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REVIEW

Laser photochemistry of organometallic compounds related to applications in microelectronics

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Photochemistry of organometallic compounds achieves a marriage of a rich variety of organometallic chemistry and the full potential of electronically excited states of molecules. The application of lasers as light sources adds a great many new features to these studies, which cannot be attained by other means, because lasers provide light of such a high quality, e.g. a high-intensity, energetic (i.e. wavelength) purity, a high degree of coherence, and a high spatial and temporal resolution. Laser photochemistry of organometallic compounds, such as laser photochemical vapor deposition (LPCVD), laser ablation, and photochemical dry etching, forms the basis of many important industrial processes which sustain the present-day microelectronics industries. Lasers are used not only to photodissociate organometallic molecules, but to monitor the reaction steps by probing the starting material, chemical intermediate, or final product by many laser-based spectroscopic methods. Although it is a very young area of science (the first laser was operated in 1960), this research area is now really ebullient, as a result of strong interest from both the fundamental and the practical sides. Laser photochemistry of organometallic compounds extends a wide and fertile research frontier, full of challenge and novel possibilities. In the present review, the present status of laser (ultraviolet and visible) photochemistry of organometallic compounds related to these industrial applications is briefly reviewed, with special emphasis on the basic studies of the relevant photochemistry and their relationship to photochemical processes on solid surfaces.

Keywords: Laser, photochemistry, organometallic compounds, chemical vapor deposition, dry etching, laser ablation

INTRODUCTION

The use of lasers in semiconductor technology continues to expand year after year. The continued decrease in integrated circuit (IC) dimensions increases the importance of laser applications in semiconductor processing procedures. Besides such applications as wafer positioning, marking and redundant memory repair, direct on-chip processing by the use of laser photochemical vapor deposition (LPCVD) has come to occupy a very important position. Laser etching of metals, semiconductors or organic polymer materials forms another category of processes essential in semiconductor technology. Reactive chemicals such as halogens and halogenated alkyls are frequently used in the reactive dry etching processes. Laser ablation processes, in which the atoms, ions or molecules which constitute the surface of metals or semiconductors are ablated, are also very important procedures in many industrial processes such as photolithographic mask preparation. These three processes are intimately related to each other. Organometallic molecules play an essential role in these processes: they are used as starting materials in LPCVD, and they are formed as a result of the reactive dry etching procedure, or the laser ablation of metals in an organic atmosphere.

In the present review, the present status of investigations related to LPCVD, reactive dry etching and laser ablation processes with ultraviolet and visible lasers is briefly reviewed from the standpoint of the involvement, and the very important role, of organometallic compounds. Because the present author is a physical photochemist, the emphasis is put on the mechanistic aspects of these processes. The intimate relationships of these studies with photochemistry on solid surfaces are discussed. The author believes that the general scope in this field can be obtained from this review, although a complete coverage of the literature is not intended. Compounds containing boron, silicon, phosphorus and arsenic are included. Besides organometallic compounds, related compounds such as metal hydrides and halides are added when it is thought appropriate to do so. Our recent studies related to the gas-phase reaction of organometallic compounds,[1] LPCVD,[2–7] reactive dry etching,[8–14] and laser ablation[15–19] are included. Reference is also made to our other review articles[20,21] written from the standpoint of surface photochemistry. A database of photodissociation of simple molecules including organometallics has been compiled by the present author.[22]

PHOTODISSOCIATION OF ORGANOMETALLIC COMPOUNDS IN THE GAS PHASE

Uses of lasers in photochemistry

The development of laser-based investigations has given an invaluable impetus to photochemistry. Molecules can be excited to well-defined energy levels (to a single vibrational or rovibrational level if desired), and much finer details in the reaction mechanism can be unraveled using energetically pure laser light. Time-resolved studies with pulse lasers realize the clarification of the time course of photochemical dissociation reaction to the picosecond, or even to the femtosecond, domain. The high degree of coherence enables many types of nonlinear processes to occur. A molecule can absorb two, three, or even some tens of photons at one time (multiphoton absorption process). Many types of laser spectroscopy such as laser-induced fluorescence (LIF), resonant multiphoton ionization (REMPI), laser photoacoustic spectroscopy, laser magnetic resonance, Doppler-free absorption spectroscopy, and coherent anti-Stokes Raman spectroscopy (CARS) can be used for the detection of atoms, molecules, ions, and free radicals with high sensitivity and selectivity.

Photochemistry of organometallic compounds

Organometallic compounds occupy a very peculiar position in the field of photochemistry in their own right. The presence of carbon–metal bonds with a variety of chemical properties highlights the photochemical behavior of these compounds. However, the investigations of these compounds are still at an early stage. The book by Geoffroy and Wrighton[23] treats mostly coordination compounds. Their description of compounds with direct metal–carbon bonds, except for metal carbonyls, is limited. The higher excited states of a limited number of organometallic compounds are included in the book by Robin.[24]

The photodissociation reactions of compounds with direct metal–carbon bonds are fundamentally important reactions, directly related to applications for microelectronics. Laser light must be absorbed by these molecules to cause the photodissociation. It must coincide with their absorption bands. The absorption bands of simple organometallic compounds corresponding to a few of their lower excited states are usually located in the ultraviolet (UV) or vacuum ultraviolet (VUV) region. In typical saturated compounds they correspond either to the valence excitation in which an electron in the carbon–metal σ-bond is excited into the σ^*-bond (the asterisk represents the antibonding orbital), the Rydberg excitation in which an electron in the σ-bond is excited to a Rydberg orbital, or a mixture of both.[24] In any case, the excitation brings the molecule from the potential curve of the ground state into that of one of those excited states (See Fig. 1). Bond scission occurs as the result of excitation of the molecule onto the potential energy curve leading to dissociation [Fig. 1(a)]. Alternatively, the molecule is excited onto one of the 'bound' excited states. Then the molecule transfers to a dissociative potential curve after it experiences a certain mode of molecular vibration [Fig. 1(b)]. The former and the latter dissociation process are called 'direct dissociation' and 'predissociation', respectively.

Absorption spectra and their interpretation

The absorption spectral data of organometallic compounds in the gaseous phase are of fundamental importance to the elucidation of the photodissociation reaction in the LPCVD processes. However, the storage of these data in our repertoire is very limited.[24–34] Some of the published absorption spectra are reproduced in Fig. 2.[25–28] Molecular orbital calculations with various degrees of approximation have been made for some organometallic compounds. *Ab initio* molecular orbital calculations on silane and disilane have been made for the assignment of VUV

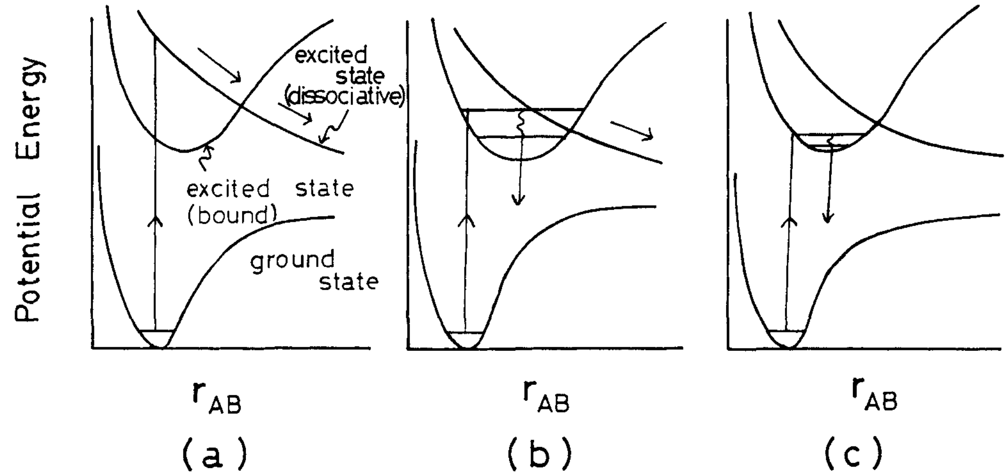


Figure 1 Potential curves of a molecule (schematic) and photodissociation process. (a) Direct dissociation; (b) predissociation; (c) no dissociation (emission is observed).

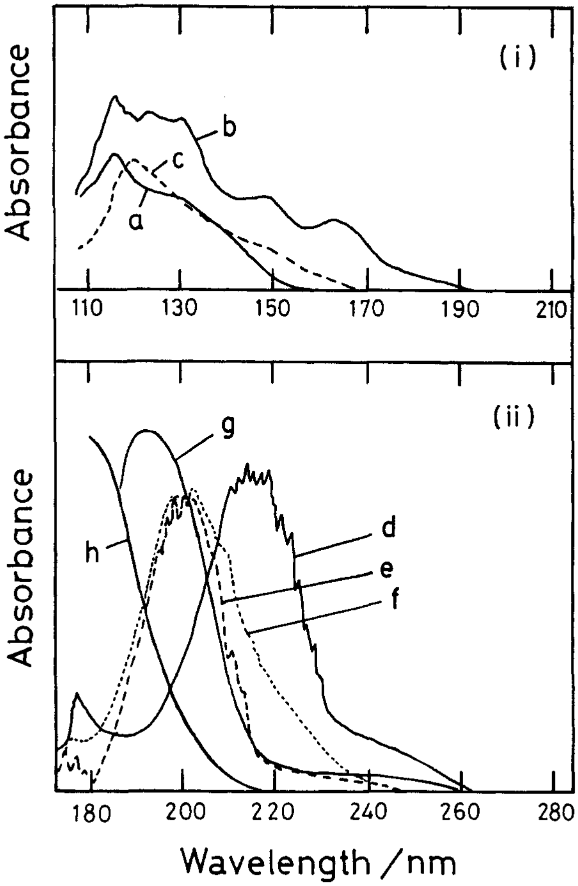


Figure 2 Examples of absorption spectra of organometallic compounds (adapted from Refs 25–28): a, SiH_4; b, Si_2H_6; c, GeH_4; d, $Cd(CH_3)_2$; e, $Hg(CH_3)_2$; f, $Zn(CH_3)_2$; g, $Ga(CH_3)_3$; h, AsH_3. A different ordinate scale is used for curves d–f and curves g and h.

photoabsorption spectra.[7] Strong peaks in their absorption spectra are attributed primarily to Rydberg transitions of the silicon–hydrogen (Si–H) and silicon–silicon (Si–Si) bonding electrons to the 4*s*, 4*p* and 4*d* orbitals, with substantial contributions of the valence excitations. Fernandez *et al.*[31,32,35,36] measured and interpreted by *ab initio* configuration interaction (CT) calculations the VUV spectra of SnH_4,[35,36] $SnCl_4$ and $Sn(CH_3)_4$,[31] and SnH_3CH_3.[32] For example, the first two bands of the VUV spectrum of the last compound are attributed to a_1 and e transitions towards the Rydberg *s*-orbital. Their calculation shows that the HOMO involves primarily a tin–carbon (Sn–C) bond. Although the absorption spectral data of organometallic compounds in the adsorbed state on a solid surface are frequently of more direct importance to LPCVD (*vide infra*), these data are almost lacking except for some very limited cases.[37,38] The continued studies of these fundamental molecular properties are essential for the development of organometallic photochemistry related to microelectronics.

Photodissociation of organometallic compounds in the gas phase

Investigations of photodissociation of organometallic molecules in earlier days included those made on dimethylcadmium ($(CH_3)_2Cd$),[39] dirhenium and dimanganese decacarbonyl ($M_2(CO)_{10}$), M=Re,Mn[40] etc. by Bersohn *et al.* Jonah *et al.*[39] photolyzed dimethylcadmium by polarized light (a 1000 W xenon–mercury arc). Annular distributions of cadmium atoms detected as a deposit clarified the details of the photodissociation mechanism. Cadmium atoms and methyl radicals were found to fly apart perpendicular to the electric vector of the incident light. This shows that the transition moment is perpendicular to the molecular axis and that fragments separate along the molecular axis. For dirhenium decacarbonyl,[40] the photodissociation at 300 nm gave only metal–metal bond cleavage.

One of the photochemical investigations of organometallic compounds in the gaseous phase is illustrated here, taking the photodissociation of tetramethyltin[1] as an example. The vapor of tetramethyltin has been photodissociated in a molecular beam using an excimer laser (ArF) at 193 nm. The primary processes which are energetically possible are shown in Eqns [1] and [2].

$$\mathrm{Sn(CH_3)_4} \to \mathrm{Sn(CH_3)_3 + CH_3} \qquad \Delta H = 252\ \mathrm{kJ\ mol^{-1}} \qquad [1]$$

$$\phantom{\mathrm{Sn(CH_3)_4}} \to \mathrm{Sn(CH_3)_2 + 2CH_3} \qquad \Delta H = 499.8\ \mathrm{kJ\ mol^{-1}} \qquad [2]$$

Dissociation into more than three fragments is common in the photodissociation of alkyl metals, such as trimethylgallium ($\mathrm{Ga(GH_3)_3}$)[27] or dimethylcadmium ($\mathrm{Cd(CH_3)_2}$).[39] The methyl radical ($\mathrm{CH_3}$) is produced by this dissociation reaction. In order to elucidate the finer details in these reactions, the translational energy distribution of methyl radicals has been examined by the measurement of their time-of-flight (TOF). The TOF obtained (Fig. 3) has been transformed into the translational energy distribution. The resulting distribution has been found to be well represented by a sum of two prior distributions with a restricted number of vibrational degrees of freedom, these two corresponding to the two reaction pathways, [1] and [2] mentioned above. This experiment has made it clear that both of the reaction paths [1] and [2] occur under the experimental conditions.

The accumulation of experimental data on the photodissociation reactions of organometallic molecules in the gas phase is of fundamental importance, since they provide an important clue in elucidating the reaction mechanism in LPCVD, reactive dry etching, etc. Compared with the cases of small inorganic and organic molecules,[41] however, the existing data on organometallic compounds are scarce. Typical data on the photodissociation of some simple organometallic compounds in the gas phase are given in Table 1. The present author has published a compilation of the data on the photodissociation in the gas phase of simple molecules including organometallic molecules.[22] As a matter of fact, investigations of these organometallic compounds are much accelerated recently by the development of industrial needs related to LPCVD.

Among other research works on gas-phase organometallic photochemistry related to LPCVD, multiphoton dissociation of trimethylgallium in the 420–520 nm range was studied by Mitchell *et al.*[27] This process gave neutral fragments, including gallium atoms and a metastable molecular fragment which was assigned as methylgallium ($\mathrm{GaCH_3}$). Yardley *et al.*[42] studied the fragmentation and molecular dynamics in the laser (352, 248, 193 nm) photodissociation of iron pentacarbonyl ($\mathrm{Fe(CO)_5}$). Fragmentation of a high degree was observed. These authors suggested the sequential loss of carbon monoxide (CO). Motooka *et al.*[43] measured the light emission of aluminum atoms and CH radicals in the gas-phase photolysis of trimethylaluminum at 248 nm. They proposed a model involving a cascade one-photon process.

Table 1 Typical examples of primary processes in the photodissociation reaction of organometallic and related compounds in the gas phase

Compound	Reaction[a]	Wavelength (nm)[b]	Ref.
$\mathrm{SiH_4}$	$\mathrm{SiH_2+2H}$ (ϕ = 0.83) $\mathrm{SiH_3+H}$ (ϕ = 0.17)	147	101
$\mathrm{PH_3}$	$\mathrm{PH_2(\tilde{X},\tilde{A})+H}$	193	102
$\mathrm{AsH_3}$	$\mathrm{AsH_2(\tilde{X},\tilde{A})+H}$	193	103
$\mathrm{Zn(CH_3)_2}$	$\mathrm{Zn+2CH_3(\tilde{X})}$	248	104
$\mathrm{Cd(CH_3)_2}$	$\mathrm{Cd+2CH_3(\tilde{X})}$	248	39,104
$\mathrm{Hg(CH_3)_2}$	$\mathrm{Hg+2CH_3(\tilde{X})}$	248	105
$\mathrm{Sn(CH_3)_4}$	$\mathrm{Sn(CH_3)_3+CH_3}$ $\mathrm{Sn(CH_3)_2+2CH_3}$	193	1
$\mathrm{ZnI_2}$	$\mathrm{ZnI(X,B)+I}$	193	106
$\mathrm{CdBr_2}$	$\mathrm{CdBr(X,B)+Br}$	193	107
$\mathrm{CdI_2}$	$\mathrm{CdI(X,B)+I}$	193	108
$\mathrm{HgCl_2}$	$\mathrm{HgCl(X,B)+Cl}$	172	109
$\mathrm{HgBr_2}$	$\mathrm{HgBr(X,B)+Br}$	193	110
$\mathrm{HgI_2}$	$\mathrm{HgI(X,B)+I}$	193	111
$\mathrm{AsI_3}$	$\mathrm{AsI_2(\tilde{X})+I}$	300	112
$\mathrm{Cr(CO)_6}$	$\mathrm{Cr(CO)_5+CO}$	355	113,114
$\mathrm{Fe(CO)_5}$	$\mathrm{Fe(CO)_4+CO}$	352	42
$\mathrm{Re_2(CO)_{10}}$	$\mathrm{2\ Re(CO)_5}$	300	40

[a] X or $\tilde{X}$, electronic ground state; A, $\tilde{A}$, B, etc., electronically excited states. [b] 193, 248, 355 nm, lasers (see Table 3); 300 nm, second harmonic of a dye laser; 147 nm, xenon lamp; 172 nm, xenon excimer fluorescence; 352 nm, frequency-tripled Nd:YAG laser.

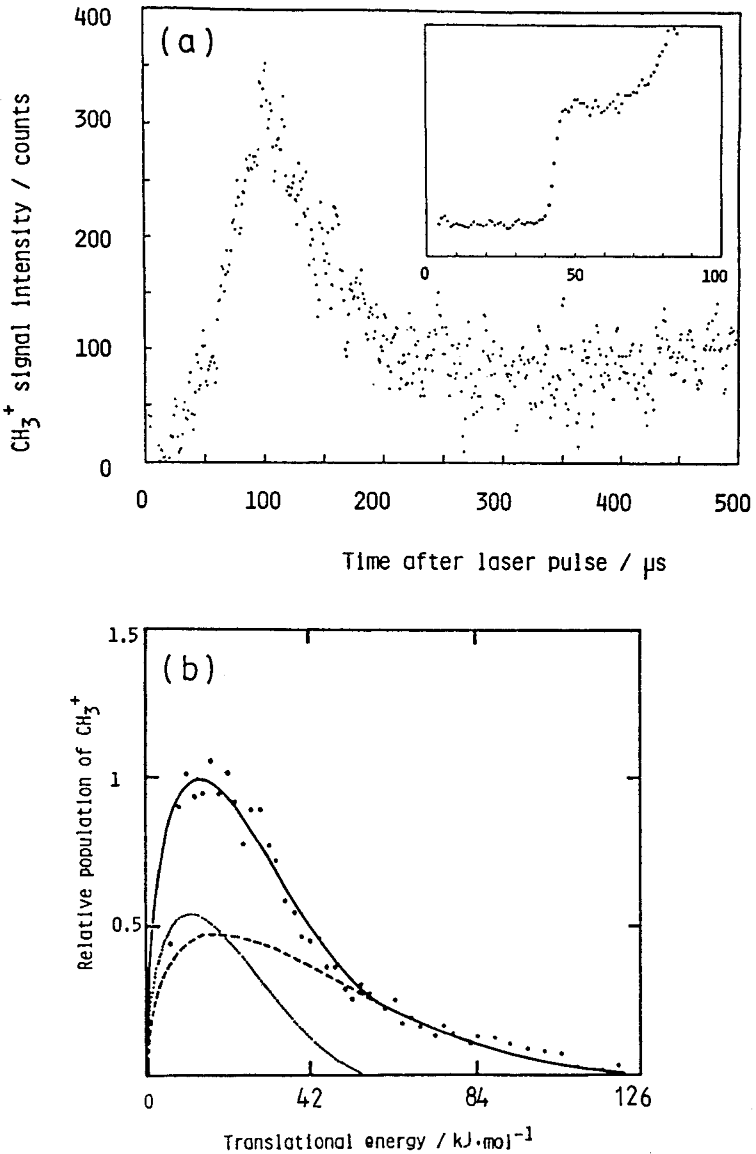


Figure 3 TOF distribution of the methyl radical on the photodissociation of $Sn(CH_3)_4$ at 193 nm (a), and translational energy distribution of the methyl radical calculated from the TOF curve (b). The inset in (a) is the TOF distribution of the methyl radical from solid $Sn(CH_3)_4$ (from Ref. 1, with permission).

LASER PHOTOCHEMICAL VAPOR DEPOSITION (LPCVD)

Although chemical vapor deposition (CVD) processes can be achieved with a variety of energy sources to break the metal–ligand bonds, e.g. thermal energy or plasmas, LPCVD[44] has many advantages over the others. Compared with the thermal CVD process, LPCVD can cause the photodecomposition of selected molecules in the mixture, because the photon energy, especially that from lasers, can sever only chemical bonds in those molecules which absorb the photons. LPCVD enables low-temperature film growth processes to occur eliminating the heating of the substrates which may cause unnecessary surface diffusion of the deposited material leading to the smear-out of the pattern. Moreover, LPCVD has high spatial resolution. The laser light can be focused on a spatially confined area, allowing the maskless 'direct writing' of a metal deposit in the form of a narrow line, or any pattern free from the smear-out which may occur in thermal CVD. The latter point is very important in the fabrication of a densely packed VLSI (very large scale integrated) circuits. Compared with plasma CVD, LPCVD is free from the damage due to highly energetic charged species as ions and electrons inherent in plasmas. This eliminates the smear-out of drawn lines and dopant profiles.

Examples of LPCVD

LPCVD was pioneered by Deutsch *et al.*[45] in 1979. They prepared metal films of aluminium and cadmium from trimethylaluminium and dimethylcadmium, respectively, on a quartz substrate. They used the second harmonic (257.2 nm) of a continuous wave (CW) argon ion laser. Since then, the deposition of other metal films has been reported. Those include zinc from dimethylzinc,[46,47] molybdenum from $Mo(CO)_6$,[48,49] iron from $Fe(CO)_5$,[50] chromium from $Cr(CO)_6$, tungsten from $W(CO)_6$,[48–50] etc. A copper ion laser or an excimer laser (KrF, 248 nm or ArF, 193 nm) was used in these cases. Boyer *et al.*[51] used an ArF excimer laser (193 nm) with the silane/N_2O mixture to cause the direct photolytic reaction to obtain a silicon dioxide (SiO_2) film. Andreatta *et al.*[52] reported the photolytic deposition of silicon and germanium by the photodissociation of SiH_4/N_2 or GeH_4/He mixtures using ArF (193 nm) or KrF (248 nm) excimer lasers. The photoconducting layer of gallium arsenide (GaAs) was prepared from trimethylgallium together with arsine (AsH_3), by use of the frequency-doubled Neodymium:Yttrium Aluminium Garnet (Nd:YAG) laser light (532 nm).[53] Bedair *et al.*[54] reported the direct writing of GaAs, InGaAs and GaAsP from trimethylgallium, trimethylindium, arsine and phosphine by LPCVD using focused light of an argon ion laser.

A carbon dioxide laser has been extensively used in CVD, for example, of silicon from silane (SiH_4). This type of laser CVD is not included in this review, because the dissociation process involved seems to be essentially pyrolytic. However, Hanabusa *et al.*[55] reported that the tuning of the laser to excite silane in the vibrational ground state (v = 0) into the vibrationally excited state (v = 1) was essential for the deposition, excluding any thermal effect.

Compounds used in LPCVD

In the LPCVD process, the vapor of an organometallic compound, neat or diluted in inert gases such as helium or argon, is supplied onto solid substrates. Laser light is irradiated either vertically or parallel to the substrate surface, as shown schematically in Fig. 4, to cause the dissociation of the organometallic compound, either in the adsorbed state or in the gaseous phase, respectively. Metallic or semiconductor films are formed on the substrate. Vertical irradiation is essential in maskless direct writing. Parallel irradiation is suitable for large-area deposition. The compounds used in LPCVD processes are limited by their volatilities and light absorptivities. They must have a high enough vapor pressure at the operating temperature. They must also absorb the irradiated laser light to cause the direct photolytic reaction.

Frequently used materials are silane (SiH_4) and disilane (Si_2H_6) for the formation of silicon,[52,55] SiO_2[51] or Si_3N_4.[56] Trialkyl compounds of the Group III elements, e.g. trimethylaluminum ($Al_2(CH_3)_6$),[45,46] trimethylgallium ($Ga(CH_3)_3$),[2,3] or trimethylindium ($In(CH_3)_3$)[4,5] are used to prepare the respective metallic films. These are used together with hydrides or trialkyls of the Group V elements, phosphine (PH_3), arsine (AsH_3), trimethylphosphine ($P(CH_3)_3$), or trimethylarsine ($As(CH_3)_3$) in the fabrication of the III–V semiconductors such as GaP,[57] InP,[58] GaAs,[59,60] etc. The Group II alkyls, such as dimethylcadmium ($Cd(CH_3)_2$) and dimethylzinc ($Zn(CH_3)_2$), are used with the Group VI alkyls, such as diethyltellurium ($Te(C_2H_5)_2$)[61] to make the II–VI semiconductors, e.g. CdTe.

Although all of these processes are called LPCVD in this review, the formation of such a semiconductor crystal on another crystal under the precise control of crystal growth is more accurately called

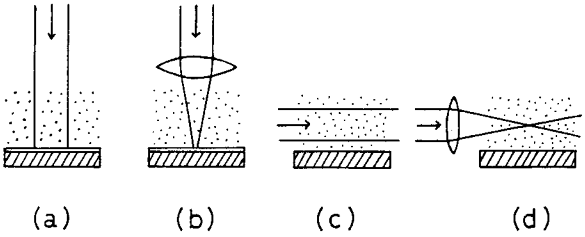


Figure 4 Irradiation of laser light vertical and parallel to the substrate surface in LPCVD. (a) vertical; (b) vertical (focused). (c) horizontal; (d) horizontal (focused).

photostimulated metalorganic vapor phase epitaxy (MOVPE).[59,61]

Metal carbonyls of refractory metals, e.g. $Fe(CO)_5$, $Cr(CO)_6$ and $W(CO)_6$ are used to deposit the respective metallic film.[48–50] These metallic films, as well as lead film from tetraethyllead ($Pb(C_2H_5)_4$),[62] are used in the repair of pinhole defects in photolithographic masks.

The organometallic compounds frequently used in LPCVD are listed in Table 2. The boiling point data are shown together with the electronic absorption data. These two properties are very important in relation to use in LPCVD processes.

Lasers used in LPCVD

Because the absorption bands of these organometallic compounds are found in the UV or VUV region, the relevant light sources are excimer lasers (KrF, 248 nm or ArF, 193 nm) or the fourth harmonic (266 nm) of a Nd:YAG laser. Although another light source — synchrotron radiation (SR or SOR) — has begun to be used,[63] the importance of lasers are increasing, considering their reasonable size and price. One of the drawbacks of lasers comes from their very merit, i.e. the fixed wavelength. The agreement of the wavelengths of the absorption bands of the organometallic compounds with those of lasers has to be accomplished by the proper choice of compounds, since we have little freedom in the choice of laser wavelengths. The situation is improved if we have a tunable UV or VUV laser source. The development of free-electron lasers tunable in the UV and VUV region is anticipated in this context.

Data on the lasers which can be used in LPCVD are given in Table 3. Both pulsed and continuously operating (continuous wave, CW) lasers are listed.

The metallic, semiconductor, and insulator films which have been prepared by LPCVD with UV or visible lasers are listed in Table 4, together with their precursors. Besides the examples already mentioned, the deposition of zinc oxide (ZnO),[64] $TiSi_2$,[65] gold,[66] AlGaAs,[67] CdTe[61] and HgCdTe[68] are also reported. One of the merits of LPCVD is that one can prepare materials with various compositions by adjusting the process variables, such as the ratio of precursors. Doping or alloying can be carried out easily by LPCVD.

Table 2 Typical organometallic compounds used in LPCVD processes

Compound	M.p. (°C)	B.p. (°C)	Edge[a] (nm)	Max.[b] (nm)	Ref.[c]	Laser[d] (nm)	Ref.[e]
$Zn(CH_3)_2$	−29.2	44	250	200	26	257	46,47
$Cd(CH_3)_2$	−4.5	105.2	260	218	26	257	45,46
$Al_2(CH_3)_6$	15.2	125.4	260	200	74	257	45,46
$Ga(CH_3)_3$	−15.7	55.7	260	193	28,29	248	2,3,71
$In(CH_3)_3$	88.4	50[g]	—	215	34	248	4,5
SiH_4	−185	−111.8	160	141	25	193(m)[f]	52
Si_2H_6	−132.5	−14.5	195	164	25	193	56
GeH_4	−165	−90	170	149	25	193(m)[f]	52
$Sn(CH_3)_4$	−54	78	225	—	1	257	45
$Pb(C_2H_5)_4$	−135	198	—	—	—	257	62
PH_3	−133	−87	220	180	30	—	
AsH_3	−117	−55	220	< 180	30	193	67
$As(CH_3)_3$	—	50.1	240	200	29	193	60
$Te(C_2H_5)_2$	—	137–138	—	—	—	248	61
$Cr(CO)_6$	152–153	160(s)[h]	—	—	—	260(m)[d]	48
$W(CO)_6$	~150	—[h]	—	—	—	260(m)[d]	48
$Mo(CO)_6$	150	—				260(m)[d]	48
$Fe(CO)_5$	−20	103	~400		33	248,193	50
$Ni(CO)_4$	−25	42.3	—		—	476.2	69

[a] The long-wavelength edge of the absorption band. [b] An intensity maximum of the absorption band. [c] Ref. for spectra. [d] The wavelength of the laser used in LPCVD. [e] Ref. for LPCVD. [f] Multiphoton absorption. [g] At 23.8 Torr. [h] Sublimed.

Table 3 Lasers used in LPCVD processes[a]

Name	Wavelength (nm)	Pulse/CW	Pulse width (ns) /Repetition rate (Hz)	Typical power
(a) Gas lasers				
Excimer ArF	193	Pulse	17/200	200 mJ
Excimer KrF	248	Pulse	23/200	300 mJ
Excimer XeCl	308	Pulse	17/200	150 mJ
Excimer XeF	351	Pulse	20/200	100 mJ
Nitrogen	337.1	Pulse	10/100	9 mJ
Argon ion	488,514.5,etc.	Continuous wave	—	3–5 W (all lines)
(2nd)[b]	257.2	Continuous wave	—	
Krypton ion	647.1,568.2,etc.	Continuous wave	—	0.75 W (all lines)
Helium–neon	632.8	Continuous wave	—	4 mW
Copper vapor	510,578	Pulse	$25-40/(4-6)\times10^3$	2–8 mJ
Gold vapor	312	Pulse	$15-60/(2-20)\times10^3$	
(b) Solid lasers				
Nd:YAG	1064	Pulse	8–9/10	300 mJ
(2nd)[b]	532	Pulse	6–7/10	150 mJ
(3rd)[b]	355	Pulse	5–6/10	60 mJ
(4th)[b]	266	Pulse	4–5/10	20 mJ
(c) Dye lasers				
Excimer laser-pumped	217–1000	Pulse	10/100	10 mJ
Nitrogen laser-pumped	300–700	Pulse	7/20	0.9 mJ
Nd:YAG laser-pumped	195–5000	Pulse	10/30	100 mJ

[a] This table is meant only to give examples of each type of laser. The carbon dioxide laser is not included here. [b] Second, third and fourth harmonics of the laser.

Photolytic and thermal (pyrolytic) dissociation

One of the fundamental issues in the mechanism of LPCVD is whether the dissociation occurs thermally (i.e. pyrolytically) or photolytically. The dissociation reation is called thermal when the energy of the laser light is thermalized (i.e. distributed among all the degrees of freedom of the total system including the solid substrate) before the dissociation of the chemical bond occurs. In contrast, the reaction is called photolytic when the bond dissociation occurs directly before the thermalization of the energy. Experimentally, the dissociation in a particular case can be judged as photolytic when the wavelength dependence of the dissociation follows the absorption spectrum of the organometallic molecule. In the thermal (pyrolytic) case, the wavelength dependence would not show such a dependence because the light absorption of the solid substrate can cause deposition, and the solid substrates, which are either metal or semiconductor, usually have absorption bands extending to the near-ultraviolet or visible region. The LPCVD processes of aluminium, cadmium, zinc, etc. with UV light[45–51] can be considered as photolytic. The excitation of the molecules to the excited states can be either a one-photon or a multiphoton process. The latter process can occur in the focused irradiation of laser light.

We have made a mechanistic study of the LPCVD process of trimethylgallium and have concluded that the dissociation occurs photolytically at 248 nm,[2,3] based on the wavelength dependence of the density of gallium atoms (a reaction intermediate) probed by the laser-induced fluorescence technique (*vide infra*). More than two photons are necessary to obtain gallium atoms in this case (see Fig. 5). A similar result has been obtained for the LPCVD of indium from trimethylindium.[4,5]

Kräuter *et al.*[69] in their deposition of nickel from $Ni(CO)_4$ with a krypton ion laser (476.2, 530.9 and 647.1 nm) found that the deposition rate was independent of the laser wavelength, and they considered that the reaction was thermally activated and not influenced by multiphoton dissociation. Bedair

Table 4 Metal, semiconductor or insulator films prepared by LPCVD

Prepared film	Precursor	Wavelength (nm)	Ref.
Zinc	$Zn(CH_3)_2$	257	46,47
ZnO	$Zn(CH_3)_2/NO_2$ or N_2O	248,193	64
Cadmium	$Cd(CH_3)_2$	257	45,46
Aluminum	$Al_2(CH_3)_6$	257	45–47
Gallium	$Ga(CH_3)_3$	248	2,3
Indium	$In(CH_3)_3$	248	4,5
Silicon	SiH_4	248,193	52
Si_3N_4[a]	$SiH_4,Si_2H_6/NH_3$	193	56
SiO_2	SiH_4/N_2O	193	51
$TiSi_2$[a]	$SiH_4/TiCl_4$	193	65
Germanium	GeH_4	248,193	52
Tin	$Sn(CH_3)_4$	257	45
Lead	$Pb(C_2H_5)_4$	257	62
Chromium	$Cr(CO)_6$	260,248,193	48,50,70
Tungsten	$W(CO)_6$	260,248,193	48,50
Molybdenum	$Mo(CO)_6$	260,248,193	48
Iron	$Fe(CO)_5$	248,193	50
Nickel	$Ni(CO)_4$	476.2,530.9,647.1	69
Gold	$(CH_3)_2Au(hfac)$[b]	514	66
GaP	$Ga(CH_3)_3/P(t\text{-}C_4H_9)_3$	514.5	57
GaAs	$Ga(CH_3)_3/AsH_3$	532	53,54,71,72
	$Ga(CH_3)_3/As(CH_3)_3$	193	60
InP	$(CH_3)_3IP(CH_3)_3/P(CH_3)_3$	193	58
AlGaAs	$Al_2(CH_3)_6/Ga(CH_3)_3/AsH_3$	193	67
InGaAs	$In(CH_3)_3/Ga(CH_3)_3/AsH_3$	[c]	54
GaAsP	$Ga(CH_3)_3/AsH_3/PH_3$	[c]	54
CdTe	$Cd(CH_3)_2/Te(C_2H_5)_2$	248,193	61
HgCdTe	$Hg(CH_3)_2/Cd(CH_3)_2/Te(CH_3)_2$	193	68

[a] These formulae correspond to the stoichiometric composition. The composition can be varied by changing the process variables. [b] hfac, hexafluoroacetylacetonate. [c] focused Ar^+ laser beam (wavelength not specified).

et al.[54] assume that both pyrolytic and photolytic processes seem to contribute in their deposition of a III–V compound. In practice some involvement of thermal effects cannot be eliminated even in the 'photolytic' case, especially when one uses a pulse laser. The absorbed light energy which is not consumed in the photolytic dissociation is eventually changed into thermal energy, causing some increase in the temperature of the system. Moreover, the involvement of thermal processes has been found to be very important for film preparation in many cases. The thermal energy assists the further progress of the dissociation reactions. In the actual film-forming process, the intact metal atoms must diffuse on the surface to form surface metal clusters, and these clusters are eventually changed into the film. The kinetic energy of diffusion on the surface (for which we have for the moment no effective means of measurement) must be supplied by thermal energy. Rytz-Froidevaux *et al.*[37] deposited cadmium from dimethylcadmium at various wavelengths between 337 and 676 nm. In their case the deposition was initiated by multiphoton dissociation of $Cd(CH_3)_2$ molecules and continued by their pyrolysis at the laser-heated metallic deposit. Yokoyama *et al.*[70] prepared a chromium film by LPCVD of $Cr(CO)_6$ using a KrF excimer laser. Remarkable film quality dependence on laser intensity suggested the photothermal effect. Photoinduced surface heating was found to be very important for obtaining a metallic film of good quality.

Sometimes lasers are used as a secondary source of thermal metalorganic CVD (MOCVD) to 'assist' or 'enhance' deposition. In these cases the substrates are kept at a high temperature. Aoyagi and co-workers[71,72] used an argon ion laser (514.5–457.9 nm) in the deposition of GaAs from $Ga(CH_3)_3$ and AsH_3 on a substrate heated to 500–680 °C, and found a large

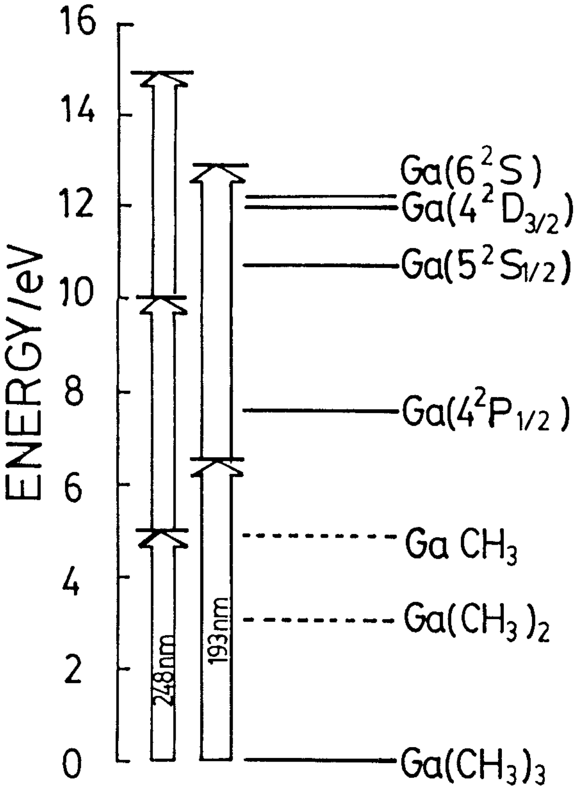


Figure 5 Energy level diagram of trimethylgallium and its fragment radicals and the gallium atom (drawn using the data from Ref. 27).

enhancement of the deposition rate for the lower temperature region (500–600 °C). Balk *et al.*[28] studied a UV laser-assisted growth of GaAs from three trialkylgallium (methyl, ethyl, isobutyl) compounds and AsH_3, on a substrate heated above *ca* 700 °C using an ArF excimer laser (193 nm). In the 'laser-assisted' case, the enhancement in the growth rate is found in the relatively lower-temperature side of the measured range.

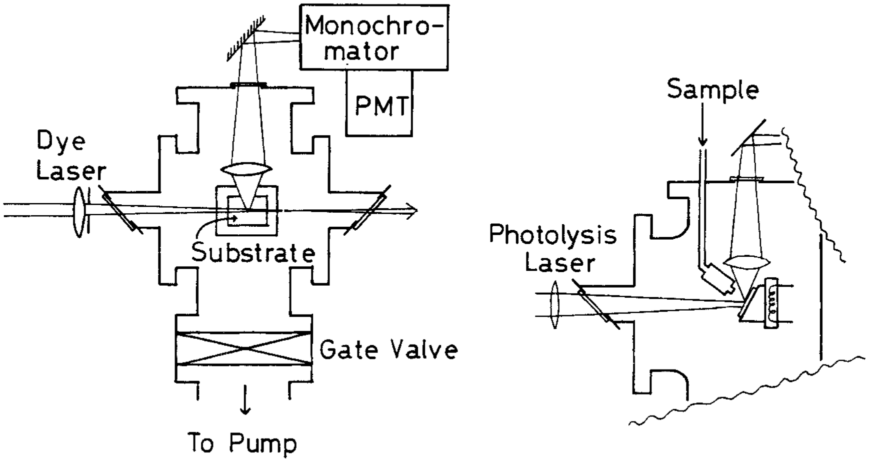
Decomposition in the adsorbed state or in the gaseous state

Dissociation reactions in the LPCVD processes can occur in the adsorbed state of organometallic molecules on the solid substrate, in the gaseous phase above the substrate, or both. The molecules can adsorb on the substrate physically or chemically. Dissociation in the adsorbed state is facilitated when the laser light irradiates vertically onto the substrate. In contrast, dissociation in the gaseous state can be effected also by irradiation parallel to the substrate surface. These two processes can also be distinguished by the temperature dependence of the CVD rates.[2,3,73,74] Because the lower temperature favors adsorption, the process can be judged to occur in the adsorbed state when it is more favored at low temperatures. In the LPCVD of trimethylaluminum and dimethylcadmium at 257.2 nm, Ehrlich *et al.*[73,74] found that the former compound showed a decrease of deposition rate with an increase in temperature, whilst the latter compound showed no significant rate change with temperature. They concluded that decomposition predominated in the van der Waals surface film and in the gas phase for the former and latter compound, respectively. The pressure dependence showing a Brunauer–Emmett–Teller (BET)-type adsorption isotherm[73,74] gives further support for the occurrence of dissociation in the adsorbed state.

In our case of the photodissociation of trimethylgallium at 248 nm,[2,3] we have measured the density of gallium atoms, a reaction intermediate, above the substrate (quartz) surface by the laser-induced fluorescence technique. The experimental set-up is shown schematically in Fig. 6. Trimethylgallium (diluted in argon) has been ejected as a pulsed beam. The dependence of the reaction rates, judged from the density of gallium atoms, on the back-pressure of trimethylgallium beam as shown in Fig. 7 leads to the conclusion that the reaction occurred essentially in the adsorbed state.[2]

Wood *et al.*[75] analyzed their experiments on dimethylcadmium with the frequency-doubled 514.5 nm light from a cw argon ion laser by the dependence of the writing rate on the spot size, and concluded that the bulk of decomposition occurred in the gas phase. The enhancement of photochemical reaction on solid surfaces is due to the interplay of a number of surface phenomena, including the large surface density of the reactant, spectral broadening and a shift to the long-wavelength side (see below), and enhancement of the electric field due to surface contouring.[38] From the industrial point of view, dissociation on the solid surface (in the adsorbed states) is preferable to that in the gaseous phase, since a sharp profile of the deposit can be made and highly integrated circuits can be fabricated.

It is to be noted that the electronic absorption bands of molecules adsorbed on solid surfaces generally extend to a longer wavelength compared with those in the gaseous phase.[37,38] This must be always kept in



(a) (b)

Figure 6 Schematic view of LIF measurement in the LPCVD of gallium from $Ga(CH_3)_3$: (a) front view; (b) side view.

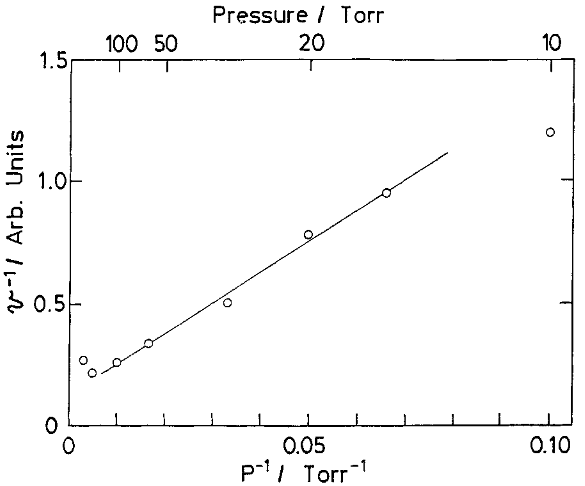


Figure 7 Dependence of the reciprocal of the time-integrated LIF intensity of gallium atoms (v^{-1}) on the reciprocal of the back-pressure of the nozzle (P^{-1}), in the LPCVD of trimethylgallium at 248 nm (from Ref. 2, with permission).

mind when one judges whether a particular dissociation process is photolytic or not.

Detection of the reaction intermediate

In general, the detection and quantitative measurements of reaction intermediates are very important in the elucidation of reaction mechanisms. The clarification of the reaction mechanism of the LPCVD processes is essential to the determination of the best conditions for the reaction and to its design. Several groups made mechanistic investigations of LPCVD processes by the observation of reaction intermediates. Lasers are essential not only for photodissociation but also as a probe in these measurements. Examples of investigations by laser-induced fluorescence (LIF), multiphoton ionization (MPI), laser Raman, coherent anti-Stokes Raman, and laser IR spectroscopy are illustrated below. Lasers are used in all of these measurements as an essential means of detection.

Laser-induced fluorescence (LIF)

An example of the experimental set-up is shown in Fig. 6.[2,3] After the vapor of an organometallic compound has been photodissociated by a UV laser, the reaction intermediate formed in its electronically ground state (hence nonfluorescent by itself) is excited by the probe laser light into its fluorescent excited state. A dye laser is usually used as the probe laser. The resulting fluorescence is measured to discover the identity of molecules and their distribution among the vibrational or rotational levels, and the spatial density of the reaction intermediate. We can make the measurement in the spatially and temporally resolved fashion, because we can pass the probe laser light exactly into the space to be measured, at a selected time delay after the photodissociation laser pulse. In the LPCVD of trimethylgallium[2,3] or trimethylindium,[4,5] the

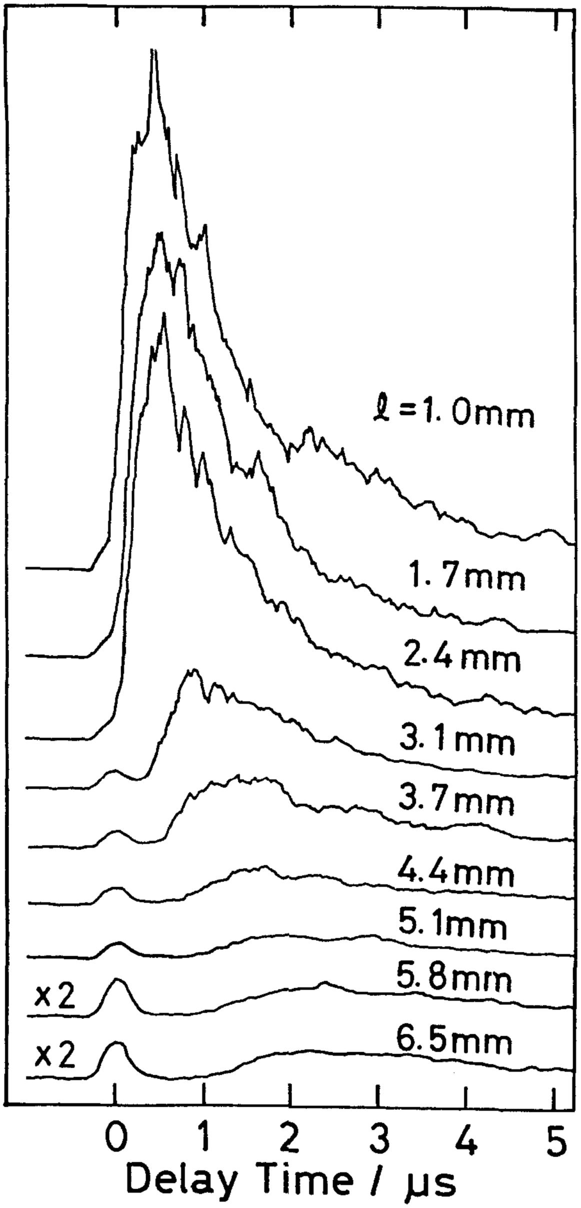


Figure 8 Temporal variation of laser-induced fluorescence (LIF) measured at various heights (ℓ mm) above the substrate surface in the LPCVD of trimethylgallium at 248 nm (from Ref. 2, with permission).

temporal variation of the LIF of gallium or indium atoms detected at various heights above the substrate surface (Fig. 8) reveals that the dissociation reaction occurs in the adsorbed state on the solid surfaces, since the peak of the LIF intensity shifts to a later time for a larger distance from the substrate surface. (This conclusion is in agreement with that drawn from the pressure effect mentioned above.) This is the first application of LIF to the LPCVD of organometallic compounds. For inorganic silicon compounds, LIF detection was used in the determination of spatial concentrations of silicon atoms in the glow discharge of silane,[76] silicon atoms[77] and Si_2[78] from the thermal CVD of silane, and HSiCl[79] in the thermal CVD of dichlorosilane, respectively.

Multiphoton ionization (MPI)

The fragment to be measured is ionized by the multiphoton absorption of the probe light (see Fig. 9). As a probe light source, a tunable dye laser is usually used. The probe laser light is focused in the sample cell to cause multiphoton absorption. This methodology can be applied irrespective of whether the fragment does or does not give fluorescence; therefore it is more general than the LIF method. There are many studies on the MPI of organometallic compounds in the gas phase. Examples are shown in Table 5. When the MPI process includes an intermediate level which is a real molecular electronic state, the MPI process is called resonance-enhanced MPI (REMPI). The intensity of ions increases by several orders of magnitude by this resonance effect, compared with the nonresonant case. Therefore, REMPI is a very highly sensitive, and also a highly selective analytical method, which seems,

Table 5 Examples of the ions obtained as a result of multiphoton ionization (MPI) processes of organometallic compounds

Compound	Observed ion	Ref.
$B(C_2H_5)_3$	$B(C_2H_5)_3^+$	115
$Al_2(CH_3)_6$	Al^+	115
$Zn(CH_3)_2$	$Zn(CH_3)_2^+, ZnCH_3^+, Zn^+$	116
$Ga(CH_3)_3$	$GaCH_3^+, Ga^+$	27,115
$In(CH_3)_3$	In^+	115
$Sn(CH_3)_4$	Sn^+	117
$Hg(CH_3)_2$	$Hg(CH_3)_2^+, HgCH_3^+, Hg^+$	118
$Pb(C_6H_5)_4$	Pb^+	117
$HgCl_2$	Hg^+	117
$HgBr_2$	Hg^+	117
$SnCl_4$	Sn^+	117
$Cr(CO)_6$	Cr^+	117,121
$Mn_2(CO)_{10}$	Mn^+	117,120
$Fe(CO)_5$	Fe^+	119,122
$Co_2(CO)_8$	Co^+	117
$Mo(CO)_6$	Mo^+	117
$W(CO)_6$	W^+	117,121
$Cr(C_6H_6)_2$	Cr^+	117
$Fe(C_5H_5)_2$	Fe^+	117,122,123
$Ni(C_5H_5)_2$	Ni^+	117,124

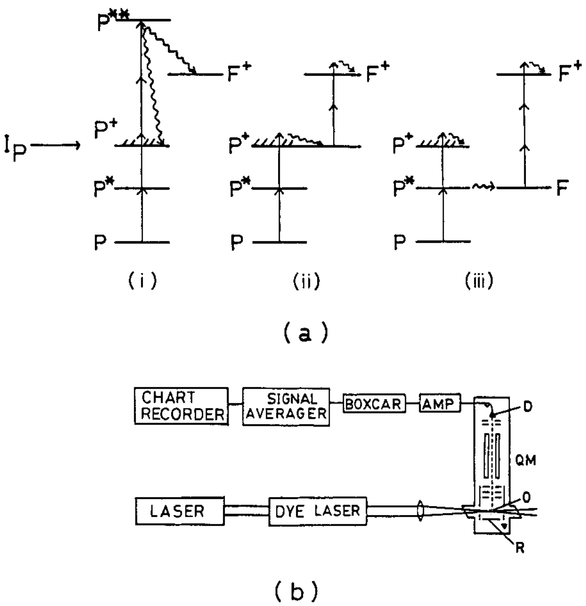


Figure 9 MPI and MPI/dissociation measurement. (a) Three types of MPI processes: (i) autoionization from the superexcited state; (ii) the case when parent ions are formed first, then fragmentation occurs; (iii) the case when fragmentation occurs first, and then ionization follows. P, parent molecule in the ground state; P*, parent in the intermediate excited state; P**, parent in the superexcited state (above the ionization threshold); P^+, parent ion; F, fragment (neutral); F^+, fragment ion. I_p indicates the level corresponding to the ionization potential. (b) A schematic view of an MPI/dissociation measurement system. QM, quadrupole mass spectrometer; O, reaction region. A molecular beam of sample gas is introduced from the front (vertically into the plane of the paper), and laser light is focused into this region. R, repeller; D, ion detector.

however, scarcely to be applied so far to the analysis of the LPCVD process.

Laser Raman spectroscopy

This technique was used to detect SiH_4 in the thermal CVD of this molecule in the spatially resolved fashion.[80] The density profile showed a considerable depletion of silane in the gas phase near the heated (745 °C) substrate. The depletion could be caused by a diffusion-controlled concentration gradient as silane reacts on the surface and/or by gas-phase reactions.

Coherent anti-Stokes Raman spectroscopy (CARS)

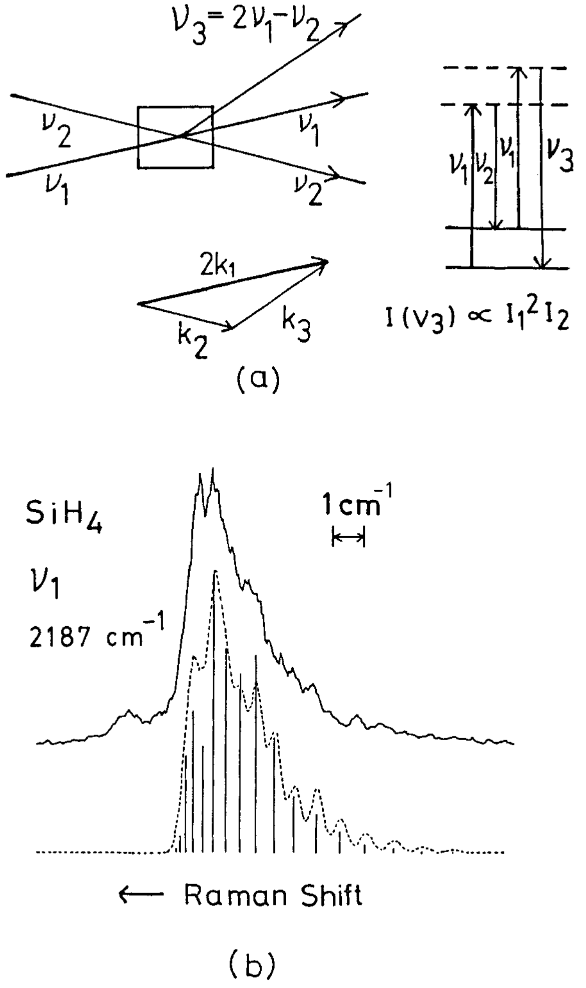


Figure 10 CARS measurement. (a) Two dye laser beams and CARS light: energy diagram and phase-matching conditions. (b) An example of the CARS signal: the ν_1 mode of SiH_4 (adapted from Ref. 6).

Two dye lasers are used. One of them is operated at a fixed wave number (ν_1). The wave number of the other (ν_2) is tuned [Fig. 10(a)]. When the difference in the wave number ($\nu_1 - \nu_2$) is coincident with the wave number of the molecular vibration of the intermediate, a laser-like intense light beam ($2\nu_1 - \nu_2$) is generated in a direction determined by the directions of the two lasers by the phase-matching conditions. This is a very sensitive detection method for the species with a large third-order dielectric susceptibility ($\chi^{(3)}$). An example of CARS measurements on silane[6] is given in Fig. 10(b).

Laser IR spectroscopy

Higashi and co-workers[81–83] studied LPCVD of trimethylaluminum at 248 and 193 nm on a sapphire substrate by IR spectroscopy whose sensitivity was enhanced by a pulsed photoacoustic measurement. The source of tunable IR radiation was visible light from a dye laser driven by a Nd:YAG laser. The laser pulse was introduced into a high-pressure hydrogen (H_2) cell which emitted the third Stokes radiation in the infrared region (2.7–3.4 μm). They observed the signal of the adsborbed methyl group and its desorption by 193 nm irradiation.

Absorption and emission spectroscopy

Osmundsen *et al.*[84] made absorption and emission spectroscopic studies of the growth of germanium (Ge) thin film by photodissociation of GeH_4 at 248 nm. They observed emission from germanium atoms and GeH. The dependence of the emission line intensity on the pump laser fluence was found to be quadratic, indicating that these species have a common precursor which is produced by the simultaneous two-photon absorption.

REACTIVE DRY ETCHING

Etching is a very important procedure in VLSI technology. In reactive dry etching, a rective gas such as a halogen or a halogenated alkyl is used instead of the liquid etchant. A brief review of this topic seems to be relevant, since organic molecules such as alkyl halides are used with metal substrates, and some organometallic fragments may appear as a result of the reaction, although it is generally believed that the halogen moiety itself works in the actual etching processes. Steinfeld and co-workers[85] performed surface etching of silicon dioxide or nitride substrates by the reactive neutral fragments, which were generated by IR-multiple photon dissociation with a carbon dioxide laser of molecules such as CF_3Br, CF_2Cl_2, or CDF_3. Ehrlich *et al.*[86] used UV laser phtolysis of methyl halides for localized photoetching (spatial resolution ~ 1 μm) of GaAs and InP with the frequency-doubled light (257.2 nm) of an argon ion (Ar^+) laser. These authors succeeded in a high-resolution etching of silicon substrates with chlorine (Cl_2) or hydrogen chloride (HCl) gas using an Ar^+ laser.[87] The same beam was used simultaneously to heat a reaction zone on the substrate. High spatial resolution (up to ~5 μm) was realized.[87] The photodissociation has been proven to be rate-determining at low surface temperatures, as found from the close correspondence between the wavelength dependence of the etching rate and the absorption strength of chlorine vapor.[88]

Mechanism of reactive dry etching

Chuang[89] classifies reactive dry etching into three categories. In the first case (spontaneous etching), the etching occurs in the absence of light. Light simply increases the etching rate. The etching of silicon with XeF_2[90] falls in this category. The etching rate is increased significantly by visible or IR laser irradiation. The second category is a passive reaction. In the system of a silicon substrate with chlorine (25 °C), chlorine molecules dissociatively adsorb on the substrate, but no etching occurs. The surface is covered with the chloride layer and the reaction does not proceed any further. This is the stage of passivation. On UV laser irradiation, etching occurs. Horiike and co-workers[91] found that the etching rate by chlorine (Cl_2) under excimer laser (308 nm) or mercury lamp irradiation decreased with the sheet resistance in the case of n-Si, whilst the reverse held for p-Si. They proposed the following mechanism. The electrons in the conduction band play an important role in the etching process, and they react with chlorine to form chloride ion (Cl^-). Then chloride ion reacts with silicon in the etching process. The third case, the diffusive reaction, is found for silver or copper substrates with chlorine (Cl_2). For example, in the cases of copper and chlorine, even under the partial chlorination of the surface, visible or UV laser causes etching. The chloride ion (Cl^-) has been found to penetrate deep (some tens of nanometers) into the bulk of a copper substrate.

Measurements of desorbing species

Measurements on the identity and energetics of the desorbing species in reactive dry etching processes can give essential information on the reaction mechanisms. Davis *et al.*[92] studied the dynamics of laser-stimulated etching of germanium by bromine, by the measurement of TOF distribution of the product, $GeBr_2$. Its translational energy distribution was found to be hyperthermal, i.e. relatively rich in high-energy species. Marsh *et al.*[93] made a TOF study of the methyl (CH_3) radical on the photolysis of CH_3Cl on a nickel (111) surface at 193 and 248 nm. Judging from the TOF data, direct photolysis and electron-induced fragmentation of CH_3Cl was observed at 193 nm, while only the latter was observed at 248 nm.

The desorbing species in the etching process of a silicon substrate with chlorine (Cl_2) has been studied by TOF mass spectroscopy.[10–12] Laser irradiation at 193, 248 or 351 nm (*ca* 10 mJ cm^{-2}) of a multilayer of chlorine or CH_3Cl on an silicon wafer at 100 K leads to photodissociation of these molecules and formation of photoetching products. The species ejected from the surface are detected by a quadrupole mass spectrometer equipped with an electron bombardment ionizer. The kinetic energy distribution of chlorine atoms (Cl) and methyl radicals (CH_3) is bimodal for thin deposition of parent molecules on the substrates. The Maxwell–Boltzmann fit of the results reveals two components in kinetic energy: ~4.2 and 42 kJ mol^{-1}. The etching products (SiCl and $SiCl_2$) have kinetic energies of 4.2 kJ mol^{-1}.

Halogen on metal substrates

Bromine (Br_2) adsorbed on various substrates at low temperature (~77 K) has been studied by resonance Raman spectroscopy,[8,9] and it was concluded that bromine molecules are not dissociated in the measured energy range (16000–20000 cm^{-1}), even above the dissociation limit of the B state in gasious bromine (Br_2) molecules (19578 cm^{-1}). Bäuerle[94] performed the reactive dry etching of a silicon substrate by chlorine (Cl_2) using an argon ion laser (514.5, 488, 457.9 nm), and concluded that the chlorine atomic species formed by the dissociation in the gas phase are necessary, together with photogenerated carriers within the surface of a silicon substrate, to achieve the etching reaction.

LASER ABLATION

The ablation of metals or semiconductors by laser light is not only an important fundamental phenomenon in laser processing, but also a highly intriguing physicochemical process in itself. The ablation of metals in the atmosphere of an organic compound can lead to the formation of organometallic compounds.

Pulsed laser irradiation at 248 nm has been used to ablate silicon atoms from a silicon (100) wafer.[13] The mechanism has been examined by LIF analysis of the silicon products. The probed silicon atoms have been shown to leave the wafer surface with an average translational energy of 10.5 kJ mol^{-1}. The distribution of the translational energy is well represented by a theoretical model of non-cascade ablation processes.

Reaction of metal ions with organic molecules in the gas phase

Ion–molecular reactions of metal ions and organic or organometallic molecules has extended a rich field of organometallic chemistry.[95–100] Laser ablation has been used as the method of generation of metal ions, as pioneered by Freiser and co-workers,[97] and the reaction of these metal ions with a variety of organic molecules in the gas phase has been studied. Ion cyclotron resonance or Fourier transform mass spectroscopy have been used in these studies from which many important features of the reactions of metal ions with organic molecules have emerged. It is, however, beyond the scope of the present review to cover all of these features. Only a brief summary of our recent results is given below.

Laser ablation–molecular beam method

We have developed a very simple and versatile method, by combining the laser ablation of metal substrates in vacuum and the injection of a pulsed molecular beam of many organic compounds nearby (see Fig. 11). Laser light is focused on the surface of a metal substrate, which is located close to the entrance region of a quadrupole mass spectrometer before the einzel lenses which attract the ions into the quadrupoles. The metal ions and photoelectrons ejected in the process of multiphoton absorption of the metal diffuse into the entrance region. A pulsed molecular beam of an organic or organometallic compound is injected into the entrance region. The ion–molecular reaction

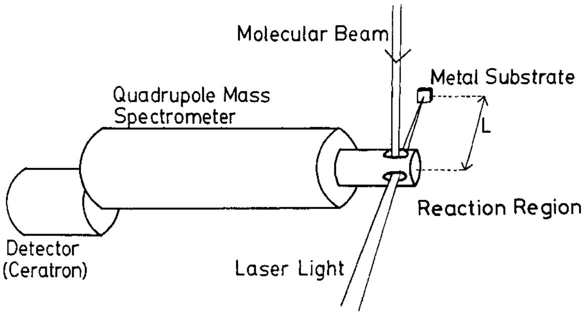


Figure 11 A schematic view of the laser ablation–molecular beam apparatus (adapted from Ref. 16).

Table 6 Typical results in ion–molecular reactions by the laser ablation–molecular beam method

Substrate metal	Molecules in the beam	Complex ions produced	Fragment ions produced	Laser wavelength (nm)	Ref.
Aluminum	$Sn(CH_3)_4$	None	$Sn(CH_3)_n^+(n = 0–3)$	532,355	15,17
Niobium	$Mn_2(CO)_{10}$	$NbCO^+$,$NbMn^+$ $NbMnCO^+$, $NbMn_2(CO)_n^+(n = 0–6)$ and/or $NbMn(CO)_n^+(n = 2–8)$	$Mn_2(CO)_n^+(n = 5,4,0)$,$MnCO^+$,Mn^+	532	16,17
Copper	$Mn_2(CO)_{10}$	$CuCO^+$ $CuMn_2(CO)_n^+(n = 0–10)$ and/or $CuMn(CO)_n^+(n = 0–10)$	$Mn_2(CO)_n^+(n = 0–5,10)$,$MnCO^+$	532	18
Titanium	$(C_2H_5)_3N$	$-2H_2, -3H_2, -(C_2H_6+H_2)$, $-(C_2H_6+2H_2)^a$		532	18
Vandadium	$(C_2H_5)_3H$	$-2H_2, 3H_2, -C_2H_6$, $-(C_2H_6+H_2)^a$		532	18
Chromium	$(C_2H_5)_3N$	$Cr(C_2H_5)_3N^+, -H_2{}^a$		532	18
Manganese	$(C_2H_5)_3N$	$Mn(C_2H_5)_3N^+$		532	18
Iron	$(C_2H_5)_3N$	$-C_2H_6{}^a$ $-H_2,{}^a$		532	18

[a] The symbol – (minus) shows the loss of neutral molecule(s) or atom(s) from the complex ion $(C_2H_5)_3N^+$ (see text).

occurs, along with the electron–molecular reaction in the entrance region. The resulting ions have been detected by the quadrupole mass spectromer.[15–19] Some examples of the results are given below (see Table 6).

Dimanganese decacarbonyl

A niobium or a copper substrate has been used together with the molecular beam of dimanganese decarcarbonyl, and the substrate surface has been irradiated with a tightly focused beam of the green second harmonic (532 nm) of a Nd:YAG laser.[16,17] Besides the substrate ions and the fragment ions originating from the compound in the molecular beam, a variety of complex ions containing both substrate metal atoms and molecules in the molecular beam are observed, as shown in Fig. 12. The ions observed for the niobium (Nb) substrate are $NbCO^+$, $NbMn^+$, $NbMnCO^+$, $NbMn_2(CO)_n^+$ ($n = 0–6$) and/or $NbMn(CO)_n^+$ ($n = 2–8$). For the copper substrate, a complete series of ions up to the species without any loss of the CO moiety, i.e. $CuMn_2(CO)_n^+$ ($n = 0–10$) and/or $CuMn(CO)_n^+$ ($n = 0–10$) is found.

Tetramethyltin

When an aluminum substrate was used with a molecular beam of tetramethyltin in the less focused condition of the laser beam,[15] only the fragment ions of the organometallic compound were found. These fragment ions are produced by the reaction of the molecules with the photoelectrons from the irradiated metal surfaces, as confirmed by (1) the arrival time in the reaction region after the pulse-laser irradiation on the metal surface, (2) the effect of a magnetic field applied vertically to the path of the metal ions and photoelectrons, and (3) the similarity of the mass pattern to that in the electron impact.

Amines

A variety of first-row transition metals ranging from titanium to iron has been used as substrate metal together with a molecular beam of ethylamine, diethylamine or triethylamine.[18] The distinction in the properties of the early and later transition metals is apparent, as seen in Table 6. For later first period transition metals (chromium, manganese, iron), the 1:1 complex ions composed of the metal ion and amine are found together with those with a loss of some hydrogen molecules (or hydrogen atoms). In contrast, for early transition metals (titanium, vanadium and niobium), the ions are obtained with a loss of ethane and hydrogen molecules. The characteristics of each transition element reveal themselves in these ion–molecular reactions.

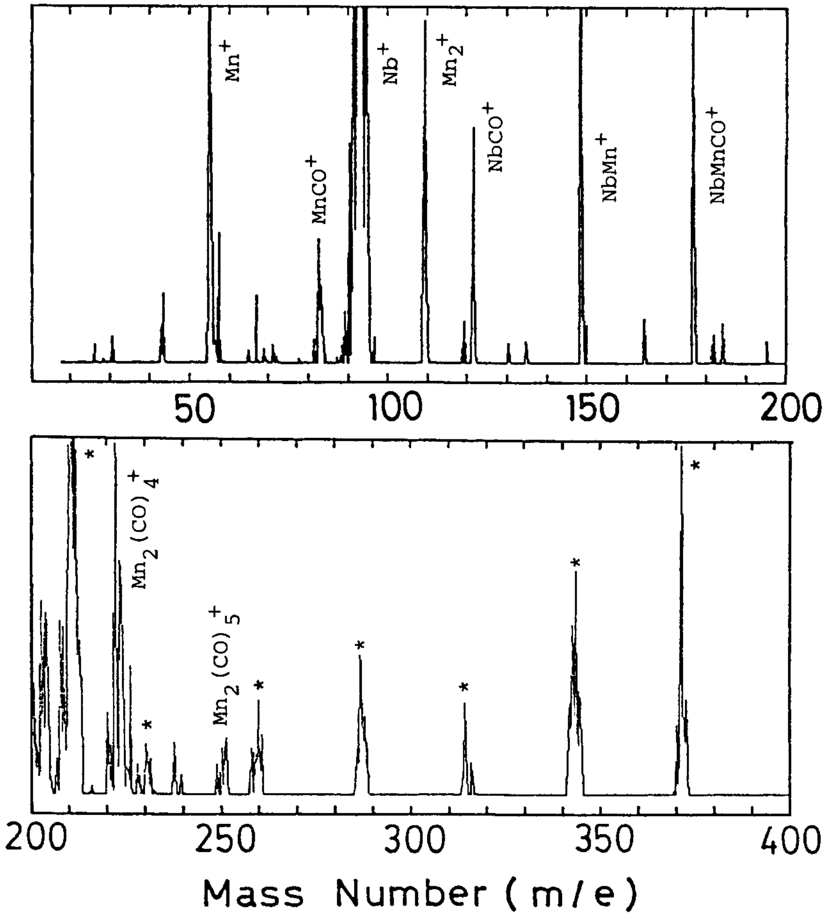


Figure 12 An example of mass spectra obtained in the laser ablation–molecular beam experiment on a niobium substrate and a molecular beam of $Mn_2(CO)_{10}$. The signals with asterisks are due to $NbMn_2(CO)_n^+$, $n = 0–6$ and/or $NbMn(CO)_n^+$, $n = 2–8$ (from Ref. 16, with permission).

Benzene

Reaction of metal ions and benzene has been examined for a variety of metal substrates.[17,19] For transition metals, we observe complex ions composed of the substrate metal ion and the benzene moiety, along with benzene ions. Loss of hydrogen atoms is found in some cases. (Application of a magnetic field reveals that the benzene ions are given by reaction with electrons.) In contrast, typical elements sparingly form complex ions in the experimental conditions.

CONCLUSIONS

The present review has addressed the topic of laser photochemistry of organometallic compounds, its fundamental aspects and problems related to LPCVD, reactive dry etching and laser ablation, all of which support the contemporary microelectronics technology. Laser photochemistry of organometallic compounds is a very young, and rapidly developing, area. In addition to its value as the photochemistry of a variety of metal- or metalloid-containing compounds, it constitutes a basic science for many important industrial applications as mentioned above. The needs of industry urge its continuing development. However, compared with the rapid development of industrial applications, the progress of the fundamental science is still limited. Much is left to be done. The number of organometallic compounds used in LPCVD is rather limited so far. The design of molecules suited to application in LPCVD should lead to further progress in this technique. The accumulation of fundamental data of electronic spectra and gas-phase reactions of many organometallic molecules will be very helpful. More extensive studies in the mechanisms in LPCVD processes should be done. Laser-based analytical techniques are very useful in these studies. New types of laser-based methods are anticipated. The development of the laser itself is very important. The investigations of LPCVD and reactive dry etching will be much more accelerated when we have more efficient methods for the study of surface processes, because many important steps in LPCVD and reactive dry etching involve processes on solid surfaces. Laser ablation of metals in organic atmospheres will be useful for the development of many types of solvent-free organometallic reactions, and also for the better understanding of the mechanism of photocatalysis by metals, metal clusters and organometallic compounds.

There are many other important fields in which laser photochemistry of organometallics should play its due role, e.g. photocatalysis by metals and metal clusters, photoelectrochemistry on modified semiconductor electrodes, mechanistic studies of the reactions of metal-containing biomolecules, photodeposition of superconductors, photocatalytic image formation, etc. These are only a few examples, and there are certainly more to come. Indeed, the laser photochemistry of organometallic compounds appears to be an unfailing spring which awaits exploitation by inspired people.

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