Pulsed Laser Deposition Manufacturing of Diamond-Like Carbon Films

Current technologies used to produce high performance diamond-like carbon (DLC) all suffer from various drawbacks in terms of the characteristics of the films they yield, their deposition speed, maximum film thickness, and the range of substrate materials with which they can be used. These drawbacks have so far limited DLC deployment in industrial markets. An excimer laser based technique has been developed which offers the ability to achieve thick films having good adhesion, low internal stress and high hardness, all of which translate into increased durability. Furthermore, the excimer laser technique does not involve heating the substrate, meaning that it can be used with a wide range of substrates, including polymers.

Shortcomings of Current DLC Technologies

DLCs exist in a number of different forms; the hardest of these is called tetrahedral amorphous carbon (ta-C), which ideally consists purely of sp^3 bonded carbon atoms. But, real world DLCs always contain at least some fraction of sp^2 bonds, and often some impurities including hydrogen. However, a ta-C film having a sp^3 content of more than 50% has a hardness of over 40 GPa and a low friction coefficient, making it highly useful for controlling wear. A common major mechanical limitation of high purity ta-C films has been the build-up of internal compressive stress in the coating. With existing fabrication methods, this stress has typically limited film thickness to 0.2 µm or less before the risk of delamination from the substrate becomes too significant. However, many applications ideally require coatings as thick as 2 µm. The most obvious way to relieve this stress is through thermal annealing. Unfortunately, traditional annealing (e.g. bulk heating of the substrate) itself presents two problems. First, when raised to temperatures above 200°C, sp^3 films begin to convert into the sp^2 (graphite) form. Second, the need for a heating cycle limits the range of substrate materials to those which can withstand high temperatures, ruling out the use of most polymers. Furthermore, from a practical standpoint, the time required for one or more heating and cooling cycles may limit production throughput and increase process cost.

The Excimer Laser Advantage

Successful film growth can now be accomplished through pulsed laser deposition (PLD). Specifically, a high pulse energy excimer laser, operating at a wavelength of 248 nm, is used to ablate a graphite target inside a vacuum chamber. This creates a ta-C film on a substrate which is moderately heated (~90°C) inside the vacuum chamber. The fast evaporation of the target material induced by the high photon energy (5 eV), short temporal width (30 ns) and the high fluence of the excimer laser pulses generates atomic species with a high degree of ionization and high kinetic energies. In particular, the mean kinetic energies in the plume obtained through excimer laser-based PLD are in the range of 30 eV to 80 eV for laser fluences of 5 J/cm^2 to 20 J/cm^2, which is significantly higher than the energies associated with thermal evaporation and ion sputtering deposition methods. This is critical, since increasing the kinetic energy of the atoms generally translates into a film with greater tetrahedral (sp^3) diamond-like carbon content.

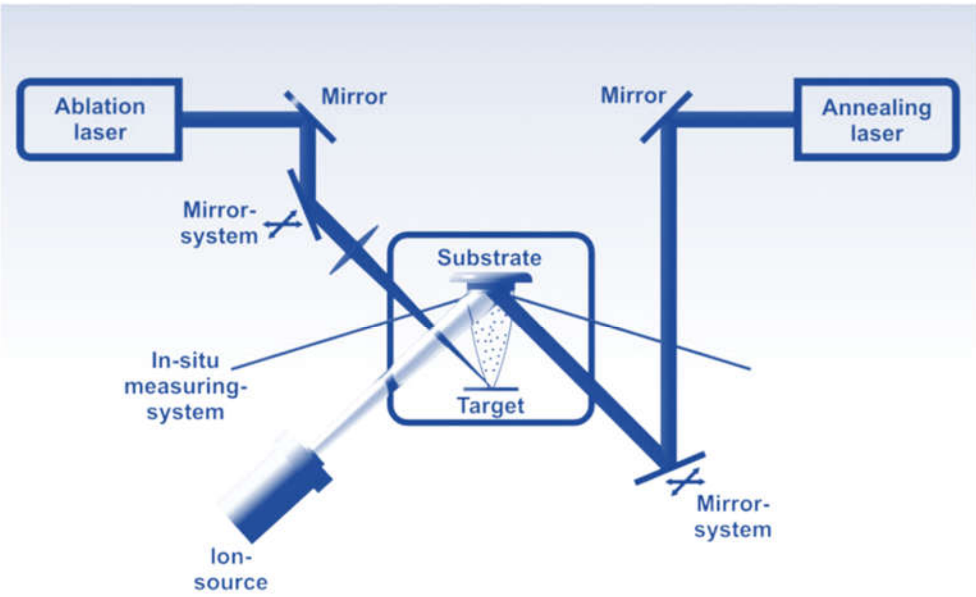

Fig. 1: Schematic of the experimental set-up used for the preparation of stress-free, ta-C films.

This two-step process developed by the group of Professor Weissmantel at the Laser Institute Mittweida in Germany utilizes a second excimer laser to perform low-temperature annealing of the silicon. They have shown that the use of repeated deposition and annealing cycles can deliver thick (>2 µm) films having no internal stress and high hardness, and can be applied to a wide range of substrates, including temperature sensitive materials such as polymers.

Figure 2 demonstrates this relationship by plotting the sp^3 content of PLD grown ta-C films, determined by means of electron-energy-loss spectroscopy (EELS). The maximum sp^3 content of 85 % is obtained at fluences in the range of 10 J/cm^2 to 20 J/cm^2.

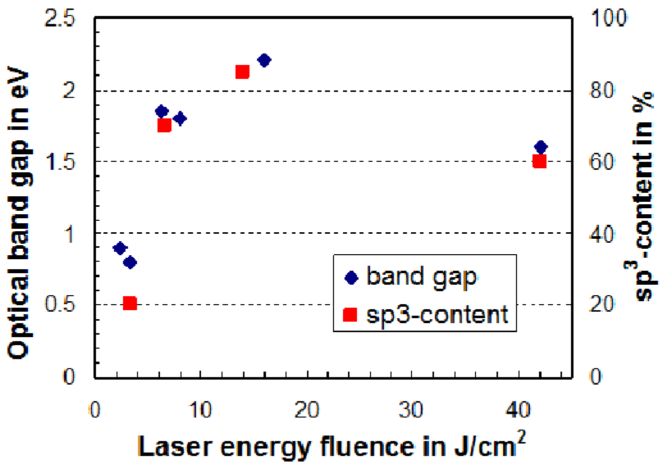

Fig 2: The sp^3-content and optical energy band gap of PLD grown ta-C films as a function of laser fluence.

Properties measured on ta-C films prepared at optimum parameters.

The film thickness was simultaneously determined by optical interference (by measuring the reflected intensity of the laser beam). The figure shows the variation in total stress as a function of film thickness during production of a 1 µm thick ta-C film on silicon. In this case, 20 successive sub-layers of 50 nm thickness were deposited and annealed, both by excimer laser. The total residual stress depends on the number of excimer pulses per area and on the excimer laser fluence; the total residual stress in the final completed film is only 0.1 GPa. Moreover, from the plot of normalized reflected intensity vs. film thickness it is also concluded that the optical band gap, and therefore the sp^3 content, is not influenced by the excimer laser annealing process, because there are no indications of an increase in film absorption.

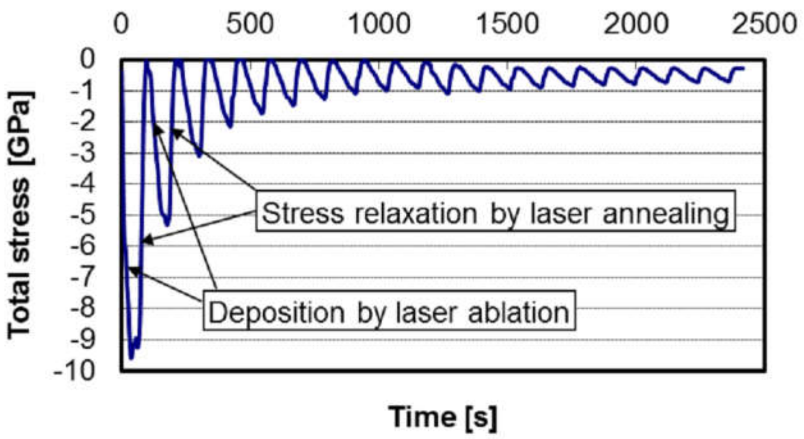

Fig 3: Total stress during the preparation of a 1 µm thick ta-C film on a 400 µm thick silicon substrate, produced by successive deposition and annealing at an ablation fluence of 12 J/cm^2 and an annealing fluence of 150 mJ/cm^2).

Adherence for 2 µm thick ta-C films was also quantified by conventional scratch testing. Since the adherence of the excimer laser produced ta-C films on steel substrates was not sufficient for some applications, intermediate layers were employed. Best adherence was obtained with boron carbide and tungsten carbide (WC) intermediate layers, which are also deposited by excimer laser ablation immediately prior to the ta-C deposition. The optimal thickness of these layers depends mainly on substrate roughness, being about 80 nm for N1 polished substrates. This approach yielded maximum critical loads around 35 N for various steels (including 100Cr6, HSS and nitride steels) with both carbides as intermediate layers, and 55 N for WC hard metal with WC as the intermediate layer. The values of the critical loads at which film damage occurred during scratching are comparable with the adhesion values reported in the literature for currently used DLC coatings.

Depending on the parameter settings in pulsed laser deposition, the formation of particulates or droplets can be observed. These particulates consist of graphite, and their size depends on the laser fluence at the target surface. At fluencies that were optimal for ta-C film growth, particulate size was of the order of 100 – 200 nm. The number of particulates in the films was minimized by using an unstable resonator along with an optimized laser spot on the target. Research has shown that particulate density in 2.5 µm thick films is generally in the range of $3x10^5$ to $2x10^6$ per cm^2, resulting in an average surface roughness of about 5 nm to 20 nm, when the ta-C films are deposited on polished silicon of 2 nm average surface roughness.

Measurement Results and Commercialization Aspects

Testing data from 2 µm thick, stress-free, high hardness ta-C films prepared with this optimized setup are summarized in the table. The films were found to be completely amorphous with a density approaching that of diamond, which is the consequence of the high sp^3 content. The average surface roughness of films deposited on N1 polished steel substrates was measured with a DEKTAK surface profilometer, and was generally found to be not significantly higher than the roughness of the substrate, indicating a very smooth film. Most importantly, extraordinarily high values of hardness and Young's modulus were measured for 2 µm thick films prepared on both steel and WC hard-metal substrates. The measurements were performed by using a dynamic indentation method with a Berkovich indenter according to ISO 14577. The values given in the table are the mean of 10 measurements, each using maximum loads of 50 mN, resulting in maximum indentation depths of about 100 nm.

Achieved layer thickness on WC and steel	5 µm
Structure	amorphous
sp^3 content	80 – 85 %
Optical energy band gap	1.8 - 2.2 eV
Density	3.1 – 3.3 g/cm^3
Internal stress - without excimer annealing - with excimer annealing	8-12 GPa → 0 GPa
Hardness	60 – 70 GPa
Young´s modulus	750 – 920 GPa
Friction coefficient	0.10 – 0.20
Thermal conductivity	9.2×10^{-2} W/cm K
Refractive index (visible range)	2.45 – 2.55
Extinction coefficient (at 248 nm)	0.35
Absorption coefficient (at 248 nm)	1.8×10^5 cm^{-1}

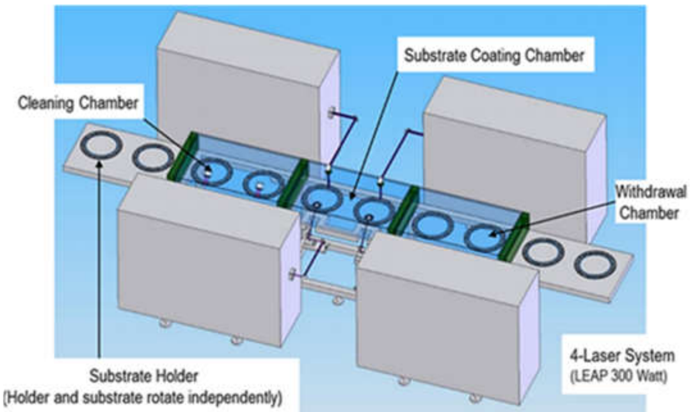

Fig 4: Concept of a continuous DLC coating system based on four high power excimer lasers.

While the excimer laser deposition and annealing method clearly produces high hardness films with excellent physical characteristics, successful deployment in industry requires that the process also meet certain goals in terms of speed and cost. One concept for a high throughput industrial system utilizes four excimer lasers in a pass-through, in-line arrangement, as shown in the figure. Depending on throughput requirements, high-power excimer lasers with up to 600 W average output power are commercially available. This setup is meant for ta-C coating of plane substrates, which are positioned in a rotating carrier. Both the loading and unloading modules act as airlocks, enabling parts to be supplied to the main chamber without ever breaking its vacuum. Furthermore, pre-cleaning of the substrates by ion beam bombardment can be performed in the loading module. The deposition and annealing processes are carried out in the coating module, and can be performed simultaneously to maximize throughput. The carriers are rotated in order to bring each part to the proper position, and any number of successive deposition and annealing steps can then be accommodated. When ta-C film deposition is complete, the parts are translated into the unloading module, which can also be used for additional post-processing steps, such as micro-structuring or marking.

Based on the deposition rates achieved in the laboratory, a system such as this could produce 0.5 m^2 of 1 µm thick ta-C film in 60 minutes. The total cost per square meter for a continuous process are estimated to be €500, when considering investment costs, consumables, maintenance, electrical energy and staff.

In conclusion, high purity, high sp^3 content DLCs have long been known to have desirable physical properties, but problems with fabrication technology have limited their use in many applications. Now, an excimer laser deposition and annealing method appears to solve many of these problems and also delivers the cost and throughput characteristics required for widespread industrial adoption.

Coherent LEAP Excimer Laser

LEAP excimer lasers at 248 nm and 308 nm are employed in materials research applications and industrial pulsed laser deposition production systems. They are available with UV output power from 80 W to 300 W. The LEAP laser is proven for a broad range of large-area ablation tasks including pulsed laser deposition, ablative thin film lift-off separation and ultra-precise micropatterning.

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