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Review

The fundamentals of chemical vapour deposition

W. A. BRYANT
Westinghouse Research and Development Center, Pittsburgh, Pennsylvania, USA

Fundamentals of the chemical vapour deposition process are described and examples given of its application. The most important aspects of the process are reviewed; these include deposit structure (with its relation to process parameters), process control through application of the principles of thermodynamics and reaction kinetics (with emphasis on deposit thickness uniformity, deposit composition control and deposit–substrate adherence) and basic design features of the equipment used.

1. Introduction

The origin of chemical vapour deposition is popularly traced to the early work of van Arkel and de Boer [1]. However, the patent literature suggests that much earlier, in 1890, de Lodyguine [2] prepared tungsten deposits on carbon lamp filaments by hydrogen reducing WCl_6. Activity in the field increased dramatically about 15 to 20 years ago and has continued unabated since that time.

A simple definition of chemical vapour deposition (CVD) is the condensation of a compound or compounds from the gas phase on to a substrate where reaction occurs to produce a solid deposit. The process is shown schematically in Fig. 1. The gaseous compound bearing the deposit material, if not already in the vapour state, is formed by volatilization from either a liquid or solid feed and is caused to flow either by a pressure differential or the action of a carrier gas to the substrate.

In the special case of a transport system, where the deposit and the reactant are of the same material, volatilization is accompanied by reaction of the reactant with a gaseous transport agent. The reverse of this reaction produces the solid deposit. Transport depends upon the difference in equilibrium constant for the temperatures of the reactant source and the substrate. This variant of the CVD process has been studied extensively by Schäfer [3].

Since the vapour will condense on any relatively cool surface with which it contacts, it is necessary that all parts of the deposition system be at least as hot as the vapour source. The reaction portion of the system is generally much hotter than the vapour source but considerably below the melting temperature of the deposit.

Volatility considerations are also important in two other aspects of the CVD process: unwanted reaction products must be gaseous to permit their removal from the deposition system, and the deposit must have sufficiently low vapour pressure to prevent its volatilization.

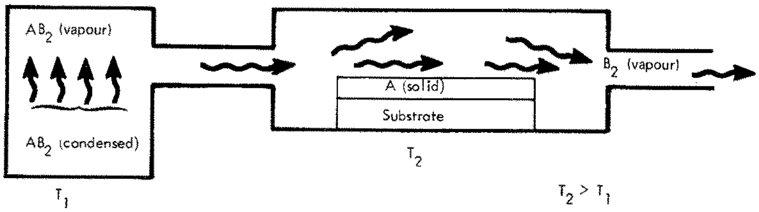

Figure 1 Schematic representation of a CVD process.

The deposition reaction is generally either one of thermal decomposition (such as depicted in Fig.

1) or chemical reduction, in which case another reactant gas is added to the system. Examples of these types of reactions are given in the following equations.

$$Ni(CO)_{4\,(g)} = Ni_{(s)} + 2CO_{2\,(g)} \qquad (1)$$

$$WF_{6\,(g)} + 3H_{2\,(g)} = W_{(s)} + 6HF_{(g)} \qquad (2)$$

Thermal decomposition most frequently involves the use of organo-metallic compounds, but can also be applied to halides and other simple inorganic compounds. Where the temperature of decomposition of a halide is impractically high, which can be the case, for example, for the refractory metal halides, sub-halides have been used at more moderate reaction temperatures [4, 5]. The same types of reactants are used in chemical reduction deposition reactions. A survey of the many reactant compounds suitable for use in the CVD process has been made by Buck [6].

The reducing agent most usually employed in chemical reduction is hydrogen, however metal vapours can be used. As an example of the latter, zinc vapour has been reacted with H_2S and water vapour to form deposits of ZnS [7] and ZnO [8] respectively. The substrate can also act as reductant, as in the case of WF_6 reduction by silicon [9, 10]. Naturally, only a very thin deposit can be produced by this method.

The substrate can supply one element of a compound or alloy deposit in situations where the element is not required as reductant but merely diffuses into the deposit. In the TiC coating of cemented carbide tool inserts it is believed that much of the carbon in the TiC originated in the substrate, even though a hydrocarbon gas was used as one of the reactants [11]. Reactant is also supplied by the substrate in the preparation of autodoped thin films for semiconductor application. This variant of the CVD process necessarily requires high deposition temperature to provide an appreciable amount of substrate element to the deposit.

The process of chemical vapour deposition finds its greatest application in the preparation of coatings, and in the production of materials to finished size for those materials that are not easily fabricated by more conventional means. Most elements can also be deposited by either electrodeposition or physical vapour deposition (which is meant to include sputtering, ion-plating, and vacuum evaporation). However, the latter process is incapable of depositing such high melting-temperature elements as tungsten, tantalum, or carbon. Electrodeposition techniques are not available for depositing certain commercially important elements such as molybdenum, tungsten, and silicon [12]. The CVD process has the added advantage of being able to deposit many alloys as well as compounds including oxides, nitrides, and carbides.

CVD materials find application in a number of fields. The following are but a small fraction of the total number of applications. Hard coatings of such materials as TiC and Al_2O_3 have been prepared on cutting tools. CVD coatings can also provide corrosion protection, using such deposits as tantalum, BN, $MoSi_2$, and SiC. Steel has been coated with tungsten to minimize erosion. Free standing shapes have been produced from materials whose fabricability by more conventional means is limited. Foremost among these materials are the refractory metals and their alloys. Most recent work has been concentrated in the fields of solid state electronic devices and energy conversion. The chemical vapour deposition of electronic materials has been the subject of two recent reviews [13, 14]. Emphasis has been placed on the formation and doping of epitaxial films of such materials as silicon, GaAs, and germanium. For energy conversion the CVD process provides materials for nuclear fission product retention, solar energy collection, and superconduction. Significant advances in the area of composite materials have been possible through application of the CVD process in preparing fibres of such materials as carbon boron and SiC, coating the fibres with a multitude of materials and infiltrating open structures to provide a matrix.

Several key aspects of chemical vapour deposition are described in the following sections. These include deposit structure and its relation to deposition parameters, control of process through an understanding of its thermodynamics and kinetics, and the basic features of the design of the equipment. The discussion will be restricted to open tube systems, i.e. systems in which reaction product gas is continually removed and reactant gas(es) are continually supplied, but this restriction is not overly confining since only a very small fraction of CVD processes are carried out in closed tube systems. Hybrid CVD processes such as reactive sputtering, reactive ion-plating and plasma-activated deposition are not discussed.

2. Structure of CVD deposits

CVD deposits form by a nucleation and growth mechanism. Nucleation is preceded by the adsorption and diffusion of atoms on the surface of the substrate. Modern nucleation theory [15] has been shown to be applicable to chemical vapour deposition [16, 17] even though the process is by nature a multicomponent system. Stable nuclei (normally consisting of only a few atoms) form at preferred sites on the substrate surface. Their growth proceeds by the addition of individual atoms both directly from the reactant gas stream and from surface diffusion across the uncovered portions of the substrate. Atom additions during this growth process generally occur at positions of lowest free energy, such as steps or kinks, and proceed to form crystallites.

In certain instances these crystallites are very thin and, prior to their coalescence, resemble islands in their appearance. A thin single crystal deposit is formed upon coalescence. Successive layers, corresponding to the "two-dimensional growth" of Joyce *et al.* [18], have been observed to form in an identical manner [19–21]. The single crystal deposit may or may not bear an epitaxial relation with the substrate. As shown by Blank and Russell [22], preferred nucleation at locations of defects in the substrate surface (rather than at preferred lattice sites), coupled with relatively low reactant concentration, can produce a low nucleation density. Nucleation at other sites is suppressed by local gas depletion. In the relative absence of substrate imperfections and at greater (though still low) super saturation, epitaxial deposits are favoured.

Fairly equi-axed nuclei can also form. During growth into crystallites the nucleations become faceted. Atom addition occurs preferentially at ledges formed by the propagation of spiral dislocations and by the mutual impingement of crystallites. Ledges (steps) have been observed on the sides of individual crystallites of tungsten when the growth rate normal to the substrate was greater than the lateral one [23]. Since the likelihood of all the crystallites growing in the same orientation is remote (nucleation orientation is little affected by the orientation of the substrate) coalescence produces a polycrystalline deposit.

From the preceding discussion it is apparent that the nature of the substrate surface can have a very profound effect on the structure of the deposit formed upon it. In addition, substrate effects have also been noted in experiments in which the minimum temperature for deposition was found to depend upon the choice of substrate material. This same dependence is responsible for the observation that growth will sometimes cease after only a very thin deposit layer has formed to provide complete coverage of the substrate. The preferred adsorption of certain impurity gases on the susbtrate has also been found to influence deposition rate and deposit morphology. Nucleation rate is strongly influenced by the choice of substrate material. The means for selective growth afforded by this relation has been used to advantage in the CVD formation of integrated circuits. Masking materials on which nucleation is not favoured have been employed in this application [24, 25].

Other structures, besides single crystal and polycrystalline ones, can be produced by the CVD process. These structures are discussed below, as are more detailed descriptions of the structures already mentioned. The remainder of this section is devoted to the influence on structure of the parameters of temperature, pressure, and composition of reactant gas.

2.1. Polycrystalline deposits.

The polycrystalline structure, often comprising columnar grains possessing a high degree of preferred orientation, is the form invariably found in deposits intended for structural applications. The preferred orientation develops, in the absence of epitaxy, by growth from the randomly oriented nucleation layer first formed on the substrate. This layer may not become continuous until a thickness of several hundred angstroms is reached. Deposit growth proceeds by the more rapid growth of preferentially oriented grains at the expense of their less favourably oriented neighbours. This process of selective growth has been discussed in detail by Van der Drift [26]. Thus, when a thickness of 20 to 50 μm has been reached, the deposit is preferentially oriented and the grains still growing from that point outward from the substrate become columnar in shape (Fig. 2). In extreme cases this preferred growth can produce a virtual single crystal deposit in its last portion to be formed [27].

Intercrystalline micro-porosity may form in the region of preferred orientation if the growth rate is controlled by gas phase mass transport whereas fully dense deposits are formed when the growth rate is dictated by a mechanism occurring on the

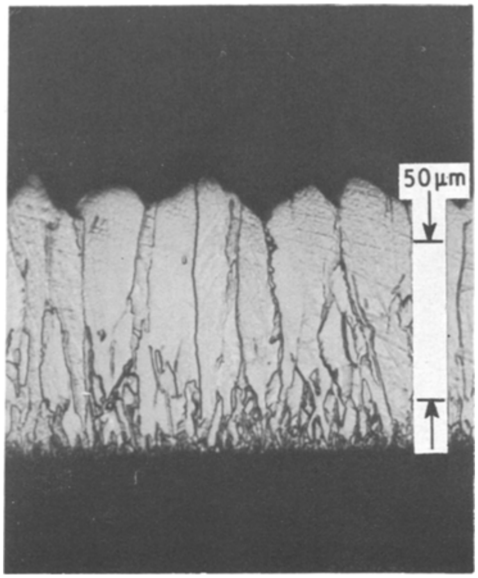

Figure 2 Typical CVD polycrystalline deposit (Ta–10W).

solid surface. (These two modes of growth rate control are discussed in a subsequent section of this review). In models proposed by Holman and Huegel [28], reactant concentration, and hence growth rate, is greatest at or near the tips of the growing crystallites under conditions of mass transport control, since the tips extend furthest into the boundary layer of the gas stream over which a concentration gradient of reactant exists. This enhanced growth rate, being greater than that near the intercrystalline boundaries, can produce grown-in boundary porosity, but on the other hand, fully dense deposits can be expected from the uniform surface concentration of reactants that accompanies rate control by a surface mechanism.

The degree of preferred orientation is dependent upon process variables, including the choice of deposit-bearing reactant. The mechanism involved in this dependence has not been determined. The effects of process parameters on preferred orientation have been studied for tungsten [29–35], silicon [36, 37] and rhenium [38, 39]. This particular form of structural anisotropy is highly desirable for applications involving thermionic emission [33] but can be detrimental where short term strength in a direction normal to the growth direction is required [40–42].

Formation of the columnar structure can be prevented. An equi-axed structure has been achieved in tungsten by imparting mechanical energy (in the form of cold work) to the deposit during its formation by having it stroked with tungsten wires [43]. The energy supplied in this manner lowered the activation barrier to nucleation sufficiently to permit new grains to form as deposition proceeded. A typical microstructure produced by this means of enhanced nucleation is compared to the normal columnar growth in Fig. 3. However, in this instance, the very fine grains of tungsten have been produced on that portion of a rotating substrate which had been intermittently contacted by the fixturing device of the deposit during the early stage of deposition rather than by continued contacting by wires. This same mechanism of producing fine-grained deposits has been encountered in fluidized bed deposition, where the mechanical energy is supplied by collisions of the bed particles.

The equi-axed structure of tungsten formed by this method of cold working is subject to recrystallization [43]. This behaviour is unlike that found for the columnar form of the same material [44], and presumably also for the equi-axed product prepared by methods involving no appreciable amounts of cold work (see below).

Polycrystalline CVD sturctures are susceptible to elevated temperature grain growth as are metals and alloys formed by other means. This grain growth is especially pronounced when the structure

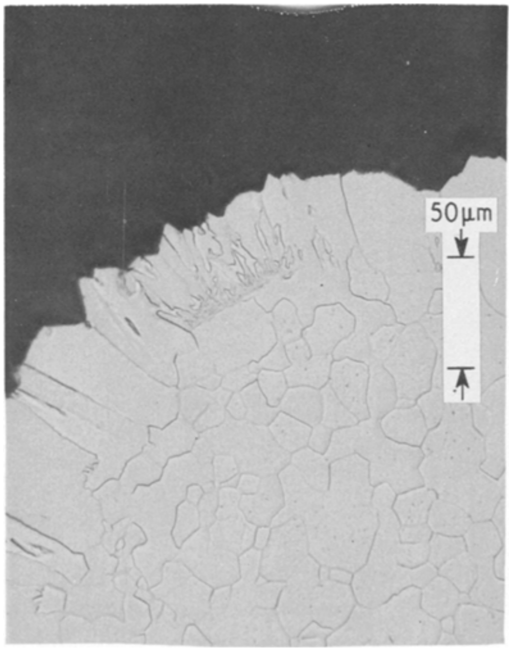

Figure 3 Fine-grained CVD tungsten deposit prepared by cold working during deposition.

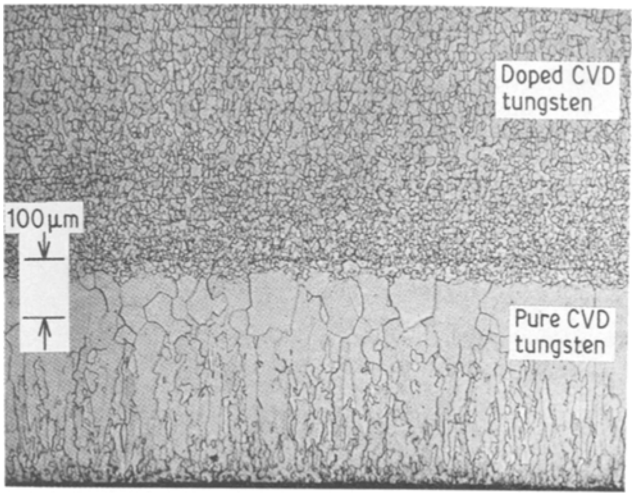

Figure 4 Thorium acetylacetonate doped and undoped CVD tungsten following annealing for 75 min at 2070° C.

is randomly oriented and equi-axed. As noted earlier this is the structure observed, in the absence of epitaxy, to form at the substrate surface prior to initiation of preferential growth. Failure to remove this layer of random orientation prior to annealing a deposit produces extensive grain growth which can proceed into the columnar structure and eventually consume it [45]. In the absence of the randomly oriented layer, preferentially oriented deposits exhibit considerable resistance to grain growth, since most of the grain boundaries are necessarily of the low angle type. Further resistance to grain growth in this structure is provided by grain boundary voids or gas-containing bubbles. These voids or bubbles form as the result of the agglomeration of atomic or molecular sized "impurities" during post deposition heat treatment. These "impurities" were once thought to be composed solely of a gas or gases present in the deposition system; for example, fluorine and/or a fluorine-containing gaseous compound such as WF_4 [46] are normally found in CVD tungsten prepared from WF_6. More recent evidence [47] however, suggests, that these "impurities" are in fact excess vacancies formed during deposition and that their coalescence with gas atoms or molecules provides the voids or bubbles. The presence of these grains boundary voids, although beneficial to retarding recrystallization and grain growth, has a deleterious effect on both short time [40, 42] and extended time [48–50] high temperature mechanical properties. The interaction between these and the applied stress has been analysed by Stiegler, *et al.* [51].

The presence of extrinsic "impurities" (those purposely added to the deposition system by the introduction of one or more additional reactant gases) can result in both the formation and stabilization of an equi-axed structure (Fig. 4). The stabilizing micro-constituent can be either a void (or bubble) or a second phase particle. Tungsten has been stabilized by the former means by the introduction of potassium [52], oxygen [53], and ammonia [54] and by the latter means by the incorporation of silicon [55], carbon [56, 57] and HfN [58]. Structural refinement has also been reported for silicon by the addition of SiC and Si_3N_4 [59], while air and oxygen have been added to the reactant stream of $Ni(CO)_4$ to produce refined nickel [60].

2.2. Epitaxial deposits

Epitaxial deposits are most often encountered in the growth of single crystals and thin films for electronic applications, however, epitaxial polycrystalline films (such as appear in the unworked portion of the specimen shown in Fig. 3) are not uncommon. As with non-epitaxial films, epitaxial films can form by a nucleation and growth mechanism, but it should be possible for them to form by monolayer formation where either the contact angle between deposit and substrate [15] is zero, or the depositing atoms lack sufficient mobility to diffuse over the surface of the substrate. A third possibility for film formation exists: in physical vapour deposition three dimensional islands (formed by nucleation and growth) have been found surrounded by a deposit monolayer [61, 62]. This hybrid mechanism of film formation is explainable by calculations of misfit strain energy and misfit dislocation energy [63].

Two types of epitaxy exist; homoepitaxy and heteroepitaxy. As their names imply the former describes the case where deposit and substrate are of the same material, and the latter when the deposit and substrate materials are different. In heteroepitaxy, islands of the deposit are generally free to form in several orientations, thus a polycrystalline film is usually formed following coalescence. It is possible, however, for the film to be recrystallized into a single crystal film if coalescence has occurred very early in the deposition process [64]. This early coalescence is favoured by high deposition (nucleation) rate and the presence of a limited amount of surface contamination which tends to decrease the misorientation of islands by restricting the number of types of preferred nuleaction sites on the substrate. In homoepitaxy the formation of a single crystal film is favoured by low deposition (nucleation) rate and a clean substrate, since both factors enhance the formation of nuclei of identical orientation.

Structural perfection is important in epitaxial films for electronic device application. These imperfections (including stacking faults, twins, growth pyramids, and dislocations) have a pronounced influence on device performance [65]. The incidence of imperfections is largely controlled by the condition of the substrate surface (and even the method of growth of the substrate [66]) and can therefore be minimized by proper surface preparation techniques including the important one of *in situ* etching.

Stacking fault formation [9, 67] and twin formation [68] in homoepitaxial silicon have been studied in detail. The origin of growth pyramids has usually been traced to the presence of contamination on the surface of the substrate.

It has been calculated for a simple one dimensional model that at substrate-coating lattice misfits of greater than 14%, dislocations form with no activation energy [69]. Thus at a misfit value lower than this critical value, exact correspondence between the lattices of coating and substrate is possible. One would expect misfit to be accommodated both by dislocations and elastic strain since this arrangement represents a lower energy situation than the one in which misfit is totally accommodated by elastic strain. The number of such defects would be expected to increase with increasing deposition rate (increasing nucleation rate) and decreasing deposition temperature (decreasing atomic mobility). The effect on nucleation rate of both substrate orientation [70, 71] and choice of substrate material [72] have been studied.

Other factors besides substrate surface condition and deposit-substrate lattice misfit affect the achievement of epitaxy. These factors include regions of polycrystallinity or subgrains which intersect the substrate surface and thermal stresses resulting from a temperature gradient existing across the thickness of the substrate. The existence of thermal stresses of sufficient magnitude to produce curvature of thin substrates has been reported [73].

Additional information on the chemical vapour deposition of epitaxial thin films, including descriptions of specific deposition systems, doping, applications, and methods of evaluation has been presented in two recent reviews of the subject [13, 14].

2.3. Powder formation

At sufficiently high reactant concentration and gas temperature (not deposition temperature, which is taken to mean the temperature of the substrate) the frequency of molecular collisions within the gas phase is great enough to cause homogeneous nucleation and the growth of a powder product. Where a continuous solid deposit is desired, powder formation is naturally to be avoided since its occurrence adversely affects the deposit density, lowers the deposition rate, and creates problems of equipment maintenance. In addition, once they are settled on to the substrate, particles serve as nucleation sites for the formation of nodules [74, 75], which form because of the accelerated growth caused by their protrusion into the boundary layer of the reactant gas stream.

Powder formation is not always undesirable. By observing the patterns of light scattered by homogeneously formed solid particles, the gas flow patterns in a CVD reactor have been visualized [76]. Powder formed in this manner can be the desired final product. An extensive discussion of this process for preparing carbon black and ultrafine powders of TiO_2 and SiO_2 has been given by Mezey [77]. CVD processes for producing powders of tantalum nitride [78], nickel [79], UO_2 [80], TaC [81], silicon [82], and many other compounds [83] have been described.

2.4. Other structures

Chemical vapour deposition has also been extensively applied to the formation of both prismatic and whisker-like single crystals. Growth of the low index planes of prismatic crystals occurs by the formation of new monolayers following "two dimensional" nucleation [15]. Whisker growth does not require "two dimensional" nucleation. Frank [84] has shown that the intersection of a substrate surface by a screw dislocation having its Burgers vector normal to the surface provides a growth step by which a whisker can form. Continued growth occurs by the adsorption of atoms on to the sides of the whisker followed by diffusion to the tip [85]. The growth rate is determined by the geometry of the whisker, and the concentration and stay time of absorbed atoms on the whisker.

A wide range of crystal morphologies is possible within one material's system depending upon the deposition temperature and concentration of reactants. This has been demonstrated, for example, in the formation of single crystals of TiN [86] and TiC [87].

One application of CVD grown metal whiskers deserves mention because of its unusual nature: arrays of tungsten whiskers having spacings on the order of several wave lengths of visible light have been used to trap almost all light which is incident upon them [88]. This new material shows great promise for the collection and conversion of solar energy.

Amorphous film deposits have also been prepared by the CVD process. Such films have useful insulating and passivating properties and thus find application in a number of electronic devices. Amorphous deposits are formed at lower temperature than their crystalline counterparts since at these temperatures the mobility of adsorbed atoms is slight. Thus they tend to stay at their adsorption site and thereby avoid moving to more energetically favourable sites where nucleation could occur. Upon heating to a temperature well above their deposition temperatures, amorphous films of Ta_2O_5 and Nb_2O_5 have been made to crystallize [89]. Other materials from which amorphous deposits have been prepared include SiO_2 [74, 90–93], silicon [94], Si_3N_4 [95], Al_2O_3 [75, 96], aluminium oxynitride [97], and both phosphosilicate and borosilicate glasses [98–101]. An extensive study of CVD glass films for electronic passivation has recently been published [102].

A highly anisotropic structure has been observed to occur in both pyrolytic carbon and boron nitride deposited at high temperature. An example of such a deposit showing the typical cone-shaped crystallites is provided by Fig. 5. In this structure (turbostratic) the basal planes are all approximately parallel but otherwise little crystallographic ordering is observed.

Two final structures, which have been observed to occur in chemical vapour deposition, are those termed botryoidal and dendritic. The latter, which has the form of a loose agglomeration of crystallites, is typified by the rhenium deposit of Fig. 6. Botryoidal structure has been defined as having the appearance of a bunch of grapes. Since both structures are very porous and irregular in their surface coverage, little application of them is expected.

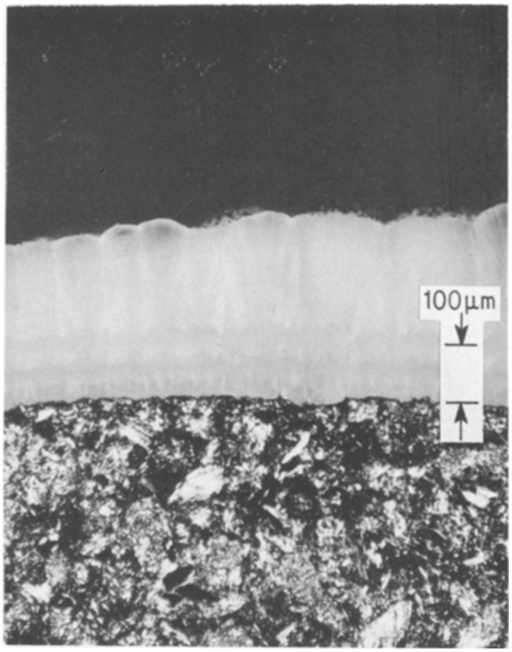

Figure 5 Turbostratic CVD boron nitride deposit on graphite.

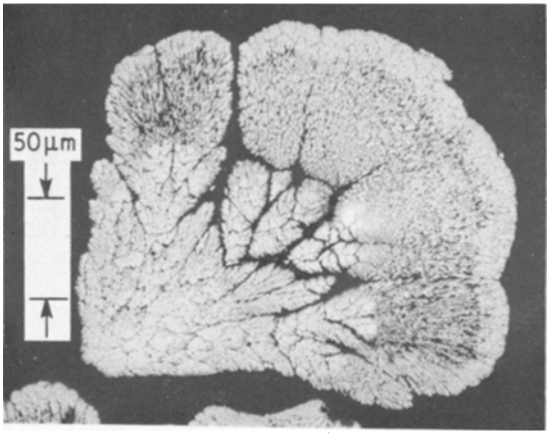

Figure 6 Dendritic CVD rhenium deposit.

TABLE I Effect of temperature and pressure on the microstructure of fluoride CVD tungsten produced at $H_2/WF_6 \approx 6$

Temp. (°C)	760 torr		0.1 torr	
	Microstructure	Reference	Microstructure	Reference
250	No deposition	[106, 107]	fine grained (< 1 μm)	[108]
350	Less coarse grained	[56]		
500	Coarse grained	[30, 109]		
600	Coarse grained	[56, 30, 109]		
650	Coarse grained	[106, 30, 109]		
700	Coarse grained	[109]		
750	Botryoidal	[56]		
800	Dendritic, powder	[110]		
900	Dendritic	[106]		
1000	Dendritic	[106]	Whiskers, fine grained (< 1 μm)	[108]
1350			Epitaxial	[111]

2.5. Dependence of structure on deposition parameters

Previous mention has been made of the influence of the nature of the substrate on the structure of deposit obtained, especially in the case of epitaxial deposits. Substantial influence is also exerted by the deposition parameters of temperature and reactant supersaturation, defined as the ratio of the partial pressure of reactant gas adjacent to the substrate to the value in equilibrium with the substrate. Consider, for example, the data of Table I for tungsten prepared by the hydrogen reduction of WF_6. At high supersaturation (corresponding to a system pressure of one atmosphere) the polycrystalline structure formed at low temperature is relatively coarse grained and with decreasing temperature, by analogy with the deposition of tantalum and niobium [103], grain structure would be expected to become finer until at sufficiently low temperature amorphous deposits would be formed. With increasing temperature the mobility of the adsorbed atoms increases to produce a decreased nucleation density and increased growth rates which in turn produce a coarser grain structure. As the temperature is further increased the microstructure changes through the consecutive stages shown in the table. At sufficiently high combined values of temperature and supersaturation, solid is nucleated homogeneously in the gas phase to produce powder of fine particle size.

Only at very low supersaturation and high temperature can epitaxial tungsten deposits be formed (Table I). Epitaxy results from the nucleation of a particular orientation that is preferred as the result of its interfacial free energy being lower than that of other possible orientations. However, as the supersaturation is increased, the nucleation rate of other orientations becomes sufficiently great that the epitaxial relation is lost. At lower temperatures fine grained polycrystalline structures and whiskers have been observed. Tungsten whiskers have also been prepared at somewhat greater WF_6 concentration, but at much lower temperature [88].

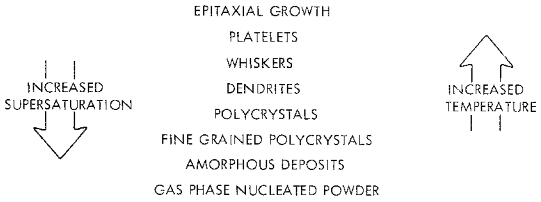

Figure 7 The effects of supersaturation and temperature on the structure formed by physical vapour deposition (according to Blocher).

Blocher [104] has described the structural dependence on supersaturation and temperature of materials prepared by physical vapour deposition as occurring according to the sequence shown in Fig. 7. From the previous discussion it is apparent that the same sort of dependencies exist for CVD materials. One obvious discrepancy exists in the case of homogeneous gas-phase nucleation. However, in the preparation of Al_2O_3 by a CVD process [105] the formation of powder was accomplished at relatively low temperature in agreement with the observations of Fig. 7 for physical vapour deposition.

3. Process control

The successful employment of a CVD process is dependent upon the thermodynamics and kinetics of the chosen deposition reaction. Not only must the reaction be thermodynamically possible but it must proceed at an economically permissible rate.

Consideration must also be given to the potential problem areas of deposit–substrate adherence, non-uniformity of deposit thickness and non-uniformity of deposit composition. These factors, and, where existant, their interrelationships, are discussed in this section.

3.1. Thermodynamics

Before considering the use of a CVD reaction it must first be determined that the reaction is thermodynamically possible. This will be the case if the calculated concentrations (partial pressures) of the reactants under conditions of chemical equilibrium are less than their chosen initial concentrations. (Preferably the equilibrium concentrations will be considerably less, for if not, the gas stream will be quickly depleted of sufficient reactant to achieve the maximum deposition rate dictated by the kinetics of the system and instead the rate will be thermodynamically limited.) The calculation of the equilibrium concentrations from the equilibrium constant might involve some trial and error since the number of gas species could be greater than two, the number of independent relations. One relation is the expression for the equilibrium constant in terms of the standard free energy of the reaction and the temperature and the other results from the condition that the system pressure is the sum of partial pressures. Some deposit-bearing reactants possess more than one valence state. In this case, the reaction must contain the reactant in its most stable valence state.

With sufficient calculation the complete range of deposition parameters (temperature, pressure, starting gas composition) over which the CVD reaction is thermodynamically possible can be ascertained. In this approach it has been assumed that reactions and species other than the overall deposition reaction and its species could be ignored, which may not be a valid assumption. Reactions may occur in the gas stream. Reactant and product gases might possibly reactant with the substrate and/or deposit. Such an etching reaction has been described by Loonam [112], who showed in detail how the formation of a lower valence compound by the reactant attack of the deposit could greatly reduce deposition efficiency (fractional conversion of deposit-bearing reactant to solid deposit). Deposit etching reactions have also been reported for the deposition of silicon from $SiCl_4$ [113–115] and germanium from $GeCl_4$ [116]. Weight loss of the substrate by etching has been reported for many materials combinations including the titanium coating of niobium [5], the Ta_2O_5 coating of silicon [117], the silicon coating of Al_2O_3 [118], and the $GaAs_{1-x}P_x$ coating of germanium [119]. Etching reactions, besides adversely affecting deposition efficiency and rate, are among several [120–122] possible mechanisms by which unwanted doping is introduced into epitaxially grown thin films.

The possibility of multiple reactions can, for critical applications, dictate the employment of a more inclusive thermodynamic analysis. Lander and Germer [123] made one of the earliest and most thorough thermodynamic analyses when they studied the equilibrium gas phase composition and deposit impurity content of molybdenum, tungsten, and chromium formed from their respective carbonyls. With the popularization of computing equipment, even more extensive calculations have been made in which all possibly occurring species are considered. The concentrations of all species corresponding to the minimization of free energy for the system are determined. Examples of such analyses are contained in the literature for the deposition of such diverse materials as TiC [124], Ti–Si–C [125], $GaAs_{1-x}P_x$ [126], $Al_xGa_{1-x}As$ [127], $In_{1-x}Ga_xAs$ [128], B_4C [129], GaAs [130], GaP [130], silicon [132, 133], and doped tungsten [52]. From the results of these calculations the identities and equilibrium concentrations of the predominant species are determined, and hence the overall governing chemical reaction is identified. With sufficient calculation, deposition diagrams showing the composition of deposit to be expected for various sets of parameters have been prepared [134, 135]. In these calculations it has been assumed that deposition rate was controlled by gas-phase mass transport, since only then would it be reasonable to further assume the gas at the substrate surface was of equilibrium composition. The close agreement between calculated and experimentally determined deposit composition found for many of the above materials deomonstrates the accuracy of the approach. It would be very interesting to apply similar thermodynamic calculations to a determination of the deposition parameters required to form single phase deposits of materials such as the nitrides of vanadium, tantalum, and niobium and borides of hafnium and zirconium. Purely empirical efforts at producing these compounds have been totally successful [136, 137].

Where deposit-bearing reactant is generated *in situ* by reaction between its elements, the reactant may be a mixture of compounds rather than a single compound. Thermodynamic calculations based on the principle of free energy minimization have been used to determine the makeup of reactant for the formation of $HfCl_4$ and the sub-halides $HfCl_3$ and $HfCl_2$ [138].

3.2. Kinetics

Employment of the reactants and parameter levels indicated by thermodynamic analysis to be necessary for deposition is not of itself sufficient to guarantee the deposition. The process must also be kinetically favourable. As a case in point, the deposition of Al_2O_3 by the reaction of oxygen and $AlCl_3$ is thermodynamically favourable, but its growth rate has been found to be exceedingly slow [139].

An understanding of the growth kinetics of a CVD process is necessary for its control (except for the deposition of epitaxial films, where the rate of formation is governed by neucleation. This form of rate control is not discussed in this article).

The effect of temperature on deposition growth rate is shown qualitatively by the plot of Fig. 8. The regions of this plot labelled A, B, and C (assuming no thermodynamic limitation) represent rate control by a reaction occurring at or near the substrate surface, rate control by mass transport in the gas stream, and rate limitation due to homogeneous gas phase nucleation of product, respectively. The possible surface reactions, which can control the process rate for the simple deposition of a single element (and which are seen to be very temperature dependent), include: (b) adsorption of reactant(s) on to the substrate surface; (c) chemical reaction on the surface (this could also include surface diffusion); and (d) desorption of product gas(es) from the surface. These reactions are collectively referred to as kinetic steps in the overall process.

Mass transport includes the two steps of (a) transport of reactant(s) to the substrate and (e) transport of product gas(es) away from the substrate. The total process of chemical vapour deposition is generally assumed to consist of these steps occurring in the sequence (a), (b), (c), (d), and (e).

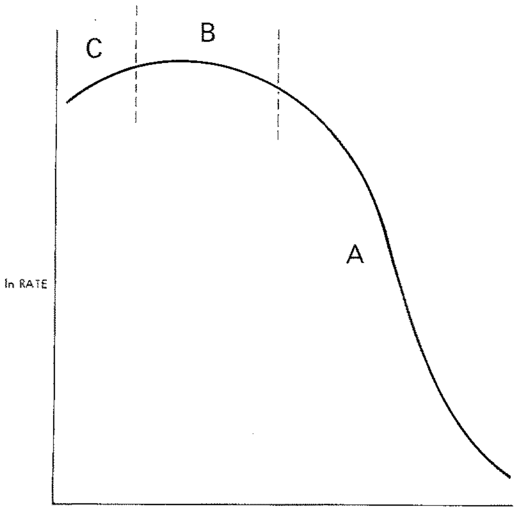

Figure 8 The effect of temperature on deposition rate.

In a majority of systems the resistance to deposition probably derives from both mass transport and surface kinetic contributions. Usually, however, one mechanism predominates and its resistance is assumed to be the total resistance.

If maximum deposition rate is desired, those conditions producing mass transport control should be utilized, and these conditions may also be determined by methods other than the one just described. By maintaining a constant deposition temperature, data of rate as a function of pressure (with constant starting gas composition and flow rate) can be used. Transport control, and hence maximum rate, is indicated by a relative independence of rate on pressure. With the other parameters held constant the region of mass transport control at high mass flow rates is indicated by a dependence of deposition rate on flow rate. (As shown by Schlichting [140], this dependence, in theory, involves the flow rate to the 1/2 power.) At both higher and lower mass flow rates the deposition rate is independent of mass flow signifying control by surface kinetics and natural convection, respectively.

An accurate model which describes the deposition rate as it is controlled by mass transport will permit prediction of the maximum rate attainable. In such a model it is generally assumed that the total resistance to mass transport is contained within a relatively thin layer of gas which lies adjacent to the surface of the substrate. Other assumptions include the absence of gas phase reactions and the attainment of compositional equilibrium by the gas on the surface of the substrate (i.e., the absence of surface kinetic resistances).

Either a film model or a boundary layer model can be used to formulate a relation for deposition growth rate. In a film model only the conditions at the boundaries of the film need to be known. (The physical properties of the film are assumed to be constant over its thickness, which is unaffected by mass transfer and bulk flow.) The deposition rate, R is described by a relation such as

$$R = \frac{M}{\phi} k_g \Delta Y \tag{3}$$

in which M and ϕ are the molecular weight and density of the deposit, respectively, k_g is a mass transfer coefficient and ΔY is a diffusion potential. A mass transfer coefficient can be obtained by using the Chilton–Colburm analogy between heat and mass transfer [141]. The validity of this approach has been demonstrated for multicomponent gas mixtures by Carlton and Oxley [142, 143]. It is important to consider the contribution of the convection to mass transport since many CVD systems operate at low flow rates, pressures at or not much below atmospheric, and with gases of widely different specific gravities. Incorporation of this effect into the rate equation is accomplished by a proper selection of the heat transfer coefficient, values of which can be found for many system geometries in texts on heat transfer such as that by McAdams [144]. Expressions for multicomponent gas diffusion potentials have been developed [145, 146]. With the gas composition known on the stream side of the film, it remains only to calculate the gas composition at the substrate surface. The assumptions of a condition of thermodynamic equilibrium there and the existence of a single predominate chemical reaction, together with the use of mass balances, make the calculation feasible.

A film model has been used to accurately represent the deposition of tungsten by the hydrogen reduction of WF_6 at relatively high temperature and pressure [142]. Later investigations further established that mass transport is rate-controlling in this deposition system under these conditions [147, 148]. The film theory of mass transport has been described in some detail in [146] and [149].

In a boundary layer model [150], provision is made for the effects of mass transfer and bulk flow on the thickness of the layer. Fluxes of the gaseous species are due to diffusion and forced convection. Examples of several variations of this type of model (including description of simplifying assumptions) have appeared in the literature [113, 52, 76, 151, 152]. In these models fluid properties are assumed to be independent of gas composition, and thus a parabolic velocity profile persists in the bulk stream of the gas, which is separated from the susbtrate by the boundary layer. Other models, which consider a more uniform velocity profile (resulting from a consideration of the variation of fluid properties with composition within the bulk stream), have also been employed [153–155]. The velocity profile in these models has been described as "plug flow" or "rod-like flow". Marked improvement to the boundary layer approach has been provided by considering the effect on mass diffusion of thermal diffusion. This was demonstrated by van der Putte, *et al.* [156] for the deposition of silicon. The coupled effect of heat and mass transfer is most significant in systems where the substrate is small and the reaction chamber is of the cold wall type, for under these conditions the difference in temperature between the gas stream and the substrate is maximized. The effect of free convection has been included in a boundary layer model [157] and has been found to be fairly accurate for linear stream velocities above certain critical values.

Another type of mass transport model (a stagnation-flow model), applicable to the situation where a high velocity reactant gas stream impinges on a substrate positioned normal to the flow axis, has been described [158].

Any model for mass transport control requires a knowledge of the gas composition at the substrate surface. As noted previously, this composition is best determined from calculations based on minimization of total free energy in a system assumed to contain all possible gaseous and solid species. An approximation to the surface composition can be readily obtained where the equilibrium for an assumed single overall reaction lies far to the product side. In this case the surface concentration of deposit-bearing reactant will approach a value of zero.

Although conducive to the attainment of a maximum deposition rate, operation under conditions of mass transport control is not always desirable. This rate is determined by the concentration of reactant in the gas phase, which decreases as the gas stream proceeds through the reactor. To obtain deposits of uniform thickness (but at lower rate) over an extended substrate area, operation under conditions of surface kinetics control (and uniform temperature) is required. It has been possible in this manner to evenly coat the internal surfaces of a porous body such as a carbon fibre yarn [159], to bond the individual tungsten spheres held in a packed bed [160], to infiltrate porous structures with BN [161] and to form many more composite structures. It is important to keep in mind, however, that at sufficient depletion of reactant from the stream mass transport control will supplant surface kinetics control.

The achievement of uniform deposit thickness by employment of surface kinetics control is also predicated upon the substrate being composed of a single material. Where this condition is not satisfied, the separate materials may have sufficiently different influences on the sticking behaviour of the deposit bearing species for one portion of the substrate to receive diffusion spill-over from the other and thus be coated to a greater thickness [162].

In studies of surface kinetics rate control, rates can be expressed by relations based on Langmuir–Hinshelwood adsorption isotherm relations [163, 164]. These relations are predicated upon the competitive adsorption between reactant gases and have been used to study the kinetics of deposition of nickel [165], iron [166], boron [167, 168], and tungsten [169]. Experimental deposition rates are substituted into each rate relation (one for each possible rate limiting mechanism). Determination of the relation which best fits the experimental data provides the appropriate rate relation and identifies the controlling mechanism. The necessary substrate surface gas compositions cannot be calculated by thermodynamic means (as they can in mass transport control) since the surface composition is not the equilibrium one. To determine the surface composition it is necessary to substitute experimental deposition rates into a rate equation for mass transport. The bulk stream composition is then obtainable from mass balances.

Rate equations for surface kinetics control can also be formulated on the basis of absolute reaction rate theory [170]. This approach has been demonstrated in determinations of the rate controlling mechanisms of tungsten deposition from WF_6 [171], and GaAs deposition from GaCl and $AsCl_3$ [172]. Deposition rate control by a combination of both kinetic and mass transport resistances has been identified [173, 96], and an example of rate equation formulation for this condition has been described by Spacil and Wulff [154].

Besides varying deposition parameters such as temperature, pressure, and ratio of reactant gases, several other approaches are used to acquire changes in deposition rates. In the region of mass transport control dilution of the gas stream can be accomplished by adding either an inert or product gas. Surface reaction rates can be altered by gaseous additions which affect the catalytic behaviour of the substrate. For example, the rate of tungsten deposition from WF_6 has been slowed by the addition of HCl, oxygen, and water vapour [106, 174] and both decreased and increased (depending upon temperature) by the addition of $MoCl_5$ [175]. The growth rate of ZnS has been shown to increase markedly when the zinc vapour reactant contained a small amount of aluminium or copper [176].

Homogeneous, gas phase reactions can also determine the deposition rate. Sladek [177] has suggested that many CVD deposits might be formed by diffusion to the substrate of product formed in the gas stream. Strong support for a homogeneous mechanism of solid deposit formation is provided by the work of Cochet *et al* [178] who were able to experimentally measure the temperature and composition profiles of the gas stream in a CVD system for preparing Si_3N_4. The kinetics of rate control by both homogeneous and heterogeneous mechanisms has been investigated for the thermal decomposition of $W(CO)_6$ [179]. Failure to account for homogeneous reactions can produce anomalous results in the studies of the kinetics of heterogeneous reactions, as has been demonstrated in the deposition of TiO_2 [180], silicon [181], SnO_2 [182], and SiO_2 [90–92]. The possibility of encountering homogeneous reactions is lessened by using a lower temperature, lower reactant concentration, higher gas stream velocity, smaller substrate area, and cooling of the reaction chamber walls.

The deposition kinetics of compound or alloy formation are much more complex than those for single elements because of the greater possibilities for the chemical reaction path. For example, the paths taken in the deposition of SiC and TiC have been shown to be totally different, for only in the former is an elemental intermediate formed [183], while in the latter elemental titanium is not formed [184]. One special case of compound formation should be mentioned. In it, the substrate provides one of the elements by diffusion into the deposit. Where this diffusion step is rate-limiting a specific process advantage is possible. In the coating of the inner surfaces of graphite or carbon tubes of great length-to-bore ratio with refractory metal carbides, control by the mechanism permitted the attainment of uniformly thick deposits [185, 186]. This degree of uniformity would not have been possible if rate control by any other mechanism had been operative. Solid state diffusion control is also an effective (though slow) means of uniformly coating very large substrate areas as has been demonstrated in the chromium coating of large coils of mild steel [187].

Solid state diffusion is often rate-limiting in the form of chemical vapour deposition known as pack cementation. (This process produces diffusion coatings of alloys and is based on the gas phase transport of coating species established by the activity of the coating species being lower in the coated part than it is in the source material.) This process has been described by Walsh [188].

3.3. Deposit–substrate adherence

Consideration must be given to other factors in process control. One such factor is the adherence of the deposit to the substrate, especially in applications where the deposit is to serve as a protective coating. (Even where the substrate merely serves as a mandrel for the production of a free-standing article, adherence is still important if the substrate is of considerable surface area. In such cases, it is possible for separate portions of the deposit to be adherent and non-adherent owing to differences in gas composition caused by reactant depletion as it flows over the substrate. This situation can produce regions of high stress concentration at the boundaries between adherent and non-adherent deposit that are great enough to cause deposit cracking.) The adherence must be great enough to withstand both in-service stresses and those stresses encountered during cool-down from the deposit temperature, which occur as a result of differences in thermal contraction between coating and substrate, phase transformation of one of the components, or a number of other possible causes [189].

Any factor which serves to decrease the number of substrate–deposit interatomic bonds or to substitute weaker bonds for stronger ones will increase the likelihood of non-adherence. One such factor is gas phase reaction which produces a powdery deposit [92]. Other possible sources of non-adherence which have been identified include the formation of brittle intermetallic compounds at the coating–substrate interface [190], low nucleation density resulting in large grain size of deposit and possible intergranular porosity at the interface [191], hydriding of the substrate [192], and the formation of interfacial Kirkendall porosity [193]. Reference compilations of phase diagrams can aid in the proper selection materials and deposition temperature to minimize or eliminate these problems. Contamination of the substrate prior to deposition, often in the form of an inherent thin oxide film [194], must also be considered. An oxide film can often be reduced within the deposition chamber prior to deposition by heating the substrate to sufficient temperature in the presence of hydrogen. Thermodynamic analysis is useful in the selection of parameters for this reduction.

An additional source of non-adherence is the chemical attack of the substrate by a gaseous product of the deposition reaction to produce a stable, mechanically weak compound at the coating–substrate interface. The extent of this source of non-adherence is evident from the number of recent reports of its occurrence [195–199, 117]. The prediction and subsequent avoidance of substrate chemical attack have been made with the aid of simple thermodynamic calculations [200, 201]. Consider, for example, the plating of tantalum with tungsten by the reaction

$$\mathrm{WF}_{6\,(g)} + 3\mathrm{H}_{2\,(g)} = \mathrm{W}_{(s)} + 6\mathrm{HF}_{(g)}. \qquad (4)$$

The corresponding substrate attack reaction would be

$$2\mathrm{HF}_{(g)} + \mathrm{Ta}_{(s)} = \mathrm{TaF}_{2\,(s)} + \mathrm{H}_{2\,(g)}. \qquad (5)$$

As long as the total free energy change for reaction (4) is less than that for reaction (5) an adherent deposit of tungsten can be applied to the tantalum, assuming that the other causes of non-adherence previously mentioned are also avoided. Where differences in the standard free energies for the deposition and substrate attack reactions are sufficiently large, corrections to these values for partial pressures being other than one atmosphere may be neglected. This situation provides considerable simplification of adherence prediction, since it is only necessary to compare the respective standard free energy changes of the two reactions.

It is possible that those deposition parameters

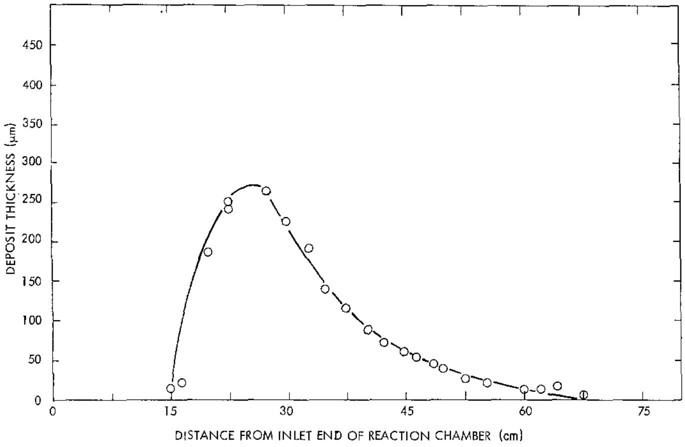

Figure 9 Typical deposit thickness profile obtained with the flow-through CVD process.

found by calculation to be necessary to the avoidance of substrate attack are not compatible with achieving reasonable deposition rates. In such a circumstance it is advisable to use the parameters required for deposit adherence until such time as the substrate is covered. This time will normally be of the order of only a few minutes. Further buildup of the deposit's thickness can then proceed using parameters favourable to high deposition rate since now the substrate is no longer in contact with the deposition atmosphere.

Adherence has also been enhanced by the use of an intermediate coating applied to the substrate. In the deposition of TiC on to a steel substrate a previous deposit of cobalt has increased the adherence of the TiC [202]. This particular case of improved adherence has been related to the increased mobility of carbon atoms on the cobalt surface to provide a greater nucleation density [203]. An intermediate coating could also improve adherence where its coefficient of thermal expansion was intermediate to those of the final coating and the substrate. In this way the introduction of the intermediate coating would serve to produce, in effect, a graded structure with respect to thermally induced stresses. A refinement has been described in which the intermediate layer has a graded composition, varying in this particular application from pure GaAs to pure GaP [204]. Finally, an intermediate layer can eliminate non-adherence caused by substrate attack [197, 199, 205].

3.4. Deposit thickness uniformity

In attempting to deposit a single element over a substrate of considerable surface area by the standard procedure of continually flowing the reactant gases over the substrate, a deposit thickness profile similar to that shown schematically in Fig. 9 is likely obtained [206]. This non-uniformity of deposit thickness is caused by the continual depletion of reactants and formation of product gas as the stream moves over the substrate. Experimental data [206] on the deposition of tungsten by the hydrogen reduction of WF_6 showing this variation of gas composition are given in Fig. 10. Reactant depletion affects the kinetics of deposition when the process is under mass transport control. Controlling deposition by surface kinetics, although helpful, does not provide the total solution, since at the lower pressures which favour this control mode the stream reactant concentration can be quickly lowered to a level where mass transport becomes controlling. One alternative approach involves altering the flow pattern of gas, and there have been attempts such as periodically reversing the gas flow direction [207], rotating the substrate, combining gas flow reversal and substrate rotation [208], stirring the gas [209], periodically re-positioning the substrate [210], imposing a temperature gradient over the length of the substrate and tilting the substrate to increase its downstream projection into the boundary layer [76]. These modifications either have not been totally successful or could not be applied to substrates of considerable surface area. Only in cases where a simple substrate configuration such as a wire [52], rod [211–213] or ribbon [214] permitted relative motion of the substrate and deposition chamber (and thus require deposition over only a short length of substrate at any one time) has uniform deposit thickness been achieved over considerable lengths.

A new CVD refinement in which the reactant gases are introduced in a pulsating rather than in a

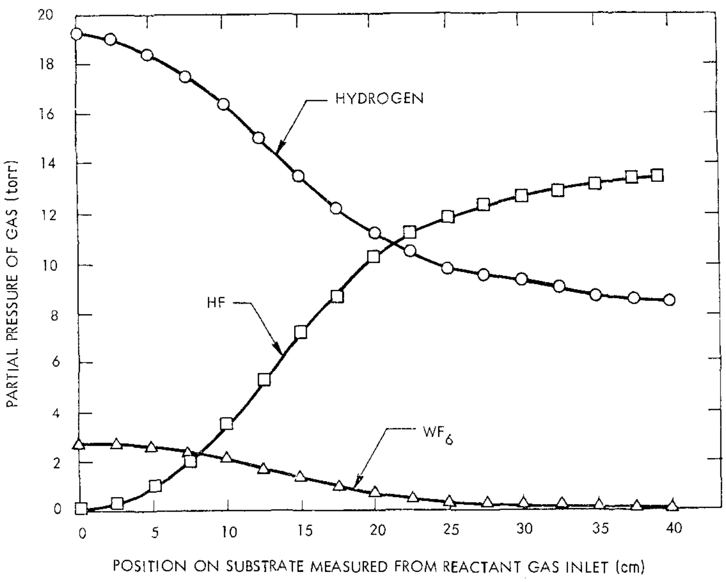

Figure 10 Typical gas composition profile found in the flow-through CVD process.

continuous flow manner has shown promise of overcoming the problem of deposit thickness nonuniformity [215]. In this technique, known quantities of reactant gases are injected into a previously evacuated reaction chamber where they almost instantly blanket the substrate with a gas of uniform composition. Naturally, this composition changes during the time in which the gas is confined to the reaction chamber but the composition at any time is likely to be invariant with respect to position on the substrate. During evacuation of the spent gases, fresh reactant gases are being accumulated in reservoirs of known volume for the next injection. Successive repetitions of the evacuation–injection cycle are used to form a deposit of uniform thickness.

3.5. Deposit compositional uniformity

In alloy deposition another factor must be dealt with, in addition to all the others already considered. In all likelihood the deposition kinetics of the separate elements are sufficiently different to provide a compositional variation across the dimension of the deposit paralleling the direction of gas flow, besides the thickness variability often found in the standard flow-through process. The difference in kinetics stems from the difference in stabilities among the reactants and is exemplified by studies on alloy systems of tungsten–cobalt [216], chromium–titanium [5], tungsten–rhenium [209, 217–219] and tantalum–tungsten–hafnium [220].

The pulsing variant of the CVD process (de-

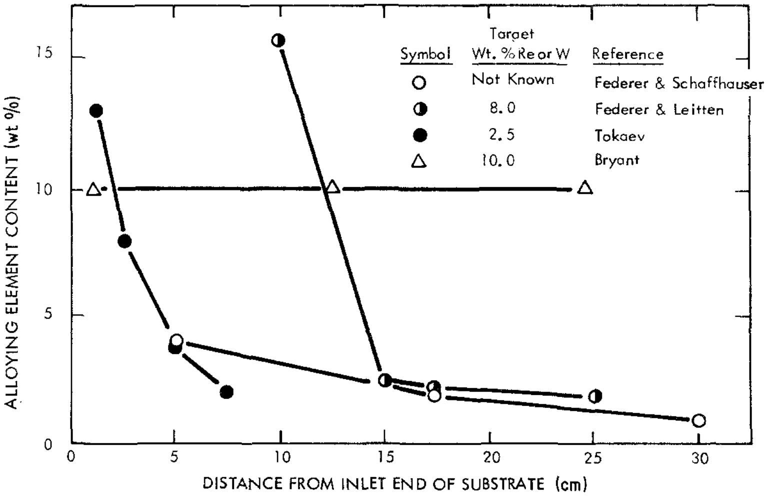

Figure 11 Comparison of alloy composition achieved by the flow-through and pulsing variants of the CVD process.

scribed previously) has been successfully used to prepare a homogeneous tantalum–tungsten alloy [220, 221]. Fig. 11 compares the uniformity of alloy content resulting from this method with that obtained by the flow-through process. In this technique the reactant gases can be either injected simultaneously or sequentially. With the latter mode of operation micro-layers of each element are produced which must subsequently be homogenized to form an alloy. This sequential approach requires longer deposition time and affords the possibility of Kirkendall void formation. On the other hand simultaneous injection requires more extensive experimentation to establish the composition of the reactant gas mixture since it is very unlikely that the individual gases can be used in the proportion in which the elements are found in the alloy. For ternary and higher order alloys, some combination of simultaneous and sequential pulsing may prove best.

4. Deposition equipment

Each setup of experimental equipment contains a number of common components. These include a vapour source (a vaporizer or, if the reactant is a vapour at room temperature, a gas cylinder), a deposition chamber and, assuming sub-atmospheric operation, a vacuum pump or aspirator.

4.1 Feed systems

Generation of a reactant vapour pressure considerably in excess of the deposition pressure permits unaided transport of reactant from the vaporizer. Vapour pressure data, such as in [222], are invaluable in this regard. If a high vaporizer pressure is not practical, the generated vapour can be transported with the aid of a carrier gas, which can be either inert or the reducing gas in the deposition reaction. Although convenient, this method has its drawback: the reactant concentration is known with certainty only if the entraining stream is saturated with reactant, which is not the case if the stream residence time in the vaporizer is too short (the result of high flow rate and/or low surface area of reactant), or the reactant is entrained in the form of liquid droplets.

Other methods of reactant feeding include metering liquid into the reaction chamber and vaporizing entrained solid particles [223]. In many systems it is desirable to generate the reactant gas *in situ* rather than to vaporize a solid or liquid feed, which eliminates the problems associated with handling reactants, many of which are hygroscopic and/or toxic. On the other hand, it must be recognized that the vaporous feed generated in this manner may be a mixture of gases rather than a single gas, as has been encountered in the generation of zirconium iodides [224] and niobium chlorides [223]. Regardless of the means of vapour formation and transport, transfer lines must be kept at least as hot as the vapour source to prevent condensation of reactant but not so hot as to cause premature reduction or dissociation. This condition also applies to any volatile impurity which may be present in the reactant.

Feed systems generally include a means for monitoring and regulating gas flow. Many types of flow meters can be used. The rotameter type requires auxiliary valves to maintain the local pressure for which the flow meter tube was calibrated. Electronic types, whose signal is a measure of the cooling effect of the mass flow of gas on a hot wire, are among the most convenient to use but are not readily adaptable to use with a gas other than the one for which they were originally calibrated. In more elaborate systems, such as those required by the pulsing variant of CVD, additional components are employed in the feed system. In this particular variant such items as known-volume reservoirs, air-operated valves and a programmer are used [220].

Many systems are provided with units for puriyfing the non-deposit-bearing reactant gas(es). The most common of these are palladium or palladium-silver diffusion cells which are used to purify hydrogen. Hydrogen has also been purified by passage over heated chips of copper or titanium, or by flow through molecular sieves. The most common carrier gas, helium, has been purified by passage through a liquid nitrogen trap and alternatively by flow over heated platinum wool followed by liquid nitrogen trapping.

4.2. Reaction chambers

One breakdown of reactor design can be made according to the wall temperature relative to the substrate temperature. In hot-wall reaction chambers these temperatures are approximately equal while in cold-wall reactors the wall temperature is considerably lower and is often not much above ambient.

In cold-wall chambers the substrate is heated by inductive coupling (either directly or by using of a susceptor), direct electrical resistance, electrical resistance of a heater contained within the substrate or infrared heating. The foremost advantage of a cold-wall design is that deposition on the reactor walls is prevented or at least minimized. It follows that reactant is conserved and the frequency with which the reactor must be cleaned is minimal. A further advantage is the reduced possibility of the occurrence of gas phase powder formation since the stream temperature is usually much lower than that of the substrate. However, cold-wall methods of heating are not applicable to all systems because of the size, shape and composition of the substrate. Resistance heating is limited to substrates of relatively small cross-sectional area and fairly high electrical resistivity. Temperature control is sometimes difficult in resistance or induction heating since the thickness of the coated substrate, and hence the resistance or inductive coupling is time dependent. Hot spots can develop on inductively heated mandrels where the shapes of the work coil and the mandrel are not exactly matched and their separation distance is small. At these hot spots increased deposition rate and/or changes in microstructure may result. Substrates which are semiconductors or insulators cannot be inductively heated because of their high electrical resistivity. The temperatures attainable by infrared heating are relatively low.

Hot-wall units offer several advantages: sharp temperature profiles can be achieved and temperature control is relatively easy. However, unwanted deposition on the walls and perhaps in the gas phase can prove to be uneconomical and even ruinous to the deposit on the substrate.

The size and shape of the reaction chamber are dictated by the size and, to some extent, the shape of the substrate. If the size of the chamber is too large relative to the size of the substrate, much reactant will pass through the chamber without being reacted. If the chamber is too small, a low velocity gas stream may be prematurely depleted of reactant and thereby cause formation of an unevenly thick deposit. This effect is accentuated in a hot-wall reactor. The shape of the chamber is best made similar to that of the substrate (or its susceptor), especially where the distance of separation is not great. This precaution provides a comparable gas flow pattern over all portions of the substrate and thus helps the formation of deposits of uniform thickness and microstructure. The gas flow pattern is also influenced by the design of the reaction chamber's exhaust port, as has been demonstrated by Chin [225]. A further subdivision in reactor designs occurs between vertical and horizontal reactors. In the former the direction of gas flow is vertical and the plane of deposition is normal to it, while in the latter both the flow and deposition plane are horizontal. (In a hybrid design, termed a barrel reactor, gas flow is vertical and parallel to the plane of deposition.)

In many CVD systems, some contribution to the total gas flow is made by free (natural) convection. This contribution is significant for ratios of Gr/Re^2 (Grashof number/Reynolds number^2) of about 0.3 and greater [226]. In vertical reactors free convection produces a flow pattern which is torus shaped with the flow direction being downward near the walls and upward at the axis [227]. If the area of substrate surface to be coated is not small compared to the width dimension of the reaction chamber the flow pattern can produce deposits of non-uniform thickness. One method of apparently surmounting this problem has been described wherein the incoming gas is made to flow downward through a bundle of small bore tubes [228]. Product gas exits both by reverse flow through the interstices of the tube and by downward flow past the substrate.

In the horizontal reactor of Eversteyn *et al.* [76], it has been shown that for relatively high flow rate combined free (vertical) and forced (horizontal) convection produced a turbulent stream which was separated from the substrate by a stagnant layer of gas. For values of Gr/Re^2 greater than 0.8 in this type of reactor free convection vortexes have been observed, while for a slight free convective contribution the streamlines are all straight and characteristic of forced convection alone [229]. Other work has shown the layer adjacent to the substrate to be laminar rather than static [230]. There is some evidence that deposit thickness is less variable in a horizontal reactor than in a vertical one [114].

A special type of reactor is the fluidized bed type, in which either seed particles have been built up to form granules [153], or coatings have been applied to a dissimilar material, either bulk [231, 232] or particulate [233–238] in form. Consideration has to be given to the ratio of the sizes of bed and reactor. Ratios which are too low cause low deposition efficiency, while ratios which are too high seriously limit deposition rate. Another type of reactor used to coat moving particulate substrates is the rotating drum [239].

4.3. Exhaust systems

Many CVD processes are best carried out at reduced pressure where they are thermodynamically more favourable and the decreased reactant concentration is less likely to produce gas phase nucleation and other unwanted deposit structures. Vacuum pumps and aspirators are used for this purpose. Where the expense of an evacuation system is not warranted, and thus only operation at atmospheric pressure is possible, the partial pressures of reactants can be kept low by dilution of the stream with an inert gas. A possible drawback to this approach is the large gas phase diffusional resistance provided by the inert gas.

Vacuum pumps must be protected against the deleterious effects of effluent gases. Many of these gases, especially those resulting from the use of reactant halides, are extremely corrosive, particularly when they are hot. Problems of abrasion can also result from particulate solids being entrained in the exhaust stream. Cold traps are frequently used to cool the gases. Corrosive products can be trapped chemically. Hydrogen halides in product gas have been neutralized with sodium and calcium compounds [110]. HF product gas has been trapped by passage through granules of sodium carbonate [240]. Unspent reactant can be stripped from the effluent stream by passing it over a heated substrate of large surface area to produce further deposition. This precaution is necessary whenever either the reactant or the deposited material is expensive. Much of the untrapped gaseous product leaving the pump can be collected in a water scrubber to prevent its entering the atmosphere.

4.4. Other system design considerations

An additional important factor in the design of equipment for chemical vapour deposition is the choice of materials for the various components. Corrosion caused by improper selection can result in impure deposits and the formation of unwanted compounds (sub-halides, for example) which can condense and plug the deposition system. These same problems can arise if the equipment is not leak tight, forming unwanted species in the equipment. In recent years several sophisticated techniques have been applied to the monitoring of CVD systems. Both temperature and gas composition profiles have been obtained by the use of very small sensing probes (thermocouples and capillaries leading, respectively, to temperature indicators and mass spectrometers). Composition profiles have also been studied by the use of both Raman scattering and resonance fluorescence spectroscopy, where the use of probes, which might affect the pattern of gas flow, is not required [241]. The Raman effect has also been used to measure temperature gradients in this CVD system. Average gas stream compositions have been determined by the use of gas chromatography [242]. Finally, growth rates have been continuously monitored with infrared detectors [243, 244] and with a laser system [245].

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