] and is a consequence of the ferroelectric nature of the material. This gives rise to a spontaneous polarisation within the crystal, resulting in physically distinguishable –z and +z faces. The etch rate of the –z face is far greater than that of the +z face, which appears to be completely unaffected by the acid mixture [2]. This differential etch property is frequently used to identify the presence of ferroelectric domains within a crystal, and can also be used as a tool for producing three dimensional structures on the surface of ferroelectrics, such as micro-cantilevers [3].

In this paper we report on advances in creating sub-micron scale structures in iron doped single crystal lithium niobate (Fe:$LiNbO_3$) using the light-induced frustration of etching

(LIFE) process, first observed by Barry *et al* [4] and further investigated by Boyland *et al* [5]. We have studied the influence of the different variables in much greater depth than previously, and have developed a more extensive understanding of the process taking place, allowing us to develop the ability of this technique for structuring lithium niobate.

The LIFE process uses the differential etch rate of z-cut lithium niobate combined with the presence of visible (blue-green) laser light, focussed on to the -z crystal face which is *simultaneously* being exposed to the acid. The light modifies the etching characteristics of the crystal; doped lithium niobate is used intentionally to enhance the absorption of such visible-wavelength light. Increasing the Fe concentration also serves to enhance the photovoltaic effect and the photoconductivity; two important factors in determining the resultant scale-length and regular patterning observed in the LIFE process.

In Barry's original paper [4], a surprising discovery was made; when the –z face of a lithium niobate crystal was exposed to an acid mixture, whilst undergoing exposure to 488 nm blue light from an argon ion laser, the etching rate was found to be reduced to near zero. It had been expected that etching would be enhanced by the presence of light; instead it was found to be reduced or frustrated. In total, three different regimes of etching were observed. Where the beam was most intense (> 100 W cm^{-2}), etching was completely frustrated, while the areas of the crystal that were not exposed to light experienced etching as normal. However, in the regions of intermediate or low intensity (in the wings of the incident laser beam for example) between these normally etched and etch-frustrated areas, a small area of partial frustration of etching was seen, characterised

by the formation of submicron scale features. Boyland [5] showed that it was possible to modify the technique to favour the deliberate creation of such features instead of achieving complete frustration, by reducing the laser intensity to below some threshold level.

We report here the results of a thorough study of the influence of factors that can be used to control the features that are produced, such as the iron dopant concentration, the duration of etching and the intensity of the light. We also discuss the complex and often visually striking patterns that are formed and present a study of the SEM images using 2-dimensional Fourier transform analysis.

Experimental Method

The lithium niobate crystal was placed in a specially designed acid-resistant cell, made from PTFE. This allowed exposure of the –z face of the crystal to the etchant, a 2:1 mixture of nitric (HNO_3) and hydrofluoric (HF) acids. The crystal was, at the same time, illuminated from below, by a 300 mW continuous wave green laser beam at 532nm, produced by a frequency-doubled Nd:YAG laser. The effects of beam size and hence intensity were investigated by adjusting the position of a focussing lens placed before the crystal. Experiments were also conducted using crystals of different iron dopant concentration (0.2 % to 0.01 %) over varying times of exposure. Samples were subsequently examined by Scanning Electron Microscopy (SEM).

Results

Following etching in the presence of loosely focussed green laser light incident on the –z crystal surface, we observed extended areas (<1mm) of intricate patterns showing small complex structures and features of regular periodic nature.

Figure 1(a) shows an SEM image of a site created on a 0.03 % Fe:$LiNbO_3$ crystal. The incident laser beam had a Gaussian profile and was tightly focussed to a spot size of $\omega_0 \approx$ 25 μm. The three regimes of etching, mentioned earlier, are visible, and more apparent in fig. 1(b). At the edge of the site (labelled A), etching has taken place as usual, while in the centre (C), etching has been largely prevented. The effect of total frustration of etching on surface topography can be clearly seen from the surface profiler trace, shown in figure 2. Surrounding the total frustration is an area of partial frustration (region B), consisting of intricate patterns made of lines and dots. The patterns become denser towards the centre of the site where the laser intensity is at its maximum.

The size of the site and the structures that are formed at a particular point on the crystal are highly dependent on the local laser intensity, etching time, and hence the total laser exposure. Figure 3(a) shows a site that was created using a deliberately defocused beam, with a larger spot size ($\omega_0 \approx$ 80 μm), and therefore a correspondingly lower power density. The iron dopant concentration was 0.1% in this experiment. The SEM image reveals a much larger site than previously (with a diameter of approximately 2mm compared to the 350 μm of the previous experiment), consisting mostly of partially etch-frustrated features. The expanded view, fig 3(b) shows a representative example of the

complex and visually intriguing patterns which are formed towards the edge of the site. It is clear from this figure that the pattern formation is deterministic and follows rules of both symmetry and scale.

Figure 4 further illustrates the difference in the structures that are formed within the partially etch-frustrated region of the site. The crystal used here was again 0.1% Fe-doped lithium niobate. Figure 4(a) was taken at the extreme edge of the site, while figure 4(f) shows the centre. The other images were taken at regular intervals between the edge and the centre of the site. Figure 4(a) shows the typical pattern found at the edges, where the laser intensity is very low; the structures are well spread out and have narrow line widths. It is also clear that some of the lines are composed of even smaller point-like structures. It appears that the lines form along one of three directions, 120° apart, suggesting a close affinity for patterning along the three equivalent trigonal axes of the crystal unit cell. As we move closer to the centre, figures 4(b) and 4(c) show denser packing of the structures, with the etch-frustrated lines curving around one-another to fill the available space. This trend continues with images shown in figures 4(d) and 4(e), until the centre, 4(f), where the intensity is greatest, the etching is almost totally frustrated and the packing density is high enough to prevent any observable orientational preference.

The concentration of the iron dopant also determines the shape and extent of the patterns that are formed. Dopant concentrations between 0.03 to 0.2% give broadly similar results, however, a concentration of 0.01 % Fe produces a very different looking site as

illustrated by figure 5. This image represents the entire site, and when compared to similar pictures taken on other samples it is clear that the structures are much wider (approximately 2.5 μm) than those obtained using higher dopant concentrations (approximately 0.5 μm wide). There is also far less variation in both line density and width over the whole of the site.

The results discussed thus far were obtained using the *simultaneous* exposure of the sample to acid and laser light, for at least one hour. However, we have also observed that if a sample was left in the acid, with the illuminating laser turned off, these structures remained. Additionally, the height difference between the structures and the surrounding area continued to increase, indicating that once formed the structures can continue to grow, without the presence of light. Their etch-resistant nature therefore seems to require initial exposure to light to start, but once formed, the features remain etch-resistant. However the sequential process; illumination *followed* by etching, produces no etch resistance.

The final aspect we investigated was the influence of the duration of etching. Figure 6 shows the widths of the lines formed after 3 different etching times (20, 40 and 80 minutes), at different positions from the centre of the site. As before, close to the centre no lines are formed; only the smaller 'dots', with high packing density. Further out from the centre, thick lines are observed, which become narrower as the distance from the centre increases. Longer etching times produce larger sites, but the relationship between width and distance stays approximately the same. The 20 minute sample had only one

area, near the edge of the site, which showed lines with widths that could be measured. We have observed, however, that structures begin to form after only five seconds of simultaneous exposure to acid and light, although lines do not develop after this short time.

We are currently attempting to seed ordered and highly periodic line growth via a structured illumination pattern, rather than an unstructured Gaussian beam, using a phase mask or other interferometric technique. It is clear that the mechanism for line formation is already predisposed to such regular periodic structuring, as shown in figure 7. In this case, the illumination was such that a central totally frustrated region was formed, while around the edge of the region, 120° oriented array of lines appeared. As shown in the expanded view in figure 7(b), these lines are not random in their spacing. The growth appears to favour a quasi-periodic patterning, to the extent that lines that are initially too closely spaced will terminate (as shown by the # in the figure) whereas lines that are of the 'correct' spacing (shown by *) will grow and increase in extent. As discussed further below, this behaviour is characteristic of a charge-mediated process, where charge generated at or near the surface seeks to minimise the energy due to repulsion with neighbouring charge of the same polarity. Regular ordered arrays represent the minimisation of energy of such mobile charge. This is to be compared to the picture shown in figure 8, where highly complex patterning has occurred, with some obvious scale-length, but the density of packing is too high to allow unrestricted growth of periodic lines.

Discussion

We have shown that it is possible to produce large areas of submicron structures on the –z face of iron doped lithium niobate, using the light induced frustration of etching technique. The formation of structures is highly dependant on the local laser intensity, iron concentration and the duration of etching. Patterns have been seen to form after only 5 seconds of exposure to acid and light. The SEM images presented in figures 3 - 5 show patterns that cover areas of millimetre dimensions; with lines that form preferentially along one of three directions at 120° to each other (this is particularly evident at the edges of the site as shown in figure 7, where structures have room to grow). It is evident that this behaviour is related to the underlying trigonal symmetry of the crystal. At the centre of the site, where the laser intensity is greatest, features are tightly packed together, forming a smooth unetched area, if the light is sufficiently intense, but towards the edges of the site lines form that can extend for distances greater than hundreds of microns.

We have used 2 dimensional Fourier transform analysis to find the spatial frequencies present in the SEM images and figure 9 shows three typical examples of the transform results. Figure 9(a), using an SEM image taken at the edge of a site confirms that there are indeed three favoured directions, while 9(c), using an image taken at the centre of the site does not have any corresponding directionality, but shows a characteristic scale length. Figure 9(b) is between these two extremes and shows lobes in the Fourier transform pattern that are broader, representing more variation in the directions of the lines from the 3 favoured directions. It is clear that these preferred directions mirror the underlying trigonal crystal symmetry of lithium niobate, but at present we are still

investigating both the origin of these structures and the implications of the micron scale lengths observed.

It is thought that the observed patterns are formed initially from localised spots, which are created by the interaction of light with the iron dopant, through the photovoltaic effect. The number of spots that are formed is dependant on the intensity of the light, hence at the centre many spots form and are therefore tightly packed. However, at the edges the laser intensity is lower, due to the Gaussian beam profile, so fewer spots occur. These may then grow as the surrounding areas are etched away, and so form lines. More complicated patterns can then arise to fill the space between the lines.

The existence of etch hillocks formed during chemical etching of the –z face of lithium niobate is well known, and was first reported by Niizeki *et al* in 1967 [6]. These etch resistant centres are revealed during normal etching (ie without the presence of light), resulting in etch hillocks on the –z surface and corresponding etch pits on the +z crystal face. The origin of these features is thought to be due to the presence of microdomains, which are very small needle-like domains of opposite polarity to the surrounding bulk area [7]. A microdomain on the –z face of the crystal would be positively charged, (a small area of +z character) and would therefore resist etching, resulting in a hillock. Later studies by Holstein [8] suggest that dislocations can also be responsible for the formation of etch hillocks and pits, with large pits being attributed to microdomains, and smaller pits due to dislocations. The experiments by these authors provide some interesting parallels to our results, but with some significant differences. The presence of

microdomains would explain the raised, etch-resistant areas we observe in the LIFE process. However, this would imply that the laser light is creating the microdomains, and in the case of total frustration, a very large-area microdomain. However, the light needs to be present simultaneously with the acid for frustrated etching to occur; exposure to light, followed by etching does not give rise to any features. Therefore, if indeed domains are formed, then they are unlikely to be permanent. As only one face is exposed in our experiments, it is not known whether corresponding etch pits could be formed, if both sides were etched (although etching of both sides of a LIFE sample after the initial experiment does not produce any topographical features on the +z face). This further suggests that any domain inversion is only temporary. Temporary formation of surface domains is all that is required however, to instigate etch frustration. Even a superficial cap of domain inverted material will prevent etching, and will hence shield material underneath.

An alternative mechanism is that of charge liberation within the crystal following exposure to laser light, caused by the photovoltaic effect. Subsequent migration of the charge to the surface region between the crystal and the acid etchant, then serves to frustrate etching. The formation of quasi-periodic structures, as seen in figure 7, suggests a charge mediated mechanism: the surface charges will arrange themselves into their lowest energy configuration, and hence form periodic surface patterns, in this case leading away from the centre of the site.

Our next direction must clearly be to further understand, and thereby control the exact periodicity, and consequently seed the growth rather than have it occur naturally. This would make the LIFE technique of significant technical as well as scientific interest, and could be used for efficient fabrication of devices.

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Figures

Captions

Figure 1(a): Typical site formed during the LIFE process on 0.03% Fe-doped $LiNbO_3$,

Figure 1(b): Magnified image showing the partially-frustrated structures that are formed near the edges of the site.

Figure 2: Surface profile of the LIFE site, showing the etch-resistant nature, after 2 hours exposure to etchant.

Figure 3(a): A larger LIFE site produced using 0.1% Fe:$LiNbO_3$ and a defocused beam

Figure 3(b): Magnified view showing large areas of complex feature formation.

Figure 4: Types of structures formed in a LIFE experiment for a 0.1% Fe:doped sample, at various points over the site. a) is on the edge of the site, and f) is at the centre of the site.

Figure 5: LIFE sample using 0.01% Fe-doped $LiNbO_3$; patterns are very different to those formed using a 0.1% dopant concentration.

Figure 6: Variation of line width with position from the centre of the site, for 3 different etching times.

Figure 7: 0.03% Fe-doped LIFE sample, after 8 mins etching. Note the clear 120° edge symmetry in (a) and the regular line spacing and evidence of quasi-periodic growth in (b)

Figure 8: A LIFE sample produced using 0.1% Fe:$LiNbO_3$ crystal; complex patterns are formed, with evident trigonal symmetry, over extended areas.

Figure 9: SEM images taken at various points of a site, and their corresponding Fourier transforms. a) edge of site, c) centre of site

Figure 1

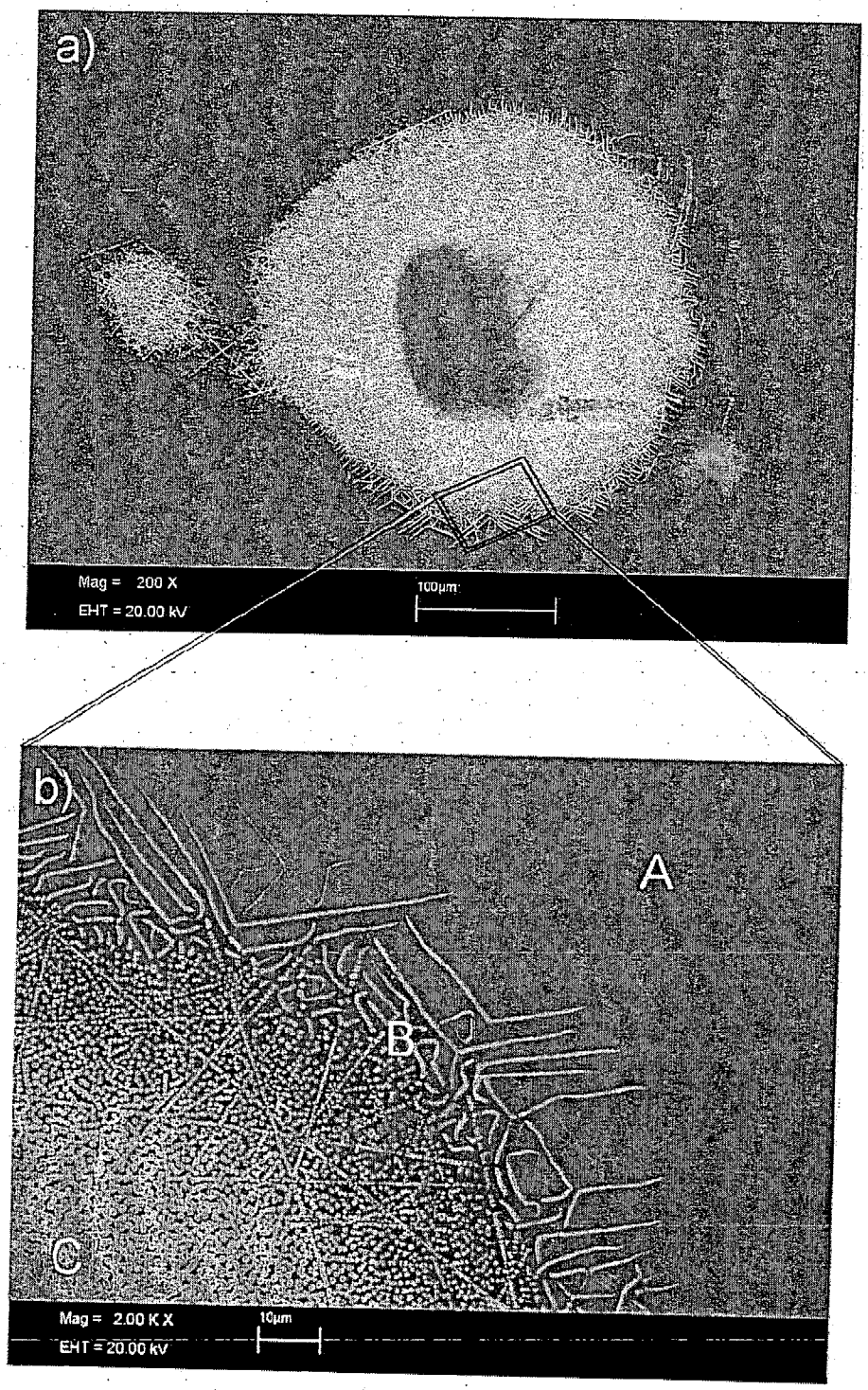
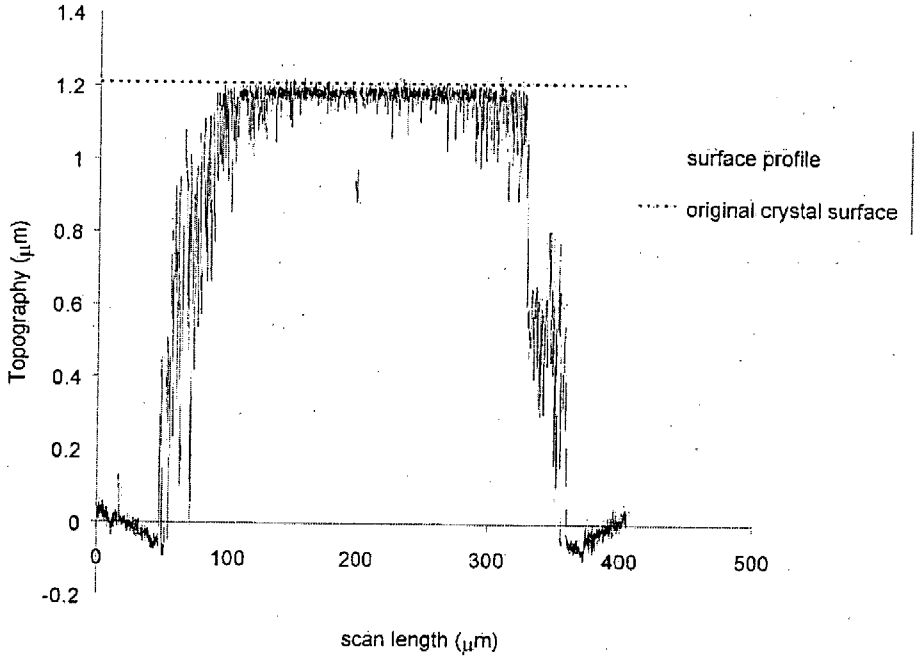


Figure 2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scan length (μm)
surface profile
original crystal surface

Figure 3

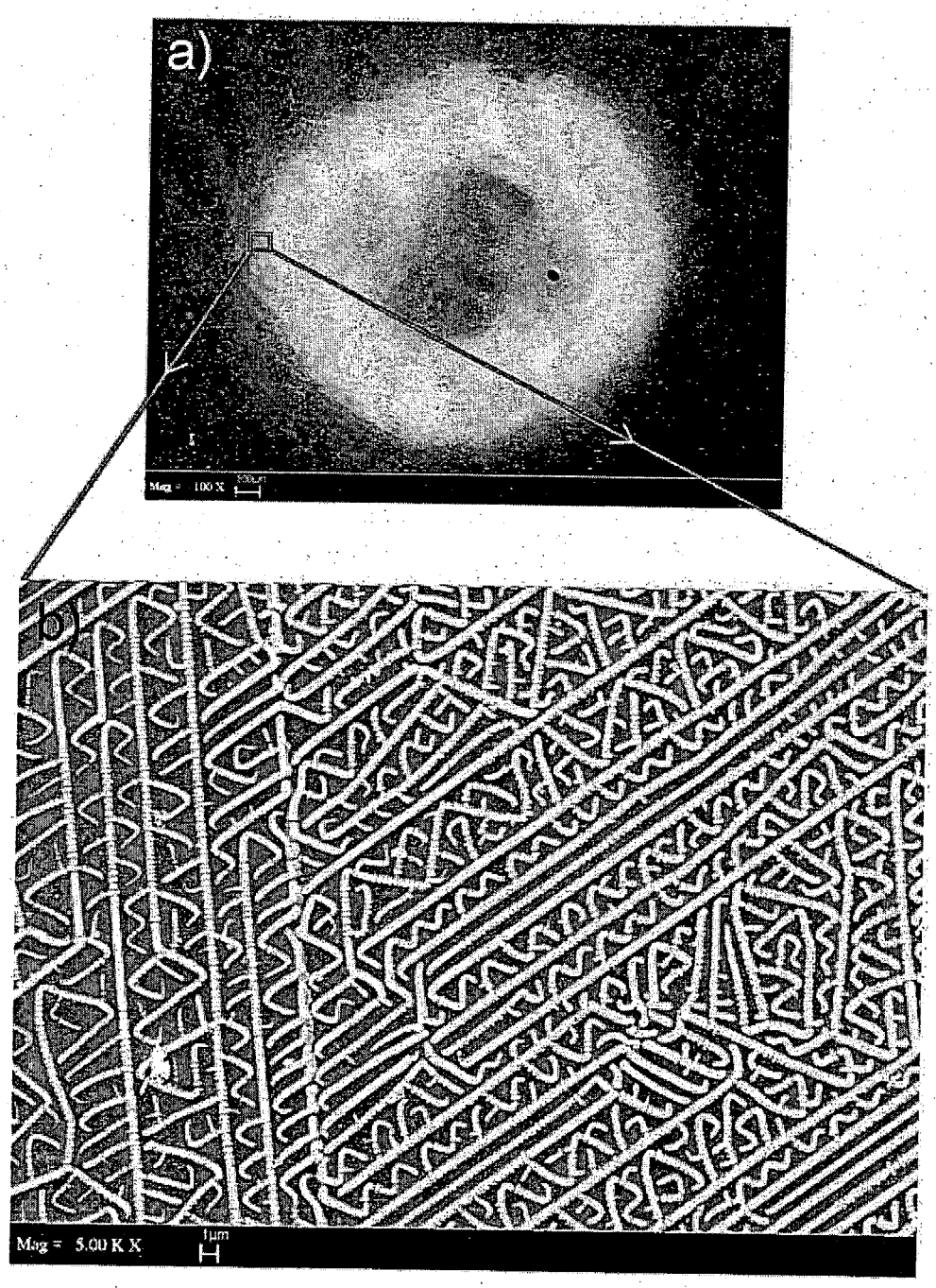


Figure 4

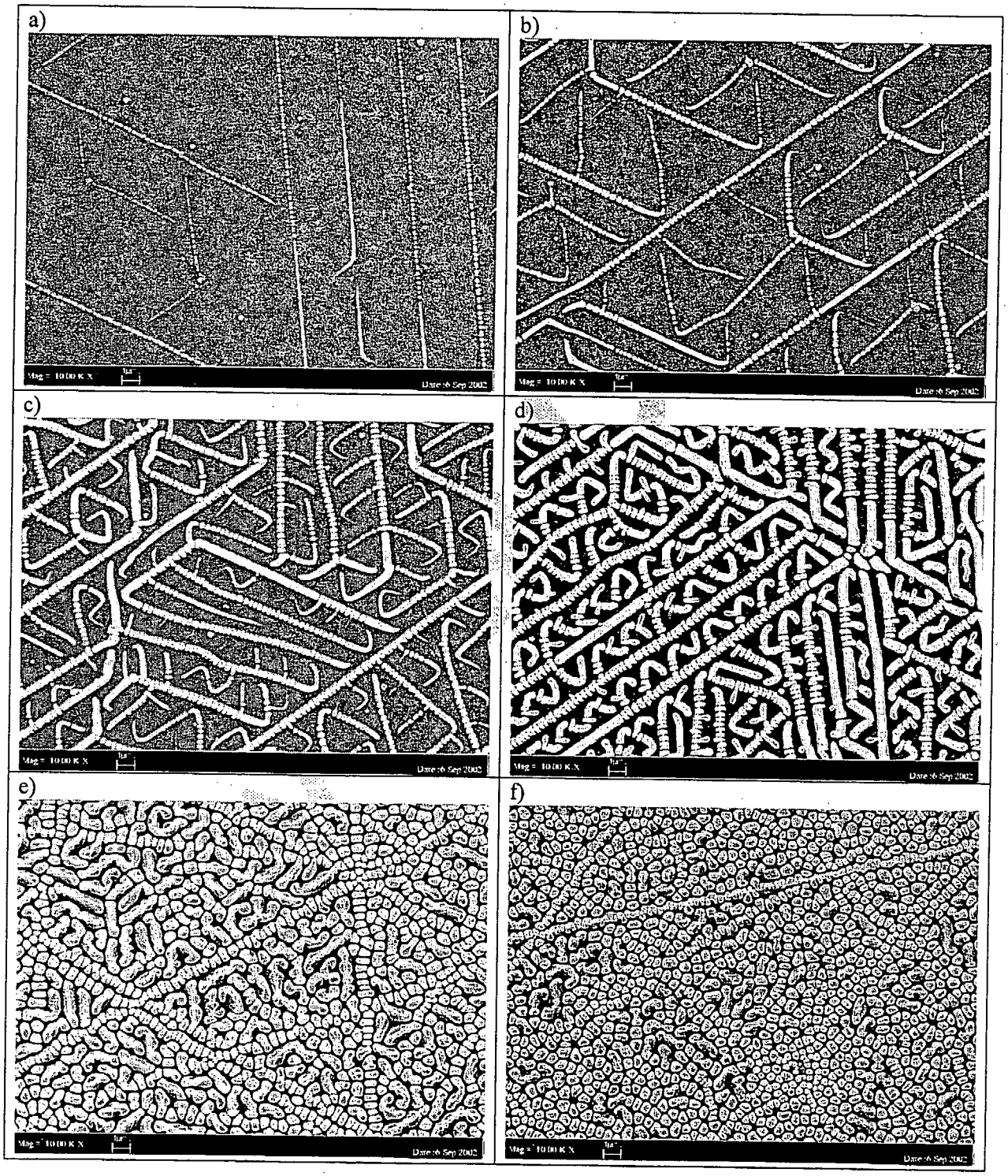


Figure 5

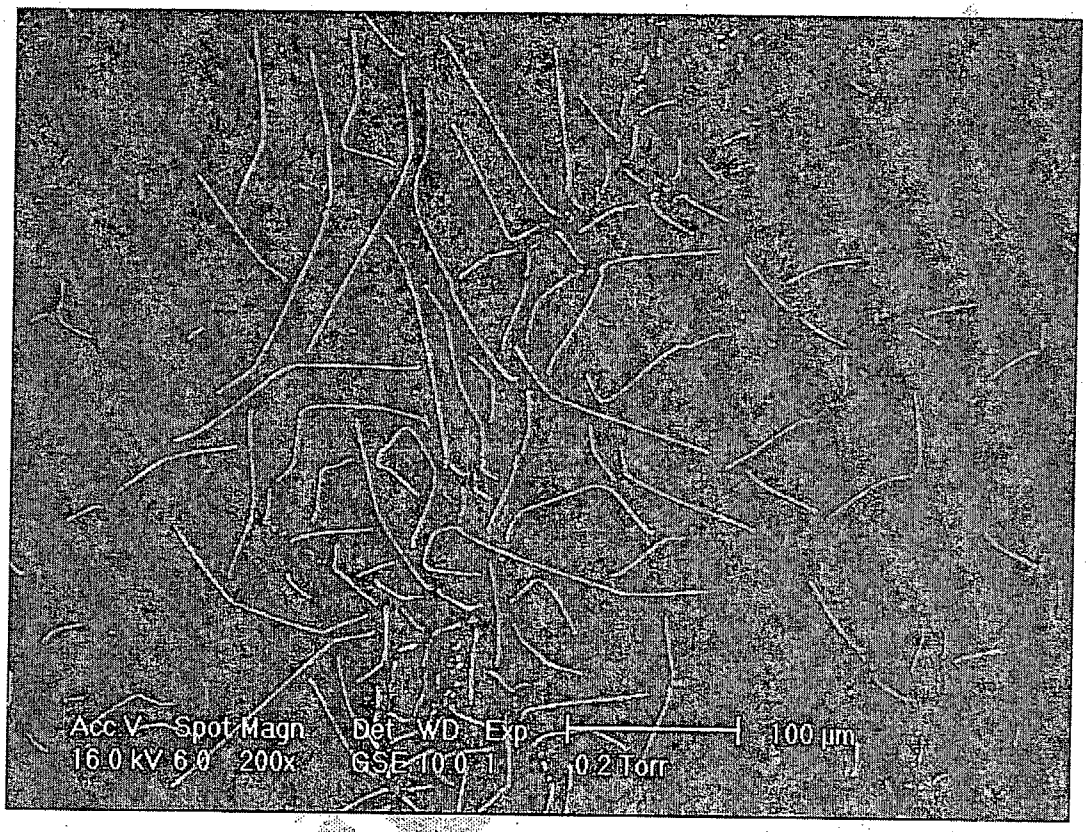
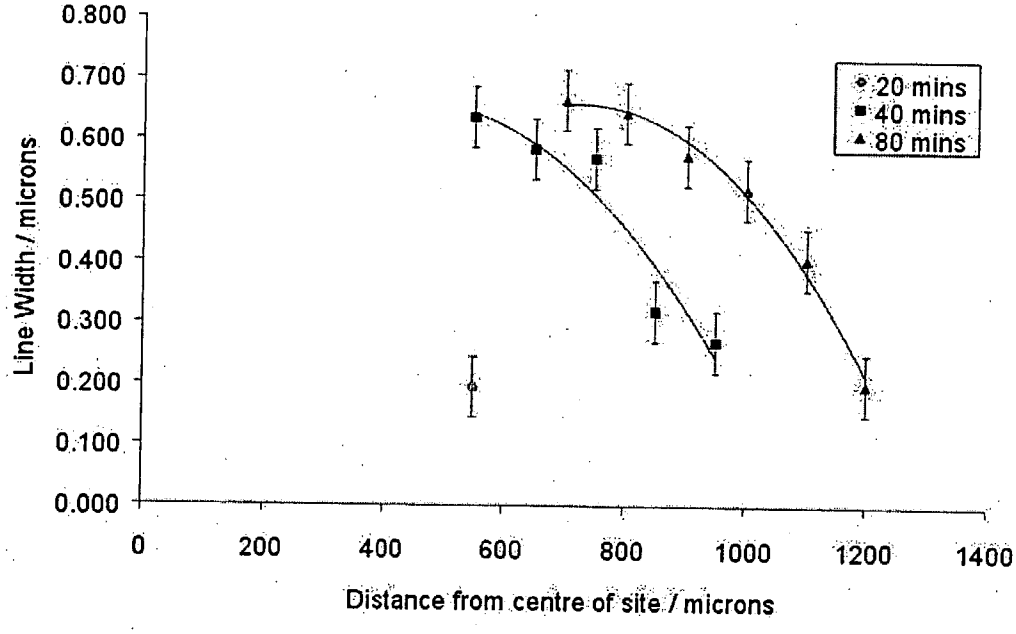


Figure 6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800
1000
1200
1400
Distance from centre of site / microns
20 mins
40 mins
80 mins

Figure 7

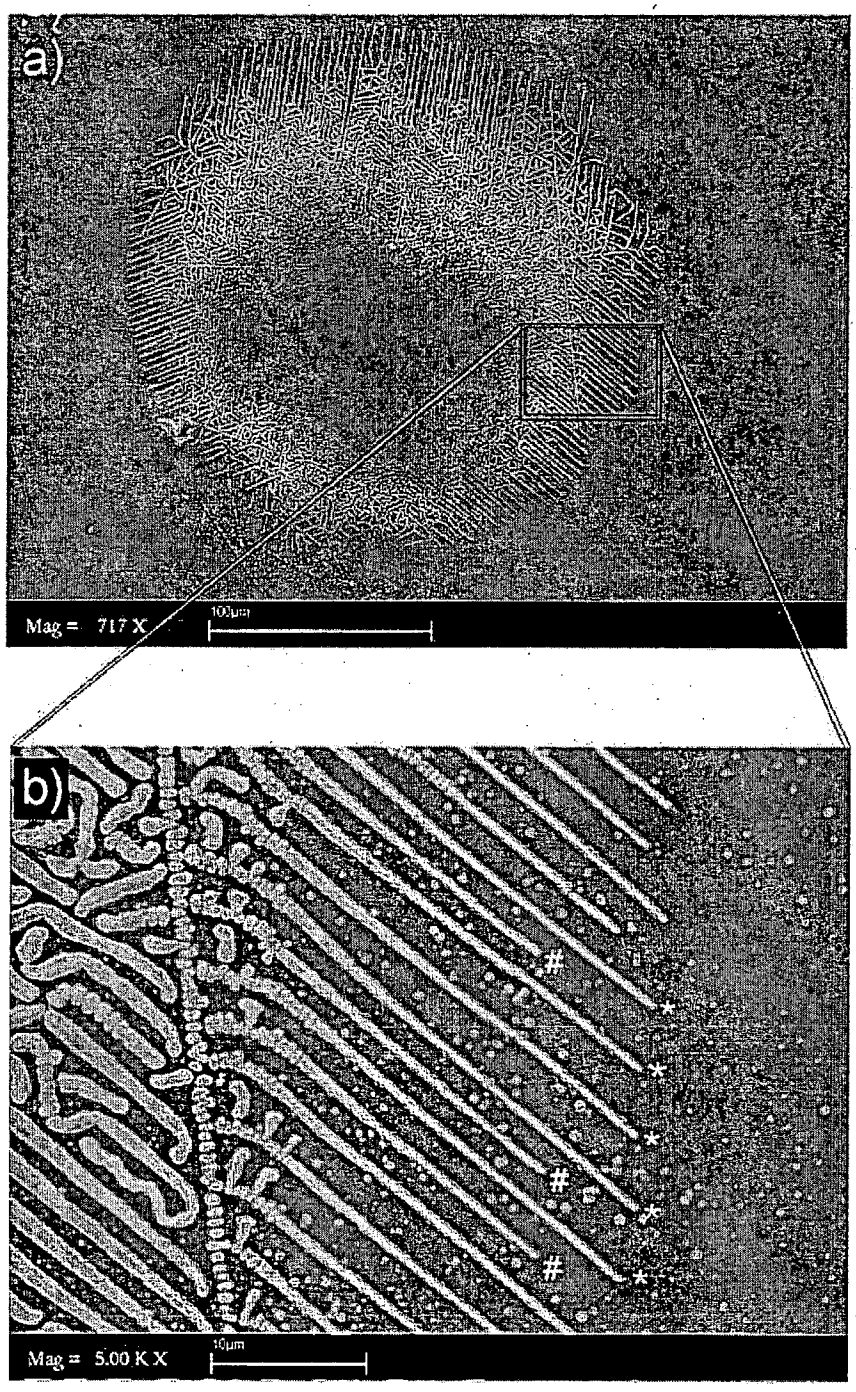


Figure 8

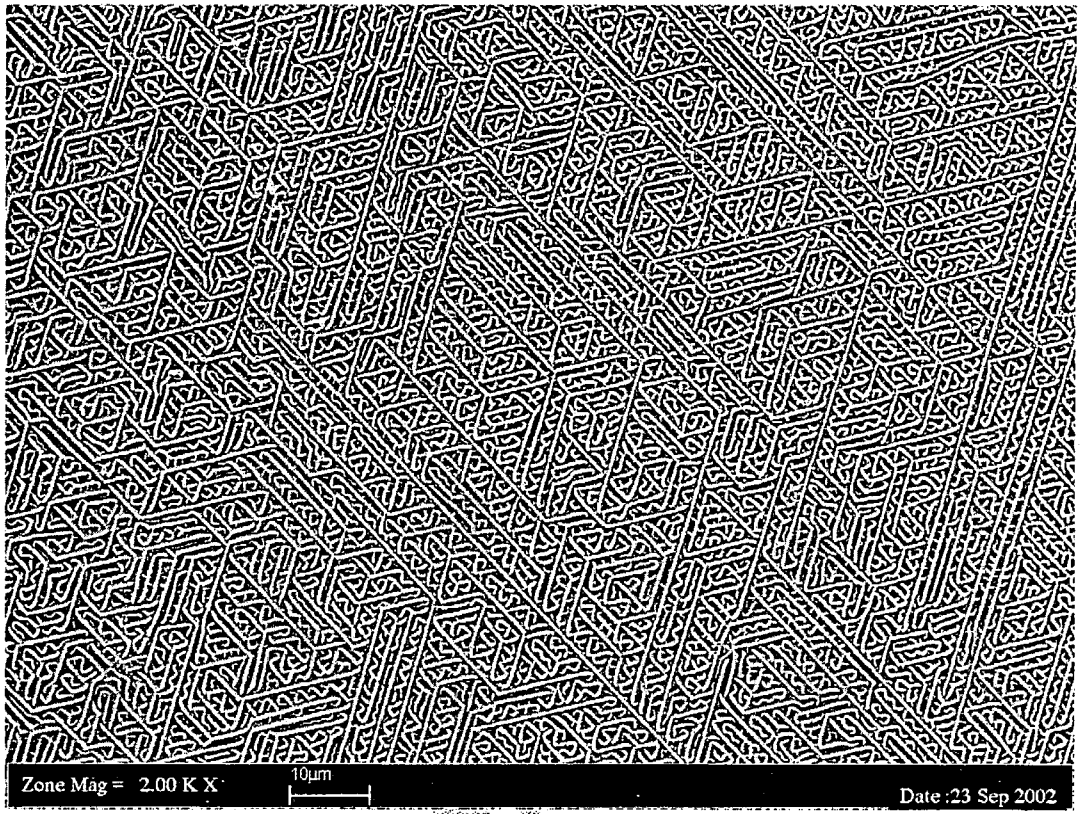
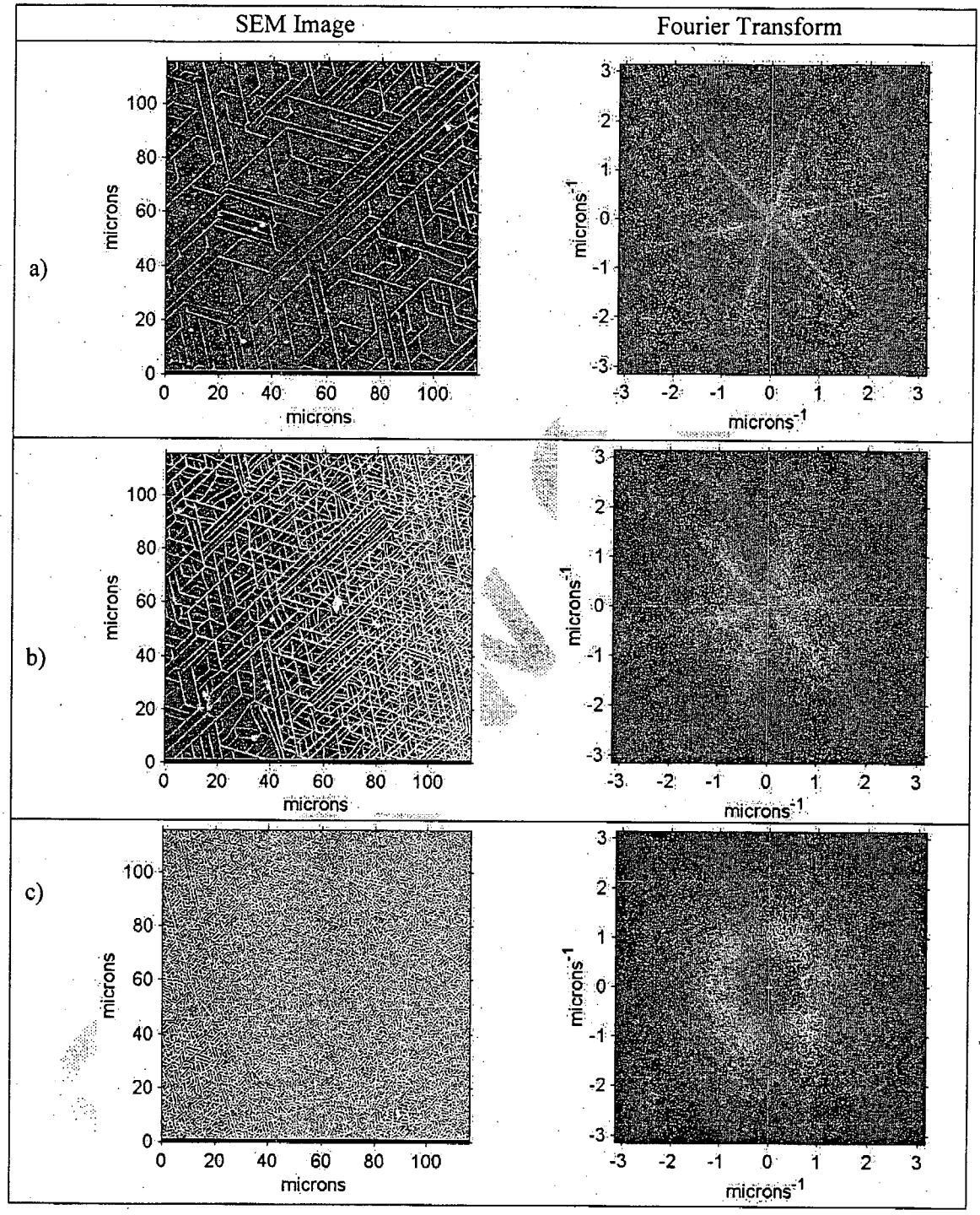


Figure 9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Fourier Transform
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microns^{-1}
microns^{-1}
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