LASER ABLATION OF POLYMERS – A 20-YEAR PERSPECTIVE

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1. Introduction

Although the title of this talk refers to 'Laser Ablation' as a general phenomenon as applied to polymers, it will really deal with the more limited topic of 'Ultraviolet Laser Ablation of Organic Polymers'. This field attracted interest only when a simple and convenient source of laser radiation in the ultraviolet (UV) region became available with the invention of the excimer laser in the 1970's. Studies on the interaction of UV laser pulses with solid organic matter such as synthetic polymers and biological tissue led to the discovery in 1982 [1-4] of the phenomenon of "Ablative PhotoDecomposition (APD)", which results in the breakup of the covalent-bonded structure of the organic solid by the photons and the expulsion of the fragments at supersonic velocities. The result is an etch pattern in the solid with a geometry that is defined by the light beam. The principal technological advantages in using UV laser radiation rather than visible or infrared laser radiation for this purpose were realized even at the time of the discovery of this phenomenon. These are the precision (± 2000 A) to which the depth of the cut can be controlled by adjusting the number of pulses and the fluence of the laser and the lack of thermal damage to the substrate to a microscopic level. Its extendability to cutting or etching tissue was also quickly realized [5].

2. Scientific Studies

It is likely that the term 'ablation' was used in connection with laser interaction with materials for the first time in 1982 [1b]. It was meant to signify an explosive burst of matter consisting of atoms, small molecules and pieces of a polymer chain that was expelled at supersonic velocity from a surface that was being irradiated with a laser pulse. The entire process that results in ablation can be dissected (purely for interpretive purposes) into (1) an absorption of the photons, (2) the breakup of the solid, and (3) ejection of the products from the irradiated surface [6]. Every aspect of this scheme has been the subject of intense physico-chemical research by numerous groups over the past 18 years. *If this analysis is limited to ablation of organic polymers by UV photons,* the first absorption step by the chromophores in the polymer, is well-understood at low photon intensities, i.e., at a few w/ cm^2. But APD is a non-linear phenomenon which is observed only when the photon intensities are greater than a threshold value of 1 Mw/ cm^2. At these high intensities, the absorption process may no longer be limited to one photon per chromophore. The second step is the breakup of the polymer chain into numerous fragments. In spite of all the effort that has been devoted to this field, there has been no exhaustive quantitative study of the chemistry of the decomposition of even a single organic polymer under a variety of experimental conditions. This has necessarily resulted in a wide range of interpretations and much controversy regarding the mechanism of the process. The third step is the explosive ejection of the products of the laser decomposition. Here again, the scientific studies have been fragmentary rather than systematic thus adding fuel to the discussions !

3. Applications of APD

Two applications of APD, one in the semiconductor industry and one in ophthalmic surgery, have reached such remarkable levels of growth and world-wide acceptance that they account for almost the entire technological interest in APD today. In the semiconductor industry, the etching of polyimide films (either as free-standing films or as a coating on a metal or ceramic substrate) by excimer laser pulses has revolutionized the use of polyimide as an insulating layer in chip packaging and for nozzles in the ink-jet printer industry.

It is worth taking a moment to look at the state of technology in the mid 1980's when polyimide was being seriously considered as a material for packaging chips. In the U.S., the polyimide of choice was PMDA-ODA and in its imide form there was no practical way to drill or etch via holes in the material. It was therefore necessary to do the drilling by chemical etchants in a polyamic acid film and then conduct a final baking step in which the imidization took place. Apart from the poor control that chemical drilling of the polyamic acid film involved, there was also the serious shrinkage in the final baking step (about 20%) which played havoc with the tolerances. Drilling with an excimer laser and APD simplified these operations by allowing the drilling to be done on the polyimide film itself and there was no longer a need for chemical etchants at all. As soon as reliable, industrial-quality excimer lasers became available by 1988, this technology was readily accepted in semiconductor manufacturing. In turn, this led to the drilling of the nozzles in ink-jet printers by the same technology. These nozzles are made to severe tolerance, yet their cost had to be so little that when an ink reservoir is replaced the nozzles can be discarded. Drilling the jet holes in a polyimide wall allowed this to become commercially viable.

In both these applications, drilling holes in a polyimide film is only one of numerous steps in the manufacture of a product. It is therefore impossible to calculate the dollar value added to the product by this step. But it can be categorically stated that it is the possibility to use APD to drill these holes that has created these technologies. The laser along with the necessary projection optics with a train to feed the work and a computer to control the process usually costs 1 – 2 million dollars. The total value of such equipment in use today is believed to be over 500 million dollars and growing at an annual rate > 15%.

The application of APD to the recontouring of the curvature of the human cornea in order to correct for defective vision is now fully accepted in ophthalmic surgery in more than 50 countries and more than 2 million people have benefited from it. It had been known to ophthalmic surgeons even at the beginning of the 20th century that the correction of myopia, astigmatism and hyperopia can be achieved if the cornea can be etched to depths of the order of tens of microns. What was missing was a tool that would give the surgeon control over tissue removal that was good to ± 2 mμ. APD has made this possible and computer control has effectively eliminated the possibility of human error in the establishment of the depth of the etching. Last but not the least, the lack of thermal damage to the volume of tissue that underlies or adjoins the etched surface (of the cornea) that is one of the key features of APD has prevented the loss of clarity in the treated eye.

What APD has to offer to surgery is actually a tool that lets a surgeon use it not just in the eye but for all living tissue as well. It is the first time in the entire history of surgery which runs to more than 4 millenia that a non-contact method of cutting (or drilling) with incredible precision has become available. Thus another application which has become well established although only in research laboratories is the use of APD for the dissection of single biological cells and the their isolation for DNA amplification.

As different medical and biological specialties come to understand the potential of APD and in parallel, the cost of a set-up for the procedure becomes acceptable, one can fully expect other novel procedures to be discovered in the coming years.

4. References

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