JOURNAL OF MATERIALS SCIENCE 30 (1995) 4751–4760

Synthesis of fluorinated diamond films using a laser technique

P. A. MOLIAN
Mechanical Engineering Department, Iowa State University, Ames, IA 50011, USA
B. JANVRIN, A. M. MOLIAN
Laser Science Company, Inc., Ames, IA 50010, USA

A laser chemical vapour deposition process for growing fluorinated diamond thin films on two bearing materials, SiC and 440 C stainless steel, is described. The type of laser, carbon feedstock, laser-precursor gas interactions, and deposition conditions have been established. Raman spectroscopy analysis revealed that the films deposited on SiC consisted of a mixture of diamond and graphite, while the films on 440 C steel were composed of diamond, diamond-like carbon and graphite. The feasibility of diamond formation using laser light–gas interactions is explained.

1. Introduction

Numerous space tribosystem components such as gimbal bearings require solid lubricants to resist extreme environments including variable temperature, radiation exposure, and a variety of atmospheres from ultra-high vacuum to highly oxidizing or corrosive environments [1, 2]. Liquid lubricants could not be applied because of their volatility due to high vapour pressure, and degradation due to temperature variation and an atomic oxygen environment.

A new solid lubricant, vigorously investigated in recent years, is diamond film because of its ability to overcome some of the current limitations of solid lubricants, such as higher friction coefficient than obtainable with hydrodynamic lubrication, high wear due to solid–solid contact and inadequate cooling capacity. Fluorinating the diamond films would be even more preferable to enhance their stability at extreme temperatures and in chemically reactive environments.

Fluorinated diamonds are excellent for an atomic oxygen environment and other harsh operating environments. For example, blower motor bearings in chemical laser satellite communication systems are subjected to a halogen atmosphere and can have improved performance through fluorinated diamond coating [1]. Fluorinated carbon exhibits a low surface energy and gives rise to excellent shearing. Diamond is a superhard material and can provide the highest wear resistance. Diamond, being four to five times higher than copper in thermal conductivity, can also provide a heat dissipation capability.

Fluorinated carbon films are capable of performing better than the currently used space lubricants including MoS_2, lead and PTFE. This paper describes a method of depositing fluorinated diamond films on space bearing materials.

2. Laser chemical vapour deposition

Diamond thin films are produced by a variety of chemical vapour deposition (CVD) procedures including plasma, microwave, hot filament, ion beam, and electron beam. Numerous papers dealing with CVD diamond synthesis have appeared in recent years [3–13]. Most of the CVD processes suffer from low deposition rate and coverage, high substrate temperature, and the presence of hydrogen and graphite impurities. New methods are required for the fabrication of diamond thin films to overcome the limitations of existing methods and possibly to improve the quality of diamond films. One such method is laser-induced CVD (LCVD) where a laser beam serves as an energy source for decomposing the gases and for raising the surface temperature of the substrate for deposition. Laser technology for diamond film fabrication is very new, and to date only a handful of publications are available that address directly on the CVD diamond growth. Lasers are capable of providing economical and technical benefits through reduced fabrication time and better quality over the existing diamond CVD technology. Some of the unique features of LCVD are its clean source of energy, the possibility of obtaining a high deposition rate, a low substrate temperature, selective-area deposition, and better surface integrity.

Most of the reported work on laser-induced CVD for diamond deposition involved the use of an excimer laser and photochemical decomposition of gaseous molecules. The laser beam was incident either normal or parallel to the substrate surface. A summary of data available on LCVD for diamond growth is given in Table I. The chief advantage of laser CVD is low-temperature deposition. For excimer laser-induced CVD, CH_4 is not used as a precursor because it does not absorb the excimer wavelength. Recently, a different laser method, beginning with carbon ion

0022–2461 © *1995 Chapman & Hall 1995*

TABLE I Literature data on laser CVD growth of diamond

Reference	Experimental details	Remarks
Goto *et al.*[7]	ArF laser, CCl_4 feed 450 °C substrate temp	Atomic hydrogen is needed
Tyndall and Hacker[8]	KrF laser, CH_3COOH 20 °C substrate temp	Neither diamond seed nor atomic hydrogen needed
Celii *et al.* [9]	ArF laser + hot filament technique	Diamond is suppressed
Janvrin [10]	ArF laser using numerous precursors	Atomic hydrogen is needed Low substrate temp. 200 °C
Molian *et al.* [11]	CO_2 laser using CH_4/H_2	Good quality diamond
Thaler [12]	CO_2 laser using SF_6/CH_4	Hydrogen-free, amorphous diamond
Chapliev *et al.* [13]	KrF laser + plasma CVD	Selective-area deposition

implantation and followed by pulsed excimer laser melting, was developed to produce defect-free, single-crystalline diamond films on a copper substrate [6].

A recent development in diamond thin films has been the fluorination of diamond which has been suggested as a means of reducing the coefficients of friction of diamond surfaces when adsorbed water or oxygen is present [14]. Fluorine atoms can provide the passivation of the surface resisting the diffusion of oxygen. This factor is very significant in space applications where atomic oxygen is present. In this work, the objectives were (1) to develop a laser CVD technique for growing fluorinated diamond films on SiC and 440 C steel substrates using halogenated methane precursors, and (2) to characterize the films with scanning electron microscope and Raman spectroscopy.

3. Experimental details

3.1. Substrates

Two bearing materials, namely SiC (alpha) and 440C stainless steel, were selected as substrates because the major objective was to provide solid lubrication for bearings to be used in space. These two different substrates were also chosen to explore the potential of a substrate and its surface as a catalyst site to facilitate the laser/gas/surface reactions on diamond film growth and morphology. No scratching and seeding of the surface with diamond powders was done to increase the nucleation rate, because the laser beam in normal radiation mode can "clean" such seeding.

SiC is an excellent substrate for diamond growth due to lattice matching. It is also the material for next-generation space bearings because SiC bearings are about 50% of the weight of steel bearings, SiC has a very high elastic modulus and hence can be designed for high preload (reduces torque or friction), SiC can be made to geometric precision, has excellent chemical resistance and has increased life for precision MMAs and actuator designs. Three different sources of SiC were used. These include Carborundum (Hexaloy Grade SA), Norton (NC 203) and ESK Engineered Ceramics (EKasic HD)

The SiC substrates obtained from Carborundum and Norton were sintered alpha (hexagonal) and contained some impurities. EKasic grade is a high-purity SiC (99.5%) and was produced by hot isostatic pressing (HIP). The steel substrates were obtained as flat specimens as well as in the form of ball bearings.

TABLE II Specifications of the laser systems used

	Laser type		
	Nd:YAG	ArF-excimer	KrF-excimer
Wavelength (nm)	1060	193	248
Average power (W)	10	10	30
Pulse length (S)	300×10^{-6}	17×10^{-9}	23×10^{-9}
Pulse energy (mJ)	$1\text{–}3 \times 10^3$	100	300
Pulse rate (Hz)	1–10	1–100	1–100

3.2. Lasers

Lasers can decompose gaseous molecules by pyrolysis and photolysis mechanisms. In laser pyrolysis, the gases are excited by the beam irradiation, and the substrate is heated to the desired temperature by controlling the power and irradiation time of the beam. The excited gases then decompose by collision with the hot surface. The laser-driven reactions are significantly different from other CVD sources for a given heat input because the focused beam produces higher temperatures in a smaller volume [15]. In the laser photolysis process, the photons break the chemical bonds of the gaseous molecules and allow the products to be deposited on the substrate. An important requirement in photolysis is that the gases should absorb the laser radiation.

In this work, we used both approaches to synthesize diamond films. A summary of the lasers used in this work is given in Table II.

3.3. Carbon feedstock

Traditionally, CH_4 diluted in hydrogen is employed as a precursor by most CVD methods. In LCVD, CH_4 is not a suitable gas because the decomposition of CH_4 can occur only with wavelengths of light less than 160 nm [16]. The precursor gases used were CCl_4

TABLE III Laser–precursor interactions

Laser		Precursor		
Nd:YAG	Excimer	CF_4	F_2	CCl_4
1064 nm wavelength; provide thermal mechanisms; photolytic effects are none or minimal	193–351 nm wavelength; provide photolytic as well as pyrolytic mechanisms	Cannot be photolytically decomposed with excimer lasers; can be thermally decomposed to C–F species at 1500 °C	Can be photolytically decomposed by wavelength less than 400 nm; can also be thermally cracked at 1500 °C	Can be photolytically decomposed at wavelength less than 250 nm; can be thermally dissociated at 600 °C

and/or 1% CF_4/1% F_2/98% He (designated X) mixed with and without hydrogen. Laser–gas interactions are given in Table III.

It has previously been demonstrated by many researchers that the addition of a small amount of oxygen to the precursor gases can reduce the graphite formation and can also increase the diamond deposition rate. This is explained as being due to the production of atomic hydrogen by chemical reactions to form H^+ and OH^-. In this work, oxygen was added to the C–F–H system in some experiments.

The effect of preheating of the precursor gases on the diamond growth was also examined in some experiments. Preheating was accomplished by flowing the gases over a tungsten filament suspended in a quartz tube which in turn was heated in a small furnace up to 1000 °C. However, tungsten was identified in the film and hence the filament was replaced by a stainless steel tube which contained fins to activate the precursor gases.

3.4. Laser chemical synthesis

Diamond growth experiments were conducted in a chemical vapour deposition reactor (CVD). A schematic diagram of the CVD chamber and laser processing is shown in Fig. 1. The six-way vacuum chamber can be evacuated to less than 10^{-7} torr (1 torr = 133.322 Pa) by means of diffusion and mechanical pumps. This chamber has provisions for the laser-beam window, heating the substrate up to 1000 °C and mounting of the target. An inlet for the gas flow into the chamber is also shown in Fig. 1. A lens behind each of the two windows is located in order to focus the beam on the gaseous medium or on the substrate. Although Fig. 1 shows a dual-beam arrangement, all the experiments were carried out only using a single beam in parallel or normal radiation of the laser beam. The beam was either 1064 nm Nd:YAG for pyrolysis or 193 nm/248 nm excimer beam for photolysis. Over 100 experiments involving variation of laser parameters, gas flow and substrate conditions, were conducted. The substrates were ultrasonically cleaned in methanol prior to and after deposition.

3.5. Analysis and characterization

Two analytical instruments were used to characterize laser-grown diamond films.

(i) Scanning electron microscope: wavelength dispersive X-ray analysis coupled with SEM was used to evaluate the presence of carbon and fluorine, the morphology of diamond crystallites, uniformity and coverage area.

(ii) Raman microprobe spectroscope: diamond films differ from amorphous carbon, graphite, glassy carbon and other forms of carbon by their light-scattering properties. The Raman spectroscope is most widely used for signature diagnosis of diamond film. In the Raman spectrum, diamond has a peak at 1332 cm^{-1}, graphite has a peak at 1580 cm^{-1} and diamond-like carbon has peaks at 1345 and 1550 cm^{-1}.

4. Results and discussion

In laser CVD, the nucleation and growth mechanisms are dependent on the method of laser irradiation, namely normal incidence or parallel incidence to the substrate, or both, using a dual-beam approach. In parallel incidence, lasers can induce chemical reactions homogeneously within the gas phase and reaction products are diffusion driven towards the substrate surface giving rise to thin films. There is no damage to the substrate by this process. In normal incidence, the laser beam causes heterogeneous reactions to occur at the gas–solid interface. Such reactions facilitate the vapour–solid condensation on the surface. In this work, we have observed that homogeneous reactions by parallel laser irradiation of the precursor gas volume did not lead to any deposition. Hence experiments and results are reported only on the normal incidence.

In normal incidence, solid surfaces are potential sites for decomposing the gaseous molecules. Depending upon the energy density of the laser beam, various other processes can also take place, such as etching, melting and vaporization. The interactions between the laser beam and the substrate in the presence of a gaseous environment during perpendicular radiation are summarized in Fig. 2. Laser energy density should be reduced in order to prevent damage to the thin film by etching, melting and vaporization. The energy density should also be sufficient for decomposition of gases.

4.1. Nd:YAG pyrolytic deposition

The pulsed Nd:YAG laser is an intense thermal source and can decompose the gases heterogeneously

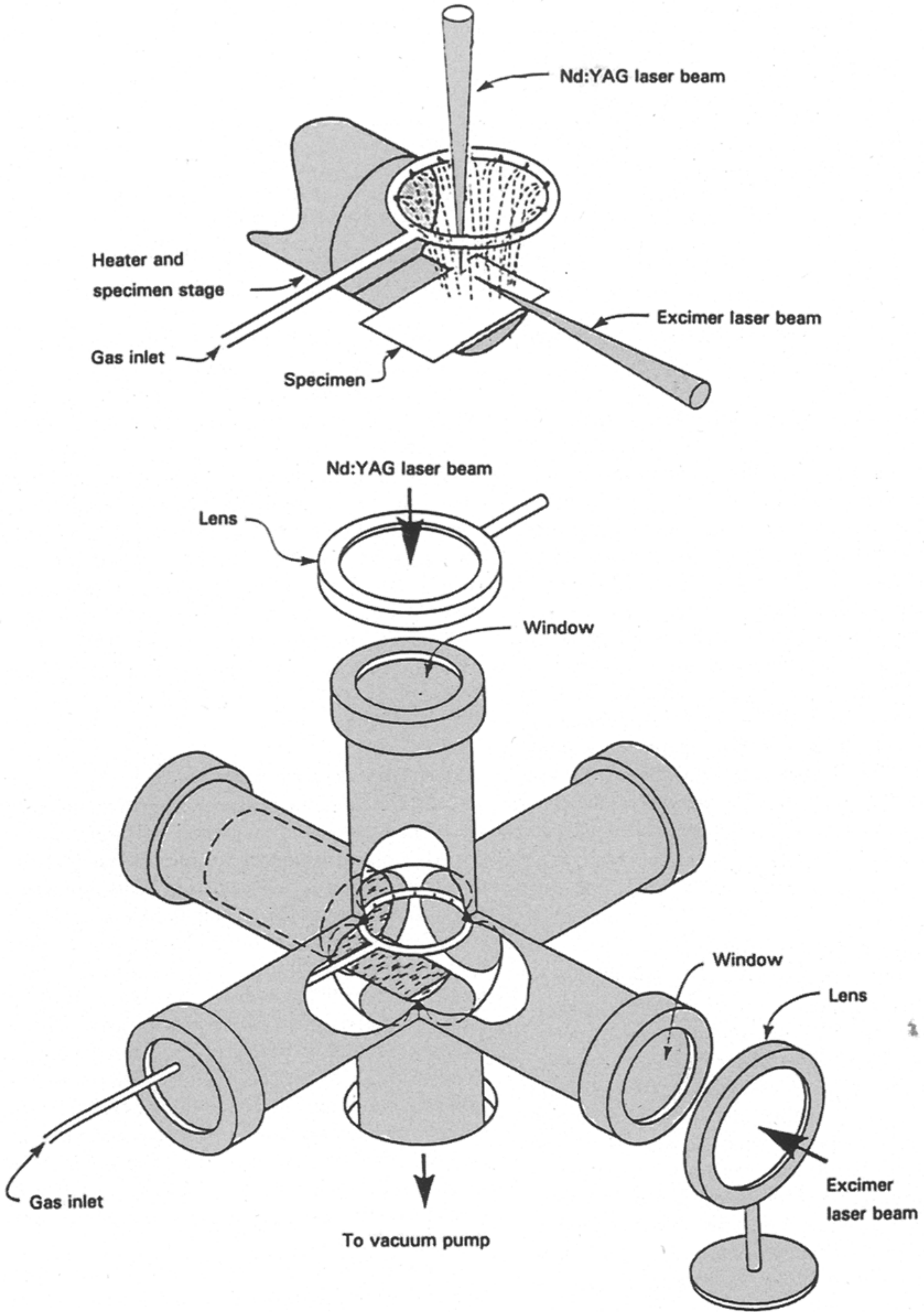

Figure 1 Schematic diagram showing laser CVD apparatus. A single laser beam (YAG or excimer) only was used for each experiment.

at the solid surface. All the Nd : YAG laser – processed samples exhibited fringes indicating thin-film formation. However, an examination of these samples under SEM and wavelength dispersive X-ray microprobe showed no signs of fluorine or carbon. Raman spectroscopy also confirmed the absence of any form of carbon. We have also conducted experiments with and without gaseous precursor to identify the differences. It seems that no reaction occurred at the SiC surface. Increasing the energy density of the laser beam led to microhole drilling. Neither carbon nor fluorine was detected surrounding the microholes.

The basis for using pyrolytic CVD using Nd : YAG laser to synthesize diamond was from the work of Rudder *et al.* [17] who deposited high-quality diamond films by thermal CVD of CF_4/F_2. Mass spectrometric analysis of thermal CVD of CF_4/F_2 revealed the presence of F, F_2 and CFX radicals [17]. Rudder *et al.* concluded that atomic fluorine behaves in a similar manner to hydrogen, namely that it etches away

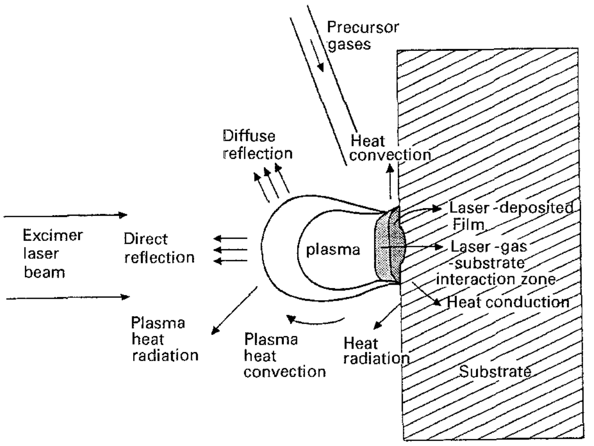

Figure 2 Laser CVD interaction processes during perpendicular irradiation of the laser beam on the substrate surface.

the non-diamond phases. In our work, even though the Nd:YAG laser decomposed pyrolytically CF_4 molecules to excited radicals of CF_3 (by thermally dissociating the gases at the hot substrate surface) and the surface binding of sp^3 structures through laser assistance have been improved, no evidence of diamond on SiC was observed.

4.2. Excimer laser photolytic deposition

Because the Nd:YAG laser pyrolysis did not induce deposition, we considered photochemical decomposition of carbon feedstock using excimer lasers. Experiments were carried out both using 23 ns pulsed 248 nm KrF excimer laser and 17 ns pulsed 193 nm ArF excimer laser. In laser photochemical reactions, the gaseous precursor must absorb the photons directly and the photon energy must be larger than the binding energy of the gases. CCl_4 and F_2 used as precursor gases in this study can be dissociated by the wavelengths 193 and 248 nm. Table IV gives the supporting data [16]. The dissociation of F_2 into atomic species is accompanied by a heat release of 37 kcal mol^{-1}. CF_4 is photolytically stable but can be thermally cracked at temperatures of 1500 °C or more, while CCl_4 can be dissociated photolytically as well as thermally at 600 °C. The absorption wavelength for CF_4 is 160 nm and the bond energy for C–F is 120 kcal which is much higher than that of the photon energy of the KrF beam (114 kcal).

A previous study indicated the possibility of obtaining diamond films with CCl_4/H_2 gas mixture in excimer laser CVD if atomic hydrogen is made available. It is envisioned in our work that F_2 molecules decomposed to the small-size fluorine atoms (photolytically) will provide the same capability as that of atomic hydrogen in etching non-diamond phases.

TABLE IV Photochemistry of precursor gases

Gas	Binding energy (ev)	Absorption wavelength (nm)	Dissociation
F_2	1.5	< 400	$F_2 \rightarrow 2F$
CCl_4	3.0	< 250	$CCl_4 \rightarrow CCl + Cl_2 + Cl$

4.2.1. *SiC substrate*

Let us first examine laser–gas–SiC interactions. The photon absorption spectrum of SiC substrate shows that approximately 30% of laser energy will be absorbed at a wavelength 248 nm [18]. The binding energy of the Si–C bond is 104 kcal mol^{-1} and hence photodissociation of SiC into silicon and carbon can readily occur both at 193 and 248 nm. The silicon and carbon atoms released from photo and thermal dissociation can react with fluorine and chlorine radicals produced by the photodissociation of CCl_4 and F_2. Fluorine has a higher electronegativity than chlorine and hence can react with silicon and carbon to form SiF_4 and CF_4. In addition, fluorine can etch graphite.

Initially, Carborundum and Norton SiC were used as substrates. No evidence of any carbon deposition was observed. This was surprising, considering the fact that SiC is an excellent substrate for diamond growth and lasers were capable of decomposing the gases. Several experiments with varying process parameters were carried out, but the results remained negative. Some possible explanations are:

1. the presence of impurities on the substrate surface may prevent the nucleation of carbon by surface catalytic reactions;
2. the heterogeneous reaction rate of the gas decomposition at the SiC surface may be slow because of the chemical inertness of SiC;
3. the time may not be adequate for the nucleation of carbon.

Because Carborundum and Norton SiC samples contained impurities, a high-purity grade SiC (EKasic HD, SiC = 99.5%) was procured from ESK engineered ceramics. This particular grade, as claimed by the manufacturer, serves as the best substrate for diamond growth. Initial experiments using EKasic HD grade SiC as the substrate did not provide satisfactory results. Continued experimentation indicated that excimer laser growth of diamond film on SiC substrate is critically dependent upon laser parameters and the purity of SiC. High energy densities of the order of 2–4 J cm^{-2} are required to decompose the gases at the SiC surface. In contrast, a pulse energy density of 0.7 J cm^{-2} is sufficient to deposit carbon film on 440 C stainless steel. Flowing gas at high rates followed by impingement of a high energy-density laser beam generated a film on SiC that consisted of a mixture of graphite and diamond (Figs 3 and 4). Laser CVD films exhibited ball-like morphological features of diamond and graphite structures rather than the typical octahedral features of diamond.

Numerous process conditions were then attempted with the objective of eliminating graphite phase from the deposited film. These variables include:

wavelength	193 nm (ArF) and 248 nm (KrF)
energy density	1–5 J cm^{-2}
repetition rate	50–100 Hz

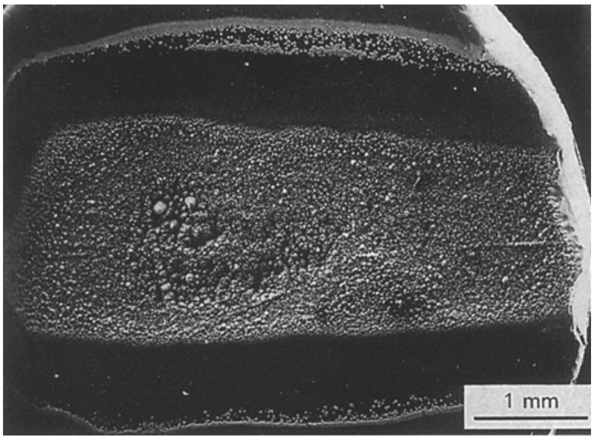

Figure 3 Scanning electron micrograph of a top view of laser-grown films on SiC.

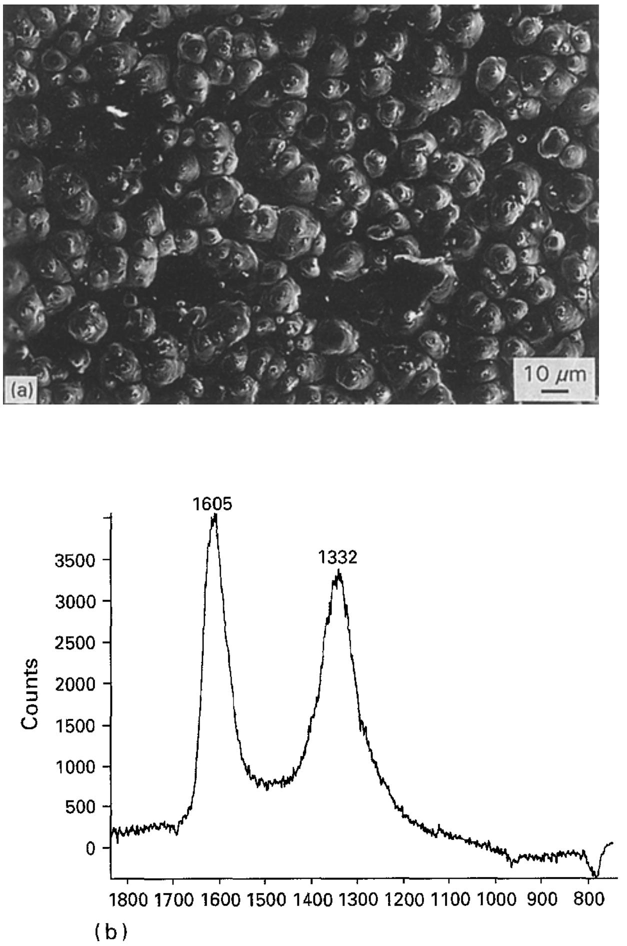

Figure 4 (a) Scanning electron micrograph of a laser-grown film on SiC showing the ball-like morphology of diamond. (b) Raman spectrum of (a) showing peaks for diamond and graphite. Note the absence of SiC peaks at 786 and 965 cm^{-1}.

TABLE V Excimer laser CVD experiments for SIC substrate

Sample	Laser parameters	Precursor gas
57	193 nm ArF, 2 J cm^{-2} 50 Hz	$X^a + H_2 + O_2$
58	193 nm ArF, 2 J cm^{-2} 50 Hz	$X + CCl_4$
64	193 nm ArF, 2 J cm^{-2}, 100 Hz	$X + H_2 + O_2$
65	193 nm ArF, 2 J cm^{-2}, 100 Hz	$X + CCl_4$
73 and 74	248 nm KrF 4 J cm^{-2}, 100 Hz	$X + H_2 + O_2$

$X = 1\%\ CF_4/1\%\ F_2/98\%$ He.

gas flow	X = 200–3000 standard $cm^3\ min^{-1}$ (gas) CCl_4 = 0.1–1 g min^{-1} (liquid)
total gas pressure	0.2 torr to atmospheric
gas flow pattern	simultaneous flow of both X and CCl_4, or injection of one gas after the other
gas preheating	1000 °C
gas additive	O_2 at 50 standard $cm^3\ min^{-1}$
substrate preheat	20–500 °C
deposition time	15–30 min

A large number of experiments, covering the effects of above-mentioned variables, were carried out. The experimental conditions for representative samples are given in Table V.

The rationale for using ArF wavelength (193 nm) was its ability to dissociate CCl_4 and F_2 more efficiently than KrF wavelength (248 nm). Results, however, indicated no major difference on the films grown using either wavelength of light. The films grown by 193 nm light had smaller coverage zones (due to the small spot size of the ArF beam), possessed finer structures and exhibited sharper peaks in the Raman spectrum. Although 193 nm wavelength is a better choice, the drawbacks include the energy stability of the beam in the laser cavity, the use of vacuum (or inert gas) in the beam delivery system, and the smaller beam.

The energy density of the laser beam was found to play a significant role in the adhesion and coverage area of the film. In this work, energy density was varied by changing the beam size (through defocusing the beam) rather than changing the pulse energy. Adhesion of the film was substantially improved (as determined in the friction test) by using higher energy density, possibly due to increased substrate temperature. Better film quality, in terms of Raman spectrum peaks, was also obtained.

Repetition rate influences the film thickness through its effects on chemical reactions. Laser pulses with repetition rates less than 50 Hz did not produce useful films. Higher repetition rate (> 50 Hz) increases the coverage zone and should be used wherever possible. This is quite different from laser ablation, where low repetition rates (< 10 Hz) are often used.

The volumetric or mass flow rate of the precursor gases is important for laser – gas reactions. Gas flows of 1000–3000 standard $cm^{-3}\ min^{-1}$ X and 0.1–1 g min^{-1} CCl_4 were found to be satisfactory. If the gas flow is not properly adjusted, there is no reaction at the

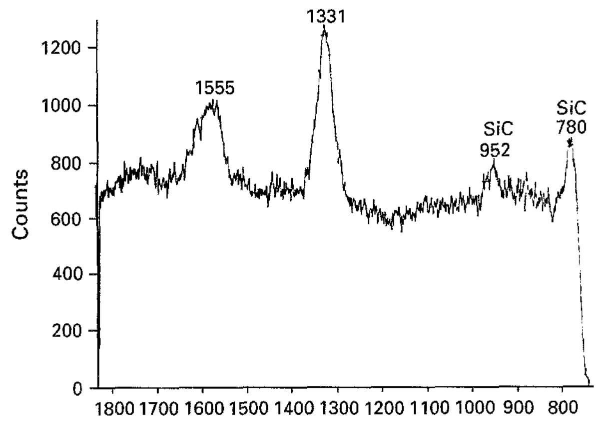

Figure 5 Raman spectrum of sample 57 showing diamond and graphite peaks in addition to SiC peaks.

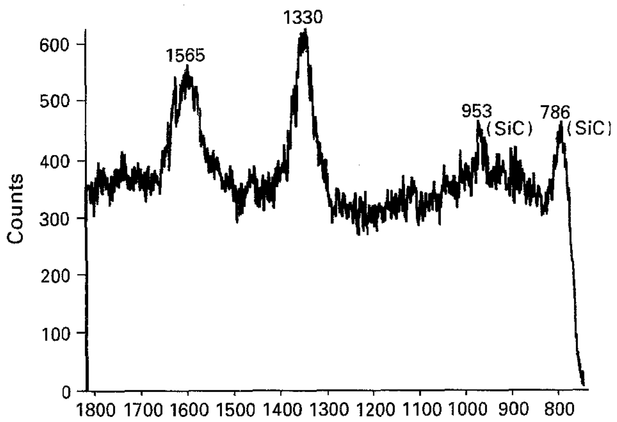

Figure 6 Raman spectrum of sample 58 showing diamond and graphite peaks in addition to SiC peaks.

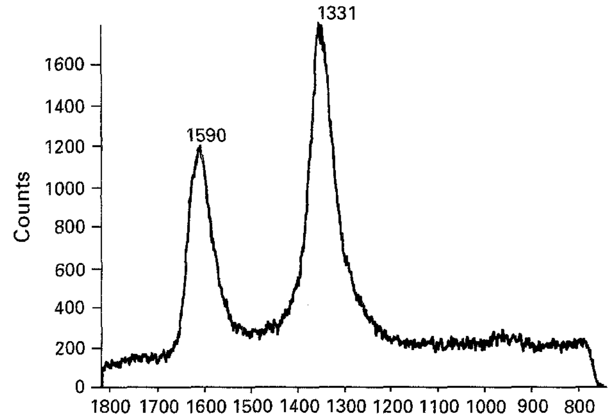

Figure 7 Raman spectrum of sample 64 showing diamond and graphite peaks. Note the absence of SiC peaks.

substrate surface. It is worth mentioning that a small plasma jet forms at the laser–gas interaction zone only at the flow rates specified. The effect of gas flow injection was also investigated. Experiments involving simultaneous flow of CCl_4 and X, delivery of X for 5 min followed by flow of CCl_4 (or vice versa) for 5 min, were carried out. The resulting differences were negligible.

The gas pressure in the CVD chamber should be held at less than 10 torr. Higher gas pressure generally leads to complete absorption of laser beam energy before it reaches the substrate surface.

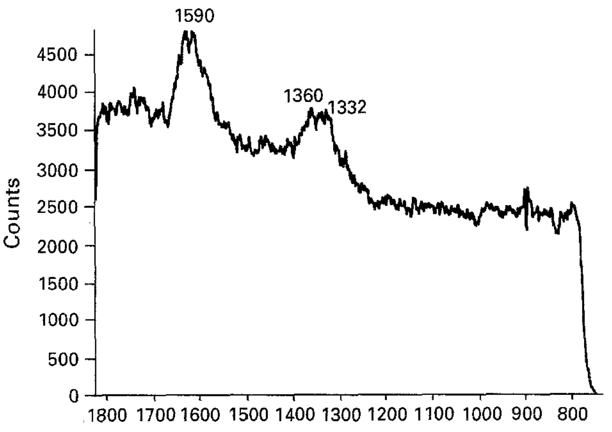

Figure 8 Raman spectrum of sample 65 showing diamond and graphite peaks. Note the absence of SiC peaks.

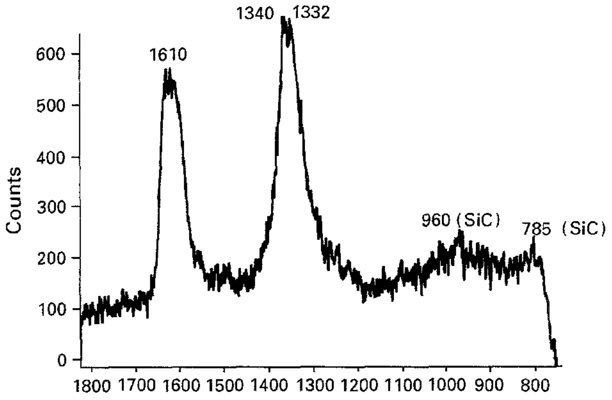

Figure 9 Raman spectrum of sample 73 showing diamond and graphite peaks in addition to SiC peaks.

Substrate preheating up to 500 °C did not affect the film growth process.

An increase in the film thickness was noted with an increase in deposition time.

Gas preheating had no effect on the film formation.

The addition of oxygen enhanced diamond structures.

Raman spectroscopy analysis of all the samples revealed the presence of a mixture of diamond and graphite in laser-irradiated regions. Figs 5–9 are representative Raman spectra of laser-grown films while Fig. 10 is a spectrum of hot-filament CVD-deposited diamond film (on silicon substrate). Fig. 10 is only for comparison purposes. The following conclusions may be drawn from Raman analysis. Diamond and graphite films were deposited irrespective of the precursor gases being $X + H_2 + O_2$ or $X + CCl_4$ (Figs 5 and 6). However, these films contained some SiC peaks. An increase in the pulse repetition rate from 50 Hz to 100 Hz (compare samples 57 with 64, and 58 with 65) eliminated SiC peaks from the Raman spectra. Addition of oxygen to the precursor gases reduced the graphite growth (based on the ratio of diamond and

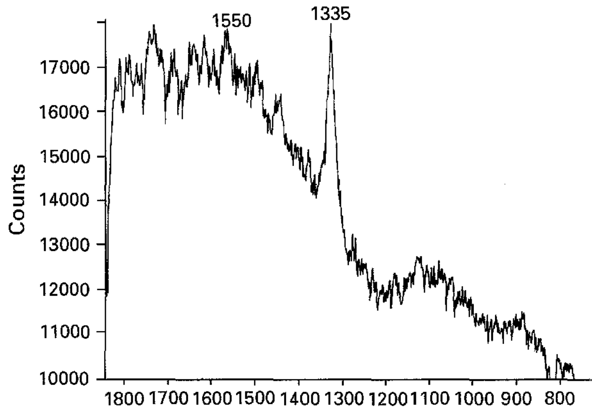

Figure 10 Raman spectrum of hot-filament CVD-grown diamond film on silicon.

TABLE VI Excimer laser CVD on steel substrates

Sample	Precursor gas flow	Laser parameters	Observations
35	X, 10 torr, 3000 standard cm^3 min^{-1}	1 J cm^{-2} 50 Hz	Green plume, black film
36	$\mathrm{X + H_2}$, 10 torr, 3000 standard cm^3 min^{-1}	1 J cm^{-2} 50 Hz	Green plume black film
38	$\mathrm{X + CCl_4}$, 2 torr, $\mathrm{CCl_4}$ 0.1 g × 3000 standard cm^3 min^{-1}	0.8 J cm^{-2} 50 Hz	Black film
40	$\mathrm{CCl_4 + H_2}$, 0.5 torr, $\mathrm{CCl_4}$ 1 g min^{-1}	0.8 J cm^{-2} 50 Hz	Black film
46	$\mathrm{X + CCl_4 +}$ $\mathrm{H_2}$ 2 torr, X 3000 standard cm^3 min^{-1} $\mathrm{CCl_4}$ 1.5 g min^{-1}	0.7 J cm^{-2} 100 Hz	Black film
50	Repeat 46 for longer time		Black film

graphite peaks in samples 57 and 64). Furthermore, $\mathrm{X + H_2 + O_2}$ serves as a better precursor than $\mathrm{X + CCl_4}$. A significant feature is that the 193 nm ArF beam is more efficient than the 248 nm KrF in depositing fluorinated carbon films (compare Fig. 7 with Fig. 9).

In summary, a mixture of diamond and graphite was deposited on SiC substrates. Variation of laser parameters and other experimental conditions did not completely eliminate the graphite. Graphite content could be minimized by the addition of oxygen and using an ArF laser beam. Fluorine was not capable of etching the non-diamond phases, possibly due to lower amounts (1%) of fluorine. It appears that removal of graphite requires significant quantities of fluorine. Additionally, diamond-stabilizing radicals such as $\mathrm{CF_3}$ may not have been present in sufficient quantities for the preferential growth and stabilization of diamond.

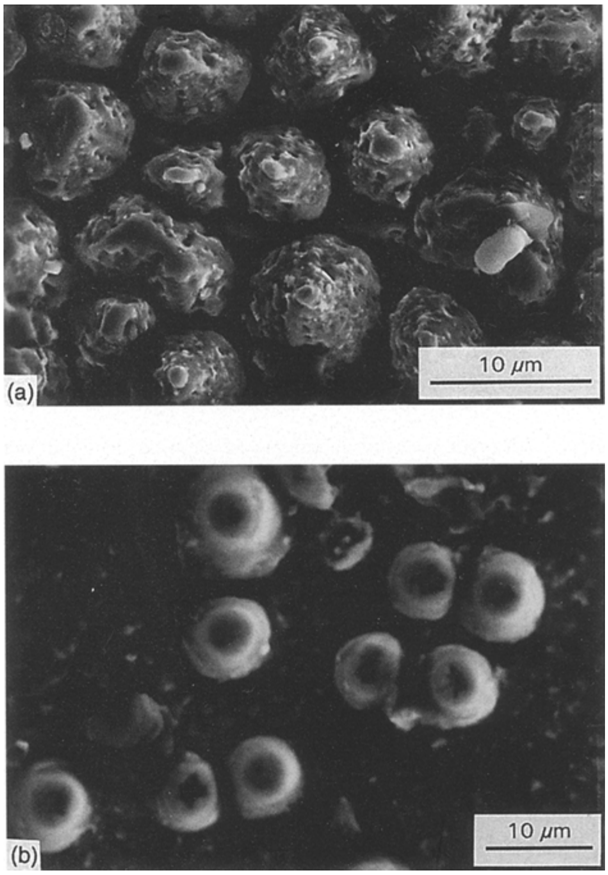

Figure 11 Scanning electron micrographs of samples (a) 35 and (b) 50 showing ball-like diamond structures.

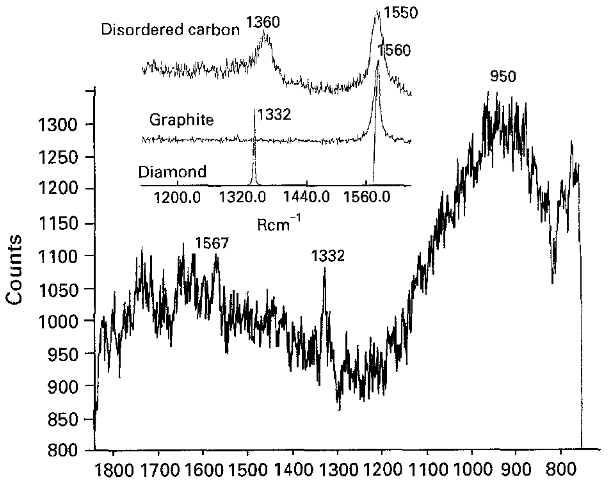

Figure 12 Raman spectrum of sample 35 showing diamond and DLC.

4.2.2. 440 C stainless steel substrate

Table VI lists representative experimental conditions used to deposit diamond films on a stainless steel substrate. Only KrF beam was used. Fig. 11 shows SEM micrographs of samples 35 and 50 illustrating the ball-like morphology of diamond and other carbon structures. Figs 12–16 are the Raman spectra of steel samples showing peaks for diamond, diamond-like carbon and graphite. In addition, a strong, broad peak centred at 950 cm^{-1} is also observed. ArF-beam laser CVD yielded much better Raman spectra than

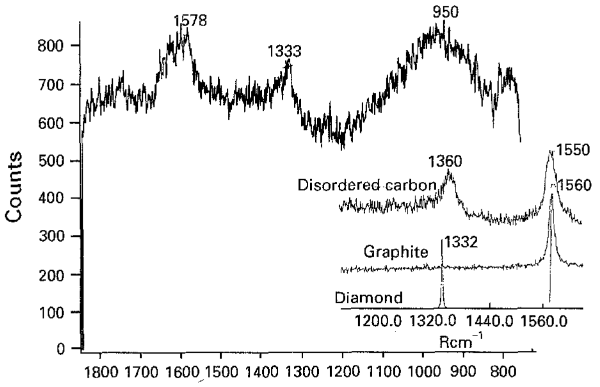

Figure 13 Raman spectrum of sample 38 showing diamond and graphite.

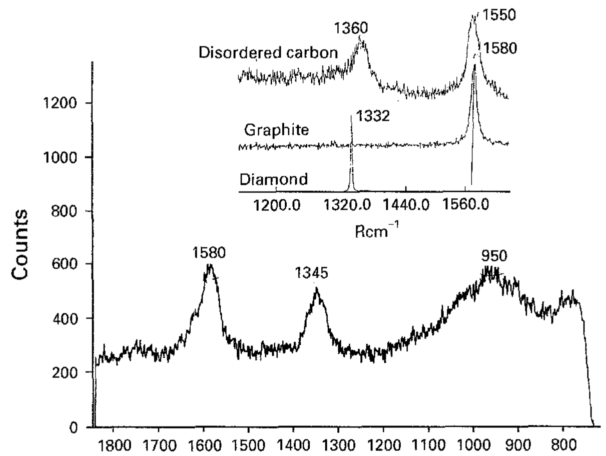

Figure 14 Raman spectrum of sample 40 showing DLC and graphite.

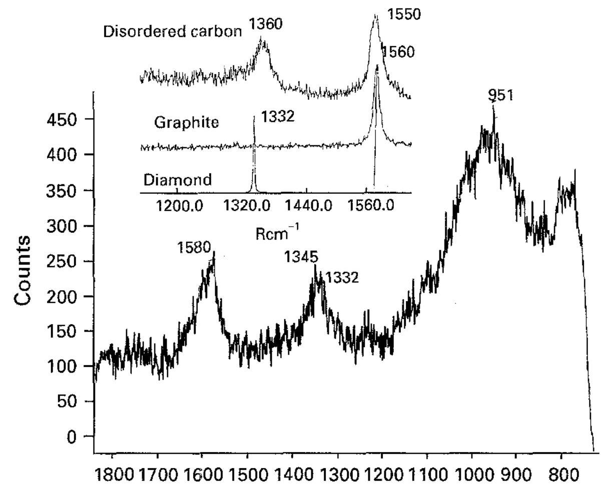

Figure 15 Raman spectrum of sample 46 showing diamond, DLC and graphite.

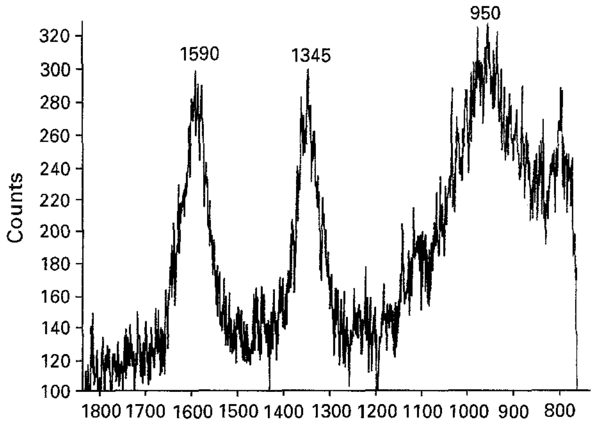

Figure 16 Raman spectrum of sample 50 showing DLC and graphite.

KrF beam laser CVD. It should be emphasized that the peak usually occurring at 950 cm^{-1} is absent in ArF-beam processed samples.

The significant differences between SiC and steel substrates are that the film grown on SiC exhibited diamond and graphite peaks in the Raman spectrum while the film on steel showed peaks for diamond, graphite, diamond-like carbon and an unidentified peak at 950 cm^{-1}. In addition, the peaks in the Raman spectrum for films grown on SiC had higher intensity (counts) than for steel.

5. Conclusion

A laser CVD process was developed for depositing a mixture of diamond, graphite and diamond-like carbon films on bearing material substrates including SiC and 440 C stainless steel. A Nd:YAG laser for creating photothermal effects and an excimer laser for generating photochemical reactions of a gaseous precursor mixture of halogenated methane and halogen were employed for this purpose. The type of laser, carbon feedstock, laser–precursor gas interactions, and deposition conditions have been established. Scanning electron microscopy, wavelength dispersive X-ray analysis, and Raman spectroscopy analysis of laser-grown films revealed that the films deposited on SiC consisted of a mixture of diamond and graphite and the films on 440 C steel were composed of diamond, diamond-like carbon and graphite. Efforts to eliminate the graphite from the film were unsuccessful.

Acknowledgement

This work was financially supported by Strategic Defense Initiative Organization under the contract number DAAL 03-91-C-0041.

References

1. L. L. FEHRENBACHER, in “Engineered Materials for Advanced Friction and Wear Applications”, Proceedings of the International Conference (ASM, Metals Park, OH, 1988) p. 169.
2. M.E. CAMPBELL, J. B. LOSER and E. SNEEGAS, “Solid lubricants,” NASA-SP 50, May 1966, Cleveland, OH.
3. M. B. PETERSON and M. KANAKIA, in “Engineered Materials for Advanced Friction and Wear Applications”, Proceedings of the International Conference (ASM, 1988) p. 153.
4. T. SPALVINS, *ibid.*, p. 203.
5. Y. TZENG, M. YOSHIKAWA, M. MURAKAWA and A. FELDMAN (eds), “Applications of diamond films and related materials”, (Elsevier Science, Auburn, AL, 1991).
6. J. NARAYAN, V. P. GODBOLE and C. W. WHITE, *Science* **252**, (1991) 416.

7. Y. GOTO, T. YAGI and H. NAGAI, *Mater. Res. Soc. Proc.* **129**, (1989) 213.
8. G. Y. TYNDALL and N. P. HACKER, "KrF laser-induced CVD of diamond", presented at 1990 Materials Research Society, November 1990 Boston (MRS).
9. F. G. CELII, H. H. NELSON and P. E. PEHRESON, *J. Mater. Res.* **5** (1990) 2337.
10. B. C. JANVRIN, MS thesis, Iowa State University (1990).
11. P. MOLIAN and A. WASCHEK, *J. Mater. Sci.* (1992).
12. S. L. THALER, in "Applications of diamond films and related materials", edited by Y. Tzeng, M. Yoshikawa, M. Murakawa and A. Feldman (Elsevier Science 1991) p. 857.
13. N. I. CHAPLIEV *et al*, *ibid.*, p. 417.
14. D. L. PATTERSON, R. E. HAUGE and J. L. MARGRAVE, *Mater. Res. Soc. Symp. Proc.* **140** (1989).
15. D. BAUERLE, "Chemical processing with lasers" (Springer, New York, 1986).
16. H. OKABE, "Photochemistry of small molecules" (Wiley, New York, 1978).
17. R. A. RUDDER, J. D. POST HILL and R. J. MARKUNAS, *Electron. Lett.* **25** (1989) 1220.
18. M. MURAHARA, H. ARAI and T. MATSUMURA, *MRS Proc.* **129** (1989) 315.

Received 28 October 1992
and accepted 22 April 1993