Novel Aspects of Materials Processing by Ultrafast Lasers: From Electronic to Biological and Cultural Heritage Applications

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Abstract. Materials processing by ultrafast lasers offers several distinct possibilities for micro/nano scale applications. This is due to the unique characteristics of the laser-matter interactions involved, when sub-picosecond pulses are employed. Prospects arising will be discussed in the context of surface and in bulk laser induced modifications. In particular, examples of diverse applications including the development and functionalization of laser engineered surfaces, the laser transfer of biomolecules and the functionalization of 3D structures constructed by three-photon stereolithography will be presented. Furthermore, the removal of molecular substrates by ultrafast laser ablation will be discussed with emphasis placed on assessing the photochemical changes induced in the remaining bulk material. The results indicate that in femtosecond laser processing of organic materials, besides the well acknowledged morphological advantages, a second fundamental factor responsible for its success pertains to the selective chemical effects. This is crucial for the laser cleaning of sensitive painted artworks.

1. Introduction
There are several features in materials processing by ultrafast lasers which make it attractive for sophisticated applications [1-3]. These include: the absence of laser interactions with the ablated material since material ejection begins several ps after irradiation, the lower ablation threshold required in many cases, the reduction of undesirable thermal effects and the ejection of directional energetic particles in ablation, which may allow low temperature growth of thin films.

In addition to the above features, there are other aspects which have been more recently established and may be exploited for expanding the breadth and novelty of applications. For example, ultrafast laser interactions with materials induce non-equilibrium surface and volume structural modifications, which may give rise to complex and unusual structures. Furthermore, in interactions with molecular substrates, the photochemical effects are minimal, allowing new routes for chemical processing. The
use of temporally shaped ultrafast pulses may provide an additional route for controlling and optimizing the outcome of processing and finally, the exploitation of filamentation effects which may be produced open the way for sophisticated material processing and remote analytical applications. Recent examples of materials processing by ultrafast lasers and their eventual functionalization on the basis of these latter issues will be presented and discussed in this work.

2. Development of responsive structured surfaces: Wetting properties of microstructured Si surfaces.

A variety of laser systems have been used for the structuring of Si surfaces, in the presence of reactive gases and primarily SF₆ [4-6]. The irradiated surfaces consist of cones or spikes whose morphology depends on the irradiation conditions. The spikes height and tip diameter, their nanocomposition, the existence of secondary peaks and the degree of periodicity and distance are crucial for the surface properties observed. For laser pulses of ns duration, a phenomenological interpretation of the initial surface morphology obtained has been based on the initial formation of capillary waves and existence of chemical etching effects. However, for ultrashort laser processing the mechanism is rather ambiguous.

The optical and electronic properties of microstructured Si have been studied in detail and form the basis for sensor and field emission applications [7, 8]. Here, we focus on the wetting properties of laser structured Si surfaces, which may give rise to a new class of applications. It has been long established that a high surface roughness may be used for tailoring its wetting properties. Based on this effect, applications ranging from electronic, microfluidic, adjustable lenses and self-cleaning coatings have been proposed.

In this work, flat n-type Si was microstructured by ultrafast lasers (Ti:Sap and KrF lasers emitting pulses of 180 and 500 fs at 800 and 248nm correspondingly) in the presence of different pressures of SF₆. By selecting the irradiation conditions (laser fluence, rep. rate, pulse duration, wavelength and SF₆ pressure) it was possible to control the features of the spikes obtained. The laser pulse duration was found to be important for the surface morphology attained. In particular, for ultrashort pulses spikes of narrower periodic distributions could be obtained allowing a good control over the surface properties. On the flat and structured Si samples, a 3 μl drop of nanopure water was placed and the contact angle was measured by the sessile drop method (see Figure 1). This Figure demonstrates the existence of a moderate hydrophilic behaviour for the flat surface and a strongly hydrophobic behaviour for the laser structured surface.

**Figure 1.** Contact angles of 3μl nanopure water drops on n-type Si (100) (a) flat (unstructured) surface and (b) structured surface. Insert: A SEM picture of the corresponding Si surface produced by a Ti:Sap laser processing in the presence of 500 Torr SF₆.

The contact angle results as a compromise of the surface tensions involved at the interfaces between solid and liquid, liquid and air and solid and air as described by the fundamental Young’s equation and its modification for structured surfaces. For flat n-type Si, a contact angle of 67º was measured, which is much smaller than that of the 151º observed for the structured Si, as shown in Figure 1. As predicted by the theoretical models, for a similar surface chemistry the contact angle of the drop and therefore the wetting properties depend on the size shape, periodicity and distance of the spikes which determine the surface morphology. Since these features can be controlled by choosing the appropriate laser irradiation parameters (e.g. laser fluence), surface regions with graded morphology and therefore wettabiltiy can be formed and exploited for inducing drop motion. The contact angle formed as a function of laser fluence is shown in Figure 2.
A drop placed on one end of this treated surface may glide in a controllable manner towards regions of increasing hydrophilicity due to the contact angle hysteresis along the contact line of the drop. The implementation of ultrafast lasers for surface engineering is critical in this respect since it allows the control of surface morphology (shape and dimensions of spikes, degree of periodicity) with high resolution and diversity. For example, temporally shaped ultrafast laser pulses may give rise to surface morphologies which range from hydrophilic to strongly hydrophobic for the same laser fluence. This is due to the different surface morphologies obtained depending on the interaction dynamics which operate for temporal differences in the laser energy dissipation on the target. The structuring of surfaces of other materials, as for example polymers, has also given rise to similar observations and can be used for dynamic contact angle changes. Moreover, methods for fully controlling the wettability and motion of a drop on laser structured Si or other surfaces in a reversible fashion are investigated by incorporating standard electrowetting or photo-switching techniques.

3. Transfer of biomolecules and functionalization of 3D structures.

3.1. Surface patterned biomolecules:
Laser-induced forward transfer (LIFT) is an established technique for the transfer of a thin film of material from a transparent carrier to a receiving substrate. Usually, the receiving substrate is placed in parallel and at close proximity to the thin film carrier, in air or under vacuum. A single laser pulse is focussed at the interface between the transparent carrier of the thin film leading into an ablation process under confined conditions as shown in Figure 3.
Recently, the ablation mechanism and dynamics of transfer have been studied in detail. These studies have indicated that depending on the type of material (i.e. absorptivity, thermal diffusivity etc.) the laser parameters involved, such as the wavelength, intensity, focal spot size and most important the pulse duration are crucial for the quality and spatial resolution of the material transferred and deposited onto the substrate opposite [9-11].

LIFT is a direct write (DW) technique, similar to the well established matrix-assisted pulsed laser evaporation (MAPLE), which originated from the Naval Research Laboratory [12]. Micrometric patterns of arrays may be formed by both techniques either by direct precision scanning of the supporting carrier and receiving substrate or by using a mask on the receiving substrate. Patterns have been obtained by both techniques for a broad range of materials. Direct transfer by LIFT, which does not require the existence and evaporation of a matrix as in MAPLE [13] has been shown to produce sub-micron good quality features when femtosecond laser pulses are employed.

Furthermore, it has been recently demonstrated that for femtosecond LIFT realized by means of a KrF laser emitting pulses of 500 fs duration at 248 nm there is a window of laser parameters which are appropriate for the microprinting of sensitive biological materials such as the lamda bacteriophage DNA, and proteins (e.g. bovine serum albumine (BSA)) with minimal damage and by maintaining their biological function.

The functionality of printed DNA was demonstrated in hybridization reactions [14]. Features down to 50 μm have been obtained in patterns of high density resolution which makes the femtosecond LIFT a good candidate for biosensor applications. Figure 4, shows a comparative study by Schlieren imaging (shadowgraphy), when using femtosecond and nanosecond laser transfer of lamda phage DNA [14].
Besides the expected minimization of any thermal effects when using ultrashort laser pulses, it is clear from Figure 2, that the femtosecond LIFT leads to a highly directional transfer and in consequence better spatial resolution.

3.2. Three dimensional (3D) biomolecular patterning:
The sensitivity of biosensors based on two dimensional (2D) biomolecular patterns restricted in the form of arrays or other shapes may be increased dramatically by developing 3D biosensitive structures without sacrificing the overall size of the device. This may be achieved by rapid prototyping of materials susceptible to further functionalization [15]. The organic-inorganic hybrid Ormocer is such a material. Ormocer is a liquid fully transparent at ca. 1μm and absorbing strongly in the region of 330 nm. Following absorption, it is polymerised into a glassy stable polymer. Two-photon polymerization of Ormocer by means of ultrafast lasers emitting at 800 nm has been applied for the microfabrication of 3D structures [16]. In this work we used an Yb laser emitting pulses of 200 fs duration at 1.028 μm. By three-photon polymerization 3D structures as the one shown in Figure 5 could be obtained [17]. Biotin was photolytically immomilized on the surface of this structure and further derivatized by fluorescently labeled avidin. In Molecular Biology the biotin/avidin system is a usual precursor for attaching biological molecules. A fluorescent microscopy image of a component with immobilized biotin streptavidin is shown in Figure 6.

![Figure 5. A SEM picture of a component obtained by three-photon polymerization of ormocer.](image)

![Figure 6. Fluorescent microscopy image of a component with immobilized biotin and streptavidin.](image)

4. Removal of molecular substrates
In the previous section it was shown the high quality and control which may be attained in inducing morphological surface modifications by ultrafast lasers. Yet, when processing molecular substrates in several important applications such as the laser cleaning of painted artworks, the degree of photochemical processes which are induced is of prime importance. For this particular application, the existence of photochemical effects in the remaining bulk substrate were studied in model systems comprised by varnishes (dammar and mastic) doped with a photosensitive compounds (e.g. 9-iodophenanthrene (PhenI)) of known photochemistry. Molecular byproducts such as the PhenH, produced in the bulk substrate were probed by laser induced fluorescence (LIF) after ablation. This technique had been previously established for other model systems [18-20]. For the purposes of this work the LIF signals of PhenI obtained following ablation by a 30ns and a 500 fs KrF lasers emitting at 248 nm are compared in Figure 7.
Figure 7. Comparison of the product LIF spectra from PhenI (1% wt) doped dammar irradiated above the ablation threshold by a single fs and a ns laser pulse (λ=248nm). In both cases the LIF spectra were obtained with a KrF laser probe beam (λ=248nm, 30ns) under the same conditions.

Figure 8 shows the fluorescence intensity as a function of laser fluence for the cases of mastic and dammar. The results indicate that photoproduction formation is limited for the ultrafast laser ablation.

Furthermore, considering the different absorptivities of dammar and mastic at 248 nm, Figure 8 demonstrates that ablation by the femtosecond laser is largely independent from the absorptivity of the samples. This is consistent with the efficient operation of multiphoton processes in this case, which also allows processing at much lower fluences and a better spatial resolution than for ablation with the nanosecond laser. Concluding, ultrafast laser removal of molecular substrates, enables processing with high precision, which is independent from the optical properties of the substrate and involves minimal photochemical effects. These features open up new avenues in using lasers for demanding cleaning applications of sensitive painted artworks, as for example in modern paintings conservation.

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References

[1] Kawata S, Sun H-B, Tanaka T, Takada 2001 *Nature* **412** 697

[2] Mills J D, Kazansky P G, Bricchi E, Baumberg J J 2002 *Appl. Phys. Lett.* **82** (2) 196

[3] Liu X, Du D, Mourou G 1997 *IEEE J. Quantum Electron.* **33**(10) 1706

[4] Her T-H, Finlay R J, Wu C, Deliwala S, Mazur E 1998 *Appl. Phys. Lett.* **73** 1673

[5] Pedraza A J, Fowlkes J D, Lowndes D H 1999 *Appl. Phys. Lett.* **74** 2322

[6] Dolgaev S I, Lavrishev S V, Lyalin A A, Simakin A V, Voronov V V, Shafeev G A 2001 *Appl. Phys. A* **73** 177

[7] Carey J E, Crouch C H, Mazur E 2003 *Optics and Photonics News* **14**(2) 32

[8] Zorba V, Alexandrou I, Zergioti I, Neumeister A, Manousaki A, Fotakis C, Ducati C, Amaratunga G A J 2004 *Thin Solid Films* **453** 492

[9] Toth Z, Szorenly T, Toth A L 1993 *Appl. Surf. Science* **69** 317

[10] Zergioti I, Papazoglou D G, Karaikou A, Fotakis C, Gamaly E, Rode A 2003 *Appl. Surf. Science* **208-209** 177

[11] Hopp B, Smausz T, Antal Zs, Kresz N, Bor Zs, Chrisey D 2004 *J. Appl. Phys.* **96** 3478

[12] Chrisey D B, Piqué A, McGill R A, Horwitz J S, Ringesei R B, Bubb D M, Wu P K 2003 *Chem. Rev.* **103**(2) 553

[13] Ringeisen B R, Chrisey D B, Pique A, Young H D, Modi R, Bucaro M, Jones-Meehan J, Spargo B J 2002 *Biomaterials* **23** 161

[14] Zergioti I, Karaïskou A, Papazoglou D G, Fotakis C, Kapsetaki M, Kafetzopoulos D 2005 *Appl. Phys. Lett.* **86** 103902

[15] Wanke M C, Lehmann O, Muller K, Wen Q, Stuke M 1997 *Sciences* **275** 1284

[16] Serbin J, Ovsjanikov A, Chichkov B 2004 *Optics Express* **12** 5221

[17] Farsari M, Filippidis G, Fotakis C 2005 *Optics Lett.* **30** 3180

[18] Athanassiou A, Andreou E, Anglos D, Georgiou S, Fotakis C 1999 *Appl. Phys. A* **86** S285

[19] Georgiou S 2004 *Adv. Polym. Sci* **168** 1

[20] Bounos G, Athanassiou A, Anglos D, Georgiou S, Fotakis C 2004 *J. Phys. Chem B* **108** (22) 7050