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Tailored Surface Modification by Ion Implantation and Laser Treatment

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Summary. An important trend in materials science is the use of increasingly sophisticated methods to control composition and microstructure during processing. Near-surface modification by ion implantation and laser treatment is one of these new methods for tailoring material properties. Novel materials have been formed which are far from thermodynamic equilibrium and which exhibit unexpected and useful properties. The most extensively studied property changes include modified electrical properties of semiconductors and improved wear, hardness, and corrosion resistance of metals. The high degree of control available with energetic beams allows relations between microstructure and properties to be systematically investigated at the atomic level. This article illustrates how ion and laser beam modification is being applied to advance both the technology and the exploratory science of materials.

Ion implantation and laser treatment (*1–15*) have increasingly come into use for controlled modification of the near-surface of materials. This area is collectively referred to as directed energy processing and includes the use of ion, laser, and electron beams to provide intense sources of atomic species, heat, and electronic excitation. Although there is a significant amount of work with electron beams, we focus only on ion and laser beams in this article, since the basic effects can generally be achieved with either electrons or laser light.

Surface and interface properties are critical to the performance of materials in many applications, ranging from the operation of semiconductor electronics to the corrosion and wear of metal components. The trends of increased reliability and of miniaturization, with the resulting increase in surface-to-volume ratios, place even greater requirements on surfaces. As a result, processes for tailoring the near-surface properties of materials independently of the bulk properties are gaining increased attention.

Ion and laser beam modification of the near-surface of materials is having an impact on both technology and exploratory science. This can best be appreciated in the context of two broader themes throughout materials science. First, there is increased interest in the development of advanced materials with improved properties. Polymers, ceramics, rapidly solidified materials, and surface-modified materials all rely heavily on the controlled formation of new materials and microstructures. In many cases a key aspect of the ability to tailor the properties of materials is a high degree of control of parameters influencing the microstructure during processing. Ion and laser beams are simply a subset of the techniques in this area, with the control necessary to open a new window to materials science.

The second theme is the ability to relate the microstructure and chemistry of materials to their properties. This quest has a long and distinguished history, going back to such notable successes as understanding the role of dislocations in the mechanical response of materials. The newer approaches bring an increasing degree of sophistication to the ability to control the microstructure and composition of materials. Ion implantation allows the near-surface region to be selectively and continuously changed in composition (Fig. 1a). Laser surface melting permits selective heating and melting of the surface region (Fig. 1b). These methods for locally mixing and moving atoms and rapidly heating and quenching the solid can lead to novel and extremely homogeneous metallurgical microstructures. Also, the two techniques complement each other in the sense that ion implantation allows selective alteration, but may leave damage requiring subsequent thermal annealing, whereas laser annealing allows selective heat treatment of materials, which can be used to remove damage and to induce rapid solidification for the formation of specific microstructures.

Both ion and laser beams give selective near-surface treatment of materials in ways that allow systems to be moved far from thermal equilibrium. Large amounts of energy are deposited into small volumes on time scales which can be exceedingly short; thus the system is rapidly quenched from a highly excited state, allowing the observation of transient phenomena and metastable material states not previously seen. This nonequilibrium aspect is the single most important common denominator between the various directed energy processes and best distinguishes many of the new and exciting developments involving these beams. Thus, ion and laser beams are proving to be powerful laboratory tools for the investigation of the science of materials.

Surface Modification

Directed energy beams are primarily used to modify materials in two ways: to controllably alter the composition and to rapidly heat (or excite) the surface (Fig. 1). The basic processes involve the introduction of atoms and atomic displacements and localized excitation of electrons leading to heating or to modification of surface chemical reactions; all of

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these processes can result in the formation of new material phases with useful properties (see Table 1). Characteristic depths of treatment vary, but they typically range from ~100 nm for ion beams and fast pulsed lasers up to ~1 mm for laser treatments of longer duration. Directed energy beams offer versatility and control in the treatment of materials (Fig. 2) and can be applied as a finishing process without appreciably altering the dimensions or bulk properties.

Although relatively new, directed energy techniques have already had a considerable impact on materials processing (Fig. 2). Semiconductors have seen the most extensive commercial application of ion beams. At the beginning of the last decade, ion implantation, in conjunction with furnace annealing, was developed as a controlled method for the electrical doping of silicon. Because of its reproducibility and compatibility with planar processing, ion implantation was rapidly adopted throughout the semiconductor industry. This process was one of the essential steps in the development of low-power integrated circuits, making possible digital watches, hand calculators, and microprocessors. Today, essentially every silicon integrated circuit (IC) produced has undergone one or more implantation steps. Implantation and ion (plasma) etching are part of the general trend in the semiconductor industry toward dry, physically based processes to achieve improved repeatability and dimensional control. At present, the role of laser surface modification is more limited in IC manufacturing. Lasers are used to selectively vaporize interconnections and resistors for the purpose of altering logic paths, excluding bad memory cells, and adjusting (trimming) resistors on fabricated wafers; more tangential uses include scribing and labeling IC's.

In metals, laser modification of surfaces (see Fig. 3) has seen considerable use in the transformation hardening of ferrous alloys. This process is widely used in the automotive industry with CO_2 lasers for hardening engine and drive-train components (cylinder liners, piston rings, crankshafts, and so on) to reduce sliding wear and fatigue. There is also considerable interest in the use of lasers for alloying materials into metal surfaces and for rapidly solidifying the near-surface region of existing alloys. These processes can result in unique microstructures with greatly increased hardness, corrosion resistance, or other useful surface properties (see Table 1).

Many newer uses of ion beams and lasers for tailoring surfaces are in the exploratory stage. These include studies of rapid heating with lasers, surface alloying with ion beams, and laser-induced deposition and etching on semiconductor and metal surfaces in contact with gases or liquids (see Fig. 2). Other areas being investigated include ion beam modification of ceramics to increase toughness, ion bombardment of polymers to modify conductivity, ion implantation of insulators to form light guides, and ion irradiation during deposition to increase adhesion and improve properties of metallic and ceramic films. Although not considered in this review, there are well-established uses of lasers and ion beams for which surface modification is not the primary objective, such as laser cutting, welding, drilling, and ion sputter-etching of surfaces.

Processes

Ion implantation. The ability to exercise control at the atomic level in a surface treatment process is the key factor in the tremendous rise in the use of ion implantation over the past 10 years. The introduction of elements is not dependent on such thermodynamic limitations as equilibrium solid solubility or on atomic diffusion rates, so that the widest possible range of material combinations is available. The implantation process begins by forming a plasma containing the element of interest, from which a beam of ions is extracted, focused, accelerated, and (usually) magnetically separated to obtain only the ion with the desired mass and energy. Any element in the periodic table can be accelerated, and the number and depth profile of the implanted ions can be predetermined by directing a specific energy distribution and total charge of ions to the surface.

Ions slow to rest in $\sim 10^{-12}$ second by collisions with the electrons and nuclei

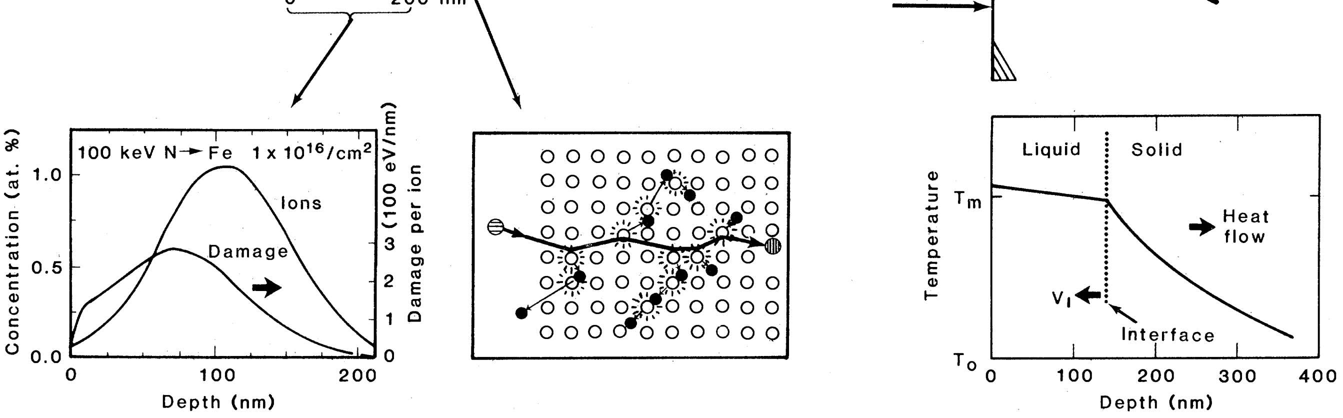

Fig. 1. Schematic diagram of (a) ion and (b) laser beam treatment of a surface.

Table 1. Materials properties influenced by directed energy beam processes.

Mechanical	Chemical	Electromagnetic
Wear	Corrosion	Superconductivity
Friction	Oxidation	Semiconductor doping
Hardness	Electrochemistry	Photoconductivity
Adhesion	Catalysis	Resistivity
Fatigue		Magnetic properties
Toughness		Reflectivity
Ductility		Dielectric constant

to produce a nearly Gaussian depth probability distribution in the solid (Fig. 1a). Atomic displacements produced by the collisions leave a cascade of vacancies and interstitial atoms, as well as more complex clusters of defects. Every atom in the implanted region is typically displaced several times for a 1 percent change in atomic composition. For light ions (such as helium) the displacements are widely separated, whereas for heavier ions and targets (for instance, tantalum in iron) a large fraction of the atoms are displaced within the ion's cascade volume. Defect accumulation and phase transformations depend on the density of displacements in the cascade. Much of the displacement damage is removed (annealed) by migration and annihilation of defects during implantation; however, removal of all defects often requires subsequent heating.

A number of special processes—sputtering, enhanced diffusion, radiation-enhanced segregation, ion beam mixing—become important in establishing the final composition profiles at high implantation fluences. For example, sputtering typically removes two to five atoms from the surface per incident ion (Fig. 1a), and thus limits the total change in concentration that can be achieved to between about 50 and 20 atom percent, depending on the ion, energy, and target. Collisionally induced atom rearrangements and motion can produce mixing of deposited single or multilayered films to obtain alloy compositions otherwise limited by sputtering. Other combined processes, including cluster beam deposition (for example, 1000 atoms in a cluster of charge +1 accelerated to the surface) and ion implantation during film deposition, are being explored to achieve thicker layers.

Laser treatment. Laser treatment of a surface involves directing a high-power beam of laser light onto the surface (Fig. 1b). A certain fraction of this light is absorbed near the surface by excitation of the electronic system and subsequently converted to heat by carrier scattering and phonon formation. Both pulsed and continuous wave (CW) lasers are used, some typical examples being pulsed ruby, Nd:YAG(neodymium:yttrium aluminum garnet), and excimer lasers, and CW argon and CO_2 lasers. Since the electron-lattice relaxation times are typically $\lesssim 10^{-12}$ second, for pulsed lasers the interaction time (see Fig. 3) is determined by the pulse length, whereas for CW lasers the interaction time is determined by the beam size and speed of sweeping the beam. Typical pulse times range from 100 nsec to the picosecond regime, whereas for CW laser treatments interaction times $\gtrsim 1$ msec are usual. Electron beams are also used for surface treatments in both pulsed (~100 nsec) and CW modes, but are not discussed in detail here because results with electron beams are quite similar to results with lasers. Pulsed ion beams have received relatively little attention.

Absorption of laser energy into a surface depends on the wavelength of the light and the optical properties of the material. Absorption depths are shallow in metals, typically ~10 nm, and can be shallow or deep in semiconductors, depending on whether the wavelength is sufficient to excite carriers across the band gap. In addition, absorption depends on impurities, structural state, and surface conditions. For example, the absorption of ruby laser light by amorphous silicon is much greater than by crystalline silicon; in aluminum, where about 90 percent of the ruby light is

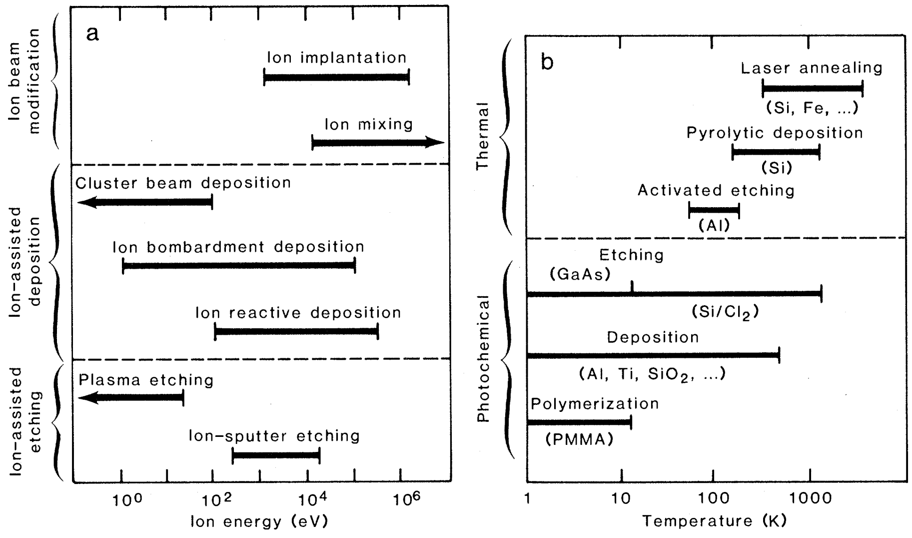

Fig. 2. Schematic representation of various (a) ion beam and (b) laser processes shown as a function of the typical range of ion energies and surface temperatures, respectively.

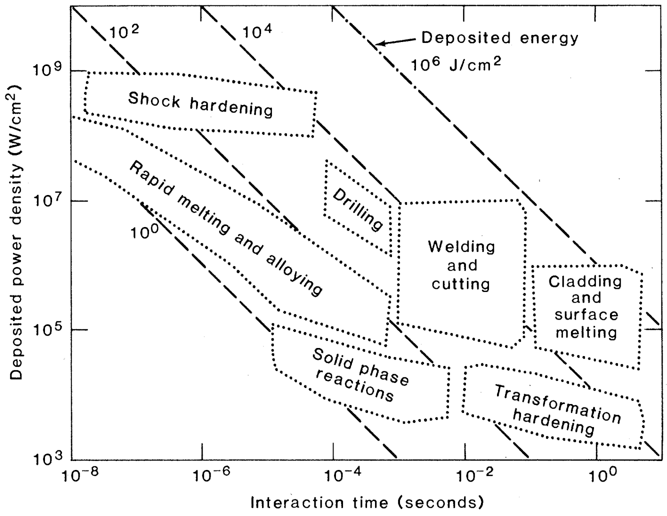

Fig. 3. Relation between the deposited power density and the interaction time for various laser surface treatment processes.

reflected, small changes in surface conditions due to roughening or alloying can significantly increase the amount of energy absorbed. At high energies surface vaporization, plasma formation, and blow-off limit energy deposition.

Key parameters in the laser treatment of surfaces are the energy deposited, interaction time, conversion of deposited energy to heat, and subsequent heat flow. These, together with the material thermophysical parameters (heat capacity, thermal conductivity, heat of melting, and others), allow one to determine the sample temperature history as a function of depth and time. A schematic temperature profile is illustrated in Fig. 1b shortly after the end of a fast (order of 10 nsec) laser pulse. The thermal profiles are calculated by numerical techniques; of particular interest are the melt depth, solidification (liquid-solid interface) velocity, and cooling (quench) rate after solidification. With 10-nsec laser pulses, melt depths may extend to ~ 0.1 μm, solidification velocities range from 1 to 20 m/sec, and quench rates are $\sim 10^8$ to 10^{10} K/sec. At 1-msec pulse lengths, characteristic melt depths extend to many tens of micrometers, solidification velocities are ~ 10 cm/sec, and quench rates are $\sim 10^6$ K/sec.

Most studies of laser surface treatments have been concerned with physical effects. More recently there has been increased interest in using lasers to control surface chemical reactions with liquid or gaseous species (see Fig. 2b). In many of the latter cases the nature of the electronic excitations at surface plays a critical role in surface changes.

Microstructures

A special aspect of ion implantation and laser heating of surfaces is the uniform and reproducible range of microstructures that can be obtained (*1–3, 5, 6, 12, 16*). Equilibrium homogeneous microstructures can be formed, and alloys with high densities of exceedingly fine precipitates are readily obtained. Metastable solid solutions and supersaturated substitutional solutions exceeding equilibrium solubilities by one to two orders of magnitude are often achieved. Fine-grain polycrystalline structures are also obtained, especially by laser melting. In addition, both ion implantation and laser melting techniques are well suited for forming amorphous phases, and new metastable crystalline phases can also be formed directly or upon heat treatment of amorphous alloys.

The resulting microstructure depends on the composition as well as the implantation or laser treatment conditions. Implantation introduces high densities of defects, leading to such unique microstructures as dense dislocation networks, high vacancy concentrations, or even superlattices of voids or gas bubbles. In the case of laser melting, very fine dendritic or cellular dendritic microstructures can be formed. Increasing the solidification rate of metals leads to a transition in the microstructure from dendritic, to cellular dendritic, to planar growth fronts. Also, higher solidification rates and steeper temperature gradients in the solid imply fast cooling and lead to shorter diffusion lengths and finer microstructures.

Solidification from the melt by laser or electron beam heating is only one of several approaches to rapid solidification (*17, 18*). Other approaches include depositing a liquid onto a cold surface by splat cooling, spinning, or vapor quenching. Except for the latter, laser melting provides the ultimate in cooling rates and control of conditions, since the melted region and substrate are in an intimate and known condition of thermal contact. The high energy density within single ion cascades ($\sim 10^{-2}$ to 10 eV per atom) and short energy deposition times ($\sim 10^{-12}$ second per ion) have caused investigators to consider the analogy between ion implantation and melt quenching on an atomic scale. For very dense cascades one may consider the ion cascade region to be quenched from a high-energy state or "temperature." Thus, during cooling, thermodynamic states that are available in the absence of long-range atomic motion can be reached. This fast quenching from a high-energy state accounts for some of the similarities in microstructures obtained between laser- and ion-bombarded surfaces. For example, similar metastable phase diagrams have been found for Ni-implanted Al and melt-quenched Al(Ni) alloys. The major differences between ion-implanted and laser melt-quenched materials occur when sufficient time is available during melt quenching for segregation in the liquid phase or at the liquid-solid interface; such segregation is usually suppressed in the implanted case.

New Material Properties

In many cases the microstructures formed by ion implantation and laser heating can be predicted, and it is possible to characterize these microstructures in detail by a wide variety of modern surface analytical techniques (transmission analytical electron microscopies, ion beam analysis, Auger electron and x-ray photoemission spectroscopies, scanning electron microscopy, and so on). However, the resulting properties can seldom be predicted, and many new and unexpected effects have been observed. A summary of various kinds of properties influenced by directed energy processing is given in Table 1. The difficulty in predicting changes in the properties reflects the limited atomic-level understanding of the relations between materials properties and microstructure. In addition, for mechanical properties a better description is needed of the composite behavior of thin layers on substrates.

The properties of new materials formed by implantation or laser alloying of deposited layers are closely related to those of surface layers formed by thin-film deposition techniques. However, surface modification by ion and laser beams is distinct from many film deposition techniques in that layers can be formed with greater purity, better adhesion, and additional controls on composition and microstructure.

Implantation of metals. Of the wide variety of surface property changes observed in implanted metals (see Table 1), mechanical properties of surfaces, especially friction and wear, have been the most extensively studied (*19–21*). Particular emphasis has been given to the study of nitrogen implantation of steels. This emphasis is due to both the previously known improvement obtained by nitriding certain steels and the ease of obtaining intense nitrogen ion beams. For certain steels nitrogen implantation increases wear resistance and improves lifetimes of tools (*20*). In particular, for precision molding tools and dies, improvements of up to an order of magnitude over normal life have been reported. These improvements have their origin in the fine dispersion of nitride precipitates, and/or nitrogen in solid solution, depending on the implantation temperature and the material. These microstructural changes can harden the surface layer and, in certain cases, change the wear mechanism; both effects can improve wear resistance. Some of the most dramatic effects of nitrogen implantation have been observed for implantation of titanium alloys; for instance, for Ti6Al4V (a titanium alloy containing 6 percent aluminum and 4 percent vanadium by weight) reductions by a factor of 3 in unlubricated friction and by a factor of 1000 in wear volume were found (*22*). Another area being explored is the treatment of titanium alloys used for hip prostheses to reduce the degradation of these artificial hip joints that results from wear between the titanium alloy ball and the polyethylene socket.

From a materials science viewpoint, the influence of metastable alloys on surface properties is of great interest. For example, nitrogen implantation does not improve the wear behavior of hard bearing steels, whereas implantation of about 20 atom percent titanium and 20 atom percent carbon does. The titanium and carbon implantation transforms the surface of a wide variety of steels—ferritic, austenitic, and martensitic—from crystalline to an amorphous alloy, which exhibits about a factor of 2 reduction in unlubricated coefficient of friction (*23*). Figure 4 shows an example of the reduction in friction and change in wear surface morphology for a soft, type 304 austenitic steel. In addition, the implanted surface layers of the steels show reductions (by about a factor of 2 to 5) in the wear rate in pin-on-disk lifetime tests until the implanted region is worn through. This amorphous alloy is a new phase which had not been obtained previously; it is not accessible by melt quenching because of the high melting point and insolubility of the TiC phase in liquid iron alloys. The reduced friction for this alloy has been shown to require the presence of the amorphous layer in the wear track; crystalline alloys of the same composition do not exhibit reduced friction (*23*). Furthermore, the wear reductions remain substantial for Hertzian stresses exceeding the bulk yield stress by as much as 50 percent for both soft steels and hard bearing steels.

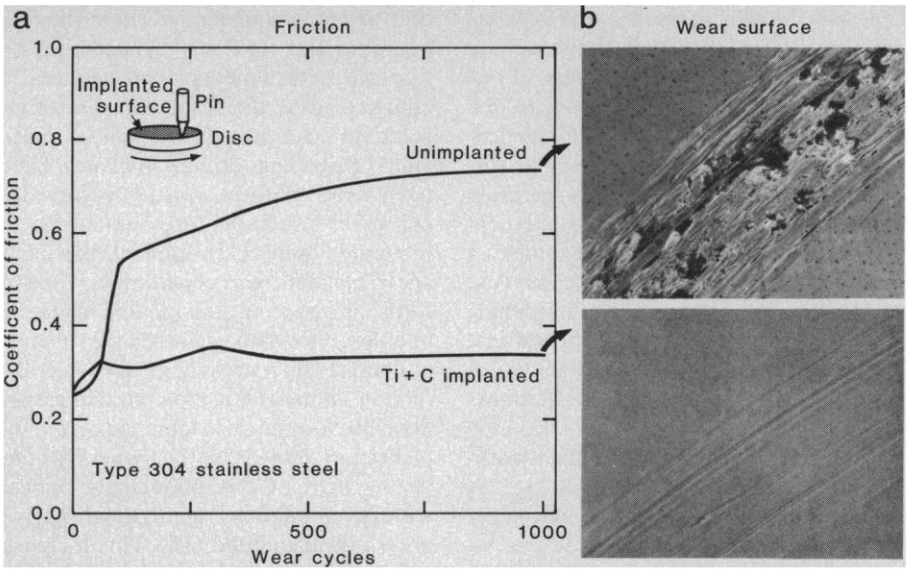

Fig. 4. Unlubricated coefficient of friction versus number of wear cycles with and without titanium and carbon implantation alloying to form an amorphous iron (20 atom percent Ti, 20 atom percent C) layer in type 304 stainless steel. Scanning electron micrographs of the surface are shown after 1000 wear cycles in each case. [After (*23*)]

Corrosion studies have also exploited the ability to form both conventional and new alloys by ion implantation (*19, 24, 25*). Chromium-alloyed iron layers have shown corrosion resistance equal or superior to that of conventional high-chrome stainless steels. As an example of a new alloy, tantalum in solution in iron would be expected to have a beneficial chemical effect in a corrosive environment, but this alloy cannot be formed by conventional metallurgy because of the negligible solubility of tantalum in iron. Implantation of tantalum to form a homogeneous alloy with iron showed that passive film formation which provides good protection does indeed occur (*25*). Furthermore, the tantalum alloy continued to exhibit reduced oxidation long after the thickness of the surface alloy had been dissolved, presumably because of preferential dissolution of iron from the alloy.

Another interesting application of ion implantation to modify metals is in the area of superconductivity (*26*). The strong influence of hydrogen on the superconducting transition temperature of palladium and palladium/noble-metal alloys was explored by low-temperature hydrogen implantation (*27*). Superconducting transition temperatures were increased to as much as 16 K for hydrogen-implanted $Pd_{0.55}Cu_{0.45}$. The only other method for introducing hydrogen at the necessary high concentrations is high-pressure loading of hydrogen.

Laser-treated metals. Laser treatment also leads to a wide variety of changes in metal surface properties, including increased hardness, strength, corrosion resistance, wear resistance, and fatigue life (*6, 10–12*). An advantage of laser treatment over ion beams is the greater depths that can be conveniently treated ($\gtrsim 10$ μm, compared to $\lesssim 1$ μm by implantation) with currently available equipment. A second advantage is that laser treatment can frequently be performed in air or in a controlled atmosphere. Laser modification of metallic surfaces can be divided into four categories: (i) transformation hardening, (ii) surface alloying, (iii) rapid solidification (glazing), and (iv) shock hardening. These areas are categorized in Fig. 3 in terms of deposited laser power and interaction time.

Transformation hardening of ferrous alloys (*28*) has become widely used in manufacturing to harden metal components in internal combustion engines. This solid-phase process utilizes lasers with defocused beams and absorptive coatings on the treated surface to enhance the energy deposition. The surface region must be heated but not melted, and sufficient carbon must be present in the steel. Hardening is accomplished by heating the surface material above the critical temperature for transformation to the austenite phase, and subsequent cooling at a sufficiently rapid rate to form a martensite phase. Cast iron can also be hardened by martensite formation; however, if graphite instead of pearlite is initially present, longer treatment times are required for the necessary carbon diffusion. The formation of martensite on the surface produces a hard surface layer without appreciably changing the bulk properties or dimensions.

In laser surface alloying, deposited films are melted by high-power laser beams to form an alloy consisting of the film and substrate atoms (*16*). This process allows the formation of surface alloys with improved properties and is being explored for a number of applications, with special emphasis on corrosion resistance. For example, corrosion studies (*29*) have shown that laser-formed alloys containing 29 percent chromium and 13 percent nickel (by weight) in iron exhibit excellent corrosion resistance and that such layers on conventional steels are far superior in corrosive environments to conventional type 304 stainless steel (19 percent chromium, 8 percent nickel). In addition to deposited films or coatings, the alloying material may be added by feeding wire or powder to the surface during laser irradiation. This process can lead to very thick alloyed layers that can be machined or polished after treatment to form metal components (*16*).

Rapid solidification by laser beam melting can result in amorphous phase formation for certain alloy compositions or, in other cases, in alloys with extremely fine dendritic or columnar dendritic microstructures (*16–18*). The surface hardness of these alloys is often increased substantially (from 50 percent to a factor of 2 or more). For example, a combination of laser melting and heat treatment to fully utilize hardening mechanisms throughout the melted and heat-affected region has been shown to be effective for increasing the hardness of a variety of steels (for example, low-carbon steel, casting alloys, cold-working and hot-working steels) (*30*).

Shock hardening involves extremely high-power laser pulses ($\sim 10^9$ W/cm^2) to induce surface vaporization for short times ($\leq 10^{-7}$ second). The rapid expansion of vaporized material produces a shock wave that propagates into the material and produces work hardening.

Semiconductors, insulators, and other materials. Ion implantation is widely used to introduce electrical dopants into silicon (*31*). Indeed, this was the first commercial application of ion implantation because it provided precise control not only of the number of dopants but also of their lateral and depth distributions. However, implantation produces damage that must be removed—for example, by furnace heating (annealing)—for electrical doping of semiconductors. There have been extensive studies of pulsed laser annealing in the nanosecond time regime, CW laser annealing in the millisecond regime, and rapid thermal annealing (~1 to 10 seconds) with high-intensity lamps to remove the implantation damage while retaining high dopant concentrations (*7–9*). Rapid thermal annealing introduces minimal stress since the entire wafer is uniformly heated, and it appears very promising for semiconductor processing applications (*7*). Rapid thermal annealing of compound semiconductors is of particular interest because it can lead to more complete activation of implanted electrical dopants while minimizing preferential loss of volatile species (for instance, arsenic from GaAs, which produces deep traps). The primary advantages are less stringent requirements on capping materials (to prevent sublimation of the more volatile element) and the increased concentrations of dopants that can be activated without decreasing the carrier mobility.

Implantation damage has also been utilized to induce property changes in a variety of materials. For example, it has been used in compound semiconductors to electrically isolate regions and in silicon to remove unwanted impurities by gettering them to the damaged region during heat treatments. Damage-induced changes in the dielectric constant of insulating materials (for instance, fused silica glass and lithium niobate) have been used to form optical waveguides and other structures for potential use in integrated optics (*32*). Implantation damage in magnetic garnet material is used to form propagating tracks for magnetic bubbles. This damage introduces a lateral compressive stress that alters the direction of magnetization in the garnet film. In ferroelectric ceramics ion implantation increases the sensitivity to visible light of this nonvolatile optical storage medium by approximately five orders of magnitude (*33*). This increase results from the contribution of the implantation damage, as well as chemically active implanted species, in reducing conductivity and increasing photosensitivity. In ceramics implantation studies have shown improvements in hardness and toughness of implanted surfaces due to both damage addition and chemical changes (*34*). In polymers, large changes in conductivity of the implanted region have been reported with increases in conductivity of up to 14 orders of magnitude (*35*).

A novel example of implantation in semiconductors which is now under investigation is the formation of buried silicon dioxide or silicon nitride layers by implantation of oxygen or nitrogen (*36*). A buried layer of oxide can be formed while maintaining a single-crystal silicon layer over the buried insulating layer if sufficiently high ion fluences, energies, and temperatures are used. This type of structure is referred to as SOI (silicon-on-insulator) and is of particular interest for its potential application to very large scale integrated (VLSI) circuits. Potential advantages of circuits formed from SOI include low power requirements, high speed, high radiation tolerance, and prevention of latch-up (runaway current flow between neighboring transistors that is increasingly difficult to prevent as feature sizes decrease). Various approaches to SOI have been considered for many years, but the difficulty in reliably and economically obtaining device-quality single-crystal silicon layers ~0.5 μm thick on insulators has prevented the development of this technology.

Another approach being explored for SOI formation is the use of CW lasers or electron beams to induce melting and crystallization of deposited polycrystalline silicon layers, typically over oxide layers on silicon (*37*). The objective in this work is to seed and sweep a single-crystal growth front laterally over large distances without defect formation. At present, low-angle grain boundary formation is a primary difficulty, but high-quality, 0.5-μm-thick single-crystal areas of about 50 by 100 μm can be obtained. Thus, although no single method has emerged for forming superior quality SOI structures, the progress demonstrates the many possibilities that exist for the creation of unique three-dimensional structures by ion implantation and laser heating processes.

Another new area of active research is the use of lasers for chemical processing (*13, 38, 39*). In this area chemical reactions that can be driven by localized heating or electronic excitation with lasers are exploited for selectively depositing, etching, or electrically doping materials (Fig. 2b). For example, thermal deposition of silicon from silane (SiH_4) gas can be assisted by heating, the rate-limiting step being the breaking of hydrogen-silicon bonds. In photochemical deposition processes photons may electronically induce the breaking of specific bonds, for example, in the low-temperature deposition of metals and insulators from gas-phase or adsorbed phase parent molecules (such as Si_3N_4, SiO_2, or Al). An example of laser etching is the case of Si and GaAs in Cl_2 gas. Laser etching and deposition on surfaces have also been demonstrated through liquids. One major interest in the use of laser chemical processes is in direct writing with focused laser spots as a complement to large-area processing for electronic applications. Another interest is in selective laser etching and deposition on silicon by laser projection through masks for VLSI uses. For III-V semiconductors a primary motivation is the greater degree of processing control, as is available for silicon.

New Materials Science

In the preceding section we gave a flavor of materials modification and studies of the relations between surface properties and surface microstructures with directed energy beams. In this section we highlight a philosophically different area of studies, but one of equal importance to materials science. This is the use of ion beams to explore fundamental processes in materials science. The result of such studies is an increased knowledge of basic parameters, processes, and mechanisms, which can improve materials processing and reliability and can advance our basic understanding of materials science. To illustrate this area we discuss first ion implantation in metals and then pulsed laser melting of silicon.

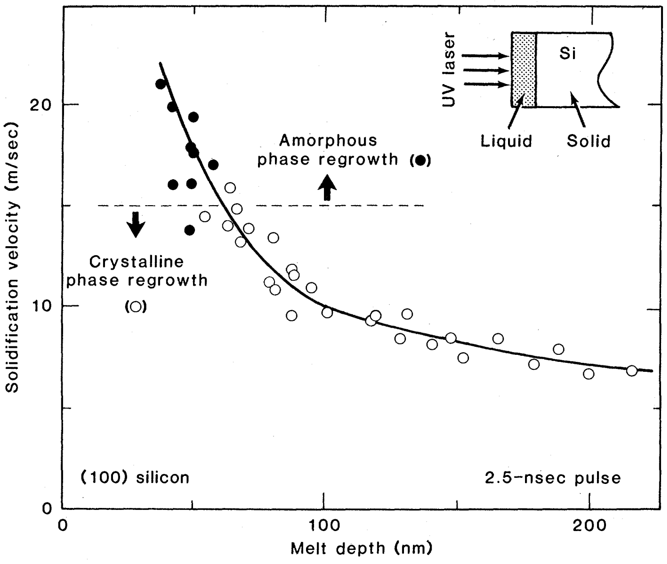

Fig. 5. Solidification velocities for various melt depths into a (100)-oriented silicon crystal as measured by the transient conductance technique with ultraviolet (UV) (347 nm) laser light pulses 2.5 nsec long (*51*). Above about 15 m/sec the silicon cannot continue to solidify into the crystalline state and is observed to form the amorphous phase.

The controlled introduction of elements and defects by ion implantation offers an ideal way to explore alloying, trapping, and phase transformations in metals (*40–42*). Both kinetics and equilibria in metal alloying reactions have been investigated. Because of the shallow depths involved, diffusivities can be extended downward by more than four orders of magnitude compared to those in conventional sectioning techniques, which extends them into a temperature range relevant to metallurgical tempering and aging heat treatments. For substitutional solutes it has been shown—for example, in iron and beryllium—that the measured diffusivities are characteristic of bulk measurements (*40*). In addition, the solubilities for solutes are obtained at quite low temperatures, where dilute solution theory often allows a general description of the enthalpy of solution. The phase boundary studies have been extended to ternary systems by forming multilayer concentration profiles. For example, various phase boundaries near the beryllium-rich corner of the BeFeAl ternary were obtained where the highly disparate melting points essentially preclude such measurements by conventional metallurgical approaches.

Ion implantation also allows detailed investigation of trapping mechanisms for impurities which lead to degradation of conventional alloys. For example, many studies have focused on hydrogen trapping in metals, which is relevant to hydrogen embrittlement, a process that leads to undesired fracture of alloys due to localized hydrogen accumulation at internal boundaries. The hydrogen studies have taken advantage of the ability to controllably introduce both defects and gas atoms by ion implantation (*43, 44*). These studies have allowed precise measurements of the binding energies of hydrogen trapped at a variety of defects. In the case of hydrogen in iron, such studies provided the first identification of the atomic structure and binding energy for a hydrogen-vacancy center in a metal (*45*). The hydrogen location observed from such measurements was subsequently verified by theoretical calculations (*46*). Hydrogen trapping by defect clusters and helium gas bubbles has also been observed (*47*). These ion beam studies of hydrogen in metals have allowed the independent determination of both hydrogen trap energies and surface recombination rates, important parameters which are difficult to separate in gas permeation studies. Such studies have been particularly relevant to the materials issues of tritium fueling, inventory, and permeation at the first wall of magnetic confinement fusion reactors.

Another area of focus of the trapping studies is metalloid (antimony, tin, phosphorus, and so on) trapping in body-centered cubic (bcc) iron. This area is relevant to temper embrittlement, a brittle fracture process involving the accumulation of metalloids at prior grain boundaries in ferritic steels operated in the temperature range 300° to 600°C (for instance, in turbine blades). Implantation studies involving temper embrittling species have shown that the interfacial boundaries between precipitates and the bcc iron matrix act as traps that can immobilize unwanted metalloids (*48*). These ion beam investigations have focused on the trapping of antimony implanted in bcc iron containing TiC precipitates that were previously introduced by implantation metallurgy techniques.

Phase transformation studies by ion implantation allow detailed investigation of the formation of metastable substitutional solutions, metastable crystalline phases, and amorphous alloy phases by systematic variation of composition and crystal lattice disorder (*41, 42*). The ability to induce the crystalline-to-amorphous transition by ion implantation depends on the damage density of individual ion cascades, as well as alloy composition and temperature. In alloy formation studies with aluminum, implantation and laser (or electron beam) melt quenching studies have been combined (*5*). This approach has allowed the direct comparison of alloy formation by implantation and by melt quenching under identical conditions of solute concentration and purity. In addition, metastable phase diagrams have been constructed and explored under various conditions. Also, it has been discovered that by these combined techniques nucleation times in liquids can be measured for the first time in the nanosecond time regime. For example, AlSb, a simple cubic phase, has a nucleation time of 15 ± 10 nsec in molten aluminum at concentrations of several percent antimony, whereas the complex Al_3Ni_2 phase has a nucleation time of $\gtrsim 1$ μsec in liquid aluminum (*49*).

New materials science studies with lasers are exemplified by the solidification of silicon at high rates (*8, 9, 50, 51*). Through the ability to rapidly melt thin layers of silicon with nanosecond and picosecond lasers, it has been possible to explore basic questions of solidification from the melt at very high velocities. Early results involving formation of metastable solutions and nonequilibrium segregation at the liquid-solid interface have been discussed (*9*). More recently, dynamic electrical conductance measurements have allowed the motion of the liquid-solid interface to be measured during pulsed melting (*51*). An example from this work involving the rapid solidification of silicon is shown in Fig. 5. These techniques, together with ion implantation to form amorphous silicon, have been used to study the amorphous-to-liquid phase transition and, for the first time, to determine the free-energy diagram for amorphous silicon up to the melting point (*51*). These high-temperature measurements were impossible previously, because of the rapid crystallization in the solid phase. From such measurements the increase in the free energy ($\sim$1/8 eV per atom) and the lowering of the melting point ($\sim$200 K) of the amorphous phase relative to the crystalline phase of silicon have been obtained (*50–*

52). Also, it has been found that there is an orientation-dependent limiting velocity for solidification into the crystalline phase [for example, ≈15 m/sec for (100)-oriented silicon, as shown in Fig. 5] (51). At higher velocities silicon can no longer grow epitaxially, but instead solidifies into the amorphous state. These studies are bringing new understanding to the old field of crystal growth because of their ability to probe regions much further from thermal equilibrium than were previously accessible.

Perspectives and Conclusions

We have explored the use of ion and laser beams for modifying the near-surface properties of materials, emphasizing that this is only one of many new approaches in materials science to better control material microstructure and chemistry during processing. In contrast, conventional metallurgical processing of alloys, including hot and cold working, casting, and powder metallurgy, focus on bulk alloying to control the properties of materials. Although the conventional process of alloy casting is very effective, there are two inherent limitations in terms of materials formation: high-melting-point phases are difficult to introduce and cooling of the alloys from the melt is slow so that segregation can occur over large distances. Because of the melt dimensions and the slow cooling, it is not possible to move very far from thermodynamic equilibrium. In bulk processing these limitations are partially overcome by powder metallurgy, in which powders are mixed and sintered together so that segregation is limited to the scale of the particle size. In surface processing these limitations are naturally circumvented by ion and laser beams. Homogeneous materials with a wide variety of tailored near-surface structures can be formed. Also, multiphase microstructures can be formed on an exceedingly fine scale. Fewer constraints of thermal equilibrium are met and materials can be formed that are much further from thermal equilibrium. Furthermore, the properties of materials can be explored continuously through a wide range of compositions without introducing new variables, and thus interrelationships between microstructure and properties of materials can be explored in detail. These techniques are also being used to explore new aspects of materials science, such as trapping mechanisms and nonequilibrium solidification phenomena.

As a result of the control and reproducibility, standard commercial techniques have emerged for ion implantation doping of silicon and for laser transformation hardening of steel components. Many other uses of ion and laser beams for surface modification are under active consideration or exploratory development for commercial use. The primary limitation of this approach is that usually only thin layers are formed, so that applications must be avoided where local penetration of the layer will lead to catastrophic failure. Directed energy processes are energy-efficient, and they are also materials-efficient in the sense of use of critical or strategic materials. Since the surface region is selectively treated, these treatments can be used as finishing steps, allowing surfaces to be engineered for optimum properties independent of bulk property requirements. Also, the treated region is an intimate part of the substrate, so that problems of adhesion are usually avoided. An anticipated area of fruitful future research is the combining of film deposition and directed energy beams to form thicker layers with special control of microstructure and properties.

In summary, the use of directed energy processes is extremely diverse and offers considerable scope for fundamental materials science studies, as well as for new applications to materials processing. The power of these techniques lie in their control, selectivity, and wide applicability and in the relaxation of the usual constraints of thermal equilibrium. One anticipates that there will be many important developments yet to come in this new field which will improve our control and understanding of materials.

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