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Laser Processing of Novel Functional Materials

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Abstract: Laser processing and laser ablation are the subject of fascinating fundamental studies and are used in various industrial processes. The applications of laser ablation range from microstructuring of nearly all materials, to the production of thin crystalline films with special properties, and micro-spectroscopy. Our projects in the field of laser ablation encompass both applied and fundamental research. In detail, we are working on the design and structuring of novel photopolymers for laser applications, on the development of advanced methods for the microstructuring of glassy carbon, and the pulsed laser deposition of perovskite films used in electrocatalysis. Additionally, emission or plasma spectroscopy is used to study the pulsed laser deposition process, and as tool for trace analysis of heterogeneous samples.

Keywords: Emission spectroscopy · Laser ablation · Microoptics · Microstructuring · Photopolymer · Pulsed laser deposition

Introduction

At the ripe age of 40 years, the laser has become a mature technological device with many applications. This was not always true, of course. For many years, the laser was viewed as 'an answer in search of a question'. That is, it was seen as an elegant device, but one with no real useful application outside of fundamental scientific research. In the last two to three decades however, numerous laser applications have moved from the laboratory to the industrial workplace or the commercial market. Lasers are unique energy sources characterized by their spectral purity, spatial and temporal coherence, and high peak intensity. One property of lasers, however, that of high intensity, did not immediately lead to 'delicate' applications but rather to those requiring 'brute force'. That is, the laser was used in applications for removing material or heating. The first realistic applications involved cutting, drilling, and welding, and the laser was little more advanced than a saw, a drill, or a torch. Vastly more expensive than traditional tools, however, the laser only slowly found niche uses where its advantages made up for the added cost and complexity.

An important development in the field of laser ablation was the application of lasers to generate a plasma at the surface, where the resulting spectral emission could be used for elemental analysis. Laser ablation of polymers was discovered in 1982, nearly simultaneously by two groups (Kawamura *et al.* [1] and Srinivasan and Mayne-Banton [2]). Srinivasan probably also used first the term laser ablation which is now common language. The discovery of laser ablation of polymers sparked research in this field in many groups around the world [3–5]. Nowadays, laser ablation of polymers is industrially used to prepare the via-holes in multi-chip modules through polyimide at IBM, and for the production of the nozzles for inkjet printers (also polyimide). Another important development of laser ablation started in 1983, when the first deposition of a superconducting film by laser ablation was reported, but became only well-known after the reinvention in 1987 for thin films of high-temperature superconductors (Y-Ba-Cu-Oxides).

Several other laser ablation-based methods 'came of age' in the late 1980s. Particularly spectacular has been the growth of laser-based medical procedures, such as laser-based ophthalmology; in dermatology for the removal of birthmarks, tattoos and smoothing of wrinkled skin; laser surgery for internal arthroscopic cutting and for arterial angioplasty; and projections for dental applications.

Laser ablation based microanalysis techniques have also become very successful, *e.g.* matrix-assisted laser desorption/ionization (MALDI) has revolutionized the identification and study of large molecular weight biomolecules and polymers. Finally, extremely high power laser ablation has paved the way to the generation of pulsed table-top X-ray and neutron sources. As a paradigm for the evolving sophistication, laser ablation has now become a tool for graffiti removal, and more delicately for art restoration, *e.g.* of paintings and parchments. Excellent summaries on various aspects of laser ablation can be found in the following books [6–12].

The principle of laser ablation can be described in the following simplified way. When an intense laser beam (pulsed or continuous wave) interacts with the

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surface of a material, various processes are taking place. Above a certain (material, wavelength, and pulselength dependent) threshold, removal of material is observed. This process is termed laser ablation. The ablated area is defined by the dimensions of the laser beam, allowing structuring in the micron to sub-micron range (diffraction limit = $\lambda/2$). The ablation parameters of different materials are dependent on the laser and material properties. Generally speaking, the high photon energies of UV lasers are capable of direct bond breaking in organic materials or polymers, *i.e.* photochemistry, while longer wavelengths mainly initiate thermal reactions. With short laser pulses, *i.e.* fs-lasers, even transparent materials can be structured due to processes such as multiphoton absorption. UV lasers are mainly applied for high-resolution applications (microlithography), while IR lasers (CO_2-lasers) are used for cutting and welding (*e.g.* in the automotive industry).

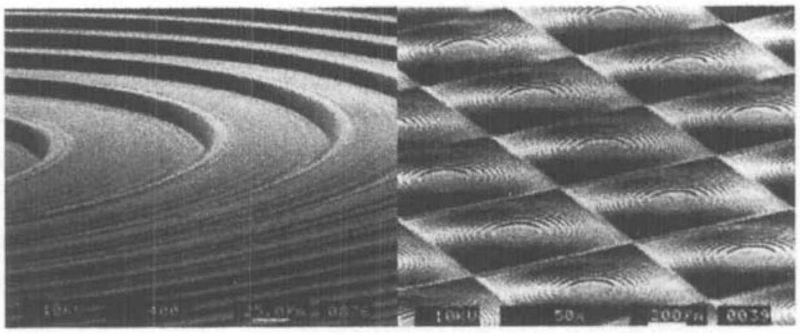

Fig. 1. SEM images of diffractive lenses fabricated by laser ablation. Magnification of one lens (left) and array of lenses (right) ablated with 308 nm using a step and repeat mode.

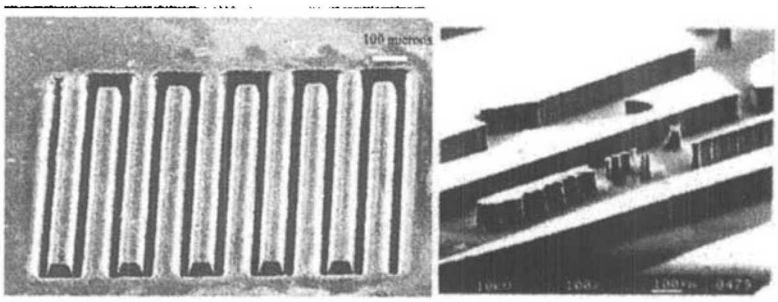

Fig. 2. SEM image of a test pattern with meander structure in glassy carbon (after ultrasonic cleaning), produced by 308 nm laser ablation with a pin hole mask. 20 pulses at each position with a fluence of ~ 60 J cm^{-2} (left). Random structure in glassy carbon, produced by a combination of etching techniques (right).

Research Projects

The following aspects of laser ablation are investigated in research projects of our group.

• *Microstructuring*

Fabrication of Microoptical Elements by Laser Ablation [13–15]. For this project, specially designed phase masks, fabricated by electron beam lithography, are applied to create complex three-dimensional structures. Examples of fabricated microoptical elements include gratings and Fresnel lenses. In Fig. 1 (left), a magnified view of a Fresnel lens and a lens array (right) produced by laser ablation are shown.

Structuring of Carbon Materials by Laser Ablation and Other Techniques. Carbon materials are important for various electrochemical applications. Laser processing and other techniques are applied for the development and design of microstructured electrodes for fuel cells. The meander structure in Fig. 2 (left) was created by laser ablation. These structures may be used for the gas distribution in glassy carbon electrodes of model fuel cells. The random structure in Fig. 2 (right) was obtained by a combination of different techniques.

Development and Test of New Polymers for Laser Ablation [16–21]. Novel photopolymers, designed for laser ablation, reveal low threshold fluences for ablation and high etch rates at low laser fluences. The decomposition products of these polymers are mainly gaseous and do not contaminate the surface. These polymers are therefore promising candidates for creation of microoptical elements by laser ablation. In Fig. 3, a comparison of structures (*i.e.* Siemens star) ablated into a special designed polymer (top) and a standard polymer (polyimide, bottom) are shown. The deposited debris is clearly visible in the case of polyimide, while it is absent for the designed polymer.

Fundamental laser ablation studies [22–25]. Various spectroscopic techniques are applied to study the ablation mecha-

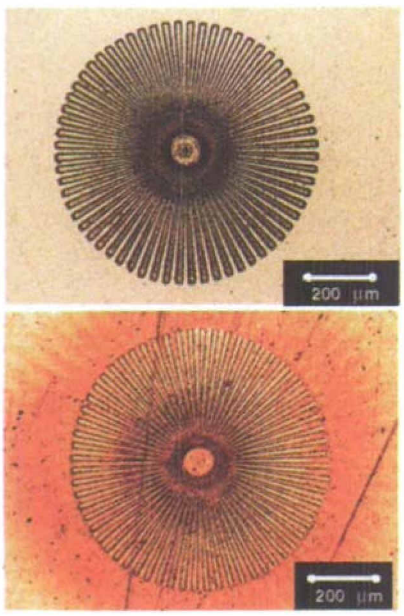

Fig. 3. SEM images of 'Siemens star' fabricated by laser ablation. Siemens stars were produced in a designed polymer (top) and in polyimide (bottom) using five laser pulses at 308 nm.

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nism that is still controversial. Examples of applied techniques are diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, Raman-microscopy, time-of-flight mass spectrometry (TOF-MS) in cooperation with Washington State University, X-ray photoelectron spectroscopy (XPS) and various time resolved techniques, *e.g.* ns-shadowgraphy and ns-interference fringes to probe surface morphological changes caused by laser irradiation in cooperation with Osaka University.

• *Thin Film Deposition*

Thin films of crystalline materials are produced to study the catalytic activity and the oxygen reduction mechanism of electrodes used *e.g.* Zn/air batteries [26]. These materials, such as perovskites, are prepared by pulsed laser deposition (PLD) with a special set-up, *i.e.* crossed reactive gas pulse PLD [27]. Thin single crystalline films are prepared and studied with various analytical techniques, *e.g.* XPS, X-ray diffraction (XRD), Rutherford backscattering (RBS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM), at PSI or at our collaboration partners at University of Zürich and University of Augsburg. Fig. 4 (left) shows a cross-sectional HR-TEM micrograph of a film. The lattice planes (top) are oriented perpendicular to the MgO (001) substrate (bottom), showing the epitaxial growth of the film. In Fig. 4 (right), the corresponding XRD spectrum is shown, confirming the crystalline structure of the perovskite film ($La_{0.6}Ca_{0.4}CoO_3$).

• *Plasma-Emission Spectroscopy, or LIBS*

In-situ *Diagnostic Tool During Pulsed Laser Deposition.* Emission spectroscopy is applied to study the ablation process during reactive gas pulse PLD, to gain a better understanding of the interaction of the gas pulse with the ablation plume and to develop an on-line diagnostic tool for film growth. A much brighter ablation plume is observed for the reactive gas pulse PLD (Fig. 5, top), as compared to deposition without reactive gas pulse (bottom). The corresponding emission spectra with and without reactive gas pulse are shown in Fig. 6. The influence of the gas pulse is clearly visible, *i.e.* higher intensities in the case of the reactive gas pulse PLD.

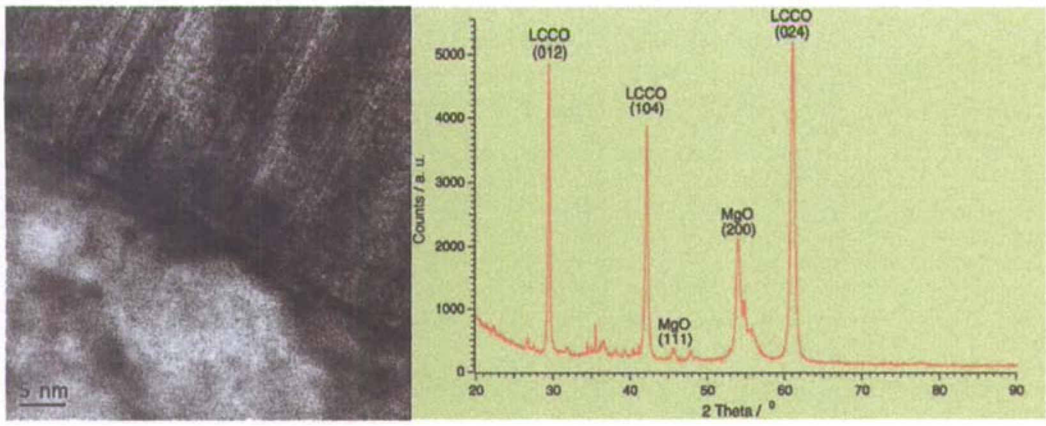

Fig. 4. High resolution TEM image (left) of perovskite film fabricated with pulsed laser deposition and corresponding XRD spectra (right).

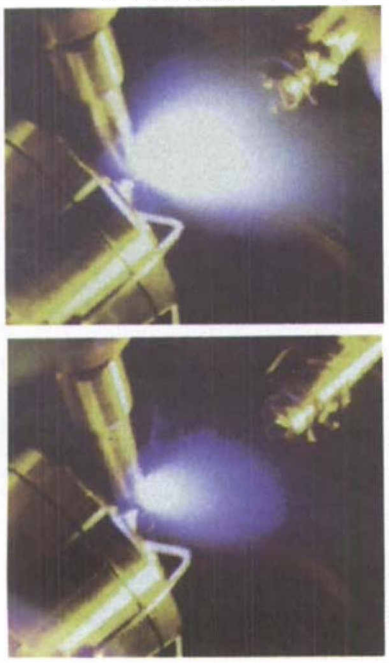

Fig. 5. Images of the PLD process with reactive gas pulse (top) and without (bottom).

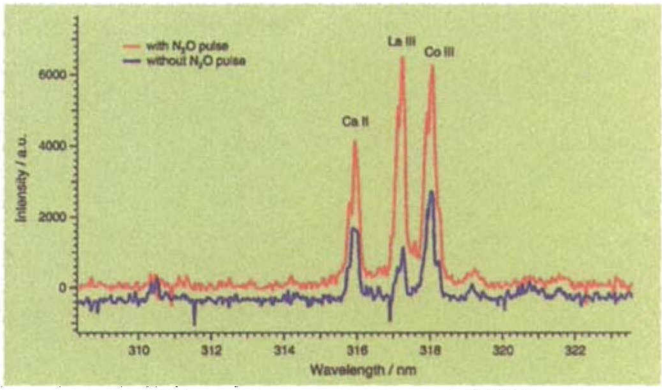

Fig. 6. Optical emission spectra corresponding to the images in Fig. 5.

Emission Spectroscopy for Trace Analysis [28]. LIBS can also be used for trace analysis of metals in complex matrices. This technique can be designed for mobile, remote use (it has even been suggested as an analytical technique for the next Mars mission). We are studying the fundamental processes of emission spectroscopy and the influence of various parameters, *e.g.* water content and particle size of the matrix, on the performance of this technique. The results are correlated with data from another laser ablation based analytical method, *i.e.* laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at ETH Zürich. The detection limit for LIBS depends on the element, but is typically in the ppm range.

Summary

Laser processing and laser ablation are mature techniques that are used in various applied and fundamental projects. The applications of laser ablation range from microstructuring of many materials to thin film production and micro-spectroscopy. Both aspects, applied and fundamental, are currently studied in our project. Specifically, we are investigating the design and structuring of novel polymers, advanced methods for the microstructuring of glassy carbon, and the pulsed laser deposition of perovskite films for electrocatalysis. Additionally, emission or plasma spectroscopy is used to study the PLD process and as tool for trace analysis.

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