Microfabrication in Foturan™ Photosensitive Glass Using Focused Ion Beam

C J Anthony, P T Docker , P D Prewett and K C Jiang

Abstract— **The fabrication of nano-dimensional features in the photoetchable glass Foturan^{TM}, using focused ion beam technology has been characterized. To date, most microfabrication in this material has used UV lithography and UV lasers, with minimum feature size of around 10μm determined by the grain structure, though there has been some recent work using high energy proton irradiation. Focused ion beam technology offers two potential advantages: features are etched directly without post bake or HF wet etch and features can be generated with lateral and depth resolution on the nanoscale. Initial test features were milled to a depth of 1.46μm, without distortion due to charging, at a milling rate of 0.23μm^3/nC, in agreement with our simulations.**

Index Terms— **Focused Ion beam, Foturan, photosensitive glass**

I. INTRODUCTION

The photoetchable glass Foturan^{TM} is a very promising new material for the manufacture of MEMS and MOEMS devices with features on the micron scale. It is a lithium aluminium silicate glass containing silver oxide as a nucleating agent with positively charged Cerium ions to provide light sensitivity [1]-[3]. The material properties of Foturan^{TM} make it of great interest for numerous applications in Microsystems technology ranging from MOEMS to lab-on-a-chip [4],[5]. There is a requirement for components to be made in glass with micron scale resolution, for example to provide optical functionality, electrical or thermal isolation combined with chemical inertness. Conventional machining techniques such as drilling, grinding, milling and moulding cannot achieve the required micron scale features. Wet etching of glass with HF acid is isotropic because of its amorphous nature, preventing the formation of higher aspect ratio dense features. Foturan^{TM} is therefore of considerable interest for its photosensitivity and its post exposure anisotropic etch capability. Currently this glass is processed using a three step process. A glass wafer is exposed to ultra-violet light typically in the 250-350nm range through a quartz-chromium patterned mask. The exposure of the wafer in the prescribed area causes a release of electrons from the Ce++ donor ion. These electrons then recombine with the Ag+ ions to form Ag atoms. The wafer is then placed in a furnace at 600 degrees centigrade where the exposed parts are crystallized causing the atoms of silver to agglomerate into small fragments. Further heat treatment leads to the formation of lithium metasilicate. The final stage of processing is to etch the wafer using hydrofluoric acid. The exposed areas etch preferentially over the unexposed areas by a ratio of 20:1. Typical minimum hole feature sizes are in the region of 10μm limited by the grain size of the exposed and postbaked material [6]. Applications to date include chromatographic columns, sensors for aggressive chemicals, high temperature environments, filters, cooling systems, medical implants, or inkjet printer heads [4].

Recent work has investigated the use of femstosecond pulse UV excimer lasers to expose Foturan^{TM} wafers using a direct write technique eliminating the requirement for the manufacture of masks [7]-[9]. Feature resolution of 10μm has been reported. Gomez-Morilla et al have reported the first example of Foturan^{TM} patterning by a direct write ion beam method, using a focused and scanned beam of MeV proton beams with a diameter of 2-3μm [10]. The very high energy of the beam produces an exposure depth of ~60μm. Postbake and HF etch produce features of this depth with lateral dimensions in the 10μm range.

We now report work to investigate focused ion beam (FIB) patterning of Foturan™ glass with the aim of producing better lateral and depth resolution and to extend its range of applications. FIB etch processing has the additional advantage of removing the postbake and wet etch steps. An initial study by Docker et al [11] showed the feasibility of using FIB to etch nano-dimensional features in Foturan™ but no mill rate was determined and effects due to different feature dimensions were not investigated. The present work rectifies these deficiencies with FIB etch experiments using a Ga$^+$ beam of 30keV energy focused to a spot size of <100nm. The experiments were supported by computer simulated ion impact analysis using the Monte Carlo program "The Stopping and Range of Ions in Matter" (SRIM) [12].

II. MODELLING

The effects of ion beam impact on solid surfaces are strongly

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dependent on ion energy and size. For example the MeV proton beams used by Gomez-Morilla et al will produce no sputter etch due to momentum transfer to surface atoms because the lightest of all ions (protons) are deposited deep into the surface; ion implantation damage due to nuclear stopping is the dominant mechanism [13], together with secondary electron generation. The latter mechanism means that high energy H^+ patterning of Foturan™ has similarities to photon exposure, though the electron effects are enhanced by some momentum transfer impact damage (low for protons). In any event, post exposure wet etch is required to reveal the ion impact effects whether due to Ag agglomeration or physical disruption. Heavy metal FIB etching, on the other hand, provides strong sputtering because of the higher mass of $^{69,71}Ga^+$ and its two orders of magnitude lower energy at 30keV. (Heavy metal sputtering typically peaks at energies just above 50keV [14]). This is confirmed by modelling using SRIM software.

SRIM software does not accept chemical bond information hence the Foturan™ composition as obtained from the manufacturer, as shown in Table I, was reduced to an approximate elemental composition for SRIM, as shown in Table II.

TABLE I. COMPOSITION OF FOTURAN™

Compound	%	Compound	%
SiO_2	75-85	ZnO	0-2
Li_2O	7-11	Sb_2O_3	0.3
K_2O	3-6	Ag_2O	0.1
Al_2O_3	3-6	CeO_2	0.015
Na_2O	1-2		

TABLE II. ELEMENTAL COMPOSITION FOR MODELLING USING SRIM.

Element	%	Element	%
O	60	Al	3
Si	25	Na	1
Li	7	Zn	1
K	3		

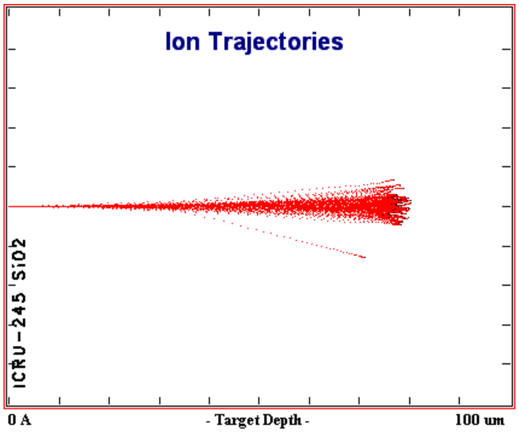

Figure 1. SRIM trajectory predictions for protons at 2.5MeV in Foturan™

The ion trajectories predicted by SRIM are shown in figs 1 and 2. Fig1 shows most 2.5MeV protons coming to rest at depths of 60µm or more - too deep to produce sputtering, as confirmed by running the sputter yield module of the SRIM suite. For the same material composition, the SRIM software predicts a mean projected range for 30keV Ga+ ions in Foturan™ three orders of magnitude lower at 50nm (see fig 2). The beam energy is deposited much closer to the surface so that the momentum transfer effect of sputtering is far greater than in the proton case. The associated sputter yield predicted by SRIM is 5 atoms per gallium ion. The FIB direct write approach thus patterns the glass by a sputter mechanism, whereas the proton implantation method patterns by creating Ag sites, as with the UV lithography and UV laser technologies. From the predicted sputter yield of 5 atoms per ion and from knowledge of the glass density and atomic composition, the sputter etch rate can be predicted. To do this, Foturan™ is assumed to be homogeneously composed of a single atom whose mass is determined from the weighted average of the elemental composition. This average mass pseudo element is then used to determine the atoms per unit volume from the glass density of $2.37g/cm^3$ [15]. The predicted etch rate calculated in this way is $0.44µm^3/nC$ for 30keV Ga+ impact. This will be correct to an order of magnitude and takes account of the different atomic masses and associated cross sections. However, no allowance is made for chemical complexes, which is the most likely source of errors.

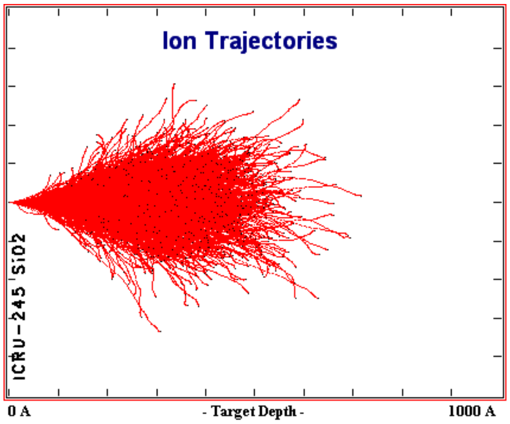

Figure 2. SRIM trajectory predictions for 30keV Ga^+ ions in Foturan™

III. EXPERIMENT

The FIB etch experiments were conducted using a Strata DB235 xP FIB/SEM workstation from FEI Inc. This is a dual beam system with coincident electron and ion beams integrated into a single piece of equipment. The sample holder is located on a motorized stage, which allows for movement in the X, Y and Z-axes, with rotation and tilt. Imaging can be done solely via the SEM, which reduces exposure to the ion beam, since the latter etches the substrate continuously during live imaging.

Immediate SEM imaging after FIB processing prevents exposure to atmospheric contaminants between etch and inspection cycles. The SEM incorporates a high brightness field emission electron source for low energy imaging of insulating samples with low electron damage. Energy Dispersive X-ray analysis (EDX) provides elemental analysis. The pattern control system is the Elphy Quantum from Raith GmbH. This lithography attachment produces micro and nano structures by means of electron beam writing via the SEM or using the focused ion beam column. A key component of the system is an electron flood gun charge neutralisation unit which allows controlled ion beam irradiation of the glass sample. When an insulator such as Foturan™ is irradiated with an ion beam, it charges positively at the ion impact location. This surface charge disrupts the incoming beam causing deflection, destroying the fidelity of the pattern. This can be overcome by use of the electron flood system to neutralize the charge build up. However for simplicity, in the work here, a thin surface coating of gold has been used to overcome the effects of charging. This gold layer is thin enough not to effect the calculation of the sputter rates from the relatively large trenches.

The FIB etch process utilised a 1µs spot dwell time and a 50% overlap of each spot in the pixellated raster scan. The beam currents were in the range 1-7nA and were set to maintain a pattern current density of approximately 30pA/µm^2 corresponding to a current dependent spot size of between 40 and 150 nm. The pattern raster times were adjusted such that all features were etched to the same depth.

IV. EXPERIMENTAL RESULTS

Trenches, tracks and holes have been etched into the Foturan™ surface as shown in figs 3 to 8. The FIB has also been used to cut a cross section through the FIB fabricated structures (figs 3, 6, 8), to allow determination of etch depth and etch profiles via the SEM imaging function. Etch depths have also been confirmed by AFM (Burleigh ARIS-3300).

Trenches of length 10µm and width 3, 5, & 7.5µm are shown in fig 3, with a sidewall roughness of ~0.1µm being observed in the close up image of the 3 µm trench in fig 4. Trenches of 25x10µm, positioned to have a separation of 3µm and 5 µm have been etched to produce 3µm and 5µm wide tracks. A raised cross produced at the intersection of these tracks is shown in fig 6. A set of milled circular holes of diameter 1, 3, and 5µm diameter are shown in fig 7. The SEM and AFM measurements show that the patterns have been cut to a depth of 1.46 µm, corresponding to an etch rate of 0.23µm^3/nC, almost exactly half of the predicted etch rate of 0.44µm^3/nC derived in section 2. The discrepancy between the two is likely to be due to the sputtering of complexes from the Foturan which the SRIM software can not predict.

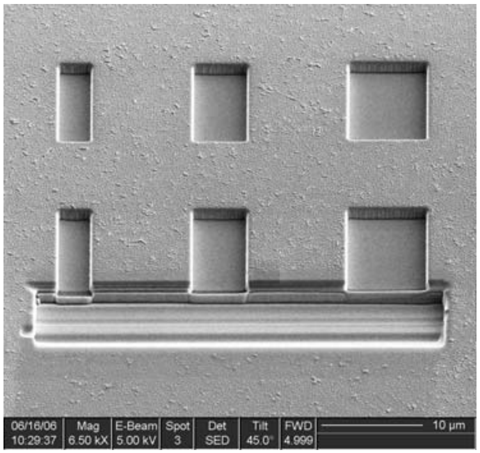

Figure 3. 10x 3, 5, 7.5µm FIB etched trenches. The trench at the bottom is sloped to reveal cross sections by tilted specimen SEM.

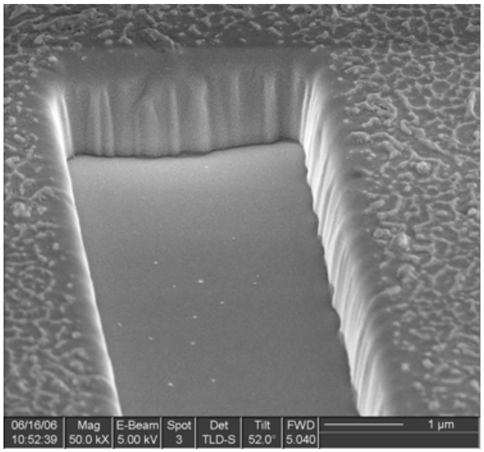

Figure 4. 3 µm wide FIB milled trench.

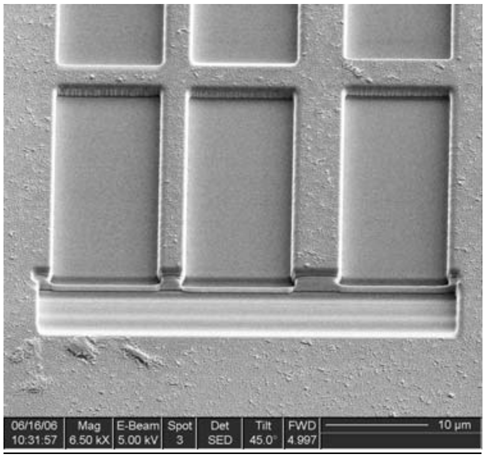

Figure 5. 3 and 5 µm wide tracks created by varying space between adjacent etched patterns.

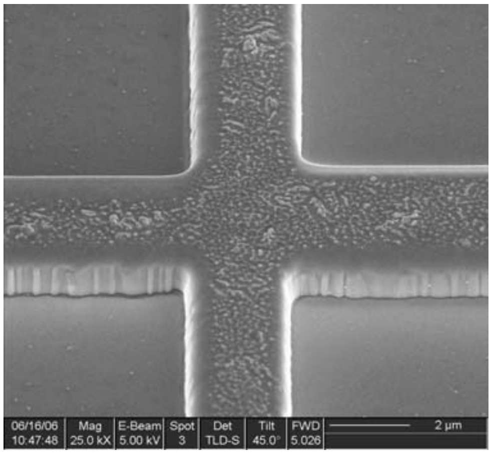

Figure 6. Intersecting tracks created by FIB etch

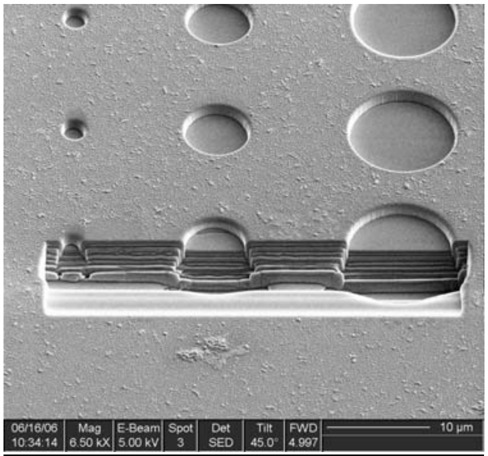

Figure 7. Etched holes of 1, 3 and 5 μm diameter, showing cross section cut.

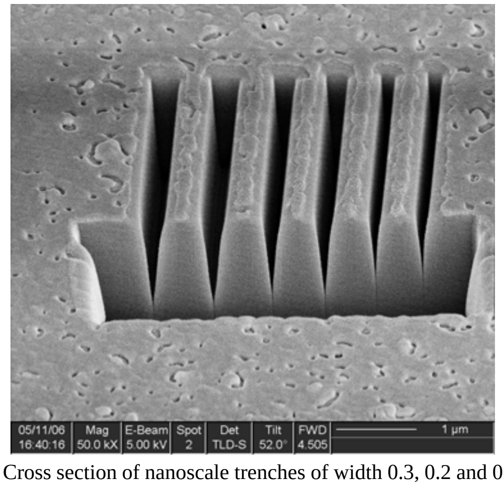

Figure 8. Cross section of nanoscale trenches of width 0.3, 0.2 and 0.1 μm and maximum depth 1μm

When nanoscale width trenches were etched (fig 8), it was seen that re-deposition on the side walls limited the achievable aspect ratio of the trenches producing V-shaped profiles. These profiles can be improved by "finishing" the trench edges with a lower beam current mill just at the edges. It is also possible to improve the profile by using reactive gas injection available within the FIB system, as sputtered species react with the gas and are removed before settling on the sidewalls. Our system currently uses iodine as an enhanced etch for dielectrics but XeF^2 is another candidate for chemically assisted etching of glasses [16]. Ideally the gas should be tailored to the chemistry of the Foturan™ for this approach to be effective.

V. Discussions and Conclusions

A study of focused ion beam fabrication on the important new photosensitive glass Foturan™ has been carried out, following the proton irradiation studies of Gomez-Morilla et al. Monte Carlo TRIM simulation highlights the pre-eminent role of sputter etching in the case of Ga^+ FIB at 30keV beam energy, with all the energy being deposited within 60nm of the surface. In contrast, the 2-3 MeV scanning proton beam used by Gomez-Morilla et al penetrates 60μm into the glass. In their case the "exposure" of the photosensitive glass from the surface by the beam is almost certainly due to electron generation by the decelerating protons with displacement damage being small for such light ions and confined to a thin layer at the maximum depth.

In our Ga^+ FIB case the microfabrication fabrication experiments are consistent with the SRIM calculations with the sputtering mechanism dominant, so that depth resolution of etch on the scale of a few tens of nm should be achievable. Lateral scattering is negligible and feature resolution will theoretically be determined by the ultimate probes size (in our case ~10nm). We have not yet investigated the ultimate resolution in these preliminary experiments and this will be the subject of future work.

In the meantime, this initial work has demonstrated the utility of Ga^+ FIB etch processing of the new Foturan™ photosensitive glass with etch depth and lateral dimensions on the micron scale with nanoscale wall roughness determined by the probe size and scanning strategy. We report for the first time the experimental sputter yield of $0.23\mu m^3/nC$ for 30keV Ga^+ irradiation of Foturan™, which is in reasonable agreement with calculations based on an average pseudo-atom approach.

The value of FIB, because of its superior lateral and depth resolution, will be in the fabrication of smaller, shallower and smoother sidewall features than can be achieved using optical, proton beam or electron beam techniques. As such it will be used to complement these larger feature scale fabrication techniques available, so as to enable the creation of the complex structures required for MOEMS and lab-on-a-chip applications.

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REFERENCES

[1] Borelli NF, Morse DL, Bellman RH, Morgan WL, ‘Photolytic technique for producing microlenses in photosensitive glass’, Appl. Opt. 24,p 2520-2525 (1985)

[2] Smith PG,’Some light on Glass Technol. 20, p149-(157 1979)

[3] Hulsenberg D, Bruntsch R,’Glasses and glass-ceramics for application in micromechanics’, J. Non-Cryst. Solids, 129 p199-205 (1991)

[4] Dietrich TR, Braham A, Diebel J, Lacher M, Ruf A, ‘Photoetchable glass for microsystems: tips for atomic force microscopy’, J.Micromech.Microeng., 3, p187-189, (1993)

[5] Diebel J, Abraham M, Dietrich TR, Lacher M, ‘Ultra long glass tips for atomic force microscope’, J. Micromech. Microeng. 6 p254-260 (1996)

[6] Dietrich TR, Ehrfeld W, Lacher M, Speit B, ‘Fabrication technologies for Microsystems utilizing photoetchable glass’ Microelectric Engineering 30 p497-504 (1996)

[7] Livingston FE, Helvajian H, ‘The variable UV laser exposure processing of photosensitive glass-ceramics: maskless micro-to meso-scale structure fabrication’, Applied Physics A-materials science and processing, 81(8), p1569-1581, (2005)

[8] Cheng Y, Sugioka, Midorikawa k,’Microfabrication of 3D hollow structures embedded in glass by femtosecond laser for lab-on-chip applications’, Applied surface science, 248(1-4) p172-176 (2005)

[9] Kim J, Berberoglu H, Xu XF, Fabrication of microstructures in photoetchable glass ceramics using excimer and femtosecond lasers’, Journal of microlithography and Microsystems, 3(3) p478-485 (2004)

[10] Gomez-Morilla I, Abraham MH, de Kerckhove DG, ‘Micropatterning of Foturan photosensitive glass following exposure to MeV proton beams’, J. Micromech Microeng., 15 p706-709 (2005)

[11] Docker PT, Teng J, Prewett PD, Jiang KC, "Fabrication of nano-dimensional features in FOTURAN using focused ion beam technology", to be published in, Proceedings of 2006 Conference on Multi-Material Micro manufacture, Grenoble, France, 20-22 September 2006

[12] Ziegler JF, Biersack JP, and Littmark U. In The Stopping and Range of Ions in Matter, volume 1, New York, 1985. Pergamon

[13] Lindhard J and Sharff M, Phys. Rev. 124, 1961, pp128

[14] Prewett PD and Mair GLR, “Focused ion beams from liquid metal ion sources”, Taunton, Somerset, England : Research Studies Press ; New York : Wiley, 1991.

[15] Cheng Y, Sugioka K, Masuda M, Shihoyama K, Toyoda K, and Midorikawa K, Optical gratings embedded in photosensitive glass by photochemical reaction using a femtosecond laser, Optics Express, Vol. 11, Issue 15, pp. 1809-1816, 2003.

[16] Randolph SJ, Fowlkes JD, and. Rack PD, Focused electron-beam-induced etching of silicon dioxide, J. Appl. Phys. 98, 034902 (2005)