Brite-EuRam CONTRACT N° BRPR - CT98 - 0749
Brite-EuRam PROJECT N° BE97 - 4669

PROJECT TITLE:

AMBIENT TEMPERATURE DEPOSITION OF HARD DIAMOND-LIKE CARBON COATINGS

DIAMCO

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PUBLISHABLE SYNTHESIS REPORT

Reference period for the Report:	From October 1, 1998 to January 31, 2002
Start date of the Project:	October 1, 1998
Duration of the Project:	40 months
Date of the issue of the Report:	March, 2002

CONTENTS

1. SUMMARY

A pre-industrial prototype of a plasma reactor operating in a Distributed Electron Cyclotron Resonance (DECR) configuration and corresponding processing routes have been successfully designed and developed for ambient temperature deposition of diamond-like carbon (DLC) protective coatings on large area, thermally sensitive substrates. Unambiguous and physically sound relationships between the processing parameters specific to this machine and the physical properties of the DLC coatings were established initially and the research subsequently focused on reaching a better understanding of the fundamental properties of the DLC thin films.

A low energy, high current electron gun has been developed in an attempt to combine plasma processing with polarisation of thick dielectric substrates by fast electron injection. The new electron gun produces substrate electron current densities of 1 mA/cm^2 and enables well controlled biasing of dielectric substrates whatever their thickness or shape.

Substantial progress has been accomplished in understanding the nucleation and growth processes. New light was shed on the role of energy density deposited in elastic collision cascades and its impact on the nucleation dynamics. Physical mechanisms responsible of carbon and hydrogen incorporation were analysed in detail. Interaction between external and intrinsic stress fields and their impact on the DLC microstructure, hybridisation and optoelectronic properties has been demonstrated. Stress mediated nucleation was shown to lead to formation of auto-correlated nano-structured DLC films. Process-induced defects have been identified for specific demonstrators and correlated to the process parameters. Ways around these problems have been found.

Successful demonstrators included coated plastic optical components for use in sunglasses and helmet visors. These demonstrated superior scratch resistance, decorative added value and excellent stability and durability. A further demonstrator significantly enhanced the moisture resistance of microelectronic assemblies and hence their reliability. This work is continuing as an industrial development and promoted novel industrial applications. Innovative aspects of the DECR equipment may now be incorporated into commercial equipment.

2. CONSORTIUM

The consortium was made up of 7 partners from 5 Member States (France, Germany, Ireland, Italy and the UK). The partnership was vertically integrated with expertise contributed from four major European manufacturers acting as end-users who intend to implement the new coating technology in the corresponding industrial sectors. The industrial and research laboratories focused on process development as well as process control methodology and evaluation of the coatings. The coatings were fabricated on a pre-industrial scale machine designed by one of the industrial partners. Industrial activities, corporate strategy and/or main R&D activities of the individual partners is described below.

2.1 Centre National de la Recherche Scientifique (CNRS), Laboratory "PHASE" *(Coordinator)*

The CNRS is a major French research organisation. The two CNRS laboratories involved in this project are PHASE-Strasbourg and LEMD-Grenoble, as scientific and financial co-ordinators respectively.

The CNRS-PHASE Laboratory in Strasbourg (PHysics and Applications of SEmiconductors) (http://www-phase.c-strasbourg.fr) is an autonomous laboratory of the CNRS linked to Louis Pasteur University in Strasbourg. Since its creation in 1960 it has built up expertise in the field of fabrication and modification of semiconductor materials for microelectronic and photovoltaic device applications, and in ion beam and photon beam related techniques (laser processing, medium to high energy ion implantation and nuclear related analytical tools). The Laboratory has also extensive experience in analysis of defects in semiconductors, band-gap engineering and material characterisation, as well as modelling of the related phenomena. It has acquired an international reputation as an R&D performer in the field of radiation detectors and solar cells.

The research activity of the PHASE Laboratory is organised around four scientific themes (bulk semiconductors, thin films, nanostructures, and equipment design) and three main services (clean room facilities, implantation and nuclear analysis, materials characterisation). The PHASE staff includes about 75 people including 22 senior scientists.

2.2 Centre National de la Recherche Scientifique (CNRS), Laboratory "LEMD" *(Partner)*

The CNRS-LEMD Laboratory (Laboratoire d'Electrostatique et de Matériaux Diélectriques) (http://www.polycnrs-gre.fr) is a R&D performer with well established expertise in plasma-based processing of dielectric materials. The permanent LEMD staff includes 15 research scientists and 4 engineers. The Laboratory has acquired an extensive experience in plasma processing (etching and deposition) and in designing DECR plasma reactors. LEMD has recently patented the new technique of plasma deposition on dielectrics. The process is based on substrate biasing by fast electron injection (PFEI). The CNRS-LEMD has been successful in transferring know-how in the field of plasma deposition to a variety of industries in France and in Europe (SCHEIDER-ELECTRIC, PIRELLI, NITRUVID, TORNIER, HYDRO-QUEBEC etc.). It has an established reputation for successful participation in EU research programmes. The expertise of CNRS-LEMD and of CNRS-PHASE are complementary and their combination helped to efficiently attain the project objectives.

2.3 RADSTONE Technology Plc *(End-user)*

Over the last 30 years Radstone Technology (http://www.radstone.com/) has become a world leader in the fabrication of custom designed and standard product electronic systems for a diverse range of markets and applications. The company successfully achieved a full listing of it's shares on the London Stock Exchange at the end of February 1994. Radstone Technology is a highly innovative company and has a strong R&D effort which has put the company in a prime position for offering advanced Power Wiring Board (PWB) technology to the market.

Radstone Technology currently designs and uses advanced PWBs incorporating thick copper thermal management cores, epoxy bonding layers and thin patterned copper foils for electrical interconnection. These form the base substrate for the high functionality electronic assemblies provided by Radstone Technology into high performance applications requiring excellent reliability in harsh environmental conditions. Full facilities for characterisation and assessment of laminate based substrates are available to Radstone Technology. Such laminates are naturally poor heat conductors and have too high a coefficient of thermal expansion (CTE) to match the electronic devices mounted on them. Additionally the polymeric materials currently used to conformally coat finished electronic assemblies, while reducing failures due to electro migration, do not prevent moisture ingress through the coating to the surface of the assembly.

This project targeted development of sealing layers to reduce or eliminate moisture ingress through the polymeric conformal coating layer**.**

The equipment available at Radstone Technology constitute a modern facility for the design and assessment of state of the art electronic assemblies. These facilities have been made available to the project as required, since none, with the exception of design workstations, are in continuous use. The company holds ISO9001 registration.

2.4 Centro Technologie del Vuoto (Ce.Te.V) *(End-user)*

Ce.Te.V. (http://www.cetev.com) was established in 1988 and presently is a Joint Stock Company between Galileo Avionica and Meteor, both within the Finmeccanica group. Its R&D activities are finalised towards an effective industrial utilisation of new processes and equipment developed. Presently 20 people are employed: 4 senior researchers, 4 graduate researchers, 8 technicians and 4 administrative. Furthermore many agreements with universities and research centres are running for the National and International advice and co-operation.

Ce.Te.V. activities include a specialised production line for high quality optical treatments certified for defence and space applications. Facilities include almost 2000 m^2 of covered area of which 700 m^2 constitute clean rooms of different class level (from 100 to 10000) and controlled areas. Current Ce.Te.V. operating plants are equipped with highly innovative PVD techniques (Electron Beam Gun, Sputtering, Ion Assisted Deposition, Ion Beam Sputtering Deposition, Ion Plating). Particular effort is devoted to PE-CVD techniques using 4 specialised equipments. In addition, a line for sub-micron photolithography has been installed for large area substrates (wire chamber detectors). Most of the plants at Ce.Te.V. have been designed, engineered and produced in house improving knowledge of plant manufacturing and special process set-up. Ce.Te.V. expertise helped attaining project objectives using an alternative processing route

2.5 INTERCAST EUROPE S.p.A. *(End-user)*

INTERCAST EUROPE S.p.A (http://www.intercast.it) is a SME founded in 1976, in its facility in Parma (Italy) manufactures plastic sunglass lenses (for fashion and sport activities) transparent plastic sheets, visors for goggles, face shields for labour protection etc. Intercast Europe employs 100 people, 10 of which are dedicated to R&D and Quality Control activity. Ten years ago the subsidiary SOLARLENS Co LTD. was founded based in Bangkok (Thailand) with 250 people to produce sun lenses for the Far East and American market. Every month over 25 tons of allylic resins are transformed in 2 million pairs of lenses and more than 100000 sheets in hard resin thermoformable. The production of lenses exceeds 20 million pairs per year and are distributed all over the world. Intercast Europe laboratory co-operates with national and international research centres to certificate his new products and follow all technical developments in optical field.

2.6 ROTH & RAU *(End-user)*

Created in 1990 near Chemnitz, Germany (http://www.roth-rau.de), Roth & Rau is an SME company of 60 employees. Its core business activity concerns design and manufacture of plasma and ion beam technology equipment for research, development and industrial purposes. Roth & Rau has 3 Departments devoted to:

- In line Plasma Equipment design end manufacture.
- Special Plasma and Ion Beam Systems .
- Hard coating department.

Roth & Rau develops the following equipment:

- Microwave ECR (Electron Cyclotron Resonance) plasma sources for plasma etching and/or deposition equipment.
- Microwave linear plasma sources particularly well suited for large area plasma processes like cleaning, surface modification and activation, polymerisation and thin film deposition.
- Kaufman type ion beam sources (hot cathode).
- ECR ion beam sources.
- Complete equipment for ion and plasma sources for etching and/or deposition.
- Coating service.

Roth & Rau has considerable experience in the equipment design and production. Most machines are sold in Germany while other customers are in Taiwan, India, USA, Europe and Saudi Arabia. Since 1997 Roth & Rau has had offices in the Far East and India.

Roth & Rau expertise in DLC coating, plasma processing and equipment manufacturing played a major role in the project.

2.7 National Microelectronics Research Centre (NMRC) *(Partner)*

The Irish **National Microelectronics Research Centre (NMRC)** (http://www.nmrc.ie/, http://www.nmrc.ie/access/) was established in 1981 with a staff of 20 people. Since then, it has grown to become the largest multidisciplinary research centre in Ireland and has achieved the scale necessary to compete in the international R&D market. The centre now has a critical mass in excess of 200 research staff along with a significant research infrastructure currently valued at over IR£80 million (E101 million). NMRC has a dual mission, firstly to be a Centre of Excellence in selected Information and Communication Technologies (ICT) fields, and secondly to be a key part of the national science, technology and innovation infrastructure. This is achieved through supporting existing indigenous and multinational industry, providing highly skilled staff for Irish industry and stimulating new industrial development and inward investment from foreign companies.

Since its foundation, NMRC has collaborated successfully with industrial concerns in other European countries under the auspices of various EU research programmes such as ESPRIT, BRITE/EURAM, BCR and RACE. In 1990, an agreement with the European Space Agency (ESA) established an ESA Microelectronics Technology Support Laboratory (MTSL) in the NMRC. In 1992, under the European Large Scale Facility (LSF) programme, NMRC was appointed as a centre of excellence in Microelectronics Reliability, Failure Analysis and Reverse Engineering. The research currently undertaken by NMRC may broadly be defined under the following headings:

- **Device Fabrication**
  Silicon, Compound Semiconductor Growth & Fabrication, Microsystems Devices.
- **Photonics**
  LEDs, VCSELS, Sub-millimetre wave devices, optical communications, laser metrology.
- **Nanotechnology**
  Nanometer-scale device handling, Sub-micron lithography.
- **Sensors, Transducers & Microsystems**
  Radiation sensors, Ultrasonics, Optical Biosensors, etc.
- **Microelectronic Packaging & Reliability**
  Additive PCB processes, Lead-free solder evaluation, Microsystems Packaging Development. Power Device. Packaging.
- **Modelling & Computer Aided Design**
  Finite Element, mechanical & electrical modelling, MOS Device Simulation, 3-D Fluid Dynamic Thermal Simulation, IC layout.
- **Materials Characterisation**
  Thermo-Mechanical Property Measurement (CTE, Young's Modulus, Phase Transition Temps, Poisson's Ratio, Thermal Diffusivity, etc), Electrical Property Measurements, Thermal Conductivity Measurement, Tensile & Compressive Strengths, Fatigue Testing.
- **Microstructural Evaluation.**
- **Environmental Sciences**
  Eco-friendly Wafer & PCB cleaning techniques, Toxic Metal Sensors.
- **Test & Analysis Services**
  Reliability Tests, Reverse Engineering, Failure Analysis, Material Property Measurements.

Through its participation in international R&D consortia over the last 18 years, NMRC has developed its R&D expertise and technology portfolio, which provides the basis for the support of the long-term sustainable and competitive development of the ICT & Electronics sectors in Ireland and Europe.

The main technical role of NMRC in the DIAMCO project was in materials characterisation and reliability evaluation.

3. Technical challenge and methodology

DLC films display a unique combination of exceptional and desirable properties [1-7 and ref. therein]. These include high hardness, high abrasive and adhesive wear resistance with low coefficients of static and dynamic friction in non lubricated operations, chemically inert to both acids and alkalis, lack of magnetic response, an optical gap ranging from zero to a few eV and high electrical resistivity. The physical properties of the DLC thin films are strongly interrelated and depend on the deposition technique and growth conditions [8]. They are highly adjustable for special requirements. DLC films can be made electrically conductive or having the wetting properties of Teflon. DLC coatings are commercially used in thin-film magnetic rigid discs for wear and corrosion resistance and in aggressive tribological environments such as metal cutting. Diamond-Like Carbon (DLC) has potential uses in the optical, acoustic, corrosion resistant and electronic device markets.

The potentially attractive properties of DLC coatings will remain irrelevant on the industrial scale as long the specific problems limiting the applicability of the material, such as adhesion and intrinsic stress, remain unsolved. Large surface DLC coating and growth of DLC films of several microns in thickness are still impossible on the industrial scale and represent challenging tasks for research and development.

The goal of the DIAMCO project was to develop a low cost and technically reliable new DLC coating processes and equipment for distinct industrial applications. The work was performed in three phases:

1. A prototype laboratory equipment (DIAMCO machine) was designed and built by the Consortium. It has been subsequently used as a key experimental tool for process development and optimisation.
2. Using a variety of experimental techniques the DLC fundamental physical properties were carefully analysed and unambiguously correlated to the process parameters. The corresponding database was established and used for process optimisation.
3. DLC coatings were deposited on various demonstrator substrates. The processing conditions for each demonstrator were subsequently optimised taking into account the earlier defined specifications. The prospects for industrial implementation were carefully analysed and discussed in detail with the end-users.

4. TECHNICAL ACHIEVEMENTS

4.1 Pre-industrial prototypes

4.1.1 DIAMCO machine : pre-industrial laboratory prototype : general concept and potential for innovation

One of the principal achievement of the DIAMCO Consortium was the design and construction of a distributed electron cyclotron resonance (DECR) plasma laboratory prototype reactor [9]. The pre-competitive prototype equipment targeted the following objectives:

- To develop an environmentally friendly DLC deposition process independent of thermodynamic effects and operating at ambient temperature, with a consequent improvement in the thermal budget performance.
- To fulfil stringent requirements of deposition uniformity on large size substrates and over a variety of substrate materials at reduced equipment and processing costs
- To enable the plasma cleaning, seeding and deposition processing steps to be integrated within a multistep "in situ" operation offering increased manufacturing flexibility.
- To demonstrate potential for easy scale-up of the equipment and an increase in the substrate throughput.

The approach proposed has been based on a reactor configuration where electron cyclotron resonance is coupled with peripheral multipolar magnetic field confinement in order to improve plasma uniformity and enhance plasma density. The reactor design is schematically represented in FIG.1.

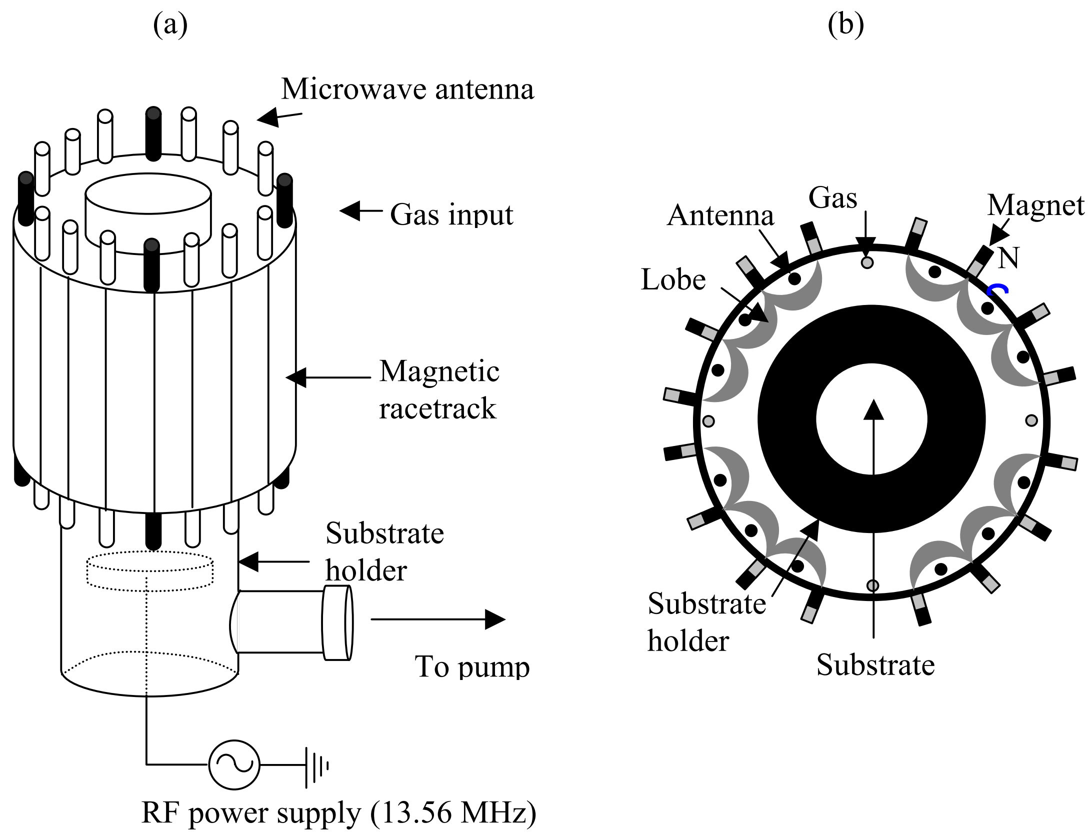

FIG 1. Schematic views of the DECR reactor: (a) general view, (b) axial cross section.

We refer to this configuration using an abbreviation “DECR” meaning Distributed Electron Cyclotron Resonance. The microwave generator operates at a frequency of 2.45 GHz and powers the reactor with microwave energy radiated by 12 antennas. The antennas, parallel to the axis of cylindrical reactor, are located in the vicinity of the magnetic field "race tracks". The role of the multipolar magnetic field is to confine fast electrons produced by cyclotron resonance, as well as the plasma.

At sufficiently low pressure (10^{-3}-10^{-4} Torr) the plasma generated in the vicinity of the antennas diffuses under the influence of the density gradients. A uniformly distributed, cold (i.e. free of high energy electrons), high density (10^{11} - 10^{12} ion/cm^3) diffusion plasma is obtained across the reactor volume, allowing for the processing of large sized substrates and/or 3D objects. A substrate is immersed in a DECR plasma and repetitively pulse biased to a negative voltage, thereby accelerating ions across the plasma sheath into the substrate. The proposed design of the DECR reactor enables deposition of DLC films using a carbon rich precursor like acetylene or using a graphite target immersed in a noble gas plasma. In order to achieve this a water-cooled graphite sputtering target is placed on the top flange of the plasma chamber. It is equipped with a dark shield to avoid unwanted discharges and is operated by a 3kW, -1000V pulsed DC power supply. The graphite target acts as sputtering source producing neutral carbon atoms which eventually become ionised.

The DECR prototype equipment, designed jointly by ROTH&RAU and CNRS and subsequently manufactured, assembled and tested by ROTH&RAU has been used since February 2000 by CNRS-PHASE. It is called here after the “DIAMCO Machine”. The general performance and reliability of the DIAMCO machine have been carefully assessed and the objectives assigned have been attained. The DIAMCO machine operates in conformity with the requirements listed in the DIAMCO Specification Booklet.

In a DECR reactor a cold plasma of uniform density is distributed across a large volume and/or area enabling large area substrates or 3D substrates to be subimplanted or coated. The substrates treated in the DIAMCO machine include planar objects up to 300 mm in diameter and/or 3D objects such as plastic lenses and/or printed wiring boards with soldered microelectronic components. In principle there is no physical limit to the scaling up of the DECR reactors and adapting the process to much larger substrate sizes.

Most of the industrial plasma reactors use RF power for plasma excitation. Although efficient for a variety of applications, such systems have a common weakness of having the RF power applied directly to the substrate holder. This reduces the range of the applicable bias values and, more importantly, generates a "hot" plasma where ion energies cover a broad range, depending on the RF bias amplitude. In such configurations monoenergetic processing and fine tuning of ion energy are not feasible.

Microwave power excitation combined with DECR configuration produces a "cold" plasma where ion energies are thermal (several eV). If a bias of several tenth or several hundreds Volts is applied to the substrate, the ions are accelerated to the corresponding energy, but the half-width of the ion energy distribution remains of the order of several eV. Such quasi - monoenergetic ions are extremely useful when material structure is energy dependent and a well defined ion energy is required for a specific application. The DIAMCO machine enables the ion energy to be adjusted accordingly to the process requirements. The general view of the DIAMCO machine is shown in FIG.2.

The DIAMCO machine offers considerable flexibility in both substrate handling and plasma processing. The computer control system is user friendly, precise and comfortable. The presence of the modem enables flexible and efficient maintenance performed at minimum cost. The DIAMCO machine remains stable at low plasma pressures (below 0.5 mTorr). Vertical movement of the substrate holder enables the substrate current to be de-coupled from the substrate bias. Using C_2H_2 as precursor the DIAMCO machine offers a remarkable processing flexibility and high deposition rates (from 100 to 600 A/min).

Under certain conditions (using a sputtering source in an Ar plasma) the machine enables nucleation and growth of nano-structured thin films. The DIAMCO machine represents potential for innovation as it produces a substantial flux of secondary electrons of tuneable energy. When optimised, the secondary electron-based technology might enable efficient biasing of dielectric substrates. The general performance of the DIAMCO machine validates the DECR configuration as appropriate for coating large size substrates.

FIG. 2: General view of the DIAMCO machine

The industrial manufacturing aspects of the machine and of the corresponding technology are as follows:

- The plasma cleaning, seeding and deposition processing steps are integrated within a multi-step "in situ" operation. The corresponding manufacturing flexibility offers the potential for a reduction in equipment and processing costs.
- In certain cases adequate adhesion may be obtained via an “in situ” plasma treatment without an additional adhesion promoting interlayer. This allows for lower processing cost and increased substrate throughput.
- The environmentally friendly cleaning, seeding and deposition processes are independent of thermodynamic effects and operate at ambient temperature, with consequent improvements in the thermal budget requirement and the potential to coat thermally sensitive substrates.
- The deposition process using DECR plasma combined with the floating potential opens new possibilities for industrial manufacturing, where low processing cost and enhanced process reliability are successfully combined.

4.1.2 Low energy, high current electron gun

In accordance with the objectives of the DIAMCO project a low energy, high current electron gun has been developed in an attempt to combine plasma processing with polarisation of thick dielectric substrates by fast electron injection.

The electron beam is extracted from a DECR plasma source operating at a microwave frequency of 2.45 GHz. The electron gun is implemented on a DECR processing reactor equipped with a load-lock chamber. The substrate-holder (150 mm in diameter) can be translated from the load-lock to any position in the reactor chamber.

In presence of the plasma in the processing chamber the electron gun enables an efficient biasing of dielectric substrates via electron flooding when the following conditions are fulfilled:

- Electron current is high enough to compensate the ion current collected on the substrate.
- Electron mean free path is long enough for the electron beam to reach the substrate with an energy equal to the energy of extraction.

The experimental results obtained under these conditions are shown in Fig.3 where the electron current extracted from the auxiliary plasma and the bias voltage induced on an isolated substrate-holder are plotted as a function of the extraction voltage.

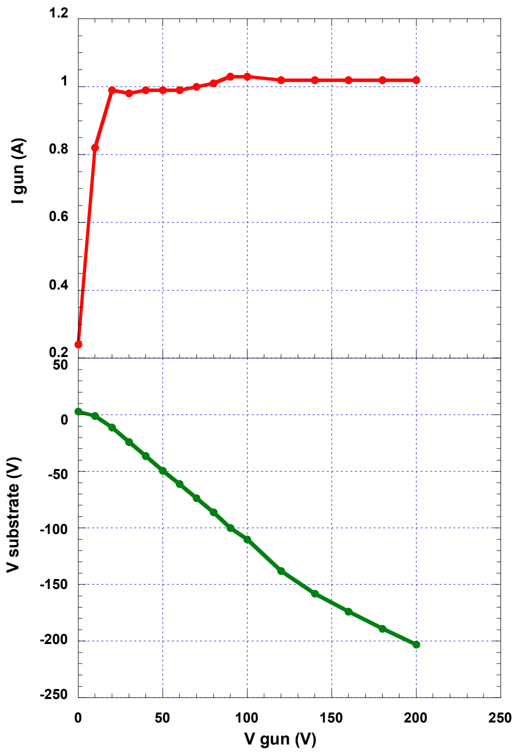

Fig. 3 Electron current extracted from the electron gun (top) and the D.C. bias voltage induced by electron flooding on an isolated substrate-holder (bottom) plotted as a function of the extraction voltage

We observe that once the current saturation is reached the electron current is of the order of 1A and remains nearly independent of the extraction voltage. The new electron gun produces the substrate electron current densities of 1 mA/cm^2 and enables well controlled biasing of dielectric substrates within the range from ~ -10 to -100 V whatever the substrate's thickness or shape. The results obtained validate the new technique of electron shower biasing for plasma coating process designed for dielectric substrates.

4.2 DLC hard coatings: DECR processing route

4.2.1 Experimental approach

Investigation of DLC properties requires a complex, cross-disciplinary approach. The difficulties specific to this material where no long range order exists have generated a significant amount of controversial data in the literature. The structural complexity as well as the significant intrinsic tensile stress have been responsible for the persistence of a gap between the potentially interesting and promising DLC properties and it's currently very limited industrial applications.

In this context the DIAMCO Consortium has been successful in shedding new light on the DLC physical structure and properties, and in promoting novel industrial applications. The progress achieved by the Consortium results from its ability of networking a variety of techniques and bringing together expertise in:

- Spectroscopic ellipsometry
- Infrared spectroscopy
- Raman spectroscopy
- Positron annihilation spectroscopy
- X-ray induced photoelectron spectroscopy (XPS)
- Elastic Energy Loss spectroscopy (EELS)
- High Resolution Transmission Electron Microscopy
- Confocal optical microscopy
- Atomic force microscopy (AFM)
- Nuclear reaction analysis
- Elastic Recoil Detection Analysis (ERDA)
- Rutherford Backscattering Spectroscopy (RBS)

4.2.2 DLC nucleation: deposited energy density, stress fields and microstructure

Understanding DLC growth would not be possible without taking into account the complex processes of energy deposition by energetic ions. An energetic ion interacts with the substrate material and dissipates energy. Energy is dissipated in binary collisions via elastic and inelastic collisions as well as phonons. Atomic bonds are broken, substrate atoms are displaced, and redistribution of the bonds occurs.

If the DLC deposition process occurs in the presence of Ar in the plasma, the energy deposited by argon ions in atomic collision cascades leads to bond breaking and redistribution. If the deposited energy density is high enough, the resulting DLC morphology is dominated by the presence of nano-structures of variable density and shape [10]. The AFM views of the nano-objects grown at a low Ar plasma pressure and at the RF bias of -80 V are shown in Figures 4 and 5. FIG.4 shows that the nano-objects form randomly distributed, basket-like clusters separated from one another by several microns of apparently flat surface. The distribution of the nano-objects (islands) is attributed the strain mediated nucleation processes. The nucleation of an individual island is initiated at a point corresponding to a surface singularity. The growing nucleus creates a stress field where the surface energy is enhanced and the nucleation probability is increased. The new nucleation sites are formed preferably in this area. Each new site creates a new stress field, etc. The zone of enhanced nucleation probability extends radially and eventually results in the formation of a “basket like" network of islands of various sizes, similar in shape. A close-up in Figure 5 shows the morphology of individual nano-objects within the cluster. Interestingly, the planar area clearly seen between the individual nano-objects corresponds to a graphitic carbon layer ~80 Å thick. The nano-structure formation process brings a new light on the impact of energy deposition on hybridisation and interface structure.

The XPS analysis shows that the sp^3 ratio increases as the angle of electron emergence decreases thereby indicating that sp^3 carbon is outermost within the film structure. This result strongly suggests that sp^3 rich hillocks reside in a sp^2 rich "ocean". The fact that the XPS argon signal disappears at 10° emergence angle indicates that integration of argon occurs mainly within the sp^2 bonded regions. We conclude that the surface topography and microstructure of the plasma deposited DLC thins films strongly depend on the deposited energy density and the high dose rate effects which may lead to a stress-mediated nucleation.

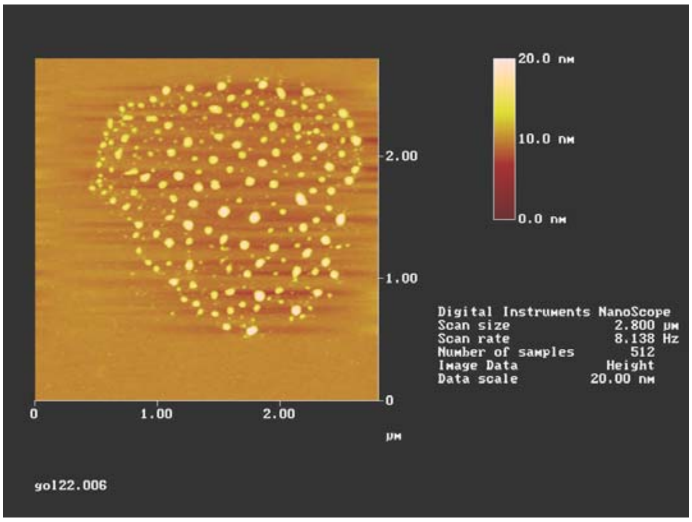

FIG. 4 : AFM image of nanostructured DLC deposited using the RF bias of -80 V.

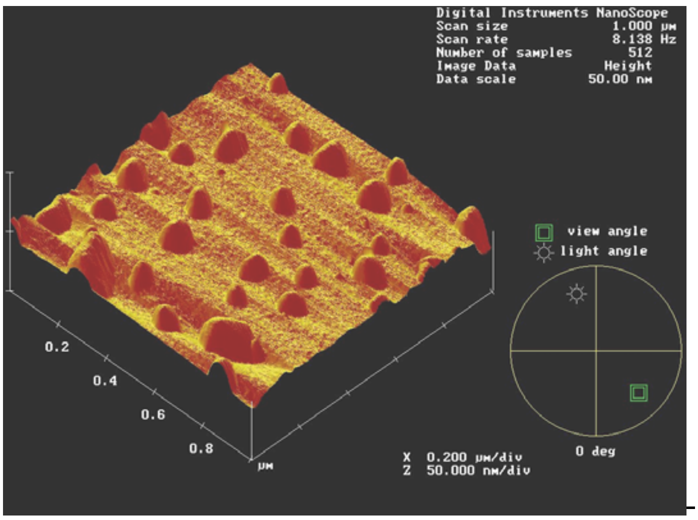

FIG. 5 : AFM angle view of the sample shown in FIG.4
(Vertical scale has been intentionally enhanced)

We conclude that if the energy density is high enough the bond redistribution may lead to nucleation of the sp^3 bonded clusters. The sp^3 bonded clusters generate stress field. Within the range of the stress field the surface energy is increased thus enhancing the nucleation probability. The DLC nucleation and growth processes are controlled by the self-consistent, mutual interaction between the sp^3 hybridisation and stress-fields.

4.2.3 DLC growth: incorporation of hydrogen

DLC may integrate a significant amount of hydrogen which varies between several atomic % up to almost 70 at.% [2, 8]. The hydrogen content may be determined using the resonant (6.385 MeV) nuclear reaction analysis (NRA):

$$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma.$$

The NRA (or ERDA) provide information on a total amount of integrated hydrogen, without distinction between the hydrogen bound to carbon atoms and unbound hydrogen dissolved in the material.

The emerging overall picture of the hydrogen integration process may be described as follows:

- Hydrogen incorporation within DLC films results from the competition between chemisorption, subplantation and ion bombardment enhanced desorption of hydrogen.
- Energy deposited by ion bombardment stimulates the release of hydrogen thus reducing the amount of integrated hydrogen. Hydrogen desorption is controlled by the ion current density and occurs within a period of time of about 0.1s after ion impact.
- Increase in the hydrogen incorporation leads to a decrease in the film density.
- Increase in the deposition rate leads to a decrease in the hydrogen content (see FIG. 6).

During the DLC growth the hydrogen and carbon atoms compete for the access to the available carbon dangling bonds. One would therefore expect the DLC growth rate to be correlated to the hydrogen content. Such correlation indeed emerges from this work. When various results relating to hydrogen integration are assembled within the same plot they show a coherent trend shown in FIG. 6: the smaller the hydrogen integration rate, the higher the DLC growth rate. The trend is observed for a variety of experimental conditions.

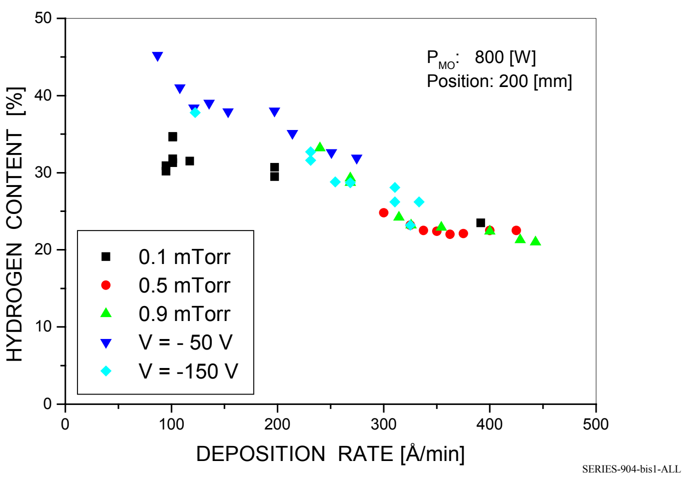

FIG. 6 : Deposition rate as a function of hydrogen content

The conclusion emerging from FIG.6 appears to be intuitively obvious: the release of hydrogen liberates atomic bonds thus enhancing carbon integration rate. The minimum hydrogen concentration of about 20% seen in FIG.6 is characteristic of the acetylene plasma.

4.2.4 DLC growth: incorporation of argon

Using the RBS technique we have measured the amount of argon integrated within the growing DLC film. The results obtained may be fitted (continuous line) by the analytical expression:

$$y = 3.5\,[1-\exp(-0.1\,x)]$$

where "y" represents the argon content (in at.%) and "x" the argon flow (in sccm). Assuming that such fit is physically sound the pre-exponential factor of 3.5 corresponds to the argon solubility limit (in at.%) in DLC. To our knowledge this is the first time the solubility of argon in DLC has been assessed experimentally.

The results obtained in this work provide experimental evidence that the presence of argon within the plasma leads simultaneously to an enhancement in the DLC sputtering yield and in the sp^3 hybridised carbon fraction. It also leads to a significant shrinkage of the DLC optical gap. The reduction of the gap is attributed to the enhancement of the sp^3 hybridised fraction and the resulting intrinsic tensile stress. The effect is also attributed to the enhancement of disorder within the sp^2 hybridised carbon fraction induced by ion bombardment.

4.2.5 DLC growth: substrate bias, hybridisation and density

The Electron Energy Loss Spectroscopy analysis (EELS) was used in order to determine the sp^3-hybridised carbon fraction. The results are shown in FIG. 7 (black squares) together with the data obtained by other authors.

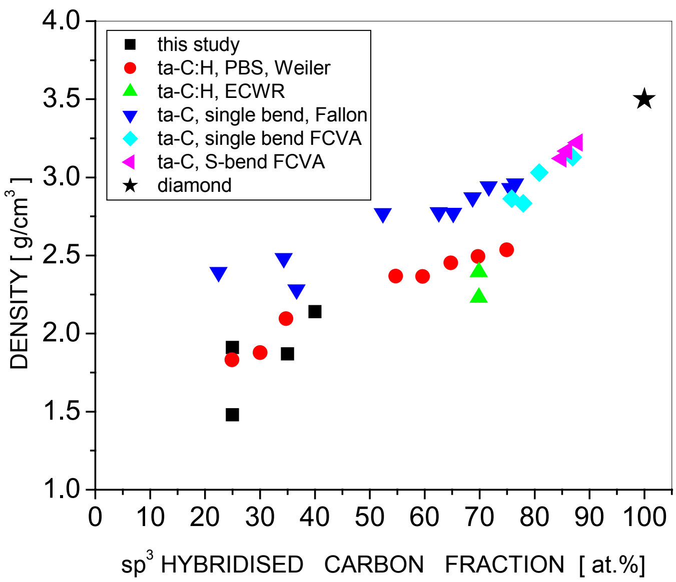

FIG. 7 : Comparison between the DIAMCO data and the data from the literature. The results correspond to a variety of plasma systems. Black squares: this study. Red circles: ref. [3]. Green up triangle: ref. [11]. Dark blue triangles: ref. [12]. Pink triangles: ref.[13]. Blue square: ref. [14]. Black star: diamond.

FIG. 8 represents the relationship between the substrate bias and hybridisation obtained in this work. The behaviour observed is consistent with the literature and provides useful guidance for the process development and optimisation.

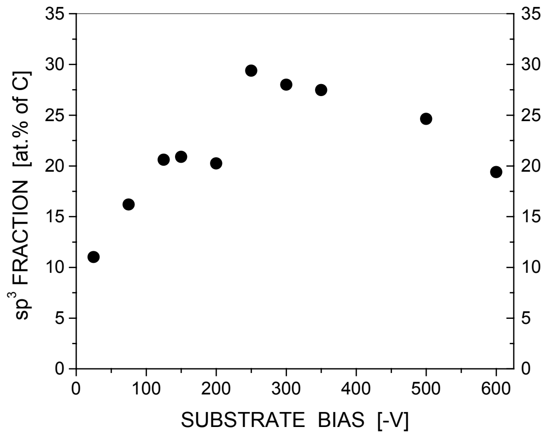

FIG.8 : Impact of the bias on hybridisation for the C_2H_2 plasma

We conclude that the microstructure of the DLC coatings produced in this work contains between 25 and 40 at.% of the sp^3 hybridised carbon forming clusters of variable size and surrounded by the sp^2 hybridised carbon network.

4.3 DLC hard coatings: IPPA-PECVD processing route

An alternative technology developed in this project is based on two processes:

- The radio-frequency PE-CVD using capacitive RF power coupling, and
- The Physical Vapour Deposition (PVD) technique operating under Ion Plating Plasma Assisted (IPPA) conditions (i.e. energetic ion bombardment of substrates during film growth).

The proposed technology enables deposition of the DLC-containing super-hard multi-layer coatings for plastic optical components. The mutli-layer coatings consist of:

- Semi-organic layers deposited directly on the substrate by PE-CVD and acting as matching and pre-hardening layers.
- Metal layers enabling an improved DLC adhesion and increased reflectivity and deposited by IPPA PVD.
- DLC layers grown at the top of the multi-layer stack using PE-CVD.

Metal layers have been deposited using different Physical Vapour Deposition techniques, such as pulsed DC magnetron sputtering and thermal evaporation from crucibles. In all these cases the condensation of the metallic film was carried out under Ion Plating Plasma Assisted (IPPA) conditions. The IPPA approach has shown to appreciably improve the overall mechanical and environmental stability of the coatings.

The semi-organic and metal layers have been deposited in separate reaction chambers in order to prevent contamination of the PVD sources.

The goal of the experimental work was to:

- Develop and optimise the design of the multi-layer structure and of the materials used
- Optimise the processing parameters (such as the bias, pressure, gas flow, etc.).

Two types of multi-layer structures have been fully developed and characterised:

- Type 1: substrate / semi-organic coating / DLC layer
- Type 2: substrate / semi-organic coating / metal layer / DLC layer

Type 1 structure has shown superior scratch resistance and durability with respect to top-quality lacquers available on the market.

Type 2 structure displays beautiful chromatic effects of interferential nature. Mechanical durability of the Type 2 structure is comparable to the good quality lacquers.

4.4 Demonstrators: hard coatings for sunglasses and helmet visors

Multi-layer structures of Type 1 and 2 described in paragraph 4.3 have been applied to solar lenses made of different plastic materials (such as poly-carbonate (PC), allylic resins, poly-amides) and helmet visors made of PC. All the coated demonstrators have been tested in terms of the optical quality, abrasion resistance (falling sand test, Sutherland test with rubber and steel wool) and environmental durability (thermal shock test in boiling and cool water alternately, humidity cycles in climatic room). Helmet visors have been tested also using a so called ‘vice test’ in which the substrate is bent until cracks appear within the coating.

In comparison to the top quality lacquers available on the market the demonstrators coated with the Type 1 multi-layer structure have shown superior mechanical and environmental durability. The high refractive index of the DLC top layer (which is about 2 in the VIS range) increases the reflectivity and produces a mirror effect. The decorative effect of such coatings is neutral.

Demonstrators coated with Type 2 multi-layer structure display attractive interference colours depending upon the thickness of the DLC top layer. The mechanical and environmental durability of such coatings is comparable, but not superior, to the good quality lacquers and standard decorative mirrors. However, the decorative aspect of such coatings is quite impressive. Further improvements in quality might be obtained if the metal and semi-organic layers were deposited sequentially in situ, in the same vacuum cycle.

4.5 Demonstrators: reliability enhancement of electronic assemblies

The requirements of this demonstrator were to employ DLC in combination with standard materials currently used in the industry to reduce the rate of moisture ingress in assemblies destined for harsh environment applications. The driver for this demonstrator was enhanced reliability with regard to both electro migration and corrosion. Electro-migration failure in electronic systems occurs when ionic conduction between biased conductors produces dendritic growth resulting in electrical leakage paths. Corrosion failures are due to dissolved contaminates introduced by moisture ingress. A typical harsh environment producing corrosion risk might be a sea borne application with high levels of salt in the atmosphere. Current techniques to reduce electro-migration work by interposing a physical barrier between conductors but provide poor moisture resistance. Improving moisture resistance would further reduce electro-migration and provide protection against ingress of corrosive materials.

Evaluation techniques developed during the project have provided quantitative data on the degree reduction of moisture transmission by the use of a thin sealing layer DLC. These results indicated a reduction in moisture transmission and this data has been confirmed qualitatively using industry standard Surface Insulation Resistance (SIR) tests. It is hoped to undertake further work to extend the process to low aspect 3D structures and to fully qualify the process to withstand the thermal and mechanical stresses encountered by electronic systems in harsh environment applications.

5. Exploitation and Follow-up Actions

The exploitation of the technology generated from the DIAMCO project potentially involves the technologies developed for the DIAMCO machine, the coating of solar protection lenses and helmet visors and the protection of electronic assemblies from moisture ingress.

DIAMCO Plasma Machine

The DIAMCO machine includes a number of innovative features not previously included in equipment marketed by Roth & Rau. A number of these are now included in new machines currently manufactured by this partner including the computer control system and the provision of remote maintenance facilities both of which were first utilised and successfully operated in the DIAMCO machine.

Other potential innovations resulting from the DIAMCO project include:

- Biasing of dielectric substrates by a flux of tuneable secondary electrons
- Potential to nucleate and grow nano-structured thin films
- Use of multiple in-situ process steps to reduce processing coasts
- Validation the use of DECR configurations for successful coating large area substrates.

These potential innovations may be included in future machines from Roth & Rau depending on market demand.

Coating of Sunglasses and Helmet Visors

The market for sunglasses is very fashion dependant and both the technical enhancement and cosmetic appearance of the coated lenses must be considered in evaluating the potential for market exploitation of the lens coating technology successfully developed during the DIAMCO project.

One process developed with DIAMCO produced improved mechanical properties for the lens while offering only limited cosmetic value. The alternative multi-layer processes developed offered good cosmetic variations but only no significant improvement in mechanical and environmental durability as compared to the good quality lacquers currently used.

Further work is envisaged following the end of the DIAMCO project to investigate in-situ processing which may offer better mechanical properties of the multilayer coatings developed during the project to improve market potential.

Enhanced Moisture Resistance in Electronic Assemblies

The DIAMCO project has successfully demonstrated the potential for improving the moisture resistance. Following the end of the project contacts have been initiated with other interested parties and work is planned to complete process proving and to fully assess the market potential of the technology developed with DIAMCO.

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7. Collaboration sought

The partners within the DIAMCO projects plan to exploit the technologies developed both within their organisations and via the extensive industry contacts at their disposal. One such contact is already active arising from the moisture resistant coating part of the project.