

**RECENT
DEVELOPMENTS IN
SURFACE COATING
AND MODIFICATION
PROCESSES**

RECENT DEVELOPMENTS IN SURFACE COATING AND MODIFICATION PROCESSES

Papers presented at a Seminar organized by the
Tribology Group of the Institution of Mechanical
Engineers and held at the Institution of Mechanical
Engineers on 10 October 1985.

Published by
Mechanical Engineering Publications Limited for

CONTENTS

THE ORIGINAL IS
OF LACK PP.

Introduction <i>J. Halling</i>	1
Chemical vapour deposition (CVD) for surface modification <i>M. L. Hitchman</i>	3
Principles of ion plating <i>D. G. Teer and R. D. Arnell</i>	21
Applications of ion plating <i>D. G. Teer</i>	29
Surface modification using Dynamic Recoil Mixing <i>A. E. Hill, J. S. Colligon and H. Kheyrandish</i>	35
Ion implantation <i>G. Dearnaley and W. A. Grant</i>	43
The laser's other role <i>W. M. Steen and V. M. Weerasinghe</i>	49
Designing and producing engineering surfaces <i>B. J. Gill</i>	53

Introduction

J HALLING, MEng, PhD, DSc, DIC, FCGI, FIM, FIProdE, CEng, FIMechE, FRSA

INTRODUCTION

The majority of engineering failures arise from deficiencies of the surface material in dealing with fatigue, friction, wear, corrosion, electrical and thermal contacts etc. Although in some instances these failures are exacerbated by high surface stress due to bending and/or torsion, it must be stressed that the surface material is the only part of any component which has to coexist with the external environment such as contacting surfaces and chemical attack. It follows that designers should choose bulk material from the standpoint of structural and economic criteria and surface material to deal with the external conditions. Surface technology deals with the methods for achieving these desired surface requirements and their behaviour in service.

The achievement of desirable surface properties involves either surface coating technology or processes which modify the properties of the bulk material to meet the surface demands. In a sense surface modification processes are themselves a rather special example of surface coating. In the past it has been traditional practice to manufacture components from a single material and to use surface modification processes to produce desired surface properties. Recent developments have not only produced improved modification methods but perhaps more significantly have created totally reliable surface coating technologies.

As loads, speeds and operating temperatures continue to increase attention has become increasingly focussed onto materials such as ceramics. Such materials are difficult to shape into the complex geometries of many engineering components but they can be readily deposited as coatings onto traditional materials shaped by the established cutting and forming processes. Such an approach is now well established in the cutting tool industry where its success augurs well for many other applications.

CRITERIA FOR THE EVALUATION OF SURFACE PROCESSES

With the very wide range of surface processes already available and the probability of new processes being developed it is perhaps useful to consider those factors which assist in the choice of the most appropriate process for any particular application. A good designer will of course choose "horses for courses"

and recognise that if a coat of paint is adequate there is no merit in choosing expensive high technology solutions. The factors likely to be of most interest are as follows:

a) For both coating and surface modification processes:

1. The process must give significant functional improvement, the degree of improvement being related to the additional costs involved. As an example; if the coating of a cutting tool doubles the productivity of a machine tool an increased tool cost of an order of magnitude may be justified.

When considering the economics of processes one should ideally include not only manufacturing costs but service costs such as reduction in energy due to lower friction and material costs often minimised by using coatings of expensive materials on cheaper substrates.

2. The process should provide uniform coatings or degree of modification on the complex geometries of most engineering components. With line of sight processes this usually involves the use of complex manipulative devices. In other processes this may be achieved by the mechanics of the process, e.g. vapour deposition and plasma nitriding.
3. Ideally the process should operate at relatively low temperatures so that the properties of the substrate are unaffected. This is essential when operating on polymers and even on steels one desires to avoid post process heat treatments to restore lost properties. This problem arises with the Chemical Vapour Deposition process.
4. With the increasing restrictions imposed by legislation the process should be free from pollution and safety hazards.
5. The process will be more attractive if it can be readily incorporated into a modern continuous production line. In this context processes must be capable of automation with a minimum of manual operation.

b) For coating processes:

1. The process should be capable of coating any material or combination of materials onto any substrate material. Such flexibility will often justify the large capital

investment inherent in the new processes.

2. The process must produce bonding of the coating with total integrity. Such bonding is dependent on three factors, the cleanliness of the surfaces, the energy of the process and, most importantly, the generation of a graded interface between the substrate and the coating rather than a plane of discontinuity.
3. The process should be able to control the structure of the surface. In some practical application one may require porosity of the surface layers whilst in other cases one requires porous free dense structures.
4. Most applications will require control of the surface finish of the coating. In some situations this is most readily achieved by coatings which simply replicate the finish of the substrate. This is particularly important with hard coatings where finish machining is an expensive process.

Chemical vapour deposition (CVD) for surface modification

M L HITCHMAN, Bsc, DPhil, CChem, FRSC
University of Strathclyde

SYNOPSIS A review of CVD processes and reactors is given with examples of CVD coatings and their properties. The principles underlying the preparation of coatings by CVD are discussed and illustrations of the applications of these principles to specific coating materials are given.

1. INTRODUCTION

Chemical vapour deposition (CVD) is the formation of a solid layer from the gaseous phase via a chemical reaction. It is to be distinguished from purely physical processes such as evaporation, sublimation and sputtering. By analogy with electroplating it is sometimes known as gas plating.

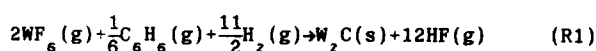
This article provides an overview of CVD. First of all, the requirements of a typical CVD apparatus are discussed and then illustrations of types of CVD processes are given. The geometry of reactors used in CVD varies widely, and typical configurations are next indicated. Since CVD is, by definition, a chemical process and since for controlled deposition endothermic reactions are preferred, energy has to be inputted to both initiate and sustain growth. Methods of initiating CVD processes are therefore reviewed. Examples of the types of layers and materials which can be prepared by CVD are then given, and important properties of CVD layers are summarised. This rather practically oriented section of the article is concluded by a consideration of the advantages and disadvantages of CVD relative to other deposition procedures.

Underlying all CVD processes are basic physicochemical principles, and without an understanding of these one has to resort to purely empirical procedures in order to optimise deposition parameters. Therefore, it is important to discuss the chemistry and gas dynamics in a CVD reactor and to consider the relative roles of these two types of process. This is done and the relevance of the principles are illustrated by reference to the deposition of specific coatings.

2. CVD APPARATUS

The exact arrangement of a CVD apparatus can vary widely, often depending on the particular applications. The basic requirements of a CVD apparatus can, however, be illustrated by reference to a generalised system. Figure 1 shows a schematic arrangement for the production of tungsten carbide coatings. The

overall reaction can be written as:



The apparatus can be thought of as being made up of several constituent parts and these are now briefly considered.

2.1 Source material

The simplest form of source material to handle is one which is a gas at normal temperatures and pressures since commercial supplies in gas cylinders of the required purity and composition can usually be obtained. Sometimes, though, it is necessary to use precursors which are liquids, or even solids, under ambient conditions. Then higher temperatures and/or low pressures have to be employed in order to transport the material to the reactor, often with the aid of a carrier gas. In the example of Figure 1, one reactant, hydrogen, is a gas but the other two are liquids. Benzene vapour is produced by controlled heating and argon carries the vapour to the reactor. The tungsten hexafluoride has a boiling point of 17.1°C and so at room temperature its vapour pressure is generally sufficient to generate a high enough partial pressure for the CVD process. However, care must be taken to ensure that no condensation of the vapour occurs in the pipework leading to the reactor; often heating tapes are wound round the pipes to avoid this.

2.2 Gas handling

As will become apparent when discussing the influence of gas flow on deposition (Sections 12 and 13), it is essential to be able to control total and relative gas flows. This may be done with conventional, manually controlled flow meters, but there is an increasing use of mass flow controllers (1) with electronic feedback for automatic control. The sequencing of gas flows may also be controlled either manually or automatically, with the latter being especially useful and desirable when reactants are hazardous or toxic.

2.3 Reactor

Shown schematically in Fig. 1 is a vertical, hot wall reactor. This is a very common configuration for the preparation of coatings by CVD (e.g. 2 - 4). Other configurations are illustrated in Section 4. Important considerations in reactor design include control of temperature and gas dynamics in order to ensure that uniform and reproducible growth characteristics are obtained. Temperature control may be effected in several ways and these are discussed in Section 5.1 below. The total pressure in the reactor is often at, just above or only slightly below atmospheric pressure. In such cases the gas flow near the substrate has an important influence on deposition, and if uniform growth over any given sample or from one sample to another is to be achieved considerable care has to be taken in designing the geometrical arrangement of the samples (Section 13). The problems associated with the influence of gas flow on growth uniformity can be alleviated by reducing the pressure in the reactor (5). This may be done by having a pumping system (e.g. a rotary pump and/or a blower) downstream of the reactor. This reduces the influence of convection and enhances the rate of diffusion, which if it is rapid compared with the rate of growth leads to very uniform layers, even for complicated geometries (5). The effects of temperature and gas flow on growth characteristics are discussed in Sections 11 - 13.

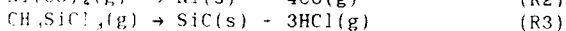
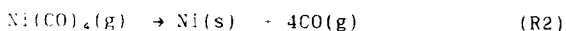
2.4 Exhaust of by-products

The gaseous by-products from a CVD reactor can often have unpleasant properties, as in the case of the tungsten carbide deposition reaction (R1). They cannot, therefore, be directly vented to the atmosphere, but must be trapped in some way; chemical and physical methods of removal of the product gas and any excess reactant gases are illustrated in Fig. 1. With a reduced pressure reactor the traps may be before and/or after the pumping system, depending on the nature of the exhaust gases.

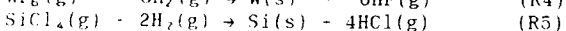
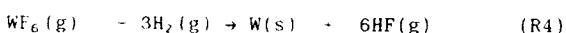
3. TYPES OF CVD PROCESSES

There are a wide range of reactions which are used for the purposes of CVD, but most, if not all, of them conveniently fall into one or more of four main groups.

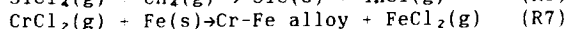
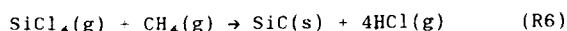
(a) Thermal decomposition reactions - These reactions are also known as pyrolytic reactions and they mostly involve the metal carbonyls, hydrides, and halides, and organometallic compounds. Some representative reactions are:



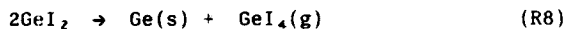
(b) Reduction reactions - The reducing agent in these reactions is usually hydrogen. Some typical examples are:



(c) Displacement or exchange reactions - Some examples of these reactions are:



(d) Disproportionation reactions - An example of these reactions is:



Some CVD coating processes may involve several types of reactions simultaneously. An example is reaction (R1) for the deposition of tungsten carbide.

4. TYPES OF REACTOR

Figure 1 illustrates a vertical, hot wall reactor. As mentioned this is a common configuration for the CVD of coatings, but other geometries such as horizontal reactors are possible. Whatever the exact geometry, though, the reactors are usually tubular in design. This is a useful advantage since the flow conditions and transport phenomena in such reactors are analogous to those often encountered in chemical engineering and so this can facilitate the understanding of the gas dynamics and mass transport in the reactor. The feature of the hot wall also has a number of advantages. First, very careful control of the temperature throughout the reactor can be maintained and, in fact, by having a combination of several heating elements it is possible to have a number of zones with differing temperatures to allow fine control of the CVD process. Second, there are no significant temperature gradients normal to the flow and so the rate of decomposition of the reactants is uniform across the whole cross section of the reactor. The fact that there is a uniform temperature across the reactor means, of course, that the material being deposited grows on the walls as a dense, adherent layer as well as on the substrate and there is little particulate contamination of the layer on the substrate. After a number of depositions in the reactor the deposit on the walls may be quite thick and start to flake off, so at that stage the reactor has to be cleaned. Particulate deposits on the reactor walls can also be a problem in cold wall reactors where the whole reactor is not enveloped by a furnace, and heating of the substrate alone occurs (Section 5). In this type of reactor since only the substrate is heated to the deposition temperature, there is a steep temperature gradient as one moves away from the substrate surface. The walls of the reactor will thus certainly be colder than the surface temperature, but, depending on the geometry and deposition temperature, they may still be at a sufficiently high temperature to allow some deposition on them. This deposition is often rather patchy and poorly adherent and so there is a risk of particulate contamination of the substrate. In addition, because of the steep temperature gradients the gas flow and mass transport in a cold wall reactor is much more complex than in hot wall systems. This can lead to considerable complications in controlling the growth of CVD layers, particularly the uniformity and structure of the layers. In spite of these various disadvantages cold wall reactors are used for the preparation of CVD layers, especially for cases where there is a low activation energy for deposition. In such

cases in a hot wall reactor gas phase nucleation can occur and this leads to very poor quality, non-adherent deposits. In a cold wall reactor by having the bulk of the gas at a lower temperature than the substrate surface, gas phase nucleation can be minimised and deposition then only occurs by heterogeneous processes which are much more conducive to producing good quality layers.

Figure 2 shows four different geometries for cold wall reactors. The designs are actually for reactors used for the epitaxial deposition of silicon (6), but similar geometries could be used for coating deposition as well. The schematic flow lines illustrate the complexity of the gas dynamics in cold wall reactors, and considerable effort has been put into trying to elucidate the gas flow and mass transfer in such reactors (e.g. 7 - 10).

5. METHODS OF ENERGY INPUT FOR CVD

5.1 Thermal CVD

As indicated in the discussion of hot and cold wall reactors, the traditional method of initiating and controlling CVD processes is by the input of thermal energy. In the case of hot wall reactors this is usually done by thermal radiation with the CVD reactor inside an oven or furnace. For cold wall reactors the most common form of energy input is by r.f. induction heating of a conducting substrate or susceptor (i.e. substrate support). More recently heating by photoradiation with high intensity photons from quartz iodine or tungsten filament lamps has been increasingly used, particularly for silicon deposition (11).

5.2 Plasma CVD

One of the main disadvantages of all types of thermal CVD is that the high temperatures often required to sustain the deposition process can cause thermal damage to the substrate; for example, crystalline stress may be introduced. A solution to these problems is to use other forms of energy input which allow deposition at lower temperatures. A method that has been extensively investigated and widely applied over the last few years is the use of plasmas. Since for many CVD processes with plasmas some heating is still required, although because of the additional energy input from the plasma temperatures are typically several hundred degrees lower than in conventional thermal CVD, the technique is often known as plasma enhanced CVD (PECVD) or plasma assisted CVD (PACVD).

In PACVD a high frequency r.f. field (e.g. 50kHz - 10MHz) with power inputs of typically 50W - 1kW is applied either by capacitive or inductive coupling to the reactor containing the reactant gases, which in order to sustain a plasma have to be at reduced pressure (e.g. 0.01-10 Torr). Excited free electrons produced in the plasma collide with gas molecules to produce reactive ions and secondary electrons. The substrates are usually supported on one or more heated electrodes in the reactor and impingement of the ionised gaseous species on the substrate surfaces leads to deposition reactions. Layers grown by PACVD are generally amorphous

in nature and are of good quality. Coatings which have been produced by PACVD include boron nitride (12-14), silicon carbide (15) and titanium carbide (16,17), and steels have been plasma carburised (18) and nitrided (15). The field of PACVD has been usefully reviewed in a number of places (e.g. 15,19).

5.3 Other methods

For the preparation of coatings little, if anything, has been done to investigate other methods of initiating CVD processes. For other applications of CVD layers, particularly in the semiconductor industry, much higher frequency radiation has been used to initiate CVD reactions and has given rise to the technique known as photochemical or photosensitised CVD.

In order for any form of electromagnetic radiation to interact with a molecule there must be absorption of the energy by the molecule from the radiation. Gaseous reactants such as used in CVD processes are commonly simple inorganic species with energy continuum at shorter wavelengths and higher energies than the region of the spectrum usually associated with photochemical reactions so that there is no, or only weak, absorption. In such cases, therefore, a suitable additional reactant needs to be introduced into the system to act as a sensitising agent. An example is in the deposition of silicon dioxide from a mixture of silane, nitrous oxide and mercury vapour (20, 21). The silane and nitrous oxide are mixed at room temperature in a flow system and the gas mixture is passed over a mercury surface before it is fed into the reactor chamber, which is kept at a reduced pressure (0.7-2.0 Torr). The reactor is illuminated through a quartz window with intense u.v. light from a mercury lamp and deposition occurs on the substrate lying on a heated susceptor (75-175°C). The mercury atoms are raised to an excited state by the u.v. radiation. Excited mercury atoms colliding with nitrous oxide molecules generate excited oxygen atoms which can then react with silane molecules to form silicon dioxide. Because of the high energy of the u.v. radiation the temperature required for oxide deposition is significantly less than for conventional thermal CVD (e.g. 450°C for low temperature oxide (LTO) (22)). The oxide properties, though, are comparable to those of LTO (21).

Photochemical CVD allows very low temperature deposition but, as indicated above, it is rather limited in its application because of the weak absorption of the u.v. radiation by the gaseous reactants. Also because the entire illuminated volume of gas reacts, unwanted deposition on reactor walls occurs and deposition of silicon dioxide is less than 20nm min⁻¹. The use of lasers gives one the possibility both of higher power inputs, and hence increased reaction and deposition rates, and of concentrating the input into a very small reaction volume. Recently, a method has been described (23) for the direct laser induced deposition of silicon dioxide. The reaction between silane and nitrous oxide is brought about by photodissociation of the nitrous oxide with a pulsed ArF (193nm)

laser. Layers of silicon dioxide are produced over a wide deposition temperature range (20-600°C) with deposition rates as high as 300nm min⁻¹. One particularly attractive feature of laser induced CVD is the possibility of focussing on a small region and of scanning to other positions to provide localised deposition and thus coating substrates in specific areas.

Another way of using lasers for deposition in limited areas is for the production of localised heating. The principle of this technique is to choose the laser wavelength such that the gaseous reactants are transparent and the substrate is absorbing. As mentioned above, conventional thermal CVD can introduce a lot of thermal stress and damage into the substrate. With laser heating this problem can be circumvented by using a laser beam of optimum energy which only heats a thin layer of substrate surface. A recent example of this type of laser CVD is the deposition of thin tungsten and iron coatings in both spot and line geometries (24,25).

From this brief review it can be seen the CVD processes have been initiated with radiant energy of wavelengths ranging from $\sim 10^4\text{m}$ (r.f. plasmas at 50kHz) to $\sim 10^{-7}\text{m}$ (e.g. photochemical or laser induced CVD). It is unlikely that there will be much scope for exploring the use of wavelengths much outside this range. Wavelengths much shorter than 10^{-7}m lead into the X-ray and γ -ray regions of the electromagnetic spectrum and into the hazards that handling such high energy radiation present. Wavelengths much longer than 10^4m will have too little energy to initiate chemical or thermal processes. It may be interesting, though to look at forms of irradiation other than electro-magnetic radiation, such as sound waves. For catalytic processes high intensity ultrasound, for example, has the potential for initiating unusual reactions at low temperatures and on a large scale (26). This has led to the suggestion of using ultrasonic waves as a means of bringing about CVD reactions (27). No work, though, has to our knowledge, been done on this type of energy input.

6. EXAMPLES OF CVD COATINGS

Table 1(a) provides an indication of the wide range of coatings which can be prepared by CVD. Table 1(b) shows that layers may be amorphous, polycrystalline or single crystal; although for coatings one is scarcely interested in single crystal material. One of the main advantages of CVD over physical deposition techniques (e.g. evaporation, sputtering) is the ability to produce composite materials either by simultaneous or successive deposition steps. An example of successive coatings is the triphase of titanium carbide/titanium carbonitride/titanium nitride which is commonly offered as a coating for high speed tools (4). An example of simultaneous deposition is the preparation of titanium carbonitride which can be deposited from organic nitrides which act as carbon and nitrogen sources (2,28,29).

7 SUBSTRATES

Table 2 gives examples of the combination of coatings and substrates which are currently in production or which have been developed to varying extents. However, although a wide range of coatings have been put on an equally wide range of substrates it is not always a simple matter to match the coating and the substrate. This point is considered further below (Section 8.2).

8 PROPERTIES OF CVD COATINGS

8.1 Hardness

One of the main reasons for coating a substrate material is to protect the substrate against excessive wear, for example on cutting tools or ball bearings. Therefore one of the properties of such a coating is that it must be hard. Figure 3 shows the relative hardness of a number of coatings and the advantage of coating steel with, say, titanium nitride or titanium carbide is apparent.

Hardness is a necessary but not sufficient criterion of a coating for protection against wear. In addition to hardness, coatings should have low coefficients of friction against themselves and against other coatings or substrate materials in order to reduce wear. Figure 4 shows (30) the tribological behaviour of different hard coatings for a pin with a spherical end rubbing against a rotating disk. For both dry and humid air, tests were done without lubrication, but one might expect the high moisture content of the humid air (> 94% relative humidity) to provide some lubrication. This is supported by the fact that in general both friction coefficients and wear rates are less in humid air than in dry air. The greatest wear rates of both ball and disk are for steel and steel ($10^{-13} - 10^{-14}\text{m}^2\text{N}^{-1}$) which is not unexpected for a metal with a low hardness ($\sim 900\text{kp mm}^{-2}$) and high coefficient of friction (~ 0.8 in dry air). A low wear rate ($\sim 10^{-15}\text{m}^2\text{N}^{-1}$) for the silicon carbide disc with a steel ball is also what one might expect for a hard coating (silicon carbide $\sim 2500\text{kp mm}^{-2}$) being rubbed by a soft surface (steel $\sim 900\text{kp mm}^{-2}$) with a low coefficient of friction (~ 0.2 for steel and silicon carbide), but, perhaps less expectedly, the low coefficient of friction also dramatically reduces wear of the steel ball as well ($\sim 10^{-16}\text{m}^2\text{N}^{-1}$). Very low wear rates are found for hard coatings rubbing against each other with low friction coefficients (e.g. titanium carbide and silicon carbide). However, there are clearly other factors affecting wear rates for, for example, with the case of the hard titanium nitride ball and silicon carbide disk which appear to have a low, average value for the coefficient of friction in dry air (~ 0.2) the wear rates of both surfaces are relatively high ($\sim 10^{-14}\text{m}^2\text{N}^{-1}$ for the titanium nitride ball in dry air and $\sim 10^{-13}\text{m}^2\text{N}^{-1}$ for the silicon carbide disc).

Other factors which might be expected to influence the behaviour of materials under mechanical load will be intrinsic stresses, defect concentrations, grain size, orientation of microstructures, metastability of phases, degree of macro- and microporosity, and extent of incorporated impurities in the coatings.

Table 1 Examples of coatings prepared by CVD

(a) A classification by chemical form.

Metals	: Be, Al, Ti, Nb, Ta, Cr, Mo, W, Re
Graphite and carbides	: C, B ₄ C, SiC, TiC, Cr ₃ C ₂ , WC
Nitrides	: BN, TiN, TaN, Si ₃ N ₄
Boron and borides	: B, TaB ₂ , WB, FeB, NiB
Silicon and silicides	: Si and the different silicides of Mo, Fe, Ni
Oxides	: Al ₂ O ₃ , SiO, SiO ₂
Organic compounds	: PTFE

(b) A classification by application, crystalline form and use.

General Application	Type of Layer Grown	Use	Example
Electronic	Epitaxial (single crystal)	a) Light emitting diodes	GaAs, GaAs _{1-x} P _x
		b) Radiation detectors	CdS
		c) Integrated circuits	Pb _{1-x} Sn _x Te Si
	Poly-crystalline Amorphous	Transparent conductors Encapsulation and passivation of devices	SnO ₂ Glasses
Coatings	Poly-crystalline	a) For metal cutting tools	TiC
		b) For corrosion protection	Ta on steel

Table 2 Examples of coating and substrate combinations

Coatings																
Substrates	Al ₂ O ₃	Cr	Mo	W	WC	TiC	TiN	Si	SiC	Si ₃ N ₄	Silicides	B	Borides	B ₄ C	BN	PTFE
Ceramic	D		D	D		P			D	D		P				
Graphite, Diamond		D	D	D	D	D	D	D	D	I		F		P	P	P
Aluminium oxide	D	D	D	D		P	D		D	D		P				
Cemented carbides	D	D	D	D	D	I	I	D				P				
Glass, quartz	P		D	D		P						P	D			D
Silicon	D															
Tantalum, niobium	P	D				P	P		D		D	D	P	D	P	
Molybdenum		D	D	D		P	P		D		D	D	P	D	P	
Tungsten		D		D	D	P	D	D	D		D	D	P	D	P	
Nickel alloys		D	D	D		P	D				D	D	I	D	P	
Cobalt alloys		P	D	D		P					D		D			
Copper alloys			D	D		P							P			P
Steel Alloys		I	D	D		I	I			D	D		P			D
Non-alloyed steel		D				P	D				D		P			D
Stainless steel		D				P	D				D	P	P	P	P	D
Key:	Industrial processes	I				Developed technique	D				Partially developed technique	P				

Furthermore, hard coatings can only deform elastically with a fracture strain of ~2% and so these materials cannot withstand mechanical overloading without risk of cracking. Certainly, cracking and flaking are well known phenomena in cemented carbide cutting tools and this is one of the reasons why cemented carbide inserts are not widely used in interrupted cutting operations. And this leads on to the consideration of another important property of CVD coatings - adhesion.

8.2 Adhesion

Obviously the adherence of a layer to the substrate will play as important, if not more important, a role as hardness and friction in determining the wearability of a coating. For example, after a prolonged period of running time at high speeds titanium carbide coated ball bearing elements can deteriorate due to a loss of cohesion between coating and substrate leading to chip-offs within the coating. This lack of cohesive or adhesive bond strength which can often be the cause for the mechanical failure of a coated tool or work piece is of a complex nature and is not well understood. Clearly, though, as well as depending on deposition parameters such as temperature and time, it will also depend on the degree of compatibility between the coating and substrate. So, for example, cemented carbides are very favourable substrate materials for titanium carbide and titanium carbonitride coatings since they have similar physical properties to the coatings. If, however, steel is used as a substrate thermal treatments need to be carried out after the deposition in order to release stresses and strains built into the interfacial region.

One way of overcoming incompatibility is to form an interfacial transition zone between the final coating and the substrate. This zone can be as thin as a single atomic layer or it can extend to nearly a millimetre. For the thicker transition zones one has effectively a new phase between the coating and the substrate and a three body instead of a two body composite. Sometimes an interfacial zone is formed by interdiffusion of the coating and substrate materials so that there is a "buffer" region with properties intermediate between coating and substrate; within this "buffer" region stresses caused by mismatch of crystallographic parameters, differences in thermal expansion coefficients, and microstructural defects can be released.

Another important factor in promoting adhesion is the cleanliness of the substrate prior to deposition. This is not only because impurities on the surface can physically block the deposition of a coating and so lead to a discontinuous, flaky layer, but also because they can markedly affect the mode and amount of nucleation of the depositing material. Some preliminary studies have shown, for example, that (30) a combination of cobalt binder metal and dissolved carbon in cemented carbide substrates leads to a dramatic increase in nucleation rate of titanium carbide layers. Also it is known from practical experience that improved adherence between coating and substrate is obtained with increasing nucleation density; this is not unexpected

since the larger the number of growth sites the less the amount of coarse grain growth and the greater the number of anchorage points for adhesion promotion. As with the factors affecting adhesion it is difficult, however, to get a quantitative correlation between adhesion and deposition parameters. This is partly because it is not always easy to reproduce exactly deposition conditions, especially surface characteristics, from one run to the next, but it is also due to the problems of measuring quantitatively and reproducibly the adhesion itself.

One technique which has been relatively highly developed for measuring adhesion and attempting to correlate it to industrially important properties is the Scratch Test. The method is based on a model of Benjamin and Weaver (31) and consists of scratching the coated surface with a diamond stylus of defined radius of curvature at a given velocity and under a progressively increasing load until the coating cracks, locally flakes off and eventually is removed entirely from the scratch channel. The critical load at which the coating begins to lose its load bearing capacity, characterised by the first appearance of cracks or local flaking, is taken as a measure of the coating adhesion strength of the substrate. There is good evidence in many cases for relating this onset of failure with the practical limit of usefulness of a coating. The principle of the technique, its application to a range of coatings, and its further development for the determination of critical load by acoustic emission have been usefully illustrated by Hintermann (30).

8.3 Purity and composition

The composition of a layer will obviously affect its properties, and sometimes it only requires very small traces of a foreign species to give dramatic changes in layer characteristics. This is especially the case for layers for semiconductor applications, but it can also apply to coatings as well. For example, the CVD of silicon nitride from a gas mixture of silicon tetrachloride, ammonia and hydrogen produces preferentially an amorphous or α -crystalline layer (32). Introduction of less than 3% of titanium nitride by adding to the gas mixture a flow of titanium tetrachloride produces either an α - or a mixed ($\alpha + \beta$)-crystalline layer - Fig. 5. In this particular case the additional titanium nitride was introduced intentionally but if unintentional incorporation occurred from, for example, the substrate then this could result in a less adherent layer since the titanium nitride/silicon nitride ($\alpha + \beta$) composite has large crystal grains compared with the very fine grain structure of α -crystalline silicon nitride. Since one of the features of CVD is that it allows the production of extremely high purity materials then unintentional impurity incorporation will almost certainly come from the substrate; thus the control and cleanliness of the substrate surface is once again apparent.

We have already mentioned that one of the attractive features of CVD is the ability to use it for the production of composite layers, and this is desirable, of course, in order to

bestow new and improved properties on coatings. In discussing adhesion, we have indicated the usefulness of depositing successive layers to form a heterogeneous structure, but desirable layer properties can also be achieved by simultaneous deposition of several constituents to form a more homogeneous type of structure. An example of this type of layer is the formation of titanium carbonitride coatings. These coatings are known to provide good protection against wear and corrosion for both cemented carbide (33) and steel substrates (34). They are traditionally formed from mixtures of nitrogen/methane/hydrogen/titanium tetrachloride at temperatures ~1000°C. The high deposition temperature can, however, lead to excessive grain growth and substrate distortion, especially for steel substrates, and consequently give poorly adhering layers. Recently, Bonetti-Lang and co-workers (28) have investigated lower temperature deposition (550°C-850°C) using organic compounds, such as hydrazines, nitrides and amines, as carbon and nitrogen sources. When compared with standard titanium carbide coatings the composite titanium carbonitride layers showed lifetimes up to seven times longer for cutting inserts and one and a half times longer for simulated milling tests. The scale-up of an organic nitride based CVD titanium carbonitride coat process for industrial production has been described by Bonetti and Wahl (29).

8.4 Thickness

The thickness of coatings prepared by CVD can vary within wide limits, from rather less than 0.1µm to greater than 100µm, depending upon the type and application of the coating. Using the Scratch Test, a positive linear relationship between critical load and coating thickness has been found (30). However, it is not clear whether this correlation is due to a real change of the physical properties at the interface or simply due to the higher load needed to produce the same deformation in layers of different thicknesses. Whatever the reason, improved wear characteristics cannot be obtained by continuing to increase layer thickness indefinitely since one has also to satisfy requirements dictated by the cutting or forming requirements of the tooling. For coatings which are intended to change the wear properties of a surface thicknesses are generally in the 1-10µm range.

9. ADVANTAGES AND DISADVANTAGES OF CVD

The discussion of Sections 2 - 8 above has been largely in terms of the preparation of coatings for improved cutting wear. There are, though, other reasons for coating substrate materials. Improved wear for applications where there is abrasion due to sliding and rolling contacts is also important, as is protection against corrosion and oxidation. The particular examples which have been given in the above discussions illustrate, however, the general advantages and disadvantages of preparing coatings by CVD. These are summarised below.

9.1 Advantages

A large range of elements and compounds can be prepared by CVD, far greater than can be

achieved by physical techniques such as evaporation or sputtering. This range extends over metallic, ceramic and polymeric materials with the possibility of producing layers of varying degrees of crystallinity, from monocrystalline deposits in some instances through the more commonly obtained polycrystalline films to completely amorphous layers in other cases. Another important advantage of the production of all these layers by CVD is the ability to vary the composition from a very high degree of purity and perfection in the case of single crystal materials to a carefully controlled stoichiometry for polycrystalline and amorphous layers. This important feature of CVD processes, which is much less readily obtainable by physical deposition techniques, can not only lead to layer properties which are desirable but which also may be unique.

9.2 Disadvantages

Although a large number of different types of coating have been prepared on a wide range of substrates, there are instances where coatings do not adhere well to the substrate. Therefore for the preparation of CVD layers the coating and substrate must be compatible. Not unrelated to this requirement is the fact that most depositions involve elevated temperatures and this can limit the choice of substrate material because of problems of possible deformation or modification of the substrate.

Clearly CVD is not a technique which will necessarily provide a universal solution to all coating problems. Nevertheless, it is a technique which is sufficiently versatile and with distinctive enough features to make it an attractive possibility for many instances where it is desired to coat a substrate in order to give protection against abrasion, corrosion and erosion.

10. PRINCIPLES OF CVD

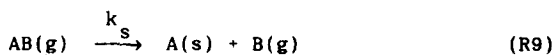
All that has been said thus far has been of a qualitative and empirical nature. However, in order to produce satisfactory coatings for any particular application it would obviously be very valuable to have a basic understanding of how important features of CVD layers, such as growth rate, uniformity, composition, structure and mechanical properties, are dependent, in general, on the growth conditions and, more particularly, on the chemistry of the CVD process. This is a very complex subject and a considerable amount of work has been done in trying to elucidate the effect of reactor parameters on layer characteristics (35-37). Here we can only briefly outline the principles involved and illustrate one or two aspects of the roles of reactor design and CVD chemistry in determining features of layer growth.

Figure 6 shows schematically the various processes which will be involved in forming a solid layer on a surface by decomposition of an initial gaseous species. It can be seen that factors which may have an influence on layer growth will include gas phase reactions, reactant transport to the surface, adsorption of reactant, surface diffusion and reactions, desorption of by-products, and transport of these by-products away from the surface. An

overall reaction, which we can write very simply as in the examples given in Section 3 above, is clearly made up of a number of individual processes, each of which in turn may be far from simple. So in order to obtain some insight into the ways in which the various processes can influence layer growth we shall simplify the total picture by considering just two general types of process - transport and chemical kinetics.

11. CHEMICAL KINETICS IN CVD

Let us consider a simple CVD process of the form



corresponding to the deposition of solid A from gaseous AB with B as a gaseous by-product. The rate of the deposition reaction (j_k) will be proportional to the concentration of AB at the surface (C_s^{AB}) and this is represented by

$$j_k = k_s C_s^{AB} \quad (1)$$

where k_s is the proportionality constant, known as the reaction rate constant. The units of j_k can be, for example, moles $cm^{-2}s^{-1}$ and with the corresponding units of C_s^{AB} being moles cm^{-3} then the units of k_s are $cm s^{-1}$; growth rates in terms of increase of layer thickness per unit time (e.g. $cm s^{-1}$) are obtained from j_k by multiplying by the molecular weight of the layer and dividing by its density.

The dependence of the deposition rate on temperature reflects the variation with temperature of the rate constant, and this is described by the Arrhenius equation

$$k_s = A \exp(-E/RT) \quad (2)$$

where E ($J \text{ mole}^{-1}$) is the activation energy required to overcome the energy barrier to deposition, T is the thermodynamic temperature (K), R is the molar gas constant ($J \text{ mole}^{-1}K^{-1}$), and A is a term which describes the molecular rearrangement involved in going from the gaseous state to an adsorbed state on the surface. For an endothermic activation, where E has a positive value, it is seen that the rate of reaction will increase exponentially with temperature - curve A in Fig. 7. An increased rate of deposition means an increased rate of consumption of the gaseous reactant and this reactant has thus to be replaced from the bulk of the vapour. This leads on to a consideration of transport in CVD.

12. TRANSPORT IN CVD

In the bulk of the vapour the distribution of gaseous species is determined essentially by convective transfer (35) and since this is generally an efficient means of transport the concentration distribution will be uniform. Close to the reaction surface, on the other hand, the gas velocity falls due to frictional forces at the surface and the transfer of matter is then largely diffusive. Diffusional transport is not as efficient as convective transport and so any significant consumption of the gaseous species as a result of chemical reaction on the surface leads to depletion of the gaseous species near the surface - Fig. 8. The rate of diffusional transport (j_t) to

the surface will be proportional to the concentration gradient at the surface and if a linear approximation is made for the concentrations profile then we have (curve B in Fig. 8)

$$j_t = D(C_g^{AB} - C_s^{AB})/d \quad (3)$$

where C_g^{AB} and C_s^{AB} are, respectively, the concentrations of the gaseous species AB in the bulk of the gas and at the surface, d is the approximate distance over which diffusional transport is occurring (known as the diffusion layer thickness), and the proportionality constant D is called the diffusion coefficient. The units of j_t will be the same as those of j_k (e.g. moles $cm^{-2}s^{-1}$) and so with the units of C_g^{AB} and C_s^{AB} as moles cm^{-3} and of d as cm , the units of D will be $cm^2 s^{-1}$. For convenience the ratio D/d can be written as k_t , which will have the units $cm s^{-1}$. By analogy with k_s , k_t can be considered as the rate constant for diffusional transport to the surface. Under given conditions of temperature and of bulk concentration of gaseous species the maximum rate of transport to the surface will obviously be when the surface concentration is zero ($C_s^{AB} = 0$) and one then has the transport limited or limiting diffusional rate ($j_{t,L}$)

$$j_{t,L} = k_t C_g^{AB} \quad (4)$$

The concentration profile corresponding to this condition is shown by curve C in Fig. 8. However, although we consider k_t as a rate constant it has a very much weaker temperature dependence than k_s (10,35). It can be shown that (35)

$$k_t \propto T^{-1/6} \quad (5)$$

and the resulting effect on the rate of transport to the surface is shown by curve B in Fig. 7.

13. COMBINED CHEMICAL KINETICS AND TRANSPORT

Clearly, for there to be continuity at the surface the kinetic rate of deposition must equal the rate of arrival of AB at the surface and so equations (1) and (3) may be equated, the unknown surface concentration C_s^{AB} can be eliminated and the following expressions obtained for the overall rate of reaction (j)

$$j = k_s k_t C_g^{AB} / (k_s - k_t) \quad (6)$$

or on inverting

$$1/j = (1/k_t C_g^{AB}) + (1/k_s C_g^{AB}) \quad (7)$$

The plot for the overall growth as a function of temperature corresponding to these last two equations is shown by curve C in Fig. 7. Although the curves in Fig. 7 have been calculated for a specific deposition (that of silicon from silicon tetrachloride - reaction (R5)), they nevertheless show the general temperature dependence of most CVD processes. In particular, it can be seen that over a wide temperature range the overall rate of deposition has contributions from both transport and kinetic processes. Equation (7) perhaps shows this most clearly. If the rate of layer growth is regarded as being equivalent to a current in an electrical circuit (35) then equation (7) shows that the deposition process

can be likened to a series resistive network made up of the resistance of transport (R_t) and the resistance to the surface reaction (R_s) with the current (or rate of growth) being determined by the relative values of these two resistances. So when the kinetic rate is much higher than the rate of transport (i.e. at high temperatures) then the transport resistance is much greater than the reaction resistance and the overall rate is controlled by the limiting transport of species to the surface, and in Fig. 7 curve C merges into curve B for the transport limited diffusional rate - equation (4). At low temperatures, on the other hand, the kinetic rate is much lower than the rate of transport (or the reaction resistance is much greater than the transport resistance) so there is no depletion of reactant AB near the surface ($C_s^B = C_g^B$ - curve A in Fig. 8), the overall rate is controlled by the chemical kinetics (equation (1) with $C_s^B = C_g^B$) and curve C of Fig. 7 merges into curve A for the kinetic rate of growth.

The various conditions mentioned above for the two extremes of transport control of growth and kinetic control are summarised by the first five criteria given in Table 3.

Table 3: Conditions for transport and kinetic control of a CVD process.

Transport Control	Kinetic Control
$R_t \gg R_s$	$R_s \gg R_t$
$k_t (=D/d) \ll k_s$	$k_s \gg k_t$
$j = k_t C_s^B$	$j = k_s C_s^B$
$C_s^B \ll C_g^B$	$C_s^B = C_g^B$
$j \propto T^{1/6}$	$j \propto \exp(-E/RT)$
$\partial j / \partial u \neq \text{constant}$	$\partial j / \partial u = 0$

The last criterion shows how the growth rate is dependent on the flow velocity (u) of the bulk of the gas. In the case of transport control the criterion is obtained by considering an expression (35) for the diffusion layer thickness (d)

$$d \sim (lD/u)^{1/2} \quad (8)$$

where l is a characteristic length such as the distance along the susceptor. Coupling equation (8) with equation (3) shows that under transport controlled conditions a significant and often useful enhancement of growth rate can be achieved by increasing the gas velocity. However, from equation (8) it will also be noted that for reactors such as those shown in Fig. 2(b) and (c) the diffusion layer thickness increases as one moves along the susceptor away from the entry point of the gases into the reactor (i.e. for larger values of the characteristic length l). This means that if CVD is being carried out under transport, or mainly transport, control the growth rate on a downstream substrate will be less than that on an upstream one; if the substrate is sufficiently long there can even be non-uniform growth on one substrate. This undesirable effect of growth non-uniformity can be counteracted and largely overcome by using a sloping susceptor, as in fact shown in Fig. 2 (b) and (c). By sloping the susceptor in this way the distance between the susceptor and reactor wall is reduced leading to a diminution in cross sectional area for the gas flow. Since gas

flows are always controlled so that there is a constant volume flow, the linear velocity (u) is thereby increased as l increases and by careful design the ratio l/u in equation (8) remains constant.

If deposition is carried out under conditions where kinetic control prevails, then these problems associated with the gas flow do not arise since the growth rate is low enough not to cause any depletion of the reactant at the substrate surface ($C_s^B = C_g^B$ - curve A in Fig. 8) and there is thus no transport contribution to, and hence no effect of the gas velocity on, growth. It might therefore be thought that the sensible thing to do to avoid the complications associated with mass transport is to always ensure that growth is under kinetic control. Figure 7 reminds us, however, that kinetic control occurs at low temperatures and there may be a number of reasons why low temperature growth is not desirable. For example, a relatively thick coating might be required and the low growth rate could mean an unacceptably long time for the deposition. Or the quality of the film (e.g. the degree of crystallinity) obtained with low temperature deposition might not be compatible with the properties demanded for a particular application. And even if growth at low temperatures is acceptable, because of the exponential dependence on temperature of the growth rate (equation (2)) there can be problems in achieving sufficiently good temperature control to ensure that there is exactly the same surface temperature over a given substrate or from one substrate to another.

For these various reasons CVD of coatings is often carried out under conditions where, if there is not complete control by transport, there is at least some degree of transport control, and as a result consideration has to be given to the types of problem associated with non-uniform growth discussed above. Unfortunately in many instances the solution is not quite as simple as might have been implied by the discussion about sloping susceptors. That procedure works well for substrates with a simple geometry, but for substrates with more complex shapes it does not overcome the problem of non-uniform gas flow over different parts of the substrate. As can be imagined large protruberances and deep crevices can give rise to flow eddies and undisturbed regions, and under otherwise overall transport controlled conditions there will be deposition that is far from uniform with the additional possibility of poor step coverage. The only real solution to this type of problem is to carry out deposition under conditions where there is less transport control. This means, of course, more kinetic control, but in addition to obtaining that by growing at lower temperatures there is another way of achieving it - by reducing the pressure in the reactor.

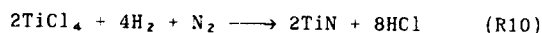
By considering equations (3) and (8) it can be seen that the rate of transport is proportional to $D^{1/2}$. From the classical kinetic theory of gases it is known that $D \propto 1/(Total Pressure P)$ and so the rate of transport will be proportional to $1/P^{1/2}$. Therefore by adding a pumping system to the CVD reactor (e.g. placing a pump at the end of the

exhaust line in Fig. 1) the pressure in the reactor can be reduced to, say, 100mTorr and the rate of transport enhanced by a factor ~ 100 . Of course, lowering the pressure in a reactor means that the concentration of gas available for reaction is also lowered, but this does not necessarily mean that the growth rate will be correspondingly lowered (cf. equation (1)). When operating in a reactor at atmospheric pressure the reactant gas is almost invariably diluted with a carrier gas (e.g. the argon in Fig. 1), but in reduced pressure reactors pure reactant gases are often used. Thus while there may be a difference of $\sim 10^4$ in total reactor pressure between a reduced pressure and an atmospheric pressure reactor, the partial pressure of a reactant (p_{AB}) in the two reactors may differ by less than 1:10 and the relative growth rates achieved will also therefore lie in this range. Very uniform growth on a large number of closely spaced substrates can be achieved in a reduced pressure reactor and this shows that such a reactor is a useful means of overcoming problems of transport controlled growth (5). Of course, if there is no transport control there must be kinetic control and, as already mentioned, this means there must be very careful control of the temperature in the reactor. For this reason reduced pressure systems usually have hot wall reactors, where the reactor is completely encased in a well lagged furnace. With care temperature control to better than $\pm 1^\circ\text{C}$ can be achieved with modern resistance heated furnaces and a thickness uniformity of better than $\pm 5\%$ both on a given substrate and from one substrate to another can be obtained (38).

Having discussed very briefly and simply some of the basic principles of CVD we shall now finally illustrate these principles by reference to two particular coating processes.

14. APPLICATIONS OF PRINCIPLES OF CVD TO COATING PROCESSES

The first coating process to be considered is the deposition of titanium nitride (TiN) onto a titanium carbide coated substrate with a composition of 94 weight per cent of tungsten carbide and 6 weight per cent of cobalt, as reported by Kim and Chun (39). Figure 9 shows a schematic of the experimental arrangement. The deposition is from a mixture of titanium tetrachloride, hydrogen and nitrogen, with the hydrogen acting both as a reducing agent in the reaction



and as a carrier gas for the TiCl_4 vapour, which is formed by bubbling the hydrogen through a thermostatically controlled reservoir containing liquid TiCl_4 . The reactor is a hot wall system in a horizontal, resistance heated furnace. The deposition conditions are summarised in Table 4.

Figure 10 showing the effect of temperature on growth rate is given in the form of an Arrhenius plot of $\log(\text{deposition rate})$ vs $1/T$. From equation (2) we would expect at the lower temperature end a linear plot with a slope of $-E/R$, while at higher temperatures we would expect from equation (5) an almost horizontal plot, or certainly one with a much lower slope than in the kinetic region. Figure 10 is seen to conform to these expectations. However, some care is needed in interpreting the sort of plot given in Fig. 10, since, as Fig. 7 shows, there is a rather gradual transition from kinetics to transport over a wide temperature range. An Arrhenius plot being a log/linear plot leads one to think in terms of two distinct regions - a kinetically controlled region and a transport controlled region - with

Table 4: Deposition conditions for titanium nitride (39)

Flow rates ($\text{cm}^3\text{min}^{-1}$)		Temperature ($^\circ\text{C}$)	Gas partial pressures (atm)		
H_2	N_2		TiCl_4	H_2	N_2
100-500	100-500	1050	0.030	0.485	0.485
300	300	900-1150	0.030	0.485	0.485
250	250	1050	0.015-0.040	0.480-0.493	0.505-0.467

Note: Total pressure in reactor = 1 atm; Deposition time in all cases = 1 hr

only a short transition between the two. Figure 7 shows that transport can have a significant effect on growth even at low temperatures so in such plots the linear low temperature portion of the curve, while having the major features of kinetic control (cf. Table 3), will in fact show some characteristics of mixed control. For example, the activation energy being for a mixed process will depend on flow rates. This effect is shown in Fig. 11, where Arrhenius plots have been calculated using the same parameters as used for the calculation of Fig. 7, but with varying flow rates. Some caution is thus required in obtaining from Arrhenius plots kinetic information which may be of importance in understanding factors affecting layer characteristics.

The high temperature region ($> \sim 1000^\circ\text{C}$) will similarly have a contribution from kinetics, but nevertheless will be expected to show the main features of transport control. This is supported by Fig. 12 which shows that as expected from equation (3) and (8), the growth rate is linearly dependent on the square root of total flow rate, at least for flow rates $< \sim 700 \text{ cm}^3\text{min}^{-1}$. Above $700 \text{ cm}^3\text{min}^{-1}$ there is a deviation from linearity, but this is in accord with a more detailed theoretical analysis (36) which shows that at a constant temperature while growth may be purely transport controlled at low flow rates, the growth becomes under mixed control at higher gas flow rates - Fig. 13. This shift in the shape of the curves with flow rate occurs because as one uses higher and higher flow rates then at a given temperature there will be less and less transport limitation on growth and more and more kinetic contribution to the overall growth.

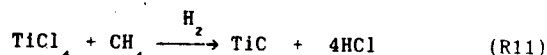
From the point of view of layer quality, scanning electron micrographs show that TiN crystal size shows a steady increase with temperature over the range 950°C to 1150°C , which encompasses a mixed transport/kinetic controlled region and a transport controlled region. This behaviour is understandable in terms of an increased rate of crystal growth with temperature - the faster the growth of nuclei the larger will be the final crystallite size. SEM pictures also show that there is an increase in crystal size with total gas flow rate for flow rates up to $\sim 700 \text{ cm}^3\text{min}^{-1}$ but that beyond that flow crystal size becomes almost independent of flow rate. The increase in crystal size with flow rate at low flows simply reflects the increased growth rate due to more rapid transport - the more rapid the layer growth the more rapid the crystal growth. At high flows there is a larger kinetic contribution to total growth, less dependence of growth rate on flow (cf. Fig. 13), and hence a correspondingly smaller dependence of crystal size on flow.

An increase in the partial pressure of TiCl_4 (PTTC) will also increase growth rate (cf. equation (6)), but in this case it is found that there is a decrease of TiN crystal size with PTTC. The reason this occurs is that increasing PTTC not only increases overall growth, but also increases the rate of crystal nucleation. A higher nucleation rate will mean that for the same total amount of material

deposited there will be a larger quantity of smaller crystals formed, and this is clearly the dominating effect of increasing PTTC.

These observations and the earlier observation (Section 8.2) that more adherent layers are generally formed with increased nucleation density, would suggest that good conditions for depositing TiN coatings are a high partial pressure of TiCl_4 (e.g. $\sim 0.03 \text{ atm}$), low total gas flow rates (e.g. $\sim 200 \text{ cm}^3\text{min}^{-1}$) and low deposition temperature (e.g. $\sim 950^\circ\text{C}$). Such conditions are often used in practice, but they will give rise to mixed kinetic and transport control and so due consideration will need to be taken of uniformity requirements. It would not be desirable to increase the flow rate to try and reduce the effect of transport since this leads to larger crystallites. One option to try and get more kinetic control would be to reduce the growth temperature even further, provided, of course, that longer growth times for a given layer thickness are acceptable and also that higher deposition temperatures are not needed for other reasons, such as giving some alloying, sintering or annealing of the coating to make it more adherent and compact.

Another way to obtain less effect of gas flow is to reduce the reactor pressure, as suggested in Section 13. Chun and co-workers (40) have investigated this possibility for the deposition of titanium carbide (TiC) from titanium tetrachloride, methane and hydrogen.



For this deposition process it was found that not only was a finer grain structure obtained at lower temperatures, as with TiN, but that the grain size of the TiC was much finer with a decrease in the total pressure as well.

The example of TiC is a good one to conclude this discussion of the applications of the principles of CVD, for while it usefully illustrates the basic principles of transport and kinetics discussed in Section 13 it also shows on more detailed examination that there can be other factors influencing layer growth and characteristics. For example, it has been found that (40) the composition of the substrate has a marked influence on the growth, especially during the initial stages. The higher the cobalt content of a steel substrate the higher the growth rate and this is attributed to the promotion by the cobalt of the diffusion of carbon out of the steel into the depositing material. This merely underlines, however, the point which we have been trying to make in the second half of this review. Namely, that, while CVD is undoubtedly a useful and valuable technique for carrying out surface modification, there is a continual need for more basic studies in order to obtain a more fundamental understanding of the various processes in order that the technique of CVD can be fully exploited for the preparation of surface coatings.

REFERENCES

1. Kern W and Ban V S in Thin Film Processes, Academic Press, 1978, p.257
2. Bonetti-Lang M, Bonetti R, Hintermann H E, and Lohmann D, in Proc Eighth Int Conf CVD, Electrochemical Society, New Jersey, 1981, p.606.
3. Stolz M, Hieber K and Wieczorek C, Thin Solid Films 1983, 100, 209
4. Pódob M T and Hegi R, in Proc Fourth European Conf CVD, Philips, Eindhoven, 1983, p.479
5. Hitchman M L, Kane J and Widmer A E, Thin Solid Films, 1979, 59, 231
6. Berkman S, Ban V S and Goldsmith N in Heteroepitaxial Semiconductors for Electronic Devices, Springer-Verlag, Berlin, 1978, p.264
7. Ban V S, J. Electrochem. Soc., 1978, 125, 317
8. Sugawara K, J. Electrochem. Soc., 1972, 119, 1749
9. Manke C W and Donaghey L F, J. Electrochem. Soc., 1977, 124, 561
10. Hitchman M L, J. Crystal Growth, 1980, 48, 394
11. Hammond M L Solid State Tech. 1979, 22(12), 61
12. Stirling H F, Alexander J H and Joyce R J, Special Ceram., 1968, 4, 139
13. Feist W M, Steele S R and Readey D W in Physics of Thin Films, Academic Press, New York, 1969, 5, 237.
14. Hyder S B and Yep T O, J. Electrochem Soc., 1976, 123, 1721
15. Ojha S M in Physics of Thin Films, Academic Press, New York, 1982, 12, 237
16. Hazelwood F J and Iordanis P C, Proc Conf Ion Plating Allied Tech, Edinburgh, 1977, p.248
17. Hazelwood F J, Proc Int Conf Adv Surf Coat Technol, London, 1978, p.29
18. Grube W I and Cay J G, Metall. Trans. A, 1978, 9A, 1421
19. Hollahan J R and Rosler R S, in Thin Film Processes, Academic Press, New York, 1978, p.335
20. Kim H M, Tai S S, Groves S L and Schuegraf K K, in Proc Eighth Int Conf CVD, Electrochemical Society, New Jersey, 1981, p.258
21. Sarkozy R F, in Proc Fourth European Conf CVD, Philips, Eindhoven, 1983, p.230
22. Logar R E, Herring R B and Wauk M T, Electrochem. Soc. Ext. Abstr., 1978, 78-2, 603
23. Boyer P K, Roche G A, Ritchie W H and Collins G J, Appl. Phys. Letts., 1982, 40, 716
24. Allen S D, Trigubo A B and Liu Y C, in Proc Eighth Int Conf CVD, Electrochemical Society, New Jersey, 1981, p.267
25. Allen S D and Trigubo A B, J. Appl. Phys. 1983, 54, 1641
26. News item, Ind. Res. Develop., June 1982, p.70
27. Hitchman M L, Vacuum, 1984, 34, 979
28. Bonetti-Lang M, Bonetti R, Hintermann H E and Lohmann D, Int. J. Refractory and Hard Metals, 1982, 9, 161
29. Bonetti R and Wahl H, in Proc Fourth European Conf CVD, Philips, Eindhoven, 1983, p.510
30. Hintermann H E, Annals CIRP, 1982, 31, 435
31. Benjamin P and Weaver C, Proc Roy Soc. 1960 254A, 163
32. Hirai T, Hayashi S and Tanaka A, in Proc Fourth European Conf CVD, Philips, Eindhoven, 1983, p.503
33. Schintmeister W and Packer O, J. Vac. Sci. Technol., 1975, 12, 743
34. Yaws C L and Wakefield G, in Proc Fourth Int Conf CVD, Electrochemical Society, New Jersey, 1973, p.577
35. Hitchman M L in Progr. in Crystal Growth and Characterisation, Pergamon Press, Oxford, 1981, p.249
36. Hitchman M L and Curtis B J, ibid. p.283
37. Hitchman M L, Vacuum, 1984, 34, 377
38. Hitchman M L, in Proc Seventh Int Conf CVD, Electrochemical Society, New Jersey, 1979, p.59.
39. Kim K S and Chun J S, in Proc Fourth European Conf CVD, Philips, Eindhoven 1983, p.517
40. Lee C W and Chun J S, in Proc Eighth Int Conf CVD, Electrochemical Society, New Jersey, 1981, p.540.