Laser processing of micro and nano structures at the National Centre for Laser Applications, Galway

Tony Flaherty

There are a number of techniques in use in the National Centre for Laser Applications for the production of patterns and structures on the micro, nano and molecular scale. These techniques are aimed at developing processes in the bio-sensor and bio-medical fields. The two principal approaches are the drilling and machining of shaped holes and channels for drug delivery and bio-sensors, respectively, and the fabrication of regular nano-scale features on surfaces for superior (- enhanced, or inhibited) biological interaction. Here we outline some of the techniques used and illustrate them with examples of some of the structures which have been achieved to date.

Micro- Engineering of Surfaces

Two approaches have been used at the NCLA to achieve shaped channels and tapered holes: Overlapping of Gaussian spots, and dynamic masking of an Excimer beam.

Overlapping of Gaussian Spots.

The aim of this work was to develop a process for machining holes in polymers with custom tapers. The lasers used were two Q-switched DPSS lasers emitting in the UV range: an AVIA 355nm laser from Coherent. with repetition rates from 10 kHz to 100 kHz, pulse duration from 12 ns to 25 ns, and a HIPPO from Spectra Physics at 266 nm wavelength with repetition rates from 30 kHz to 300 kHz, pulse duration from 9 to 13ns. For beam delivery and motion of the beam across the work piece both lasers were equipped with galvo scan heads. The machining strategy was optimised, based on varying fluence, direction of scan and percentage beam overlap with respect to depth of material removed, and especially, the roughness of the remaining surface.

Figure 1 shows the output of a model which was used to predict surface roughness for a given beam overlap. The results of these studies gave a machining strategy which produced flat features, 1 micron deep in polyimide with rms roughness of approximately 50 nm (compared to a native roughness of 25- 40 nm). Figure 2 shows a profile of a step machined in polyimide, allowing a visual comparison between the native and machined surfaces. By successively machining deeper layers, a tapered structure can be fabricated, and obviously, with the control offered by the galvo scanning system, the angle of taper can be varied over the depth of the entire structure. Illustrating this approach, Figures 3 and 4 show a profile and image, respectively of a structure with several distinct machined layers.

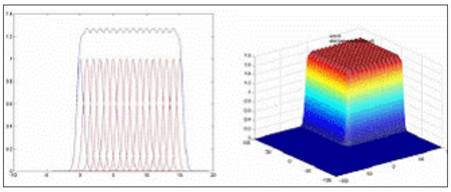
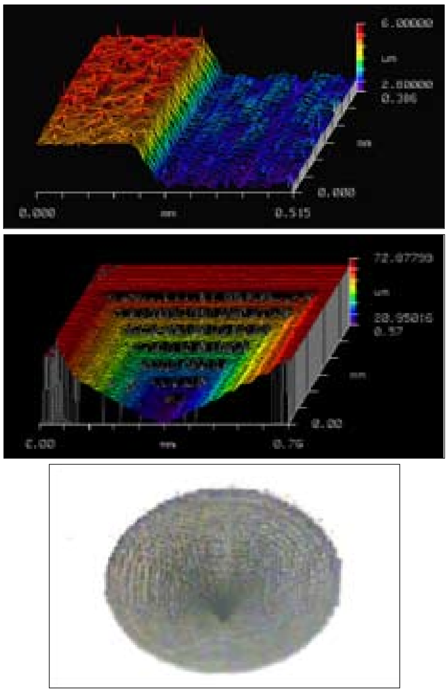


Figure 1. Model of the overlapping beams, used to predict machined sample roughness



Figures 2 to 4. Step machined in polyimide. (Top to bottom) Figure 2. Step machined in polyimide using overlapping Gaussian pulses from a DPSS laser; Figure 3. Profile of custom taper machined in polyimide using overlapping scans from DPSS laser with galvo-scanner; Figure 4. Micrograph of tapered hole machined using overlapping pulses strategy.

Dynamic Masking

An alternative approach to the fabrication of shaped holes and channels is based on the use of dynamic pinholes. These are masks used in image projection systems (in cojunction with an excimer laser) whose shape can be controlled in real time. The masks consist of four blades mounted in a square or rectangular shape, with independent control on the position of each of the four blades. These masks are designed to address a number of issues that arise with the use of static masks, such as the leading-edge and trailing-edge taper seen when the sample is in motion (mask-dragging), the changing cross-sectional profile when direction of sample motion changes and the occasional requirement for variations in depth or width of the channels.

A common problem seen in the case of the mask-dragging technique is the phenomenon of lead-in and lead-out taper. By synchronising the sample motion system with the pinhole, this taper can be eliminated. Figure 5 shows a 3-d plot illustrating channel sections machined using an ArF excimer laser at 193 nm, where the trailing edge has been eliminated (leading edge remains for illustration). Figure 6 shows the effect on micro- channel shape of varying the separation of the blades perpendicular to the direction of machining of the sample.

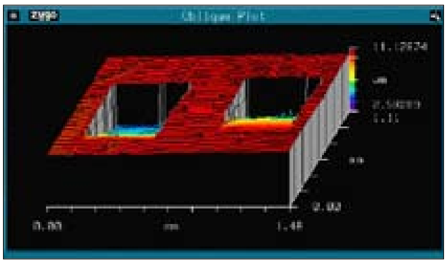


Figure 5. Two representations of 3-D profile of features machined using an Excimer laser and dynamic mask, illustrating the elimination of the trailing edge.

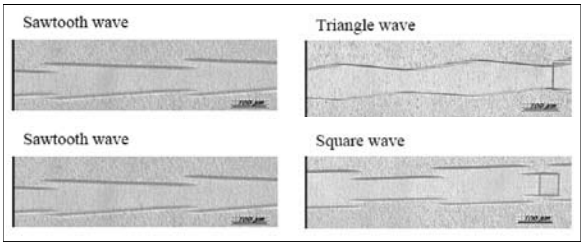


Figure 6. Micrographs of channels machined in Perspex. The width of the mask was varied as the sample moved under the laser. Programmed depth variations are also possible by varying mask length, in the direction of sample movement.

Engineering Surfaces on the Nano Scale (and beyond)

The second main area of application at NCLA has been the development of methods to treat polymer surfaces in order to encourage colonisation by living cells, either for clinical implantation or *in-vitro* tissue engineering applications. The aim of the study was to investigate the potential of short wavelength periodic surface structures for improved interaction with biological media (osteoblast cells, studied *in-vitro*).

Polymers were treated by a number of methods; using an ArF Excimer laser at 193nm to machine periodic arrays of patterns in the surface; the periodicity of the patterns was varied from a few hundred nanometers to 10 µm; or using an Excimer lamp to modify the chemistry of the surface layer by breaking surface bonds and incorporating atmospheric oxygen. Surface structures of samples treated by the first method were examined using Scanning Electron Microscopy (SEM), White Light Intereferometry and Atomic Force Microscopy (AFM) and surfaces of samples treated with the second method were examined by using contact angle measurements which indicated a higher surface energy.

Laser treatments

A number of optical set-ups have been used in conjunction with the Excimer laser, to generate nanometer- scale structures. These include the use of phase masks and a phenomenon known as LIPSS- (Laser Induced Periodic Surface Structures) to create regular interference patterns on the substrate; also the use of microbeads which act as arrays of lenses to focus the laser radiation onto the sample.

The phase mask used was a grating of 668 nm period etched in fused silica. The mask creates interference between the -1 and +1 diffracted orders which form a pattern on the sample surface with features with a similar period as the grating. Coverage was increased by either using “step and repeat” indexing or by translating the sample continuously. Figure 7 shows an array of lines machined on the surface of polyimide using the phase grating and an Excimer laser.

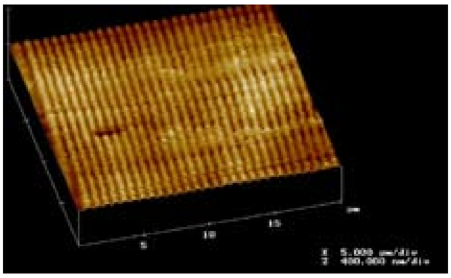


Figure 7. AFM image of a grooved sample showing the effect of the phase mask. The period of the array approximates to that of the phase mask (in this case, 670 nm).

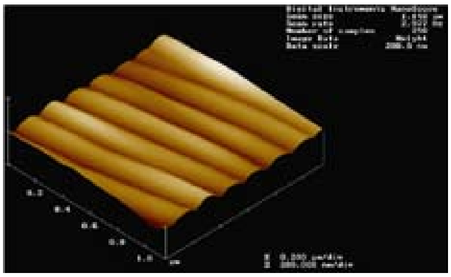
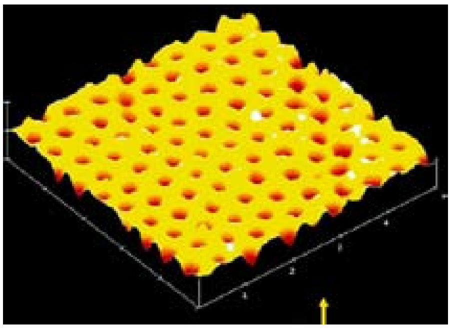


Figure 8. The LIPSS effect in polyimide. The wavelength of the periodic features is 180 nm.

Figure 8 shows the results of LIPSS treatment. The LIPSS effect is thought to arise from localised melting and reorganisation due to interference between surface- scattered polarised laser radiation and incident radiation from the same beam. It is dependant on laser wavelength and angle of incidence. The features are normally more clearly defined than those generated using a phase mask and, since it is a non-ablative process, there is no re-deposited debris. Periods in the range 200 to 1000 nm have been fabricated at NCLA.

Microbeads, small spherical beads of silica, are applied in solution to the surface of a sample. They self-organise into a tightly-packed array of lenslets, focusing a large laser spot into an array of tiny spots, each etching of a correspondingly small hole. Bead diameters used had diameters of 3 µm and 520 nm, and the resulting etched holes had diameters of 950 nm and 350 nm respectively. Hole depths ranged from 50 to 100 nm. The 350 nm holes are shown in figures 9.



Figures 9. An AFM image of 320 nm holes in polyimide.

UV lamp treatments

The final method of surface modification to be discussed involves using a short wavelength (172 nm) Excimer lamp to alter the surface chemistry. The UV photons break polymer bonds close to the surface, allowing the incorporation of oxygen or other desirable functional groups. This can substantially change the way the material interacts with its environment, particularly with biological media. The study evaluated the effectiveness of this treatment on polymeric biomaterials, to improve their water contact angle (hydrophillicity) and thereby enhance their interaction with biological environments.

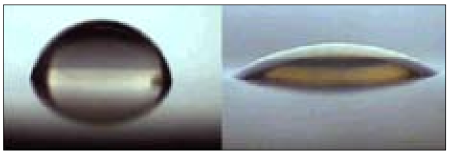


Figure 10. Water droplets in contact with a nylon surface before (left) and after UV surface exposure.

The polymeric biomaterials studied included Nylon 12, Ultra-high molecular weight polyethylene (UHMWPE), Low-density polyethylene (LDPE), Sarlink and polycaprolactone (PCL). Water contact angle, surface free energy and X-Ray Photoelectron Spectroscopy (XPS) measurements were performed on the polymers to analyse the chemical changes on the surfaces, immediately after UV treatment and over the following 28 days.

A decrease in water contact angle and an increase in surface free energy and its base component were observed directly after treatment as shown in figure 10. The decrease in contact angle indicates an addition of polar functional groups to the surfaces and hence an increase in wettability. With the exception of PCL, ‘ageing’ or hydrophobic recovery (shelf life of the treated surfaces) was found to be rapid over the first 1-3 days but then slowed down; the polymer surfaces were more hydrophilic than the untreated surfaces after 28 days, the duration of the study. XPS measurements confirmed surface energy results, indicating that there is an increase in the oxygen content at the expense of the carbon and nitrogen at the surface of the polymers. The various results obtained demonstrate that UV treatment at 172nm wavelength successfully modifies polymeric biomaterial surfaces by increasing wettability and surface energy and thus has significant potential for improving biomaterial/cell interactions.

In conclusion, a range of standard and novel laser and optical techniques are in use in the NCLA for generating complex, functional structures in materials at the micro- nano- and molecular levels. Some practical issues remain to be resolved in applying the techniques economically to real-world applications, but are expected to be overcome as developmental work continues, and new exciting applications emerge.

Acknowledgements
I would like to acknowledge the contribution of my colleagues at NCLA and the financial support of the Enterprise Ireland Commercialisation Fund for this research.

Contact
Tony Flaherty
National Centre for Laser Applications, National University of Ireland
Galway, Ireland
E: tony.flaherty@nuigalway.ie

See Observations pXX