

**UV FEL light source for industrial processing**

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### **ABSTRACT**

Short-wavelength UV light is strongly absorbed by most materials, creating the opportunity to drive near-surface thermal or chemical processes. The resulting modifications have a wide range of prospective applications, but few have been developed because of the low capacity and high unit cost of light from present sources. We analyze the light source requirements for large-scale applications to polymers and metals. We describe meeting them with free electron laser whose design is described in a companion paper in this session. This machine will deliver 1.0 to 2.5 kW between 190nm and 350nm with options in the visible and IR, and serve to further develop FEL technology for much higher powered machines. We gratefully acknowledge support for this work from the Commonwealth of Virginia Center for Innovative Technologies and The U.S. Department of Energy.

**Keywords: laser processing, FEL, surface processing, UV light, economic analysis.**

## 1. Introduction

The situation of American industry has been widely discussed and we need here to recall only certain key points. The return on capital in manufacturing in recent years eroded deeply enough to become no longer competitive with other investment opportunities, prompting efforts to restore earnings performance by cost reduction, often through unprecedented downsizing. Though reports of record earnings are now commonplace, they certainly cannot persist long in the face of lower cost competition from former third-world nations determined to raise living standards by moving up the chain from agrarian economies to basic manufacturing to advanced manufacturing to technology leadership. No doubt some benefit may be realized from further downsizing, but "shrinking to greatness" has limits. Increasing earnings through increased physical volume of existing and kindred products is possible only if new, better-performing technology can be deployed and if sufficient capital can be obtained. A more inviting competitive strategy is to seek increased earnings through leveraging the existing manufacturing investment base: adding value to existing products. Surface modification offers exactly this opportunity.

## 2. Polymer Surface Processing

Synthetic fibers and textiles made from them illustrate many important aspects. Surface modification by wet chemical processing is already well established, with anti-stain treatments for carpet as probably the most familiar example. 1994 saw world-wide production of about 40 billion pounds of synthetic and artificial fibers [1]. Taking  $0.2 \text{ m}^2/\text{g}$  ( $91 \text{ m}^2/\text{lb}$ ) as an average textile fiber surface area, another view of 1994 production is 1.4 million square miles of surface area, about  $3/8$  of the land area of the United States. However the costs that can be tolerated for developing this real estate severely limit what can be done. Throughout 1995 the selling price of benchmark polyester staple (used for blending) and yarn both stayed just below a dollar a pound [2]. Accepting a 20% cost increase for surface modification is equivalent to only 0.2 cents/ $\text{m}^2$  if all the surface of every fiber must be treated. The constraint can be relaxed considerably by instead modifying the surface of a fabric instead of the surface of every fiber in it, as a later example will show, but 5 cents/ $\text{m}^2$  of fabric is still limiting. Packaging, especially high performance packaging for food, is a more or less comparably large opportunity for polymer surface modification. Surface area per unit of packaging is larger than might be apparent, since typical package construction such as the familiar single-serve juice box incorporates many layers, each with its own surface issues. Nonetheless, modestly greater costs can be tolerated. The point to be seen here is that the potential scale of the applications is large enough to impact even the largest corporations, but that the cost horizons are far below where surface modifications other than wet chemistry have found widespread use. Certainly it is hard to anticipate that the surface processing technologies familiar from the electronics industry can ever reach the necessary cost/capacity horizons.

Short wavelength ultra-violet light appears promising as a means of surface modification. The ability of UV to drive transitions in organic molecules such as the initiation of radical chemistry has been known for decades and is widely used for lithography-based patterning. The high processing temperatures used for thermoplastic polymers (polyesters, nylons) appear incompatible with photoinitiators so that affordable, radical-initiated chemistry probably requires driving  $\pi - \pi^*$  transitions directly, typically at wavelengths below 200 nm. As an example of what can be achieved, delivering 1 - 3 J/ $\text{cm}^2$  at 193 nm to nylon converts surface amide groups to non-leachable amines, which exhibit broad-spectrum antimicrobial activity [3]. Films of this material could be used as enhanced-safety food packaging or fabrics as air filters to reduce the risk of airborne pathogens without themselves adversely affecting indoor air quality. A second strategy is to activate a gas phase species which then reacts with the surface, e.g., photo-assisted etching by oxygen. A third strategy is to activate a species on the surface. For example, the surface of polyimide (and probably other polymers) can be hydroxylated by irradiating a thin water layer with 172 nm light from a  $\text{Xe}_2^*$  excimer lamp [4]. Improvements result, such as increased adhesion of subsequently deposited metal for printed wire boards. The requirement in all instances is light of a wavelength that drives the transition that makes the radical; presently only the ArF (193 nm) and  $\text{F}_2$  (157 nm) excimer lasers, and the  $\text{Xe}_2^*$  (172 nm) excimer lamp are available.

The other family of polymer surface modification processes enabled by short wavelength UV is best understood as rapid thermal processing (RTP). Energy is deposited in a thin, near-surface layer only, raising its temperature sufficiently to bring about the desired transformation. The energy is delivered so rapidly that solid state heat conduction has no opportunity to move heat out of the surface layer before transformation conditions are reached. Further, the energy deposition is so brief and the total energy is so small that the underlying bulk can rapidly quench the heated surface. The benefit of UV light is to provide access to absorbances so high that all the energy delivered is deposited within less than a micron of the surface. IR light at a wavelength where absorbance is sufficiently intense is also effective. For example, polyimide's absorbance throughout the 190 nm - 250 nm wavelength range exceeds  $2 \times 10^5 \text{ cm}^{-1}$ , i.e., one micron is five absorption lengths. In contrast, nylon shows such high absorbance only in a narrow band centered near 190 nm. In addition to the requirement for near-surface energy deposition, RTP requires that deposition takes place so rapidly that heat transfer cannot move a significant amount of the energy away from its deposition site. The low thermal conductivity of polymers makes it easy for the few tens of nanoseconds pulse lengths from excimer lasers to fulfill this requirement.

A simple way to view polymer RTP applications is in terms of the effect of increasing energy deposition per unit area. In the range of a few tens of millijoules, the outermost micron or so of PET (poly ethylene terephthalate) is heated above the crystalline melting temperature and then cooled too rapidly by heat transfer to the underlying bulk for crystallization to occur, so that the surface remains amorphous [5]. The amorphous surface exhibits markedly improved adhesion in a number of applications [6]. Approximately the original degree of crystallinity can be restored by briefly raising the surface temperature to 140 - 180 C [7], typical of existing heat-setting practice. Delivering similar energy from a 248 nm KrF<sup>F</sup> excimer laser to a polyimide surface increased subsequent adhesion to copper foil by more than a factor of three [8].

Increasing energy deposition to several tenths of a joule, but at per-pulse fluence below the ablation threshold, melts the surface [9]. Melting releases retained strain energy in drawn fibers or films in the presence of the strong thermal gradient, giving rise to convection cells that freeze in upon cooling. Discussion continues as to the mechanistic details [10]. Nonetheless, the process imparts micron-scale roughness to films or fibers that markedly enhance their friction, wetting, filtration and visual appearance [11]. Irradiating with polarized UV light permits reducing the dimensional scale of the roughness from the "native" few-micron range [12] to a 0.1 - 0.2 microns [13]. Increasing energy deposition to tens of joules induces pyrolysis of the near-surface material [14]. For polyimide irradiation with a 248 nm excimer laser, a structure consisting of sub-micron carbon clusters in a matrix of the original polymer results [15]. Further energy deposition at 248 nm results in extensive graphitization, attaining near-metallic conductivity at about  $40 \text{ J/cm}^2$  [16]. True metallic character and significant current-carrying capability can be achieved by using the modest conductivity achieved at lower fluence to directly electroplate copper [17].

Delivering the energy rapidly with respect to absorption depth raises the temperature of the absorbing region sufficiently to vaporize and eject some of it: photoablation. The topic has been extensively reviewed [18]. Much of the ejected material is small molecular fragments, viewed as evidence of decomposition [19]. The tens of nanoseconds pulses typical of excimer lasers are long with respect to the ablation timeframe, so that certainly at least some of the decomposition must be due to action of the light on the plume of ejected material [20]. Nonetheless, robust polymers (e.g., poly tetrafluoro ethylene, PTFE) can be deposited with conventional excimer laser pulses [21]. Short pulse lasers appear to overcome the plume problem [22], raising hope that pulsed laser deposition (PLD) can give rise to a versatile, solvent-free technology for applying polymeric coatings. However, present laser costs limit prospective applications to all but a few high value applications [27]

### 3. Micromachining

A reasonable definition of micromachining is technology to create features in solid objects smaller than attainable by established "mechanical contact" and kindred methods such as drilling, cutting, punching,

or electrical discharge machining. Technologies where lithography is a critical step (e.g., LIGA) are usually not included. In point of fact, micromachining often turns out to be laser cutting. Three microfluidic examples give some notion of micromachining's potential scope. First, the 40 billion pounds of artificial fiber noted earlier were all made by extruding a polymer melt or (much less commonly) solution through a very special capillary array plate, a spinneret. Fiber manufacturers closely guard the details of their spinnerets, but some aspects are clear. The market pull for more natural-like quality drives synthetic fibers toward ever smaller cross-sections and toward non-circular shapes, placing ever-increasing demands on spinneret technology to make the capillaries that will yield such fibers. Further, making all those pounds of fiber requires many spinnerets indeed. A second example is the orifice plate in every fuel injector in every cylinder of every automobile made and many light trucks. The size and dispersion of the fuel droplets from the orifice plate affects the generation of pollutants during combustion and hence the difficulty of attaining ever more stringent emission standards. A third example is the orifice array found in ink jet printer heads, probably totaling much more than a billion holes annually. Desired improvements over conventional technology for all three applications include smaller size, greater aspect ratio, variable cross-section and materials versatility. However, these must not come at the sacrifice of production scale and unit cost.

An ideal micromachining operation should illuminate on the workpiece exactly the outline of the material to be removed. The energy should be delivered so rapidly that heat loss to adjacent material does not raise the temperature sufficiently to adversely affect properties (collateral damage) or impair energy efficiency: on the order of picoseconds. The pulse length should also be short enough to have completed before the energy-absorbing plume of ejected material could form, less than a nanosecond. The wavelength should be chosen that results in an absorbance such that the available pulse energy is only modestly more than enough to vaporize the absorbing volume. The repetition rate should be high enough that the plume of ejected material just clears before the next pulse arrives, as high as megahertz. Though CO<sub>2</sub> lasers find extensive use in metal cutting, their shorter wavelength and better beam quality seems to give the edge to Nd:YAG's for precision applications. Excimer lasers suffer from pulse length in excess of the plume generation time as well as beam quality issues, though UV's strong absorption by so many materials makes the use of excimer lasers appealing otherwise. An issue not to be forgotten is that all laser cutting so far operates by precisely moving the workpiece with respect to a stationary illumination system. Certainly the accuracy and speed of the positioning system will at some point become more limiting than the laser performance.

#### 4. Metal Surface Processing

Despite their displacement by polymers in some highly visible locations, metals will continue to be the dominant material of construction for the foreseeable future. In common with the polymers, many of the desired performance improvements for metals are surface-related, especially durability enhancements such as better corrosion, wear, and fatigue resistance. Others have a significant surface aspect: more environmentally benign fabrication and finishing processes that eliminate waste streams from traditional wet chemistry and more versatile adhesive-based joining technologies.

Metal surface processing with lasers is dominantly rapid thermal processing. One class of applications transforms the native surface so as to obtain more favorable microstructure: laser hardening, tempering, annealing, or glazing depending on the temperature to which the surface was raised. The opportunity to have widely different states of heat treatment at the surface and in the bulk is not available with conventional technologies and allows uniquely favorable performance to be obtained for the whole component. Laser surface hardening was found to increase the fatigue life of 1045 steel by two orders of magnitude [23] and to virtually eliminate water drop erosion of stainless steel turbine blades [24]. The other major family of applications alters surface chemistry as well. The added components can come from surface segregation of already-present alloying elements, previous thin film deposition or even be fed into the irradiation zone. For example, the Cr/Fe ratio on the surface of the widely used 304 stainless steel can be increased six-fold by careful laser melting [25]. The same alloy's friction coefficient can be reduced four-fold by Ti surface alloying through laser melting a previously applied Ti film [26].

#### 5. Light Sources

The preceding three sections discuss some of the most appealing applications for processing with strongly absorbed light. Taking advantage of them faces two major kinds of economic constraints. The first is that the value added can support only a limited unit cost for the light used in processing. Since these products are not now in the marketplace, definitive values for cost tolerance are not available. Rather, we estimate them on the basis of what is tolerated for surface modification by other means. Hopefully the unique values described above will command higher prices that will make the present estimates conservative. The second is that the surface processing must be integrated into existing production schemes to have any prospect of being affordable, i.e., surface processing rates must match existing work flows. Table 1 gives the resulting light source requirements for polymer surface processing.

Table 1: Illustrative Polymer Surface Processing Light Source Requirements

<u>Application</u>	<u>Light Needed</u> (J/cm <sup>2</sup> @ wavelength)	<u>Cost Tolerance</u> (cents)	<u>Typical Power</u> (kW)
Film amorphization	0.03 @ 248 nm (PET)	5/m <sup>2</sup> : 15/kJ	10
Surface texturing	1 @ 248 nm (PET) 1 @ 193 nm (nylon)	5/m <sup>2</sup> : 0.5/kJ	30
Antimicrobial carpet	2 @ 193 nm (nylon)	55/m <sup>2</sup> : 0.2/kJ	100
Electrical conductivity	40 @ 248 nm (polyimide)	\$5/m <sup>2</sup> (?): 1.25/kJ	10 (?)

The requirements for micromachining are hard to state so explicitly. Laser cutting so far is only considered when existing technology cannot create the part. The tolerable cost is then the value of whatever having the part permits one to do and the required production rate is also specific to the application. Another way to view these issues is by comparison to other machining technologies and laser cutting is then just another way to remove material. For psec laser pulse lengths, the required energy approaches the vaporization enthalpy of the removed material [20]. If we imagine an ink jet print head as 100 cylindrical holes having a diameter of 100 microns diameter and 300 microns depth, about 250 microliters of material must be removed, roughly a third of a milligram. No matter what value is chosen for the vaporization energy and for a non-ideality correction factor, the total energy per piece can hardly exceed several joules. One point to be seen is that production economics are more likely to be dominated by the fixed costs of workstation and its maintenance than by the cost of the light. An expected major cost impact of the light source will be rate at which it delivers pulses, because the pulse rate determines the cutting speed and thus the production rate. Over some range upward from the typical present kilohertz pulse rate, piece cost will fall directly as pulse rate goes upward. The first limit to be encountered will probably be the speed of repositioning to the next hole or the speed of changing pieces, but clever manufacturing engineers will be able to push the limit back for large numbers of identical pieces.

The requirements for metal surface processing are much more like those for polymers, especially if the end use design and the unit cost of light permit treating metal stock forms prior to fabrication rather than finished parts. In that case, costs must be in line with existing finishing operations, leading again to cents to tenths of a cent per kilojoule and very large power requirements, and treatments would presumably be done by the materials supplier. The other family of applications is piece treating, where again the comparison is to conventional treatment costs and might be done by job shops akin to platers and heat treaters.

Translating these research findings to large-scale manufacturing requires suitable light sources, where "suitability" may be summarized from the above as pico-second pulses of 175 nm - 300 nm UV light at megahertz repetition rate for less than a cent per kilojoule, scaleable to tens of kilowatts. The light sources used to demonstrate the applications are excimer lasers, but they have not been able to approach

these performance levels, even after twenty years of development. A major problem is inherent to the physics of conventional light sources: removal of waste heat from the active medium. As described subsequently [28], the free electron laser (FEL) offers different physics for converting electrical energy to light, simply the interaction of an electron beam with a periodic magnetic field (wiggler). The energy not converted to light consists of an electron beam departing from laser at the speed of light, making waste energy removal inherent to the light-generating process. Driving the FEL with superconducting RF cavities sharply reduces the cost of the light produced by allowing both 100% duty cycle operation and nearly complete recovery of energy from the beam after the wiggler. A further cost reduction yet might be attained by operating in the IR rather than the UV, which is expected to capture all the RTP applications, sacrificing only the applications that require chemical radicals.

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