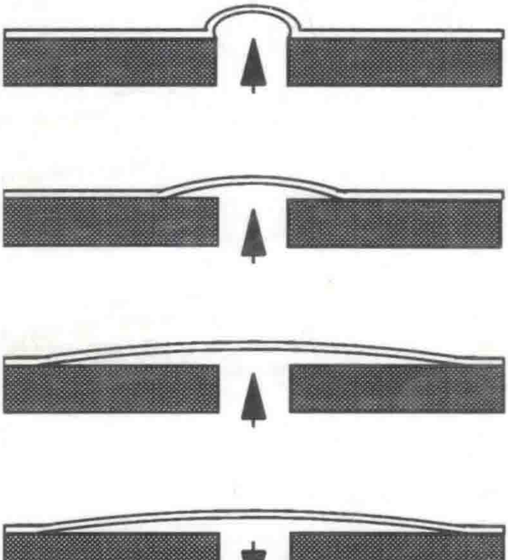
METALLIZED PLASTICS

FUNDAMENTALS AND APPLICATIONS



EDITED BY
K.L. MITTAL

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Preface

This volume embodies the proceedings of the Fourth Symposium on Metallized Plastics: Fundamental and Applied Aspects held under the auspices of the Dielectric Science and Technology Division of the Electrochemical Society in Honolulu, Hawaii, May 17–21, 1993. This event was a continuation of the series of symposia initiated in 1988 to address the burgeoning topic of metallized plastics. The previous symposia in this series were held as follows: the premier one in Chicago, October 10–12, 1998, the second in Montreal, Canada, May 7–10, 1990, and the third in Phoenix, Arizona, October 13–18, 1991. The proceedings of these three symposia have been duly documented.[1,2,3]

The final technical program for the fourth symposium comprised 40 invited and contributed papers covering both fundamental and applied aspects. Both overviews and original research contributions were included, and the authors represented many different disciplines. This patently confirmed the high level of interest and the interdisciplinary nature of the topic of metallized plastics.

As pointed out earlier[1], there are a legion of applications for metallized plastics, ranging from the very mundane (e.g., as decorative coatings) to high-tech (in microelectronics). Even a cursory look at the current literature will evince that the topic of metallized plastics is pursued with very keen interest, and all signals indicate that this high tempo of interest and R&D activity will continue unabated.

As for the present volume, it contains a total of 28 papers covering many ramifications of metallized plastics. It should be recorded that although the symposium was held in 1993, the authors were asked to update the information before inclusion in this volume; hence, the material is quite up-to-date. Also, it must be documented that all manuscripts were rigorously peer-reviewed and suitably revised before acceptance. In other words, this volume is not merely a compilation of as-received manuscripts, rather, it represents a compendium that has passed peer scrutiny.

The volume is divided into three parts: Part I, "Metallization Techniques and Properties of Metal Deposits," Part II, "Investigation of Interfacial Interactions," and Part III, "Plastic Surface Modification and Adhesion Aspects of Metallized Plastics." The topics covered include: various metallization techniques for a variety of plastic substrates; various properties of metal deposits; metal diffusion during metallization of high-temperature polymers; investigation of metal/polymer interfacial interactions using a variety of techniques, viz., ESCA, SIMS, HREELS, UV photoemission; theoretical studies of metal/polymer interfaces; computer simulation of dielectric relaxation at metal/insulator interfaces; surface modification of plastics by a host of techniques including wet chemical, plasma, ion bombardment and its influence on adhesion; adhesion aspects of metallized plastics including the use of blister test to study dynamic fracture mechanism of thin metallized plastics.

This and earlier volumes[1-3] offer bountiful information concerning many aspects of metallized plastics. I sincerely hope that anyone with serious or tangential interest in this topic will find great value in this latest book, which represents the cumulative wisdom of contemporary researchers and technologists in this arena.

Now comes the pleasant task of thanking those who helped in more ways than one. First and foremost, it is my sincere pleasure to mention that this symposium was jointly organized by yours truly, Dr. John R. Susko (formerly of IBM Endicott) and Professor Katsuhiko Nakamae (Kobe University, Japan), and thanks are extended to them. Thanks are also due to the appropriate officials of the Dielectric Science and Technology Division of the Electrochemical Society for sponsoring this event. My sincere thanks are extended to the unsung heroes (reviewers) for their many useful comments, which are *sine qua non* to maintain the highest standard of publications. My appreciation goes to my wife, Usha, for retyping some of the manuscripts and making the requisite corrections in others. I deeply appreciate the interest and patience of Anita Lekhwani of Marcel Dekker, Inc. Without the cooperation, interest and contributions of the authors this book would not have seen the light of day.

K. L. Mittal

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Part II. Investigation of Interfacial Interactions

Part III. Plastic Surface Modification and Adhesion Aspects of Metallized Plastics

Designing of Organometallics for Vapor Phase Metallization of Plastics

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Chemical vapor phase deposition (CVD) of metal films from organometallic precursors has become an increasingly active area of research. As well as affording a method for the generation of pure metal films, the technique allows deposition of metals under far milder conditions than those necessitated by conventional techniques. The advent of laser induced deposition offers scope not only for the deposition of metals on relatively fragile materials such as plastics but also the generation of microscale structures and patterning. In this review the design criteria for organometallic precursors for vapor phase metalization of plastics are discussed. Organometallic compounds of Ni, Pd and Pt are discussed.

THE CRITERIA

For an organometallic compound to be suitable for chemical vapor phase deposition it must fulfill several criteria. A CVD source compound must (1) be volatile, (2) be stable enough to undergo vapor phase transport to the substrate, (3) have weak metal to ligand bonds or a readily accessible decomposition route. Ideally it will be stable to air, light and moisture and be readily synthesized in high yield from commercially available starting materials. Hopefully, it will be non–toxic. In addition, the ligands attached to the metal must be (1) volatile, (2) stable against dissociation both in the gas phase and at the growing metal film surface and (3) desorb from both the plastic and metal surfaces without leaving residual contamination. For the deposition of corrosion resistant metals as conducting contacts on plastics there are additional requirements: (1) deposition should take place at ambient or close to ambient temperatures to avoid degradation of the plastic — this necessitates light or radiation induced deposition, (2) the organometallic complex should not react at the plastic surface in the absence of incident radiation initiating decomposition, (3) the incident radiation should not "burn" the plastic substrate, (4) the incident light (or radiation) should initiate decomposition only at the surface, and not in the gas phase as this would only lead to random deposition, and (5) the resultant metal film should adhere firmly to the surface.

LIGANDS

Early workers in the field favored the commercially available binary metal carbonyl complexes as CVD sources. These species are already in the zerovalent state and it was felt that the carbonyl groups would be readily lost on thermolysis or photolysis as had been demonstrated through simple substitution chemistry in solution. Furthermore, Mond et al.[1] had demonstrated in the last century that the reversible reaction of nickel with carbon monoxide afforded an excellent method for the production of pure nickel, a process still used industrially today.

$$\text{Ni(impure)+4CO} \rightarrow \text{volatile Ni(CO)}_4 \rightarrow \text{Ni(pure)+4CO}$$

However, as will be described below, deposition of thin films is a complex process involving reactivity both in the gas phase and at the surface and it was found that although binary metal carbonyls had many advantages, their suitability for the deposition of pure metal films is rarely one of them! With hindsight it is easy to rationalize why? Photolysis or thermolysis causes ejection of one or more carbonyl groups from the metal center. The unsaturated fragment binds to a nucleation site at the surface. Carbon monoxide on a metal surface can then undergo homolysis of the C–O bonds resulting in both carbon and oxygen contamination of the metal particles.

The elements of the nickel group are unique in that apart from the extensively studied $Ni(CO)_4$, binary metal carbonyl complexes are only known in low temperature matrices.[2] It is therefore necessary to utilize different complexes for the deposition of thin films of palladium and platinum.

This has led to the use of relatively novel organometallic complexes. For platinum deposition, the organometallics: $Pt(CO)_2Cl_2$,[3,4] $Pt(acac)_2$,[4,5] $Pt(F_3acac)_2$,[6] $Pt(PF_3)_4$,[7] $PtL_2(Me)R\{R{=}CH_3, \eta^1\text{–}CH_2CH{=}CH_2, CH{=}CH_2, C(CH_3)_3; L{=}CH_3NC$, 1,5–cycloocta-diene)[8-10]}, $Pt(\eta^5\text{–}C_5H_5)(CH_3)_3$ and $Pt(\eta^5\text{–}C_5H_4CH_3)\,(CH_3)_3$,[11-18] and $Pt(\eta^5\text{–}C_5H_5)\,(\eta^3\text{–}C_3H_5)$,[19,20] have been explored, although only $Pt(\eta^5\text{–}C_5H_5)(CH_3)_3$ has been explicitly considered for deposition on plastics.[18] For palladium deposition, the spin coating and subsequent photolysis of palladium acetate[21-28] has been the organometallic of choice for the metallization of plastics. Other palladium organometallic complexes $Pd(\eta^3\text{–}C_3H_5)_2$ and $Pd(\eta^3\text{–}CH_2C(CH_3)CH_2)_2$,[29] have been considered for the deposition of palladium thin films. Palladium has been photolytically deposited on Teflon™, Kapton™ and Ultem™ successfully using $Pd(\eta^5\text{–}C_5H_5)(\eta^3\text{–}C_3H_5)$.[30-35]

Generally, gas phase deposition is undertaken either in vacuum or in the presence of a carrier gas at ambient or reduced pressures. The carrier gas of choice is dihydrogen either alone or mixed with an inert gas such as dinitrogen or argon. There are good chemical reasons for the use of dihydrogen as will be explained below, but its high thermal conductivity may also play a significant part in assisting thermal decomposition in a flow system. Decomposition is commonly initiated by photolysis or pyrolysis (thermally). Photoassisted deposition has the advantage of low temperatures and more control over microstructure. Plasmas may also be used even at quite low temperatures, although the harsh conditions inherent in the use of plasma can be demanding on the deposition substrate, and lead to ligand decomposition (and subsequent incorporation of contaminants in the film).

In the last few years, studies have concentrated on the deposition of platinum thin films due to its superior resistance to corrosion. Although the carbon levels of platinum films deposited thermally is high (10–40 percent), recent workers have found that introduction of dihydrogen leads to dramatic reductions in the carbon content. Indeed platinum films containing less than 1 percent carbon have been reported.[12] It has been shown that in the presence of dihydrogen, catalytic hydrogenation of the organic ligands takes place leading to the formation of relatively inert saturated hydrocarbons that are readily eliminated[9,14] as shown below.

$$Pt(\eta^5\text{–}C_5H_5)(CH_3)_3 + 4H_2 \rightarrow Pt + C_5H_{10} + 3CH_4$$

Photoassisted deposition of platinum films has been investigated in conjunction with thermal deposition and as an initiation method in its own right. When used in conjunction with thermal methods, photolysis leads to an enhancement of the rate of deposition but appears to have little effect on the impurity levels. Films deposition solely by photolytic means also have high carbon content although there is evidence to suggest that the use of dihydrogen will decrease the carbon content of films produced by laser photolysis.[12]

Far fewer studies have been made with palladium than with platinum. This may be due to more limited chemistry available for the synthesis of suitable precursors since Pd(IV) is not a common oxidation state for palladium. Studies have concentrated on thermal decomposition from $Pd(\eta^3\text{–}C_3H_5)_2$ (and substituted analogs) and photodeposition from $Pd(\eta^5\text{–}C_5H_5)(\eta^3\text{–}C_3H_5)$.[29,30]

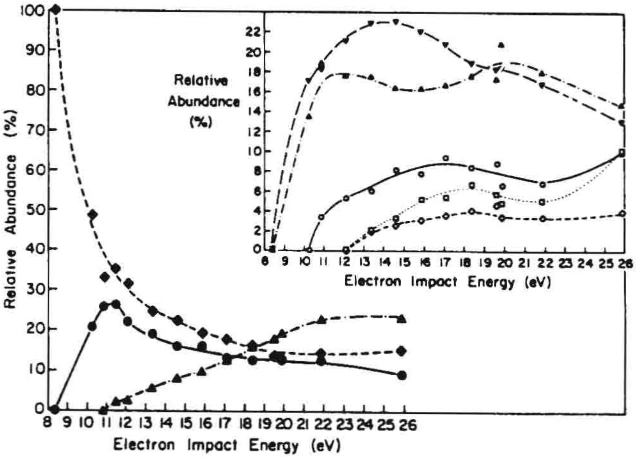

Figure 1. The breakdown diagrams for $Pd(C_5H_5)(C_3H_5)$ derived from electron impact ionization efficiency curves (IEC's). Relative intensities (abundance) are plotted as a function of electron impact energy, with an intensity of 100% implying that this is the only observed fragment. **Main Plots:** ♦ – – – parent $Pd(C_5H_5)(C_3H_5)^+$ ion, • $C_3H_5^+$ ion, ▲ — · — · $C_3H_3^+$ ion. **Corner inset plots:** ◊ – – – Pd^+ ion, ○— $PdC_5H_5^+$ ion, ☐ · · · · $PdC_3H_5^+$ ion, Δ –·–·– $C_5H_5^+$ ion, ∇ ——— $C_5H_6^+$ ion. Ion yields were collected in a magnetic sector mass spectrometer following ionization and fragmentation from electron impact. Taken from ref. 12.

DECOMPOSITION PATHWAYS

A surprising feature in deposition studies has been the marked differences in the decomposition mechanisms of isostructural precursors of palladium and platinum. This is evident