Translated from *Uspekhi Khimii*, **59**, 177–196 (1990) U.D.C. 621.315.592

Laser-induced chemical deposition from the gas phase

V V Teslenko

ABSTRACT. The results of the study of the chemical reactions involved in the deposition of various substances from the gas phase using the pulsed, quasi-continuous, and continuous laser radiation in the wavelength range 0.193–10.6 μm have been summarised. Particular attention has been paid to the deposition of inorganic substances, including non-metals (C, Si, Ge, etc.), metals (Cu, Au, Zn, Cd, Al, Cr, Mo, W, Ni), and a number of simple compounds. Detailed experimental data are given on the influence of the radiation parameters (wavelength, duration and spacing of the pulses, intensity of radiation, shape and position of the laser beam) and the nature of the reagents (hydrides, halides, carbonyls, alkyl organometallic compounds, etc.) on the rate of deposition and the composition of the deposit. The characteristics of photolytic deposition reactions and their possible applications have been examined.

The bibliography contains 202 references.

Contents

I.	Introduction	103
II.	Deposition of non-metals	103
III.	Deposition of metals	106
IV.	Deposition of inorganic compounds	109
V.	Characteristics of laser-induced chemical deposition reactions	111
VI.	Possible applications of laser-induced deposition processes	112
VII.	Summary	112

I. Introduction

Reactions involving chemical deposition from the gas phase are finding extensive practical application. In addition to the traditional method in which the reagents are heated, the attention of chemists in recent years has been drawn to other methods of initiating chemical reactions, such as plasma excitation and laser irradiation.

The first paper on the chemical deposition of carbon induced by the radiation of a CO_2 laser appeared in 1972.[1] In the period up to 1980, not more than ten papers on this topic[2–9] were published, but by 1988 the number of papers, reports, and patents exceeded 200. Most of the credit for this goes to specialists in electronics, who not only carried out a large number of studies but also published a whole series of reviews,[10–18] although these are short and highly specialised.

The chemical processes of deposition from the gas phase induced by laser radiation have a wider practical importance, however.[19–24] They can be regarded as a new field of laser chemistry, adjoining, for example, the field of gas-phase laser chemistry.[25–27] This has made it appropriate to publish the present review, which has the following aims: 1) to summarise the experimental data for the period 1980–1987; 2) to describe the principal characteristics of laser-induced chemical deposition reactions; and 3) to examine the possible applications of the process.

The possibility of laser-induced chemical deposition reactions was studied in detail by a number of authors.[8,16,23,28] Here it is sufficient to note that this method can apparently be used to bring about all reactions of chemical deposition from the gas phase (a list of reactions has been published[29–31]), and also a number of other reactions, in particular the decomposition of transition metal halides, such as $TiCl_4$.[32] Two main types of reaction are distinguished, depending on the nature of the interaction of the laser-radiation with the substance: 1) laser-chemical reactions, in which the electromagnetic energy is used up only in the rupture of bonds in the starting materials, and is not converted into thermal energy; and 2) laser-thermal reactions, in which the reagent is first heated, and then undergoes thermochemical transformation. In the English-language literature, these reaction types are described as photolytic and pyrolytic respectively.

The minimum size of the reaction zone is comparable with the wavelength of the radiation; the value attainable in practice is 0.5 μm for photolytic processes, and several μm for pyrolytic processes.[33] Assemblies for carrying out laser-induced deposition are of three main types: in the first type, the laser radiation interacts with a gas in a free space (power synthesis),[34] in the second it interacts close to the surface of a support (deposition of amorphous and microcrystalline coatings),[35–38] and in the third it interacts when the beam reaches the surface of the support (formation of point deposits and non-planar bands, growth of rods, preparation of polycrystalline coatings).[39–41] In addition, there are combined assemblies, for example assemblies using crossed beams.[42–49] The most frequently used are assemblies with the perpendicular configuration, in which the laser beam is directed on to the support, and assemblies with the parallel configuration, in which a beam with a circular or rectangular cross-section is passed several millimetres above the surface of a planar support.

II. Deposition of non-metals

Carbon is obtained by the pyrolysis of hydrocarbons.[1,3,50–56] The production of spiral bands with a width of 0.35 mm on a ceramic rod with a diameter of 3.5 mm by irradiating it in a hydrocarbon atmosphere with a CO_2 laser has been described.[3] The same radiation with metallic supports was used to grow fibrous graphite crystals with a diameter of less than 1 μm and diamond-like films.[50,51] The technical assembly "Kvant-12" has been used to obtain films with a thickness of up to 40 μm on a metal or ceramic support.[52] The decomposition of acetone vapour by heating glass, mica, and crystalline glass supports by radiation with a power of up to 1 W and wavelength λ = 0.53 um (diameter of the focal spot

50 μm) made it possible to obtain rods of polycrystalline graphite with a diameter of 40 μm and a length of up to 3 mm; except for the initial period, the rate of growth (70–230 μm min^{-1}) was proportional to the radiation power.[56] The deposition of carbon from C_2H_2, C_2H_4, and CH_4 on graphite, tungsten, and aluminium oxide supports heated by the radiation of an Ar^+ laser has been described.[53,54] The deposit was obtained in two forms. When the laser beam scanned the surface of the support at a rate of 42 μm s^{-1}, non-planar polycrystalline bands with widths of 5–26 μm were deposited. Stationary irradiation of the support gave cylindrical carbon rods with a diameter of 10–70 μm and a length of up to 1 mm. The volume rate of deposition of carbon from acetylene increased non-linearly with increase in the intensity of the irradiation (I); no deposition was detected at I < 54 kW cm^{-2}, and at I > 292 kW cm^{-2}, homogeneous deposition took place close to the surface of the support to give flakes of carbon black. The range of values of I in which heterogeneous deposition of carbon was observed with C_2H_4 and CH_4 were used was greater, and corresponded to 82–760 kW cm^{-2} and 1055–2190 kW cm^{-2} respectively.[53] The measured axial rates of growth of the carbon rod at different temperatures and pressures are given in Fig. 1. The rate of deposition in the temperature range 1500–2500 °C at partial pressures $p_{C_2H_2}$ in the range 6.7–98 kPa had values in the range 0.2–35 μm s^{-1}; up to 2000 °C, the activation energy was 200 kJ mol^{-1}, and the order of the reaction with respect to C_2H_2 was close to 1. Above 2200 °C, the activation energy decreased, apparently indicating that the process moves from the kinetic into the diffusion range.[54] All the processes described were pyrolytic.

The photolytic decomposition of C_2H_4 under the influence of a CO_2 laser (pulse energy E = 0.7 J) at a pressure of 665 Pa has been carried out on an assembly with the parallel configuration.[55] A carbon layer with an area of 5 mm^2 and a thickness of 0.1 μm was deposited on an NaCl support at a distance of 1 mm from the focus (dose D = 300 J cm^{-2}) after pulse irradiation with 50 000 pulses. The carbon had an amorphous structure with the inclusion of individual crystallites of carbyne and lamellar graphite. In the pulse irradiation of ethylene, thermal equilibrium was not established, so that unstable phases were deposited.

High-intensity ultraviolet radiation brings about the formation of a plasma, from which carbon-containing radicals and ions may diffuse to the surface of a support situated 2–3 mm from the focus, and react on it to give carbon. Thus focussing radiation with λ = 308 nm and a power W = 5 MW with a pulse duration τ = 7.5 ns and a pulse repetition frequency ν = 5 Hz gave an intensity of radiation I = 10^5 kW cm^{-2}.[55] On passage through the laser plasma, naphthalene vapour decomposed, and carbon was deposited on the support (polished SiO_2) as a diamond-like coating with a thickness of about 1 μm. The degree of transformation (and rate of deposition) increased when a magnetic or electric field was used,[40,55] as a result of the increase in the rate of the transport of the active species from the generation zone to the surface of the support.

The largest number of papers has been devoted to the deposition of silicon,[5,7,38,42–44,46,48,54,57–83] indicating the considerable practical interest in this process.

When assemblies with the perpendicular configuration were used, the support was heated by the radiation to 900–1400 °C, so that the deposit had a crystalline structure. Silicon is often deposited using a CO_2 laser,[57,59,69,73] and SiH_4 or a mixture of $SiCl_4$ and H_2 as the reagent.[59] In the last study, polycrystalline coatings with a particle size of 8 μm were obtained at a temperature of the quartz support equal to 900 °C (W = 18.9 W). The rate of deposition v was 5.1 μm min^{-1}, and increased with increase in temperature; saturation took place at a radiation power W = 20 W. The activation energy of the process E_a = 154 kJ mol^{-1}. When the support is heated by the radiation of an Ar^+ laser[74] to 1400 K (at p_{SiH_4} = 13.3 kPa), the temperature dependence of the rate of deposition of polycrystalline silicon is described by an Arrhenius equation with E_a = 195 kJ mol^{-1}. The characteristic deviation of the experimental points from the Arrhenius straight line at temperatures above 1400 K indicates that the process moves from the kinetic into the diffusion range. Under these conditions, the process remains in the kinetic range to a higher temperature than in the ordinary pyrolysis of SiH_4.

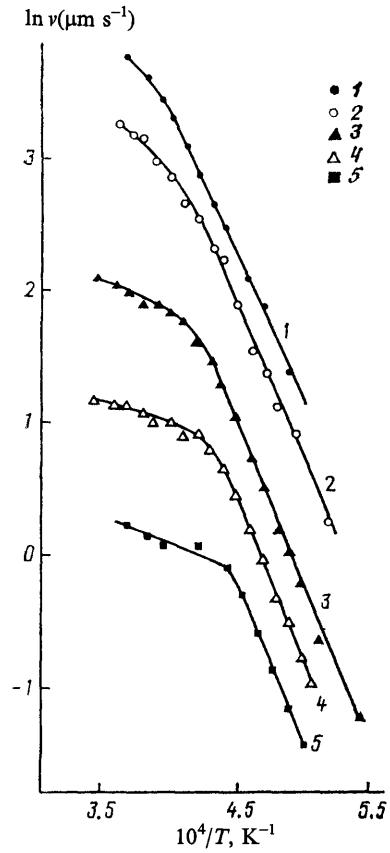


Figure 1. Temperature dependence of the rate of deposition of carbon from C_2H_2 at different partial pressures, kPa: *1*, 98.0, *2*, 66.5, *3*, 26.6, *4*, 13.3, *5*, 6.7.[54]

Single crystals of Si have been deposited using laser radiation with a wavelength of 530.9 nm.[63] Faceted rods with a length of several millimetres and a diameter of about 0.1 mm have been grown on silicon supports with the (100), (110), (111) orientation at 1650 K and p_{SiH_4} = 13.3 kPa at a rate of 30 μm s^{-1}. The axes of the rods coincided with the [100] or [110] directions, irrespective of the orientation of the support. The profile of the growing end of the rod resembled a parabola. Silane and a laser beam with a diameter d = 22 μm were used in the experiments. At deposition temperatures of 1450 K and 1550 K the rods were polycrystalline.

The dependence of the rate of deposition and structure of silicon on the angle of incidence of the radiation, I, p_{SiH_4}, and the temperature of the support (T_s) has been studied.[43,71] With decrease in the angle of incidence from 90° to 0°, the structure of the deposit changed from polycrystalline to amorphous,[71] and the deposition was quenched at a low radiation intensity.[43]

The production of films of amorphous hydrogenated silicon (*a*-Si:H) on assemblies with the parallel configuration is based on the excitation and dissociation of SiH_4 molecules, which show strong resonance absorption at certain wavenumbers in the infrared range (mainly 913.3 cm^{-1}). Mass-spectrometric measurements showed that the action of the laser beam increases the concentration of H_2 and SiH_n^+ ($n = 0-4$); $Si_2H_n^+$ ($n = 1-7$) peaks were also observed, indicating the formation of disilane as a result of the high density of radicals in the irradiated volume.[65,66]

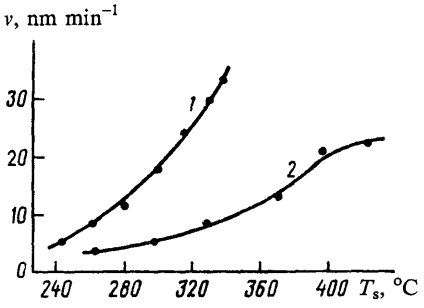


Figure 2. Temperature dependence of the rate of deposition of amorphous silicon at $I = 250$ W cm^{-2}: *1*, $p_{SiH_4} = 0.57$ kPa, $p_{tot} = 1.33$ kPa, gas consumption 5.75 cm^3 s^{-1}; *2*, $p_{SiH_4} = 0.43$ kPa, $p_{tot} = 1.05$ kPa, gas consumption 4.25 cm^3 s^{-1}.[57]

Although dissociation in the gas phase takes place even at room temperature, an appreciable rate of heterogeneous deposition is achieved only on a support heated above 200 °C. Fig. 2 gives data on the temperature dependence of the rate of deposition of silicon.[57] The maximum rate of deposition is limited on the one hand by the formation of a powder, and on the other hand by the decrease in the silane concentration as it is used up. The diameter of the laser beam d and the distance from the support are also important. Thus at $T_s = 310$ °C and $W = 65-80$ W, the rate of deposition at $d = 7.5$ mm is approximately twice that at $d = 4.0$ mm. The explanation for this unexpected result was that in a narrow beam, the degree of dissociation rapidly reaches a limiting value with increase in I, whereas in a broad beam, a larger number of reagent molecules are involved in the process.

The concentration of hydrogen in the deposit and the nature of the bonds it forms with silicon depend markedly on T_s. The infrared spectra showed that films with a thickness of 1 μm contained SiH_2 and SiH groups. Heating at 350–450 °C led to a decrease in the hydrogen concentration (mainly as a result of the decomposition of SiH_2), and heating at 550–650 °C led to crystallisation of the deposit.

Similar results were obtained[64,68–70] on supports of borosilicate glass (including glass coated with Pt, Mo, or a mixture of In and Sn oxides), aluminium, single crystals of silicon, and aluminium oxide. Radiation with $\lambda = 10.6$ μm and $I = 0.1-1.0$ kW cm^{-2} was used. The temperature of the support was 200–650 °C. In studies by Gattuso and co-workers,[64] the main experiments were carried out at $T_s = 300$ °C, $p_{SiH_4} = 800$ Pa, $W = 70$ W, and $d = 6$ mm. The rate of deposition increased linearly at first, for 60 min, after which a stationary value was established. The stationary value v depends on the rate of consumption of the gas, and with change in the latter from 2 $cm^3 s^{-1}$ to 4 $cm^3 s^{-1}$, v increased from 6.0 nm min^{-1} to 16 nm min^{-1}. The rate of deposition also increased with increase in T_s, W, and p_{SiH_4}. The maximum value of v was limited by the side process of powder formation. The addition of H_2 or HCl to silane was recommended, to suppress homogeneous deposition.

A model of the deposition including the gas-phase decomposition of SiH_4 to SiH_2 and H_2, the diffusion of SiH_2 free radicals to the support, and their reaction on the solid surface to give a deposit has been proposed.[68] In the opinion of the authors cited, the limiting stage is the first of these stages, which determines the exponential dependence of the rate of growth of the deposit on the temperature of the gas T_g. T_g was calculated by assuming that the absorbed energy of the laser beam is equal to the energy lost as a result of thermal conductivity. For pure silane at a pressure $p_{SiH_4} =$ 665 to 1064 Pa, $T_s = 200-400$ °C, and $W = 20-40$ W, the value of T_g was 440–550 °C. The dependence of v on T_g gave $E_a =$ 190 kJ mol^{-1}.[69,70] This value coincides with the activation energy of the pyrolysis of SiH_4, and is close to the value 220 kJ mol^{-1} obtained for the decomposition of SiH_4 to Si_2H_6, H_2, and *a*-Si:H powder under the influence of laser radiation with $\lambda = 9.77$ μm.[73]

Radiation with $\lambda = 193$ nm has been used to obtain an *a*-Si:H coating from disilane.[67,78] At a temperature of the glass support of 200–400 °C and a pressure in the system of 133 Pa, the rate of deposition reached 5.5 nm s^{-1}. The concentration of hydrogen in the deposit depended on T_s, and had the values 17, 9.3, and 7.2 at.% at 200, 300, and 400 °C respectively.

The deposition of germanium from GeH_2 has been carried out[60,62,83] in an assembly with the perpendicular configuration using excimer ArF, KrF, and XeCl lasers ($\nu = 20$ Hz). The laser beam was focussed at a point 1–4 cm from the base of the reactor. By moving the latter along the optical axis, the value of I was varied in the range 1–20 mW cm^{-2}. The duration of the process was about 400 s. Fig. 3 gives the dependence of the initial rate of growth v_0 of the germanium film on the intensity and wavelength of the radiation. The XeCl laser did not induce the reaction. The difference in the action of the radiation of the ArF and KrF lasers is due to the characteristics of the absorption of the radiation by the gas and the deposit. In the opinion of the authors cited,[62] the decrease in v_0 on intensive irradiation is due to the volatilisation of the substance. The average temperature of the support, however, did not exceed 120 °C. It is suggested that a chain reaction is initiated by the two-photon dissociation of GeH_4 to GeH_2 and then takes place according to the scheme shown in Fig. 4. The deposition takes place as a result of the gas-phase diffusion of atomic Ge and Ge_2H_6 to the surface of the support; the concentration of germanium in the gas phase as the support was approached passed through a maximum at a distance of approximately 1.5 mm from it. In the opinion of the authors cited,[83] the low activation energy of this process ($E_a =$ 8.3 kJ mol^{-1}) compared with the pyrolysis of group IV hydrides indicates that the deposition is limited by one of the gas-phase reactions or by the desorption of hydrogen.

An amorphous hydrogenated *a*-SiGe:H alloy was obtained on a support heated to 200 °C by irradiating a mixture of Si_2H_6, GeH_4, and H_2 (λ = 193 nm, τ = 10 ns, ν = 100 Hz, pulse energy E = 15–20 J).[84] Chain radical reactions in the gas phase at a total pressure of 133–250 Pa began as a result of the absorption of one photon by the Si_2H_6 molecule. The intermediate reaction products were Si_2H_5, SiH_3, SiH_2, SiH, and H. The reaction of these radicals with GeH_4 gave $SiGeH_6$, GeH_2, and GeH_3. The proportion of silicon transferred to the deposit was higher than that of germanium.

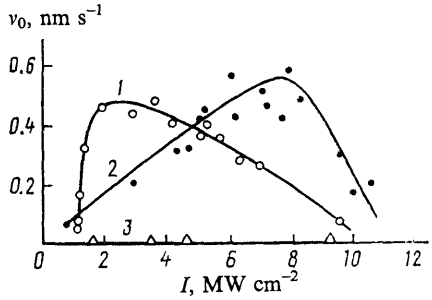


Figure 3. Dependence of the initial rate of deposition of Ge on the energy density of ArF (*1*), KrF (*2*), and XeCl (*3*) lasers.[62]

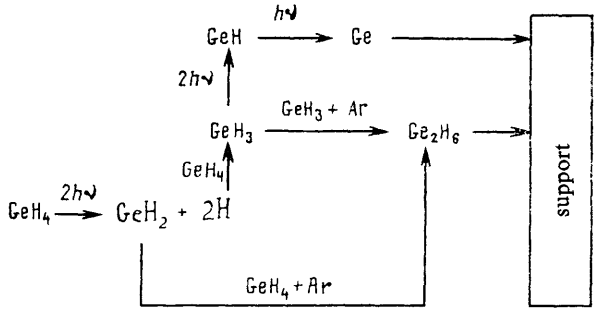


Figure 4. Principal reactions taking place on the irradiation of GeH_4 using a KrF laser (λ = 248 nm).[83]

The rate of decomposition of PH_3 in the optical breakdown of the gas with the formation of a PH_x deposit[85] remains unchanged on going successively from the $P(10)$ line to the $P(32)$ line of a CO_2 laser, and shows a clearly defined threshold. The deposition threshold is determined by the energy and frequency of the pulses, and also by the pressure of PH_3 and the inert gas (Ne).

Data have also been published[86] on the deposition of As from AsH_3, Se from $SeMe_2$, and Te from $TeMe_2$, Te_2Me_2, and $TeEt_2$.

Thus hydrides are most frequently used for the deposition of non-metals. In photolytic processes, radiation in the infrared or visible ranges is used. The principal characteristics of these processes are the increased extent of the kinetic range of the reaction on coordinates concentration–temperature and the possible use of high reagent concentrations without the risk of powder deposition. Photolytic processes are generally carried out in one of three ways: 1) using multi-photon absorption of the radiation of a CO_2 laser (often accompanied by relaxation and heating of the hydride); 2) by chain reactions induced by the absorption of photons with an energy greater than 4 eV; and 3) by optical breakdown of the gas. The last method is apparently complicated by the fact that the threshold conditions of breakdown and the stability of the laser plasma depend to a marked extent on the local composition of the gas and the hydrodynamic characteristics of the system.

III. Deposition of metals

In modern industry, the deposition of metals from the gas phase by the reduction of halides using hydrogen has acquired the greatest importance. In laser-induced chemical deposition, decomposition reactions have found preferential application.

Copper has been deposited from its bis(hexafluoroacetylacetonate) at pressures of 1.3 Pa [87] or 0.4 Pa [88] on silica supports heated by the radiation of an Ar^+ laser. The volume rate of deposition increased from 50 $\mu m^3 s^{-1}$ to 300 $\mu m^3 s^{-1}$ with increase in I from 400 kW cm^{-2} to 600 kW cm^{-2}. The main impurity was oxygen (up to 10 mass %). Au was deposited similarly from its dimethyl(pentane-2,4-dionate) at a pressure of 1.0 Pa; at I = 400 kW cm^{-2} the rate of the process was 1 $\mu m\ s^{-1}$.[89]

Zinc and cadmium have been deposited using $ZnMe_2$ and $CdMe_2$. The thermal and spectral properties of these compounds are similar,[90,91] so that they show identical behaviour in laser decomposition processes. These processes can be examined for the case of the deposition of cadmium.[48,92–104]

The radiation of a Kr^+ laser with λ = 520.8–568.2 nm has been used to heat GaAs supports.[98] At W = 70–300 mW and d = 10 μm the temperature of the support was 235–1000 °C. The process was carried out by decomposing $CdMe_2$ at atmospheric pressure in a hydrogen carrier; the partial pressure of $CdMe_2$ was 20 Pa. The cadmium deposit obtained at T_s < 550 °C was formed within the focal spot. At higher values of T_s, the deposition also took place beyond its limits. A typical rate of deposition was 20 nm s^{-1}.

When radiation with a shorter wavelength, λ = 257 nm, was used, the process took place mainly by the non-thermal decomposition of $CdMe_2$, and mainly in the gas phase, and not in the adsorbed layer. The rate of deposition was linearly dependent on the partial pressure of $CdMe_2$ and the intensity of the irradiation. At I > 2 W cm^{-2}, a deviation from the linear relationship towards lower values of v was observed, due to the decreased concentration of the reagent in the volume of the laser beam. The addition of an inert gas led to a sharp decrease in the total rate of deposition as a result of the decreased rate of gas-phase diffusion of atomic cadmium to the surface of the support. Under these conditions, the role of adsorbed $CdMe_2$ increased, with a simultaneous increase in the sensitivity of the process towards energetic non-uniformity of the surface and interference of the incident and reflected laser beams.[97]

When radiation with λ = 193 nm was used, the deposition took place only as a result of the decomposition of $CdMe_2$ in the gas phase.[99] The concentration of Cd in the gas phase on irradiation with a pulse ArF laser was proportional to I, corresponding to single-stage photodissociation. A definite role was also played, however, by processes in the adsorbed layer, which the authors cited[99] called "prenucleation". In an experiment in which the support (Si or SiO_2) was kept in a $CdMe_2$ atmosphere, the

non-adsorbed $CdMe_2$ was removed, and the support was irradiated by a beam with a characteristic shape, the formation of a deposit was not observed. The reaction vessel was then filled with $CdMe_2$ again to a pressure of up to 0.20 kPa, and the support was irradiated by a broad uniform beam. This gave a deposit whose shape coincided with that of the beam used in the first stage of the experiment. If however in the first stage the irradiated support did not carry an adsorbed layer of $CdMe_2$, a deposit with the characteristic shape was not formed in the second stage.

Aluminium has been obtained by decomposing the compound $AlC_{12}H_{27}$,[105,106] but more frequently by decomposing $AlMe_3$.[10,11,14,98–100,105–110] As with $CdMe_2$, several types of radiation have been used for the deposition.

For example, when a GaAs support was heated to 400 °C by the radiation of a continuous Kr^+ laser with λ = 520.8–568.2 nm, and a mixture of hydrogen and $AlMe_3$ with a partial pressure of 1.3 kPa was passed through the reaction vessel at atmospheric pressure, rods with a diameter of 20–90 μm were obtained at the focal spot.[98] The deposit contained amorphous Al and crystalline Al_3C_4. The length of the rods depended on the intensity of the radiation, and did not exceed 0.5 mm. The roughness of the surface of the rods obtained was attributed[98] to the turbulence of the gas stream. Change in the gas consumption from 1.0 litre h^{-1} to 4.4 litre h^{-1}, however, had no influence on the course of the process or the form of the deposit. The rate of growth of the rods decreased continuously with time (for example, in the first 120 s the rate decreased from 7 μm s^{-1} to 1 μm s^{-1}) as a consequence of the non-isothermal nature of the process; with increase in the thickness of the layer, the growth surface moved out of the focus, and the intensity of irradiation (and hence the temperature) decreased. When the beam was focussed at a point 30 μm from the surface of the support, an increase in the rate of growth to a maximum value at the focus of the laser beam was observed at first, after which the rate decreased.

In the range 442–460 nm, $AlMe_3$ has three absorption bands at 443.6, 445.1, and 446.2 nm. Radiation with these wavelengths has been used to deposit aluminium.[100] A potential of up to 2 kV was applied to the support to attract the ions. The latter reached the surface having a higher energy, and this increased considerably the quality of the coatings obtained.

Radiation with λ = 257 nm did not lead to heating of a support of silicon or its oxide, but acted directed on $AlMe_3$ in the gas phase or in the adsorbed layer.[10] At room temperature and a pressure of several hPa, trimethylaluminium is extensively dimerised. The quantum yield of aluminium in the gas phase was appreciably lower than that in the adsorbed layer.

At λ = 248 nm, Al atoms in the gas phase are formed by a cascade process, each stage of which is initiated by one-photon absorption.[109] The main chain of transformations is described by the scheme

$$Al_2Me_6 \rightarrow AlMe_3 \rightarrow AlMe_2 \rightarrow AlMe \rightarrow Al.$$

C_2H_6 is a side product of the deposition.

An advantage of the use of radiation with λ = 193 nm is that when it is directed on to the surface, a high quantum yield is achieved in the non-thermal photo-desorption of methyl groups. This makes it possible to obtain highly pure aluminium.[107]

The reactions of $GaMe_3$ and $InMe_3$ in the visible and ultraviolet ranges are similar.[111–113] The deposition of In by the decomposition of InI at λ = 193 nm has also been proposed.[114] The deposit, with a thickness of 0.3 μm, did not contain iodine.

Tetraethyllead has an absorption band at 242 nm, and is characterised by an appreciable photon absorption cross-section at 257.3 nm. The rate of deposition of lead at this wavelength is directly proportional to the $PbEt_4$ pressure and the intensity of the radiation; at p_{PbEt_4} = 500 Pa and I = 600 W cm^{-2}, the rate of deposition reaches 8 nm s^{-1}.[115] Increase in the partial pressure of He from 13.3 kPa to 79.8 kPa leads to an almost two-fold decrease in the rate of deposition. This is due to the decrease in the rate of diffusion of Pb atoms in the gas phase, which indicates that a predominant role is played by photolytic decomposition.[115]

Titanium has been obtained by decomposing its tetrachloride on supports of $LiNbO_3$ and SiO_2 at the focal spot (d = 4 μm) of a quasi-continuous Ar^+ laser (W = 5 mW, λ = 257 nm).[32] At an intensity of radiation of 50 kW cm^{-2}, the temperature in the spot did not exceed 30 °C. In the opinion of the authors cited,[32] the main reactions take place in the adsorbed layer. Irradiation of gas with a high concentration of the tetrachloride ($\geqslant$1.0 kPa) or gas containing hydrogen leads to the reduction of $TiCl_4$ to $TiCl_3$ and its deposition on the surface of the support as "hail". Sharp focussing of the radiation on the surface suppresses the gas-phase deposition, and the reactions in the adsorbed layer are complete with the formation of metallic titanium. In this case the deposition mechanism is possibly autocatalytic.[32]

Chromium can be obtained by decomposing its hexacarbonyl.[14,116–119] The use of radiation with λ = 248 nm gave black fragmentary films with a columnar structure in an assembly with the parallel configuration, and light silvery coatings in an assembly with the perpendicular configuration.[14] The main impurity was oxygen (up to 7 mass %), but its concentration can be decreased by using an improved reactor and an improved vacuum system.

The decomposition of $Cr(CO)_6$ under the influence of radiation with wavelengths of 193, 249, and 308 nm has been carried out with both the parallel and the perpendicular relative arrangements of the beam and the support.[118] In the last case, coatings with strong adhesive power were obtained on quartz, Pyrex, Suprasil, and aluminium. At τ = 10 ns, E = 8–12 mJ, and ν = 10–60 Hz, the pulse rate of deposition was independent of ν, and had the values 0.010, 0.028, and 0.005 nm $pulse^{-1}$ for λ = 193, 249, and 308 respectively (the thickness of the coatings did not exceed 300 nm).

Japanese workers[119] obtained chromium films on an assembly with the perpendicular configuration (λ = 248 nm, ν = 50 Hz, I = 1–9 MW cm^{-2}, average energy density 140 J cm^{-2}). The quartz support was not heated specially during the process. The deposition was carried out from argon at atmospheric pressure and $p_{Cr(CO)_6}$ = 40–90 Pa. The deposits contained approximately 50% chromium, 20–50% oxygen, and up to 30% carbon, depending on the intensity of the radiation. The films with the lowest concentration of oxygen had a metallic lustre and strong adhesive power, but their electrical conductivity was lower than that of chromium by a factor of 500. The purity of the films obtained was much lower than that of the coatings described by Boyer and co-workers,[14] apparently due to the high partial pressure of Ar in the reactor.

Molybdenum has been obtained from $Mo(CO)_6$.[14,116,118,120,121] At a low temperature of the support, the deposit contained large quantities of oxygen and carbon. Thus the pulse irradiation (λ = 248 nm) of molybdenum carbonyl adsorbed on Si (100) gave at 150–200 K a deposit with the composition $MoCO_{0.3}$ with a quantum yield close to 1.[120] By comparing the deposition processes taking place at room temperature under the influence of radiation with λ = 157, 193, 248, and 308 nm, Solanki and co-workers[116] found that the lowest concentration of carbon in the deposit and the

highest rate of deposition were achieved at 248 nm. According to Flynn and co-workers,[118] however, the rate of deposition at 193 nm is slightly greater than that at 248 nm.

The deposition of Mo by the optical breakdown of the gas using the radiation of a pulse CO_2 laser has been described.[121] Argon was added to the gas to facilitate breakdown.

Tungsten deposits have been obtained by two reactions: by decomposing tungsten carbonyl,[14,116,118,122] and by reducing tungsten hexafluoride with hydrogen.[122–127]

The deposition of tungsten from its carbonyl is similar to that of molybdenum. The rate of deposition at 257 nm increases in proportion to the increase in I to 1 kW cm^{-2} (Fig. 5). At λ = 193 nm, other conditions being equal, the rate of deposition is three times greater.[118]

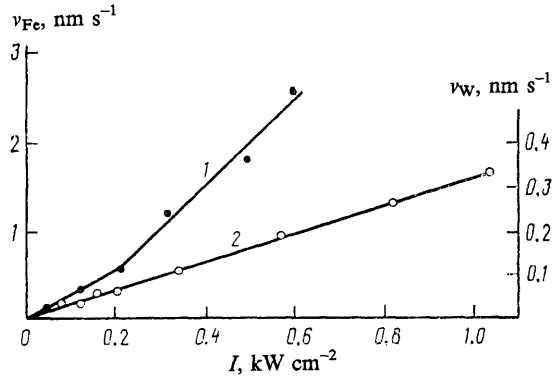


Figure 5. Dependence of the rate of deposition of W (*2*) and Fe (*1*) on a quartz support on the intensity of radiation with λ = 257 nm at pressures $p_{W(CO)_6}$ = 27 Pa and $p_{Fe(CO)_5}$ = 67 Pa.[128]

Tungsten has been deposited from WF_6 by irradiating a quartz support with a CO_2 laser with a power of 40 W.[122] Under these conditions, the greatest thickness of the tungsten film obtained was limited to 250–500 nm, depending on the conditions of irradiation and the concentration of the reagents. Three stages of the process are readily distinguished: 1) induction, 2) intensive, 3) attenuated. The duration of the induction stage decreases with increase in the radiation power; this can be attributed to the increased rate of attainment of the "threshold temperature" of the surface of the support. The second stage is short; it corresponds to the attainment of the maximum rate of deposition, the magnitude of which depends on I (or more accurately on T_s) and p. The decrease in the rate of deposition in the third stage is due to the decrease in the temperature of the support as a result of the reflection of the radiation by the tungsten film formed. Increase in the intensity of the radiation should of course have led to continuation of the deposition process, but this possibility was not studied experimentally.

The deposition of tungsten on a silicon support heated by the radiation of a Kr^+ laser (λ = 468–530 nm), not absorbed by the gaseous reagents (p_{H_2} = 53.2 kPa, p_{WF_6} = 26.6 kPa), has been described.[123] The beam with a power of 3–4 W was focussed on the support to give a spot with a diameter of 20 μm, and moved over the surface at a rate of 0.2–2.0 mm s^{-1}. With slower movement and a power greater than 4 W, fusion of silicon was observed. Since in the wavelength range used Si and W have similar absorbing power, it was possible to obtain thick deposits and to grow coatings by repeated irradiation. Similar results were obtained by other workers.[126]

Manganese has been obtained by decomposing $Mn_2(CO)_{10}$ under the influence of radiation with a power of 1–40 mW (λ = 337.4–356.4 nm, I = 3–150 kW cm^{-2}). When the beam scanned a ZnS support heated to 100 °C, bands of Mn with a thickness of 30–800 nm were deposited.[129]

$Fe(CO)_5$ has been used to obtain iron coatings.[122–124,127] The irradiation of a quartz support with a CO_2 laser with a power of 5.5 W gave the same self-limiting process as in the deposition of tungsten from its hexafluoride. Thus at $p_{Fe(CO)_5}$ = 3.6 kPa, the thickness of the film after 3 ms was 50 nm, which did not increase on subsequent irradiation. An interesting feature is that for a lower radiation power, the growth was more prolonged; for example, for a radiation power of 2.2 W, a coating with a thickness of 1 μm was formed in 1 s. The radiation of an Ar^+ laser has also been used to heat the support.[130]

In the ultraviolet range, photolytic deposition of iron takes place. The use of radiation with λ = 257 nm led to the continuous growth of the deposit at a rate which depended on the intensity of the radiation (see Fig. 5). The break on the straight line apparently indicates a change in the deposition mechanism.[128] The decomposition of $Fe(CO)_5$ has also been carried out using the fourth harmonic of a neodymium laser (λ = 266 nm, τ = 15 ns, ν = 25 Hz, W = 0.01–0.3 mW).[131] The film, deposited in a focal spot with d = 150 μm, had strong adhesive power, but the film deposited beyond the spot had low adhesive power. This indicates that the deposition was not due to the thermal decomposition of the carbonyl. The rate of deposition at p = 130 Pa and W = 0.25 mW was 0.25 nm s^{-1}; it decreased non-linearly with increase in the Ar pressure to 80 kPa, and increased in proportion to p and W. In the opinion of the authors cited, this indicates an unsaturated one-photon decomposition mechanism.

Nickel has been deposited from $Ni(CO)_4$.[8,123,124,132–136] When a quartz support was irradiated by a low-power CO_2 laser, self-limitation of the deposition was observed.[123,124,132,136] The maximum rate of deposition increased non-linearly with increase in the power from 0.3 μm s^{-1} at W = 0.4 W to 3 μm s^{-1} at W = 2 W. The dependence of the duration of the induction stage on the intensity of the radiation indicates that the reaction rate is determined not only by the temperature of the support. For a high value of I, a decisive influence on the course of the deposition may be shown by the rates of nucleation and the gas-phase reactions.[124] The activation energy of the deposition of nickel on steel, glass, and silicon supports was 90 kJ mol^{-1}, which is characteristic of a pyrolytic process. When the radiation of a Kr^+ laser was used, the diameter of the undulating deposit was much greater than the value of d, and increased during continuous radiation, evidently as a result of the heating of the non-irradiated parts of the support due to its thermal conductivity. The dependence of the rate of growth of the Ni rods on I is shown in Fig. 6. It can be seen from Fig. 6 that deposition does not take place below a certain threshold value of I. This is followed by a plateau, on which the rate of deposition remains unchanged, after which it begins to increase with subsequent increase in I. When helium, which has a high thermal conductivity, is added to the reactor, the rate of deposition decreases as a result of

the cooling of the surface by the increase in the removal of heat.[133,135] The nickel specimen obtained in this way does not contain carbon (accuracy of the determination 1%). Its electrical resistance is 1.9×10^{-5} Ω.cm (three times the tabulated value), indicating that the deposit is highly pure.

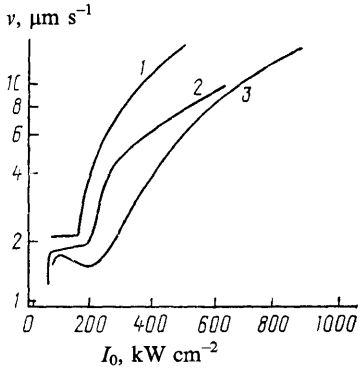


Figure 6. Dependence of the rate of growth of Ni rods on the intensity of the radiation at $p_{Ni(CO)_4}$ = 40 kPa and different focus spot diameters, μm: *1*, 22, *2*, 27, *3*, 13.5; in the experiments corresponding to curve *2*, He was added to $Ni(CO)_4$ (p_{He} = 53.3 kPa).[133]

Platinum has been deposited from $Pt(PF_3)_4$ at a pressure of 60 Pa on silicon, aluminium, graphite, quartz, and copper supports using a pulse Kr^+ laser.[137,138] The yield of the deposit decreased in the order of the supports given above (energy density in each pulse 200 mJ cm^{-2}). The quantum yield of platinum amounted to thousandths of the original quantity of $Pt(PF_3)_4$ (for example, 3.7×10^{-3} on the aluminium support). It was shown that the deposition takes place under the influence of electrons produced by the interaction of the laser radiation with the surface of the support.[137,138] The similar decomposition of $Fe(CO)_5$ and $CoEt_2(CO)_2$ under the influence of slow photoelectrons on the irradiation of glass and silver supports with the light of an Xe–Hg lamp (λ = 200–400 nm) has been described.[139] The other reactions examined above possibly also take place by this photoelectron mechanism.

Thus the metals of groups I, II, and III are most frequently deposited from organometallic compounds, and metals of groups VI, VII, and VIII from their π-complexes. The efficiency of the photolytic decomposition of these compounds at different values of λ correlates with the form of the absorption spectra. The deposits generally contain appreciable quantities of carbon and oxygen, which apparently originate in the ligands and in the air entering the reaction vessels. Dilution of the reagents with large quantities of inert gases leads to a significant decrease in the total rate of deposition and in the purity of the deposits. In contrast to the deposition of non-metals, an additional photoelectron mechanism operates in the deposition of metals.

IV. Deposition of inorganic compounds

Silicon carbide has been deposited using a CO_2 laser and a mixture of H_2 and $SiMeCl_3$.[9,50] Radiation with a power of 25 W was focussed on the surface of W, SiC, C, SiO_2, and ZrO_2 supports, so that the temperature reached 1100–1450 °C. The rate of deposition was directly proportional to p_{SiMeCl_3} in the range 0.27–13.3 kPa and inversely proportional to p_{H_2} in the range 0–10.6 kPa. The material of the support had no influence on the rate of deposition at a deposit thickness greater than 1.0 nm. The value of E_a in the absence of H_2 was 335 kJ mol^{-1}, and at p_{H_2} = 13.3 kPa, E_a was 400 kJ mol^{-1}. In the opinion of the authors cited,[9,50] the limiting stage was the decomposition of the methyl radical. The deposit was polycrystalline, and the particle size depended on the temperature of the process. Silicon carbide has also been obtained by decomposing $SiMeCl_3$ and $SiMe_2Cl_2$ on crystalline glass supports heated by the beam of an Ar^+ laser.[140] The rate of growth of the rods reached 70 μm s^{-1}. Stoichiometric SiC was deposited from $SiMe_2Cl_2$ in a nitrogen atmosphere. In a CO_2 atmosphere, codeposition of silicon and its dioxide took place. The decomposition of $SiMeCl_3$ in a stream of nitrogen led to the formation of graphite.

SiC powder has been synthesised from a mixture of SiH_4 and C_2H_4, which absorb radiation with λ = 10.59 μm.[141] In the tubular reaction vessel, the beam of a CO_2 laser with a diameter of 6 mm was directed at right angles to the stream of reagents. At the point of intersection, I = 530 W cm^{-2}, and T_g = 1100 °C. In a narrow beam (d = 2 mm) the corresponding values were 5.25 kW cm^{-2} and 1550–1750 °C. Since the time for which the reagents were in the reaction zone was constant, the diameter of the particles of the powders obtained showed little scatter. The chemical composition of the deposit could be varied by altering the reagent ratio, pressure, and intensity of the radiation.[141]

The formation of surface periodic structures from a mixture of SiH_4 and CH_4 at the points of a surface interference wave at λ = 9.27 μm has been described.[142]

The deposition of titanium carbide[127,132,143] using a carbon steel support required the powerful radiation of a CO_2 laser (0.5–1.2 kW in a spot with d = 1–2 mm). The original mixture consisted of $TiCl_4$ (1.6 kPa), CH_4 or C_2H_2 (26.6 kPa), and, sometimes, H_2 (26.6 kPa). The presence of H_2 was not necessary for the deposition of the carbide.

Titanium silicide was obtained similarly using SiH_4 instead of the hydrocarbon.[144–147] The single-crystal silicon support was heated to 400–500 °C by the radiation of a CO_2 laser with a power of 160 W. In addition, the gas was irradiated by an ArF laser (I = 100 MW cm^{-2}). Increase in the molar ratio SiH_4:$TiCl_4$ from 3 to 18 led to a change in the Si:Ti ratio in the deposit; for example, at T_s = 400 °C this ratio changed from 1.0 to 2.3. The silicide was amorphous at 400 °C, and partly crystalline at 450 °C and 500 °C. The concentration of oxygen in the deposit was 2–4 at.%, and the chlorine concentration 0.2 at.%.

Zinc oxide has been deposited in an assembly with the parallel configuration from a mixture of dimethylzinc and oxides of nitrogen, using radiation with λ = 248 nm with N_2O, and radiation with λ = 193 nm with NO_2.[14,148] The highest purity of ZnO and the highest rate of its deposition were achieved at a total pressure of 266 Pa and a $ZnMe_2$ partial pressure of 4.0 Pa. The temperature of the support varied from 20 °C to 220 °C. The coatings, with a thickness of 0.5 μm, contained less than 1% carbon and traces of nitrogen. Increase in the ratio $ZnMe_2$:NO_2 led to a change in the stoichiometry of the deposit, and this was reflected in its electrical conductivity

(the extreme values of the electrical conductivity differed by a factor of 10^4).

Aluminium oxide was deposited similarly. 50–1000 $cm^3 s^{-1}$ N_2O, 100 cm^3 s^{-1} He, and $AlMe_3$ at a partial pressure of 10.6 Pa were passed through the reaction vessel at a pressure of 133 Pa.[149] A blue fluorescence was observed along the laser beam. The rate of deposition was approximately 200 nm min^{-1} at W = 10 W and λ = 248 nm. At W = 8.2 W and λ = 193 nm, the rate was higher, but the deposit was less uniform along its thickness. The coatings obtained at a rate of deposition of 1 μm min^{-1} separated from the support on contact with air. Loose grey films were obtained at a high rate of deposition. The best coatings, containing less than 1% carbon, were obtained at T_s = 450 °C, p_{AlMe_3} = 10–15 Pa, and an N_2O consumption of 200–800 cm^3 s^{-1}.

Al_2O_3 was deposited from a mixture of $AlMe_3$ and NH_3 at a support temperature below 100 °C (radiation with λ = 193 nm was used).[150] The source of oxygen was the air entering the reactor. At a support temperature above 100 °C, ammonia became chemically active, and up to 400 °C the deposit formed consisted of a mixture of Al_2O_3 and AlN.

The preparation of indium and gallium oxides by methods similar to that used for Al_2O_3 has been proposed.[149]

Silicon oxide has been deposited in an assembly with the parallel configuration by irradiating a mixture of SiH_4 and N_2O using an ArF laser (λ = 193 nm).[14,151] At a pulse frequency of 100 Hz, the average intensity of the radiation was 40 W cm^{-2}. The laser beam passed over the support at a distance of 0.3 mm. The pressure in the reactor did not exceed 1.0 kPa. The consumption of N_2O was 800 cm^3 s^{-1}, and the consumption of N_2 containing 5% SiH_4 was 70 cm^3 s^{-1}. The silicon support was heated from 20 °C to 600 °C. The deposits obtained at temperatures up to 200 °C appeared non-uniform, and readily separated from the support. At $T_s \geqslant$ 250 °C, uniform strong deposits were obtained. The rate of deposition reached 5 nm s^{-1}. The concentration of nitrogen (as Si_3N_4) was less than 5 mass %, and the concentration of hydrogen (combined with Si atoms) was 1–4 at.%.

SiO_2 coatings were obtained similarly.[152] The laser beam has a cross-section of 5 × 20 mm, and the pulse frequency was varied from 3 Hz to 70 Hz. The dependence of the rate of deposition v on the partial pressure of N_2O was non-linear, and had a maximum at p_{N_2O} = 3.0 kPa. The rate was directly proportional to the power of the pulses. The rate of deposition was also influenced by the $N_2O:SiH_4$ ratio. With increase in the latter, the rate increased, but only to a limiting value. This saturation phenomenon is due to the existence of a limit to the transport properties of SiH_4. According to some authors,[152] the highest rate of deposition was observed at $N_2O:SiH_4$ = 50, and according to others,[153] at $N_2O:SiH_4$ = 20 (deposition in the absence of N_2 diluent). Analysis of these values led the authors cited[152] to the conclusion that the quantum yield of the photodissociation of N_2O is close to 0.01, but that the O atoms liberated in turn initiate the additional dissociation of N_2O or react with N_2O to form more photosensitive compounds, for example NO or NO_2. As a result, the extent of the transformation of N_2O to yield O is increased two-fold.

Titanium oxide has been obtained by the reaction of $TiCl_4$ with CO_2 in hydrogen by heating a quartz support by the radiation of a carbon dioxide laser with a power of 5–10 W.[6,8,127,132,144] The partial pressure of the reagents was $TiCl_4$ 1.65, CO_2 2.73, and H_2 2.73 kPa. The rate of deposition had values of 30–100 nm s^{-1} (d = 0.8–3.0 mm, τ = 0.1–1.0 s). Titanium dioxide absorbs radiation more strongly than SiO_2, so that repeated pulse irradiation of the same section of the surface gave a thicker deposit than continuous irradiation with the same duration. Moreover, on continuous irradiation the form of the surface of the deposit resembled a Gaussian curve, whereas on pulse irradiation (for example with 20 pulses in 0.1 s), the deposit had the form of a plateau; this can apparently be attributed to the ratio of the rates of diffusion and heat transfer.

Titanium oxide can be obtained by decomposing oxygen-containing organometallic compounds, for example $Ti(OCHMe_2)_4$.[154]

The laser-induced decomposition of CrO_2Cl_2 has been studied.[155] Radiation with λ = 488–515 nm was focussed on a spot with a diameter of 5 mm or 2 mm on supports of glass, fused SiO_2, or single crystals of Si and Al_2O_3. The radiation power varied from 1 mV to several W, and the CrO_2Cl_2 pressure was 13 Pa. Mass spectrometry detected an appreciable quantity of chlorine atoms in the irradiated gas. This indicates an appreciable rate of photolytic decomposition of the oxide chloride, although CrO_2Cl_2 itself absorbs at λ = 420 nm. To study the heterogeneous reactions, an irradiated fused SiO_2 support was placed in the chamber of the mass spectrometer, and the measurements were made during the reaction. The deposition took place in three stages. In the first stage, which lasted tens of seconds, slow growth of the CrO_2 film took place, and this process was accompanied by the production of a small flux of chlorine atoms. The deposition apparently involved the decomposition of CrO_2Cl_2 molecules in the gas phase or in an adsorbed layer. In the second stage, the flux of the species Cl, Cl_2, and O_2 increased sharply. The increase in the rate of the process was due to the thermal activation of the decomposition of CrO_2Cl_2 as a result of local heating of the surface by the absorption of radiation by the deposit formed in the first stage. The spontaneous acceleration took place until the thickness of the deposit was greater than the characteristic thickness of the absorbing layer. This was followed by the third stage, characterised by a stationary rate of deposition with a new increased surface temperature. Since the deposit contained Cr_2O_3, and O was detected in the gas phase, in the second and third stages the deposition was accompanied by the thermal decomposition of CrO_2, which takes place at temperatures above 400 °C. At a radiation intensity lower than 1 W cm^{-2}, only the dioxide was deposited.

Experiments carried out with the radiation of an excimer laser (λ = 193 nm) at a CrO_2Cl_2 pressure of 13 Pa showed that the composition of the deposit can be regulated by adding HCl to the gas phase; the deposit had the composition $CrO_{0.83}$ at an HCl pressure of 26.6 kPa, and $CrO_{1.5}$ in the absence of hydrogen chloride.[155]

Films of WO_3 or Fe_3O_4 have been deposited by irradiating (λ = 308 nm) a mixture of NO_2 with $W(CO)_6$ or $Fe(CO)_5$ in a reactor heated to 50 °C.[156] The carbonyls were mixed with an inert gas (Ne or He), whose partial pressure was 70–90 kPa. The deposition of WO_3 was more rapid than that of Fe_3O_4, since the absorption cross-section of $W(CO)_6$ is almost 10^2 times that of $Fe(CO)_5$.

Aluminium nitride has been deposited in an assembly with the parallel configuration from a mixture of $AlMe_3$ and NH_3 (λ = 193 nm).[150] Ammonia reacted at a support temperature above 100 °C, and with increase in the support temperature to 400 °C the mole fraction of AlN in the deposit increased almost linearly, reaching 1. Practically pure nitride was deposited at 400–500 °C.

Amorphous films of silicon nitride were obtained in assemblies with the parallel configuration from a mixture of SiH_4 and NH_3.[157] The radiation of a CO_2 laser with a power of up to 160 W (λ = 10.6 μm) was used. The temperature of the Si support was

250–450 °C, and the pressure in the reactor 1.33–2.0 kPa. The Si:N ratio in the deposit depended on the reagent ratio, and was 1.2 at $SiH_4:NH_3$ = 1000. The infrared spectrum of the deposit contained bands characteristic of Si–N, Si–H, Si–O, and N–H bonds. The concentration of hydrogen in the deposit decreased with increase in the temperature of the support. The rate of deposition was low (15 nm min^{-1}), and independent of temperature.

Coatings were obtained[158] using a low-power ArF laser (W = 0.2 W). The rate of deposition of the coatings on an area of 7.5 cm^2 was independent of the temperature of the support (200 to 600 °C), and equal to 5 nm min^{-1}. A similar study[14] showed that the rate of deposition may reach 70 nm min^{-1} (temperature of the support 200–425 °C, pressure in the reactor 266 Pa, gas consumption (cm^3 s^{-1}): SiH_4 10, NH_3 10, N_2 50). The Si:N ratio in the deposit was less than 1, the hydrogen concentration 20–30 at.%, and the oxygen concentration did not exceed 5 at.%.

The deposition of indium phosphide from the trimethyl compounds (on supports of Si, InP, InGaAs, and GaAs) was carried out using an excimer laser (E = 100–200 mJ, τ = 15 ns, ν = 20 Hz).[159–161] The dependence of the nature of the deposition on the wavelength was studied at T_s = 323 °C, a total pressure of 0.8 kPa, and gas consumptions of (cm^3 s^{-1}): Me_3InPMe_3 9, PMe_3 38, H_2 150, and He 230. At 351 nm, the reagents were transparent, but a small quantity of deposit consisting of In and O was obtained. Radiation at λ = 248 nm was absorbed by $InMe_3$, so that mainly indium was deposited. At 193 nm, both reagents absorbed radiation strongly, and InP was deposited. A typical rate of deposition was 0.03 nm $pulse^{-1}$. The composition of the deposit depended on the photon flux: a phosphorus deficit was observed at 0.01–0.03 J cm^{-2}, and a deposit with the stoichiometric composition (InP) was formed at 0.1–0.3 J cm^{-2}. The deposit obtained for a low value of the flux was amorphous, but at values greater than 0.1 J cm^{-2} it was polycrystalline, with a particle size of 5–40 nm.

Gallium arsenide has been deposited by the reaction[143]

$$GaMe_3 + AsMe_3 + H_2 \rightarrow GaAs + 2CH_4.$$

The partial pressures of $GaMe_3$, AsMe3, and H_2 were 8.6, 13, and 20 kPa respectively. The SiO_2 support was heated at the focal spot (d = 0.6 mm) to 600–900 °C by the radiation of a CO_2 laser with a power of 2–3 W for 2–12 s. At W = 3 W, the deposition took place in a ring round the centre of the beam, and the deposit was not continuous even when the thickness reached several μm. The rate of deposition was 15–50 nm s^{-1}. The composition of the deposit varied form $GaAs_{0.37}$ to $GaAs_{2.4}$, depending on the irradiation conditions.

The deposition of GaAs was carried out at atmospheric pressure from a mixture of AsH_3 and $GaMe_3$ (or $GaEt_3$) by heating supports of single-crystal Si or GaAs to 500 °C with the beam of an Ar^+ laser (I = 1.5–35 kW cm^{-2}).[162,163] Scanning with the beam gave bands with a width of 1.5–500 μm and a thickness from 20 nm to 4 μm. Auto-epitaxy was observed at a growth rate lower than 2 nm s^{-1} (high rate of scanning and low exposure in one scanning cycle).

Stepwise layer growth of GaAs took place with the mixture of $GaMe_3$, AsH_3, and H_2 (total pressure 1 kPa) was supplied intermittently with a cycle duration of 4 s.[164] A section of the support was heated intermittently to 200–500 °C by the radiation of an Ar^+ laser. In this process, the proportion of deposited Ga was 1.0, and the activation energy was the same as that without irradiation (87 kJ mol^{-1}). A model of stepwise layer epitaxy, which assumes that photocatalytic decomposition of $GaMe_3$ takes place only on the surface As atoms (but not Ga atoms) was proposed.

The auto-epitaxy of GaAs in an $AsCl_3–Ga–H_2$ gas mixture was studied using excimer KrCl, KrF, XeCl, or XeF lasers at ν = 5–70 Hz.[165] Only the radiation with λ = 249 nm increased the rate of the process (for example by a factor of almost 4 at T_s = 600 °C and W = 1.7 W); the rate of deposition was proportional to the radiation power, and had values of 0.6–1.4 nm s^{-1}. The increase in rate is apparently due to the photolytic reduction of $AsCl_3$ by hydrogen to AsCl, as confirmed indirectly by the form of the infrared spectra.

Finally, it may be noted that there are three main methods for depositing compounds: 1) the simultaneous deposition of the elements of the compound being deposited (for example, from a mixture of SiH_4 and C_2H_4, or $GeMe_3$ and AsH_3); 2) the codeposition of a substance which is gaseous under the conditions of the experiment (oxygen, nitrogen) with another substance being deposited (for example from mixtures of $ZnMe_2$ and NO_2, or SiH_4 and NH_3); and 3) the decomposition of a complex compound with preservation of the bond between the elements being deposited [for example CrO_2Cl_2 or $Ti(OCHMe_2)_4$]. Formally, the reactions involving $MeSiCl_3$, Me_2SiCl_2, and Me_3InPMe_3 are of the last type, but in fact these compounds undergo preliminary decomposition in the gas phase, so that in reality they are of the first type.

V. Characteristics of laser-induced chemical deposition reactions

The experimental data examined reveal various characteristics of laser-induced chemical deposition from the gas phase.

1. These reactions require radiation with a definite wavelength. To transfer the molecules to higher vibrational levels, the wavelength of the radiation should lie in a relatively narrow range of values (about 0.1 μm). For example, the decomposition of silane by this method requires radiation with λ = 10.59 μm, and even at 10.55 μm the photolytic reaction does not take place. On the other hand, to transfer molecules to an excited electronic state, there is a restriction only on the maximum wavelength (minimum photon energy). The experimental data indicate that in this case it is appropriate to use photons with an energy 1.2–2.0 times the bond energy.

2. The principal parameters of the deposition: the intensity of the radiation, concentration of the reagents, pulse duration, and pulse repeat frequency, show clearly defined threshold values. Below these values, only gas-phase reactions, which probably have their own restrictions, can take place.

3. Deposition takes place most readily on irradiation of the support; prenucleation is observed close to the threshold parameters, that is a small quantity of new substances is apparently formed using the surface energy of the heterogeneous support. Another way of bringing about the process is by the irradiation of the gas close to the support, when the latter acts as a "sink" for the active species generated. Finally, the process takes place with the greatest difficulty in the reaction zone in the absence of any surfaces, since homogeneous nucleation requires a relatively high supersaturation.

4. Redistribution of the absorbed laser energy before the start of the chemical transformations leads to heating of the gas and transfer of the process to a known thermochemical path. Similarly, the absorption of radiation by the deposit formed makes probable a change from a photolytic to a pyrolytic mechanism (an example is

provided by the decomposition of chromium oxide chloride). If neither the support nor the deposit absorb radiation, the rate of the process is not sensitive to the temperature of the support; formally, this means that the apparent activation energy is zero.

5. In the deposition of compounds, their composition depends not only on the ratio of the starting materials but also on their comparative photo-activity; this provides an additional "lever" for controlling the properties of the substance obtained.

6. Under certain conditions, laser radiation leads to the formation of a plasma either as a result of optical breakdown of the gas or as a result of the emission of photoelectrons from the irradiated support, so that the deposition becomes strictly plasmochemical.

These characteristics are listed with traditional chemical deposition from the gas phase in mind.

VI. Possible applications of laser-induced deposition processes

The reactions examined are used mainly to obtain fine powders,[166–175] amorphous, polycrystalline, and single-crystal films (layers, coatings),[19,57,150,165,176–180] narrow bands of unlimited length,[50,123,133,154,181–183] regular surface structures,[184–186] and parts for drawing optical fibres.[187,188] These products have potential uses in powder metallurgy, solar energy, micro-electronics, radio technology, applied optics, and the technology of protective and decorative coatings. In each of these fields, a new technological method generally has to compete with several well established and intensively developing technologies. Thus a number of methods of deposition from liquid, gas, and plasma are used successfully to obtain fine monodisperse powders.[189] In micro-electronics, surface structures are deposited using ultraviolet and X-ray lithography, and continuous films are obtained by chemical reactions with gaseous reagents, including chemical deposition from the gas phase,[190] and also ion implantation.[191] In the preparation of elements based on *a*-Si:H, the main competing method is plasmochemical deposition.[192] Optical coatings are obtained by a range of methods: physical[193] and chemical[194] deposition, including atomisation in a glow discharge, ion-beam and magnetron atomisation,[195] and laser volatilisation.[196]

The lack of the required data makes it impossible to carry out a comparative economic evaluation of different methods. According to one estimate,[169] the cost of the production of 1 kg of silicon, silicon carbide, and silicon nitride powders in an assembly with an output of 50 ton per year using a CO_2 laser with a power of 1.5 kW is 5–25 dollars (the wide range of values is due to the difference in the cost of silane, whose contribution is considerable). The production of these powders might be economically advantageous with lasers operating for many hours (ideally, many days), but this is as yet impossible.

Thus it appears unlikely that there will be any significant practical application of laser-induced chemical deposition in the foreseeable future. The situation is slightly more optimistic for the small-scale application of this method to produce made-to-order integral circuits[197] and for the repair of photo-stencils.[198] Possible developments of the method are: 1) an increase in the number of substances that can be deposited; 2) the development of new methods for obtaining particles of relatively complex shape, for example tubes, beakers, springs, etc.; 3) the production of assemblies for obtaining coatings on planar surfaces with an area greater than 100 cm^2, and also on non-planar objects (spheres, rods, tubes, etc.); 4) the discovery of new methods for controlling the structure of the material being deposited; 5) the improvement of deposition methods to increase the uniformity of the properties of the products and the reproducibility of the results; and 6) the extension of theories of the mechanism of deposition and the modelling of specific processes.

VII. Summary

The main progress in the study of laser-induced chemical processes has been made in the decomposition of gaseous hydrides, organometallic compounds, and carbonyls. Two types of process, photolytic and pyrolytic, are developing rapidly, and to some extent supplement one another.[199] Important advantages of pyrolytic processes are the short time and the local character of the heating of the support. This to some extent prevents irreversible thermal transformations (degradation, recrystallisation of the support, etc.), decreases the risk of the formation of undesirable powdered deposits, and also makes it possible to intensify mass exchange in the deposition zone. Most progress will apparently be made in photolytic reactions in the ultraviolet range, where it is possible to select photon energies sufficient for the rupture of chemical bonds.

An independent direction of research is the study of the intramolecular selectivity of deposition processes, achieved, for example, by the two-stage infrared–ultraviolet dissociation of molecules.[200] Promising possibilities are provided by the use of extremely short (femtosecond) laser pulses[201] and multi-wave laser radiation with a mixture of inert gas halides.[202]

References

1. H Lydtin *Chem. Vapor Deposit.: Proc. 3 Intern. Conf.*, 1972, p. 121
2. R S Berg, D M Mattox *Chem. Vapor Deposit.: Proc. 4 Intern. Conf.*, 1973, p. 196
3. M Anderson *Microelectr. and Reliab.*, 1973, **12** 177
4. A M Ronn, B L Earl *Chem. Phys. Lett.*, 1977, **45** 556
5. C P Christensen, K M Lakin *Appl. Phys. Lett.*, 1978, **32** 254
6. W M Steen *Adv. Surf. Coating Techn. Proc. Intern. Conf.*, London, 1978
7. M Hanabusa, A Namiki *Appl. Phys. Lett.*, 1979, **35** 626
8. S D Allen *IEEE/OSA Conf. Laser Eng. and Appl.*, Washington, 1979, p. 43
9. D V Fedoseev, V P Dorokhovich, A P Lavrent'ev, et al. *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1976, **12** 1796
10. D J Ehrlich *J. Vac. Sci. and Technol.*, 1982, **21** 23
11. D J Ehrlich, J Y Tsao *J. Vac. Sci. and Technol.*, 1983, **B1** 969
12. N Tsukada, et l. *Appl. Phys. Lett.*, 1983, **43** 189
13. D Baeuerle *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 19
14. P K Boyer, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 19
15. R T Young *Symposium on Energy Beam-Solid Interact. and Transient Therm. Processing*, New York, 1984, p. 217
16. Y Rytz-Froidevaux, et al. *Appl. Phys., Ser. A*, 1985, **37** 121
17. J G Eden *IEEE Circuits and Devices Mag.*, 1986, **2** 18
18. J E Greene, et al. *Nucl. Instrum. and Meth. Phys. Res., Ser. B*, 1987, **27** 226

19. I Gianinoni, M Musci *Nucl. Instrum. and Meth. Phys., Ser. A*, 1985, **239** 406
20. D Baeuerle *Laser und Optoelektron.*, 1985, **17** 29
21. M Hanabusa *Kagaku Kogaku*, 1985, **49** 711; Ref. *Zh. Elektronika*, 1986, 5G268
22. A Katayama *CEER Chem. Econ. and Eng. Rev.*, 1986, **18** 14
23. M Hanabusa *Rev. Laser Eng.*, 1984, **12** 526
24. M Hirose, S Yokoyama *Rev. Laser Eng.*, 1985, **13** 148
25. E Grunwald, D F Dever, P M Keene *Megawatt Infrared Laser Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1981, 135 pp.
26. V Daneu, J J J Yang in collected papers *Laser-Induced Chemical Reactions* (Translated into Russian), Izd. Mir, Moscow, 1984, p. 56
27. Yu N Molin, et al. *Infrakrasnaya Fotokhimiya* (Infrared Photochemistry), Izd. Nauka, Novosibirsk, 1985, 254 pp.
28. V V Teslenko *Izv. Akad. Nauk SSSR*, Neorg. Mater., 1989, **25** 1653
29. V M Krivoruchko *Poluchenie Tugoplavkikh Soedinenii iz Gazovoi Fazy* (The Preparation of Refractory Compounds from the Gas Phase), Atomizdat, Moscow, 1976, 120 pp.
30. E G Rakov, V V Teslenko *Khimicheskoe Osazhdenie iz Gazovoi Fazy* (Chemical Deposition from the Gas Phase), Izd. Znanie, Moscow, 1988, 47 pp.
31. A V Emyashev *Gazofaznaya Metallurgiya Tugoplavkikh Soedinenii* (The Gas-Phase Metallurgy of Refractory Compounds), Izd. Metallurgiya, Moscow, 1987, 207 pp.
32. J Y Tsao, et al. *Appl. Phys. Lett.*, 1983, **42** 559
33. R M Osgood, H H Gilgen *Ann. Rev. Mater. Sci.*, Palo Alto, 1985, **15** 549
34. J S Haggerty, W R Cannon in collected papers *Laser-Induced Chemical Reactions* (Translated into Russian), Izd. Mir, Moscow, 1984, p. 183
35. Japan. P 59-162 267; *Chem. Abstr.*, 1985, **102** 27032
36. Europ. P. 154 561; *Chem. Abstr.*, 1985, **103** 187368
37. US P. 4 579 750; *Chem. Abstr.*, 1986, **105** 15826
38. BRD P. 3 442 790; *Chem. Abstr.*, 1986, **105** 144609
39. Japan. P. 56-45 759; Ref. *Zh. Khim.*, 1982, **7** L132
40. Japan P. 60-96 759; *Chem. Abstr.*, 1985, **103** 164863
41. L A Ryabova, et al. *VI Vsesoyuznaya Konferentsiya po Rostu Kristallov* (Sixth All Union Conference on Crystal Growth), Izd. Nauka, Erevan, 1985, Vol. 2, p. 204
42. French P. 2 548 218; *Chem. Abstr.*, 1985, **103** 31249
43. T Meguro, et al. *Reza Kagaku Kenkun.*, 1984, **6** 207; *Chem. Abstr.*, 1985, **102** 157578
44. Japan. P. 60-240 122; *Chem. Abstr.*, 1986, **105** 160051
45. Japan. P. 61-30028; *Chem. Abstr.*, 1986, **105** 89147
46. Japan. P. 60-152 023; Ref. *Zh. Elektronika*, 1986, 8G153
47. Japan. P. 59-208 055; Ref. *Zh. Radiotekhnika*, 1986, 4E548
48. M Hanabusa *Techn. Rdsch.*, 1985, **77** 46
49. Japan. P. 60-53 015; Ref. *Zh. Elektronika*, 1986, 8A225
50. D V Fedoseev, I G Varshavskaya *V Vsesoyuznoe Soveshchanie po Nerezonansnomu Vzaimodeistviyu Opticheskogo Izlucheniya s Veshchestvom: Tezisy Dokladov* (Summaries of Papers Presented at the Fifth All Union Conference on the Non-resonance Interaction of Optical Radiation with Matter), Izd. Nauka, Leningrad, 1981, p. 285
51. D V Fedoseev, I G Varshavskaya *Nachtrag. Tagungsbd. 8. Tag. "Hochvakuum. Granzflaschen/Dunne Schichten"*, Dresden, 1984, p. 84
52. A V Verkova, et al. *Trudy Konferentsii po Elektronnoi Tekhnike. Seriya Elektronika SVCh* (Proceedings of the Conference on Electronics. Superhigh-Frequency Electronics Series), 1981, No. 1 (164), p. 38
53. G Leyendecker, et al. *Appl. Phys. Lett.*, 1981, **39** 921
54. D Baeuerle, G Leyendecker *Appl. Phys., Ser. B*, 1983, **28** 267
55. DDR P. 226 907; *Chem. Abstr.*, 1985, **104** 91562
56. L A Ryabova, Yu D Kalafati, I A Serbinov, et al. *Poverkhnost'*, 1987, (1) 141
57. R Bilenchi, et l. *J. Appl. Phys.*, 1982, **53** 6479
58. M Hanabusa *Thin Solid Films.*, 1983, **107** 227
59. V Baranauskas, et al. *Appl. Phys. Lett.*, 1980, **36** 930
60. R W Andreatta, et al. *Appl. Phys. Lett.*, 1982, **40** 183
61. D Baeuerle *Appl. Phys. Lett.*, 1982, **40** 819
62. R W Andreatta, et al. *J. Vac. Sci. and Technol.*, 1982, **20** 740
63. D Baeuerle *Appl. Phys., Ser. A*, 1983, **30** 147
64. T R Gattuso, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 215
65. R Bilenchi, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 199
66. R Bilenchi, et al. *Chem. Vapor Deposit.: Proc. 4 Eur. Conf. Eindhoven*, 1984, p. 194
67. A Yamad, M Konagai, K Takahashi *Japan. J. Appl. Phy.*, 1985, **24** Pt. 1, 1586
68. M Meunier, et al. *J. Non-Cryst. Solids*, 1983, **59–60** 699
69. J H Flint, et l. *Laser Assisted Deposit. Etching and Doping*, New York, 1984, p. 66
70. M Meunier, et al. *Symposium on Laser-Control. Chem. Proc. Surf.*, Boston, 1983, New York, 1984, p. 397
71. Y Pauleau, et al. *Symposium on Laser-Control. Chem. Proc. Surf.*, Boston, 1983, New York, 1984, p. 41
72. W R Imler *Laser-assisted Chemical Vapor Deposition of Hydrogenated Amorphous Silicon Alloys*, Berkeley, Univ. California, 1986, 92 pp.; *Chem. Abstr.*, 1987, **106** 76848
73. J M Jasinski, R D Estes *Chem. Phys. Lett.*, 1985, **117** 495
74. G Leyendecker, et al. *J. Electrochem. Soc.*, 1983, **130** 157
75. I Gianinoni, M Musci *J. Non-Cryst. Solids*, 1985, **77–78**, Pt. 2, p. 743
76. R Bilenchi, et al. *Appl. Phys. lett.*, 1985, **47** 279
77. H M Branz, et al. *Appl. Phys. Lett.*, 1986, **48** 171
78. A Yoshikawa, et al. *15 Conf. Solid State Devices and Mater. Tokyo*, 1983, p. 40
79. Japan. P. 60-107 824; *Chem. Abstr.*, 1986, **104** 13704
80. Japan. P. 60-109 220; *Chem. Abstr.*, 1986, **104** 27425
81. T Meguro, et al. *Japn. J. Appl. Phys.*, 1986, **25**(1) 524
82. T Toshihiro, et al. *Appl. Phys. Lett.*, 1986, **49** 971
83. J F Osmundsen, et al. *J. Appl. Phys.*, 1985, **57** 2921
84. Y Ishikawa, et al. *Appl. Phys. Japan.*, 1986, **55** 1177
85. J Blazejowski, F W Lampe *J. Appl. Phys.*, 1986, **59** 2283
86. M Stuke, R Fantoni *Laser Spectrosc. Proc. 7th Intern. Conf.*, Berlin, 1985, p. 414
87. F A Houle, C R Jones, T H Baum *Appl. Phys. Lett.*, 1985, **46** 204
88. C R Moylan, T H Baum, C R Jones *Appl. Phys., Ser. A*, 1986, **40** 1
89. T H Baum, C R Jones *Appl. Phys. Lett.*, 1985, **47** 538
90. C J Chen, R M Osgood *J. Chem. Phys.*, 1984, **81** 327
91. A M W Bakke *J. Mol. Spectrosc.*, 1972, **41** 1
92. Y Rytz-Froidevaux, et al. *Appl. Phys., Ser. A*, 1982, **27** 133

93. T H Wood, et al. *Laser Diagn. and Photochem. Proc. Semiconductor Devices*, New York, 1983, p. 35
94. T H Wood *Appl. Phys. Lett.*, 1983, **42** 409
95. S R J Brueck, D J Ehrlich *Phys. Rev. Lett.*, 1982, **48** 1678
96. R M Osgood, D J Ehrlich *Opt. Lett.*, 1982, **7** 385
97. C J Chen, R M Osgood *Phys. Rev. lett.*, 1983, **50** 1705
98. Y Rytz-Froidevaux, et al. *Phys. Lett., Ser. A*, 1981, **84** 216
99. D J Ehrlich, R M Osgood, T F Deutsch *Appl. Phys. lett.*, 1981, **38** 946
100. T F Deutsch, et al. *Appl. Phys. Lett.*, 1979, **35** 175
101. D J Ehrlich, et al. *IEEE J. Quant. Electr.*, 1980, **16** 1233
102. C J Chen, R M Osgood *Chem. Phys. Lett.*, 1983, **98** 363
103. C J Chen, et al. *Microsc. Semicond. Mater.: Proc. Inst. Phys. Conf.*, Oxford, 1983, p. 149
104. D J Ehrlich, R M Osgood *Chem. Phys. Lett.*, 1981, **79** 381
105. M Rodot, J E Bourree *Vide, Chouches Minees.*, 1985, **40** 339
106. G S Higashi, C G Fleming *Appl. Phys. Lett.*, 1986, **48** 1051
107. G S Higashi, L J Rothberg *J. Vac. Sci. and Technol., Ser. B*, 1985, **3** 1460
108. G S Higashi, et al. *Chem. Phys. Lett.*, 1985, **115** 167
109. T Motooka, et al. *J. Appl. Phys.*, 1985, **58** 4397
110. W R Iversen *Electronics*, 1986, **59**(7) 18
111. Y Rytz-Froidevaux, et al. *Symposium Laser Diagn. and Photochem. Process Semiconductor Devices*, New York, 1983, p. 29
112. M R Aylett, J Haigh, *Symposium Laser Diagn. and Photochem. Process Semiconductor Devices*, New York, 1983, p. 177
113. D Braichotte, H Van Den Bergh, *Helv. Phys. Acta*, 1986, **59** 1014
114. D B Geohegan, et al. *Symposium Laser-Control. Chem. Proc. Surf.*, New York, 1984, p. 93
115. M S Chiu, K P Shen, Y K Ku *Appl. Phys., Ser. B*, 1985, **37** 63
116. R Solanki, et al. *Appl. Phys. Lett.*, 1982, **41** 1048
117. T M Mayer, G J Fisanick *J. Appl. Phys.*, 1982, **53** 8462
118. D K Flynn, J I Steinfeld, D S Sethi *J. Appl. Phys.*, 1986, **59** 3914
119. H Yokoyama, et al. *Appl. Phys., Ser. A*, 1985, **37** 25
120. J R Creighton *J. Appl. Phys.*, 1986, **59** 410
121. T R Jervis, L R Newkirk *J. Mater. Res.*, 1986, **1** 420
122. S D Allen, A B Trigubo *J. Appl. Phys.*, 1983, **54** 1641
123. S D Allen, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 207
124. S D Allen, et al. *J. Appl. Phys.*, 1985, **58** 327
125. S D Allen, et al. *Symposium on Laser-Control Chem. Proc. Surf.*, New York, 1984, p. 1
126. G Q Zhang, et al. *J. Appl. Phys.*, 1987, **62** 673
127. S D Allen *Mater. Sci. Res.*, 1984, **17** 397
128. D J Ehrlich, et al. *J. Electrochem. Soc.*, 1981, **128** 2039
129. A H Kitai, G J Wolga *Symposium Laser Diagn. and Photochem. Process Semiconductor Devices*, New York, 1983, p. 141
130. R B Jackman, et al. *J. Appl. Phys.*, 1986, **59** 2031
131. N A Kislov, et al. *Laser/Optoelektronik*, 7, Berlin, 1986, 455
132. S D Allen *J. Appl. Phys.*, 1981, **52** 6501
133. W Krauter, et al. *Appl. Phys., Ser. A*, 1983, **31** 13
134. T R Jervis *J. Appl. Phys.*, 1985, **58** 1400
135. F Petzoldt, et al. *Appl. Phys., Ser. A*, 1984, **35** 155
136. S D Allen, et al. *J. Appl. Phys.*, 1986, **59** 1653
137. H Schröder, K L Kompa, D Masci *Appl. Phys., Ser. A*, 1985, **38** 227
138. BRD P. 3 526 830; *Chem. Abstr.*, 1986, **105** 138403
139. P M George, J L Beauchamp *Thin Solid Films*, 1980, **67** L25
140. V S Salun, I F Kanaev, et al. *Pis'ma Zh. Eksp. Teor. Fiz.*, 1987, **13** 823
141. Y Suyama, et al. *Am. Ceram. Soc. Bull.*, 1985, **64** 1356
142. F Shaapur, S D Allen *J. Appl. Phys.*, 1986, **60** 470
143. S D Allen, et al. *J. Vac. Sci. Technol.*, 1982, **20** 469
144. G A West, et al. *Appl. Phys. Lett.*, 1985, **47** 476
145. G A West, et al. *J. Vac. Sci. Technol., Ser. A*, 1985, **3** 2278
146. G A West, et al. *Conf. Lasers and Electro-Opt.*, Baltimore, Washington, 1985, p. 284
147. A Gupta, G A West, K W Beeson *J. Appl. Phys.*, 1985, **58** 3573
148. R Solanki, G J Collins *Appl. Phys. Lett.*, 1983, **42** 662
149. R Solanki *Appl. Phys. Lett.*, 1983, **43** 454
150. H Demiryont, et al. *J. Appl. Phys.*, 1986, **59** 3235
151. P K Boyer, et al. *Appl. Phys. Lett.*, 1982, **40** 716
152. A Tate, et al. *Appl. Phys., Ser. A*, 1985, **38** 221
153. H M Kim, et al. *Chem. Vapor Deposit.: Proc. 8th Intern. Conf.*, 1981, p. 258
154. G W Rice, *J. Am. Ceram. Soc.*, 1987, **70** 117
155. C Arnone, et al. *Appl. Phys.*, 1986, **48** 1018
156. M S Chiu, et al. *Lasers Manuf. Proc. 2nd Intern. Conf.:* Birmingham, 1985, Amsterdam, 1985, p. 295
157. C A West, A Gupta, *Symposium on Laser-Control Chem. Proc. Surf.*, Boston, 1983, New York, 1984, p. 61
158. T F Deutsch, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 129
159. V M Donnelly, et al. *J. Vac. Sci. Technol., Ser. A*, 1986, **4** 716
160. V M Donnelly, et al. *Appl. Phys. Lett.*, 1984, **44** 951
161. V M Donnelly, et al. *J. Appl. Phys.*, 1985, **58** 2022
162. S M Bedair, et al. *Appl. Phys. Lett.*, 1986, **48** 174
163. N H Karam, et al. *Appl. Phys. Lett.*, 1986, **49** 880
164. A Doi, et al. *Appl. Phys. Lett.*, 1986, **49** 785
165. J Nishizawa, et al. *J. Electrochem. Soc.*, 1985, **132** 1939
166. E T S Pan, et al. *Appl. Opt.*, 1987, **26** 70
167. L M Sheppard *Adv. Mater. and Process. Inc. Metal Progr.*, 1987, **131**(4) 53
168. W R Cannon, et al. *J. Am. Ceram. Soc.*, 1982, **65** 330
169. J S Haggerty *Inter. Conf. on Ultrastructure Proc. of Ceramics, Glasser and Composites*, New York, 1983, p. 353
170. J H Flint, et al. *Aerosol Sci. Technol.*, 1986, **5** 249
171. US P. 4 548 798; Ref. *Zh. Radiotekhnika*, 1986, 9E676P
172. US P. 4 558 017; *Chem. Abstr.*, 1986, **104** 134881
173. A Gupta, J T Yardley *Appl. Lasers to Indust. Chem.: Proc. SPIE*, Bellingham, 1984, p. 131
174. A Gupta, et al. *Laser Assisted Deposit and Doping*, Bellingham, WA, 1984, p. 94
175. G W Rice *J. Am. Ceram. Soc.*, 1986, **69** 183
176. Japan P. 61-12 868; *Chem. Abstr.*, 1986, **105** 15829
177. Japan. P. 61-84 379; *Chem. Abstr.*, 1986, **105** 138680
178. Japan. P. 60-92 474; *Chem. Abstr.*, 1986, **104** 93772
179. E W Sabin *Proc. Electrochem. Soc.*, 1986, **86-4**, 284; *Chem. Abstr.*, 1986, **104** 235164
180. H Demiryont, L R Thompson *Appl. Opt.*, 1986, **25** 1311
181. I P Hermann, et al. *Symposium on Laser Diagn. and Photochem. Process. Semiconductor Devices*, Boston, 1982, New York, 1983, p. 9
182. Y C Du, U Kempfer, K Piglmayer *Appl. Phys., Ser. A*, 1986, **39** 167
183. Y S Liu, et al. *J. Vac. Sci. Technol., Ser. B.*, 1985, **3** 1441

184. H H Gilgen, et al. *Symposium on Laser-Control Chem. Proc. Surf.*, New York, 1984, Vol. 29, p. 139
185. Japan. P. 60-107 824; Ref. *Zh. Khim.*, 1986, 12L38P
186. Japan. P. 60-126 820; *Chem. Abstr.*, 1986, **104** 27062
187. T F Morse, et al. *J. Lightwave Technol.*, 1986, **4** 151
188. Japan. P. 58-41 760; Ref. *Zh. Khim.*, 1985, 24M296P
189. M Haruta, B Delmon *J. Chem. Phys.*, 1986, **83** 859
190. E Reichmanis, L E Thompson *Ann. Rev. Mater. Sci.*, 1987, **17** 235
191. J F Gibbons *Nucl. Instr. Meth. Phys. Res., Ser. B.*, 1987, **21** 83
192. S A Endrikhovskii, et al. *Obzory po Elektronnoi Tekhnike* (Electronics Reviews), Ser. 6, 1986, No. 1 (1170), 60 pp.
193. V D Vvedenskii, V P Ryazanskii, G S Salishchev *Opt. Mekhan. Prom.*, 1987, (9) 47
194. B G Gribov, et al. *Opt. Mekhan. Prom.*, 1986, (5) 47
195. P J Martin *J. Mater. Sci.*, 1986, **21** 1
196. R Brauns, et al *Opt. Acta*, 1986, **33** 545
197. *Electron Prod. und Pruftechn.*, 1987, (4) 26
198. J K Tison, M G Cohen *Solid State Technol.*, 1987, **30** 113
199. V V Teslenko *Khimiya Plasmy* (Plasma Chemistry), No. 16, 1989, p. 98
200. A N Oraevskii *Khim. Vys. Energ.*, 1986, **20** 102
201. A Migus, A Antonetti, A Orszag *Recherche*, 1987, **18** 432
202. R A Sauerbrey, W L Nighan, F K Tittel *IEEE J. Quantum Electron.*, 1986, **22** 230