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Continuous wave ultra violet radiation induced frustration of etching in lithium niobate single crystals.

S. Mailis[a], C. Riziotis, P. G. R. Smith, J. G. Scott, R. W. Eason

Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ

Abstract

Illumination of the –z face of congruent lithium niobate single crystals with continuous wave ultra violet (UV) laser radiation modifies the response of the surface to subsequent acid etching. A frequency doubled Ar+ laser (λ=244 nm) was used to illuminate the –z crystal face making it resistive to HF etching and thus transforming the illuminated tracks into ridge structures. This process enables the fabrication of relief patterns in a photolithographic manner. Spatially resolved Raman spectroscopy indicates preservation of the good crystal quality after irradiation.

Submitted
Appl. Surf. Science
July 2002

PACS: 77.84.Dy, 81.65.Cf, 42.70.Mp
Keywords: Lithium niobate, Ultra violet radiation, chemical etching, surface patterning

a Corresponding author. e mail: sm@orc.soton.ac.uk, tel:++44(2380)593141 fax: :++44(2380)593142

1. Introduction

Differential etching provides a powerful tool for surface microstructuring of lithium niobate single crystals. The z faces of lithium niobate single crystals etch differentially in HF or HF:HNO_3 acid mixtures depending on the orientation of the ferroelectric domains. More specifically the –z face etches at a rate of 1.7 μm/hr in 48% HF at room temperature while the +z face remains unaffected [1]. Hence, by electric field poling parts of the surface of an initially single domain crystal it is possible to fabricate surface relief structures [2,3]. A suggested explanation of the effect is given in [1] where the microscopic bond strengths were held responsible for the observed differential etch behaviour.

Suppression of etching has also been demonstrated in the –z face of z-cut Fe:doped lithium niobate ($LiNbO_3$) single crystals using continuous wave visible laser radiation at a wavelength of 488nm [4]. An explanation for the effect involves the role of photoexited Fe ions in the crystal. Fe ions both increase the absorption of the light, and also generates mobile charge carriers which can interact with the electrochemistry of the etch process.

However in undoped crystals the number of photoexited defects at visible wavelengths is limited. As the band gap of the crystal is at E_g~4.0 eV [5] the main absorption mechanism is through intraband excitation, when ultra violet radiation with photon energy higher than the band gap is used. In this paper the latent frustration of etching induced from continuous wave (c.w.) UV laser irradiation is presented for undoped crystals.

2. Experimental procedure.

A frequency doubled Ar^+ laser (λ=244 nm) was used for the UV exposures. As shown in the outline of the experimental setup which is shown in figure 1 the laser beam was transmitted through an acousto-optic modulator (AOM) which controlled the laser power delivered on the sample. The first order diffracted light from the AOM was passed through a spatial filter, for wave-front cleanup, which also acted as a x3 beam expander, and was then directed through an optical system and was focused on the sample surface using a 35 mm plano-convex lens which was mounted on a translation stage allowing movement along the z axis. The calculated spot size on the sample surface was 1.7 μm at the focus of the lens but could be varied by changing the sample-lens distance.

The sample was mounted on a set of high precision computer controlled x-y translation stages with a positioning accuracy of 50 nm using optical encoders. The lithium niobate samples were scanned in front of the focused beam at scanning speeds that varied from 10 mm/min to 3000 mm/min. For the experiments which are presented here the exposure conditions were varied by changing the scanning speed and the laser power while the spot size was kept constant at the value of 1.7 μm.

In figure 2 a plot of the corresponding energy fluence versus the translation stage velocity for different laser powers is depicted which illustrates the range of exposure conditions. In this plot three different fluence regimes can be identified: i) for energy fluence above 200 J/cm^2 severe surface damage is observed and spatially resolved Raman spectra suggests melting of the surface ii) below 30 J/cm^2 no surface damage is observed, and iii) the intermediate fluence range regime where minimum surface damage is observed but no indication of surface melting is evident from micro-Raman

spectroscopy data. In order to avoid severe surface damage, the scanning speed was kept at high values (3000 mm/min) while the power of the beam was varied between 20 mW and 50 mW. The samples were exposed at constant speed in lines separated by 9 μm while the length of the illuminated lines was of order a few cm. After the UV exposure the samples were etched in 48% HF acid at room temperature.

3. Results and discussions

After UV illumination a set of ridges was revealed after 15 minutes of etching on the –z face. The ridges are shown in the atomic force microscope (AFM) scan of the surface presented in figure 3a. The illumination was performed at a laser power of 50 mW corresponding to an energy fluence of 30 J/cm^2 . The height of the ridges was of order 400 nm as measured with an a-step. The a-step scan which is shown in figure 3b was performed at an oblique angle with respect to the ridges in order to compensate for the poor spatial resolution of the device. Another sample was exposed to UV under the same conditions but this time etched for 1 hr. In the large area SEM scan of the surface after etching which is presented in figure 4a the illuminated part is clearly distinguished from the unexposed and uniformly etched part and the large scale uniformity of the ridges can be seen. The height of the ridges measured as before with the a-step (shown in figure 4b) is 1.7 μm. The ridge heights measured for both samples shows the expected etch contrast corresponding to total suppression of etching.

In order to assess the directional preferentiality of the process a sample was scanned along both y and x axis and then etched for 1 hr. Although the y-axis is an axis of symmetry of the crystal the differential etching process does not show any preferentiality as is shown in the SEM picture of figure 5.

In the cross ridge pattern of the SEM scan of figure 5a the horizontal ridge lay along the y direction while the vertical ridge lay along the x direction. In the detail of the cross ridge structure of figure 5b no height difference between the single ridge and the superimposed structure is observed providing further evidence for the total suppression of etching.

Apart from the z faces of the crystal, some degree of differential etching occurs for the y faces and this property has been used before as a diagnostic tool to assess the depth profile quality of periodically poled domains in lithium niobate. A similar effect has been observed also in the case of the UV illuminated areas thus, revealing the laser affected area as well as the cross section of the etch frustrated ridge structures.

Such cross sections are shown in figure 6 where a sample exposed on the –z face and along the y-axis was cut and polished to expose the y face of the crystal and was subsequently etched in 48% HF acid. Brief etching (a few minutes) provides enough optical contrast to visualise the laser affected area which extends to a depth of ~4 μm as shown in figure 6a. After further etching for 1 ½ hrs square cross section ridges are revealed corresponding to the illuminated areas shown in figure 6b.

Spatially resolved Raman spectroscopy provides evidence for the crystal quality after illumination and etching. A Micro-Raman system (Renishaw Raman RM2000) using a HeNe laser (632.8 nm) operating in confocal mode acquires spectra from an area of order 3x3 μm^2 and from a depth of order 3 μm. The Raman spectra geometry used was 180 backscattering with an orientation of: Z(YY)Z [7]. Various spectra were acquired from both exposed and exposed+etched areas and were compared with spectra from "virgin" unexposed material.

Micro Raman spectra that has been acquired from UV-illuminated but not etched samples Shows no qualitative difference between illuminated and not illuminated areas. The only difference is a slight decrease in the intensity of the spectrum acquired from the slow scanned areas which may be attributed to slight surface damage which would reduce the backscattered signal.

However, the Raman picture changes after the HF etching process. The set of micro-Raman spectra, which is presented in figure 7 was obtained from an illuminated + etched sample. The dotted line corresponds to spectrum from one of the revealed ridge structure while the solid line spectrum comes from an unexposed area. The spectrum from the unexposed + etched areas show no difference to the spectra from virgin material while the spectrum from the ridge structure exhibit red shift and broadening. Additionally the intensity ratio for some peaks appears changed. The spectra which are presented in figure 7b are intensity-normalized with respect to the 873 cm^{-1} peak (which did not show any changes apart from intensity) so that differences in peak location as well as peak intensity ratios become clearer.

The qualitative analysis of the Raman spectroscopy data, especially those from the exposed-non etched sample, supports the hypothesis that UV illumination does not destroy or otherwise alter the crystal structure of lithium niobate. The shift, broadening, and peak intensity ratio change in the spectra from the exposed + etched samples suggests perhaps structural strain on the ridge structure itself after etching.

4. Conclusions

The suppression of chemical etching of the –z face of lithium niobate single crystals using continuous wave UV illumination has been demonstrated. Gratings, consisting of arrangements of ridge structures, with good uniformity have been fabricated in a

photolithographic (exposure + development) manner irrespective of direction on the x-y crystal plane. Micro-Raman spectroscopy provides evidence for the preservation of the crystal quality after UV illumination. Finally this process shows potential for applications involving fabrication of submicron features such as gratings on the surface of lithium niobate which can be used for example as Bragg reflectors for waveguide structures.

Acknowledgements

The authors would also like to acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for funding under Grant no. GR/R47295 Claire Mormiche, in the Dept of Chemistry, Univ. of Southampton for the AFM scans, Jeremy Frey, Mark Bradley of the chemistry Department, Univ. of Southampton and Bill Brocklesby of the Optoelectronics Research Centre for the Raman spectroscopy.

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Figure captions

Fig 1. Outline of the experimental setup used for the exposures of the lithium niobate samples. The beam from a doubled Ar+ laser (244 nm) is expanded and cleaned-up by a spatial filter (S.F.), directed by an optical system to the set of x-y translation stages and is focused on the sample's surface by a plano-convex lens with a 35 mm focal length. An acousto-optic filter (A.O.M) is used to control the laser power delivered to the illuminated surface.

Fig 2. Plot of the energy fluence (J/cm^2) versus translation stage velocity (mm/min) for various laser powers (20 mW- 50 mW). The spot size is kept constant at a value of 1.7 μm. This plot summarizes the exposure conditions used in the experiments.

Fig 3. a) AFM scan of the line-exposed –z face lithium niobate surface after 15 min etching in 48% HF at room temperature. The dashed line shows the direction of the alpha-step scan. b) Alpha-step scan of the surface showing the height of the revealed periodic structures.

Fig 4. a) SEM scan of the –z face of line exposed lithium niobate surface after 1 hr etching in 48% HF at room temperature. b) Alpha step scan of the revealed periodic ridge structures showing maximum height of order 1.7 μm. The a-step scan is performed along the dashed line which is shown in fig (a).

Fig 5. SEM scans of crossed ridges on the –z face revealed after 1 hr etching of a cross illuminated sample. a) low magnification picture of the 2D network of ridges, b) detail of one cross structure.

Fig 6. Optical microscope pictures of y-face etched line exposed sample. a) brief (a few minutes) etching in 48% HF at room temperature, b) 1.5 hr etching reveals the square cross section ridges.

Fig 7. Micro-Raman spectra from illuminated + etched sample. The solid spectrum corresponds to etch frustrated areas while the dotted spectrum corresponds to non etch frustrated area.

Figure 1

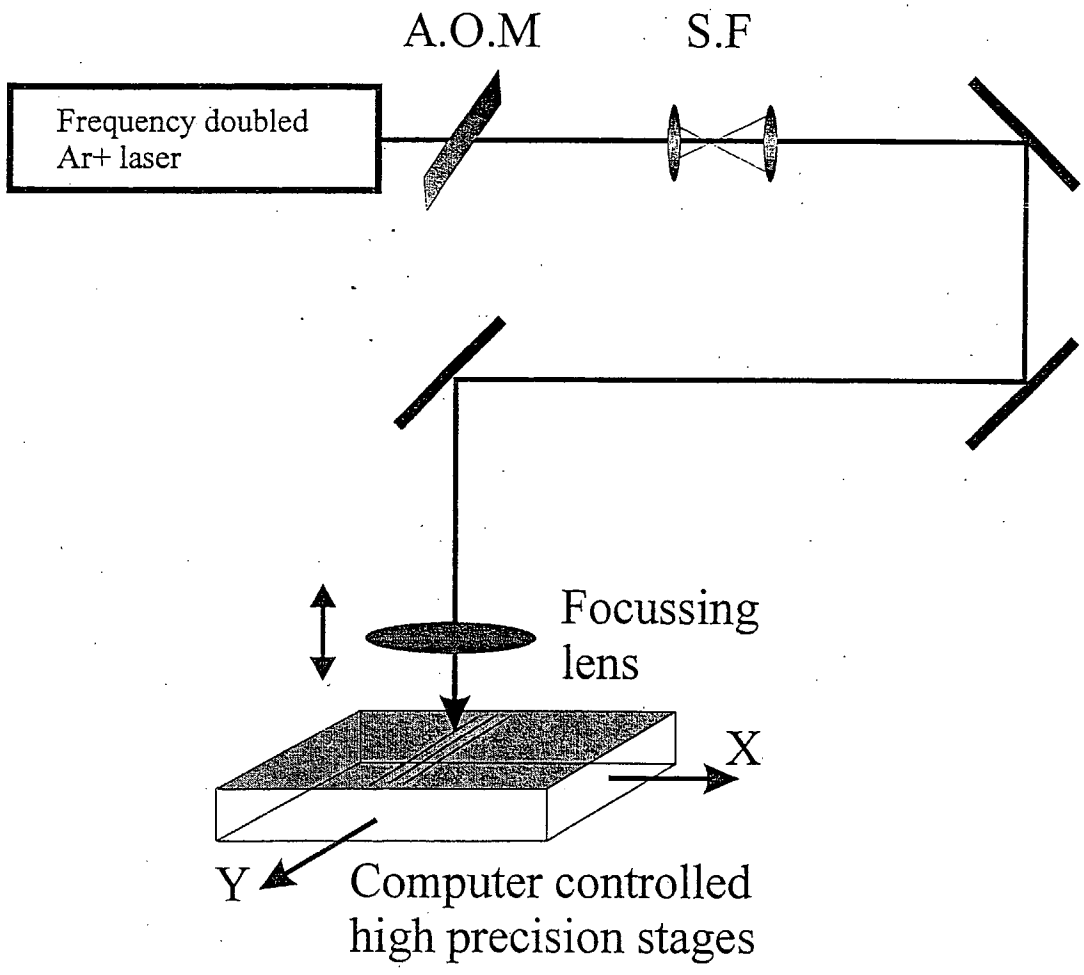

A.O.M
S.F
Frequency doubled
Ar+ laser
Focussing
lens
X
Y
Computer controlled
high precision stages

Figure 2

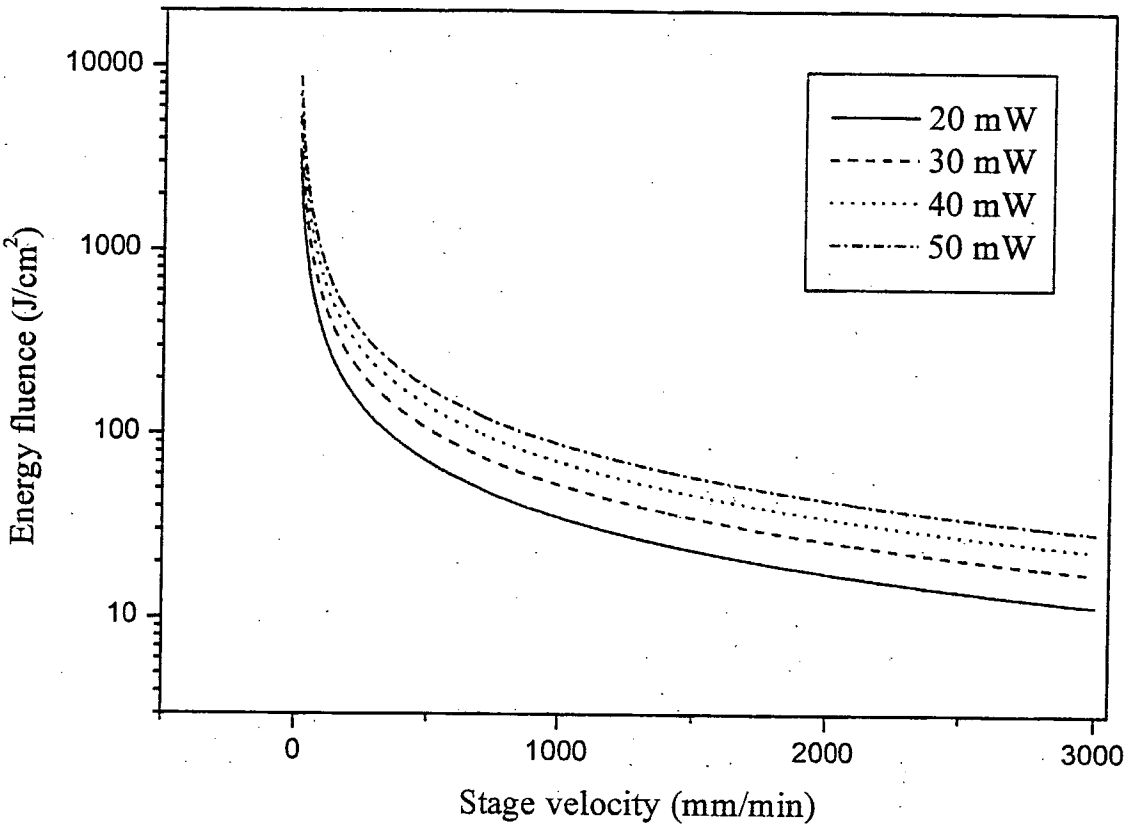
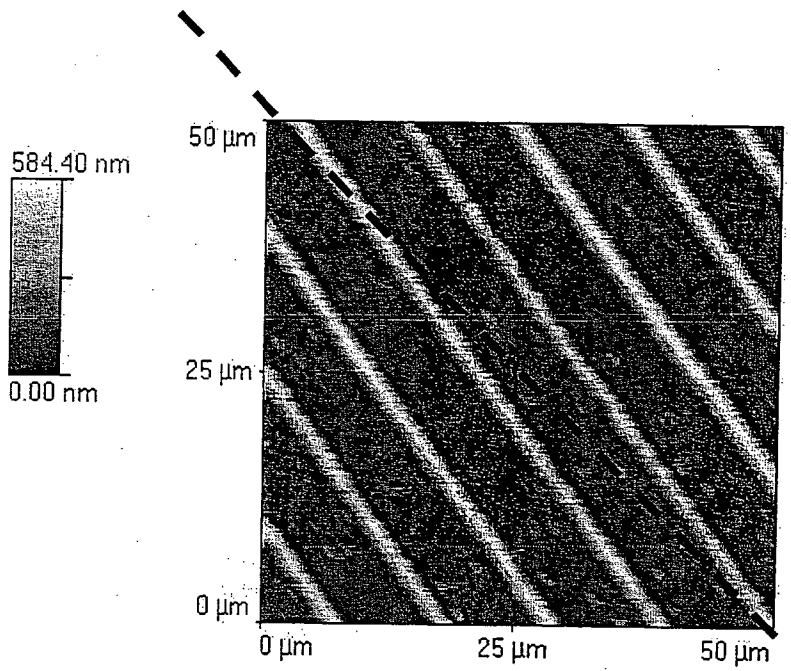

10000
1000
100
10
Energy fluence (J/cm^2)
0
1000
2000
3000
Stage velocity (mm/min)
20 mW
30 mW
40 mW
50 mW

Figure 3

a)


a-step scan line
584.40 nm
0.00 nm
50 µm
25 µm
0 µm
0 µm
25 µm
50 µm

b)

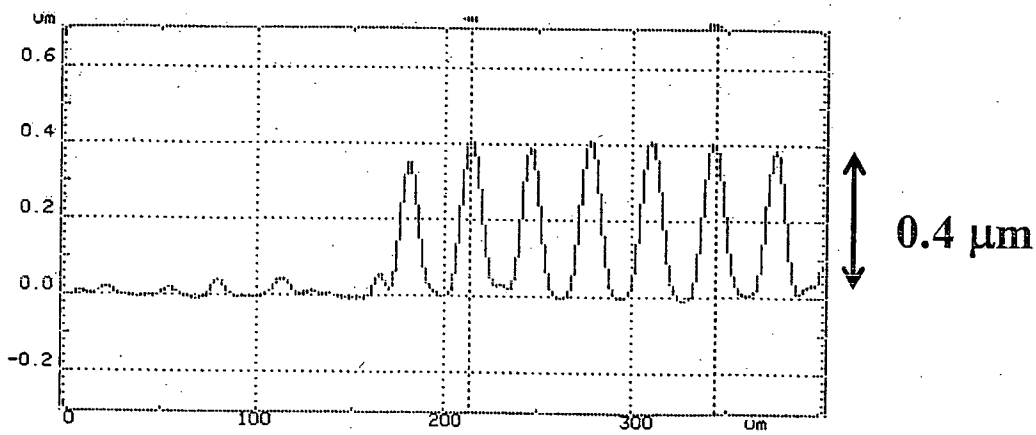
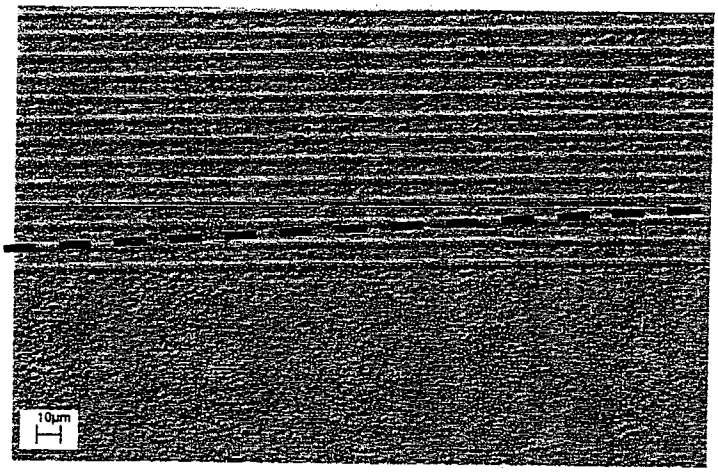

um
0.6
0.4
0.2
0.0
-0.2
0
100
200
300
um
0.4 µm

Figure 4

a)



b)

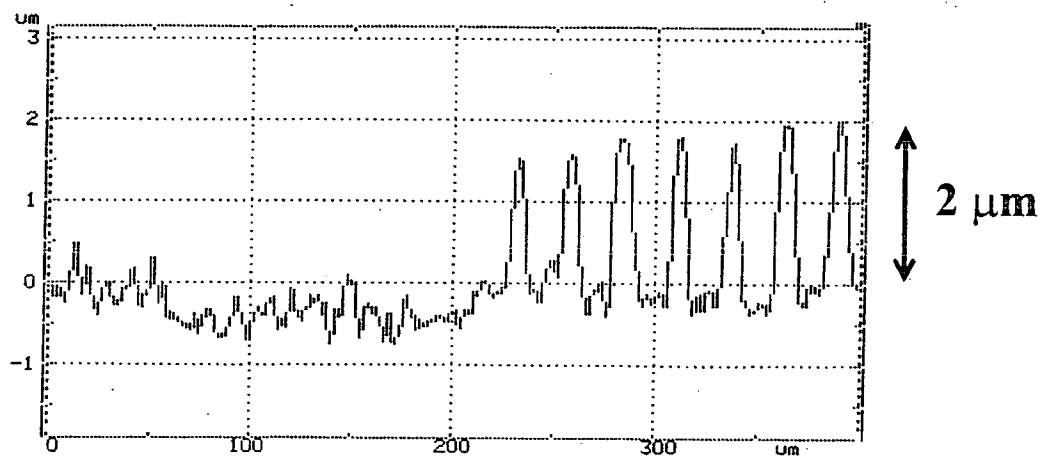
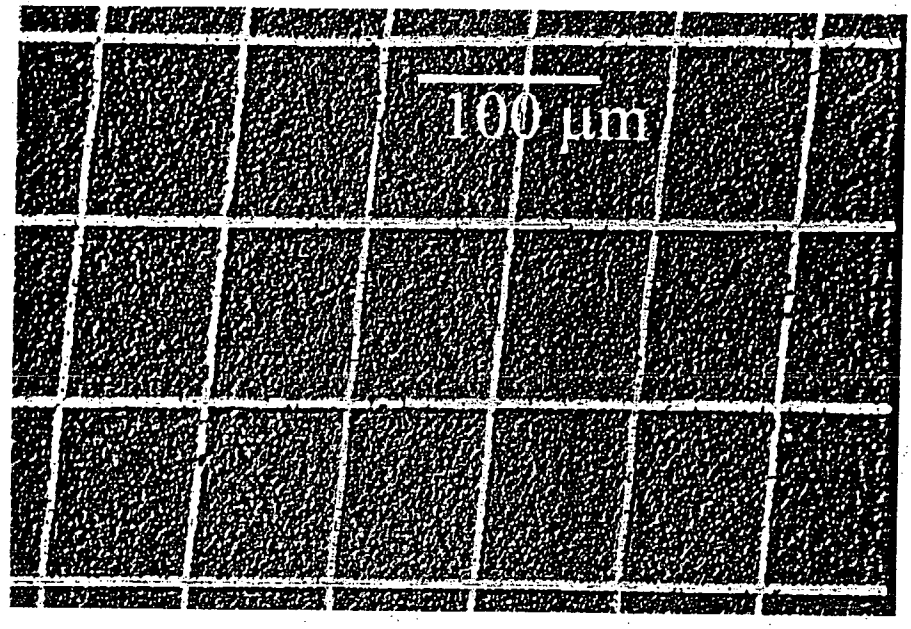
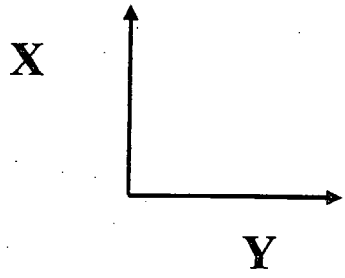


Figure 5

a)





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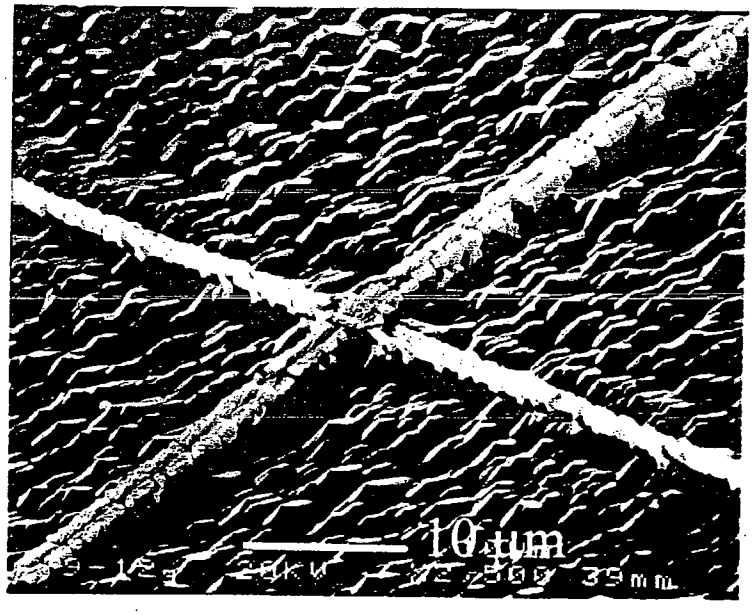


Figure 6

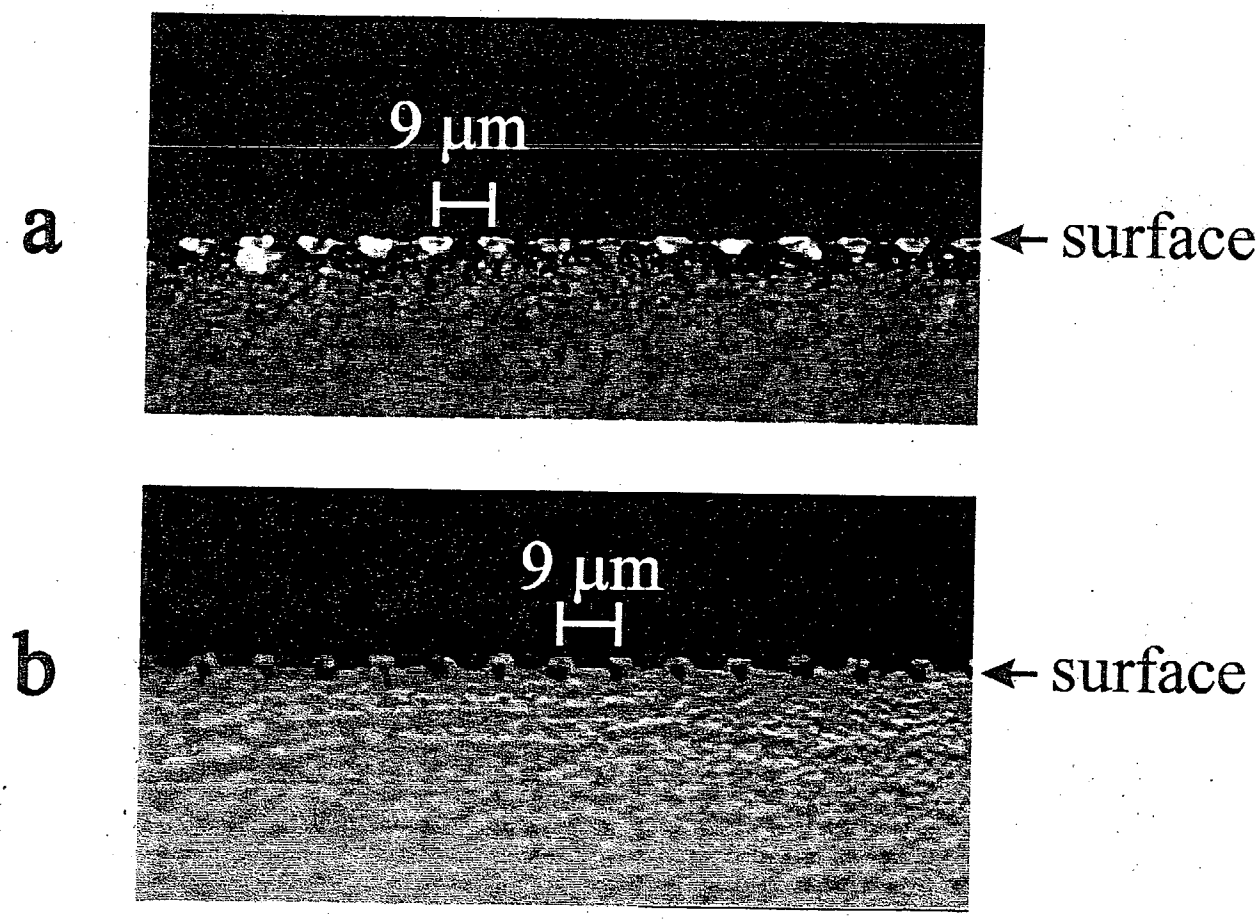
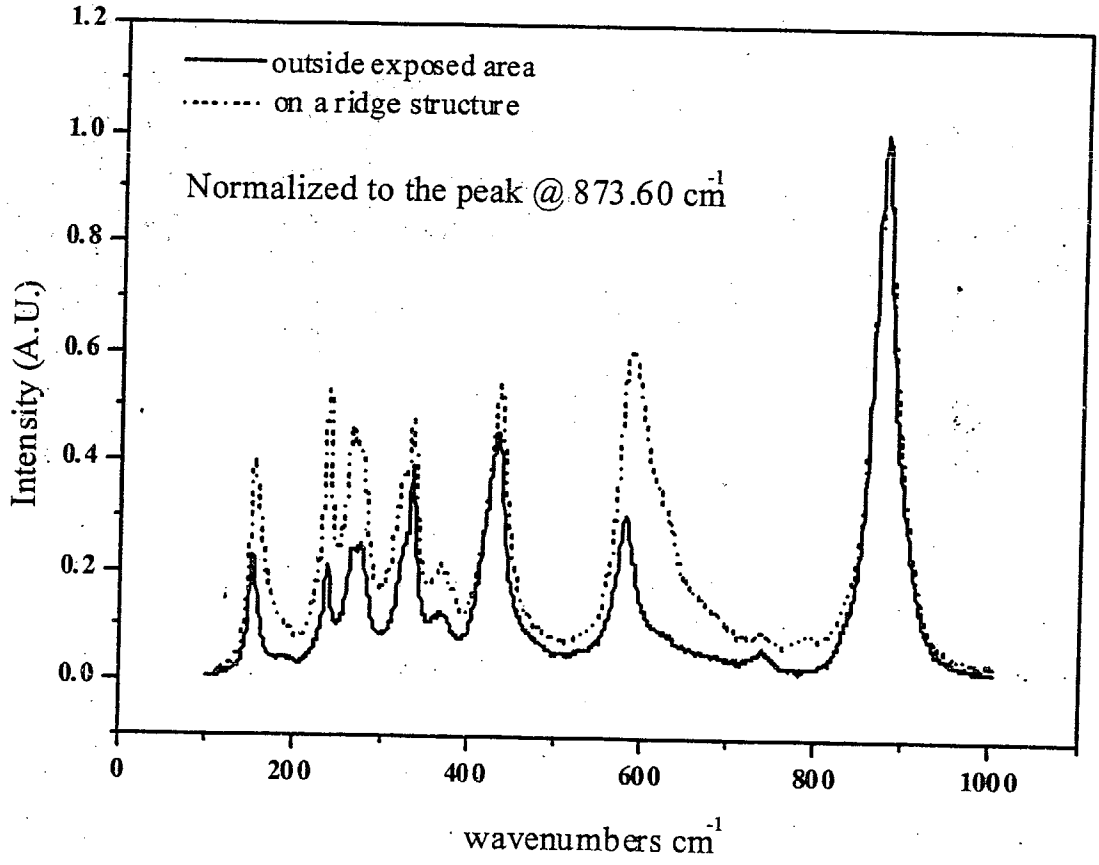


Figure 7


outside exposed area
on a ridge structure
Normalized to the peak @ 873.60 cm-1
Intensity (A.U.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
wavenumbers cm-1