

Laser chemical vapour deposition

S K ROY

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

Abstract. The special role of lasers in material processing is outlined in this article. In the background of the various chemical vapour deposition processes, the laser-induced chemical vapour deposition processes have been described. The unique aspects of pyrolytic and photolytic laser chemical vapour deposition have been stressed. Some of the recent experimental results on thin film deposition by laser have been reviewed. The problems and future of laser deposition processes have also been mentioned.

Keywords. Laser; chemical vapour deposition; LCVD; thin film.

1. Introduction

In recent times lasers are being increasingly employed in various types of material processing. Diverse types of lasers are available over a wide energy spectrum in continuous wave (CW) or pulsed mode for such uses. The unique properties of the laser beam, e.g. coherence, spectral chromaticity, low divergence and tunability, contribute in giving a concentrated beam of large energy density (irradiance) in a chosen spectral region. In addition, the laser beam can be manoeuvred to the required place of use and can be focused according to requirements. These properties have led to the laser being used for analysis, synthesis, evaporation, etching, doping, etc. in material processing (Boyd 1983) as well as in many industrial processes like drilling, cutting, welding, etc. (Ready 1978). The use of lasers in the biological and medical fields is also well known.

The laser has proved to be an important tool in material processing both in the area of fundamental development and in industrial applications. Both attributes of a laser beam, viz. heat and light, have been utilized effectively in the laser processing of materials. Figure 1 is a block diagram showing the extensive network of laser processing techniques currently being employed or investigated for possible application in semiconductor manufacturing. The present review concerns a limited aspect of laser processing, viz. laser-induced chemical vapour deposition (LCVD). LCVD is becoming an interesting new area of research in material science. It has high potential as a technique for thin film deposition and is still in the research and development stage. In the next section, we will briefly describe general chemical vapour deposition (CVD) techniques and their variants and how they are related to LCVD. After that, we will review LCVD, the mechanism and applications, and the results obtained till now. The paper will conclude with general remarks on the future possibilities of LCVD processes as a viable technology.

2. General CVD processes and their variants

As opposed to the direct processes of physical deposition like evaporation,

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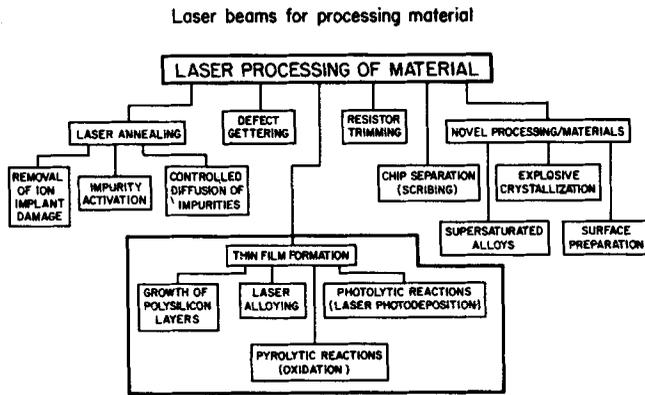


Figure 1. Block diagram showing extensive network of laser processing techniques.

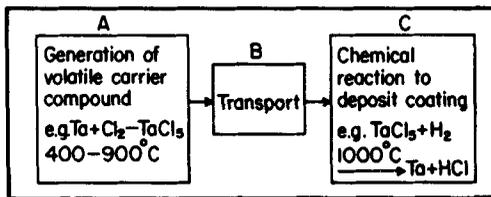
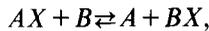


Figure 2. The basic steps in the CVD process.

sputtering, ion plating, etc. chemical vapour deposition (CVD) is a process of indirect deposition. CVD describes a broad group of processes (Powell *et al* 1966), all of which use a chemical reaction between two or more reactants in gaseous phase at or near a heated surface at a suitable temperature to produce the desired phase, a solid deposit of the material on a surface. The chemical reaction is essentially a thermal decomposition or reduction given by

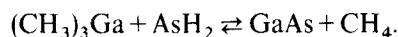


where AX is a halide and B is a reducing agent like hydrogen. General CVD consists of the three basic steps shown in figure 2: generation of volatile carrier compound, transport of volatile compound to the deposition zone, and the chemical reaction to form the solid product. The reactions are controlled by thermodynamics and thermodynamic equilibrium determines the product. A whole range of materials can be produced in thin-film mode. Originally CVD was extensively used for metallurgical coating because of its excellent work coverage, uniform reactant distribution and deposition, overall growth rate control and lower temperature growth (800–1000°C) compared to direct processes. The mechanism of growth is basically adsorption of reactants and chemical reaction controlled by diffusion and boundary layer around the surface of deposition. The growth rate depends essentially on the ratio of the partial pressures of reactants and products at a constant temperature of the surface.

The advancement of microelectronics has given a great fillip to the processing of semiconductor devices by the CVD technique. This has necessitated CVD production of semiconducting materials like Si and Ge in crystalline, polycrystalline and amorphous states, insulating materials like SiO_2 and Si_3N_4 , and metals like aluminium and tungsten and their silicides.

Low-pressure chemical vapour deposition (LPCVD) is an evolved version of CVD and can be used efficiently when product volume is more than the reactant volume. The reaction kinetics are qualitatively similar to that in atmospheric CVD, the difference being that the deposition chamber is operated at a sub-atmospheric pressure (0.3–1 torr), which results in changes in the hydrodynamics of reactant gas flow, thinner boundary layer, low temperature of operation (600–680°C) and higher surface diffusivity. The advantages are more uniform growth, lower growth rate and hence better controllability and large throughput.

Another improved variant of CVD, metal-organic chemical vapour deposition (MOCVD), is of recent interest and for special applications (Dapkus 1982). Metals that do not have simple inorganic compounds in gaseous phase, like Ga, In, Al, etc. are used in organic complex form. These are liquids with reasonable vapour pressure at or around room temperature. These compounds along with hydrides carried by a carrier gas can be jointly or severally dissociated to form compounds, stoichiometric or otherwise, that can be deposited on suitable substrates. The series of III-V compounds and alloys have been deposited by MOCVD. The reaction chemistry is pyrolysis with recombination at or near a heated surface. The typical reaction is the joint pyrolysis of a metal alkyl and a hydride, e.g.



The growth rate is related to the first order in partial pressure apart from the reactor effect for hydrodynamics of reactant flow. The layers grown have uniform composition at somewhat lower temperature (500–600°C) and very low growth rate, giving very good controllability and capability for abrupt ultra-thin junctions. The technique is eminently suited for fabrication of multilayered structures like superlattices, heterogeneous multilayer quantum wells (MQW) and a host of exotic thin-film structures.

The other variant of CVD, where a low-pressure chemical deposition is achieved with the introduction of plasma, is plasma-enhanced chemical vapour deposition (PECVD) (Hess 1986). In a suitable reactor chamber, the plasma ionizes the reactant gases by forming chemically active radicals, which, under the low pressure condition, undergo chemical reaction on the heated substrate. Nucleation of the deposit is facilitated by ion bombardment from the plasma. Deposition temperature is low (~400°C) compared to other CVD processes. The main advantages are: the technique can handle complex types of reactants which will not normally dissociate in CVD or LPCVD processes, surface diffusivity is excellent, and enhanced reaction rates are due to plasma. One of the shortcomings of the technique is the radiation damage due to plasma. This is often avoided by using remote control plasma instead of a direct one.

3. Laser-induced chemical vapour deposition (LCVD)

Like all the other CVD processes, LCVD is another approach to grow materials using the unique properties of laser outlined earlier. As will be clear in the following, LCVD promises various advantages over other CVD techniques especially in the field of microelectronics and general film growth. In some aspects there are qualitative similarities with some variants of CVD and in others the mechanism is quite different. Both attributes of the laser beam, viz. heat and light, have been

exploited in the deposition of materials by this variant of CVD (Solanki *et al* 1985; Mayo 1986). Thus LCVD can be broadly classified into two categories: pyrolytic LCVD (heat-thermal effect) and photolytic LCVD (light-wavelength effect). Figure 3 shows, schematically, the two mechanisms.

3.1 Pyrolytic LCVD

Figure 3a shows that in pyrolytic LCVD the laser light impinges upon the desired substrate, heating it locally over the beam area. Owing to the incident thermal profile of the beam, the surrounding reactant gas undergoes thermal decomposition and deposition takes place in a manner analogous to that in conventional CVD or LPCVD. Correct choice of laser can help avoid absorption in the reactant gases and aid heat absorption at the substrate surface. The spatially selective heating allows deposition at high pressure of reactant gases without gas-phase nucleation. It has been possible to deposit various materials, metals, semiconductors and insulators by this thermochemical heterogeneous reaction.

3.2 Photolytic LCVD

As figure 3b shows, in the photolytic LCVD technique the reactant gas molecules are photodissociated owing to absorption of photons of appropriate wavelength of the laser light. The beam, either by single or multi-photon absorption, excites particular vibrations of the reactant molecules and raise the internal energy to induce dissociation. The reactive species produced by such a process of bond breaking interact with substrate giving rise to the deposited film. Evidently, bond breaking is intrinsically efficient since energy is not randomly distributed throughout the internal degree of freedom of the molecules. This technique has also been used in deposition of different materials in thin film form.

3.3 Interrelationship between various CVD processes

Figure 4a shows the interrelationship between various processes including LCVD. Figure 4b shows the comparison between photo-LCVD and PECVD so far as the energy selectivity is concerned. Both these processes take place at lower temperature compared to other CVD processes, which are in essence thermally driven. The thermal dissociation reaction proceeds at a slower rate since most of the energy is spent in effecting the dissociation. On the other hand, PECVD and photo-LCVD are aided by electron/photon-induced dissociation. The narrow

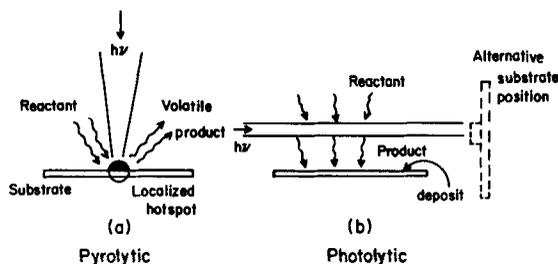


Figure 3. Schematic illustration of basic laser deposition mechanisms.

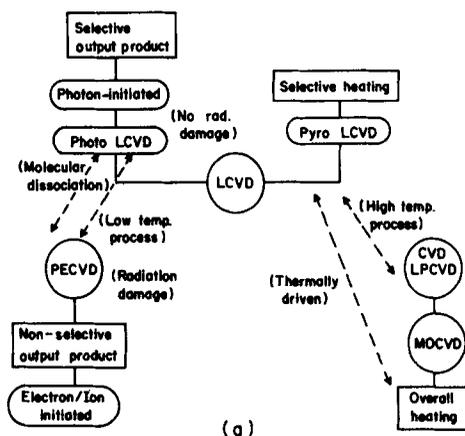
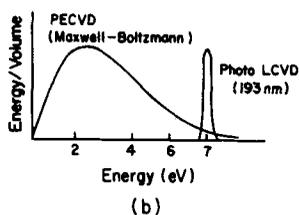


Figure 4. (a) Interrelationship between various CVD processes; (b) comparison between PECVD and photo-LCVD.



energy spectrum of photons allows dissociation into selective output channels unlike electron impact dissociation where electrons follow a broad Maxwell-Boltzmann distribution. In this respect, photo-LCVD is unique amongst the various CVD processes.

In general, idealized pyro- or photo-deposition may not be the actual case. At high intensity, deep UV can initiate a combination of thermal and photolytic chemistry. Alternatively, if a pyrolytic light source is at near-UV, photodissociation of a weakly bound complex may also occur.

3.4 Reasons for using LCVD

Though CVD has been in use for quite some time, the advent of microelectronics, specially very large scale integration (VLSI) circuits, has resulted in the development of the variants of CVD. These devices need low temperature processing to avoid a number of deleterious effects like wafer warping, inhibition of pattern transfer, defect generation and propagation, uncontrolled dopant diffusion, etc. Development of LPCVD and PECVD helped to mitigate some of the problems. On the other hand, LCVD, especially photo-LCVD, seems to have some advantages over other CVD processes, like additional flexibility and selectivity, low-temperature operation, plus well-defined, repeatable and controlled micro-region deposition capability. The pyro-LCVD, being due to a thermal effect, is suited to direct writing of small features rather than large-area deposition. On the other hand, photo-LCVD has the potential to meet most of the requirements of microelectronics. In general, LCVD give excellent step coverage and uniformity of deposition because of the planar source of depositing species which is built-in in the deposition mechanism.

4. Film deposited by LCVD

Various materials, metals, semiconductors and insulators in elemental or compound form have been deposited on a number of substrates in thin film configuration. Figure 5 shows a typical deposition system though many variants of this arrangement have been successfully used to show feasibility of deposition. Using suitable optics, the surface reaction and volume reaction photons can be expanded to effect large-area deposition. For micronic linear deposition, the substrate can be moved in X - Y directions. With computer control the deposition can be spatially directed with high resolution. In some arrangements, the substrate needs to be heated to improve adhesion and uniformity of the deposited layer. Some characterization of the materials has also been done, though more exhaustive work to understand the mechanisms of the deposition and optimization of growth parameters to achieve the required material still remain to be done.

Polycrystalline silicon was deposited on quartz substrate by pyro-LCVD using argon-ion laser (Bauerle *et al* 1982; Roy *et al* 1987). Nickel was thermally dissociated from $\text{Ni}(\text{CO})_4$ and insulating layers of TiO_2 and TiC were also deposited using CO_2 laser (Allen and Bass 1979; Allen 1981). Hydrogenated amorphous silicon (a-Si:H) was also deposited by gas-phase pyrolysis of silane (Meunier *et al* 1983). Refractory metals like W, Mo and Cr were deposited by using UV lasers in photolytic LCVD mode from the respective carbonyls (Solanki *et al* 1981). Metals like Al and Cd were deposited from organic complexes by using UV from frequency doubling of visible line by photo-LCVD (Deutsch *et al* 1979). Polycrystalline Si and Ge were deposited by photo-LCVD by using UV from excimer laser (Andreatta *et al* 1982). Blum *et al* (1983) oxidized silicon by photolytically dissociating nitrous oxide (N_2O) into nitrogen and oxygen using ArF laser beam; photons were not absorbed by silane but the latter was oxidized to give a film of insulating SiO_2 . Excimer laser has also been used for deposition of compound semiconductors like InP by photo-LCVD (Donnelly *et al* 1984).

Deposition of insulating and compound semiconducting films does present problems since most of these films have two or more constituent species. Thus formation of these compounds proceeds in two steps: extraction of volatile species from free or radical-containing precursors and subsequent reaction with another species to form the desired compound.

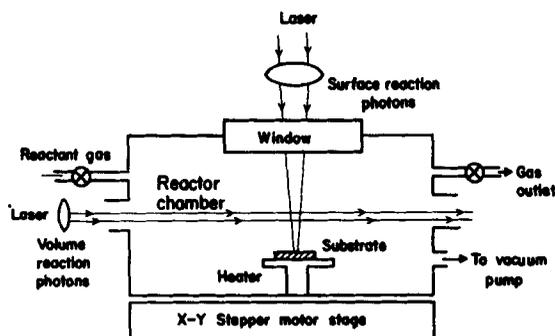


Figure 5. Typical LCVD deposition system.

5. Concluding remarks

The LCVD technique is still in its infancy, but has a host of possibilities. Progress in this technique will definitely depend on further development of suitable lasers. Higher power and larger beam aperture lasers are needed to make the process cost-effective and technologically acceptable.

Though a large number of materials in thin-film mode have been grown by LCVD, the basic mechanism is not understood well. The gas surface reaction dynamics, the interface phenomena, the mechanism of multicomponent deposition and the role of various laser parameters in the growth of required films have not been completely investigated. A quantitative understanding of the role of lasers in enhancing the rate of chemical reactions and modifying surface chemistry is needed. The detailed electrical and structural characterization of materials grown is awaited.

The technique has grown in importance because of the possible applications in microelectronics and high density integrated circuits, though its commercial exploitation has not begun yet. Some device ideas have been tried out (Tsao *et al* 1982; McWilliams *et al* 1983) but have not taken practical shape. Feasibility studies of some of the unit processes connected with device fabrication have been done. Because of possible applications in micro-region deposition, doping and etching, various device structures have been contemplated, such as superlattice, three-dimensional lattice structures, conditioning of gate arrays, restructuring masks for integrated circuits and even maskless device making. Very intensive work is needed to evaluate inherent potentialities of LCVD as a research tool for understanding gas–solid interface physics, dopant incorporation and large-area deposition, so that the technique can be promoted from the realm of research and development to a viable technology in the fabrication of future solid-state devices.

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