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INTRODUCTION

The majority of commercial applications of lasers for materials processing involve directly focusing the laser light onto the material, thereby locally raising the temperature of the material to promote the desired process. The disposition of absorbed energy in high irradiance laser-matter interactions, schematically indicated in Figure 1, includes melting, vaporization, light emission, and, at sufficiently high irradiances, plasma formation, the initiation of thermal and shock waves going into the target, and the emission of x-ray and UV photons as well as charged particles (electrons and ions) directed away from and into the material. Most of these major components of the interaction are either being used or are contemplated for use in materials processing applications, generally at low irradiances. Process control with lasers, at 8% of the laser marketplace in 1983, commands almost twice the market share of all materials processing with lasers.

![Diagram of laser interaction](image)

Fig. 1 — Interaction of a high power pulsed laser with condensed matter.
In the first section, this paper will enumerate many applications of lasers to the processing of high-technology materials. Thereafter, three sections will emphasize laser-driven shocks, x-ray lithography with x-ray emitting laser-produced plasmas, and the laser irradiated solid target as an evaporative coating source.

MATERIALS PROCESSING

As it stands today, the area of materials processing with lasers has received a strong impetus from the success of laser shaping, joining, and modification of metals.\(^2\)\(^3\)\(^4\) Shaping includes drilling, cutting, bending, laser assisted machining (turning and milling) and direct laser machining. Joining includes bonding, welding of various types (spot, seam, butt), brazing and soldering.

Surface modification treatments of metals encompass transformation hardening, surface alloying, injecting a refractory material into a surface melt layer, post processing of electroplated layers, post processing of plasma sprayed layers, and marking. Laser heat treatment for surface hardening has progressed beyond the original goal of wear reduction and has achieved increases in strength and fatigue life, improved lubrication, tempering, creation of surface carbide, etc. The importance of materials modification by "advanced, precisely controlled processing techniques, which beneficially change the alloy structure during either consolidation or joining," has been emphasized as a remaining route which may lead to structural (as distinguished from surface) properties which are increasingly difficult to obtain by alloy development alone.\(^5\) Laser processing is playing a role in the development of this new technology, e.g., with techniques to build up structures from laser-processed layers. A graph of power density regimes for metal processing with \(\text{CO}_2\) lasers is available in the literature.\(^6\)

Another class of economically important materials, semiconductors, has also been intensely investigated to determine the suitability of laser processing. Silicon has received the greatest attention, but many other materials, including GaAs, (Al,Ga)As, InSb, CdTe, HgTe, InP, GeSe, Cu-In-Se, CuInSe\(_2\), and CdS, have not been neglected.\(^7\)\(^8\)\(^9\)\(^10\)\(^11\) In the large, these investigations and applications are related to the microelectronics industry, with more forward looking aspirations for integrated optic devices.

Laser annealing of semiconductors, perhaps the most actively pursued process for these materials, now encompasses more than its initial scope, the heating and recrystallization of ion-implantation-damaged Si wafers. Annealing seats the implanted dopant at lattice sites and also heals macroscopic defects caused by ion bombardment. Removal of defects and precipitates arising from high temperature processing, epitaxial regrowth of evaporated Si on crystalline Si, crystallization of polysilicon, and the formation of metal silicide conducting paths, a form of laser-induced chemical change, are also included under the banner of laser annealing. In addition, the melting and regrowth process can be used to incorporate dopants and to tailor the profile of dopants in the regrown material in a manner different than is attainable by ion implantation. A related thermal process, the selective absorption of the 9.25 micron line of \(\text{CO}_2\) by \(\text{SiO}_2\), allows the topographic smoothing of silicon oxide features on a wafer.

Another technique addressed to semiconductor processing is laser chemical vapor deposition (LCVD). In LCVD, laser light promotes the deposition of reactants from a vapor phase onto a substrate. Since its inception about half a decade ago, LCVD has progressed to having demonstrated epitaxial growth of deposited films. LCVD has also accomplished writing a pattern of desired composition onto the substrate for local doping, for conduction paths, or for mask definition and repair. Materials deposited include metals, insulators, semiconductors (both elemental and compound), and polymers. Although the writing rate is up to 10,000x greater than in planar vapor reactions (a geometric effect which varies with feature size), the disadvantage of serial operation remains. The chemical reactions may be induced thermally (pyrolytically) or by direct chemical reaction from photon absorption in the gas (photolytically); the latter offers wavelength-selectivity among reactions and
can operate satisfactorily at lower temperatures, yielding less stress on the substrate. Other examples of reactions locally induced by lasers have been demonstrated, e.g., electroplating and chemical etching.

Additional types of materials for which laser processing is being researched include chemicals (IR photochemistry, photodissociation, photoisomerization, catalysis, photopolymerization, and vibrationally enhanced reactions), biological materials, isotopes (laser isotope separation for nuclear fission fuel), and hydrogen isotopes (inducing thermonuclear fusion reactions).

SHOCKS

As an introduction to shock processing of materials, the following sections will successively consider some of the effects which shocks produce in materials, methods of producing or driving shocks in solids, and comments on applications using those effects. The motivation for this overview is to examine the field of shock generation and to review and assess the suitability of lasers as a driver for shocks, both for research and for commercial applications.

Shock waves in materials are compressive. Like acoustic waves, which travel at the sound speed, shock waves are a manifestation of atomic movements. Since the material in and behind the shock front is compressed to a higher pressure, and because sound speed increases with pressure, the shock travels at a greater speed than the sound speed in the uncompressed material. However, the shock travels at a speed below the sound speed in the compressed material behind the front (for stable shocks in nonreactive media). The shock speed increases with the compression, i.e., with the amplitude of the shock. Thus, the highest amplitude portion of a high amplitude compression wave overtakes the lower amplitude components, resulting in a shock front at which uncompressed material is immediately adjacent to the region of highest compression the pressure, density, temperature, and some physical properties of the material change across this sharp front in a nearly discontinuous fashion. In part, these changes result from the violence of the atomic motions associated with shock waves, which can be sufficiently strong to melt or even ionize the material. Compressions as small as a few percent and up to a factor of 2 are not uncommon, with values as high as 6 having been reported. The distance over which the discontinuity takes place can be a few microns for dense, ionized material; experiments in condensed matter at room temperature anticipate probing shock fronts with micron resolution, and profiles with submicron dimensions are not unheard of. Dissipative losses, such as compression heating, decrease the amplitude of the shock as it traverses the material. The removal of the driving force initiates a decompression (rarefaction) wave which can quickly overtake the shock, thus limiting the duration of the highly compressed condition of the material. As a rule of thumb, an unconfined laser-generated shock in a homogeneous solid decays only after about twice the laser pulse duration. Many of these calculated profiles of a shock wave as it develops as shown in Figure 2, together with a photograph of a shock wave at late time in a plastic target. The unit of pressure adopted in this article and in much of the literature is the Pascal (Pa), 1 Pa = 1 Newtons/sq. meter. (1 psi = 6894.8 Pa, 1 standard atmosphere = 101,325. Pa, and 1 bar = 0.1 MPa.)

Two areas of research which benefit from shock investigations in condensed matter are astrophysics and geology. The understanding of stellar interiors is also dependent upon the study of matter at high densities, pressures, and temperatures. It has been proposed that thermonuclear fusion reactions, such as take place in stars, might be induced in the laboratory by a high velocity impact (impact fusion), a technique which has long been used to generate shocks: a somewhat related approach to fusion involves the convergent implosion of spherical or cylindrical shells, which also must take transient shock pressures into consideration. The impact of micrometeoroids on spacecraft is a further problem which can be addressed by shock experiments. The behavior of hydrogen at high pressures may be important to the study of the planets Jupiter, Saturn, and Uranus, which are constituted primarily of that element. Geologic interest in the state of matter in the core of the earth, where static pressures are 300–400 GPa and the temperature is about 5000 degrees Kelvin, has been directed to laboratory shock experiments which momentarily achieve temperatures and pressures in that range.
The overall breadth of scientific interest in shock processes in condensed matter is perhaps best surveyed in the light of the many effects which shock waves produce.

**SHOCK EFFECTS**

The passage of a shock wave results in compression heating, one of the most important effects of the shock. While high static pressures can be applied in the presence of a heat sink, if necessary, the transient nature of shocks does not allow heat dissipation sufficient time to prevent the attainment of elevated temperatures. The arrival of the rarefaction wave, on the other hand, is associated with expansion cooling, but residual thermal energy remains in the material. The net result of the atomic motions associated with the shock wave and the thermal history can include chemical breakdown, chemical synthesis, defect formation, phase changes, twinning, precipitation, recrystallization, melting, ionization, and plasma production.

Shocks also can produce mass motions on a larger, micron scale. For shock waves which traverse an interface, particularly at an angle, these motions can include hydrodynamic instabilities of fluidized materials: after shock treatment, the interface of two solid materials can resemble breakers at an ocean shore. Such effects allow the bonding or cladding of metals essentially without diffusion across the interface, which constitutes the most important commercial process for metal working with explosives. In crystalline materials, shocks can produce comminution, the reduction of crystal structure into crystallites of powder dimensions. The shock may also rotate the crystallites about into a distribution of orientations.

The release of electrons, production of defects, and the reduction of particle size in shocked materials can strongly influence the chemistry of the shocked state, and has been a focus of research. Shock-induced defects are cited as having significant effects on compressional, mechanical, electrical, optical, thermodynamic, chemical, and structural processes in shock-loaded solids.

A further example of morphological change induced by a shock is the removal of material at a free surface in the path of a shock. The reflection of the shock from the surface induces a tensile stress which can be sufficient to exceed the material’s strength. This dynamic fracture of material is called spallation. Although spallation is most easily diagnosed in macroscopic samples, the processes must also take place on the microscopic level, e.g., in powders.

Shocks not only can produce powders and rip a material apart, they have been used in the compaction and sintering of powders. Precision parts of dissimilar materials such as aluminum and steel can be fabricated from admixtures by this means. Admixtures of powders may also be induced to
chemically react by the passage of a shock front. The production of defects in shocked materials is related to catalytic activity; accordingly, defect production in and the catalytic behavior of shocked powders, which have large surface areas, is a matter of investigation. In general, the powder sizes which have been used are larger than the thickness of the shock front.

Phase changes in condensed matter have been induced by shock waves, e.g., the conversion of graphite to diamonds, martensitic transformations in stainless steel, and phase transformations in ceramic powders. Of particular interest is the design of a shock treatment which permits recovery of the sample. The largest number of metallurgical recovery experiments have been concerned with fcc metals. Hardening in metals is related to defect production, phase transformation, and morphology. All of these have been studied in shock treated metals. Several review articles on the metallurgical effects of shock waves are cited in references. Polymerization by shock waves has also been studied for various organic substances. The existence of a pressure threshold has been demonstrated in acrylamide, 5 GPa being insufficient; multiple shocks have been shown to be effective in enhancing polymerization.

Magnetic effects might be suspected to be influenced by shock passage, and indeed a few observations have been made in this area. Piezoelectric effects of shocks have been seen in the 0.01-0.9 GPa range, and piezoresistive effects in the 1-14 MPa range. Refractive index changes have been charted in the 5-50 GPa range.

The compression of atoms into close proximity to one another is necessarily influenced by the interatomic potentials, and studies have been addressed to this topic. The potentials gained from shocks, in which the material likely is at elevated temperatures, has a greatly disturbed lattice and may even be ionized, may not be directly applicable to the modelling of materials at room temperature and below.

Pressure ranges over which many of these effects have been experimentally investigated are displayed in Figure 3. Chemical experiments have also been conducted at much lower ranges, e.g., 0.5-2 MPa. Many of the effects are limited by the onset of melting at very high pressures, and thus cannot be investigated by the highest shock pressures available. For example, defect structures can be annealed out by a shock- or thermally-induced melting. At yet higher pressures, the thermal radiation emitted by a free surface of the material signals the arrival of the shock front.

SHOCK DRIVERS

The methods and machines for driving shocks in solid materials may be compared on the basis of the peak shock pressures which have been produced and measured (or inferred by suitable means) for each of the various drivers. Reported pressure ranges of experimentally measured shocks are shown in Figure 4 for several types of shock drivers operating in planar or nearly planar geometry. The maximum pressure attainable with a given driver will be dependent upon the material in which the shock is propagated, so that many materials will not be able to access the highest peak pressure of which the driver is capable. Furthermore, shocks dissipate energy as they propagate, with an attendant drop in pressure (see Figure 2, above). Techniques for generating converging shocks, e.g., shaped explosive charges, implosion of spherical or cylindrical shells, etc. are not included in the figure. The highest static pressure attained in the laboratory, 0.25 TPa (2.5 Mbar), was in a diamond anvil cell, a device which presses a sample between two gem-quality diamonds having facets a fraction of a millimeter in diameter; higher pressures than this may be achieved in future laboratory experiments.

The drivers portrayed together in any one category in Figure 4 are not necessarily identical. For example, the data for chemically explosive drivers encompass the relatively simple sandwich structure ignited by an explosive lens, as well as the chemically explosive flyer plate driver, of which several variants exist. Overall planarity is not always achieved: the sample is generally held in a cavity in a metal plate, and radially propagating shock and release waves do get set up at the boundaries.
Fig. 3 — Pressure ranges of experiments on shock effects.

Fig. 4 — Pressure ranges of shock drivers.
of the sample cavity. Also, pressure is increased by multiple shocks passing both radially and axially through the sample. The pressures attained depend primarily upon the type of explosive used, on the details of the geometry of the device, and on the materials employed.

Chemicals are not the only way to initiate an explosion. A thin material can be made to explode in response to the sudden deposition of heat in it by a large pulse of electricity. In one such device, an aluminum foil is exploded to form a plasma, which expands and accelerates a tantalum flyer plate. (It is also possible to generate shocks without a flyer plate by this method; that is, the Ta impactor also has shocks generated within it.) Impact velocities of 30 km/sec have been achieved with this "electric gun." On the low end of the pressure range, an exploding foil apparatus has been constructed according to theoretical predictions of pressures of but a few hundred MPa, to be applied in experimental studies of dislocations in crystals.

Another instrument for generating shocks is the gas gun. A gas gun expels a projectile from a barrel by the force of expanding propellant gases. The expansion of compressed gases yields more reproducible results than gases produced by ignited powders. Since the velocity of the projectile is limited by the sound speed of the compressed gas, the highest projectile speeds are obtained with gases of low molecular weight. A light gas gun projectile includes the flyer plate and a carrier called a sabot. The flyer plate is accelerated by a comparatively low pressure (a fraction of a GPa) over a relatively long time (few msec), which does not disturb the initial thermodynamic state of the flyer plate—a significant advantage for this technique of driving shocks; the temperature rise of the projectile during acceleration and prior to impact is only about 1 degree Kelvin. Single stage light gas guns can yield about 1.5 km/sec with kilogram projectiles 10 cm in diameter. In a two-stage light gas gun, the propellant gas is compressed and heated by a piston driven from a powder discharge; the projectile then can achieve higher velocities, e.g., up to about 8 km/sec.

The rail gun, or electromagnetic launcher, is a device in which the projectile essentially becomes the moving part of an electric motor. Velocities of 10 km/sec have been achieved, corresponding to shock pressures of about 1 TPa. A combined gas gun-rail gun has been reported in the construction phase, with an anticipated velocity for a 1 gram projectile of at least 15 km/sec.

A comparison of various flyer plate drivers is given in Table 1. It is readily apparent that orders of magnitude can separate the various drivers, depending on the parameter of interest. The needs of a pilot research project might be quite different than those of a production line application. For instance, a gas gun may be very useful for studying the equation of state of a metal, and yet be totally irrelevant to the surface hardening of a manufactured item by shock treatment.

Table 1 — Flyer Plate Parameters. The characteristics of projectiles, generally taking the highest speed and associated values. The drivers may be operated in parameter ranges other than those cited. The temperature shown is after acceleration and prior to impact, and is often design dependent.

<table>
<thead>
<tr>
<th>Driver</th>
<th>Thickness</th>
<th>Diam.</th>
<th>Highest</th>
<th>Mass</th>
<th>Momentum</th>
<th>Energy</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exploding foil</td>
<td>.03</td>
<td>.8</td>
<td>30.</td>
<td>.003</td>
<td>7.5</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Gas Gun 1</td>
<td>2.5</td>
<td>10.</td>
<td>1.7</td>
<td>1.1</td>
<td>1600</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>Gas Gun 2</td>
<td>1.5</td>
<td>2.8</td>
<td>8</td>
<td>.02</td>
<td>160.</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Laser</td>
<td>.001</td>
<td>.1</td>
<td>100</td>
<td>10^{-4}</td>
<td>1.</td>
<td>5 x 10^{-5}</td>
<td>7 x 10^4</td>
</tr>
<tr>
<td>Rail Gun</td>
<td>0.1</td>
<td>1.</td>
<td>10.</td>
<td>.003</td>
<td>120.</td>
<td>2.</td>
<td></td>
</tr>
</tbody>
</table>
APPLICATIONS OF LASER-GENERATED SHOCKS

The pressure profile produced by a laser pulse incident upon a material is primarily dependent upon the irradiance (power per unit area) absorbed by the material, but is also a function of other parameters, such as the laser wavelength and the details of the laser pulse's temporal profile. The mechanism by which laser pulses generate shocks in condensed materials is the ablation (vaporization and removal) of material from the absorbing surface: the momentum carried off by the evaporated or ionized surface atoms is balanced by momentum imparted to the bulk material. This momentum transfer produces the compression wave. Representative values of resulting pressures are given in Figure 5 for Nd-doped pulsed glass lasers. The data below 10 GPa pertain to absorbers covered by transparent material, a technique (applicable only to irradiances for which the transparent surface does not ionize appreciably) which confines the vapor, lengthens and increases the pressure pulse, e.g., from 60 MPa for a free surface in vacuum to 700 MPa for a confined target near 1 GW/cm$^2$.

![Figure 5 - Pressures from Nd lasers at 1.06 micron. Solid dots and open triangles are in vacuum; points below 10 GW/cm$^2$ are for overlayered targets. Definitions of irradiance vary for the different data sets.](image)

Laser irradiation has been employed both for the removal of and production of defects in silicon. Removal of defects is accomplished by laser annealing, during which a melt layer is formed (thermally, not by shock heating) at the surface of the silicon by the absorption of laser energy. The strength of laser annealing is that macroscopic defects such as dislocations, stacking faults, and precipitates are absent in the recrystallized layer, but the process also introduces defects (evidently point defects) which remain and are a disadvantage for some electron device structures. At these irradiances, below about 100 MW/cm$^2$, defect production mechanisms other than shock-generation are in view. Intentional introduction of defects at higher irradiances has been pursued as a gettering technique, using repetitively pulsed Nd lasers which can focus to about 100 GW/cm$^2$. A pulsed laser beam is impinged directly onto the back surface of the semiconductor, typically in air, to create defects. Thermal processing allows unwanted impurities to migrate to the defects where they become trapped; the laser-damaged back layer, with the impurities, may then be chemically removed. Advantages of laser irradiation over mechanical means for gettering site production have been enumerated.
Defects in crystals affect not only their electrical properties, but also their x-ray diffraction properties. For this reason, x-ray diffraction is used to characterize shocked materials. It has been shown that the intensity of x-ray diffraction from an x-ray analyzing crystal is dependent upon the degree of perfection of the lattice. In some cases, higher diffraction efficiencies can be obtained by rendering the lattice "ideally imperfect," i.e., composed of small, disoriented crystallites. In lithium fluoride, an important x-ray analyzing crystal, the requisite disorienting can be introduced by abrading and etching the surface of the crystal; however, for the more penetrating x-rays, which reach deeper than the 50 microns or so of disorder, the diffracted intensity reverts to the lower value typical of the perfect lattice. Mechanically flexing the crystal introduces sufficient disorder to yield the desired dependence of intensity with x-ray wavelength, but unfortunately at a reduced absolute value. The demonstrated ability of laser irradiation to harden metals (by introducing defects) to depths many times greater than 50 microns invites the shock processing of LiF x-ray analyzer crystals. Surface melting from direct irradiation may not be disadvantageous to the performance of analyzing crystals and may possibly be reduced with a flyer plate technique.

The laser-accelerated flyer plate technique has already been employed to shock harden aluminum alloys, with peak pressures in the 5-15 GPa range. Shock waves produced by direct laser illumination has also induced surface hardening, and increased tensile and fatigue strengths: a single laser shot can produce a hardness the same as that of a heavily hammered surface in some materials. In certain materials, hardness increases with the number of shocks. Sheet samples of an aluminum alloy have been irradiated from two sides, and hardened throughout their 1.35 mm thickness, due to a shock-induced increase in dislocation density.

One might suppose that a longer pressure pulse, at constant pressure, would give the same hardening, and deeper. Experiments with exploding foil flyer plates at constant pressure and varying shock pulse duration in Cu-8.7\%Ge reveal a more complicated result, showing a maximum in hardness. This maximum is explained on the basis of the rates of twinning and dislocation production during the shock. Similar pulse length dependence for laser generated shocks would be expected in this material.

A list of possible industrial applications, once proposed (with suggested processing schedules) for other shock drivers and largely applicable for the laser driver as well, includes tool steels, shafts, armor, punches, cutting tools, gun barrels, etc. Presently active industrial applications of shock processing by explosives, some of which are obviously not relevant to the laser driver, include rock blasting (although direct cutting of rock with lasers has been investigated), metal bonding, modification of ceramic powders, and diamond synthesis.

The synthesis of stable and metastable phases of solid materials by shock treatment has been demonstrated, and attempts have been made to shock synthesize superconductors. Superconductors have no resistance, and therefore do not introduce resistive power losses into the transmission of electrical energy through them. The main difficulty is that they must be operated below a critical temperature which is, in all superconductors thus far fabricated, too low for economical use in power transmission. Many superconducting materials exist in a metastable phase. The ability of lasers to induce phase changes by shock processing in a non-contact fashion with good control, and even to shock wires in cylindrical geometry in a pulsed-repetitive fashion, make this technology worth investigating more fully.

The higher irradiances are important in evaluating the equation of state of materials at high pressures, for which a uniform planar shock is best suited to the required precision. An advance in laser irradiation uniformity, and hence shock uniformity, has recently been achieved with Induced Spatial Incoherence, a technique for spatially and temporally homogenizing larger-scale beam structures. This technique may be transferrable to other experiments and processes requiring a uniform, focused, but essentially planar, irradiation pattern.
X-RAY LITHOGRAPHY

The pervasive influence of the microelectronics industry on commercial activities of almost all sorts is widely recognized. The overall importance of the power of information retrieving and processing equipment is poorly estimated by considering only the magnitude of annual sales volume. The recognition of the role of this industry has resulted in its sustained growth; and yet, forecasts anticipate a levelling off in the near future. The growth of the industry has been directly linked to the continued diminution of sizes on microchips, illustrated in Figure 6: the smaller the feature sizes, the greater the number of elements per chip, and the greater the capability of the resulting circuit per unit cost and, generally, the greater the speed.

![Fig. 6 — Trend of linewidth in integrated circuits. Courtesy of R.T. Bate, Texas Instruments, Inc.](image)

Present efforts to sustain growth and realize the next generation of improvement in processing power are therefore centered on techniques for further miniaturization of microcircuits. One major thrust in this effort is the attainment of commercially viable processes to produce smaller linewidth features on microchips, but with the same basic device structures as used heretofore. A more novel approach is to develop a totally new type of structure around quantum well devices. This paper will indicate ways in which processing steps with laser-produced plasmas might contribute to each of these major thrusts.

In this section, an introduction to lithographic concepts is followed by a brief summary of results of research performed at this Laboratory on the technical feasibility of attaining of small linewidths by x-ray lithography, using a laser plasma (LP) as an x-ray source. The principal advantages and limitations of this method are then outlined and areas of future work suggested, and lastly, the present status of commercial application is indicated.

LITHOGRAPHY CONCEPTS

Commercial fabrication of microcircuits includes patterning of thin films of different materials on the surface of a semiconductor, and patterning of relatively dilute concentrations of dopants near the surface. The patterning steps are performed by techniques conceptually similar to some originally employed in the printing of lithographs. Optical lithography for circuit manufacture involves placing a mask, i.e. a pattern of dark and light areas on the surface of a transparent substrate such as a glass plate, between a wafer of semiconductor material and a light source. The light exposes a photosensitive polymer layer called a photoresist which has previously been coated onto the semiconductor's
surface. Development of the exposed resist removes portions of the resist according to the pattern of exposure, the net result being a replication of the mask pattern in the polymer. Optical lithography is easily performed for feature sizes of 5 micrometers or greater, with successively greater care required as one approaches 1 micrometer, i.e. a few times the wavelength of visible light. Submicron lithography is performed with shorter photon wavelengths, or with electron beams or ion beams. Accordingly, lithography with x-ray photons is of interest, their wavelengths being orders of magnitude smaller than the visible. Applications of fine line fabrication outside the field of microelectronics, the comparison of electron, ion, x-ray, UV, and optical lithographies, the evaluation of the suitability for lithography of various types of x-ray sources, and other topics related to lithography have been well reviewed by Nagel, and will not be treated here in such detail.

**LASER PLASMA X-RAY LITHOGRAPHY FEASIBILITY**

In one suggested arrangement for a laser plasma (LP) x-ray lithography exposure facility, a high-power laser directs a pulsed beam into an exposure chamber and onto a target, typically at an irradiance near or above about $10^{13}$ W/cm$^2$ and in a focal diameter of a fraction of a millimeter. During the laser pulse, the target material is heated to a temperature sufficiently high to cause x-ray emission, about a million degrees Kelvin. The x-rays radiate away from the target in all directions, and pass through masks held in alignment with their respective semiconductor wafers. The conditions are chosen to produce x-rays which pass through the mask substrate, but not through the pattern defined on the mask. The mask substrate itself must be thin in order to achieve low x-ray absorption.

An early test of the feasibility of LP x-ray lithography was performed at this Laboratory, and exemplified many relevant characteristics of the x-ray source: source size, spectral content, emission efficiency, debris patterns, and submicron replication. A Q-switched Nd:glass laser put about 30 Joules onto an aluminum slab target in a 40 nsec pulse. The plasma emits visible, UV, and x-ray photons, as well as plasma particles (electrons and ions) and vapor. The full width at half maximum of x-rays near a kilovolt in energy was 15 nsec. An x-ray mask, composed of a gold pattern on a beryllium substrate, was held in close proximity to a silicon wafer coated with a resist. Kilovolt x rays exposed the resist through the mask, and the resulting patterns were developed by spraying with the appropriate solutions. Electrical tests were performed to assess radiation damage to the silicon by the x-rays.

The spatial distribution of x-rays emitted above 1 kilo-electron Volt (keV) was recorded with pinhole cameras of differing sensitivity and resolution. As shown in Figure 7, the highest intensity of x-ray emission originates in a region about 0.4 mm by 0.6 mm. Measurable x-radiation does arise from a much larger plume (Figure 7b). (Materials synthesis in such plumes is the subject of other work reported in these Proceedings.) The importance of the emission pattern to lithographic exposure levels, however, is more properly represented by the smaller size of the high resolution image. The penumbral blurring from this source is adequately small to attain line widths under one micron (see below) by placing the mask very near to the resist, i.e., within several tens of microns.

The spectra of LP x-ray sources above a kilovolt in photon energy are fairly distinctive, being composed of emission lines and continua, both of which are characteristic of the target material, its degree of ionization and other plasma properties. The spectrum of an aluminum target near 1 kilovolt, taken with the 40 nsec laser and given in Figure 8a, exhibits a cluster of lines about 1.6 keV which contain nearly 90% of the spectral energy above a keV, and lower-lying but nonetheless noticeable continuum contributions having low energy limits at the ionization energies of the various aluminum ions of which the plasma is composed. The continuum falls rapidly with a slope that depends on the plasma temperature; a very few photons are produced at high photon energies, and the number of these which are absorbed per shot by a wafer will fluctuate. A typical high energy LP continuum spectrum (obtained under other conditions) is indicated in Figure 8b. (The continuum of an electron impact x-ray source such as an x-ray tube has an entirely different shape, with significant continuum levels all the way out to the accelerating energy of the electrons.) There is also an intense contribution predominantly below 1 keV, composed of lines and a differently shaped continuum. If a mask...
substrate were so chosen as to allow longer wavelength, lower energy (e.g., visible) photons to expose the resist through the mask, loss of resolution by diffraction of these photons might result. This region of the spectrum was effectively absorbed by the Be mask substrate, and therefore did not contribute to the lithographic exposure.

Fig. 7 — X-ray images of an aluminium plasma (a) at high resolution (about 25 microns) showing the hottest region and (b) at low resolution (about 1 mm) showing the plume.

Fig. 8 — Spectra from laser plasmas. (a) Trace of photographic density clearly reveals the weaker lines and the continuum above about 2.1 keV. Unfolded intensity is dominated by the 1.6 keV group of lines. (b) High energy continuum, taken under other conditions.
The beryllium mask substrate was nominally 25 microns thick, and the gold pattern 500 nm thick. At these thicknesses, the absorption in the gold (beryllium) would be at least 99% of the photon energy below 0.9 (0.8) kev, 82 (49)% at 1.6 keV, and 86 (9)% at 3.0 keV. It is desired that the substrate foil be uniformly absorbing across its area. This absorption of photons in the mask and gold pattern produces heating, which in turn induces thermal expansion. According to a calculation which does not account for any other heat loads or for thermal conduction, the heating produced by the 1.6 keV photons is but a couple of degrees in Be, although the heating of the gold would be over 100 degrees C. Warpage might result, and differential expansion between substrate and pattern could possibly delaminate the mask. However, when the patterned side of the mask is placed away from the source (as in this work), so that the substrate alone absorbs the abundant UV radiation, a significant additional heat load on the substrate does result. This effect may be used to render the temperatures of substrate and pattern more nearly isothermal. Also, thermal equilibration times are less than 400/nsec exposure of 1 micron (the thermal diffusivity of beryllium is 6 x 10^-5 m²/s, and that for gold 10^-6). The gold pattern is evidently isothermal with a significant thickness of the substrate, which may retard delamination. Thus, it is important to evaluate mask substrate and pattern heating, and to do so in the light of the details photon deposition and mask design.

Another attribute of laser-produced plasmas, the emission of target material itself, can be deleterious to the mask if care is not taken. The pattern of aluminum vapor and debris, which was emitted by these solid slab targets and caught on a glass plate, is reproduced in Figure 9. The majority of debris is confined within a well defined cone of fairly large half angle, 55 degrees in the present case. Generally speaking, the debris emission prevents placing the mask in the region of most intense x-ray emission, when microcircuits are to be made. The amount of such debris can be reduced appreciably by suitable target design, e.g., a thin foil target which does not contain the large reservoir of meltable material of a slab target. It is possible to fabricate the target of a disc sufficiently thin that it is completely vaporized by the laser pulse; this disc may then be held on a thinner, larger foil for mounting. Nonetheless, some target material will always be present and may proceed by line of sight toward the mask. Having taken measures to reduce the quantity and particle size of such material, it is anticipated that the material can be caught on another film which is interposed between the source and the mask. This catcher film, of course, must be appreciably transparent to the x rays which are to expose the resist. Likely as not, the catcher film will absorb the subkilovolt x rays, which then would not be available to thermalize the mask. While these considerations have been conceptualized, they remain to be rigorously demonstrated in practice.

Exposure of polybutene-1-sulfone (PBS) resist was performed at a distance of 5 cm from the source, by a series of 90 laser shots. The mask and wafer were in close proximity to each other, 5 cm from the source at an angle of about 40 degrees from the incident laser beam, i.e., within the debris cone. With this non-optimized system, the x-ray output of about a third of the shots was significantly below the norm, due largely to insufficient optical isolation of the laser from the target in the system as it was then configured. Part of the mask was covered by a series of Be filter layers with graded x-ray attenuation; the exposure behind this step wedge was quantified and the sensitivity of the resist determined (5 J/cm²) and found to be in reasonable agreement with previous values from continuous wave x-ray exposures (14 J/cm²). More recent results with a single shot, 1 nsec exposure of PBS by a laser-produced plasma found the resist to be more sensitive than for steady exposures. Partial exposure of the resist results in partial development, such that the topography of the resist receives the mask pattern in relief, but not to the extent that the valleys descend fully to the wafer. (A similar topographical effect can be expected in exposures by photons insufficiently penetrating to reach the full depth of the resist.) In a region of the mask subject to such a partial exposure, a relief pattern showing features of 0.75 microns (the narrowest structures on the mask) was recorded (see Figure 10), thus demonstrating the feasibility of producing fine lines by this method.

In addition to the mask exposure test, a concurrent exposure test was performed on MOS capacitors, to determine whether the ionizing lithographic exposure would induce electrically significant radiation damage. Capacitors consisting of 100 nm thick aluminum dots were evaporated onto a dry silicon oxide layer on the silicon substrate. These test structures were protected by an 18 micron Be
foil (i.e., thinner than the mask substrate), and placed 5 cm from the plasma. The radiation hardness of these wafers was found to be less than in wafers not subject to ionizing lithography. Capacitance/voltage curves\textsuperscript{39} taken before and after irradiation yielded no change in shape and less of a shift than in similar tests following exposures by x-ray tubes and electron beams.\textsuperscript{41} It appears, however, that the presence of impurities in the oxide layer was the controlling factor in these findings, rather than the lithographies used.\textsuperscript{46} The impurities can evidently be avoided by appropriate processing steps.

Fig. 9 — Debris pattern recorded on a glass plate placed in front of Al targets.

EVALUATION

The advantages and disadvantages of x-ray lithography in general, and of various plasma sources in particular, have been enumerated elsewhere.\textsuperscript{33,34,35} The advantage of greatest moment, of course, is the ability to attain finer resolution than with conventional optical methods. Some of the limits on this resolution vary with system design: source size, geometrical placement of components (source, mask, wafer), and the diffraction of photons which reach the resist. Other limits are more fundamental: smearing produced by energetic photoelectrons liberated in the resist by the x-ray absorption process, and effects produced by the inevitable damage sites which are formed by ionizing radiation (e.g., electrical power losses and leakage). A systematic comparison of the electrical side-effects of laser plasma x-ray lithography remains to be carried out; initial investigations are beginning to develop a partial view. It has been found that the electrical effects of lithography with ionizing radiations are dependent on the details of the structures and materials present at the time of irradiation; for this reason, radiation hardness tests on finished devices may not give the same effects as those undergoing processing, and effects may be different for different processing agendas. Thus, the evaluation of radiation effects is likely to remain a matter for further investigation, especially as processing techniques evolve. Research in this area should be conducted with repetition and verification until the controlling parameters are well understood. Mask heating remains a consideration which is deserving of further investigation. Protection from debris is clearly a need, the details of which must be worked out. Single shot lithographic exposures have been performed with LP x-ray sources, but the variability experienced in x-ray output from these sources leads one rather to consider a multi-shot scheme.\textsuperscript{47}
In addition to reducing the heat load on the mask in a system with less energy per pulse, the precision in integrated exposure can be increased, while reducing the cost of the laser. Such an approach has been demonstrated with a 10 Hz Nd laser, although the exposure time for presently available lasers is again too long (15 to 60 min.) for a commercially attractive lithography system. The development of higher average power, repetitively pulsed lasers may have an impact here. It has been pointed out that the 1 micron wavelength of Nd lasers is not optimal for x-ray lithography, and that a greater x-ray output would be expected from shorter wavelengths. This expectation was recently corroborated experimentally with a KrF laser operating at 249 nm: a hundred shots exposed a less sensitive resist in under two minutes, a very inviting result.

Fig. 10 — Submicron replication achieved by x-ray lithography with Al plasmas.

LITHOGRAPHY APPLICATIONS STATUS

X-ray lithography has proceeded through a number of phases of development. After initial investigations were made, devices were made in low quantities to serve demonstration, research, or customized purposes. Bubble memory devices with 1 micron features have been fabricated by x-ray lithography on a production line basis by Intel. Although the center of gravity of the industry is still solidly in the optical lithography region, electron impact x-ray lithography systems and exposure sources are now on the market, e.g., Perkin-Elmer’s new step-and-repeat unit and the Micronix flood exposure unit. In addition, electron discharge plasma sources are being offered for x-ray lithography by Maxwell. The laser plasma x-ray source has been under development by Spectra Technology, and an integrated x-ray lithography system employing a laser plasma x-ray source is being developed by Hampshire Instruments.

In summary, x-ray lithography is presently in its early phases of commercial productivity. The research performed on laser plasma x-ray sources is bearing fruit in the development, now in progress, of x-ray lithographic systems for the commercial market. Further advances in optimization of the laser plasma exposure system are anticipated to enhance the strength of this application of laser technology.
EVAPORATIVE COATING

Above laser densities of about $10^5$ to $10^6$ W/cm$^2$ impinging on a solid target, vapor and other forms of material begin to be expelled from the irradiated region. These other forms include expanding plasma (above about $10^8$ to $10^9$ W/cm$^2$) and ejected liquid, e.g. globules. Various mechanisms are responsible for the ejection of liquid, including microexplosions beneath the surface, and the forcing out of liquid by the pressure pulse associated with laser-driven ablation. Despite the fact that the prospect of using laser-produced evaporation as a coating technique was pointed out early and has continued under investigation, the technique has evidently not been competitive with the numerous alternative technologies. This is likely due in part to the perception that other coating systems offer better control, higher deposition rates, and superior coating uniformity over larger areas. It remains, then, to examine whether specialized uses for laser evaporative coating offer significant advantages over other means.

An example of coating quality for the higher irradiance regimes, where ejecta are emitted, is typified by Figure 9; the uniformity of the coating would obviously be poor over most, if not all, of the available solid angle. However, such results need not be taken as optimum. Carbon films produced by pulsed laser plasma deposition (about 1 J/pulse, 9 nsec, 10 Hz, Nd laser) were smooth in thickness down to micron distances laterally, although thickness did vary gradually on a scale of centimeters. (Aluminum films prepared from rod targets in the same investigation were visibly not smooth.)

The laser source can be adjusted to emit vapor or plasma, depending on the irradiation conditions. The degree of ionization of the emitted plasma is also under control, together with the energy of the emitted plasma ions. Since the energy of the ions is dependent on the plasma temperature, the uniformity of the laser irradiation can be important. The degree of ionization can be reduced by passing the ions through a low pressure gas, to enable charge exchange to take place. Each of these parameters is reasonably reproducible, and may be diagnosed with the appropriate instrumentation. Thus, the laser coating source can be well characterized and adjusted over many of the parameters of interest.

The coating rate is dependent upon both the laser and the target parameters, as well as the geometry of the coating setup. The carbon films previously mentioned were deposited at the rate of 0.1 Angstrom/pulse, at a distance of about 5 cm. Thus, sub-Angstrom control is offered by the laser coating technique, with thicknesses of 0.1 micron being obtained in about an hour and a half. Other workers have obtained rates of under 1 to $10^6$ Angstrom/sec for various materials with peak laser powers ranging from 160 W to a GW.

These coating rates and degrees of control are within the range of possible application to the fabrication of such structures as superlattices, quantum devices, and multilayers. The laser evaporative coating source does not require the gas handling hardware of metal-organic vapor deposition systems, and is compatible with high vacuum techniques such as are found in molecular beam epitaxy systems. Other laser processes, including laser chemical vapor deposition and laser annealing, are being considered for fabricating some of these structures. It is not to be anticipated that the laser coating source will replace the various systems now in use for research fabrication. However, laser evaporative coating can reasonably be expected to find further research applications, perhaps eventually even commercial applications, but these await a more thorough compilation of the attributes of the laser evaporative source in relation to the fabrication of these novel microstructures.

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