Pure & Appl. Chem., Vol. 68, No. 5, pp. 1047–1053, 1996.
Printed in Great Britain.
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Plasmas and polymers: From laboratory to large scale commercialization

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Abstract: The use of low-pressure plasmas for materials processing, pioneered by the semiconductor industry since the 1960s, is now also a commercial reality in technologies which make extensive use of plastics (automotive, aerospace, packaging, pharmaceutical, and other industries). On hand of examples from our own experience, we show how research on plasma surface modification of polymers and plasma coating of polymers has progressed from the university laboratory, via pilot-scale operations, to full-scale commercial implementation.

1. Introduction

In this paper we describe how low-pressure plasma processes have progressed from the stage of curiosity-driven research in a university laboratory to pilot-scale development which can be transferred to industry, to large-scale industrial implementation.

We begin, in the introduction, with a brief overview how low-pressure plasma processing of materials has evolved during the past thirty years, and of some of the important scientific and technological issues we perceive at this time.

In the remaining portions we discuss two specific areas of industrial use of plasma processing, both unrelated to the semiconductor industry, namely (i) surface modification of polymers, and (ii) large-area plasma-assisted deposition of thin films onto polymeric substrates.

1.1 The Evolution of Low Pressure Plasma Processing

Although plasma science and technology can be traced back to I. Langmuir's pioneering work in the 1920s and 30s, the real "spark" to glow discharge plasma processing of materials came in the late 1960s, with the advent of modern integrated circuit technology. Electronics, in 1995 a $ 1500 billion industry world-wide, has enabled most other products, from automobiles to domestic microwave ovens, to evolve in the way we now know them. The electronics industry, in turn, is fed by the $ 100 billion annual semiconductors market, which now relies very heavily on plasma processing: In a typical semiconductor chip factory today, more than 30 percent of the equipment is plasma-based, plasma reactors which comprise an annual business in excess of $ 2 billion.

Low-pressure plasma processing is replacing traditional (e.g. wet-chemical) methods for several reasons:

(i) anisotropic plasma etching (1,2), unlike isotropic wet-chemical techniques, can define patterns below 0.25 μm, for example those required on 1-gigabit DRAM chips which will be in production before the year 2000;

(ii) plasma techniques ("dry processing") avoid the hazards and pollution associated with wet chemistry, and they are amenable to the ultra-clean, highly reproducible and automatic processing requirements of the semiconductor industry.

Since the mid-1980s we have been witnessing a gradual acceptance of plasma processing in areas other than microelectronics, namely in macroelectronics (photovoltaics, large-area displays, electro-photography) (3-5), information storage technology (6), and, more recently, in a multitude of other sectors such as the automotive, optical, biomedical, packaging, and defense industries. Major advances in vacuum technology, gas handling instrumentation, and other developments linked

with semiconductor fabrication, have helped create the very favourable climate for plasmas which we now experience. This has been aided by an explosive growth in the number of relevant technical publications, and by focused study groups such as Battelle's multiclient program of the late-1980s (7,8), and by the NRC (USA) report on "Plasma Processing of Materials", published in 1991 (9). A particularly attractive aspect of low-pressure plasma processing, one which has helped bring the powerful automotive industry "on-board", is the surface modification of polymers: Unlike plasma etching (1,2) and plasma-assisted deposition of thin films (3-6) (where material is removed from, or added to a surface, respectively), surface modification merely alters the structure and composition of a shallow (a few tens of nm at most) surface layer of polymeric materials, leaving the bulk unaffected. This finally allows us to compile the following complete inventory of low-pressure ("cold") plasma processes:

(A) Plasma etching (dry removal of conducting, semiconducting, and insulating materials).

(B) Deposition of thin films:
  - B1. "Organic" [plasma polymers, amorphous and diamond-like carbon (DLC), crystalline diamond (6,10,11)];
  - B2. "Inorganic" [(metallic, semiconducting and insulating materials (3-5)].

(C) Surface modification, whereby surface-specific properties such as adhesive bonding, wettability, biocompatibility, and the like can be drastically altered (12).

1.2 Plasma Science Issues

In spite of this proliferation of applications mentioned above, there are still many unresolved questions regarding the most efficient use of plasma processing, largely due to the inherent complexity of the plasma state. In order to ensure the high quality and the reproducibility of a given plasma process, numerous parameters must be controlled with care, such as the pressure and flow rate of the reagent gas or gas mixture, the discharge power density, the surface temperature and electrical potential of the workpiece, etc. Currently, the effects of excitation frequency, f, and of plasma-surface interactions are still only partially understood, and these are the objects of much ongoing research. For example, it has been shown (13) that the efficiency of producing electron-ion pairs is greater at microwave (MW, $f \geq 300$ MHz) frequencies than at lower excitation frequencies, for a given power density absorbed in the plasma. Indeed, the yields of other types of chemically reactive particles such as free radicals, which at 20 % or more of all species are the majority constituent, are also found to be higher in MW plasmas. As recently reviewed by Moisan *et al.* (13), this is attributed to a significantly higher fraction of energetic electrons in the tail of the EEDF and to a higher value of the electron density, n, than for lower-frequency plasmas. It is therefore not surprising that among recent generations of commercial plasma reactors, an increasing number of these systems operate at the 2.45 GHz MW frequency.

Rather than use either MW or RF (radiofrequency) power to sustain the plasma, one can combine the two power sources to generate a so-called "mixed" (or dual-) frequency plasma (14): While MW excitation generates a high concentration of active species in the gas phase, as noted above, the role of RF power is to create a negative DC self-bias voltage, V_B, on the powered, electrically isolated substrate-holder. This causes ions to be accelerated by the potential drop $(V_P - V_B)$ across the RF-induced plasma sheath, or "dark space", to their maximum kinetic energy:

$$E_{i,max} = e|V_P - V_B|, \quad (1)$$

where V_P, the plasma potential, is generally a few tens of volts positive with respect to ground. In practical situations, at often-used gas pressures of ~ 100 mTorr, the ions lose part of their energy through inelastic collisions. The average energy is then typically

$$\overline{E}_i \approx 0.4E_{i,max}. \quad (2)$$

In other words, in dual-frequency (MW-RF) processing, independent control of the RF power allows one to vary the energy of the ions bombarding the substrate surface, with values ranging from a few eV to several hundreds of eV, and with fluxes of up to ~ 10^{16} ions/cm^2-s (14), conditions comparable to the operating parameters of low-energy ion beam systems. Ion bombardment of material surfaces can lead to sputtering, breakage of chemical bonds, surface diffusion and other

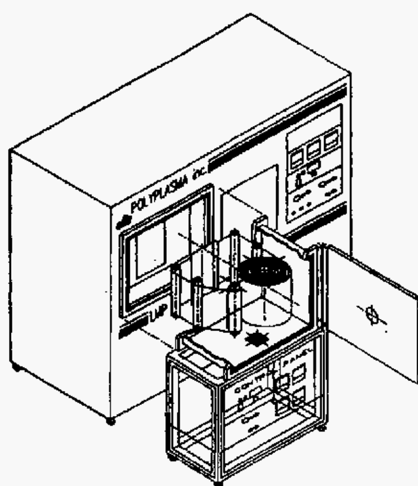
forms of energy dissipation; these can be highly beneficial, especially in the context of plasma-assisted deposition of thin films : Ion bombardment contributes to film densification and to improved adhesion, allowing one to deposit low-porosity films at lower substrate temperatures, T_s (15,16). Such observations are in accord with the transition from a porous to a densely-packed microstructure in the so-called "structure zone models" (17,18), and they have the technologically important consequence that high-quality thin films can now be deposited onto polymers with low softening temperatures like polyolefins, polyester, and the likes.

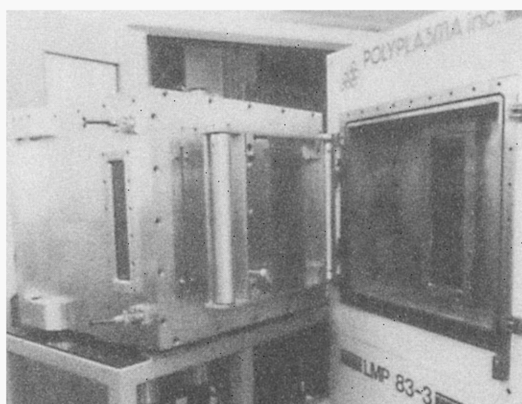
2. Pilot- and Industrial Scale Plasma Processes

2.1 Considerations for Plasma Reactor Design

Contrary to semiconductor fabrication, where plasma reactor chambers accommodate either single wafers or, at most, batches of up to two dozen wafers at a time, the situation is very different in the rapidly-growing industrial use of plasmas for the treatment of polymers. Here, one may be dealing with large or small three-dimensional objects (for example plastic containers, or automotive parts), with flexible webs such as polymer films or textiles, with fibres or yarns, or with fine powder particles. In all these cases a principal criterion for an economically viable process will likely be the highest possible material throughput which is compatible with the product specifications. Most academic research projects tend to focus on demonstrating the feasibility of a given plasma process and, hopefully, to provide some understanding of its mechanisms. In such situations small, batch-type plasma reactors are quite satisfactory and not infrequently, converted semiconductor process reactors serve this purpose well. Our laboratory at École Polytechnique has been no exception, for we have used a batch reactor with a static 200 cm^2 substrate area (15) to develop numerous MW or dual- (MW/RF) frequency processes, particularly for plasma-enhanced chemical vapor deposition (PECVD) of silicon-compound or diamond-like carbon (DLC) films (14-16), but also for etching and surface modification of polymers (19).

With the growing awareness of plasma processing in industry, the questions of possible scaleup and process economics have arisen with increasing frequency in university laboratories, including our own. For example, in regard to the plasma treatment or coating of moving flexible webs, it is impossible to answer a wide range of important questions when one uses the static, batch-type reactors mentioned above. This has incited us to design and build a pilot-scale MW/RF reactor system for plasma processing continuously moving flexible web materials up to 30 cm in width. Figures 1(a) and (b), respectively, show a schematic view and a photograph of this system: It comprises two parts, namely the "LMP 83-3" plasma reactor (20), to which we have added a web-





(a) (b)

Fig.1 Pilot-scale dual-frequency (MW/RF) PECVD roll coater for 30 cm wide webs. (a) cut-away drawing; (b) view of plasma chamber and of web-handling chamber.

handling chamber (left side of photograph). This chamber mates with the MW plasma chamber (right-hand side of photograph) via a flange plate with a vacuum seal, and it contains the synchronous motor-driven feed and uptake rolls, which permit the web substrate to be transported through the plasma zone at constant, adjustable speed, while in contact with the water-cooled RF bias electrode. The speed, of course, determines the residence time in the plasma zone; in a PECVD process this, in turn, determines the coating thickness (see section 2.2).

A second pilot-scale coating system in our laboratory, this one for coating rigid cylindrical objects, for example long tubular specimens, is illustrated in Fig. 2. The plasma is generated using a proprietary cylindrical microwave applicator, in a section of thick-walled silica glass tubing below the central cubic chamber of the vertical vacuum vessel. During a typical coating run, the cylindrical specimen is initially located in the lower tubular stainless steel section, and is then raised at constant speed through the plasma zone into the upper cylindrical section. The specimen is suspended by a Nylon chord, which is wound onto a motor-driven shaft at the top of the reactor assembly; the motor speed controls the residence time in the plasma zone which, in turn, determines the thickness of the PECVD deposit. This thickness can be measured in-situ by means of an optical thickness monitor, located in the cubic chamber (30 cm on the side, machined from a single block of aluminium), to which are also connected the pumping system, the pressure gauge, and the reagent gas inlet system. Coating of longer tubular substrates (several meters) of various diameters is also possible if this plasma system is simply equipped with tubular end sections of appropriate lengths, and with vacuum pumps capable of evacuating the larger overall volume.

2.2 PECVD on Polymeric Substrates

As already mentioned, the pilot-scale reactor systems shown in Figs. 1 and 2 are primarily intended for PECVD process development, in particular for the deposition of thin SiO_2 coatings onto polymeric substrates. In the case of flexible substrates (Fig. 1), we are currently working in two process areas:

(i) Protective coatings on Kapton® polyimide, used as a thermal blanket material in space technology; here, a ~ 300 nm SiO_2 coating acts as a protective layer against erosion by atomic oxygen in low Earth orbit (LEO) (21,22). The reactor in Fig. 2 serves this same purpose, to coat carbon fibre-epoxy composite tubes used as structural components on spacecraft.

(ii) Even thinner (a few tens of nm) SiO_2 layers are excellent barriers against the permeation of O_2, H_2O, CO_2, and aromas through flexible or rigid packaging materials (23,24).

In both of these processes the SiO_2 layer results from the plasma-chemical reaction of a volatile organosilicon compound (HMDSO), an oxidizer (N_2O or O_2), and an inert gas (Ar or He), in proportions (1:3:1).

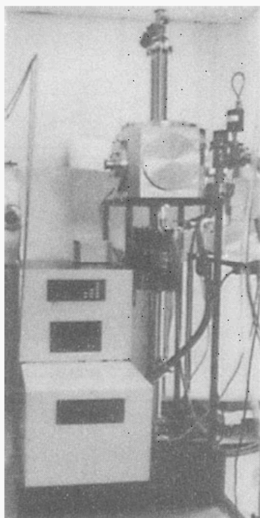


Fig.2 PECVD reactor for coating cylindrical objects, for example composite tubes.

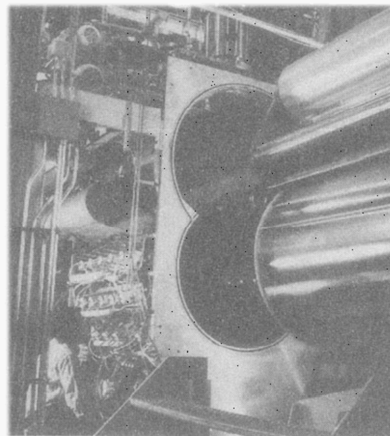


Fig.3 Industrial dual-frequency PECVD roll coater for 100 cm wide webs.

Application area (ii) above has enormous market potential, since low-cost SiO_2-coated polymers such as 0.5 mil (12 μm) polyester (PET) or polypropylene films can replace expensive and non-recyclable laminates based on PVDC or EVOH. Figure 3 shows PMI's industrial-scale, dual-frequency (RF/audio, 13.56 MHz/40 kHz) PECVD roll coater, which achieves deposition rates of about 10 nm/s to coat 100 cm wide, 12 μm PET packaging film with ~ 30 nm of SiO_2. This results in an overall oxygen permeation rate of ~ 0.6 scc/m^2/day, comparable to or better than aluminized films. The web unrolls over the lower, electrically isolated drum, to which tens of kW of 40 kHz power are applied. Oxygen is dissociated by several rows of RF plasma generators (helical resonators) surrounding the drum, and it reacts with volatile organosilicon (HMDSO) to form the dense SiO_2 coating on the PET film around the drum perimeter, assisted by ion bombardment. It should be noted that this machine can readily be converted to MW/AF or MW/RF operation (25).

A second commercial plasma coating process, this one for small, discrete parts, is illustrated in Fig. 4. The RF plasma reactor seen here comprises a large rotating and rocking Pyrex-glass vacuum chamber, into which the RF power is coupled with a coil (shown) or a clamshell electrode arrangement. In this process, batches of several thousand rubber parts for the pharmaceutical industry (rubber stoppers, closures, septums, o-rings, syringe plunger tips, ...) are loaded into the chamber and uniformly coated with a thin, lubricious layer of hydrocarbon, resulting from the plasma-chemical reaction of a propylene-helium gas mixture. Uniformity of coating is assured by the tumbling and rocking motion of the reactor while the batch is being treated. The market rationale for this process is to eliminate the need for the currently-used silicone slip agents, now considered to be a health risk.

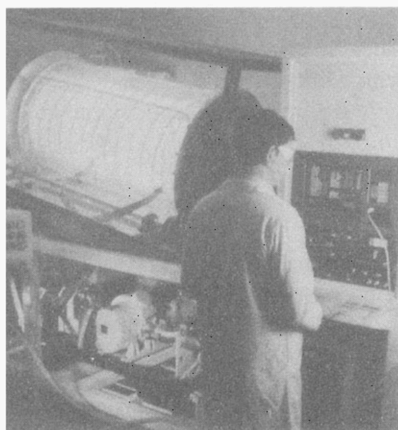


Fig.4 PECVD batch reactor with tumbling and rocking motion, for coating many small parts.

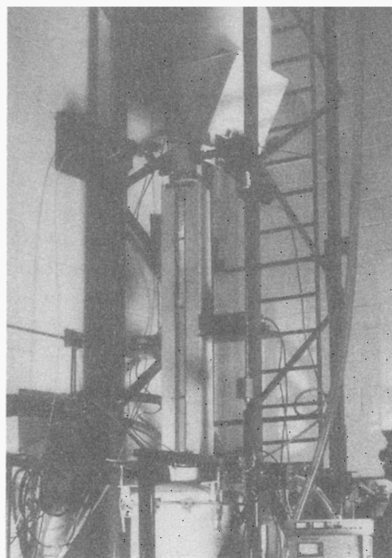


Fig.5 Tubular plasma reactor for continuous treatment of polymer powder particles.

2.3 Surface Modification of Polymers

In a recenty-published critical review (26), we have surveyed the current status of plasma surface modification of polymers for improved adhesion. This area of low-pressure plasma processing has come to prominence via numerous industrial applications, for example paint adhesion to plastic automobile parts (e.g. bumpers and dash assemblies), and improved bonding in polymer matrix composites.

Interaction mechanisms between a plasma and a polymer surface are very complex, for they include physical bombardment by energetic particles and by ultraviolet photons, and chemical reactions at and below the surface. Four main effects result from this, namely surface cleaning (removal of adsorbed contaminants and water vapor), ablation, crosslinking, and surface chemical modification (for example, grafting of new chemical functionalities). These occur together in a

complex synergy, which depends on many parameters. Nevertheless, it is possible to control the main set of parameters governing a given process, and thereby to assure reliable reproducibility of the process outcome, so important for industrial implementation.

An excellent example of property improvement of polymer matrix composites is that of thermoplastic or thermoset matrices containing plasma-treated polymeric powder particles as filler. Plasma can be used to oxygenate or nitrogenate the surface of polymer particles to increase their wettability, dispersability, loading and adhesion in liquids or polymer matrices, thereby improving product (part or coating) properties and lowering materials costs.

Figure 5 shows a vertical tubular plasma reactor (27) in which the powder particles are gravity-fed in a continuous stream through the RF plasma zone from a hopper at the top to a collecting bin at the bottom. This process, in which about 50 kg/hr of the 60 μm average diameter particles are plasma-modified, has the objective to incorporate a few atomic % of chemically-bonded oxygen into their surface. This chemical modification has dramatic beneficial effects on all the important properties of finished parts containing up to about 30 weight % of the plasma-treated filler: vastly improved abrasion resistance and reduced friction coefficient, enhanced tear strength and modulus, and reduced weight of finished parts, all these on account of the superb bond strength at the filler/matrix interface. The plasma reactor depicted in Fig. 5 uses 180 cm long clamshell-type electrodes, and up to 1 kW of RF (13.56 MHz) power, but a modified version for 2.45 GHz MW excitation is currently being tested for increased powder throughput. Other examples of particulates which can be functionalized by plasma treatment are talc, clay silicate, carbon black, and ground tire particles for use as fillers, treated pigments for paints and coatings, treated micronized waxes for inks, lubricants and coatings.

3. Conclusions

We have presented here a brief summary of research and development in low-pressure plasma processing of polymeric materials, both coating and surface modification processes. For lack of space, we could describe only results from our own experience in the university and industrial environments; many other laboratories are performing excellent work in this area, and numerous other processes have reached commercial maturity. We perceive a very great potential for growth of this particular plasma process sector in coming years.

Acknowledgments

The authors gratefully acknowledge many valuable contributions to this work by our collaborators, too numerous to be listed here. This work has been supported in part by research grants from NSERC and FCAR.

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