Kirk-Othmer Encyclopedia of Chemical Technology.

PHOTOCHEMICAL TECHNOLOGY, SURVEY

Intense research in photochemistry has provided a substantial base of photochemical technologies for industrial application. The state-of-the-art in applied photochemistry has been reviewed through 1989 (1) and subsequently benchmarked at the International Symposium on Perspectives in Photochemistry in 1992 (2). The oldest recorded continuously practiced application of photochemical technology is the processing of natural dyes of the indigo class as used in the traditional Japanese textile craft of aizome (see Dyes, natural; Textiles) (3). Practice of aizome, popular for over 10 centuries, is no longer of commercial importance.

Photoimaging is another use of photochemical technology (see Imaging technology). The first known photographic image was recorded by Nièpce in 1826 by the photocross-linking of bitumen (see Coal) coated in a thin layer on a glass plate; exposure of the plate took several days in a camera oscura (4). Bitumen is a naturally occurring mixture of oligomerized, aromatic, and unsaturated hydrocarbons which undergo cross-linking on absorption of the ultraviolet component of sunlight. Oil of lavender was used as a developer to remove uncross-linked hydrocarbon from unexposed regions of the plate to reveal the negative image (see Photography). This photochemical innovation gave rise to modern photopolymer technology which is responsible for the environmentally significant solventless coatings (qv) industry (5, 6).

Photochemical technology has been developed so as to increasingly exploit inorganic and organometallic photochemistries (2, 7), recognizing the importance of photoinduced electron transfer as the phenomenological basis of a majority of commercially successful photochemical technologies (5, 8). Use of coherent light sources in industrial applications has led to the field of photodynamic therapy as a photochemically based medical technology (9–11). The application of photochemistry to information storage and communication processes is expected (12) (see Resist materials).

1. Light Sources

Conventional, incoherent light sources suitable for industrial-scale photochemistry and the reactors exploiting them have been reviewed in depth (2). Subsequent improvements in traditional light sources have been incremental.

The exploitation of coherent sources has been a much awaited advance in photochemical technology. Application of laser sources has proved revolutionary in photoimaging (6), and enabled innovations in photodynamic therapy (9–11) and photochemical memory technologies (12). As of this writing (ca 1995), lasers (qv) have not yet proved to be of significant importance for large-scale industrial synthetic applications, but have been applied to effect various photochemistries, eg, photodecomposition of polymers, surface treatments, high precision machining of synthetic polymeric structures, and medical surgery (13). The latter two applications are examples of laser ablation, the use of laser energy to decompose solid structures to gaseous products. The mechanism of ablation has been established to involve primarily photochemical reactions (14). Availability of high powered CO_2 lasers for ablation applications on the one hand, and of electronically modulatable solid-state lasers for high bandwidth information storage, imaging, and communications applications on the other hand, both emitting in the red and near infrared (0.6–9 μm), has stimulated renewed interest in infrared photochemistry.

In 1988 the excimer lamp, a new kind of lamp, was announced (15). An excimer lamp is a gas-phase fluorescent lamp powered by an electrical (15) or microwave (16–18) discharge. It produces monochromatic, incoherent radiation in a quasi-continuous mode, ie, pulses of light at a relatively high (ca 100 Hz) repetition rate. Wavelength of emission is the same as for the corresponding excimer laser, eg, 248 nm for KrF (16), 193 nm for ArF (17), and 157 nm for F_2 (18). Efficiencies of these lamps are theoretically as high as 40% and under practical operating conditions efficiencies of ca 10% based on microwave power are obtained (16–18) for the more efficient, microwave discharge powered lamps. One application for excimer lamp photochemistry is the hardening and/or drying on-press of uv-curable inks used in the printing industry, eg, for newspaper printing (19) (see Radiation curing). Such inks (qv) are capable of the appropriate rheological characteristics for web offset printing at lower (or zero) levels of volatile solvents and, after uv-curing do not smear in contact with press components, offset to other printed surfaces, or come off on the readers' hands. Excimer lamps are also used to cure epoxy adhesives (qv) incorporating, eg, diaryliodonium or analogous trarylsulfonium salts as photo-acid sources, in the process of making laminated products such as industrial wipers, work wear, surgical drapes, etc (20). Principal application of excimer lamp technology, however, has been in the photochemical deposition of insulating layers in microelectronic fabrication.

2. Photophysics

2.1. Photochemical Laws and Sensitization

All photochemical technologies are practiced in accord with the fundamental laws of photophysics, relating to the nature of light and its interaction with matter. These are covered in detail in texts and reference books on photochemistry (see *General References*). Of interest herein are the following: (*1*) the Bunsen-Roscoe law, ie, only light which is absorbed by the reactive system is useful; (*2*) Einstein's law, ie, light absorption is quantized and each quantum absorbed activates one molecule; and (*3*) the lowest energy excited state of a given spin multiplicity is the starting point for practical photochemical processes. A corollary of the first principle is that not only must the desired component of a photochemical reaction mixture absorb light from the source to be exploited but also other components of the mixture must not absorb in the same spectral regime.

A special case applies when the photochemical reaction mixture is in the form of a thin film, eg, a radiation curable coating, a microlithographic resist, an imaging medium, or a thin, flowing film of a solution in a flow reactor. Accordingly the active light absorbing component in the mixture should optimally be present at a concentration such as to absorb ca 63% of the incident actinic radiation. Inefficient utilization of the radiation results at lower concentration and reaction occurs nonuniformly at higher concentrations (21).

In many cases of practical interest, the reactive species does not absorb light from available sources. In these cases a sensitizer is used that is capable of absorbing available radiation and subsequently transferring either the excitation energy or, in many cases, an electron to the reactive system. In principle the sensitizer does not participate in the reaction and should not affect its course. In practice this is often not the case. Diaryliodonium salts are commonly used photoinitiators for either free-radical or cationic polymerizations (5, 6, 22) (see Initiators). The diaryliodonium cations typically do not absorb significantly at wavelengths longer than 280 nm. Rather, trifluoromethylacetophenone, which absorbs the Hg arc line at 313 nm, sensitizes iodonium salt photolysis by triplet state energy transfer, ie, the excitation energy of the sensitizer is transferred to the iodonium cation. In this case, the sensitizer is recovered unchanged. Electron-transfer sensitization is often more useful in many industrial applications than energy-transfer sensitization. Thus polycyclic aromatic hydrocarbons, eg, anthracene which absorbs out to 400 nm, overlapping the emission of readily available relatively inexpensive medium pressure Hg arc lamps, also sensitize diaryliodonium cations, but sensitization occurs by electron transfer. Because efficient in-cage recombination consumes all the radical products of the reaction, anthracene sensitization is useful only for photoinitiation of cationic cures, eg, of epoxies, via the protic acid by-product.

Previous expositions of photochemical laws have distinguished prominently between states of singlet and triplet multiplicity (1). This distinction continues to be important with respect to photophysics of small organic molecules, but among inorganic and organometallic compounds, states of other multiplicities, eg, doublet and quartet states (23), play an important role. Spin conservation characterizes electronic molecular excitations and localized exciton formation in solids. Thus initially formed excited states exhibit the same multiplicity as the ground state. In the presence of heavier atoms, eg, organometallic compounds, increased spin-orbit coupling enhances facility of interconversion of spin states. Spectroscopic studies suggest that triplet manifold states of organic compounds with their characteristic photochemistries can also be accessed efficiently, with respect to internal conversion within the same spin manifold, as a consequence of multiphoton laser excitation (24).

2.2. Multiphoton Effects

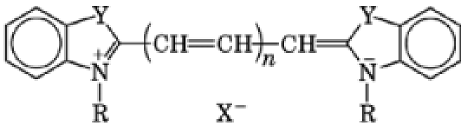
Intense laser sources are capable of producing multiphotonic excitation, allowing different photochemistries to be obtained from higher excited states than from the lowest excited state usually accessible with conventional light sources. Generation of radicals from higher excited states of diketones and photoactivation of primary radicals from monophotonic decomposition reactions of organic precursors, eg, benzophenone, benzil, and the aryl-substituted cyclohexanones, represent newer routes to laser specific photoinitiation of polymerization in radiation curing applications (5, 25), particularly for rapid curing of thick polymer specimens, as well as high contrast, submicrometer resolution microlithography.

Multiphoton processes are also undoubtedly involved in the photodegradation of polymers in intense laser fields, eg, using excimer lasers (13). Moreover, multiphoton excitation during pumping can become a significant loss factor in operation of dye lasers (26, 27). The photochemically reactive species may or may not be capable of absorption of the individual photons which cooperate to produce multiphoton excitation, but must be capable of utilizing a quantum of energy equal to that of the combined photons. Multiphoton excitation thus may be viewed as an exception to the Bunsen-Roscoe law.

2.3. Excited-State Relaxation

A further photophysical topic of intense interest is pathways for thermal relaxation of excited states in condensed phases. According to the Franck-Condon principle, photoexcitation occurs with no concurrent relaxation of atomic positions in space, either of the photoexcited chromophore or of the solvating medium. Subsequent to excitation, but typically on the picosecond time scale, atomic positions change to a new equilibrium position, sometimes termed the *thexi*-state (28). Relaxation of the solvating medium is often more dramatic than that of the chromophore itself. Photochemical reactions generally occur from the *thexi*-state, as illustrated in Figure 1. This relaxation can have practical consequences, eg, with respect to choice of the optimum medium in which to effect a particular photochemical reaction.

An illustration of the technological significance of the relaxation phenomenon can be taken from photographic chemistry. Dyes of the cyanine class where $Y = S, O, -CH{-}CH-$; $n = 0, 1, 2, 3\ldots$ $X^- =$ halide, etc, are used as spectral sensitizers to extend photochemical response of the photographic silver halides, which only absorb blue and ultraviolet light, into the visible spectral regime.



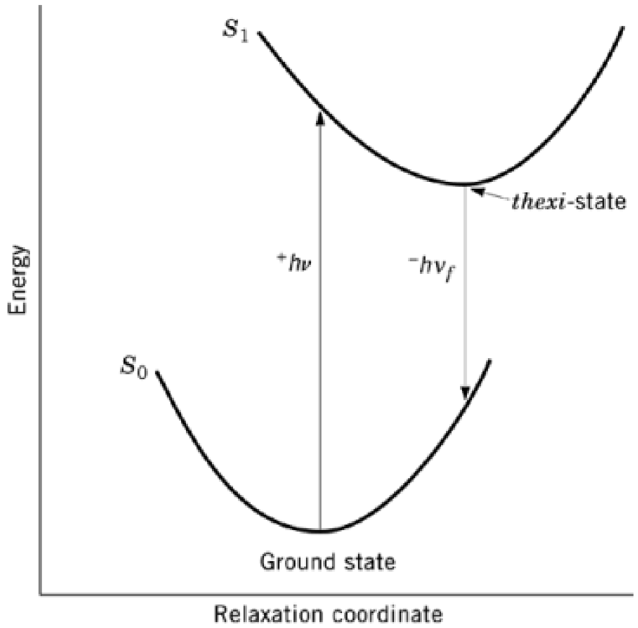


Fig. 1. Relaxation of molecule-medium system subsequent to photoexcitation where S_0 is the singlet ground state; S_1, the first excited singlet state; and $h\nu_f$, the fluorescent photon. See text.

The mechanism of this sensitization is usually understood as involving single-electron transfer from photoexcited dye into the conduction band of the silver halide crystal (29). In their ground-state conformation, cyanine dyes are usually planar. Their *thexi*-states are twisted (30) and relaxation often involves thermalization of sufficient energy so that the excited dyes are no longer capable of effecting the electron transfer exoergically. The process of spectral sensitization thus becomes inefficient. Even before *thexi*-state formation in the cyanine dye system was understood, dyes, in which the polymethine chain of the chromophore was made rigid by incorporating it into a cyclic or polycyclic residue, had been synthesized (31). These dyes proved to be more stable than their open-chain analogues and yielded more efficient sensitization, because the excited dye molecule is structurally constrained to remain in the more reactive planar configuration.

2.4. Electron-Transfer Dynamics

To a large extent, commercial photochemical technology, including radiation curing, photomedical applications, photochemical information storage, and silver halide photography, involve photoinduced electron transfer. Electron transfer is also the primary process occurring in organic photoconductors as used in office copying applications (see Electrophotography) (32); the basis for other photoinitiated, heterogeneous-phase polymerization processes (33); and a crucial player in photocatalysis. An understanding of the theory and phenomenology of photoinduced electron transfer is de rigeur for development of photochemical technology in the contemporary environment. Dynamics of light-induced electron-transfer processes in both homogeneous and heterogenous phases have been reviewed (34).

For the reaction, $D + A + h\nu \longrightarrow D^+ + A^-$, the Gibbs free energy change is given by the Weller equation (35):

$$\Delta G = F\left(E_{\mathrm{ox}}^{D} - E_{\mathrm{red}}^{A}\right) - E_{0,0} - e^2/r\epsilon$$

where F is the Faraday constant; E^{D}_{ox} is the electrochemical oxidation potential of the donor, D; E^{A}_{red} is the reduction potential of the acceptor, A; $E_{0,0}$ is the energy of the electronic transition excited by the radiation employed, usually of the *thexi*-state of the excited moiety vs the relaxed ground state; and the final term is the Coulomb expression for the energy required to effect charge separation over the D–A separation distance, r, in a medium of dielectric constant, ϵ.

The rate of the electron-transfer process, at least in solution, is defined in the usual way:

$$d(D^{+}, A^{-})/dt = k[A][D^{*}] \quad \text{or} \quad k[A^{*}][D]$$

where k is the rate constant, depending on whether D or A is energetically excited. According to usual photochemical notation, the asterisk designates the excited state species. From transition-state theory a pseudo-equilibrium constant, $K^{\neq}$, is defined:

$$K^{\neq} = hk/k_{b}T$$

where h is Planck's constant, k_{b} is the Boltzman constant, and T is the temperature in Kelvin. By convention, k is specified in units of $\mathrm{L}^{2}/mol^{2}\cdot s$). Then a free energy of activation can be defined as follows:

$$\Delta G^{\neq} = -k_{b}T \ln K^{\neq}$$

There are two approaches to estimation of $\Delta G^{\neq}$. The first is an empirical approach (36) based on dynamics of fluorescence quenching of aromatic hydrocarbons in acetonitrile solution. Accordingly,

$$\Delta G^{\neq} = \left[(\Delta G/2)^{2} + (\lambda/4)^{2}\right]^{1/2} + G/2$$

where the adjustable parameter, $\lambda = 0.42$ eV (40.4 kJ/mol), for all reactive pairs studied. Subsequent investigations have shown that λ is solvent dependent. This equation is often called the Rehm-Weller equation.

In work for which Marcus and Levich separately received the Nobel Prize, it was shown from first principles (37) and in different contexts that

$$\Delta G^{\neq} = (\lambda/4) \;\; (1 + \Delta G/\lambda)^{2} + W$$

wherein λ was defined as a medium reorganization energy which is related to the energy thermalized during relaxation of the excited state to the *thexi*-state (28). The value of λ is predictable in many cases where medium relaxation is the principal contributor to λ by a dielectric continuum approximation. The variable W incorporates the work of bringing the reactants together and separating the products.

This expression, usually called the Marcus equation, is generally applicable to all one-electron transfer processes whether photoinduced or not. Dynamics of electron transfer reflect the driving force provided by photon energy absorption in the ΔG term according to the Weller equation. Thus, if the parameters of the Weller equation can be established experimentally, only estimation of λ is required for prediction of k. It can be seen on inspection that the empirical Rehm-Weller expression is a special case of the Marcus expression; this relationship and the conditions under which the Rehm-Weller treatment applies, have been discussed (38) from a theoretical point of view. Models based on the Marcus treatment have been successfully applied to charge separation and transport in organic photoconductive layers used in electrophotography (qv), and have proven useful in the design of such systems (39).

An important consequence of the Marcus equation is the existence of the Marcus inverted region, which is not predicted by the Rehm-Weller equation. Thus, maximum electron-transfer rate occurs when $\Delta G = -\lambda$; if the reaction is more exoergic, the rate slows down in a mirror image of the relationship by which rate

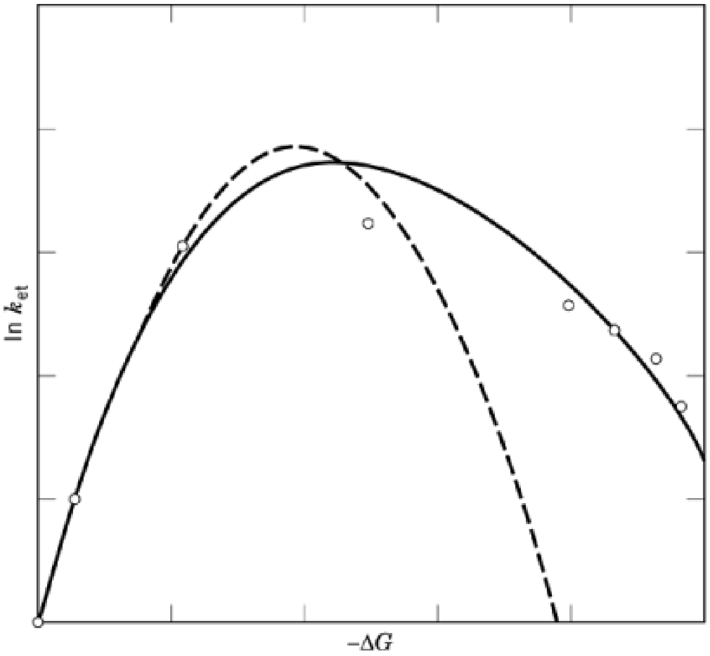


Fig. 2. Electron-transfer reaction rate, k_{et}, vs exoergicity of reaction: the dashed line is according to simple Marcus theory; the solid line and data points are experimentally determined (37).(Courtesy of The American Chemical Society.)

increases with increasing exoergicity up to the maximum, as shown in Figure 2. Experimental demonstration of the existence of the Marcus inverted regime (40) represented a validation of the Marcus model. Existence of the inverted region can be exploited in practical applications to control back-electron transfer (occurring with first-order rate constant, $k_{-\mathrm{et}}$) which competes with involvement of one or both of the charge separated products in the desired reaction (occurring with pseudo-first-order rate constant, k_{r}). Back-electron transfer is an energy wasting process (41).

Knowledge of photoinduced electron-transfer dynamics is important to technological applications. The quantum efficiency, φ, ie, the number of chemical events per number of photons absorbed of the desired electron-transfer photoreaction, reflects the competition between rate of the electron-transfer process, eg, from D^*, and the radiative and radiationless decay of the excited state, reflected in the lifetime, τ, of D^* in absence of A. Thus,

$$\phi = \left[k\,[A] \,/\, \left(k\,[A] + \tau^{-1}\right)\right]\ \left[(k_r / k_r + k_{-\mathrm{et}})\right]$$

A strategy for increasing φ by inhibiting back-electron transfer, $k_{-\mathrm{et}}$, involves molecular design so as to maximize λ for the back reaction. For example, hydrazines undergo significant intramolecular reorganization associated with pyramidal–planar reconfiguration at nitrogen, on one-electron oxidation (42). *Ab initio* molecular orbital calculations have shown that this feature of the hydrazine functional group is preserved when it is incorporated into the pyrazoline ring structure (43). Thus triarylpyrazolines can be used as especially efficient electron-transfer sensitizers of decomposition of both aryliodonium cations (44) for photoinitiation of free-radical and/or cationic polymerization processes. The theory of photoinduced electron-transfer dynamics is a tool to be used in the engineering of applied photochemical systems.

3. Applications

3.1. Photohalogenation

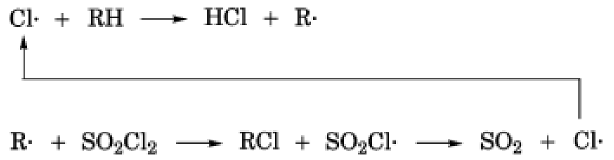
Photochemical chlorination of aliphatic hydrocarbons has been the textbook example of industrial photochemistry for decades (45). As of the mid-1990s it is still commercially important and industrial-scale halogenation has been reviewed in detail (1). In most examples of historical importance, ultraviolet radiation was used to dissociate Cl_2 to yield atomic chlorine which, in turn, abstracts a hydrogen atom from the hydrocarbon substrate yielding an organic free radical and HCl. Recombination of this radical with atomic chlorine yields a monochlorocarbon which is more susceptible to the hydrogen abstraction reaction than the parent hydrocarbon. A mixture of chlorohydrocarbons usually results by this method (see Chlorocarbons and chlorohydrocarbons). Production of trichloroethane occurs in this manner. Photohalogenation is also used for production of the insecticide lindane (γ-hexachlorocyclohexane) (see Insect control technology).

A more energy-efficient variation of photohalogenation, which has been used since the 1940s to produce chlorinated solvents, is the Kharasch process (45). Ultraviolet radiation is used to photocleave benzoyl peroxide. The radical products react with sulfuryl chloride (from SO_2 and Cl_2) to liberate atomic chlorine and initiate a radical chain process in which hydrocarbons become halogenated. Thus, for Ar = aryl,

$$(\mathrm{ArCOO})_2 + h\nu \longrightarrow 2\ \mathrm{ArCOO}\cdot$$

$$\mathrm{ArCOO}\cdot \longrightarrow \mathrm{Ar} + \mathrm{CO}_2$$

$$\mathrm{Ar} + \mathrm{SO_2Cl_2} \longrightarrow \mathrm{ArCl} + \mathrm{SO}_2 + \mathrm{Cl}\cdot$$



The most innovative photohalogenation technology developed in the latter twentieth century is that for purposes of photochlorination of poly(vinyl chloride) (PVC). More highly chlorinated products of improved thermal stability, fire resistance, and rigidity are obtained. In production, the stepwise chlorination may be effected in liquid chlorine which serves both as solvent for the polymer and reagent (46). A solid-state process has also been devised in which a bed of microparticulate PVC is fluidized with Cl_2 gas and simultaneously irradiated (47). In both cases the reaction proceeds, counterintuitively, to introduce Cl exclusively at unchlorinated carbon atoms on the polymer backbone.

3.2. Laser Photochemical Vapor Deposition

Laser pyrolytic and laser photochemical vapor deposition (LPCVD) technologies based on pyrolysis and photolysis of organometallic precursors are important to the deposition of thin inorganic films and surface patterning for the microelectronics industry (2). Owing to use of organometallics this technology is sometimes called metal organic chemical vapor deposition (MOCVD). Thin films of metals, insulators, and semiconductors can be deposited on inert surfaces by decomposition of precursors from the gas phase. The chemistry can occur either in

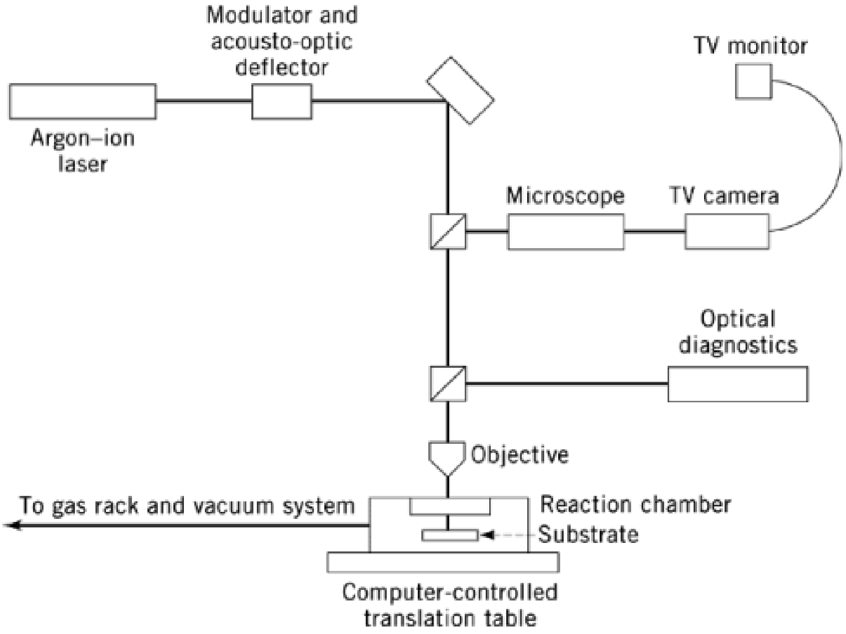


Fig. 3. Scanned laser imaging device for LPCVD in the microelectronics industry (48).(Courtesy of The American Chemical Society.)

the gas phase adjacent to the substrate or in the adsorbed state on its surface (48, 49). High resolution patterning of the surface, ie, imagewise deposition, requires that surface photochemistry via the gas-phase processes dominates; such imagewise deposition may be achieved either by writing the pattern using a scanned laser (50) or by imaging through a mask (51). A schematic diagram of a scanned laser imager for LPCVD application is shown in Figure 3 (48, 50). Principal documented applications have involved repair of electronic devices, such as fabrication masks, interconnecting gate arrays and chips, and fabrication of customized circuits. Slow deposition rates appear to have been the principal limitation of LPCVD. The majority of applications have involved metal deposition. Metal alkyls are principal precursors of metal deposits, especially aluminum, in these processes. Only the best characterized materials deposited by LPCVD, ie, metals and insulating SiO_x (49), have been incorporated into commercial electronic products as of this writing.

Distinction between pyrolytic and photochemical techniques is not clear cut. Deposition may, for example, involve thermolysis of a photochemically generated intermediate or vice versa. Photochemical techniques generally have an advantage over the pyrolytic approach in that it is not necessary to subject the substrate, even locally, to the extreme temperatures (750–1400°C) used in the purely pyrolytic processes (50). Frequency-doubled Ar ion lasers (244 nm) and excimer lasers (193 and 248 nm) are used to effect the photochemistry. Laser selection may be critical in a particular application. Where surface photochemistry is desired exclusively for high resolution patterning, decomposition of adsorbed $Cd(CH_3)_2$ or $Zn(CH_3)_2$ to yield the corresponding metal requires 193 nm photons from a ArF laser, even though the gas-phase decomposition of these precursors can be effected at 248 nm with a KrF laser. Surface energy relaxation pathways have been invoked to explain this difference. Metal carbonyls (qv) are also useful, especially for deposition of Ni, Fe, Cr, W, and Mo. These decompositions are often hybrid photochemical–pyrolytic (52). Noble or coinage metal films, Cu, Au, Ir, Pt, or Pd, are accessible by laser photolysis of volatile acetylacetonate (acac) or hexafluoroacetylacetonate (hfacac) complexes, again using excimer lasers. In these cases higher purity metal films are obtained by the pyrolytic, rather than the pure photochemical mechanism (48, 53); surface temperatures of no more than 175–225°C are required to decompose hfacac complexes.

Excimer lamps have opened the possibility of cost-effective large-area direct photochemical vapor deposition (PCVD). PCVD of stoichiometric, insulating SiO_2 onto Si wafer has been reported using SiH_4 and N_2O as gas-phase precursors and the 172-nm radiation from a Xe^*_2 lamp (54). Deposition rate in this demonstration process is ca 3 nm/min. Similarly α-Si_xC_{1-x} of useful electronic properties has been deposited on glass, also using the Xe^*_2 lamp at a rate of 50 nm/min, which is competitive with other CVD processes (55).

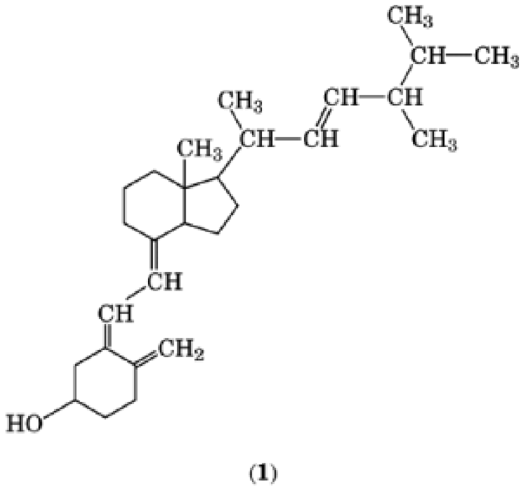
Epitaxial deposition of semiconductors (qv) by LPCVD is a promising technique for device fabrication, particularly radiation detectors, and is under intense investigation as of this writing. Studies on the deposition of crystalline, polycrystalline, or amorphous Si films have been motivated by thin-film solar cell applications. Decomposition of SiH_4 is usually pyrolytic because this common starting material does not absorb significantly beyond 160 nm; biphotonic excitation at high photon fluxes allows use of 193-nm radiation from an ArF laser to effect LPCVD of Si (56). This process is relatively inefficient. The preferred starting materials are Si_2H_6 or Si_3H_8, both of which undergo one-photon decomposition at 193 nm (57). GeH_4 absorbs at 248 nm (KrF laser) and is a useful precursor of Ge films by LPCVD; biphotonic excitation is thought to be involved, however (58). The photolytic technique is used for preparation of large-area Ge–Si alloy films from Si_2H_6–GeH_4 mixtures (59) and alternating amorphous Ge and Si structures can also be deposited photochemically for synthesis of multiquantum-well devices (60). By contrast, thermal chemical vapor depositions (CVD) of Ge yields primarily a crystalline Ge deposit (61).

Development of photochemical technology for epitaxial deposition of Group 12–16 (II–VI) semiconductors from organometallic precursors has focused on narrow band gap materials, eg, HgCdTe, CdTe, and HgTe, which are useful in near-infrared radiation detectors (62). The advantage of the photochemical technology over pyrolytic CVD is lower deposition temperature (63). MOCVD has also been used for deposition of Group 13–15 (III–V) semiconductors, eg, GaAs, InGaAs, and AlGaAs, but pyrolytic decomposition of the precursors is usually involved (49). LPCVD of the wider band gap III–V semiconductor GaN for application in blue light-emitting diodes (LEDs) has been investigated in the laboratory (64) and a hybrid photochemical–pyrolytic mechanism inferred. In addition to LPCVD of metallic layers, deposition of insulating SiO_x, primarily large-area deposition of SiO_2, has reached commercialization. As in the case of 172-nm excimer lamp photolysis, stoichiometric films result from 193-nm photooxidation of SiH_4 in the presence of N_2O (65). Photolysis of N_2O in the gas phase to form reactive oxygen atoms is most likely the primary process involved (66).

With the advent of organic optical polymers, an innovative photochemical approach to waveguide fabrication has been developed (67, 68). Accordingly a chromophore, eg, a merocyanine dye, dissolved in or bound to a thin film of an optical polymer is imagewise photobleached to tailor the index of refraction (at nonactinic wavelengths) of the polymer in precise fashion. Channel waveguides (67) and active waveguide devices, eg, directional couplers and interferometric intensity modulators (68), can be fabricated by this technique. Lasers, eg, Ar ion, are usually employed to effect photobleaching having high spatial precision. Kinetic studies indicate that one-photon processes dominate (69).

3.3. Vitamin D

Vitamin D is synthesized by photochemical means (see Vitamins). The commercial process was patented in 1985 (70). The term vitamin D is actually applied to several isomers wherein the side chain in the parent structure varies. Vitamin D_2 **1** and D_3 **2** are the most important, commercially, owing to use as animal feed additives. These compounds are synthesized from the steroids ergosterol and 7-dehydrocholesterol, respectively. The synthesis involves a photochemical ring opening (photo-Cope rearrangement) to yield the corresponding pre-vitamin D. The reaction is usually carried out in ether or alcohol using medium pressure Hg-vapor lamps which have higher output in the useful spectral regime (260–313 nm) than in the undesirable regime below 254 nm, as compared to low pressure lamps.



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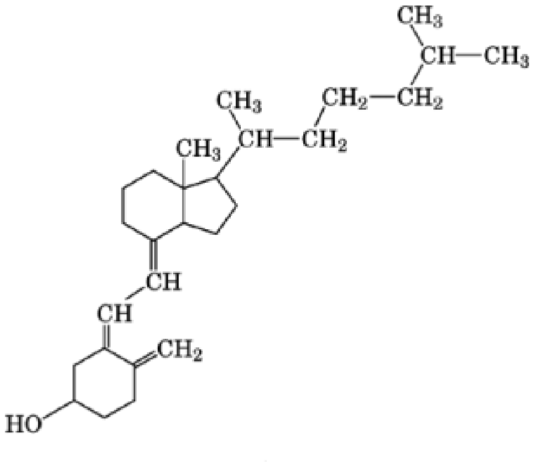


(2)

The *cis*-configuration of the 6,7-double bond in pre-vitamin D is critical to its subsequent thermal rearrangement to the active vitamin. A photochemical isomerization of pre-vitamin D to yield the inactive *trans*-isomer occurs under conditions of synthesis, and is especially detrimental if there is a significant short wavelength component, eg, 254 nm, to the radiation continuum used to effect the synthesis. This side reaction reduces overall yield of the process and limits conversion yields to ca 60% (71). Photochemical reconversion of the inactive side product, tachysterol, to pre-vitamin D allows recovery of the product which would otherwise be lost, and improves economics of the overall process (70).

3.4. Polymer-Based Technologies

Materials science aspects of polymer-based photochemical technologies have been reviewed (72). One example is the use of photoinitiated polymerization in three-dimensional engineering prototyping. In contemporary computer-aided design (CAD) a three-dimensional object is created on the computer. In this process the designer is guided by various digitally generated projections of the object on the monitor. In order to have a solid prototype for visual inspection of the final design, a photopolymerization technique, sometimes called stereolithography, is

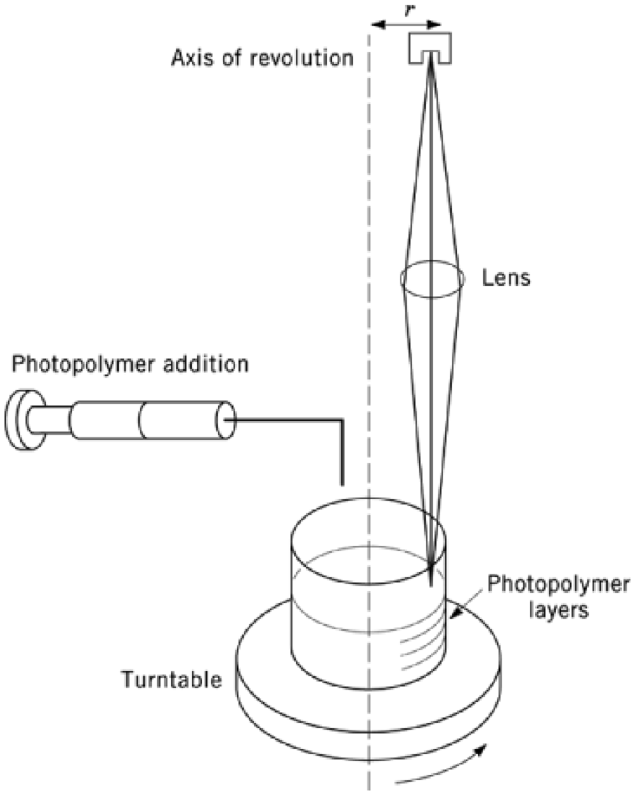


Fig. 4. Apparatus for stereolithographic generation of engineering prototypes in the CAD workflow (73).(Courtesy of The Society for Imaging Science and Technology (IS&T).)

employed. Principles of this process were first described in the open literature in 1982 (73) (see Computer-aided design and manufacturing (CAD/CAM)).

As illustrated in Figure 4, the model is created on a platform submerged in a bath that is mounted on a turntable and contains a suitable monomer including a photoinitiator responsive to a laser line. The laser is modulated by the design computer and scanned radially while the turntable rotates to write one laminar element of the design. The platform is then displaced downward by the thickness of one lamina, and the next layer created, and so forth. After the process is completed, the model is removed from the bath, washed free of unreacted monomer, and often subjected to a thermal or uv post-cure. Stereolithographic fabrication times of under one hour are commonplace. Annual sales of equipment and materials for this application now exceed $30 million in the United States (74). Because polymerization involves formation of covalent bonds rather than intermolecular van der Waals interactions, photopolymerizable materials often shrink during curing. Shrinkage of the polymer is a primary limitation of the dimensional fidelity of stereolithography (75).

Thickness of the laminar layer is determined both by the need to reproduce fine detail in the object and by the penetration depth of the actinic laser light into the monomer bath (21, 76). There is thus a trade-off between precision of detail in the model and time required for stereolithography, ie, the number of layers that have to be written, and an optimum light-absorbing initiator concentration in the monomer bath corresponding to the chosen layer thickness. Titanocene-based initiators, eg, bis-perfluorophenyltitanocene has been recommended for this application (77). Mechanistic aspects of the photochemistry of titanocenes and mechanisms of photoinitiation have been reviewed (76).

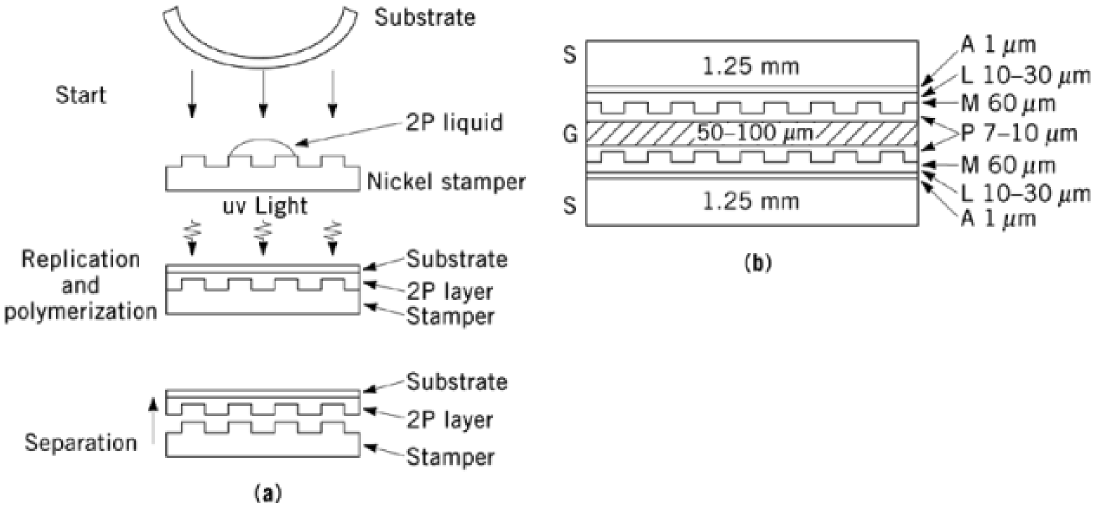
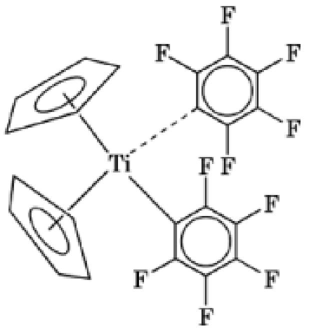
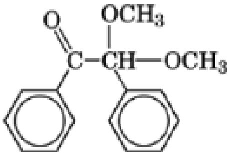


Fig. 5. (**a**) Schematic of the Philips 2P Process for video disk replication (79); (**b**) configuration of a double-sided LaserVision disk where the hole at the center is not shown. S represents the transparent substrate; A, the primer layer; L, lacquer with picture and sound information in the form of pits; M, mirror coating; and G, adhesive layer.(Courtesy of N.V. Philips' Gloeilampenfabriken.)



Photoinitiated polymerization can be used to replicate microstructured surfaces having a high degree of precision. An example is the Philips 2P Process (Fig. 5**a**) used in the fabrication of laser video disks (78). On a video disk, or compact audio disk (CD), the digitized information is recorded in the form of a spiral track of microscopic pits, typically ca 0.1-μm deep and 0.4-μm wide. Pit length and linear separations vary from 0.5–2.0 μm, and the pitch of the spiral is ca 1.0-μm between tracks (12, 79). In the 2P process the information is initially formatted onto a Ni-plated master, called a stamper, which serves as a mold. Between the stamper and the disk substrate, made from optical quality poly(methylmethacrylate) (PMMA), is injected the curable monomer incorporating a photoinitiator. The monomer is cured in place to replicate the microstructure pattern of the stamper. The polymer replica is then metallized by vapor deposition, typically Al, to make it reflective. Video disks are double sided; that is, two metallized replicas are laminated together using an appropriate adhesive to make the finished product (see Fig. 5**b**). The stamper is made by conventional photolithographic technology using a novolak photoresist imaged using an Ar ion laser at 488 nm (see Resist materials) (79).

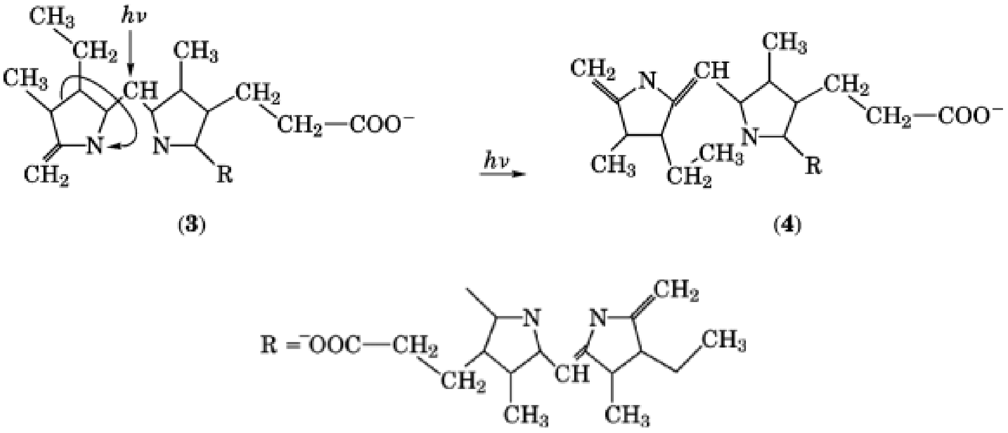
The photopolymer employed for the replication step must have extremely high dimensional stability, both during and after the curing process. In addition the light-cured polymeric replica must be hard, release easily from the stamper, and provide good adhesion to the metallic vapor coat (80). Free-radical polymerizable acrylic monomers, eg, a mixture of 2-ethylhexyl acrylate and 1,4-butanediol diacrylate, have been chosen by Philips for this application. The difunctional acrylate provides the cross-link density necessary to meet the hardness requirement for the cured polymer. The shrinkage problem is exacerbated if the cross-link density is too high, but a little shrinkage is tolerable insofar as it facilitates release of the replica from the stamper. Photoinitiation of polymerization of such mixtures is typically effected using a benzilketal-type initiator, eg, α,α-dimethoxy-α-phenylacetophenone (DMPA), responsive in the near-uv. Similar technology is employed to replicate the aspherical lenses used to focus the reading laser precisely on the pit tracks of the video disk or CD in their corresponding players (80).



3.5. Photochemical Therapies

The discipline of photomedicine has its origin (81) in observations, ca 1900, of the Danish Nobel laureate in Medicine, Niels Finsen, who recognized the photochemical basis of the disappearance during the summer of the facial lesions *lupus vulgaris*, Norwegian tuberculosis victims developed during the winter. Finsen eliminated *lupus vulgaris* by subjecting his Nordic patients to artificial light focused through a water-filled lens (to eliminate infrared) having quartz windows (to transmit uv).

A particularly successful therapeutic application of photochemistry has been the treatment of hyperbilirubinemia, otherwise known as newborn jaundice (82). Newborn jaundice, which occurs in nearly half of all newborn infants, results from high concentrations of the heme pigment, bilirubin, in the plasma, which can lead to irreversible brain damage if not controlled. The basis for photochemical treatment of newborn jaundice stems from the discovery in the 1930s (83) that bilirubin is efficiently decomposed when exposed to light. The therapeutic potential of this phenomenon resulted from the benchmark observation of an anonymous nurse that newborn jaundice disappeared in infants placed in a brightly sunlit portion of the hospital nursery (82, 84). Devices for effecting whole-body irradiation of newborns are commercially available. These utilize cool white or blue fluorescent lamps, or appropriately filtered tungsten–halogen lamps (82). The key photochemical transformation of bilirubin is a geometric isomerization about a double bond converting a (*Z,Z*)-isomer (**3**) to an (*E,Z*)-isomer (**4**) of bilirubin. The latter isomer is nontoxic (85).



(**3**) (**4**)

This is essentially the same process responsible for deactivation of photoexcited cyanine dyes.

New impetus was given to photomedicine by development of lasers that are compatible with the clinical environment. These include HeNe, Ar ion, ruby, and tunable dye lasers operating in the continuous wave (cw) mode. Prior to the advent of lasers in medicine, only the treatment of newborn jaundice, and the application of long wavelength uv irradiation in conjunction with administration (or topical application) of psoralen class sensitizers to treatment of skin diseases (86), principally psoriasis, were clinically important phototherapies.

Lasers can be coupled efficiently to fiber optic devices to deliver intense monochromatic light precisely to the desired region of the body, including internal organs (see Fiber optics). As in other cases of laser-induced photochemistry, biphotonic effects may be important (87). Lasers also offer the advantage of being able to concentrate the incident energy in a spectral bandpass matched to the absorption band of the sensitizer.

A principal application for photomedicine is the photodynamic treatment of cancer. Photochemical and clinical aspects of this topic have been reviewed (10, 11). Direct irradiation of tumors coupled with administration of a sensitizer is used to effect necrosis of the malignancy. In this process, an excited state sensitizer interacts with dissolved O_2 *in vivo* to effect conversion of the oxygen from its triplet ground state to an excited singlet state, $^1O_2$, which is highly cytotoxic. In principle, excited sensitizers in either the singlet or the triplet state can effect this conversion of molecular oxygen (8). In practice interaction of excited sensitizer and O_2 is at best a diffusion controlled reaction and the solubility of O_2 in aqueous media is only ca $10-^4$ M. The Einstein-Smoluchowski relationship predicts that excited-state lifetimes of ≥ 1 μs are required for efficient sensitization, restricting useful sensitizers, S, to those giving high yields of longer-lived triplet excited states. This also implies that dyes characterized by high triplet yields are more apt to be skin sensitizers, as $^1O_2$ is also thought to play an intermediate role in acute and chronic photodermatoses, and perhaps photocarcinogenesis (88).

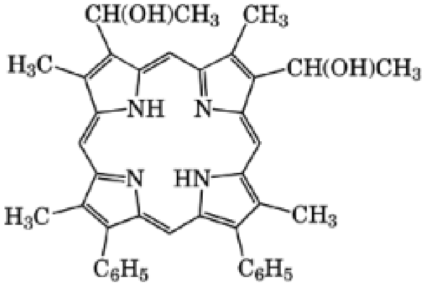
$$S + h\nu \longrightarrow S^1$$

$$S^1 \longrightarrow S^3$$

$$S^3 +^3 \mathrm{O}_2 \longrightarrow S +^1 \mathrm{O}_2 \longrightarrow \mathrm{etc}$$

As penetration of tissue by light increases more or less monotonically beyond 450 nm (89), it is desirable for sensitizer absorption bands and actinic laser lines to be located as far into the red as possible. Primarily sensitizers absorbing at ca 630 nm, matched to the 633-nm output of the HeNe laser, have been used. If the sensitizers are available, wavelengths out to 800 nm that are accessible using solid-state diode lasers might be preferable (11). Waste energy is converted to heat in tissue, and the power which can be delivered to the target area without causing thermal damage to surrounding, healthy tissue generally limits laser powers useful in photodynamic therapy. Clinical experience has shown steady-state irradiances of up to ca 200 J/cm^2 at 633 nm to be tolerable (10). Higher powers would be tolerable at longer wavelengths, owing to the lower light absorption coefficient of the tissue. On the other hand, owing to photobleaching of typical sensitizers by the light actinic for tumor necrosis, the process is characterized by strong high intensity reciprocity failure, ie, an increase in light intensity is accompanied by a subproportional decrease, if any, in irradiation time required for the same biological effect (90).

A successful sensitizer for photodynamic therapy must therefore exhibit good optical absorption properties as far into the red as possible, matched to an available laser line, as well as efficient intersystem crossing to a long-lived triplet state. In addition, it must exhibit correct pharmacological properties, specifically persistence *in vivo* on the appropriate time scale, and selective absorption into the target tumor(s) (91). The latter minimizes sensitization of healthy tissue, as well as the amount of foreign substance which must be introduced into the body. Historically, a mixture of hematoporphyrin **5** derivatives was used, but higher molecular weight oligomers of hematoporphyrin which were by-products of the derivatization reaction were primarily responsible for tumor localization (92). Oligomeric hematoporphyrins are commercially available under the name Photofrin and comprise the most commonly used sensitizer for photodynamic cancer therapy. About 5000 patients had been treated successfully for various cancers using the photodynamic method and Photofrin as of 1992 (10). Selective absorption of oligomeric hematoporphyrins to malignant tissue combined with efficient uv-excited fluorescence of the adsorbed sensitizer has led to a proposal (11) that these same compounds could be used to enable early, noninvasive detection of malignancies, eg, lung tumors, by fluorescence.



(5)

Given stringent requirements for effective sensitizers and the desire to use wavelengths further to the red for therapeutic applications, definition of newer sensitizers has been a principal area of research since about 1987. Expanded theoretical and experimental understanding of photophysics has been a key element in identifying new classes of potential sensitizers (93–98). Research has focused on cationic derivatives of Nile Blue (93), metallo-phthalocyanines (94), naphthalocyanines (95), chlorin-type compounds (96), expanded ring porphyrinoids (97), as well as porphyrins other than hematoporphyrin and its derivatives (98). This work has also been reviewed (10, 91). Instrumentation for photodynamic therapy has been reviewed (99).

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