
METALLIZED PLASTICS 5&6: FUNDAMENTAL AND APPLIED ASPECTS

Editor: K.L. Mittal



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Preface

This volume chronicles the proceedings of the 5th and 6th symposia on **Metallized Plastics: Fundamental and Applied Aspects**, held under the aegis of the Dielectric Science and Technology division of the Electrochemical Society in Los Angeles (May 5-19, 1996) and Paris (August 31-September 5, 1997) respectively. These events reflected a continuation of the series of symposia initiated in 1988 to update on a regular basis the R&D activity in the arena of metallized plastics which over the years has evinced tremendous interest from both fundamental and applied points of view. The previous symposia in this series were held as follows: the premier one in Chicago, October 10-12, 1988, the second in Montreal, Canada, May 7-10, 1990, the third in Phoenix, Arizona, October 13-18, 1991, and the fourth in Honolulu, Hawaii, May 17-21, 1993. The proceedings of these symposia have been well documented.

Both these symposia elicited an excellent response which is a testimonial to the brisk activity and interest apropos of metallized plastics. The technical programs clearly reflected an interest and need to ameliorate the existing methods and to devise new and more efficient ways to metallize plastics. Also, novel techniques to characterize metal-polymer interfaces or to monitor properties of metallized plastics were discussed. The programs for both symposia comprised both invited and contributed papers which were both overviews and original research in nature.

This volume contains a total of 29 papers (15 from the Los Angeles Symposium and 14 from the Paris Symposium) addressing many aspects and new developments in the field of metallized plastics. Of course, many more than 29 papers were presented at these symposia; but the remaining papers are not included in this volume for a variety of reasons. It should be recorded that all manuscripts were properly reviewed and suitably revised before inclusion in this volume. Also it should be underscored that the authors of the Los Angeles Symposium were asked to update the information. So the information presented in this book should be fresh and up-to-date.

This volume is divided into three parts: Part 1 "Metallization Techniques and Properties of Metal Deposits"; Part 2 "Spectroscopic Investigation of Interfacial Interactions"; and Part 3 "Surface Modification and Adhesion Aspects". The topics covered include: various metallization techniques for a variety of plastic substrates and simplification of electroless method by using plasma or UV laser

pretreatment; various properties of metal deposits; investigation of metal-polymer interfaces using a variety of spectroscopic techniques; interaction of metals with self-assembled monolayers; study of early stages of metal-polymer interface formation; surface modification of plastics by a host of techniques including plasma, excimer laser, ion beams and characterization of modified plastics surfaces; surface modification of polymers used in the low Earth Orbit space environment; adhesion aspects of metallized plastics including a quantitative adhesion test for metal coated polymer fibers and nondestructive techniques for monitoring metallized plastics adhesion.

This and the preceding volumes (1-4) offer a fountain of information and represent current commentary on the R&D activity taking place in the technologically highly important field of metallized plastics. Yours truly sincerely hopes that anyone interested in the fundamental or applied aspect of metallized plastics will find this and earlier volumes a valuable source of current information and a fountainhead of new ideas.

Acknowledgements

This is the most enjoyable part of writing a Preface, as this gives an opportunity to thank those who helped in many different ways. First, it is my sincere pleasure to mention that the Los Angeles Symposium was jointly organized by Dr. Robert Opila (Bell Labs., Lucent Technologies) and myself; and the Paris Symposium was the culmination of the efforts of Dr. F. Arefi-Khonsari and Dr. J. Amouroux (Université Paris VI) and yours truly, and my thanks are extended to these three individuals. Thanks are also due to the appropriate officials of the Dielectric Science and Technology Division of the Electrochemical Society for sponsoring these events. My sincere thanks go to the reviewers for their time and efforts in offering many valuable comments which definitely improved the quality of this publication. My appreciation goes to my wife, Usha, for making corrections in certain manuscripts. Of course, the most important individuals responsible for a book are the authors and I deeply appreciate their co-operation, interest and contributions in this endeavour.

K.L. Mittal

References:

1. K.L. Mittal and J.R. Susko (eds), *Metallized Plastics 1: Fundamental and Applied Aspects*, Plenum Press, New York (1989).
2. K.L. Mittal (ed.), *Metallized Plastics 2: Fundamental and Applied Aspects*, Plenum Press, New York (1991).
3. K.L. Mittal (ed.), *Metallized Plastics 3: Fundamental and Applied Aspects*, Plenum Press, New York (1992).
4. K.L. Mittal (ed.), *Metallized Plastics: Fundamentals and Applications*, Marcel Dekker, New York (1998).

Part 1

**METALLIZATION TECHNIQUES AND
PROPERTIES OF METAL DEPOSITS**



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ELECTROLESS METALLIZATION OF POLYMERS: SIMPLIFICATION OF THE PROCESS BY USING PLASMA OR UV-LASER PRETREATMENT

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A new method for promoting chemical adhesion of electroless metals to polymer substrates is described. Firstly, the process consists of grafting nitrogenated functional moieties onto polymer surfaces using cold-plasma or UV-laser techniques allowing sample treatment in nitrogen-containing atmospheres (N_2 or NH_3). Then, this step is followed by a surface activation process during which chemisorption of palladium (catalyst for the subsequent plating reaction) is accomplished using only a dilute acidic $PdCl_2$ solution. This method, which is based on the strong chemical affinity of palladium towards nitrogen, avoids the use of unfriendly chemicals. X-ray photoelectron spectroscopy was employed to investigate ex-situ chemical changes on the polymer surfaces (poly(styrene) and poly(tetrafluoroethylene) samples in the present work) during processing. Adhesion performance of the metal-polymer interfaces was studied by subjecting the metallized specimens to a fragmentation test.

INTRODUCTION

Metallized plastics are used today in a large variety of technological applications. This explains why metallization of polymers has attracted considerable attention and research over the last few years¹⁻⁵. Obviously, understanding and improving metal/polymer adhesion is one of the primary concerns for obtaining stability and long term reliability of the relevant manufactured products.

First, distinction should be made between the methods commonly used to metallize plastics. One of these involves metal atom deposition (e.g. via thermal evaporation or sputtering process) on the surfaces of polymers under high or medium vacuum. Different metals such as Al, Mg, Ti, Cr, Cu, Ni, Ag, Au ... have been so deposited on various polymer substrates (poly(ethylene) (PE), poly(propylene) (PP), poly(styrene) (PS), poly(ethylene terephthalate) (PET),

polyimide (PI) when not specified or Kapton[®] when specified, poly(ether imide) (Ultram[®]), poly(ether ether ketone) (PEEK), poly(ethylene oxide) (PEO), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA) ...), and much detailed chemical information (particularly in the case of metal films deposited in ultra-high vacuum) about initial growth mechanisms, interfacial reactions and influence of substrate pretreatments has been obtained using, among others, in-situ x-ray photoelectron spectroscopy (XPS). In addition to the use of the conventional physical vapor deposition (PVD) techniques mentioned above, metallization of polymer substrates can also be carried out by electroless deposition. This wet phase process involves mainly Ni or Cu deposits on catalytically active surfaces. A crucial aspect of this technology is not the method of metallization itself, but the way in which the surfaces of polymer materials can be rendered catalytically active via suitable surface pretreatments. Obviously, the problem of adhesion between the electrolessly deposited metal and the polymer surface is also strongly dependent on the type of polymer involved as well as on the nature of the process which is used to render the polymer surface catalytically active for the electroless plating (see section "State-of-the-Art"). In this context, characterization by XPS of the electrolessly deposited metal/polymer interfaces and, therefore, understanding of adhesion mechanisms appear much more complicated than in the case of evaporated or sputtered metal/polymer interface given that a wet deposition process is not compatible with direct (i.e. in-situ) UHV investigations.

As already noted, and whatever may be the application sought, electroless processes require extensive pretreatments of polymer surfaces before deposition can be carried out. The objective of the present work is to describe the potential of a new process for activating polymer surfaces and obtaining strong metal-polymer adhesion. This process involves a specific plasma or UV laser-induced chemical modification of the polymer surfaces and a subsequent palladium chemisorption. The studies carried out in the present work were mainly conducted on poly(styrene) (PS) and poly(tetrafluoroethylene) (PTFE) substrates whose surfaces were investigated by XPS after each stage of treatment. PS and PTFE were selected for the present investigation because of the absence of oxygen in their chemical structure (see reason for this in section "Results and Discussion"). Besides, PTFE was chosen because this prototype of the family of fluorinated polymers is well known for its high chemical inertness and thermal stability which leads to the fact that adhesion of any material to it requires very drastic surface pretreatments. In addition, some data concerning poly(carbonate) (PC) samples were also obtained by using time-of-flight secondary ion mass spectrometry (TOF-SIMS) in an attempt to confirm some XPS results. The data obtained as a whole have led us to develop a simplified method for palladium chemisorption and electroless metallization and to better understand adhesion mechanisms at the corresponding metal-polymer interface.

STATE-OF-THE-ART

Electroless deposition is an autocatalytic process which consists of a redox reaction in aqueous solution between the ions of the metal to be deposited and a strong reducer. However, in the case of insulating samples, such a final operation has to be preceded by an activation step leading to the formation of catalytic sites (e.g. via Pd²⁺ chemisorption) on the surface to be metallized.

Figure 1 (route (a)) describes the conventional chemical way which, historically speaking, was the first to be followed for metallizing polymer materials. This route starts generally by using a chromic or sulfochromic etching to oxidize the surface and increase its roughness. Subsequently, a two-step process is performed via a surface treatment, successively in an acidic SnCl_2 solution (sensitization step), then in an acidic PdCl_2 solution (activation step).

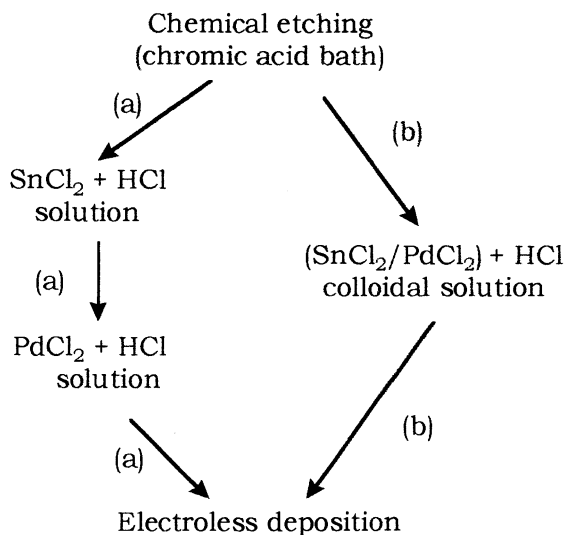
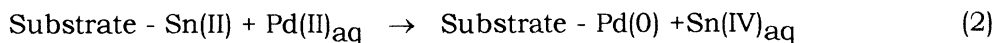
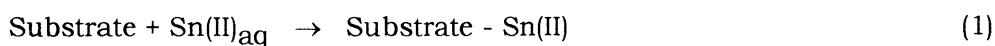
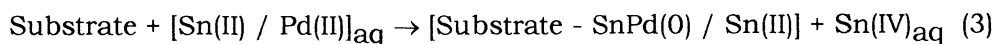


Figure 1. Schematic diagram of electroless plating processes using chemical etching pretreatment and a two-step (route a) or a one-step (route b) operation leading to surface activation (Pd chemisorption).

This two-step process is represented by some authors⁶⁻⁹ as follows:



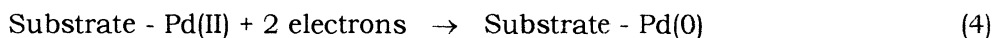
A simplification of this two-step operation was further developed by using a one-step process (Fig. 1, route (b)) which involves substrate treatment in an acidic colloidal $\text{SnCl}_2/\text{PdCl}_2$ solution which directly leads to surface activation¹⁰⁻¹³. The resulting reaction in this one-step process can be represented as follows:



In this latter case, the so-pretreated substrates were also submitted to an acceleration step by immersion in an HCl solution. In light of this one-step operation, it is often proposed^{10,11} that Sn(II) ions be used to reduce Pd(II) ions to form colloidal particles which consist of a Sn / Pd alloy core surrounded by a protective layer of Sn(II) ions. The acceleration step is then carried out to remove this protective layer which makes the colloidal particles available to catalyze the subsequent electroless process. Despite the great complexity of the operating mode of mixed $\text{SnCl}_2/\text{PdCl}_2$ solutions and the difficulties associated with their

ageing in terms of metallization efficiency, this simplified approach for obtaining surface activation is commonly used and many applications in various areas are still currently being developed¹².

Whatever the selected process (one or two-step routes) may be, reactions (2) and (3) lead us to think that palladium is chemisorbed as Pd(0) which is required to catalyse the further electroless deposition. However, other authors¹³⁻¹⁵ do not agree with this interpretation and consider that the ultimate reduction to Pd(0) becomes efficient only after a certain initiation time in the plating bath which contains a strong reducer. This initiation time which is reported to vary over a large range (some seconds to some hundreds of seconds) is mentioned by most authors. Previous works carried out in our laboratory clearly support the fact that Pd²⁺ reduction to the atomic state is a necessary step and that the reaction initiates in the solution, level with the interfacial zone between the solution and the activated substrate¹⁶. Under these conditions, the corresponding reducing step can be represented by the reaction:



In the particular case of nickel coatings, electrons necessary for the reduction are generally provided by different reducing agents such as sodium hypophosphite (NaH₂PO₂·H₂O), sodium boron hydride (NaBH₄), hydrazine (N₂H₄), or dimethylamine borane¹⁷. Electroless deposits obtained in these conditions correspond to "Ni-P", "Ni-B" alloys and "pure" Ni, respectively. In the same way, electroless copper deposition can be carried out from ionic solutions containing formaldehyde, hypophosphite, borohydride, hydrazine, dimethylamine borane ... as reducing agents¹⁸.

Whatever the selected route (a) or (b), the initial stage generally consists, as already said, of an etching of the polymer surface with a strong oxidant such as chromic acid or sulfochromic acid. For example, our previous works¹⁹ involving various polymer materials were performed by immersing the corresponding samples in a sulfochromic bath (K₂Cr₂O₇: 79 g dm⁻³; H₂SO₄: 868 ml dm⁻³) at 75°C for 1 min. Nevertheless, it should be noted that some researchers particularly concerned with environmental problems over chromium have attempted to restrict the use of chromic-containing processes. So, Karas et al.²⁰ described an adhesion promotion process for poly(ether imide) (Utem®) involving a chromium-free mild etch (treatment with potassium hydroxide after a sulfuric acid step) followed by application of a chemical adhesion promoter (via immersion into an aqueous thiourea solution). In this example, authors used a proprietary tin/palladium catalyst system and an electroless copper film was deposited.

In addition to the conventional (a) and (b) routes represented in figure 1, other processes have also been investigated and/or proposed as candidates for obtaining catalytically active polymer surfaces. For example, Viehbeck et al.²¹ describe a seeding process for activating the surface of polyimide (Kapton®) and other electroactive polymers. This process consists of reducing electrochemically the outer region of such materials when these materials are brought into contact with an electrolyte solution containing a strong organic reducing agent. In this way, the electroactive surface is used to provoke electron transfer to metal ions in solution causing metals (e.g. Pd, Pt ...) to be deposited at the surface. The deposition of such metals renders the polymer surface active towards further metal deposition from conventional electroless plating baths. In addition, Baum

et al.^{22,23} describe a selective process based on the photoreduction of potassium iron (III) oxalate in the presence of palladium (II) chloride which results in the formation of an active palladium catalyst. This process is reported to operate well on a variety of dielectric materials including polyimide (PI) films when the iron-palladium treated dielectric films are irradiated with a 500 W Hg-Xe deep UV lamp.

Another example recently reported by Rye et al.²⁴⁻²⁶ pertains to the adhesion of electrolessly deposited copper on patterned PTFE. This technology was achieved via an area-selective irradiation (electrons or x-rays) of the PTFE surface to produce crosslinking and a subsequent selective etching of the non-irradiated areas with a sodium naphthalenide solution. Cu deposition takes place in etched areas by using a $\text{SnCl}_2/\text{PdCl}_2$ one-step process followed by a Cu (II) / formaldehyde plating bath.

Several other techniques have also been reported for improving surface wettability and bondability of metal films electrolessly-deposited on polymer substrates. This was particularly stimulated in the field of microelectronics whose evolution over the last few years has encouraged new specific approaches and the replacement of purely chemical surface pretreatments. Laser-stimulated chemistry has thus become an important tool for surface chemistry and thin film processing. So, a palladium deposition process was carried out for the first time in 1989²⁷ via a localized decomposition of a Pd-acetylacetonate spin-on film deposited from a chloroform solution on polyimide (PI). In this experiment, a continuous wave (CW) argon ion laser (351 nm) was used. The decomposition of the thin solid organometallic precursor film can be considered here as a photothermal process. Further, other experiments again with a CW argon laser (515, 488 or 458 nm)²⁸ and with UV-excimer lasers (ArF^* at 193 nm, KrF^* at 248 nm, XeCl^* at 308 nm, XeF^* at 351 nm)^{29,30} were conducted on various polymer substrates (PI, PTFE, poly(phenylquinoxaline) (PPQ) ...) using as precursors mainly Pd-acetylacetonate ($\text{Pd}(\text{C}_5\text{O}_2\text{H}_7)_2$) and Pd-acetate ($\text{Pd}(\text{CH}_3\text{COO})_2$). Depending on the laser wavelength and laser fluence, the corresponding photodecomposition processes are shown to be photothermal, photolytic or both. Clearly, this technique which combines a photo-induced process with electroless plating offers great potential for producing Pd prenucleation patterns (via the use of a screen-mask to define the laser irradiation area or via a direct writing of microscale features by scanning of the laser beam focused on the specimen surface) and fast deposition, in particular, of copper lines (high activity of Pd prenucleation sites in commercial Cu plating solutions).

Prenucleation of polymer surfaces with Pd from thin metal (Pd)-organic films has also been carried out using newly developed incoherent excimer UV and vacuum UV (VUV) sources³¹⁻⁴⁰. Operation of such devices is based on excimer formation from a dielectric barrier discharge (silent discharge) in an atmosphere of a rare-gas or a rare-gas/halogen-gas mixture. Typically, emitted radiations (e.g. Ar_2^* at 126 nm, Kr_2^* at 146 nm, Xe_2^* at 172 nm, ArF^* at 193 nm, KrCl^* at 222 nm, etc.) provide an alternative to the use of excimer lasers as excimer sources allow to extend the photon emission, in particular, towards the deep UV range. In addition, it is clearly shown that decomposition processes (e.g. of organometallic precursors) are only of a photolytic nature which allows low temperature processing on thermally unstable substrates. It is also worthwhile pointing out that excimer sources can be very useful in large area processing. Under these conditions, VUV light-induced decomposition of spin-on Pd-acetate films on various substrates (polyamide (PA), PMMA, PET ...) was accomplished

through metal contact masks and patterned Pd films were obtained. The latter were subsequently reinforced by electroless copper and nickel plating processes⁴¹⁻⁴³.

As mentioned before, processes using appropriate lasers or incoherent excimer sources can lead to the direct deposition of metals (e.g. Pd) from thin solid metal-organic films. An alternative activation procedure could be the direct UV or VUV light-induced metal deposition from the gas phase. As an example, surface films obtained by adsorption from a suitable gas phase precursor (such as Cu-acetylacetonate) can be photodecomposed with the aid of excimer lasers^{44,45}. However, this laser-induced CVD (LCVD) technique is reported to have several drawbacks (e.g., complicated CVD equipment, limited growth rates) and in light of this, the route involving decomposition of thin solid metal-organic films remains largely preferable for activating a polymer surface for subsequent electroless plating³⁹.

Also, an interesting work carried out in gas phase by excimer laser processing deserves to be highlighted. This work due to Niino and Yabe⁴⁶ concerns fluoropolymers (PTFE and fluorinated ethylene propylene copolymer (FEP)) and deals with their surface chemical modification in hydrazine gas (N_2H_4) photolyzed with ArF* (193 nm) excimer laser irradiation. On the basis of hydrophilic behaviour of the so-treated surfaces, selective-area electroless plating of nickel metal was performed by using the conventional two-step process (see Fig. 1, route (a)). Although the mechanism of metal deposition was not explained, the authors suggested that the hydrophilic behaviour of chemically modified surfaces was due to the presence of amino groups. As will be shown further (see section "Results and Discussion") this fact is of prime importance. Indeed, the present work will highlight the specific affinity of palladium (the activator of the metallization reaction) towards nitrogenated species grafted on polymer surfaces.

In light of the key role played by UV and VUV irradiation in the processing techniques described above, one is surprised at the fact that plasma methods have not been more developed for pretreating polymer surfaces for further electroless metallization. As far as we know, besides the work carried out in our laboratory^{16, 19,47,48}, only a few investigations dealing with this field can be found in the literature. As an example, Ehrbar and Ganguillet⁴⁹ report a method for preparation of plastic materials (PE, acrylonitrile-butadiene-styrene copolymer (ABS), etc.) involving successively glow discharge (corona) pretreatment, immersion of the sample into a reducing solution, then into the Sn(II)/Pd(II) solution (see Fig. 1, route (a)) or into a colloidal Pd solution (see Fig. 1, route (b)) and finally into a bath of chemical copper. In the same vein, Shirk and Ceresa⁵⁰ describe a process for preparing a "sensitized or activated" polyimide (PI) by contacting the surface with a flame followed by the application of an electroless metal catalyst. In addition, these authors note that PdCl_2 is the preferred catalyst as the flame-sensitized film does not require the supplemental SnCl_2 sensitizer. Furthermore, Buchwalter et al.⁵¹ show that polymers (PI, PTFE, other fluorinated polymers, etc.) can be functionalized by means of a plasma (in H_2 , H_2O , O_2 , O_3 , N_2O , NH_3 , H_2S , N_2H_4 ... gaseous atmospheres) and that a metal-organic complex should be formed when the functionalized surface is immersed in an appropriate aqueous metal-salt solution (e.g. PdCl_2 activation solution). Copper deposition is then accomplished by using a conventional Cu plating bath. It should be noted that whatever the plasma gas used, these authors do attribute process efficiency to the formation of oxygen-containing functionalities. We will see in section

"Results and Discussion" the reasons why adhesion mechanisms between Pd and polymer surfaces activated with a PdCl_2 solution do not involve oxygenated species.

In summary, the literature data cited above point out that activity of electroless catalysts is largely dependent on surface chemistry of pretreated polymer substrates. Accordingly, Mance et al.⁵² describe how the surface chemistry modification of plastic substrates (PS, ABS ...) determines the efficiency of electroless catalysts and, therefore, allows metallization. This effect was demonstrated for polymer surfaces modified by photooxidation (254 nm UV light from a low pressure Hg lamp, plasma oxidation, or ozonation) by using subsequently a conventional colloidal $\text{SnCl}_2/\text{PdCl}_2$ solution (Fig. 1 / route (b)).

EXPERIMENTAL

All plasma and laser treatments and subsequent chemical metallizations were performed on PS and PTFE commercial samples supplied by Goodfellow Cambridge Limited, Cambridge, England. Planar sheets 2 mm in thickness were cut into 10 x 50 mm coupons and cleaned ultrasonically in ethanol before further processing.

The conventional sensitization/activation treatment using the two-step route and leading to palladium chemisorption was carried out by immersing the substrate for 3 min in a solution containing 0.1 g dm^{-3} SnCl_2 and 0.1 ml dm^{-3} (37 %) HCl, rinsing it in deionized water, immersing it for 3 min in a solution containing 0.1 g dm^{-3} PdCl_2 and 3.5 ml dm^{-3} (37 %) HCl, and rinsing it before carrying out the metallization itself. In addition, the one-step process was also carried out. It consisted of immersing the substrate for 3 min in the mixed solution whose composition (12 g dm^{-3} SnCl_2 , 0.25 g dm^{-3} PdCl_2 , 60 ml dm^{-3} HCl) was that used by Osaka et al.⁷, rinsing it in deionized water and immersing it in an acceleration solution (0.07 M HCl) for 3 min. On the basis of the literature data and taking into account the low stability of the solutions containing SnCl_2 , the mixed solutions used here were freshly prepared (they were discarded 48 h after their preparation) and kept in the absence of light, under nitrogen atmosphere. Similarly, acidic SnCl_2 solutions used in the two-step route were prepared daily.

When the simplified process developed in our laboratory was used, samples were immersed in a PdCl_2 (0.1 g dm^{-3}) acidic solution for 3 min and rinsed in deionized water.

Plasma treatments of PS and PTFE samples were performed in a parallel plate RF reactor (diameter: 30 cm ; interelectrode distance: 8 cm) operating in the Reactive Ion Etching (RIE) mode. The samples to be treated were positioned on the RF powered electrode (17 cm in diameter) which was capacitively coupled, through an impedance matching network, to a 13.56 MHz RF power supply. The experimental conditions were fixed as follows : gas (O_2 , N_2 , NH_3) flow = 100 sccm, pressure = 100 mTorr, power density = 0.5 W cm^{-2} and variable treatment duration. The pressure limit in the reactor was 1 mTorr. O_2 , NH_3 and N_2 gases used were 99.998, 99.999 and 99.995 % pure, respectively.

Laser treatments of a poly(carbonate) (PC) sample were performed previously to the present work with a Quantel Nd:YAG instrument (5th harmonic at $\lambda = 213 \text{ nm}$; pulse duration = 16 ps ; energy density = 0.10 to 0.80 mJ cm^{-2} ; beam diameter at the polymer surface = 7 mm). In the present work, the background pressure of the reaction chamber was around 0.5 Torr and the

working pressure was 7.5 Torr. The distance between the silica window and the sample surface was varied from 0.5 to 2 mm. This value corresponds to the distance travelled by the laser beam through the reactive gas. Similar experiments are in progress on PTFE samples by using an ArF excimer laser (EMG 103 MSC model) from Lambda Physik ($\lambda = 193$ nm ; pulse duration = 20 ns ; energy density up to 200 mJ cm^{-2} ; laser beam not focused). In this work, the working pressure was 0.1 Torr, the energy density about 10 mJ cm^{-2} and the distance between the silica window and the sample surface about 20 cm.

In each case, the metallization step was carried out at 85°C using the following solution (NiSO_4 , $6\text{H}_2\text{O}$: 36 g dm^{-3} , NaH_2PO_2 , H_2O : 10 g dm^{-3} , lactic acid: 29 ml dm^{-3} , thiodiglycolic acid: $< 0.1 \text{ g dm}^{-3}$) whose pH was adjusted to 5. Under these conditions, Ni-P films were electrolessly deposited onto polymer surfaces.

Immediately after each treatment, the samples were analysed by XPS in using the Riber SIA 200 spectrometer equipped with a non-monochromatic twin Al/Mg excitation source and a MAC 2 analyzer. Analyses of PS-based substrates were carried out using Mg $K\alpha$ radiation while those of PTFE-based substrates done using Al $K\alpha$ radiation. Spectra were recorded at a take-off angle of 25° with respect to the sample surface. Survey scans were recorded at an overall resolution of 2.3 eV and core level spectra at 0.9 eV. All XPS peaks were referenced to the C 1s signal, at a binding energy of 285 eV representative of the C-C and C-H environments of the polymer for PS and at 292.5 eV representative of the CF_2 environment for PTFE. Note that the use of a non-monochromatic source involves the presence of small satellite peaks due to Al or Mg $K\alpha_{3,4}$ excitation radiation. Such satellites, which appear approximately at 10 and 12 eV (for Al), and at 9 and 10 eV (for Mg) on the low-binding energy side of the main photoelectron peaks, obviously need not be considered in the present study. The peak identification was performed according to Beamson and Briggs' data⁵³. The curve fitting was carried out after background subtraction by the Shirley method, using a data-system software which allows to fix, for each component, peak energy and intensity, full-width-at-half-maximum and Gaussian-Lorentzian percentage. Samples were exposed to laboratory atmosphere for less than 2 min between plasma, or laser pretreatment and introduction in the XPS chamber.

In addition, TOF-SIMS experiments were carried out on PC substrates using a Perkin-Elmer PHI 7200 spectrometer equipped with 8 keV Cs^+ ion source and reflector-type TOF analyser. The incident ion beam was pulsed at 10 kHz with a pulse duration of about 1 ns. Analyses were carried out by rastering the ion beam ($100 \times 100 \text{ mm}$) over the sample surface. Positive and negative ion spectra were obtained under static conditions (total working ion dose of about $1 \times 10^{12} \text{ ions cm}^{-2}$). Surface charge neutralization by a pulsed electron flood was not required in the present work because of the absence of surface charge built-up due to the reduced primary dose used and to the rastering of the incident ion beam. At a mass of 28 D, mass resolution $m/\Delta m$ was about 10000.

RESULTS AND DISCUSSION

Figure 2 represents the procedures involving plasma (routes (a), (b) and (c)) and UV-laser (route (d)) processes which were explored both in previous studies and in the present work and which have led to the development of a new and simplified process (routes (c) and (d)). Route (a) using successively Sn(II) and Pd(II) solutions and leading to surface activation is a two-step operation similar to

route (a) shown in Figure 1. Accordingly, route (b) using a colloidal Sn(II)/Pd(II) solution is a one-step operation similar to route (b) as represented in Figure 1.

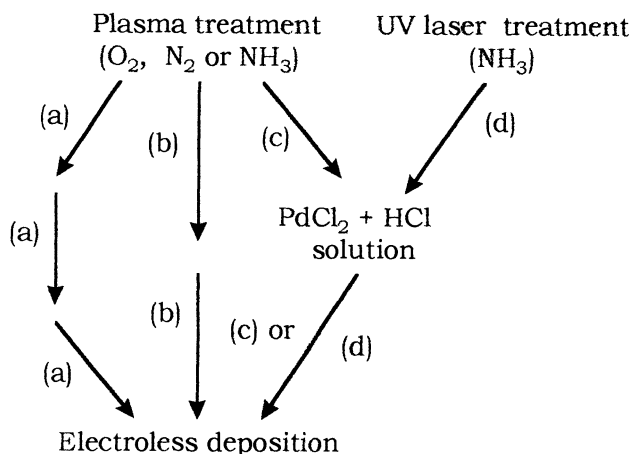


Figure 2. Schematic diagram of electroless plating processes using plasma or UV-laser pretreatment and a two-step (route (a)) or a one-step (routes (b), (c) or (d)) operation leading to surface activation (Pd chemisorption).

As shown in Figure 2, polymer surfaces were first pretreated by exposure to O_2 , N_2 or NH_3 plasmas. It is well known that O_2 and oxygen-containing plasmas are commonly used as important industrial processes for modifying polymer surface characteristics such as wettability and adhesion without altering the bulk properties of the polymer. Depending on the operation parameters a variety of oxygenated functional groups, including C-OH, C-O-C, C=O, O-C=O and CO_3 , have been reported to be surface-grafted⁵⁴⁻⁵⁸. Accordingly, nitrogen-containing plasmas give rise to primary amino groups (C-N) but the presence of C=N (imine) and C≡N (nitrile) species has also been reported⁵⁸⁻⁶¹.

Figure 3 shows XPS survey spectra of ethanol degreased PS and PTFE samples (spectra PS (1) and PTFE (1), respectively) and the same after exposure to an O_2 plasma (spectra PS (2) and PTFE (2), respectively). As expected, the degreased samples reveal only the presence of the C1s peak (at a binding energy of 285 eV) in the first case and those of C1s (292.5 eV), F1s (689.7 eV) and F2s (~35 eV) peaks in the second case, all arising from the CF_2 units of PTFE. Additional peaks are assigned to "satellites" arising from the use of a non-monochromatic source.

The net result of the interaction between PS and the reactive oxygen plasma species is the surface oxidation of the polymer. This leads to the presence of an intense O1s peak. As shown in a previous work⁴⁷, surface oxidation proceeds through opening of the aromatic ring (strong reduction of the $\pi - \pi^*$ C1s satellite) and grafting of C-OH, C-O-C and O-C=O functional groups. It should be noted here that oxygen uptake can be attributed to reactions of carbon-centred radicals, which are formed on the polymer surface and sub-surface during the plasma treatment, with oxygenated species created in the plasma as well as with O_2 when the treated samples are further exposed to the atmosphere. On the other hand, a quite different behaviour is observed in the case of PTFE substrates. Indeed, the O_2 plasma-treated samples show only a small residual

O1s peak, indicating that PTFE is resistant to oxygen attack. This result confirms the data previously published concerning both PTFE and other fluoropolymers⁶²⁻⁶⁵. A reason put forward⁶⁶ is that surface radicals generated by the plasma process react preferably with radicals from adjacent chains to form crosslinking rather than with oxygen-containing species from the plasma. However, as no

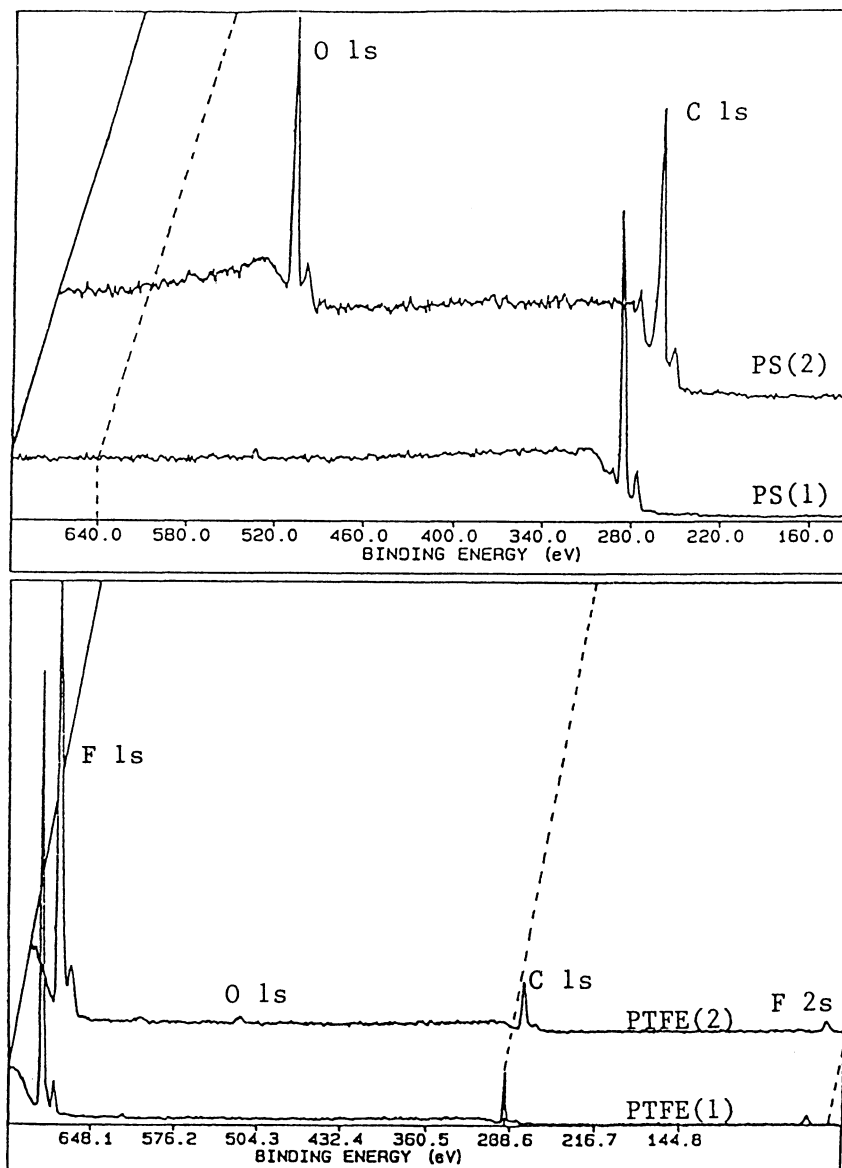


Figure 3. XPS survey spectra of ethanol-degreased poly(styrene) (PS (1)) and poly(tetrafluoroethylene) (PTFE (1)) samples. The same spectra for O₂-plasma-treated samples (PS (2) and PTFE (2), respectively) are also shown (treatment time = 1 min).

defluorination is observed, another reason which appears more plausible is that the main UV radiation (130.5 nm) emitted by atomic oxygen in the O_2 plasma is not strongly absorbed by PTFE and, therefore, does not cause breaking of surface bonds⁶⁷.

Figure 4 shows XPS spectra of ethanol degreased PS and PTFE samples after exposure to N_2 (spectra PS (3) and PTFE (3), respectively) and NH_3 (spectra PS (4) and PTFE (4), respectively) plasmas. As for PS samples, PS (3) and PS (4) spectra reveal that both nitrogenated and oxygenated functionalities are surface-grafted. The presence of oxygenated species is not at all surprising given that a number of previous studies have already detected high surface concentrations of oxygen when polymer surfaces were plasma-treated with gases not containing oxygen^{60,68-70}. This can be explained by the presence of residual O_2 and H_2O in the reactor during the plasma treatment and, as already stated, by the fact that free radicals remaining on the polymer surface after the plasma treatment are still able to react with atmospheric oxygen when samples are transferred outside the reactor. Under these conditions, the exact nature of the nitrogenated functional groups which were incorporated on the polymer surface is not easy to determine via examination of the high-energy side features of the C1s spectrum. Nevertheless, amine (C-N), amide (N-C=O) and possibly imine (C=N) functionalities should, among others, be identified⁴⁸. Similar results concerning N_2 -plasma-treated PS samples have already been reported^{58,59}. In addition, the N1s peak of N_2 or NH_3 -plasma-treated PS samples located at 399.0 eV is shown to be characteristic of N-C bonds⁵¹.

Plasma-treated fluorinated polymers have been studied to a much lesser extent than plasma-treated hydrocarbon polymers. As for the effects of N_2 or NH_3 -plasma treatments on fluorinated polymer surfaces, also much less has been reported in the literature⁷¹⁻⁷⁶ in comparison with the case of hydrocarbon polymers. Of particular interest to us is the work of Gengenbach et al.⁷⁵ relative to NH_3 -plasma-treated PTFE and fluorinated ethylene propylene copolymer (FEP). Indeed, during NH_3 -plasma treatments PTFE and FEP surfaces are reported as undergoing considerable defluorination and nitrogen uptake as amino groups. After the plasma treatment carbon-oxygen functional groups are formed as a result of complex air-oxidation phenomenon occurring when samples are exposed to the atmosphere. The aged surfaces are then reported to become oxygen-enriched. PTFE (3) and (4) spectra in Figure 4 confirm partly Gengenbach et al.' work. In both cases, the plasma process incorporates amino groups on the fluoropolymer backbone. Oxygenated functionalities are also observed probably as a result, as mentioned earlier, of the reaction of atmospheric oxygen with the free radicals created on the PTFE surface during the plasma process. However, significant differences between the N / O ratios as determined by XPS can be seen. Clearly, for a similar treatment time, the NH_3 -plasma treatment incorporates much more nitrogen (7 %) than the N_2 -plasma treatment (3 %). On the other hand, oxygen uptake (about 3 %) is quite similar in both cases. To summarize, surface functionalization of PTFE with nitrogenated species is easier with NH_3 -plasma treatment than with N_2 -plasma treatment. These results highlight the predominant role of dissociation phenomenon in the gas-phase during the plasma process and the subsequent influence of the interactions of plasma species (ions, electrons, free radicals, UV and VUV radiations) with polymer surfaces. A useful example to illustrate such effects is relative to nitridation of poly(ethylene) (PE) samples, which were exposed to MW and MW-RF

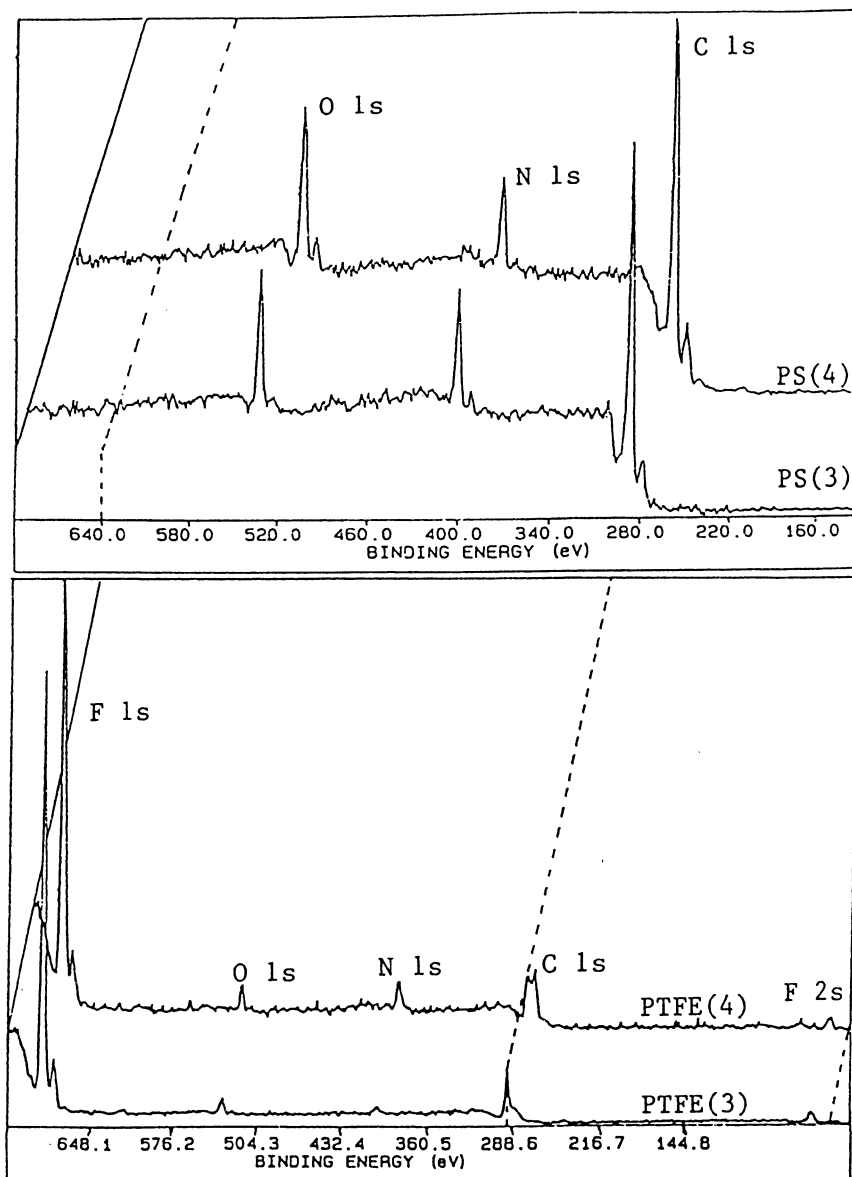


Figure 4. XPS survey spectra of ethanol-degreased PS and PTFE samples after N_2 (PS (3) and PTFE (3)) and NH_3 (PS (4) and PTFE (4)) plasmas exposure (treatment time = 1 min).

plasmas in N_2 or NH_3 environments. In these experiments^{77,78}, Klemberg-Sapieha et al. using various optical filters have shown that in the case of NH_3 plasma a very pronounced nitrogen uptake in the form of amine (C-N) groups is attributed to the influence of an intense VUV radiation (at 121.5 nm) emitted by atomic hydrogen.

In addition, XPS results shown in Figure 4 suggest some chemical modifications concerning carbon environment due, in particular, to the NH_3 plasma treatment of PTFE. Without discussing the details⁷⁹, Figure 5 represents the C1s spectrum of a NH_3 -plasma-treated PTFE sample. This spectrum is

evidently more complex than that of a virgin PTFE which contains only one component arising from the CF_2 units at 292.5 eV. As can be seen, additional contributions appear at low binding energies, which can be associated partly with defluorination process (e.g. distinguishable signals at about 291 and 288 eV) and partly with nitridation (intense signal at about 286.1 eV). The peak at 286.1 eV is assignable both to amine (C-N) and alcoholic (C-OH) functionalities. The latter functionality would result from the reaction of free radicals created on the polymer surface with the residual oxygenated species present in the reactor. Returning now to Figure 4, it can also be observed that exposure of PTFE to a N_2 plasma does not lead to an intense low binding energy "composite" band containing, in particular, a substantial contribution of C-N functionalities. Clearly, these results indicate that incorporation of nitrogen on the PTFE surface with NH_3 plasma is worthy of further detailed investigation.

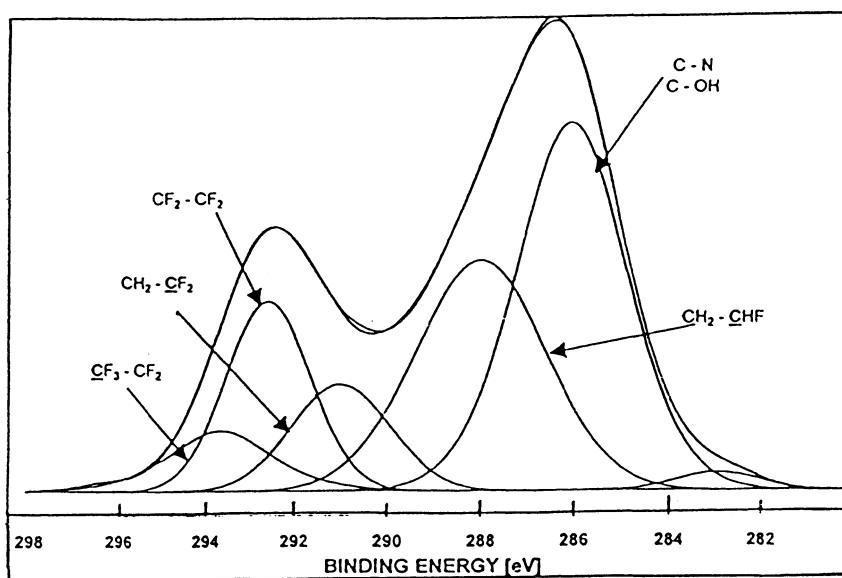


Figure 5. C1s spectrum of a PTFE sample after exposure to NH_3 plasma (treatment time = 5 min).

Let us consider now the effects of the sensitization / activation process (two-step operation / route (a)) on O_2 , N_2 or NH_3 -plasma-treated PS and PTFE substrates. The results obtained by using the one-step process (route (b)) are not given here because of the difficulties in interpreting the chemisorption mechanisms of the colloidal particles. Nevertheless, it should be noted that smaller Sn/Pd ratios are obtained when N_2 or NH_3 plasmas are used instead of O_2 plasmas. Figure 6 shows the XPS survey spectra of plasma-treated PS samples after the sensitization / activation process (route (a)).

As can be seen, the O_2 -plasma-treated sample (spectrum PS (2) / a) strongly chemisorbs Sn, and to a lower extent, Pd. On the other hand, the N_2 or NH_3 -plasma-treated samples (spectra PS (3) / a and PS (4) / a, respectively) do not adsorb any Sn but they adsorb significant concentrations of Pd. Clearly, these results highlight the selective affinity of tin towards oxygen species and, more important for the purpose of the present work, that of palladium towards nitrogenated species.

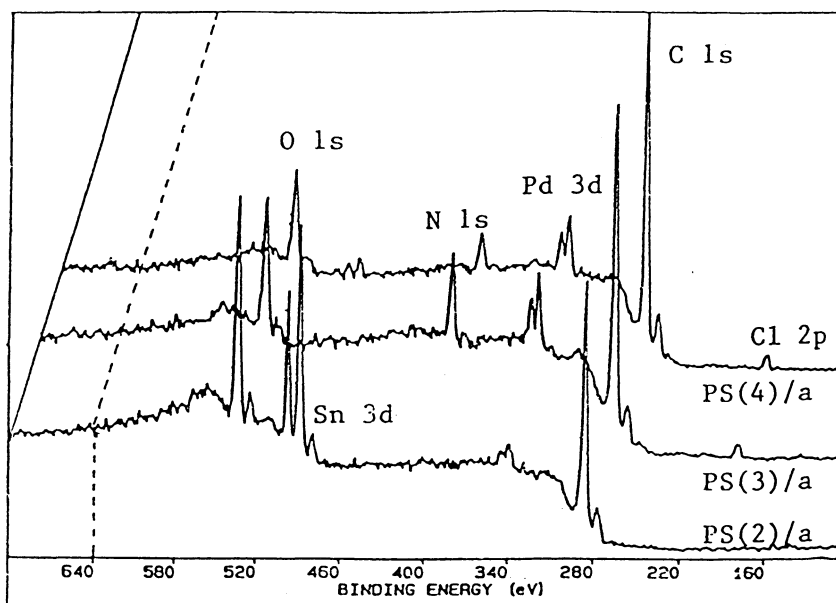


Figure 6. XPS survey spectra of O_2 (PS (2) / a), N_2 (PS (3) / a) or NH_3 (PS (4) / a) plasma-treated PS samples after sensitization / activation by using the two-step process (route (a), Figure 2).

To confirm these observations, the O_2 , N_2 and NH_3 -plasma-treated PS samples were then immersed in a simple acidic $PdCl_2$ solution (route (c)). As can be seen in Figure 7, samples previously treated in O_2 plasma do not adsorb any Pd (spectrum PS (2) / c). On the other hand, the samples on which nitrogenated species were plasma-grafted show a particular ability for chemisorbing Pd. Obviously, and irrespective of the process used (routes (a) or (c)), samples only degreased in ethanol do not present any activity towards the sensitization / activation (routes (a) or (b)) and the direct activation (route (c)) processes. Briefly, Pd chemisorption is very dependent on the nature of functional groups present or created on the polymer surface.

A similar experimental approach was then taken with PTFE substrates. O_2 -plasma-treated specimens were not considered in the data provided hereafter because such substrates do not chemically react with oxygen. Figures 8 and 9 represent XPS survey spectra of PTFE samples treated by nitrogenated-plasma, then sensitized / activated by using the two-step process ($SnCl_2$, then $PdCl_2$ solutions / route (a)) and after activation using the new way (simple $PdCl_2$ solution / route (c)), respectively. As can be seen in Figure 8, the N_2 -plasma-treated sample (spectrum PTFE (3) / a) strongly chemisorbs Sn and, to a lower extent, Pd. This is in accordance with the presence of a relatively high oxygen amount on the PTFE substrates after exposure to N_2 plasma and with the fact that nitrogen is incorporated to a much lesser extent (see spectrum PTFE (3) in Figure 4). On the other hand, spectrum PTFE (4) / a in Figure 8 relative to the NH_3 -plasma-treated sample does show, as one might expect, a lower uptake of Sn and a higher concentration of Pd. Again, the presence of nitrogenated groups chemisorbed (see spectrum PTFE (4) in Figure 4) on PTFE substrates strongly support the formation of chemical bonds between nitrogen and palladium

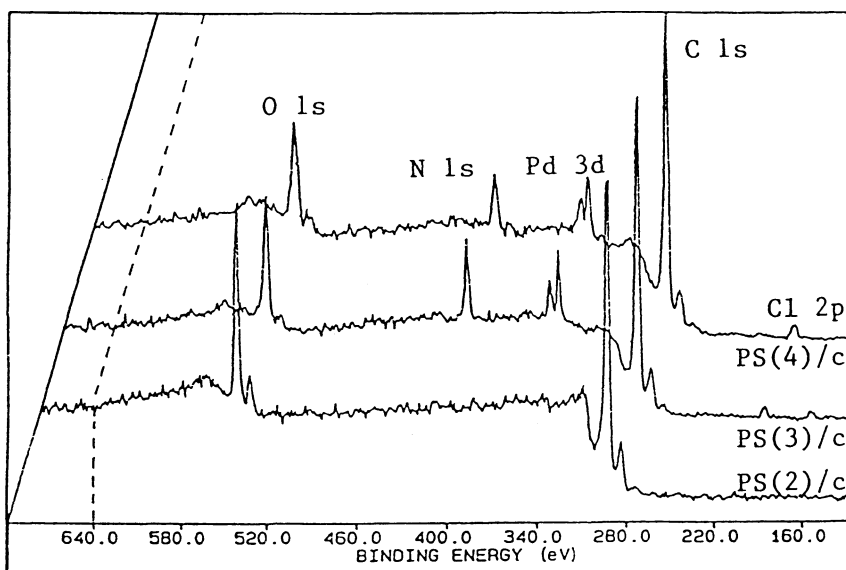


Figure 7. XPS survey spectra of O_2 (PS (2) / c), N_2 (PS (3) / c) or NH_3 (PS (4) / c), plasma treated PS samples after activation in a simple dilute acidic $PdCl_2$ solution (route (c)), Figure 2).

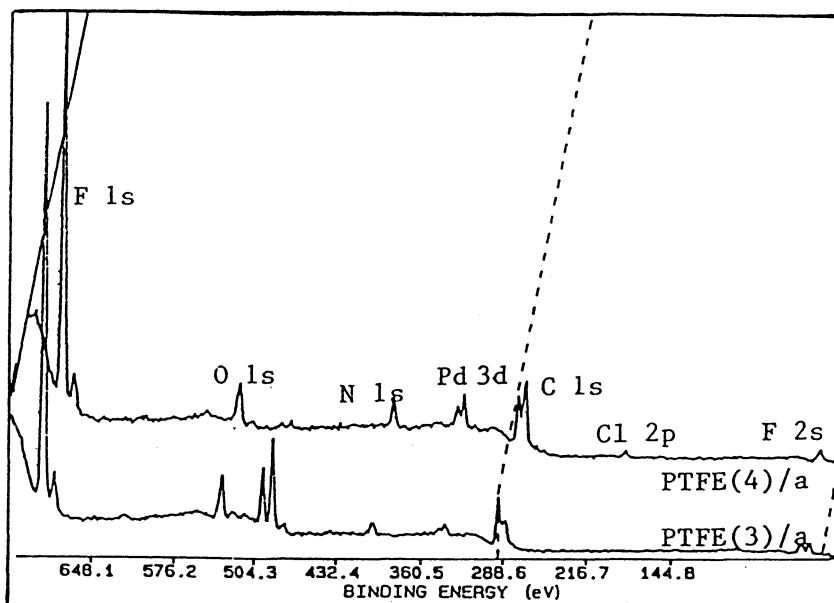


Figure 8. XPS survey spectra of N_2 (PTFE (3) / a) and NH_3 (PTFE (4) / a) plasma-treated PTFE samples after sensitization/activation by using the two-step process (route (a), Figure 2).

species. To confirm the suggested mechanism, N_2 and NH_3 -plasma-treated samples were also immersed in a simple acidic $PdCl_2$ solution (route (c)). As can be seen in Figure 9 (spectrum PTFE (4)/c), Pd is chemisorbed on the PTFE surface, when the latter has been nitrogen-enriched via a NH_3 -plasma treatment (see spectrum PTFE (4) in Figure 4).

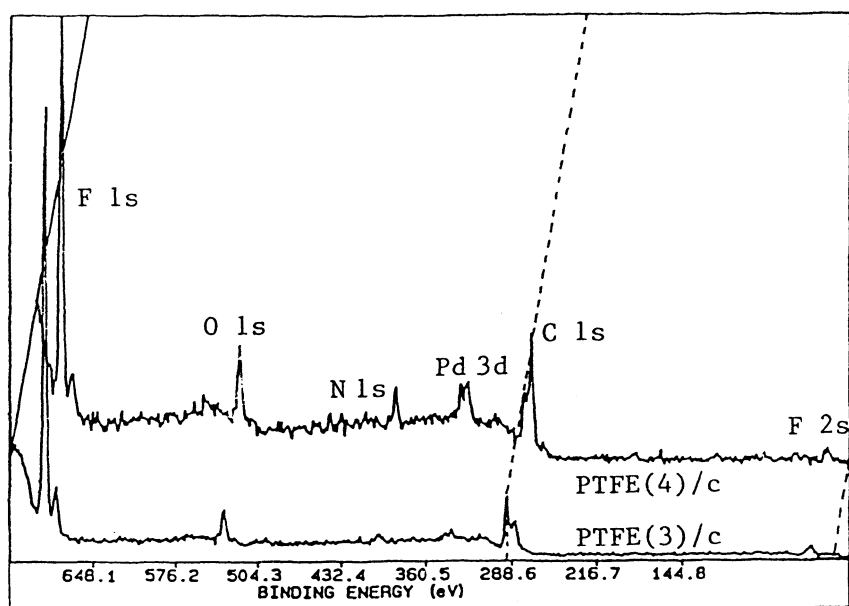


Figure 9. XPS survey spectra of N_2 (PTFE (3) / c) or NH_3 (PTFE (4) / c) plasma-treated PTFE samples after activation in a simple dilute acidic PdCl_2 solution (route (c), Figure 2).

As mentioned above in the section "State-of-the-Art", photochemically-induced surface modification of various polymers has recently stimulated much interest and many applications are in progress today in various industrial areas (microelectronics, optics, biomedical technology, etc.). In this field, UV and VUV laser radiations offer a large potential because of their capabilities to photodissociate many molecules in the gaseous state as well as to break chemical bonds at the surface of polymer materials, and such mechanisms lead to the possibility of grafting new functionalities⁸⁰. As an example, Okoshi and Murahara⁸¹, Murahara and Toyoda⁸² using an ArF excimer laser have reported how to defluorinate a PTFE surface and substitute F atoms by CH_3 groups from irradiation in a gaseous $\text{B}(\text{CH}_3)_3$ atmosphere. In a similar way, we have recently shown⁸³ that nitrogen atoms could be grafted on poly(carbonate) (PC) surfaces by laser irradiation through an ammonia atmosphere. In our work, a Nd:YAG laser (5th harmonic, $\lambda = 213 \text{ nm}$; pulse duration = 16 ps) was used. Electroless plating was then carried out on the nitrogen-grafted surfaces by using the simplified route (d) described in Figure 2. It should be noted that this process consists of an extension of route (c) which involves a plasma pretreatment.

In the present work, an ArF excimer laser ($\lambda = 193 \text{ nm}$) was used to functionalize the surface of PTFE substrates from an ammonia atmosphere. In this case, nitridation (or amination) is thought to proceed through the direct photodissociation of NH_3 molecules and the formation of amino radicals in the gas phase. It should be borne in mind that the energy of ArF excimer laser photons (6.4 eV) is higher than that of the N-H bond (4.03 eV) in ammonia molecules. In comparison, direct photodissociation is not possible in the case of a nitrogen atmosphere because the energy of the $\text{N}\equiv\text{N}$ bond is 9.82 eV. Figure 10 represents XPS survey spectra of a degreased PTFE sample prior to and after

laser irradiation under NH_3 atmosphere (spectrum PTFE (5)). After the activation process via immersion of the treated substrate in a simple acidic PdCl_2 solution (route (d)), metallization is achieved as for NH_3 or N_2 plasma-treated PTFE. As can be seen here again, nitrogenated species are grafted on the PTFE surface during the laser treatment and subsequently Pd is chemisorbed owing to its strong affinity towards nitrogen.

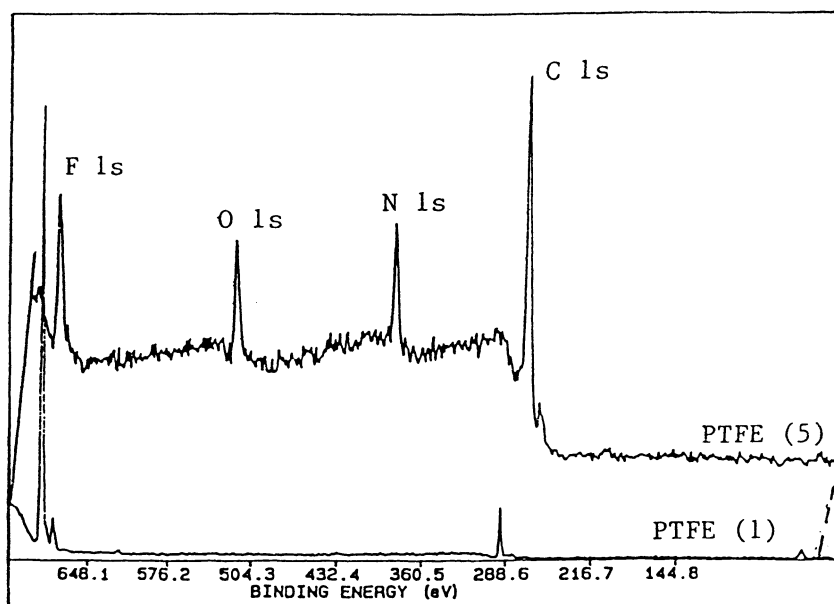


Figure 10. XPS survey spectra of a degreased PTFE sample before (PTFE (1)) and after (PTFE (5)) an ArF excimer laser treatment in a NH_3 atmosphere (treatment time: 5 min).

Irrespective of the method used (routes (a), (b), (c) or (d)) for surface activation and subsequent electroless deposition, the adhesion of the metallic layer on the polymer substrate is one of the primary concerns for achieving stability and long term reliability of the corresponding "composite" system. In the present case, it is clear that adhesion properties of the electroless plating are firstly determined by the bond strength of the catalytic nuclei to the treated-polymer surface. As for any adheree-adherend combination, several techniques are, in principle, available for measuring the practical adhesion⁸⁴⁻⁸⁷ of the specific adhering system considered in this work. Qualitatively, the adhesion of electroless coatings deposited after plasma or UV-laser pretreatment and activation process can be assessed as good, as no samples using the conventional Scotch tape test failed in our investigations. In addition, the adhesion of electroless deposits was investigated using a fragmentation test. Specimens subjected to this test were polymer substrates cut into a dog-bone shape and coated by the electroless film. In this test, which is particularly well-adapted to the case of thin and slightly deformable films deposited on ductile substrates, the coated material is strained in uniaxial tension and the development of the crack pattern is observed as a function of the applied strain⁸⁸. As an example, Figure 11 represents the fragmentation patterns obtained in the case of a NH_3 -plasma-treated PTFE sample after deposition of an electroless Ni-P coating about 500 nm in thickness. (A) and (B) SEM micrographs

are relative to samples prepared by using the conventional two-step process (route (a)) and the simplified one-step process (route (c)), respectively. In both cases, a distribution of parallel fragments is initiated upon the fragmentation operation. As can be seen, the average critical length of fragments is smaller for specimens prepared by using the simplified one-step process, which means a better adhesion of the coating to the polymer substrate.

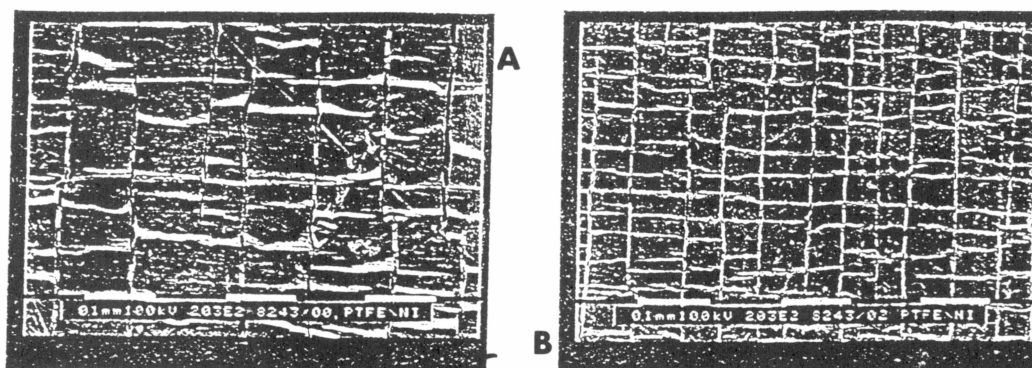


Figure 11. SEM micrographs of a fragmentation pattern (Ni-P / PTFE system) after application of a 12 % strain. The Ni-P coating is obtained (A) after the two-step process (route (a)), (B) after the one-step process (route (c), Figure 2).

CONCLUSIONS

Taking advantage of the considerable affinity of palladium for nitrogen, a new method for metallizing polymer surfaces through an electroless process has been developed. This method is based on the direct surface activation of polymer materials using (i) a gas-phase pretreatment through plasma excitation, or UV-laser irradiation in nitrogenated atmospheres and (ii) immersion of the so-treated samples in an activation bath constituted only of a dilute acidic PdCl_2 solution. In addition, it is noteworthy that the advantage of this simple process goes beyond obtaining strong adhesion at the metal-polymer interface since it makes possible, (i) the elimination of strong corrosive solutions (chromic and sulfochromic acid baths) conventionally used to pretreat polymer surfaces, which avoids costs associated with environmental constraints, and (ii) the non-use of acidic tin chloride solutions in which chemical reactions may occur (e.g., oxidation, hydrolysis, complex formation).

Based on the above considerations, it is, of course, imperative to pursue the present work with a view to optimizing the nitridation (amination) of polymer surfaces, in particular, by using plasma, or UV-laser process in the NH_3 environment. Indeed, in both treatments, it should be reminded that many parameters such as the nature of excitation sources, the geometry of reactors and the experimental conditions selected by the operator, crucially influence the gas phase and, therefore, the surface chemistry of the treated samples.

REFERENCES

1. K. L. Mittal and J. R. Susko, Editors, "Metallized Plastics 1: Fundamental and Applied Aspects," Plenum Press, New York, 1989.
2. E. Sacher, J. J. Pireaux and S. P. Kowalczyk, Editors, "Metallization of Polymer," ACS Symposium Series No 440, American Chemical Society, Washington DC, 1990.
3. K. L. Mittal, Editor, "Metallized Plastics 2: Fundamental and Applied Aspects," Plenum Press, New York, 1991.
4. K. L. Mittal, Editor, "Metallized Plastics 3: Fundamental and Applied Aspects," Plenum Press, New York, 1992.
5. K. L. Mittal, Editor, "Metallized Plastics: Fundamentals and Applications," Marcel Dekker, New York, 1998.
6. R. L. Cohen and K. W. West, *J. Electrochem. Soc.*, 120, 502 (1973).
7. T. Osaka, H. Takematsu and K. Nihei, *J. Electrochem. Soc.*, 127, 1021 (1980).
8. J. Horkans, J. Kim, C. Mc Grath and L. T. Romankiw, *J. Electrochem. Soc.*, 134, 300 (1987).
9. M. C. Burrell, G. A. Smith and J. J. Chera, *Surf. Interface Anal.*, 11, 160 (1988).
10. R. L. Cohen, J. F. D'Amico and K. W. West, *J. Electrochem. Soc.*, 118, 2042 (1971).
11. B. K. W. Baylis, A. Busuttil, N. Hedgelock and M. Schlesinger, *J. Electrochem. Soc.*, 123, 348 (1976).
12. G. O. Mallory and J. B. Hajdu, Editors, "Electroless Plating: Fundamentals and Applications," American Electroplaters and Surface Finishers Society, Orlando, 1990.
13. C. H. de Minjer and P. F. J. V. D. Boom, *J. Electrochem. Soc.*, 120, 1644 (1973).
14. R. L. Meek, *J. Electrochem. Soc.*, 122, 1478 (1975).
15. M. C. Burrell, B. R. Karas, D. F. Foust, W. V. Dumas, E. J. Lamby, W. T. Grubb and J. J. Chera, in "Metallized Plastics 1: Fundamental and Applied Aspects," K. L. Mittal and J. R. Susko, Editors, p. 223, Plenum Press, New York, 1989.
16. M. Charbonnier, M. Alami and M. Romand, *J. Appl. Electrochem.*, 28, 449 (1988).
17. D. Singh, R. Balasubramaniam and R. K. Duke, *Corrosion*, 51, 581 (1995).
18. Y. Shacham-Diamond, V. Dubin and M. Angyal, *Thin Solid Films*, 262, 93 (1995).
19. M. Alami, M. Charbonnier and M. Romand, *J. Adhesion*, 57, 77 (1996).
20. B. R. Karas, D. F. Foust, W. L. Dumas and E. J. Lamby, *J. Adhesion Sci. Technol.*, 6, 815 (1992).
21. A. Viehbeck, C. A. Kovac, S. L. Buchwalter, M. J. Goldberg and S. L. Tisdale, in "Metallization of Polymers," E. Sacher, J. J. Pireaux and S. P. Kowalczyk, Editors, p. 394, ACS Symposium Series No 440, American Chemical Society, Washington, DC, 1990.
22. T. H. Baum, D. C. Miller and T. R. O'Toole, *Chem. Mater.*, 3, 714 (1991).
23. T. H. Baum, D. C. Miller and T. R. O'Toole, in "Metallized Plastics 3: Fundamental and Applied Aspects," K. L. Mittal, Editor, p. 9, Plenum Press, New York, 1992.
24. R. R. Rye and A. J. Ricco, *J. Electrochem. Soc.*, 140, 1763 (1993).
25. R. R. Rye, G. W. Arnold and A. J. Ricco, *J. Electrochem. Soc.*, 140, 3233 (1993).

26. R. R. Rye, A. J. Howard and A. J. Ricco, *Thin Solid Films*, 262, 73 (1995).
27. Y. S. Liu and H. S. Cole, *Chemtronics*, 4, 209 (1989).
28. H. S. Cole, Y. S. Liu, J. W. Rose and R. Guida, *Appl. Phys. Lett.*, 53, 2111 (1988).
29. T. J. Hirsch, R. F. Miracky and C. Lin, *Appl. Phys. Lett.*, 46, 1357 (1990).
30. G. Shaveev, W. Marine, H. Dallaporta, L. Bellard and A. Cros, *Thin Solid Films*, 241, 52 (1994).
31. B. Eliasson, M. Hirth and U. Kogelschatz, *J. Phys. D: Appl. Phys.*, 20, 1421 (1987).
32. B. Eliasson and U. Kogelschatz, *Appl. Phys. B*, 46, 299 (1988).
33. H. Esrom and G. Wahl, *Chemtronics*, 4, 216 (1989).
34. A. Bauer, J. Ganz, K. Hesse and E. Kölher, *Appl. Surf. Sci.*, 46, 113 (1990).
35. H. Esrom and U. Kogelschatz, *Appl. Surf. Sci.*, 46, 158 (1990).
36. U. Kogelschatz, *Pure Appl. Chem.*, 62, 1667 (1990).
37. B. Gellert and U. Kogelschatz, *Appl. Phys. B*, 52, 14 (1991).
38. U. Kogelschatz, *Appl. Surf. Sci.*, 54, 410 (1992).
39. H. Esrom and U. Kogelschatz, *Thin Solid Films*, 218, 231 (1992).
40. P. Bergonzo, P. Patel, I.W. Boyd and U. Kogelschatz, *Appl. Surf. Sci.*, 54, 424 (1992).
41. H. Esrom, J. Demny and U. Kogelschatz, *Chemtronics*, 4, 202 (1989).
42. I. W. Boyd and J. Y. Zhang, *Nucl. Instrum. Methods B*, 121, 349 (1997).
43. J. Y. Zhang, H. Esrom and I. W. Boyd, *Appl. Surf. Sci.*, 96-98, 399 (1996).
44. G. Wahl and H. Esrom, *Appl. Surf. Sci.*, 46, 96 (1990).
45. J. Y. Zhang and H. Esrom, *Appl. Surf. Sci.*, 54, 465 (1991).
46. H. Niino and A. Yabe, *Appl. Phys. Lett.*, 63, 3527 (1993).
47. M. Charbonnier, M. Alami and M. Romand, *J. Electrochem. Soc.*, 143, 472 (1996).
48. M. Alami, M. Charbonnier and M. Romand, *Plasmas and Polymers*, 1, 113 (1996).
49. J. P. Ehrbar and C. Ganguillet, U.S. Patent 4,165,394 (1979).
50. A. Shirk and M. Ceresa, U.S. Patent 3,954,570 (1976).
51. L. P. Buchwalter, S. L. Buchwalter, C. R. Davis, R. D. Goldblatt, J. E. Heidenreich, S. L. Nunes, J. M. Park, R. R. Thomas, D. Tortorella and L. M. Ferreiro, European Patent, EP 0 478 975 A2 (1991).
52. A. M. Mance, R. A. Waldo, S. W. Gaarenstroom and R. R. Witherspoon, in "Metallized Plastics 3: Fundamental and Applied Aspects," K.L. Mittal, Editor, p. 29, Plenum Press, New York, 1992.
53. G. Beamson and D. Briggs, "High Resolution XPS of Organics Polymers," The Scienta ESCA 300 Database, John Wiley and Sons, Chichester, 1992.
54. S. Wu, "Polymer Interface and Adhesion", Marcel Dekker, New York, 1982.
55. D. Briggs, C. R. Kendall, A. R. Blythe and A. B. Wootton, *Polymer*, 24, 47 (1983).
56. L. J. Gerenser, J. F. Elman, M. G. Mason and J. M. Pochan, *Polymer*, 26, 1162 (1985).
57. J. M. Pochan, L. J. Gerenser and J. F. Elman, *Polymer*, 27, 1058 (1986).
58. L. J. Gerenser, *J. Adhesion Sci. Technol.*, 7, 1019 (1993).
59. R. Foerch, N. S. McIntyre, R. N. S. Sodhi and D. H. Hunter, *J. Appl. Polym. Sci.*, 40, 1903 (1990).
60. J. Lub, F. C. B. M. van Vroonhoven, E. Bruninx and A. Benninghoven, *Polymer*, 30, 40 (1989).
61. F. M. Petrat, D. Wolany, B. C. Schwede, L. Wiedmann and A. Benninghoven, *Surf. Interface Sci.*, 21, 274 (1994).

62. M. A. Golub, T. Wydeven and R. D. Cormia, *Polymer*, 30, 1576 (1989).
63. M. A. Golub, T. Wydeven and R. D. Cormia, *Langmuir*, 7, 1026 (1991).
64. M. K. Shi, A. Selmani, L. Martinu, E. Sacher, M. R. Wertheimer and A. Yelon, in "Polymer Surface Modification: Relevance to Adhesion," K. L. Mittal, Editor, p. 73, VSP, Utrecht, 1996.
65. H. J. Griesser, D. Youxian, A. E. Hughes, T. R. Gengenbach and A. W. H. Mau, *Langmuir*, 7, 2484 (1991).
66. D. Youxian, H. J. Griesser, A. W. H. Mau, R. Schmidt and J. Lieselang, *Polymer*, 32, 1126 (1991).
67. E. M. Liston, in "The Interfacial Interactions in Polymeric Composites," G. Akozali, Editor, NATO ASI Series, Series E: Applied Sciences - Vol. 230, Kluwer Academic Publishers, Dordrecht, 1993.
68. H. Yasuda, H. C. March, S. Brandt and C. N. Reilley, *J. Polym. Sci., Polym. Chem. Ed.*, 15, 991 (1977).
69. D. S. Everhart and C. N. Reilley, *Anal. Chem.*, 53, 665 (1981).
70. N. Inagaki, S. Tasaka and H. Kawai, *J. Adhesion Sci. Technol.*, 3, 637 (1989).
71. J. R. Hollahan, B. B. Stafford, R. D. Falls and S. T. Payne, *J. Appl. Polym. Sci.*, 13, 807 (1969).
72. G. C. S. Collins, A. C. Lowe and A. Nicholas, *Eur. Polym. J.*, 9, 173 (1973).
73. H. Yasuda, *J. Macromol. Sci. Chem.*, A 10, 383 (1976).
74. M. Kawakami, H. Koya and S. Gondo, *Biotechnol. Bioeng.*, 32, 369 (1988).
75. T. R. Gengenbach, X. Xie, R. C. Chatelier and H. J. Griesser, in "Plasma Surface Modification of Polymers," M. Strobel, C. S. Lyons and K. L. Mittal, Editors, p. 123, VSP, Utrecht, 1994.
76. S. L. Kaplan, E. S. Lopata and J. Smith, *Surf. Interface Anal.*, 20, 331 (1993).
77. J. E. Klemberg-Sapieha, L. Martinu, O. M. Küttel and M. R. Wertheimer, in "Metallized Plastics 2: Fundamental and Applied Aspects," K. L. Mittal, Editor, p. 315, Plenum Press, New York, 1991.
78. J. E. Klemberg-Sapieha, O. M. Küttel, L. Martinu and M. R. Wertheimer, *J. Vac. Sci. Technol.*, A 9, 2975 (1991).
79. M. Charbonnier, M. Romand and M. Alami, in preparation.
80. M. Chtaïb, E. M. Roberfroid, Y. Novis, J. J. Pireaux, R. Caudano, P. Lutgen and G. Feyder, *J. Vac. Sci. Technol.*, A 7, 3233-3237 (1989).
81. M. Okoshi and M. Murahara, *J. Mater. Res.*, 7, 1912 (1992).
82. M. Murahara and K. Toyoda, *J. Adhesion Sci. Technol.*, 9, 1601 (1995).
83. M. Charbonnier, M. Alami, M. Romand, J. P. Girardeau-Montaut and M. Afif, *Appl. Surf. Sci.*, 109/110, 206 (1997).
84. K. L. Mittal, *Electrocomponent Sci. Technol.*, 3, 21 (1976).
85. K. L. Mittal, in "Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings," K. L. Mittal, Editor, p. 5, ASTM STP 640, American Society for Testing and Materials, Philadelphia, 1978.
86. K. L. Mittal, *J. Adhesion Sci. Technol.*, 1, 247 (1987).
87. K. L. Mittal, in "Adhesion Measurement of Films and Coatings," K. L. Mittal, Editor, pp. 1-13, VSP, Utrecht, The Netherlands, 1995.
88. Y. Leterrier, Y. Wyser, J.-A. E. Månson and J. Hilborn, *J. Adhesion*, 44, 213 (1994).
89. Y. Leterrier and J.-A. E. Månson, *J. Mater. Sci. Lett.*, 16, 120 (1997).
90. Y. Leterrier, L. Boogh, J. Andersons and J.-A. E. Månson, *J. Polym. Sci. Part B, Polym. Phys.*, 35, 1449 (1997).
91. Y. Leterrier, J. Andersons, Y. Pitton and J.-A. E. Månson, *J. Polym. Sci. Part B, Polym. Phys.*, 35, 1463 (1997).



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PULSED LASER DEPOSITION OF TiN ON PMMA AND POLYIMIDE: A NOVEL ROUTE FOR POLYMER METALLIZATION

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We have developed a novel method for metallization of polymeric materials by employing a pulsed laser deposition technique. Highly metallic, adherent and hard TiN films were deposited using a KrF excimer laser ablation of high purity, stoichiometric and hot pressed TiN target at a base pressure of 1×10^{-7} Torr, and the ablated species were allowed to condense on the polymeric substrate materials. The processing parameters such as the laser fluence, pulse repetition rate, substrate-to-target distance, and substrate temperature were optimized for the fabrication of high quality metallic and adherent TiN films on PMMA and polyimide. The films were characterized by Auger electron spectroscopy, Raman spectroscopy, scanning and transmission electron microscopies, and four-point-probe electrical resistivity. Auger spectroscopy revealed that the films were close to stoichiometric TiN. The TiN films deposited on polyimide and PMMA were smooth, golden in color, and were found to be polycrystalline with an average grain size of ~ 12 nm. The adhesion of TiN films was measured by the direct pull-off method. The films were highly adherent to the polymer substrates as compared to Cu and Au films deposited by sputtering. Four-point-probe electrical resistivity measurements showed characteristic metallic behavior with a low value of resistivity, ~ 30 - $75 \mu\Omega\text{-cm}$, at room temperature. The specific resistivity was found to be a strong function of deposition temperature and reached the lowest value of $\sim 15 \mu\Omega\text{-cm}$ at room temperature for epitaxial TiN films on Si (100) deposited at 600°C by pulsed laser deposition. We also present results on the laser etching of TiN films on polymers and on the development of insulator/metal/polymer multilayer structures (AlN/TiN/polymer, DLC/TiN/polymer) for multichip modules in electronics packaging applications.

INTRODUCTION

Polymeric materials such as polyimides and poly(methyl methacrylate) (PMMA) are increasingly being used in advanced microelectronics since they have many desirable properties such as light weight, moldability, ability to form intricate shapes, corrosion resistance, and versatile electronic properties^{1,2}. In this context, metallization of polymers is an important concern in electronic applications because of demands for increased packaging density and greater reliability³. One of the major challenges in building a reliable metal/polymer structure is the adhesion between the metal and the polymer since the long term stability of the devices depends critically on the adhesion experienced at the metal-polymer interface and hence this has become an important technological problem⁴. The adhesion between a metal and a polymer is strongly dependent on the specific type of polymers and metals involved, as well as on the deposition process under which the interface between the two is formed. The most commonly used elements for metallization of polymers are Cu, Al, Ti, Ni, and Cr, and the methods of deposition have involved thermal evaporation and sputtering processes³⁻⁴. Here we propose titanium nitride metal layer on polymers since TiN films have unique and desirable properties such as low electrical resistivity, extreme hardness, and excellent mechanical and thermal properties⁵. TiN crystallizes in a B1 (NaCl-type) structure, and has complex interatomic bonding comprising of covalent, metallic, and ionic contributions. The low electrical resistivity is attributed to the contribution of nine valence electrons from the N 2p and Ti 3d orbitals⁶. The present interest in TiN thin films also stems from their desirable thermodynamical and electrical properties which open up potential applications in the microelectronics industry. For example, recent studies have shown that TiN is the most promising diffusion barrier material and is being evaluated for use in both Si and III-V compound device technologies in multilevel metallization schemes involving Al and Cu as the second layer⁷. The TiN films on polymers seem to be technologically viable for metallization for protective coating applications. The major impediment in the applications of these films on polymeric materials is the high growth temperatures employed in most commonly used chemical vapor deposition (CVD) techniques to activate the desired chemical reactions on the substrate to form a film⁸, and hence the process cannot be employed for the polymers which have low softening temperatures, for example, the softening temperatures of PMMA and polyimide are 80°C and 300°C, respectively. The reactive sputtering technique provides an alternative to this problem, and is utilized for TiN deposition at low temperatures^{9,10}. However, since polymers are soft and have a low damage threshold for ion bombardment, this technique may lead to the degradation of surfaces and adversely affect the adhesion of the deposited films.

In this paper, we report our detailed work on the processing and characterization of conducting and adherent TiN films deposited by pulsed laser deposition (PLD) on polyimide and PMMA. We show that the PLD technique is a low temperature thin film processing method which can be well adopted for metallization of polymers at room temperature, in-situ processing, and multilayer fabrication of advanced electronic materials on polymers.

EXPERIMENTAL

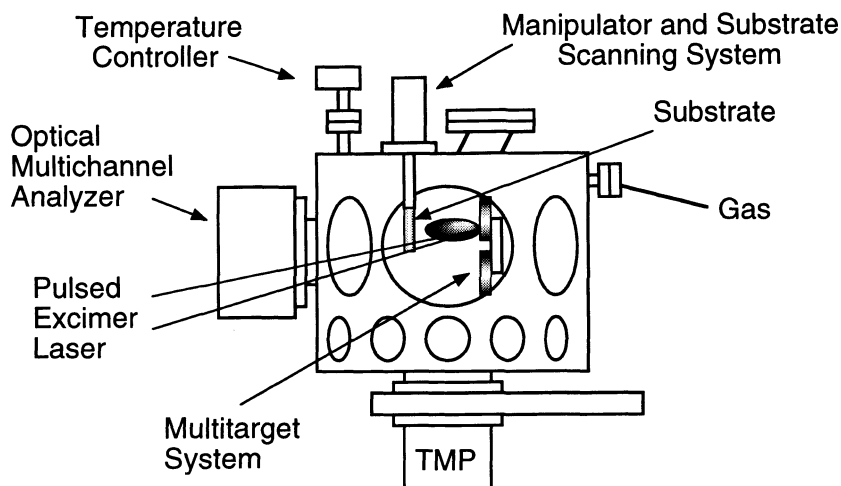


Figure 1. Schematic of the PLD technique for the fabrication of TiN thin films on polymers.

The TiN films were deposited inside a stainless steel vacuum system evacuated by a turbomolecular pump to a base pressure of 1×10^{-7} Torr. A schematic diagram of the PLD chamber is shown in Fig. 1. Radiation from a KrF excimer laser ($\lambda = 248$ nm and $\tau = 25$ ns) was used to ablate the stoichiometric and hot pressed TiN target with an energy density ranging from 2 to 10 J/cm^2 . The target was irradiated by a laser beam through a quartz window at an angle of 45° to the target surface. The laser induced vaporized material was then allowed to condense onto the polymer substrates kept at a distance of about 5 cm from the target surface. A commercially available PMMA and polyimide (supplied by DuPont) were cleaned sequentially in an ultrasonic bath of soap solution, ethyl alcohol, and isopropyl alcohol before deposition. The films were grown at various laser energy densities, substrates temperatures, and pulse repetition rates. The laser beam was also scanned over target during deposition over an area of $1 \times 1 \text{ cm}^2$ to achieve uniform films over $2.5 \times 2.5 \text{ cm}^2$ area. The multilayer structures such as AlN/TiN/polymers and diamond-like-carbon (DLC)/TiN/polymers were fabricated in-situ by the PLD method using a rotating target system. Laser deposited TiN films were characterized by Auger and Raman spectroscopies, plan-view transmission electron and scanning electron microscopies, electrical resistivity, and x-ray diffraction (XRD) technique. Auger electron spectroscopy was carried out using a JEOL JAMP 30 microprobe. The primary electron beam current was 0.3 mA at 10 keV with a beam diameter of less than 1 mm. The samples were sputter etched during analysis using a rastered 3 keV Ar^+ ion beam. Raman spectroscopy was carried out using green light (514.5 nm line) from Ar^+ ion laser. The incident light was made grazing along the plane of the TiN film and the scattered light was collected in the direction normal to the film/substrate interface. The scattered light was dispersed in a one meter 1704 spex monochromator with a resolution of 0.4 cm^{-1} and the counts were taken for one minute at each wavelength with a photomultiplier in photon counting mode. The film thickness and uniformity were also verified using α -step 200-Tencor Instrument. The adhesion measurements were carried out using the pull-off technique employing a tensile tester machine (ATS Inc).

RESULTS AND DISCUSSION

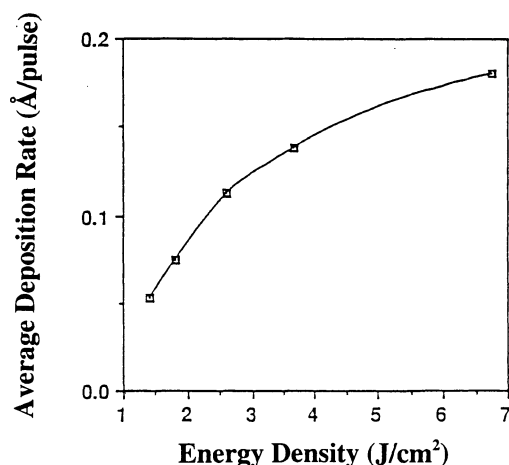


Figure 2. Deposition rate of TiN film on PMMA substrate versus laser energy density.

Pulsed laser ablation and deposition of TiN as a function of laser fluence was studied. The laser energy density significantly affects the deposition rate, and the particulate emission from the target. Figure 2 shows the average deposition rate of TiN on polymer substrates at room temperature and a base pressure of 1×10^{-7} Torr as a function of laser energy density. The curve indicates that the deposition rate increases with the laser fluence. However, at higher laser fluence, the rate of ablation is affected by laser absorption in the plasma plume. For all laser fluences, the TiN films were golden in color, which is a primary characteristic of TiN films. It should be noted that the ablation and the deposition were carried out at a base pressure of 1×10^{-7} Torr, without a nitrogen partial pressure and at room temperature. In all experiments, the TiN stoichiometric composition of the target was maintained due to highly nonequilibrium laser ablation process^{11,12}. The highly reactive nature of Ti metal species in the plasma plume is an additional factor for maintaining the TiN stoichiometry. The qualitative information on the composition of these films was obtained using Auger electron spectroscopy. Figure 3 shows typical derivative Auger electron spectrum of laser deposited TiN film on polyimide at room temperature. The two major peaks exist in the AES spectrum of TiN: one at 381 eV and the other at 418 eV. The chemical analysis of TiN using Auger electron spectroscopy is complicated because the principal Auger electron emission from nitrogen ($KL_{23}L_{23}$) occurs at an energy (381 eV) that overlaps with the Ti ($L_{3}M_{23}M_{23}$) transition at 383 eV. To circumvent this problem, the nitrogen content was characterized by the positive excursion of the combined N and Ti peaks at 382 eV and the titanium content by the negative excursion of the Ti peak at 420 eV, which essentially gives a quantitative analysis of TiN¹³. The analysis of the nitrogen stoichiometry in the film is facilitated by the following procedure. First, the ratios of the peak heights (Ti+N)/Ti, Ti/O, and (Ti+N)/O are considered to be almost independent of Auger electron signal detection. Second, the nitrogen content in the deposited film is considered high enough so that a

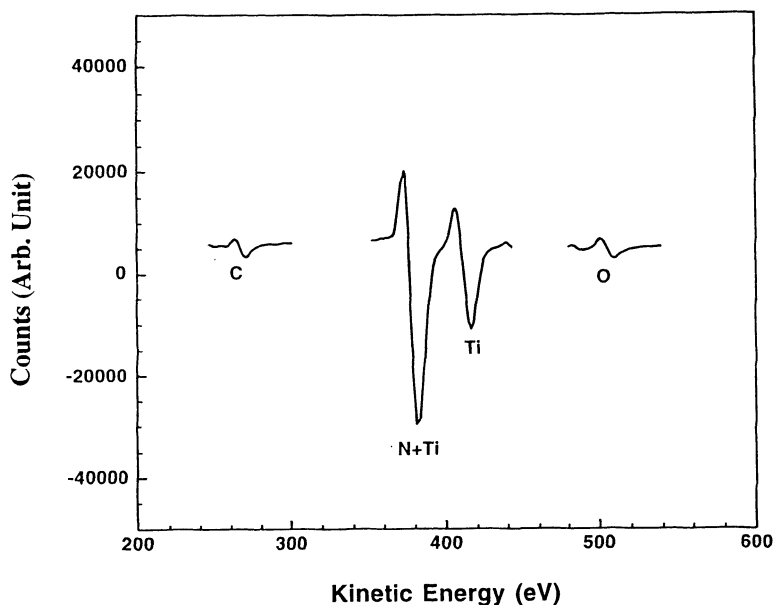


Figure 3. Auger electron spectrum of TiN film deposited at room temperature on polyimide.

slight change in the (Ti+N) peak intensity is linear with that of Ti. The Auger analysis was performed at the surface as well as in the bulk after sputtering TiN for 3 minutes to eliminate the surface oxide. The oxygen peaks which appear after sputtering are a result of gettering of oxygen present in the spectrometer by Ti. The (Ti+N)/Ti ratio remained almost constant with an average value of 1.926 over the range of temperature used in the present work. The observed carbon and oxygen lines are expected due to the atmospheric exposure of the samples. The Auger peak intensities for the Ti+N (381 eV), Ti (420 eV), O (503 eV) and C (270 eV) in the depth profiling experiment are shown in Fig. 4. This result clearly shows that the TiN films of uniform composition are formed on polymers by laser deposition from stoichiometric TiN target at room temperature and base pressure of 10^{-7} Torr.

The TiN films were also characterized by Raman spectroscopy. The scattering in the acoustical range is primarily determined by the vibrations of the Ti ions and that in the optical range by the vibrations of the N ions. Thus, the ratio of the acoustical to the optical scattering intensities provides a measure of the Ti:N ratio or stoichiometry. The spectrum of TiN polycrystalline material is characterized by acoustic peaks¹⁴ below 370 cm^{-1} and optical peaks above 500 cm^{-1} . The first order defect induced acoustic and optical phonon peaks were recorded for the TiN films deposited on PMMA at room temperature, as shown in Fig. 5. The Raman spectrum shows a main peak in the range $200\text{--}350\text{ cm}^{-1}$ which is associated with Ti atom vibrations in the absence of nitrogen. Another peak in the range of $450\text{--}550\text{ cm}^{-1}$ is associated with the titanium vacancies in the presence of nitrogen ions. These features are similar to that of the TiN target and the films obtained on (100) Si substrates. Transmission electron microscopy (TEM) studies were carried out to investigate the microstructure of the TiN films. The TEM

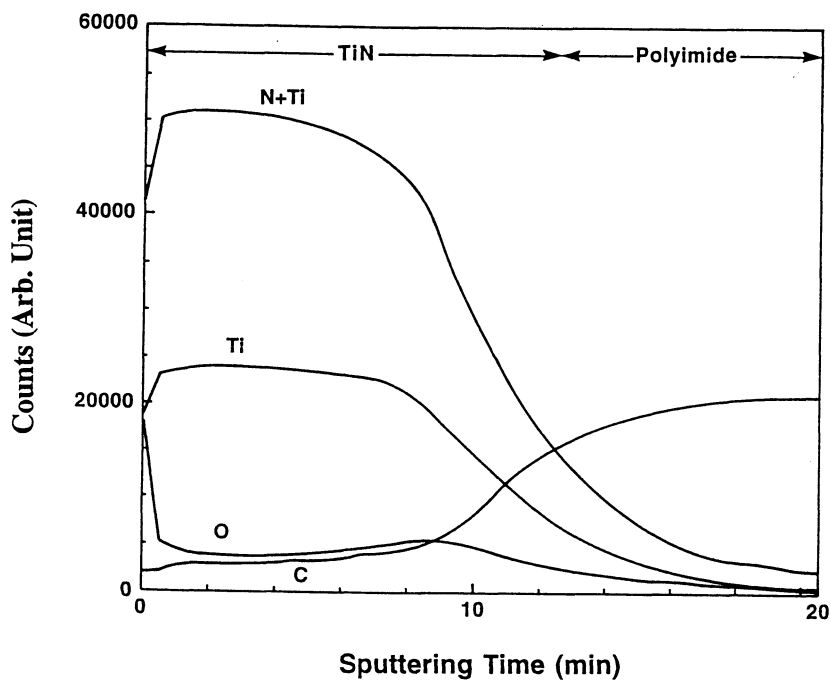


Figure 4. AES depth profiles of TiN film deposited at room temperature by PLD on polyimide.

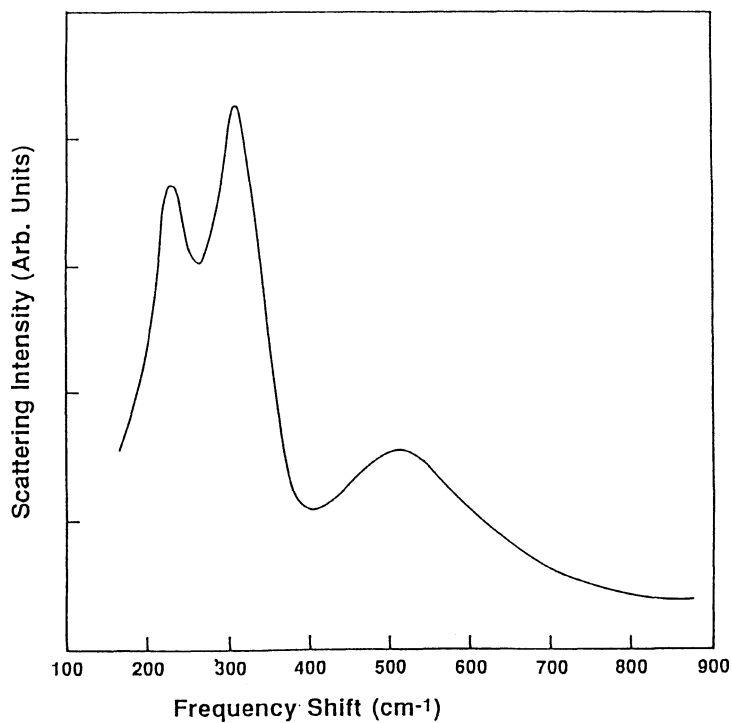


Figure 5. Raman spectrum of laser deposited TiN film at room temperature on PMMA substrate.

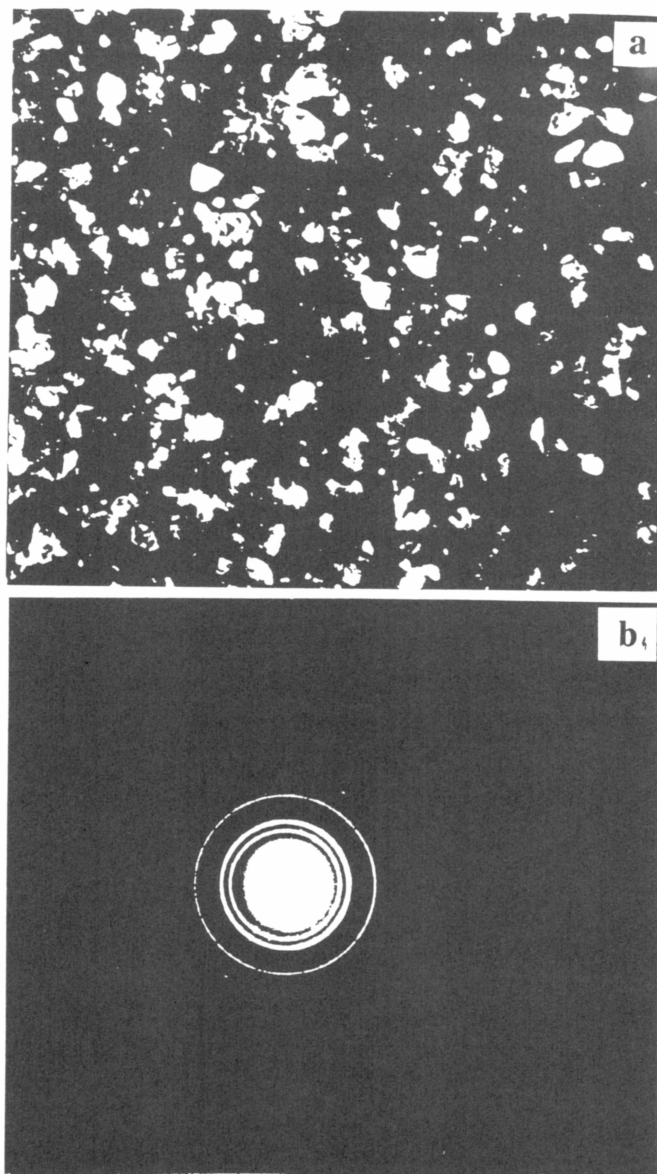


Figure 6. (a) Bright field planar TEM image of TiN film deposited at room temperature on PMMA. (b) Corresponding SAED pattern showing polycrystalline TiN film.

micrograph in Fig. 6 (a) shows that the TiN films are polycrystalline with an average grain size of 12 nm. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 6 (b). The SAED pattern clearly shows diffraction rings corresponding to (111), (200), (311), (400), and (331) planes of TiN. From the electron diffraction pattern, the lattice constant of TiN was found to be 0.421 nm which is very close to that of stoichiometric bulk TiN.

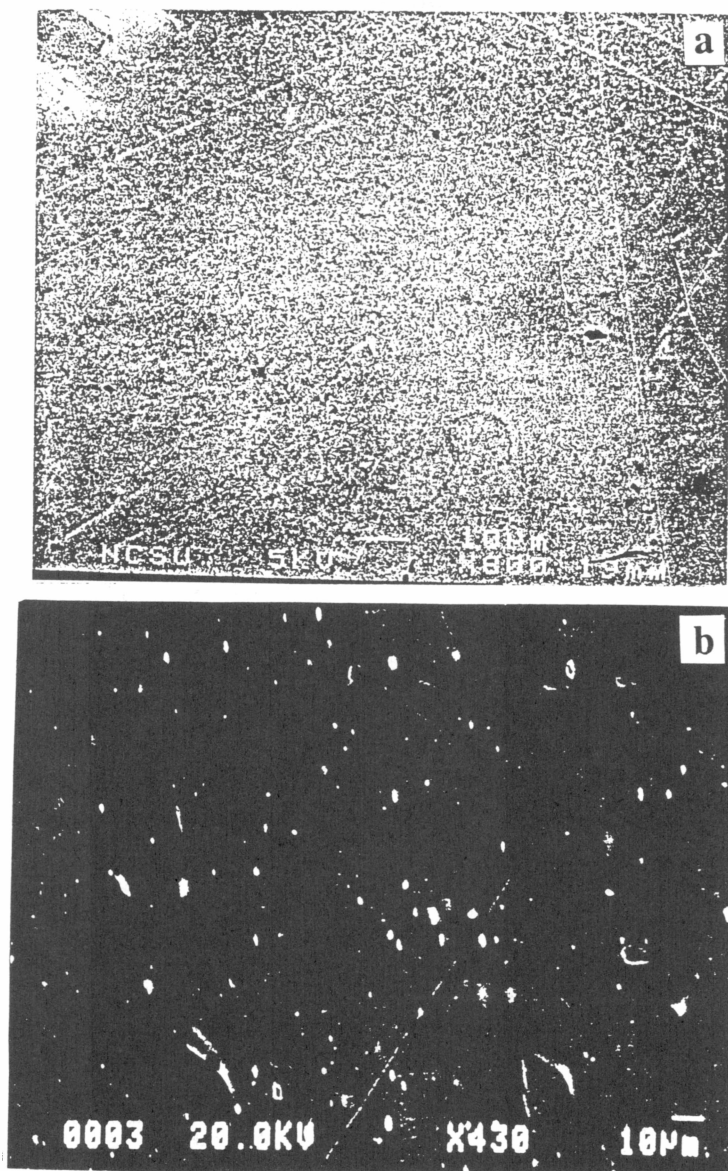


Figure 7. SEM micrographs of the TiN films on (a) polyimide and (b) PMMA deposited at room temperature by PLD.

The TiN films deposited on PMMA and polyimide substrates were examined by optical and scanning electron microscopies to study the surface smoothness of the laser deposited films. The SEM micrographs of the 50-60nm thick TiN films deposited on polyimide and PMMA at room temperature, laser fluence of $4\text{-}5\text{ J/cm}^2$ and base pressure of 1×10^{-7} Torr, are shown in Fig. 7(a) and (b), respectively. The films were found to be quite smooth and uniform. The

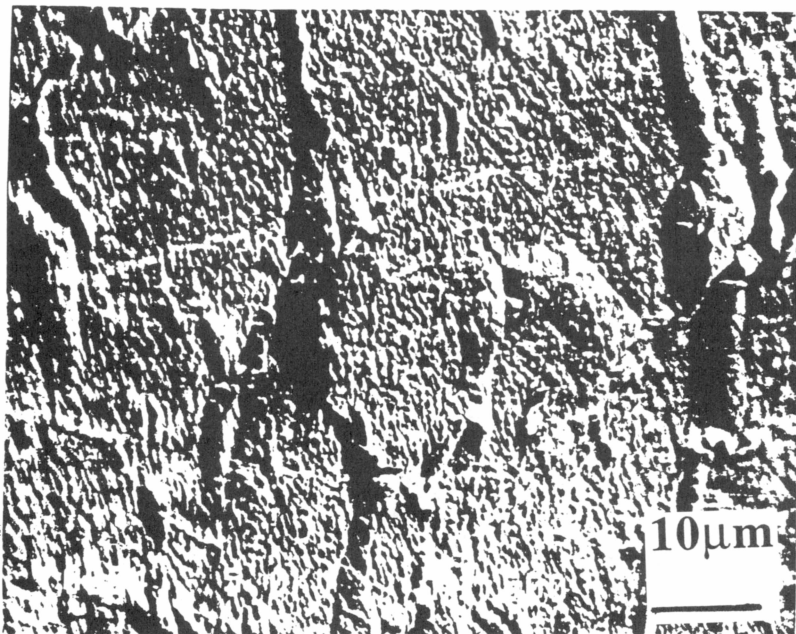


Figure 8. SEM micrographs of thicker (>100 nm) TiN film on PMMA showing peeling-off of the film.

high absorption of KrF laser by the TiN target is responsible for the uniform films with relatively low density of particles. The average particle density in all depositions at $4\text{--}5\text{ J/cm}^2$ was found to be less than 5×10^3 particles/cm². No significant effect of the pulse repetition rate on the surface morphology was observed, which indicates that the films can be grown at higher rates using the PLD technique. We have noted that as the TiN film thickness increased above a critical value, the volume strain accumulated which resulted in the peeling of the film. In the case of TiN films on PMMA, peeling of the film was observed above 80–85 nm. The films peeled off, as shown in Fig. 8, when the thickness was more than 80–85 nm. While in case of films deposited on polyimide, the interfacial bonding is much stronger than for TiN/PMMA resulting in smooth surface morphology without any peeling or cracking of the TiN films. These results are interesting since the adhesion of the metallized coatings on polymers is an important aspect of polymer metallization. It should be noted that the adhesion of a film on a substrate primarily depends on the method of thin film deposition (physical state of the depositing species), chemical properties of the participating materials (interatomic potentials and the nature of chemical bonding of the film with the substrate), physical characteristics of the substrate surface and its roughness, and substrate temperature. In our experiments, the strong adhesion of the TiN films with the polymer is expected due to the deposition of energetic (typically 20–50 eV) and excited Ti-N radicals. These radicals can form strong bonds at the interface by releasing their energies on the polymer surfaces at room temperature. To measure the adhesion of the laser deposited TiN films on polymers, the direct pull-off method^{4,15} was employed. A pulling device was

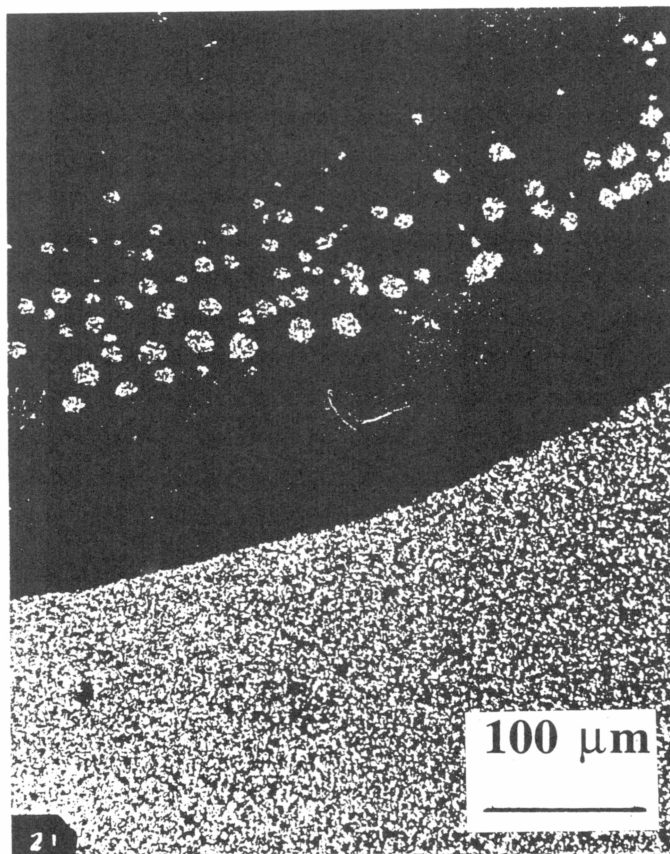


Figure 9. Optical micrograph of the detached area of TiN film from PMMA substrate after the pull-off test.

glued onto surface of the film and the bottom of the substrate. Then the film was pulled in the perpendicular direction using a tensile testing machine. The area of the pulling device was 4.31 cm^2 . A force of increasing magnitude was applied to the surface until the film was removed and the maximum force applied was measured. The area of the film detached from the substrate was measured by optical microscopy or SEM. The optical micrograph of the detached area of TiN film from the PMMA substrate is shown in Fig. 9. The pull-off forces for the TiN on PMMA and polyimide were found to be 1.85×10^7 and 5.61×10^7 Pa, respectively. These results clearly indicate the strong interfacial bonding of TiN with polymer substrates as compared to surface modified polymers and metals deposited by thermal evaporation and sputtering methods^{16,19}. We believe that the formation of energetic and excited Ti species during TiN laser ablation and the formation of a TiC bond at the interface with the polymer are likely to be responsible for the good adhesion of the TiN films. In fact, the formation of Ti-C bonds at the interface of Ti with polymers is reported for thermally evaporated Ti metal¹⁸⁻¹⁹. A low formation energy and the highly reactive nature of Ti are responsible for Ti-C bonding at the Ti-polymer interface.