

Materials processing research and development opportunities with the new generation of FEL's

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ABSTRACT

The history of materials processing teaches that each time a new processing technology becomes available, science and technology both can take a step forward. The new generation of free electron lasers now coming on line offers such an opportunity. Their high average power enables the use of fs to ps, high peak power pulses for materials processing as well as fundamental studies, with the further advantage of wavelength tunability. Taking together what has been learned with low average power fs – ps pulses, an assessment of materials processing needs, and the emerging capabilities of the new FEL's suggests what are the most promising near-term opportunities for these facilities. Progress with corresponding experiments and how they can be carried into manufacturing are described.

Keywords: free electron laser, ultrafast laser, laser micromachining, pulsed laser deposition

1. INTRODUCTION

After 25 years, the free electron laser can no longer be regarded as a novel light source technology, while it is indisputably unique. The underlying physics has been and continues to be studied extensively. The number of conferences and publications continues to grow. A consensus understanding is in place [1], though important things certainly remain to be learned, and FEL science has become embodied as FEL technology. The technology's present state has been adequate to build a number of user facilities around the world for spectroscopy and related experiments [2]. Roughly speaking, these first generation FEL's operate in the near and mid-IR to deliver individual micropulses a few picoseconds long separated by tens of nanoseconds in a format of microseconds-long macropulses at less than 100 Hz repetition rate to give less than 10 W average power [3]. These machines find extensive use for basic scientific studies, but their low average power is a problem for processing research. Enough material to assess properties cannot be produced in any realistic experimental time and the pulse format makes even microscale simulation problematical.

FEL's might have had more scientific impact if competing light sources had not deflected attention and resources. At more or less the same time as the FEL was born, so was the synchrotron light source (both at Stanford!). The versatility and multi-user capability of the latter attracted far more attention as a source of photons for inquiry, despite the higher initial cost. Efforts are being made to provide a way to depart significantly from the single user – single beam condition paradigm for FEL's [4]. Sources of photons for processing far more intense than the FEL's of the day appeared in the form of excimer lasers and more recently Ti: sapphire sub-ps machines. The successes and the shortcomings of such lasers are a source of the FEL's present opportunity. Both excimer and Ti:sapphire lasers demonstrated scientifically interesting and technologically appealing results, but deployment into manufacturing has been and will continue to be limited by cost and capacity to very high value applications.

Proposals for a new generation of FEL's took account of some of these issues and these second-generation machines are now beginning to come on line [5]. Their distinguishing features are: CW instead of macropulse/micropulse operation to give more than a hundred-fold greater average power, UV as well as IR capability, and ps or shorter micropulses. The critical enabling technology is the use of superconducting radiofrequency (SRF) accelerator with its 100% duty factor. FEL's using SRF-based accelerators can be scaled to megawatt average power if there is a reason to do so [5a] and SRF technology has been shown by experience in accelerators for nuclear physics to be sufficiently robust for industrial deployment. Calculations indicate that realistic values for the unit cost of light (< 0.1 cents/kJ) can prospectively be reached [6]. That such lasers can be built and operated successfully is not now seriously questioned. The first of the second-generation machines recently came into operation at Jefferson Lab (Thomas Jefferson National Accelerator Facility,

Newport News VA), exceeding 1.7 kW average power at 3 microns [7]. The pertinent output parameters are: 18.75 – 75 MHz (CW) PRF; 25 μ J maximum sustained pulse energy and 3 – 6 micron wavelength range [5].

2. PROCESSING APPLICATIONS

2.1. Micromachining

Turning now from the lasers themselves to what is needed for processing, we consider four areas – micromachining, pulsed laser deposition (PLD), large area thermal processing and chemical conversions. For present purposes, micromachining may be defined as cutting or drilling features smaller than can be attained by established methods such as mechanical drilling or electrical discharge machining (EDM), on the order of 100 microns for metals. Candidate applications include fuel injector orifice plates, spinnerets for synthetic fiber production, ink jet printer head orifices and aircraft boundary layer control panels. The fuel injector orifice plate dispenses fuel into the cylinder of piston engine as perhaps a dozen streams of as-small-as-possible droplets at precise angles and originating at precise locations on the plate. Performance criteria address droplet smallness and uniformity, equality of flow in the streams, accuracy of aiming of the streams, equality of flow from plate to plate and stability of performance in use. How well the orifice plate does its job has such a major impact on emissions that attaining the coming standards by after-treatment will not be a tolerable way to compensate for inadequate orifice plate performance. As long as reducing automotive emissions remains a goal, so will improving fuel injector orifice plates. Annual worldwide automotive needs well exceed 100 million holes.

World-wide capacity for polyester (PET) fiber alone exceeds 40 billion pounds [8], a number that may be put in better perspective by noting that the total length of the filaments in a pound of PET yarn is a few to several hundred kilometers. All this yarn is made as individual filaments by extruding polyester melt through small capillaries followed by drawing to establish molecular orientation and to achieve final filament size. Consumer desire since the first synthetic textiles were produced has been for a more natural-like appearance and feel, attained chiefly by decreasing fiber size and using non-round cross-sections. Only laser cutting can take the industry to the smaller and specially-shaped capillaries needed for premium priced fibers. Typical differences from the fuel injector orifice plate case are that the capillaries are all normal to the face rather than angled; the location of individual capillaries relative to each other need not be precise; desired L/D ranges from a few to several rather than values near unity.

Each ink jet printer heads has a precise array of a few hundred orifices cut into polyimide film, though metal is sometimes used. The holes are cut as an array by photo-assisted laser etching technology specific to polyimide and akin to that used for via cutting in the microelectronics industry. Annual volume well exceeds a billion holes. Consumer desire continues to be improved image quality, obtained chiefly by depositing more image elements per unit area of print, which in turn depends on decreasing printer head orifice size and perhaps increasing the number of orifices in the array and their density. The opportunity to use materials other than polymers which photoetch would permit exploring new ink formulations and new dispensing processes.

The intended application to aerostructures will enable a further step in combat aircraft performance by improved boundary layer control. On each aircraft, a few square meters of titanium alloy critical skin panels are to be provided with more than 30% coverage of less than 75 micron non-cylindrical holes for withdrawing or dispensing air. The non-constant cross section, the importance of relative hole positions make and the large piece size make the aerostructure application particularly challenging. The prospective value of laser micromachining for ceramics has been recognized since the laser drilling became possible, but no applications appear to have been achieved. The consensus understanding is that thermal and mechanical damage to material adjacent to hole initiates failure of the machined part. Yet another prospective application is to cut the channels needed in microfluidic and micromechanical devices (“MEMS”) so that materials can be used other than the silicon needed by the lithographic techniques presently employed. What MEMS devices will find a place in the market is still becoming clear, but the general pattern for most devices being considered points toward smallest channels being on the order of a few tens of microns.

A deployable laser micromachining technology needs all the elements of a total system, including a laser that generates suitable pulses of light, an optical system to condition, manipulate and deliver the beam, and a mechanical stage to manipulate the succession of workpieces. Though carbon dioxide lasers are well-established for metal cutting, they are not applied at this dimensional scale. Nd:YAG lasers may find some use at the upper end of the micromachining range. Copper vapor lasers deliver a wavelength (511 nm + 578 nm) about half that of the Nd:YAG's, with a natural 20 – 40 ns pulse length. They are now commercially available up to 75 W. The manufacturer's website [www.oxfordlasers.com],

which presumably presents the best results so far attained, at this time shows 20 micron and 50 micron holes ($L/D = 2$) in steel, 130 micron holes ($L/D = 4$) in alumina and 70 micron slots in 350 micron thick diamond.

Considerable attention is now going to Ti:sapphire laser systems using chirped pulse amplification to deliver pulse lengths in the 0.1 – 10 ps range at peak powers near 1 TW/cm^2 [9]. The consensus picture [10, 10a] of the effect on metals is that the photons transfer energy to the free electrons. They lose phase coherence within a few tenths of a picosecond after the pulse ends and diffuse outward. The electrons cool by transferring energy to the phonons in a materials-dependent time [11] on the order of a few to several ps. Because so little time is available for thermal conduction to move heat into adjacent material, many workers found that the ablation threshold energy is markedly reduced compared to nanosecond pulses [12, 13]. A further evidence for energy confinement within irradiated region is that energy efficiency, defined here as volume of material removed per unit of laser energy delivered, also increases in the same way [13a]. The corresponding picture for insulator oxides such as ceramics and optical materials [14] is that multiphoton ionization generates a small initial population of free electrons that multiplies through an avalanche cascade to become a metal-like absorber. A further five-fold reduction in threshold energy for quartz beyond the thermal transport time effect has been achieved by spreading the dose over many shots has been reported [15], suggesting that there may be more going on.

To the extent that polymers and other organics have been addressed explicitly [16, 17], a substantially similar sequence of events appears to take place. A 100-fold reduction in threshold energy has been reported for 532 nm irradiation of 6/6 nylon and PMMA with 100 ps vs microsecond pulses, but with no further threshold reduction in reducing pulse length further to 0.8 ps, consistent with polymer thermal properties compared to those of metals [18]. A unique behavior is reported for semiconductors [19]: the high level of electron excitation distorts the lattice causing direct (not phonon-mediated) melting. The use of ps pulse lasers for micromachining has been patented [20] and is commercially available [website: www.cmxr.com]. An important point about micromachining with a sub-ps laser is that for peak powers above threshold (roughly 0.1 TW/cm^2 , depending on the material), absorption is substantially independent of laser wavelength and the choice of material: high absorbance can always be achieved. Accordingly, the equipment could be optimized for laser and optical transport performance. The output power of Cu-V and amplified Ti:sapphire lasers is less than 100 W; one laser can drive one micromachining station. An issue for FEL's is that the micropulse energy is roughly 50 fold less than that of an amplified Ti:Sapphire laser.

For the nanosecond pulse lengths, a melt forms and then an ablation plume which absorbs energy from the latter portion of the laser pulse to form a plasma. The rapid heating and expansion of the plasma propagates a pressure wave back onto the workpiece, expelling much of the remaining melt but also creating a shock wave in the workpiece [21]. The plume includes material ranging size from individual atoms to sizable particles; detailed studies are available for some materials [22]. A portion of the ejected material deposits back on the entry surface as debris, which must be removed. For the picosecond time scale, ejection of material occurs long before a melt can form, in as little as 10 ps, but well after the end of the laser pulse, avoiding irradiation of the plume [23]. The shock wave into the material, the formation of a recast layer on the walls of the hole being drilled and debris adjacent to the hole are all reduced accordingly. Detailed studies of the plumes from ps pulse ablation are just beginning to become available.

The drilling of high quality holes with nanosecond or longer pulses usually proceeds by tracing the perimeter with a moving laser beam rather than by steady penetration of a fixed beam (percussion drilling). In earlier systems, the beam was fixed and a precision mechanical stage moved the workpiece. Now for the smallest holes the beam is moved with a trepanning head, rather than the workpiece, since accurately controlling both the position at rate of mechanical motion at such small dimension is difficult. A different situation may be possible with picosecond pulses. A 0.15 ps pulse laser was able to percussion drill 21 micron diameter holes through 1 mm thick quartz ($L/D = 50$), though with some damage at the entry and exit [24]. Enhanced beam trapping by the deepening hole has been found for reflective materials under typical ns pulse conditions [25], but neither the experiments nor the models pertain to high power ps pulse conditions. Moreover, how ablated material is demonstrably transported so successfully in such a long, fine capillary needs to be understood. The transport issue is important for FEL studies in another respect: plume clearing time. The ns laser ablation studies noted earlier indicate plume clearing times on the order of microseconds, corresponding to 100 kHz repetition rates, in contrast with the more than 10 MHz rate of the FEL's. We return to this subject later.

2.2. Pulsed Laser Deposition (PLD)

Pulsed laser deposition uses the material ejected by excimer laser driven ablation to deposit coatings; high temperature superconductors have gained the most attention. The conclusions of the first major review [26] remain substantially unchanged. PLD offers advantages thin film deposition including ease of compositional transfer, high energy of ablated species, option to use reactive background gases, modest substrate temperature requirement, versatility for different materials in a single apparatus and ease of prototyping novel structures. Complete equipment is commercially available and is simple for what it is. The beam from an external excimer laser is directed onto a target in the deposition chamber, which is then ablated onto an adjacent substrate. Choosing suitable angular orientations, rotating both the target and the substrate, and scanning the laser beam minimizes the development of particulate-generating surface structure on the target and promotes uniformity across the substrate. Plume clearing is less of an issue than for micromachining, since the laser beam axis is far from the surface normal and there is no need for the beam to travel down a deepening hole. The problem remains that though particulates can be minimized by careful manipulation of irradiation parameters, it is not yet possible to completely eliminate them [27]. Presently attainable levels are adequate for applications such as high temperature superconductor and magnetic thin film materials, but not for what would otherwise be quite natural PLD applications, e.g., silicon-on-insulator structures.

That debris is reduced or absent in micromachining with picosecond pulses is encouraging researchers to explore their potential as a path to particulate-free PLD. A further proposed advantage comes from the reduced energy for ablation and the greater ablation efficiency noted earlier. Perhaps because the required amplified Ti:Sapphire laser systems are so much more resource intensive than modern excimer lasers, experimental results have been slow to emerge. The short pulse length and high average power of the new generation of FEL's seems to be a natural opportunity for PLD, initially for research studies and ultimately for production. An intriguing possibility is that large scale FEL-driven PLD might ultimately see commercialization for applications such as advanced solar cells.

2.3. Large-Area Thermal Processing

Researchers using (especially) excimer lasers were able to demonstrate many desirable transformations of metal surfaces resulting in (for example) improved fatigue life for plain carbon steels [28], in elimination of water drop erosion of stainless steel blades in large steam turbines [29], and in surface enrichment of corrosion-resisting chromium in stainless steels [30]. Satisfactory agreement has been reported between calculations and experiments for a wide parameter range of excimer laser driven, melt-mediated metal surface processing [31]. However, the only metal surface processing application that appears to have gone forward into manufacturing is the use of scanned CW Nd:YAG to refine the surface grain structure of the sheet steel used for transformer laminations [32]. Certainly one factor working against manufacturing application of excimer laser driven processing is the energy required (typically 10 J/cm^2) compared to excimer laser output power and to the production rates that must be achieved in manufacturing. Energy requirements for excimer laser polymer surface processing range more widely, from $10 - 30 \text{ mJ/cm}^2$ (PET film amorphization) to $0.5 - 1.0 \text{ J/cm}^2$ (fabric surface roughening) to $5 - 10 \text{ J/cm}^2$ (imparting electrical conductivity to polyimide film) [33]. A further negative factor is that commercial viability for polymer surface applications requires a unit cost of light below a few tenths of a cent per kilojoule, certainly not attainable with excimer lasers.

Cost modeling indicates that an FEL with sufficient power to be compatible with typical manufacturing production rates may also be economically viable [6]. The economics get much better if functionally equivalent transformations can be accomplished with IR at the wavelength of the carbonyl absorbance ($5.8 - 6.1$ microns), as thermal modeling suggests, or whether UV light is indeed required. The necessary experiments are in progress. A further opportunity with the new generation of FEL's is to process enough material for end-use performance and value-in-use studies, something that could not be done with first generation machines.

2.4. Chemical Conversions

Three chemistry related opportunities are especially interesting: advanced UV photochemistry, novel metal-surface photocatalysis and vibrationally-driven organic surface photochemistry. New generation FEL's make the opportunities accessible by being able to deliver enough light to drive the reactions at a realistic rate. UV photochemistry has been studied widely since the 1920's and is presently used for chemicals manufacture only in specialty applications [34]. UV lithography and UV-curable coatings, however, are major and growing. The immediate value of a second generation FEL

once UV operation begins is to simulate processes where no suitable lamp presently exists, so as to make enough material for evaluation and to get process operating parameters for economic analyses. The high PRF of a CW UV FEL is much more compatible with lamp-like operation than the modest PRF's of other UV lasers. A second value is as a test-bed for laser photochemical reactors. The advantages of laser photochemical reactors over lamps include: more efficiently delivering light from the source to the reaction, producing only the most advantageous wavelength and being free from wavelengths that cause unwanted effects, avoiding the introduction of unwanted heat from the light source into the reactor, and delivering more intensity so that the reactor can be smaller or have a higher production rate. However, for the lasers available up to now, no combination of these advantages has been able to offset the sharply lower cost of lamps as a light source. Moreover lamps have only rarely been able to overcome the 20 – 50 fold greater cost of energy in the form of light versus fossil fuel. Still there may be merit in the notion that part-time use of a UV FEL could power a highly versatile, reasonable-capacity job shop for specialty chemicals.

A novel metal-surface photocatalysis mechanism uses ps pulses of IR light to change the selectivity of a surface chemical reaction (CO oxidation) [35], suggesting an interesting avenue of research to pursue. Briefly, the short, intense light pulse generates enough high energy electrons in the metal surface to populate normally empty states on the adsorbed species. These may be quite different states from those populated in normal UV-driven photocatalysis. The “excited” adsorbate species react along a different path from that taken where the laser beam only heats the surface, effectively providing a form of photochemistry in the IR. Care must be taken not to exceed the ablation threshold of the metal surface, or a plasma experiment ensues instead. Both first and second generation IR FEL's deliver appropriate pulses and the time between pulses at even the highest PRF is orders of magnitude longer than the few-ps reaction times reported for the excited species. An advantage for second generation machines is that their higher average power is sufficient to drive a meaningful reactor.

Vibrationally-driven photochemistry of small molecules in the gas phase has long been studied and is well understood. Efforts to similarly drive large molecules or condensed phases have found only thermal effects, attributed to rapid energy transfer from the photoexcited mode into all the others: intramolecular vibrational energy redistribution (IVR). IVR is not equally rapid for all transfers, so that molecular architecture may be chosen where an IVR bottleneck extends the residence time of energy in a certain mode or modes. The FEL's tunability valuable to provide access to wavelengths that excite such modes. Further, the FEL's high peak power can drive a mode up the excitation ladder rapidly, desirable before the excitation leaks away through IVR. The individual FEL pulses can be chirped so that anharmonicity-induced shifting in the wavelength of peak absorbance as the mode is excited does not impose an excitation bottleneck, as it might for a narrow, fixed wavelength. Success would ultimately permit certain photochemistries for surface modification to be practiced with IR instead of UV, a great operational advantage.

Considering the four groups of opportunities just discussed, those in large area thermal processing and in chemical conversions can be pursued with second generation FEL's as they are now configured. The essence of the opportunity is the high average power that enables production of significant quantities of material. The beamline and materials handling equipment needed to achieve the proper irradiance and fluence is not expected to be different from what is already built for use with other lasers, since the FEL is functioning as a CW source in these applications. The more attractive applications are based on ablation: micromachining and pulsed laser deposition. The FEL's PRF is a factor near 50 too high and the micropulse energy about a similar factor too low.

3. FEL ISSUES AND OPTIONS

Whether for micromachining or PLD, a time between pulses on the order of a few to several microseconds is desirable for clearing, but the longest time available between pulses for the Jefferson Lab FEL is 55 ns. The key determinant of the FEL's minimum PRF is pulse roundtrip time in the 8 meter-long optical cavity. Increasing the time between pulses to microseconds by decreasing the FEL's minimum PRF requires increasing the cavity length by the same factor (about 200), which is not an option. Another alternative is pulse-picking: passing only the desired pulses to the target. Pockels cells and acousto-optic modulators can switch in the required time, but it is not clear how well they would survive a constant 1.7 kW. A more robust scheme can be based on two successive polygons having a precisely stable phase relationship. The present writer has recently established decisively that first polygons will not survive such a CW beam either. Fortunately the FEL can be operated in macropulse/micropulse mode so that the average loading to the pulse picker can be reduced to 5% - 10% of full power. Aside from constructing and operating an awkward optomechanical system, the major drawback of a pulse picker is to give up nearly all of the high average power that motivated building the second generation machines in the first place.

A second issue is the need for much more energy per micropulse. Especially for micromachining, the extensive manipulation of the beam all the way from the laser to the workpiece can consume more than half of the original 25 μJ , making it difficult to achieve the irradiance needed for "ultrafast" ablation. A further impact in PLD is to lower the film deposition rate because the spot on the target must be so small in order to reach "ultrafast" conditions. Higher pulse energy could be sought by higher charge-per-bunch in the electron beam, effectively increasing beam current. There is no prospect for operating the present accelerator at sufficiently greater current to achieve the desired 25 – 50 fold increase. The most promising approach appears to be constructing a dumpable cavity in the form of an etalon with end mirrors similar to those in the FEL optical cavity and a silicon wafer switchable central mirror. Stacking of 75 micropulses in such a system has already been demonstrated [37]. The output PRF is then controlled by the PRF of the cavity dumping laser. By proper control of the loading and dumping, such a system should meet both the PRF and micropulse energy goals. Operation would, of course, be limited to the IR by the requirement for a laser-switchable cavity-dumping mirror.

A less substantial, but still important issue is manipulating the pulse length. As discussed earlier, important changes in materials response are seen in the 0.1 – 10 ps range, especially toward shorter times, making pulse length a quite desirable experimental variable. Shortening electron bunch length by a factor of ten to comparably reduce the optical pulse is not possible in the Jefferson Lab FEL. The proposed Stanford LCLS FEL will use a much higher energy electron beam (14.35 GeV vs 42 MeV) and multiple bunchers to achieve 0.1 ps directly [38], but will still not provide a variable bunch length. The most straightforward approach appears to be suitably chirping and compressing the present fixed length pulses, which has already been demonstrated for an FEL [39]. Pulse stretching/compression would best be done before the pulse stacker.

4. BEAM UTILIZATION FACILITIES

For research purposes, beam utilization facilities present few issues beyond those for any other laser system. There is no obvious reason to not simply use the micromachining, PLD, or other apparatus built to be driven by other lasers with suitable adjustments for wavelength etc. Deployment into manufacturing raises further issues. The need to minimize the unit cost of light will always favor FEL's to be large; cost becomes relatively size-insensitive above about 25 kW [6]. At production scale, a large area thermal treatment or PLD sheet coating facility, or a chemical reactor could be designed to use this much power. The less than 100 W feeds expected for micromachining stations or wafer-scale PLD's will require that some means be found to efficiently fan out and transport the original primary beam. The recently reported wavelength-specific hollow-core vacuum waveguides are appealing [40]. A further advantage of the FEL over other lasers is that a wavelength can be chosen for which beam delivery components can best be constructed. Fortunately, ablation under "ultrafast" conditions appears to be substantially wavelength-independent so that the beam delivery system can dictate the choice.

5. SUMMARY AND CONCLUSIONS

The new generation of free electron lasers now coming into service is distinguished by more-than-kilowatt average power, 100% duty factor operation, picosecond or shorter pulses and is expected to provide UV as well as IR light. They were designed with applications in mind at least as much research on FEL science and technology. The most appealing applications now in view are based on ablation: micromachining and pulsed laser deposition. The primary FEL beam is significantly higher in pulse repetition frequency and lower in energy per pulse than is optimum for ablation. Strategies based on changing the FEL itself to bring PRF in to the hundreds of kHz range, pulse energies into the hundreds of microjoules range and pulse lengths into to the 0.1 to 10 picosecond range are unattractive. Downstream conditioning of the primary beam by a pulse stretcher/compressor followed by a pulse stacker is much more appealing. Both have been demonstrated for FEL's. Applications research on large area rapid thermal processing and on chemical conversions can proceed successfully before such beam conditioning is implemented.

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