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ABSTRACT

Graded DLC based coatings and multilayers for wear resistance applications have been produced using a novel hybrid unbalanced magnetron sputtering/ low pressure CVD system. The main features of this highly flexible and scalable process are discussed. These films have been characterised using a variety of techniques including SEM, microhardness, adhesion, wear rate and lifetime tests. For example: microhardness of > 4000 Hv; excellent adhesion, Lc 115-125 N; coefficient of friction during prolonged running against WC of O.15; volumetric wear rates 1/5 of that of TiN. The process is ideally suited to large substrate size and volume production for many different kinds of applications.

1. INTRODUCTION

Diamond is an exciting material with a unique combination of physical, chemical, optical and electrical properties. These include extreme hardness, chemical inertness, high electrical resistivity, high dielectric strength, optical transparency and high thermal conductivity [1,2]. The combination of these excellent properties makes it an ideal choice for a wide range of applications in electronics, machining, tooling, optics and biomedical components.

In order to deposit high quality diamond films, harsh experimental conditions, such as very high temperatures, are necessary . For example, the substrate temperature for the deposition of diamond using CVD is around 900°C. Substrates employed for a large number of practical applications, such as glass for optical components, cannot tolerate such conditions. Additionally, the area over which diamond can be deposited is only small.

CVD involves dissociation of a suitable hydrocarbon gas such as methane or acetylene on a heated substrate. It yields coatings with good uniformity, control and reproducibility, and has the ability to coat easily complex-shaped objects. The most common CVD methods employed for diamond are either microwave plasma or hot filament CVD. The coatings produced by these methods [3-5] have cubic diamond structure (sp^3) and hardness values of 3000-12000Hv. The use of RF or DC glow discharges in plasma enhanced CVD results in a mixture of sp^3 and sp^2 bonds, yielding hardness values in the range 900-3000 Hv. These methods alone have not made a significant impact on production scale applications.

To further the applications of diamond based coatings it is necessary to lower the deposition temperature and have the capability of depositing on objects of complex geometry and on a large scale, in terms of substrate size and throughput. PVD methods, such as ion beam deposition (IBD), laser ablation, molecular beam epitaxy (MBE) and sputtering, have been used to deposit an intermediate material, diamond like carbon (DLC), which has many of the properties of diamond such high hardness, bio-compatibility and low friction; and can be deposited at very low temperatures. In general, PVD technologies involve transfer of a material from a target to the workpiece. These methods are very flexible, environmentally friendly and can be scaled easily for a wide range of materials. The development of unbalanced magnetron sputtering has recently led to great improvements in the adherence and hence usefulness of PVD DLC coatings.

Unbalanced Magnetron Sputtering

The main shortcoming of the high rate, magnetron sputtering ion plating process [6], is the decrease in the density of the ion current incident on the substrates at distances greater than about 6cm. This problem was partly overcome by Window and Savvides [7], in recognising the benefit of 'unbalancing' the magnetic field configuration of the conventional magnetrons, so that the plasma in the target region is allowed to flow out towards the substrates. This allows some of the secondary electrons produced during sputtering to follow the magnetic field lines away from the target, towards the substrates, causing further ionising collisions. The unbalancing results in enhanced levels of ionisation near the substrates since the positive species follow the electrons away from the magnetron due to their electrostatic attraction. The ions near the substrate bombard the growing film leading to dense, adherent coatings with properties previously unattainable with normal sputtering techniques.

Teer and co-workers, have designed a system that incorporates the use of multiple magnetron sputtering cathodes using the concept of unbalancing. This closed-field system was tradenamed the "Plasmag", and increases ionisation enabling the deposition of high quality reactive compounds as well as metal and multilayer films [8]. In the closed field arrangement the magnetic configuration of the magnetrons is changed. Instead of using the same polarity magnets on the outside of all magnetrons, the polarities are alternated, hence joining the magnetic fields between the magnetrons.

Combined Unbalanced Magnetron Sputtering/ Low Pressure Plasma CVD

In this paper we describe a new method for the deposition of DLC which combines the advantages of both CVD and PVD. A schematic of the process is shown in figure 1. This method combines the technologies of closed field unbalanced magnetron sputtering (CFUBMS) with low pressure plasma enhanced CVD. Many of the practical problems, such as poor adhesion to the metal substrates and non-uniform coverage of complex 3-D components have been completely resolved with this technology. This hybrid process produces DLC from the target by sputtering and from the reactive plasma by CVD. The acetylene decomposes on the surface as follows:

$$C_2H_2\ (g) \text{ --------------> } 2C\ (s) + H_2\ (g)$$

resulting in DLC and hydrogen. It has been suggested that radicals generated in the plasma etch the graphite preferentially thus increasing the of sp^3/sp^2 bonding ratio. In the plasma a complex mixture of species is present including C, CH, C_2H, and products of various recombination reactions. A system incorporating a range of in-situ diagnostics is under construction to study the surface and gas phase chemistry of this process.

2. EXPERIMENTAL

The idea of poisoning the target with carbon using hydrocarbon gas was first reported by Dimigen and Hubsch [9,10,11]. The introduction of a hydrocarbon gas (acetylene) during sputtering causes breakdown of the gas on the pure metal target surface, such that the metal and hydrocarbon are sputtered simultaneously from the poisoned target surface. This process yield metallised carbon coatings. The amount of target poisoning by the hydrocarbon will determine the final composition of the film. If total poisoning of the metal target results, the process tends to go unstable due to the non-conducting layer of carbon on the target surface, and "arcing" results. To minimise the amount of metal in the films, near to complete poisoning is required, which can be difficult to control in most cases. Good control of the degree of target poisoning is possible by closed-loop optical emission monitoring of the discharge plasma [12]. The metal discharge plasma is set to values of between 5-15% of its value for an unpoisoned surface, thus ensuring stability of the process and low levels of metal incorporation. A low RF power is applied to the substrates to promote ion assistance during film deposition. The incorporation of a small amount of metal into the film improves the some of the mechanical properties of the coatings. A schematic of the system employed in this study is shown in figure 2.

In the current process the acetylene decomposes not only on the metal target but also on the substrate to yield DLC from the gas phase. Metal targets are only used when graded and multilayers are to be deposited. For the deposition of pure DLC coatings a graphite target is utilised and DLC results from both sputtering of the target and decomposition of the acetylene gas.

Graded coatings

One of the main problems with the deposition of DLC at low temperatures, is the generation of large amounts of compressive stress. This may lead to poor coating to substrate adhesion, with large areas tending to spall off [13]. The grading of very hard alloy nitride films through various intermediate compounds, of varying compositions, has been shown to increase the scratch adhesion levels by at least 100% [14]. In the case of carbon deposition, a more intricate mixture of graded layers has been used than for other film materials. It has been found that the optimum film sequence in this case is; Ti, TiN, TiCN, TiC, C. The various compositions are graded to give smooth boundaries between the layers. This process is easily controlled by the optical emission feedback loop, and can be preprogrammed. A typical coating sequence can be seen in figure 3.

Multilayers

The deposition of multilayers of carbon and ceramics has been investigated to study changes in the film characteristics. Combinations of DLC and TiC have been deposited with different layer thicknesses to see if any benefits are apparent. The TiC layer is formed by reducing the level of acetylene entering the chamber, by adjusting the optical emission level to that of stoichiometric TiC. By pulsing the gas this process can be repeated the desired number of times to give varying multilayer combinations. However, there tends to be a certain amount of inertia present in the system due to a gradual change in target poisoning, and fine multilayer structures are hard to achieve without additional shuttering. A schematic representation of the coating structure can be seen in figure 4.

3. RESULTS

The films have been characterised for: microhardness; scratch adhesion; coefficient of friction; and volumetric wear rate. The initial graded film layer of varying composition usually makes up half the coating thickness, and leads to extremely high levels of adhesion.

Hardness and Adhesion

The Knoop microhardness of the films was measured under loads varying between 15-100g. The substrate material had a hardness of approximately 700 Hv. From figure 5, it can be seen that the monolayer carbon film had the highest measured hardness of around 4000 Kg/mm^2. At loads of over 50g the measured hardness values are lower,0 due to the influence of the substrate hardness. For the multilayer films, lower hardness values were recorded, ranging from 1500-3500 Kg/mm^2. The substrate appears to influence the hardness measurements at higher loads due to the increased penetration of the diamond. The high hardness values are probably a result of high stress levels in the carbon films. The lower hardness of the multilayer films may be due to stress relaxation of the carbon film brought about by the alternating of the structure by intermediate compounds. It can also be seen that the lowest hardness values are recorded for the finer multilayer structure, where the carbon layers are the thinnest. The adhesion was measured by friction monitored scratch testing and verified by optical and SEM examination of the scratch. The scratch tester used was developed at the University of Salford and uses the rapid increase in frictional force at coating de-adhesion to indicate the lower critical load adhesion level. The method produces results within a maximum of 10% error when compared to optical methods. Figure 6, shows the friction response of a carbon film under varying loading rates, and shows a clear indication of the coating to substrate adhesion failure. The lower critical adhesion values of the films are in the range 115-125N depending upon the loading rate used (see figure 7). The values are very high, and represent adhesion levels many times the values normally associated with carbon films. The fact that the difference between the adhesion values of the various structures is so small ($<8\%$), can be attributed to the identical nature of the initial graded layer used to optimise the adhesion. This would also explain why the adhesion does not follow the expected inverse relationship to the measured hardness [15].

Wear and Friction Coefficients

The wear rate of the films was measured by pin-on-disk tests against tungsten carbide balls, the volumetric wear was determined by relocation profilometry [15]. The wear rate of the monolayer carbon film was the lowest (~0.75x10-7 mm^3/Nm), and this was about 1/5 of the equivalent wear rate of a standard TiN coating produced in the uniform deposition and plasma system, see figure 8. The multilayer films had intermediate wear rates of less than 2x10-6 mm^3/Nm. The coefficient of friction of the films under dry running conditions against WC was very low, with the friction of the monolayer film not rising above 0.2 during running, see figure 9. The multilayer films had variable coefficients of friction of less than 0.25 during running.

CONCLUSIONS

A new hybrid closed field unbalanced magnetron/ low pressure plasma CVD system for the deposition of graded DLC multilayer coatings is described and the process features are discussed. The films produced have been shown to have superior properties to those obtained by conventional CVD and PVD methods at low temperature. In addition the system is highly flexible, readily scalable and is being used in production for a range of applications.

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Hybrid lowP, lowT, ion assisted CVD/PVD

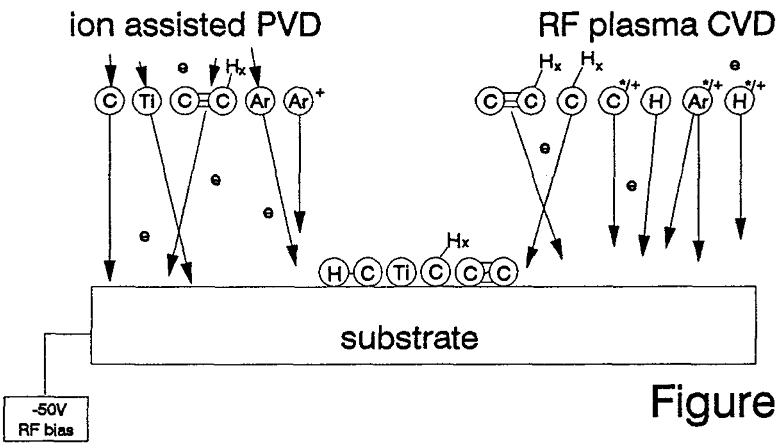


Figure 1

Schematic of a 4 magnetron closed field unbalanced magnetron sputtering system

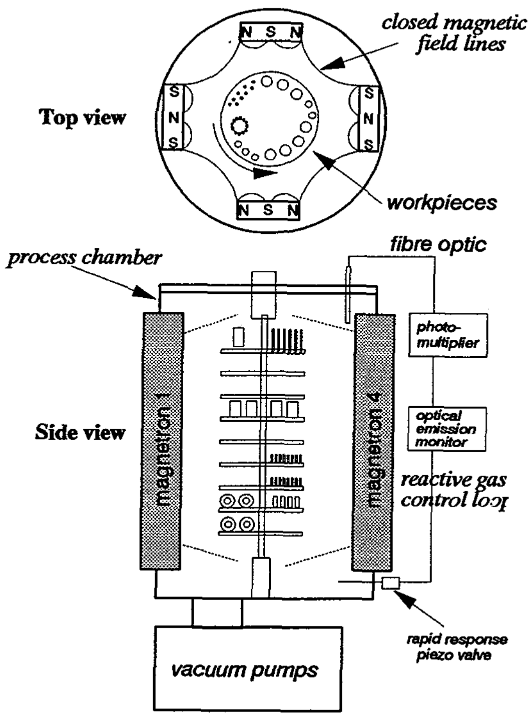


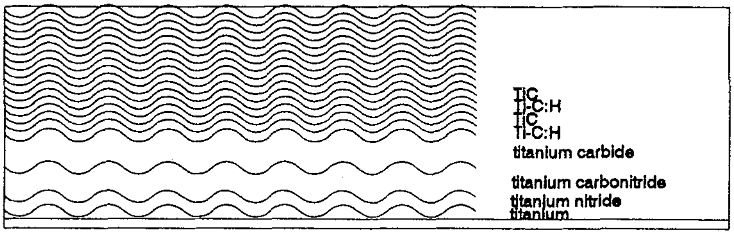
Figure 2

	Me-C:H	Me-C:H/TiC multilayer	deposition material
pump to 5x10E-5 mbar	yes	yes	
CLEANING			
input argon 3x10E-3	yes	yes	
set bias -1000 volts	yes	yes	
target 1	Ti	Ti	
target 2	Ti	Ti	
target 3	Ti	Ti	
target 4	Ti	Ti	
mags ramp 4A(15s)	all 4	all 4	
steady state 5 min	pure Ti	pure Ti	Titanium
input gas	nitrogen	nitrogen	
substrate bias volts	60-70 RF	60-70 RF	
OEM to 55%	Ti	Ti	Titanium nitride
time	25 mins	25 mins	
input gas	nitrogen/actylene	nitrogen/actylene	
OEM to 50%	Ti	Ti	Ti carbonitride
time	30 mins	30 mins	
input gas	acetylene	acetylene	
OEM to 13%	Ti	Ti	Titanium carbide
time	20 mins	20 mins	
OEM at 5%	Ti	Ti	Me-C:H
time	30 mins	x mins	
		OEM 50%	multilayer
		x mins	
		OEM 5%	
		repeat	

Figure 3 Typical Coating Routine for DLC mono and multilayer films

Schematic of the coating composition for a graded Ti-C:H coating deposited by closed field unbalanced magnetron sputtering

example: DLC/TiC multilayer



substrate

Figure 4

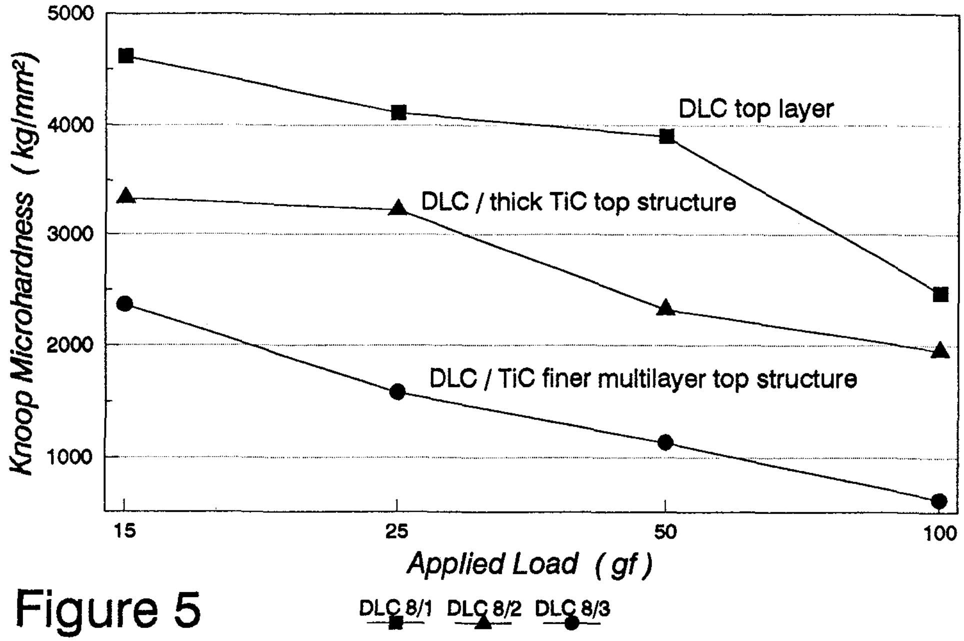


Figure 5

Variation in Knoop hardness with load (>15g hard. value influenced by substrate)

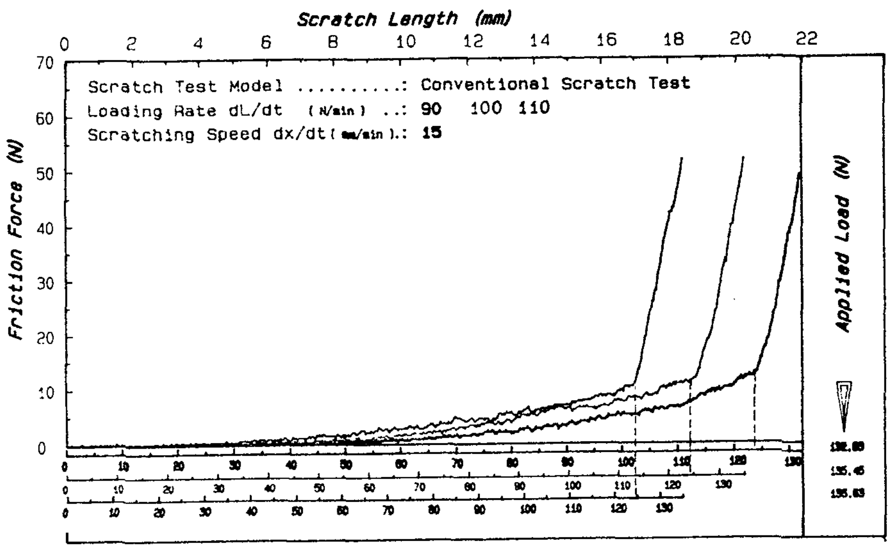


Figure 6 Variations in the friction force and the applied load with scratch length for DLC 8/1 coating deposited onto M2 tool steel by magnetron sputtering t:0 um - Ra:0 um Diamond tip radius R=200 um

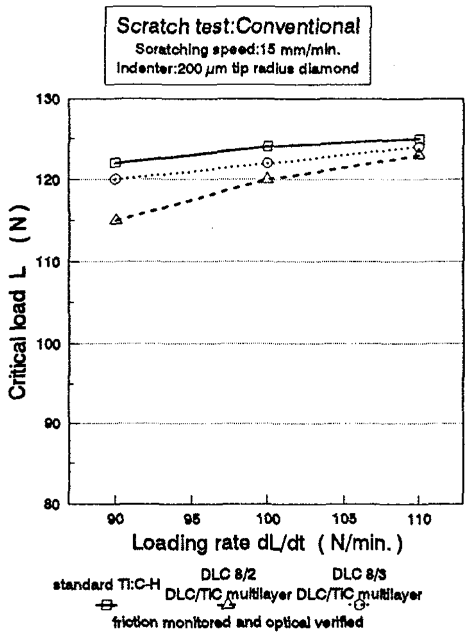


Figure 7

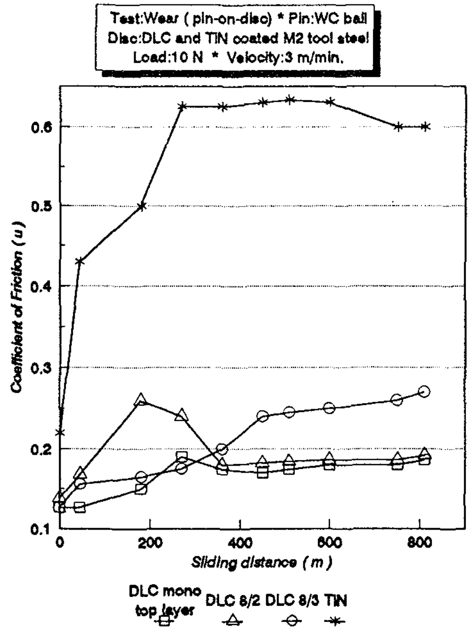


Figure 9

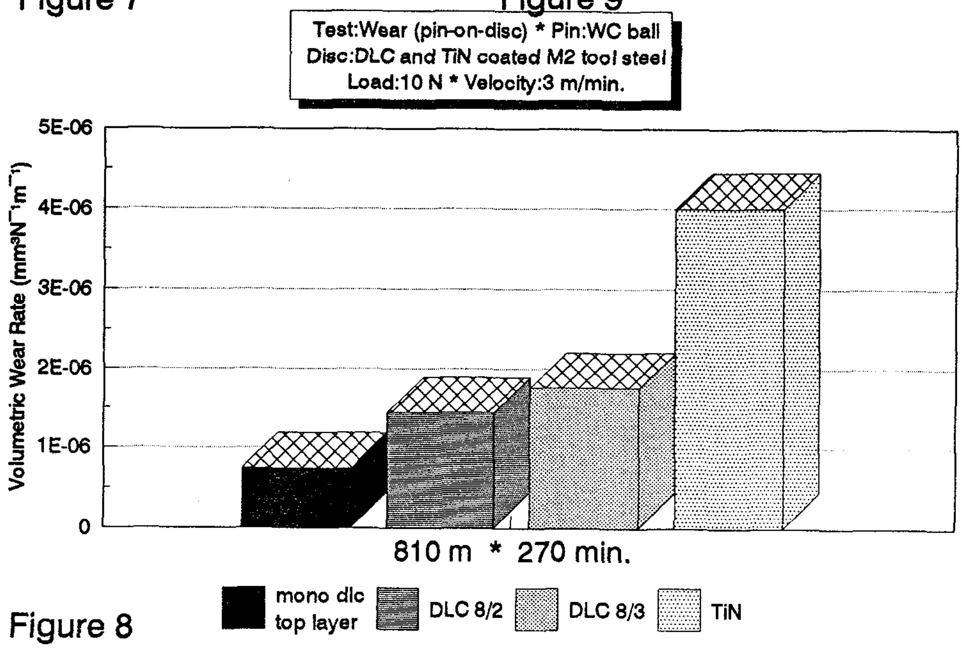


Figure 8