# CHAPTER

# 1

# INTRODUCTION

AKOS VERTES

*Department of Chemistry*
*George Washington University*
*Washington, D.C.*

RENAAT GIJBELS and FRED ADAMS

*Department of Chemistry*
*University of Antwerp (UIA)*
*Antwerp, Belgium*

After two decades of incubation, laser ionization mass analysis is rapidly gaining importance in several areas of analytical chemistry. Although in the early 1970s lasers were already claimed to be capable of directly probing and ionizing solid samples, the high hopes of a molecular microprobe have been disproved both by methodological difficulties and by poor sales statistics of several commercial instruments. It is the more mature understanding of laser–solid interaction acquired during the early applications of laser ionization that led to the redefinition of its place in analytical chemistry and to the discovery of several new methods. The pulsed laser in the new context is viewed as a tool of depositing a tunable amount of energy into a chosen degree of freedom of the material, rather than as a fast local surface heating device. Our book is centered on this concept, with special emphasis on proven or promising applications.

Laser-based methods also are at the forefront of advanced material synthesis and processing. Owing to increased efforts in the past few years we have witnessed several breakthroughs in employing the unique features of laser-driven energy deposition in solids. Laser–solid interaction is utilized in diamond synthesis, high-temperature superconductor preparation, desorption of large biomolecules, and sampling of solids for chemical analysis. Let us browse through these discoveries and their promising applications.

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Because of the unique mechanical, thermal, and electric properties of diamond, synthetic diamond production is an area of large technological importance. Earlier efforts included high-pressure and low-pressure plasma, ion beam, and combustion flame methods of preparation. Pulsed laser deposition led to the first successful synthesis of high-quality diamond films on metal substrate (Narayan et al., 1991). This result presented a landmark in the continuing effort to introduce diamond into wide areas of microelectronic applications.

Laser ablation also is part of the pulsed laser deposition technique, a promising contender for producing films of multicomponent materials such as high-transition-temperature superconductors. In the preparation of superconducting $YBa_2Cu_3O_{7-x}$ layers, laser processing also offers unique features in the oxygen atmosphere annealing step. The extreme fast heating and cooling rates achieved with lasers make it possible to reach the necessary surface temperature without substantially changing the bulk temperature. This selectivity has its obvious advantages in dealing with complex microstructures.

Another breakthrough related to laser–solid interaction came from the field of analytical chemistry. For decades, for gas phase investigation of large (bio)molecules, there has been an obstacle: above a certain molecular weight, it was impossible to volatilize these substances, therefore precluding the application of powerful analytical techniques such as mass spectrometry in their investigation. The introduction of matrix-assisted laser desorption made it possible to bring about the necessary phase transition. As a result, mass spectrometric investigation now provides unprecedented accuracy in molecular mass determination up to several hundred thousand atomic mass units (Karas et al., 1989; Beavis and Chait, 1990; Spengler and Cotter, 1990).

The general application of laser sampling of solids for analytical purposes is also in the introductory phase. Preliminary results are available for laser sampling in combination with inductively coupled plasma mass spectrometry (Denoyer et al., 1991) and with glow discharge mass spectrometry (Harrison and Bentz, 1988) for the analysis of metals, glasses, ceramics, and other hard-to-analyze insulators. The technique is far from maturity, but indications of its superior analytical sensitivity and versatility are already apparent.

The relation between these applications of laser–solid interaction is clear if we display the laser irradiances, $I_0$, and light absorption coefficients, $\alpha$, involved as illustrated in Figure 1.1.

Although preparative and analytical applications of laser–solid interaction are based on the same physical phenomenon, little or no interaction exists between these fast-growing areas. Even the two sets of journals (preparative applications: *Applied Physics Letters*, *Journal of Applied Physics*, etc.; analytical applications: *Analytical Chemistry*, *International Journal for Mass*

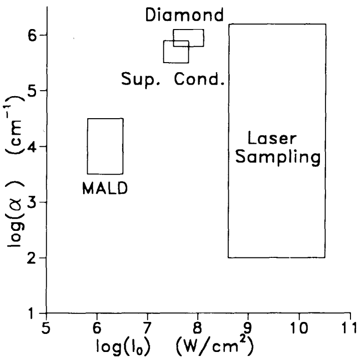

**Figure 1.1.** Map of deposited power density in some important applications of laser-induced processes: MALD, matrix-assisted laser desorption; Sup. Cond., pulsed laser deposition of high-temperature superconductor layers; Diamond, synthetic diamond formation; and laser sampling.

*Spectrometry*, etc.) and conferences are almost completely disjunct, and cross-references in the publications are scarce. Obviously the result of this parallelism is considerable waste of time and energy. On the other hand, recognition and investigation of the common elements of laser–solid interaction in the aforementioned areas can lead to cross-fertilization. One of our objectives in this volume is to blend the different fields together. That is why we have invited leading scientists from both groups to contribute.

There are continuing efforts from both the "preparative" and the "analytical" community to understand and describe the basic processes involved. Laser ablation of copper—the successful substrate for diamond film synthesis—has recently been investigated from the point of view of technological (Dreyfus, 1991) and analytical (Kimbrell and Yeung, 1988; Balazs et al., 1991) processes. Among other techniques mass spectrometry, fast photography, spectroscopy, scanning electron microscopy, and laser-based diagnostic techniques have been used to uncover the ionic, cluster, and particulate constituents of laser-induced plumes above different targets. Theoretical studies ranged from gas dynamic treatment of Knudsen layer formation (Kelly and Dreyfus, 1988) to the numerical solution of the equations of heat conduction and of plume hydrodynamics (Vertes et al., 1989; Nakamiya et al., 1990) to a two-step (isothermal + adiabatic) plasma expansion model (Singh and Narayan, 1990).

Obviously, the significance of basic studies in preparative and analytical applications of laser–solid interaction should not be underestimated. New materials and novel processing and analytical methods are expected to emerge in this area. Also the mechanisms of a number of underlying processes will no doubt eventually be unveiled.

In this volume we outline the large and fast-growing area of analytical applications: ion generation for mass analysis. As editors of this multiauthor volume, we have tried to maintain a coherent approach based on the following structure.

In Chapter 2 an elaborate overview of instrumentation is given. Starting with the history of lasers in mass spectrometry we see how the design concepts evolved in the organic and inorganic applications. Microprobing with lasers captured the imagination of instrument builders for about two decades. Separation of volatilization and ionization has been suggested as a way to increase sensitivity and selectivity of the chemical analysis. To further enrich the analytical capabilities, various combination techniques have been introduced. In these methods ion or neutral beams are used complementing the laser beam at different phases of the measurement. Chapter 2 also deals with various types of mass analyzers. Considering the special features of the laser-generated ion swarms, devoted constructions had to be developed. Magnetic sector mass spectrometers, time-of-flight mass spectrometers, Fourier transform mass spectrometers, and other less common constructions are discussed.

Chapter 3 deals with methods utilizing low and medium laser irradiance. Because molecular structure is usually not destroyed in these experiments, this irradiance range is the domain of organic analysis. The up-and-coming laser ionization method is the matrix-assisted technique, as is obvious from the programs of more than a dozen related conferences. The virtue of matrix assistance is to volatilize and ionize extremely large molecules (up to 300,000 Da as of now) by an easy and extremely fast sample preparation technique. The method is currently in the phase of vigorous development. It now seems possible to analyze mixtures of large molecules without separation and to monitor the time development of enzymatic degradation. Proteins, nucleotides, nucleosides, lipids, carbohydrates, and possibly industrial polymers are within the scope of this new technique.

With the careful selection of the ionization conditions it is possible to obtain structural information on small organic molecules. Large numbers of organic compound groups are studied and show characteristic fragmentation schemes. Comparison with electron impact fragmentation pathways is the topic of numerous current studies. Accumulating knowledge on the structure–fragmentation relationship makes this technique an important and fast tool for organic chemists.

Another promising method is based on the recognition that optimal conditions of volatilization and ionization/fragmentation may require substantially different laser parameters. While volatilization often can be achieved by infrared radiation, selective fragmentation and/or ionization can only be carried out by ultraviolet laser pulses. Optionally, a gas jet can be applied to entrain and cool the desorbed molecules. By this or a related method, ultimately one can hope for the controlled fragmentation of complex organic molecules.

In Chapter 4 the high laser irradiance regime is addressed. Owing to the elevated energy deposition in the laser–target interaction, few intramolecular bonds can survive; therefore, this regime is mainly bound to elemental analysis. Laser ablation and plasma formation—used also for material processing—exhibit special features in laser light coupling. These mechanisms have been studied both experimentally and theoretically. Laser-induced fluorescence, Langmuir-probe, and time-of-flight analyzers are used to determine density and velocity distributions of the different species in photoablated plumes. Theoretical considerations reveal spatial and temporal details of the laser-generated microplasma.

Solid sampling for elemental analysis by inductively coupled plasma or by glow discharge mass spectrometry is a promising technique, especially for the analysis of insulating materials. The plume generated by the laser shot is introduced directly to the glow discharge cell or entrained into the inductively coupled plasma torch by a gas flow. Crater characterization and analyte transport studies are underway to improve the analytical features of this new method. Although commercial laser samplers are already available from different vendors, the field of analytical applications is far from being fully exploited.

The idea of inorganic trace analysis by laser plasma ionization has been present since the conception of laser microprobe analysis. Uniform sensitivity for most of the elements and detection limits in the ppm range combined with better than $5\,\mu m$ lateral resolution have established the worthiness of this technique in the family of elemental microprobes. Instrumental considerations, analytical performance optimization, evaluation procedures, and interesting applications are discussed in Part C of Chapter 4.

Finally Chapter 5, highlights some exotic applications of laser ionization mass spectrometry. Owing to their exceptional analytical characteristics, laser ionization mass spectrometers were placed on two interplanetary space stations by scientists of the former Soviet Union. Both stations were aimed at one of the satellites of Mars named Phobos. Although, unfortunately, both space probes were lost during their trip to Mars, the care and thought that went into the design of some of the scientific payload may serve more "earthly" applications in the future. In Chapter 5 we gain a unique insight into the development of these on-board laser ionization mass spectrometers and into the operation of the prestigious Space Research Institute in Moscow.

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