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Final Report on LDRD Project: Low-Cost Pd-Catalyzed Metallization Technology for Rapid Prototyping of Electronic Substrates and Devices

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Final Report on LDRD Project: Low-cost Pd-catalyzed Metallization Technology for Rapid Prototyping of Electronic Substrates and Devices

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Abstract

A low-cost, thermally-activated, palladium-catalyzed metallization process was developed for rapid prototyping of polymeric electronic substrates and devices. The process was successfully applied in producing adhesiveless copper/polyimide laminates with high peel strengths ($> 6 \text{ lbs/in}$) and thick copper coating ($> 25 \mu\text{m}$); copper/polyimide laminates are widely used in fabricating interconnects such as printed wiring boards (PWBs) and flexible circuits. Also successfully metallized using this low-cost metallization process were: i) scaled-down models of radar-and-communication antenna and waveguide; ii) scaled-down model of pulsed-power-accelerator electrode; iii) three-dimensional micro-porous, open-cell vitreous carbon foams. Moreover, additive patterned metallization was successfully achieved by selectively printing or plotting the catalyst ink only on areas where metallization is desired, and by uniform thermal activation. Additive patterned metallization eliminates the time-consuming, costly and environmentally-unfriendly etching process that is routinely carried out in conventional subtractive patterned metallization.

A metallization process via ultraviolet (UV) irradiation activation was also demonstrated. In this process palladium-catalyst solution is first uniformly coated onto the substrate. A masking pattern is used to cover the areas where metallization is NOT wanted. UV irradiation is applied uniformly to activate the palladium catalyst and to cure the polymer carrier in areas that are not covered by the mask. Metal is then deposited by electroless plating only or by a combination of electroless and electrolytic plating. This UV-activation technique is particularly useful in additive fine-line patterned metallization. Lastly, computer models for electrolytic and electroless plating processes were developed to provide guidance in plating-process design.

Acknowledgment

We would like to acknowledge the contributions made to the project by the summer interns/student employees: R. Limary, J. D. Kurtz, T. Gilligan and J. Garmon. We would like to thank G. L. Cessac for his contribution in writing the original LDRD proposal. We would also like to acknowledge the contributions by two other original team members, G. D. Peterson and S. E. Allen, in the early stage of the LDRD project. We are also indebted to M. E. Starig, M. B. Ritchey, T. Headley and M. J. Garcia, respectively, for performing peel-strength test, SEM, TEM and FTIR analyses. Lastly, fruitful collaborations with G. Prentice of UDM, and M. Ramasubramanian, B. N. Popov and R. E. White of USC were greatly appreciated.

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1 INTRODUCTION

Full-coverage and patterned metallized polymeric substrates find wide applications in the electronic industry as well as at Sandia: i) electronic interconnects such as printed wiring boards (PWBs), flexible circuits, and interconnection cables; ii) radar and communication antenna and horns (or waveguides); iii) pulsed power accelerator components (e.g. electrodes); iv) current-collecting pads in photovoltaic modules; v) intelligent micro-electro-mechanical system devices. The goal of the LDRD project was to develop a low-cost palladium-catalyzed metallization process for rapid prototyping of electronic substrates that are made of polymers.

In full-coverage applications, polymeric substrates are conventionally metallized by one of the following three techniques: 1) sputtering or physical vapor deposition (PVD); 2) metal foil/adhesive lamination; 3) electroless plating. In sputtering or PVD metallization processes, metal is deposited directly onto a substrate under high vacuum, usually the pressure is on the order of 10^{-6} torr. Because of the high vacuum environment required, the sputtering or PVD processes are expensive in both large capital investment and high operational costs. Also, very thin metal coating is usually deposited and adhesion between metal deposit and polymeric substrate is often poor (due to chemical dissimilarity between metal coating and polymeric substrate, and the lack of adhesion-anchoring layer). In metal foil/adhesive lamination metallization, a metal foil is laminated onto a polymeric substrate support using an adhesive layer. This technique is limited to flat sheet substrate and thus is not suitable for three-dimensional complex substrates. Also, it can be expensive in that the metal foil must be sufficiently thick for web (i.e. sheet substrate) handling. Moreover, the low-molecular-weight adhesive layer can become a weak link between the metal foil and the polymeric substrate under adverse conditions (e.g. elevated temperature or high humidity). Electroless plating metallization involves first catalyzing the substrate surface by a proper catalyst (e.g. palladium metal) and subsequent deposition of metal by electroless plating. In commercial electroless plating processes, polymeric substrates are sensitized by a $\text{PdCl}_2/\text{SnCl}_2$ slurry-salt mixture; Pd^{+2} is reduced to Pd^0 chemically in an activator; and Pd^0 is attached to the substrate by electrostatic forces. Commercial electroless plating processes usually involve eleven wet processing steps for substrate-surface treatment, sensitization, Pd^{2+} reduction, washing, etc. Due to chemical dissimilarity between metal coating and polymeric substrate, and the lack of adhesion-anchoring layer, the commercial electroless plating processes also suffer from poor adhesion. More details on advantages and disadvantages of various metallization techniques for polymeric substrates can be found in Appendix I, which presents a literature survey on metallization of polymeric substrates.

The first objective of the LDRD project was to develop a low-cost, full-coverage metallization process that create strong adhesion between the metal coating and the polymeric substrate by employing an intermediate layer (which consists of catalytic palladium metal clusters embedded in a polymer matrix that has chemical properties identical or similar to that of the substrate) that serves as catalyst in electroless plating and as anchor of adhesion between the metal coating and the polymeric substrate. The metallization process developed in this LDRD project involves the following steps: a) palladium-salt-catalyst solution is coated onto the substrate; here, the catalyst solution is comprised of a palladium salt (e.g. palladium chloride or palladium acetate) dispersed in a suitable organic or inorganic polymer carrier, which is in turn dissolved in a proper solvent, depending on the substrate used. b) solvent is removed by heat drying and catalytic palladium

metal clusters are generated by thermal or heat activation. c) seed metal layer (usually a fraction of a micron thick) is deposited by electroless plating. d) the electrolessly-plated sample is dried to remove the moisture penetrated into the catalyst layer and the interface between the catalyst layer and the substrate during electroless plating. This step helps enhance the overall adhesion between the metal coating and the polymeric substrate. e) desired metal thickness is deposited via electrolytic plating. The metallization process as described above is low-cost since it does not require i) high-vacuum operation (as in sputtering or PVD deposition) or ii) thick metal foil (as in metal foil/adhesive lamination metallization; it can deposit metal to thicknesses as desired) or iii) eleven wet processing steps (as in conventional electroless plating metallization; it needs only one wet processing step, i.e. catalyst-solution coating). Equally important is that adhesion between the polymeric substrate and the metal coating is fundamentally enhanced because of the existence of the semimetallic palladium-catalyst layer. On the one hand, polymer carrier in the catalyst layer bonds well to the polymeric substrate due to chemical similarity and the interdiffusion of polymer molecules between the catalyst layer and the substrate. On the other hand, metallic palladium clusters in the catalyst layer bond well to the metal coating because of electron sharing. In other words, the intermediate catalyst layer now serves as an anchor of adhesion between the metal coating and the polymeric substrate.

The second objective was to develop an additive process for pattern metallization. Conventionally, metal patterns, such as electronic interconnects, are fabricated by the so-called subtraction process, which involves three processing steps: a) start from a full-coverage metal film (normally copper) coated onto a polymeric substrate (e.g. Kapton, a polyimide film substrate manufactured and marketed by Du Pont). b) apply a layer of photoresist (i.e. a masking polymer) to cover the interconnect circuits, or patterns. c) etch away the copper metal outside the metal patterns to obtain the desired metal interconnects, circuits or patterns. The etching process is usually time-consuming, costly and environmentally unfriendly (due to the toxic chemicals used in the etching process). The key idea of an additive metallization process is to generate catalytic palladium clusters in areas where metallization is desired. This can be accomplished by either: 1) selectively print the palladium-catalyst ink on places where metallization is wanted; or 2) selectively activate the palladium catalyst (i.e. reduce Pd^{2+} ions to Pd^0 metal) on places where metallization is needed. In the former, palladium-catalyst activation can be carried out by uniformly supplying energy, e.g. heating.; in this case resolution of the metal pattern (i.e. metal line and spacing) is controlled by printing precision. In the latter, catalyst solution can be uniformly coated onto the substrate. After drying, masking can be performed to enable selective activation by, e.g., ultraviolet irradiation. In this case resolution of the metal pattern is controlled by masking precision. With additive pattern metallization, the time-consuming, costly and environmentally unfriendly etching process is eliminated.

The third objective was to develop computer models for electroless and electrolytic plating processes in order to provide guidance for process design.

In this report, summaries of the experimental development/studies and computer modeling work are provided in the following two sections. Details of the experimental and computer-modeling works are presented in Appendices A - H.

2 EXPERIMENTAL DEVELOPMENT AND STUDIES

Technical advances or inventions made in this project on metallization of polymeric substrates are documented in two United States patent applications as presented in Appendices A and B. Fundamental studies on effects of activation conditions on formation of catalytic palladium clusters (thus catalytic activity or platability) and extent of curing or polymerization of the polymer carrier (thus adhesion between the catalyst layer and the substrate) are reported in Appendices G and H, respectively. Accordingly, only a summary of the experimental development and studies carried out is given in this section.

2.1 Substrates

This LDRD project focused on nonconductive substrates that are made of polymers. Specifically, the following substrates were successfully metallized: polyimide, epoxy polymer, carbon foams, and IBM's biopolymer (also called "green" board substrate) substrates.

2.2 Catalyst formulation

The first step in our metallization process development was to develop catalyst formulations. A catalyst formulation is normally consisted of a palladium salt (e.g. palladium chloride or palladium acetate), a polymer carrier, and a solvent (or solvents). Concentrated ammonia is usually used to mix with the palladium salt to prevent Pd^{2+} from forming undesirable complexes with the polymer carrier. Also, a surfactant (or surfactants) is often added to the catalyst formulation to improve its wetting properties. For a catalyst formulation to work, it must meet the following requirements: 1) the polymer carrier must be completely dissoluble by a solvent (or solvents, preferably nontoxic or environmentally benign) so that a solution can be made. 2) the polymer carrier should not complex with palladium ions upon mixing with the palladium salt; 3) the polymer carrier should allow palladium ions to diffuse within a solid matrix of the polymer carrier so that catalytic palladium clusters with proper size and size-distribution can be generated. 4) the polymer carrier should, chemically, be identical or similar to (or at least compatible with) the substrate so that good adhesion can be created between the substrate and the solid polymer-carrier matrix.

Three catalyst formulations were developed in this project: 1) a polyamic-acid-based, high-temperature ($> 300^\circ\text{C}$) activation formulation that is suitable for substrates such as polyimide. 2) a polyvinyl-butyral-based, low-temperature ($\sim 180^\circ\text{C}$) activation formulation that works well on substrates such as epoxy polymers. 3) a polyvinyl-chloride latex resin-based, low-temperature ($\sim 180^\circ\text{C}$) activation formulation that is suitable for substrates such as carbon foams. The first two formulations are solvent based whereas the third one is aqueous based. Detailed compositions of the three catalyst formulations are documented in Appendix A.

2.3 Full-coverage metallization via thermal activation

This process was successfully developed and applied in producing adhesiveless copper/polyimide laminates with high peel strengths ($> 6\text{ lbs/in}$) and thick copper coating ($> 25\text{ }\mu\text{m}$). Also suc-

cessfully metallized using this low-cost metallization process were: i) scaled-down models of radar-and-communication antenna and waveguide. ii) scaled-down model of pulsed-power-accelerator electrode; iii) three-dimensional micro-porous, open-cell vitreous carbon foams. The process is consisted of the following steps: a) palladium-salt-catalyst solution is coated onto the substrate. b) solvent is removed by heat drying and catalytic palladium metal clusters are generated by thermal or heat activation. c) seed metal layer (usually a fraction of a micron thick) is deposited by electroless plating. d) the electrolessly-plated sample is dried to remove the moisture penetrated into the catalyst layer and the interface between the catalyst layer and the substrate during electroless plating. This step helps enhance the overall adhesion between the metal coating and the polymeric substrate. e) desired metal thickness is deposited via electrolytic plating. Further details on this process and its applications in adhesive-less copper/polyimide laminate fabrication, carbon-foam metallization, radar reflector metallization, and toroid metallization are documented in Appendix A.

2.4 Additive pattern metallization via selective catalyst printing and thermal activation

This process was successfully developed and it is consisted of the following steps: 1) catalyst ink is printed or plotted is onto the substrate. 2) solvent is removed by heat drying and catalytic palladium metal clusters are generated by thermal or heat activation. 3) seed metal layer (a fraction of a micron thick) is deposited by electroless plating. 4) the electrolessly-plated sample is dried to remove the moisture penetrated into the catalyst layer and the interface between the catalyst layer and the substrate during electroless plating. 5) desired metal thickness is deposited via electrolytic plating. Further details on this process can be found in Appendix A.

2.5 Additive pattern metallization via selective ultraviolet irradiation activation

This process was successfully demonstrated in producing fine-line (50-micron metal line and 50-micron spacing) electronic-circuit pattern. The process is consisted of the following steps: 1) catalyst solution is coated uniformly onto the substrate; solvent is removed by uniform heating. 2) a circuit pattern mask (e.g. made of Mylar, a polyester manufactured and marketed by Du Pont) is placed on top of the dried catalyst layer. 3) the masked catalyst surface is irradiated uniformly by ultraviolet light with proper wavelength (by using proper light filters) and intensity. 3) metal is deposited by electroless plating. Further details of this metallization process and its application is presented in Appendix B.

2.6 Selective metallized samples

Selective full-coverage and pattern metallized samples are shown in Figures 1 - 8. In the full-coverage metallized samples (Figures 1 - 3), the unmetallized parts (or substrates) were fabricated by Sandia's state-of-the-art stereolithography equipment. The thickness of copper deposited was more than 25 microns and adhesion was good. In Figure 4, 0.125 inch by 9 inch copper strips were additively metallized on a 125 micron thick Kapton sheet substrate with an average copper thickness of 28 microns. The adhesion between the copper coating and the Kapton substrate was excellent with an average peel strength of 9.2 lbs/inch. Other additively metallized samples are displayed in Figures 5 - 8: from copper text to current-collecting pads to simple electronic cir-

cuits.

2.7 Effects of thermal-activation conditions on the microstructure of catalytic palladium clusters

A fundamental experimental study was carried out to examine the effects of thermal-activation conditions on the microstructure (i.e. size and distribution) of catalytic palladium clusters, which in turn affects the catalytic activity and thus the platability in electroless plating. In this study effects of activation conditions (time and temperature) on the microstructure of palladium clusters were examined using transmission electron microscopy. It was found that the size of palladium clusters depended more on the dried catalyst thickness (which in turn depends on activation conditions) at temperature above 250° C (the study employed the high-temperature activation catalyst formulation and Kapton substrate). It was also found that the average size of palladium clusters must be 4 nanometers or greater in order to achieve uniform electroless plating. Effects of activation conditions on catalytic activity were studied by electrolessly plating the activated samples. The copper coating thickness was found to be sensitive to the electroless-plating bath make-up, making it difficult to correlate palladium cluster size with plating thickness. A detailed report on this study is presented in Appendix G.

2.8 Adhesion aspect of polymeric substrate metallization

A fundamental experimental study was conducted to examine the effects of the polyamic-acid imidization extent on the overall adhesion between the copper coating and the polyimide substrate. Specifically, the effects of varying thermal-activation temperature from one hour to four hours were studied. The overall adhesive or peel strength (between the copper coating and the Kapton substrate) was measured using the IPC-TM-650 technique. The extent of polyamic-acid imidization was characterized by the Fourier Transform Infrared Spectroscopy. Preliminary IR spectra analyses indicate that the extent of imidization does affect adhesion: IR spectra show that where high adhesive peel strength was obtained, full conversion of the polyamic acid to polyimide had occurred whereas in areas of low adhesive or peel strength, imidization had only been partially completed. A detailed report on this study is presented in Appendix H.

Figure 1. Metallized sample: toroid - scaled-down model of a pulsed-power accelerator electrode

Figure 2. Metallized sample: scaled-down model of a radar-and-communication antenna

Figure 3. Metallized sample: scaled-down model of radar-and-communication waveguide

Figure 4. Additively metallized copper strips on polyimide film substrate

Figure 5. Additively metallized copper text on polyimide film substrate

Figure 6. Additively metallized copper current-collecting pads for a photovoltaic module

Figure 7. Additively metallized copper electric-circuit pattern on IBM's biopolymer substrate

Figure 8. Additively metallized simple electronic circuit on polyimide film substrate

3 ELECTROLYTIC AND ELECTROLESS PLATING PROCESS MODELING

In order to provide guidance on design of the electrolytic and electroless plating processes (with which copper metal is deposited after the substrate surface is properly catalyzed), computer models were developed.

3.1 Electrolytic plating

A two-dimensional finite-difference model was developed for predicting current-density distribution along the cathode surface (i.e. the substrate surface on which copper is deposited) for various distances of separation between the cathode and the anode (copper metal source); this was accomplished using a modified Hull cell formed by a cathode plate and an anode plate at a 45 degree angle. The adhesion of the plated copper strips (i.e. peel-strength values along the cathode surface) on the cathode side of the modified Hull cell was measured by a 90 degree peel test using the IPC-TM-650 technique. On the one hand, current density along the cathode surface was predicted by the computer model to decrease with increasing separation between the cathode and the anode. On the other hand, it was found from peel tests that adhesion decreased also with increasing separation between the cathode and the anode. Thus, the increase in adhesion was directly attributed to and correlated with the increase in current density on the cathode surface though the detailed mechanism(s) involved awaits further study. Details of the computer model and how it was used to study effects of current density on adhesion of copper electrodeposits to polyimide substrates are presented in Appendix C.

3.2 Electroless plating

A mathematical model on solution equilibrium characteristics of electroless copper plating baths (both EDTA-based and tartrate-based) was developed in order to determine the optimal process conditions (e.g. bath pH) of electroless plating, a key process in depositing copper on a polymeric substrate (e.g. polyimide). Details of this modeling work are documented in Appendix D (see also Appendix E).

A one-dimensional computer model was developed for the tartrate-based electroless-copper-plating process in order to analyze the transport of ionic species in the diffusion-dominant layer near the catalyzed-substrate surface and electrochemical reactions on the substrate surface. The model employs the mixed potential theory and takes into account of mass transport by diffusion and migration as well as Butler-Volmer kinetics on the substrate surface. In all, eight ionic species are considered in the model. A finite-difference approach with explicit time integration is used to solve the resultant set of coupled, highly nonlinear, and stiff governing equations. The model was used to predict the concentration profiles, potential response, and plating thickness as functions of time and bulk concentrations of various reactive components. Details of the computer model and a case study are presented in Appendix F.

4 LIST OF PUBLICATIONS

- 1) K. S. Chen, W. P. Morgan, and J. L. Zich 1996 "Low-cost Pd-catalyzed metallization technology for rapid prototyping of electronic substrate and devices", a *Sandia Technical Advance disclosure* filed on October 3, 1996.
- 2) K. S. Chen 1996 "Polymeric-substrate metallization research at Sandia National Laboratories", an invited paper presented at the 1996 AIMCAL (Association of Industrial Metallizers, Coaters and Laminators) Fall Conference, October 21 - 23, Atlanta, GA.
- 3) K. S. Chen, W. P. Morgan and J. L. Zich 1996 "An environmentally conscious additive plating process for patterned metallization on polymeric substrates", a paper presented at the 1996 AIChE Annual Meeting, November 10 - 15, Chicago, IL.
- 4) K. S. Chen, W. P. Morgan, and J. L. Zich 1997 "Process for metallization of a substrate", United States patent application filed on April 29, 1997. This patent application addresses the issue of polymeric-substrate metallization via palladium catalyzation and thermal activation.
- 5) K. S. Chen, W. P. Morgan, and J. L. Zich 1997 "Process for metallization of a substrate", United States patent application filed on December 8, 1997. This patent application addresses the issue of fine-line metallization of polymeric substrates via palladium catalyzation and ultraviolet activation.
- 6) M. Ramasubramanian, B. N. Popov, R. E. White, and K. S. Chen 1997 "Equilibrium characteristics of tartrate and EDTA-based electroless copper deposition baths", 1997 AESF - Surface Finish Conference Proceedings, American Electroplaters and Surface Finishers Society, Orlando, FL., session L - Research.
- 7) J. D. Kurtz 1997 "Effects of Processing Parameters on Microstructures of Palladium Catalysts as an Intermediate Layer in Polymeric Metallization", a Senior Independent Project Report, Department of Chemistry, Kalamazoo College, Kalamazoo, MI.
- 8) G. Prentice and K. S. Chen 1998 "Effects of current density on adhesion of copper electrodeposits to polyimide substrate", a paper accepted for publication in *J. of Applied Electrochemistry*.
- 9) M. Ramasubramanian, B. N. Popov, R. E. White, and K. S. Chen 1998 "Experimental study and solution equilibrium characteristics of electroless copper deposition on thermally-activated palladium-catalyzed polyimide substrates", a paper accepted for publication in *J. of Applied Electrochemistry*.
- 10) M. Ramasubramanian, B. N. Popov, R. E. White, and K. S. Chen 1998 "A mathematical model for electroless copper deposition on planar electrodes", a paper to be submitted to *J. Electrochem. Soc.*
- 11) A. Kurugangi, E. E. Kalu and K. S. Chen 1998 "A feasibility study of one-step additive pattern plating for printed wiring boards fabrications", in preparation.

5 SUMMARY AND PROJECT IMPACT

A low-cost, thermally-activated, palladium-catalyzed metallization process was developed for rapid prototyping of polymeric electronic substrates and devices. The process was successfully applied in producing adhesiveless copper/polyimide laminates with high peel strengths ($> 6 \text{ lbs/in}$) and thick copper coating ($> 25 \mu\text{m}$); copper/polyimide laminates are widely used in fabricating interconnects such as printed wiring boards (PWBs) and flexible circuits. Also successfully metallized using this low-cost metallization process were: i) scaled-down models of radar-and-communication antenna and waveguide; ii) scaled-down model of pulsed-power-accelerator electrode; iii) three-dimensional micro-porous, open-cell vitreous carbon foams. Moreover, additive patterned metallization was successfully achieved by selectively printing or plotting the catalyst ink only on areas where metallization is desired, and by uniform thermal activation. Additive patterned metallization eliminates the time-consuming, costly and environmentally-unfriendly etching process that is routinely carried out in conventional subtractive patterned metallization. A United States patent application was filed to document this invention.

A metallization process via ultraviolet (UV) irradiation activation was also demonstrated. In this process palladium-catalyst solution is first uniformly coated onto the substrate. A masking pattern is used to cover the areas where metallization is NOT wanted. UV irradiation is applied uniformly to activate the palladium catalyst and to cure the polymer carrier in areas that are not covered by the mask. Metal is then deposited by electroless/electrolytic plating. This UV-activation technique is particularly useful in additive fine-line patterned metallization. A United State patent application was filed to document this invention.

Lastly, computer models for electrolytic and electroless plating processes were developed to provide guidance in plating process design. The computer-modeling works were reported in four publications (see Appendices C, D, E and F, respectively).

The low-cost palladium-catalyzed metallization processes developed in this LDRD project have direct impacts on fabrication of electronic interconnects such as PWBs and flexible circuits. They can also potentially impact the fabrication of microelectronic interconnects, particularly in replacing aluminum (currently used as interconnect metal) by the much more conductive copper, because the catalyst layer (palladium embedded in a polymer carrier) may serve effectively as: i) a copper-diffusion barrier; ii) a dielectric material; iii) a catalyst for electroless plating. The metallization processes developed can find wide applications at Sandia, besides electronic packaging: e.g. the fabrication of pulsed-power accelerator components, advanced radar and communication antenna and horns, photovoltaic modules, and intelligent micro-electro-mechanical system devices.

Key Relevant LDRD Project Information:

Number of Technical Advance Disclosure resulting from this project:	1
Number of U. S. patent applications resulting from this project:	2
Number of refereed publications resulting from this project:	3
Number of proceeding publications resulting from this project:	1
Number of students supported by the project:	4

6 APPENDICES

Appendix A

PROCESS FOR METALLIZATION OF A SUBSTRATE

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A U. S. patent application filed on April 29, 1997 on metallization via thermal activation.

PROCESS FOR METALLIZATION OF A SUBSTRATE

This invention was made with Government support under Contract DE-AC04-94AL85000 awarded by the U. S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

This invention relates to the field of additive metallization of substrates.

Many electronic applications require patterned metallization of nonconductive substrates for interconnection among electronic devices. Examples of such applications include high density packaging (multi-chip modules), antennas, flex circuits, printed wiring boards, and flat panel
5 displays. The metallic interconnects are conventionally formed by subtractive processes. Modern additive processes attempt to overcome the drawbacks of subtractive processes.

In a subtractive metallization process, a surface of the substrate is first fully coated. Alternatively, a metal sheet can be laminated onto a flat substrate using adhesive. Selected portions of the metal plating are then etched to leave the desired patterned metallization.
10 Vacuum-assisted physical vapor deposition and sputtering deposition are often used to achieve en masse plating. Physical vapor and sputtering deposition require high vacuum, and consequentially high capital equipment and operating costs. Those deposition processes can also result in poor adhesion of the metal to the substrate.

Full coverage metal plating can also be achieved by sensitizing a surface of the substrate with
15 a palladium chloride/tin chloride bath and chemically reducing palladium ions to form catalytic clusters. Electroless plating followed by electrolytic plating deposits metal on the surface. This process can be costly due to the large number of wet processing steps, and the chemical dissimilarity between the metal coating and the substrate discourages chemical bonding therebetween. Consequently, the metal only weakly adheres to the substrate.

After full coverage metal plating, a layer of resist (a photoresist is often used) is deposited in a pattern on top of the metal layer, with the pattern corresponding to the desired metallization pattern. A subsequent etching step removes all the metal except that protected by the patterned resist layer. The etching process is usually time consuming and costly, and can require the use of materials unfriendly to the environment.

Additive processes have been proposed to overcome the environmental drawbacks of subtractive processes. The additive processes proposed achieve only thin layers of metallization, limiting their practical applications. See, e.g., Tokas et al., U.S. Patent 5,348,574. The proposed processes also suffer from poor adhesion, just as with the subtractive processes. Some of the additive processes retain resist and etching steps; consequently, they suffer from the same environmental hazards as the subtractive processes. See, e.g., Hirsch et al., U.S. Patent 5,192,581. Others have process limitations that limit their uses with widely available substrate materials. See, e.g., Orlowski et al., U.S. Patent 5,153,023. Metal/foil adhesive processes use costly thick metal foils and poorly adhering low molecular weight polymer adhesives.

Accordingly, there remains a need for improved additive metallization processes, specifically for processes that provide improved adhesion between the substrate and the metallization and that can provide the increased metallization thickness required in practical applications such as printed wiring boards.

SUMMARY OF THE INVENTION

The present invention provides an improved additive process for metallization of substrates. The improved process comprises applying a catalyst solution onto the substrate. The catalyst solution can coat an entire surface of the substrate or can be selectively applied to only a portion of a substrate surface. The concentration of solvent in the layer of catalyst solution on the substrate surface can be reduced by heating the coated substrate. Metallic clusters can be formed in the remaining catalyst layer by further heating the substrate. Electroless plating can then deposit metal onto the coated portion of the substrate. Additional metallization thickness can

be obtained by electrolytically plating the substrate after the electroless plating step. The improved process requires only one wet processing step (applying the catalyst solution onto the substrate) and does not require a high vacuum, so capital and operational costs are less than with existing processes. The improved process also does not require an etching step, avoiding the environmental hazards of chemical etching. The improved process results in improved adhesion of the metallization to the substrate and increased metallization thickness, making it suitable for a wider range of applications than existing processes.

Advantages and novel features will become apparent to those skilled in the art upon examination of the following description or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

DESCRIPTION OF THE FIGURES

The accompanying drawings, which are incorporated into and form part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

Figure 1(a-d) shows a substrate during processing according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for metallization of substrates.

Figure 1(a-d) shows a substrate during processing according to the present invention. The process comprises applying a catalyst solution 2 to a surface of a substrate 1. The catalyst solution 2 comprises a solvent, a carrier, and metal catalyst ions. The catalyst solution 2 can cover an entire surface of the substrate 1 or can be selectively applied to only a portion of a surface of substrate 1. The concentration of solvent in the layer of catalyst solution 2 on the surface of substrate 1 can be reduced by heating the substrate 1. Metallic clusters 3 can be formed in the remaining catalyst layer by further heating the substrate 1. Electroless plating can then deposit metal 4 onto the portion of the surface of substrate 1 coated with the catalyst

solution. Electrolytic plating can then deposit additional metal 5 onto the portion of the surface of substrate 1 coated with the catalyst solution.

Application performance objectives often constrain the choice of a substrate material. For example, the application might require that the substrate be a good electrical insulator. The application might require that the substrate remain stable when subjected to very high or very low temperatures, or to certain temperature variations. The application might require a substrate capable of withstanding repeated stretching or bending cycles. The application might also require that the substrate have properties compatible with other components (e.g., thermal expansion).

The present invention is suitable for use with commonly used organic polymeric substrate materials such as polyimide, polyester, polyurethane, and epoxy-based polymers. It is also suitable for use with other substrate materials such as microporous carbon foams.

The choice of substrate material affects the composition chosen for the catalyst solution. The catalyst solution comprises a suitable polymer carrier (including monomers and oligomers), catalyst ions, and a solvent or solvents. Palladium can be used as a catalyst because of its low cost. Gold, platinum, iridium, rhodium, and ruthenium can also be used as catalysts. Palladium ions can be obtained by dissolving a palladium salt (e.g., palladium chloride or palladium acetate) in the catalyst solution. Ammonium hydroxide can be used to complex the catalyst ions to prevent them from forming complexes with the polymer carrier. The catalyst solution can comprise additional components such as surfactants to improve wettability and hence uniformity of substrate coverage. The specific choices for carrier and solvent can depend on the substrate chemistry and surface features, as discussed below.

The polymer carrier can be chosen so that it achieves several basic objectives:

- The polymer carrier should be dissolved by the solvent so that a solution results.
- The polymer carrier should not complex with palladium ions on mixing with the palladium salt.
- The polymer carrier should allow palladium ions to diffuse within a solid matrix of the polymer carrier during activation.

- The polymer carrier should be identical to, similar to, or compatible with the substrate upon solidification so that good adhesion is created between the substrate and the solid matrix of the polymer carrier.

For organic polymer substrate material, numerous polymers, including monomers and

5 oligomers, can be suitable carriers. A polyamic-acid carrier can be used with solvents such as 1-methyl-2-pyrrolidinone. For example, a solution of 34.6% by weight polyamic acid, 62.35% by weight 1-methyl-2-pyrrolidinone, 0.925% by weight palladium acetate, 2.1% by weight concentrated ammonia hydroxide, and 0.025% by weight FC 430 (a fluoroaliphatic polymeric ester surfactant from 3M Corporation) forms a suitable catalyst solution. A polyamic-acid carrier
10 becomes polyimide once polymerized or cured, and therefore is especially suitable for use with polyimide substrate materials. Polyamic-acid carriers can require high curing temperatures (approximately 300 C to 330°C), and are therefore not suitable for use with substrates that cannot withstand such temperatures.

A polyvinyl butyral carrier can be used with a solvent such as a mixture of 4-methyl-2-pentanol
15 and n-butanol. For example, a solution of 4.9% by weight polyvinyl butyral, 1.45% by weight palladium chloride, 30.0% by weight 4-methyl-2-pentanol, and the remainder n-butanol forms a suitable catalyst solution.

A polyvinyl chloride latex resin carrier can be used with water as a solvent. Aqueous solutions can be less environmentally hazardous than organic solvent-based solutions. For example, a
20 solution of 18.2% by weight polyvinyl chloride latex resin, 3.3% by weight butyl cellosolve, 3.4% by weight palladium acetate, 7.5% by weight concentrated ammonium hydroxide, 5.4% by weight polyurethane resin (such as the ACRYCOL RM-8W thickening agent marketed by Rohm and Haas), 4.5% by weight Triton-X 100 (a polyethylene glycol-based surfactant marketed by Aldrich), and the remainder water forms a suitable catalyst formulation. Both the polyvinyl butyral carrier
25 and the polyvinyl chloride latex carrier can be cured at low temperatures (approximately 150°C to 190°C). Accordingly, they are suitable for use with substrates such as polyester and epoxy-based polymers that cannot withstand the high temperatures needed for curing a polyamic-acid carrier.

The catalyst solution is applied to a surface of the substrate. Dipping, spraying, slide coating, slot coating, roll coating, Meyer-rod coating, gravure coating, and draw-down processes known to those skilled in the art can coat an entire surface of the substrate. Full coating can result in full metallization of the substrate surface. Etching processes known to those skilled in the art can be used to remove selected portions of the full coating if a patterned metallization is required.

Alternatively, processes such as screen printing, flexographic printing, plotting, ink-jet printing, and gravure printing can apply catalyst solution to only selected portions of the substrate surface. The substrate surface will be metallized only where the catalyst solution was applied. Accordingly, a patterned application of catalyst solution can result in patterned substrate metallization without costly and hazardous etching processes.

Processing such as heating the substrate can reduce the concentration of solvent in the catalyst solution on the substrate surface. Solvent removal can dry the catalyst coating and allow easier handling and storage. A properly dried catalyst layer on a substrate can be stored for many years before activation. For example, a polyamic-acid catalyst solution on a polyimide substrate can be dried by heating it for 15 minutes to 60 minutes at temperatures of 50°C to 100°C. For ease of handling, the majority of the solvent should be removed. Excessive drying temperatures should be avoided because they can trap solvent beneath thick polymer carrier surface skins. Generally, heating to at least one third the boiling temperature of the solvent until at least half the solvent is removed is desirable; heating until 90% of the solvent is removed is preferred.

Thermal energy supplied to the substrate and catalyst coating activates the palladium catalyst. Thermal activation accomplishes several important tasks:

- It produces catalytic metallic palladium clusters by reducing the palladium ion to palladium metal and by diffusion of palladium metal to form clusters by nucleation and growth.
- It polymerizes or otherwise cures the polymer carrier in the catalyst coating to foster cohesive strength within the cured carrier.
- It fosters interdiffusion of molecules between the substrate and the polymer carrier, causing enhanced adhesion between the substrate and the cured polymer carrier.

In general, long exposure to temperatures sufficient to soften the substrate (i.e., above the glass transition temperature of the substrate) and cure the polymer carrier is desirable. The activation must not melt the substrate, but long exposure to sufficient temperatures promotes adhesion between the substrate and the polymer carrier. Long exposure to sufficient

5 temperatures also promotes complete cure of the polymer carrier, fostering adhesion of the palladium or other catalyst and resulting metallization to the polymer carrier. For a polyamic-acid catalyst solution on a polyimide substrate material, the catalyst-coated substrate can be subjected to activation temperatures of approximately 300°C to 330°C (320°C preferred) for at least 15 minutes. Longer times, 120 minutes or more, are preferred. For polyvinyl butyral and PVC
10 latex catalyst solutions, the catalyst coated substrate can be subjected to temperatures of approximately 150°C to 190°C for at least 15 minutes.

After thermal activation, any one of a plurality of electroless plating processes can deposit metal on the substrate. Electroless plating processes are known to those skilled in the art. See, e.g., *Electroless Plating: Fundamentals and Applications*, edited by G. O. Mallory and
15 J. B. Hajdu, 1990. Commercial copper plating baths, for example Shipley Cuposit 328, are suitable for use with the present invention (Shipley Cuposit 328 bath conditions: 3 g/L suspended copper, 7.5 g/L formaldehyde, 23°C operating temperature, 10.2 bath pH). Other metals such as gold, silver, and nickel can also be deposited. In electroless plating, reducing agents such as formaldehyde are oxidized to produce electrons. Metal ions in the plating bath consume the
20 electrons and are reduced to metal. The reduction chemical reaction proceeds in the presence of a catalyst such as palladium metal or palladium metal clusters. Palladium metal clusters greater than 5 nm in size are effective as catalysts in electroless plating processes.

Heating the substrate after electroless plating can significantly increase adhesion of the metallization to the substrate. The mechanisms involved are not yet well understood, but
25 additional heating can remove moisture at the polymer-metal interface that reduces bonding strength. Additional heating can also cause oxidation of metal at the polymer-metal interface, which can increase bonding strength and thereby improve adhesion. Additional heating can also

help further cure the polymer carrier. For example, heating for at least one hour at 80°C to 200°C (two hours at 170°C preferred) is suitable.

Existing electroless plating processes can normally deposit metal up to a few microns thick in a reasonable time. A new commercial copper bath, Circuposit 71 Full Build Electroless Copper, marketed by Shipley, can deposit 25 microns of copper in ten hours. It has also been reported that 25 micron thick copper can be deposited using commercial baths in eight to fourteen hours. See, e.g., "Electroless Plating: Fundamentals and Applications," Chapter 13, edited by Mallory and Hajdu, 1990.

Alternatively, electrolytic plating can be used to deposit additional metal to the desired thickness on the seed metal layer formed by electroless plating. Electrolytic plating is more efficient (has a higher plating rate) than electroless plating. Electrolytic plating processes comprise applying an electric current through a copper anode to provide electrons needed in the reduction chemical reaction at the cathode and are known to those skilled in the art. See, e.g., Electroplating (a chapter in Comprehensive Treatise of Electrochemistry Vol. 2, Bockris, Conway, Yeager, and White, Plenum Press, NY 1981); Fundamentals of Metal Deposition (Raub and Muller, Elsevier, Amsterdam, 1967). Commercial electrolytic plating solutions, for example the LeaRonan Glean Copper PC Plating Bath, can be used to increase the metal thickness from the seed metal layer deposited by electroless plating (LeaRonan Glean Copper PC Plating Bath composition: 12 oz./gal. copper sulfate, 25 oz./gal. sulfuric acid, 70 ppm chloride, 0.5% Copper Glean PC additive; process conditions: air agitation, 30 amps/square foot cathode current density, phosphorized copper anode).

The following non-limiting examples further illustrate the invention.

EXAMPLE 1

Polyamic-acid catalyst ink was plotted on a 5 mil thick Kapton sheet substrate using a 7475A Hewlett-Packard plotter to produce a pattern comprising ten 0.125 inch by 9 inch strips covered with catalyst solution and nine 0.0625 inch by 9 inch spacing strips (i.e., without catalyst coverage). One end of the strips were open (i.e., they were not connected to anything) but the

other ends were connected to a 1 inch by 4 inch strip that was covered with catalyst solution.

After plotting, the sample was immediately transferred to a low-temperature oven and dried at 80°C for 30 minutes. It took about 15 minutes to complete the plotting, during which time the plotted strips were air dried. After drying, the sample was further heated in a high-temperature

5 oven at 320°C for four hours. The sample was then air-cooled at room temperature until the entire sample reached room temperature. Next, the sample was placed vertically into a Shipley Cuposit 328 electroless copper bath and plated at room temperature (23°C) for 60 minutes. The electrolessly plated sample was heated in an oven at 150°C for 2 hours. After cooling the sample to room temperature, it was electrolytically plated in a LeaRonol Gleam Copper PC Plating bath at
10 room temperature for three hours at an applied current density of 5.5 amps/square foot. Peel strength test using the IPC-TM-650 technique was performed on the sample one week after electrolytic plating (the sample was left on the bench during the week). It was found that the catalyzed strips were uniformly plated (with an average copper thickness of 1.13 mil or about 28 microns) and that the adhesion between the copper coating and the Kapton substrate was
15 substantially uniform with an average peel strength of 9.2 lbs/inch.

EXAMPLE 2

A 1 inch by 3 inch by 0.25 inch microporous open-cell vitreous carbon foam with an average pore size of 80 ppi (ppi refers to pores per inch) was immersed in the polyvinyl chloride latex resin catalyst solution for 1 minute. Excess catalyst solution was blown out of the pores with

20 compressed nitrogen. The sample was then dried in an oven at 60°C for 30 minutes. After drying, the sample was further heated in an oven at 180°C for 60 minutes. After air cooling, the sample was then plated in a Shipley Cuposit 328 electroless copper bath for 60 minutes. The plated microporous carbon sample was found to be uniformly plated with good adhesion. The above process was repeated on a 1 inch by 3 inch by 0.25 inch microporous polyurethane foam with a
25 similar average pore size and the foam was uniformly plated with good adhesion.

EXAMPLE 3

A 9.25 inch by 4 inch radar reflector's concave parabolic surface was brush coated with a layer of polyvinyl butyral catalyst solution. The radar-reflector was made of epoxy polymer and was fabricated using a stereolithography technique. The coated sample was dried in an oven at 60°C for 30 minutes. After drying, the sample was further heated in an oven at 180°C for 60 minutes. After air cooling, the sample was then plated in a Shipley Cuposit 328 electroless copper bath for 15 minutes. The part was then electrolytically plated in a LeaRonol Gleam Copper PC Plating bath at room temperature for one hour at an applied current density of 20 amps/square foot. The plating on the radar-reflector surface was substantially uniform with good adhesion.

EXAMPLE 4

A toroid (3 inch outside diameter, 1 inch inside diameter, and the diameter of the circle from which the toroid was formed by rotating it is 1 inch) made of epoxy polymer using stereolithography was brush coated with a layer of polyvinyl butyral catalyst solution. The coated sample was dried in an oven at 60°C for 30 minutes. After drying, the sample was further heated in an oven at 180°C for 60 minutes. After air cooling, the sample was then plated in a Shipley Cuposit 328 electroless copper bath for 15 minutes. The part was then electrolytically plated in a LeaRonol Gleam Copper PC Plating bath at room temperature for one hour at an applied current density of 20 amps/square foot. The plating on the toroid surface was substantially uniform with good adhesion.

The particular sizes and equipment discussed above are cited merely to illustrate particular embodiments of the invention. It is contemplated that the use of the invention may involve components having different sizes and characteristics. It is intended that the scope of the invention be defined by the claims appended hereto.

ABSTRACT OF THE DISCLOSURE

An improved additive process for metallization of substrates is described whereby a catalyst solution is applied to a surface of a substrate. Metallic catalytic clusters can be formed in the catalyst solution on the substrate surface by heating the substrate. Electroless plating can then deposit metal onto the portion of the substrate surface coated with catalyst solution. Additional metallization thickness can be obtained by electrolytically plating the substrate surface after the electroless plating step.

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Appendix B

PROCESS FOR METALLIZATION OF A SUBSTRATE

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A U. S. patent application filed on December 8, 1997 on metallization via ultraviolet activation.

PROCESS FOR METALLIZATION OF A SUBSTRATE

This invention was made with Government support under Contract DE-AC04-94AL85000 awarded by the U. S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

This invention relates to the field of additive metallization of substrates.

Many electronic applications require patterned metallization of nonconductive substrates for interconnection among electronic devices. Examples of such applications include high density packaging (multi-chip modules), antennas, flex circuits, printed wiring boards, and flat panel displays. The metallic interconnects are conventionally formed by subtractive processes. Modern additive processes attempt to overcome the drawbacks of subtractive processes.

In a subtractive metallization process, a surface of the substrate is first fully coated. Alternatively, a metal sheet can be laminated onto a flat substrate using adhesive. Selected portions of the metal plating are then etched to leave the desired patterned metallization. Vacuum-assisted physical vapor deposition and sputtering deposition are often used to achieve en masse plating. Physical vapor and sputtering deposition require high vacuum, and consequentially high capital equipment and operating costs. Those deposition processes can also result in poor adhesion of the metal to the substrate.

Full coverage metal plating can also be achieved by sensitizing a surface of the substrate with a palladium chloride/tin chloride bath and chemically reducing palladium ions to form catalytic clusters. Electroless plating followed by electrolytic plating deposits metal on the surface. This process can be costly due to the large number of wet processing steps, and the chemical dissimilarity between the metal coating and the substrate discourages chemical bonding therebetween. Consequently, the metal only weakly adheres to the substrate.

After full coverage metal plating, a layer of resist (a photoresist is often used) is deposited in a pattern on top of the metal layer, with the pattern corresponding to the desired metallization pattern. A subsequent etching step removes all the metal except that protected by the patterned resist layer. The etching process is usually time consuming and costly, and can require the use of materials unfriendly to the environment.

Additive processes have been proposed to overcome the environmental drawbacks of subtractive processes. Current additive processes achieve only thin layers of metallization, limiting their practical applications. See, e.g., *Tokas et al.*, U.S. Patent 5,348,574. Current additive processes also suffer from poor adhesion, just as with the subtractive processes. Some of the additive processes retain resist and etching steps; consequently, they suffer from the same environmental hazards as the subtractive processes. See, e.g., *Hirsch et al.*, U.S. Patent 5,192,581. Others have process limitations that limit their uses with widely available substrate materials. See, e.g., *Orlowski et al.*, U.S. Patent 5,153,023. Metal/foil adhesive processes use costly thick metal foils and poorly adhering low molecular weight polymer adhesives.

Accordingly, there remains a need for improved additive metallization processes, specifically for processes that provide fine line metallization and that can provide the increased metallization thickness required in practical applications such as printed wiring boards.

SUMMARY OF THE INVENTION

The present invention provides an improved process for additive metallization of substrates. The improved process comprises applying a catalyst solution onto the substrate. The catalyst solution can coat an entire surface of the substrate or can be selectively applied to only a portion of a substrate surface. The concentration of solvent in the layer of catalyst solution on the substrate surface can be reduced by heating the coated substrate. Metallic clusters can be formed in the remaining catalyst layer by irradiating the substrate with suitable electromagnetic radiation. Masks, lithographic processes, or optical focusing can provide precision control of the cluster formation, allowing subsequent metallization steps to realize high density features.

Electroless plating can then deposit metal onto the coated portion of the substrate. Additional metallization thickness can be obtained by electrolytically plating the substrate after the electroless plating step. The improved process requires only one wet processing step (applying the catalyst solution onto the substrate) and does not require a high vacuum, so capital and operational costs are less than with existing processes. The improved process also does not require an etching step, avoiding the environmental hazards of chemical etching. The improved process results in increased metallization thickness, making it suitable for a wider range of applications than existing processes. The improved process can provide very fine metallic features, allowing high density connections.

Advantages and novel features will become apparent to those skilled in the art upon examination of the following description or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

DESCRIPTION OF THE FIGURES

The accompanying drawings, which are incorporated into and form part of the specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

Figure 1(a-d) shows a substrate during processing according to the present invention.

Figure 2 shows plating results with varying radiation wavelength.

Figure 3 shows plating results with varying radiation energy flux.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a novel process for additive metallization of substrates.

Figure 1(a-f) shows a substrate during processing according to the present invention. The process comprises applying a catalyst solution 2 to a surface of a substrate 1. The catalyst solution 2 comprises a solvent, a carrier, and metal catalyst ions. The catalyst solution 2 can cover an entire surface of the substrate 1 or can be selectively applied to only a portion of a

surface of substrate 1 using techniques known to those skilled in the art. Figure 1b shows the substrate after the concentration of solvent in the layer of catalyst solution 2 on the surface of substrate 1 has been reduced. By way of example, heating can reduce the concentration of solvent in the layer of catalyst solution 2 on the surface of substrate 1 and also dry the surface, allowing easier handling during subsequent processing.

Figure 1c shows the substrate 1 with a mask 6 mounted thereon. Mask 6 can shield portions of the substrate 1 from irradiation (represented by lines 7 in the figure). Mask 6 can have cutouts 8 corresponding to portions of the substrate 1 where metallization is desired. Irradiating the substrate 1 with appropriate electromagnetic radiation can form metallic clusters in the portions of the remaining catalyst layer not blocked by mask 6.

Figure 1d shows the substrate 1 after metallic clusters 3 have been formed in the catalyst layer 2. The portions of the catalyst layer 9 shielded by the mask 6 have no metallic clusters; the shaded portions corresponding to cutouts in the mask 6 have metallic clusters 3.

Figure 1e shows the substrate after electroless plating has deposited metal 4 onto the portions of the surface of substrate 1 containing metallic clusters. If desired, electrolytic plating can then deposit additional metal 5 onto metal deposited electrolessly, as shown in Figure 1f.

Application performance objectives often constrain the choice of a substrate material. For example, the application might require that the substrate be a good electrical insulator. The application might require that the substrate remain stable when subjected to very high or very low temperatures, or to certain temperature variations. The application might require a substrate capable of withstanding repeated stretching or bending cycles. The application might also require that the substrate have properties compatible with other components (e.g., thermal expansion). The present invention is suitable for use with, for example, commonly used organic polymeric substrate materials such as polyimide, polyester, polyurethane, and epoxy-based polymers.

The choice of substrate material affects the composition chosen for the catalyst solution. The catalyst solution comprises a suitable polymer carrier (including monomers and oligomers), catalyst ions, and a solvent or solvents. Palladium can be used as a catalyst because of its low

cost. Gold, platinum, iridium, rhodium, and ruthenium can also be used as catalysts. Palladium ions can be obtained by dissolving a palladium salt (e.g., palladium chloride or palladium acetate) in the catalyst solution. Ammonium hydroxide can be used to complex the catalyst ions to prevent them from forming complexes with the polymer carrier. The catalyst solution can comprise additional components such as surfactants to improve wettability and hence uniformity of substrate coverage. The specific choices for carrier and solvent can depend on the substrate chemistry and surface features, as discussed below.

The polymer carrier can be chosen so that it achieves several basic objectives:

- The polymer carrier should be dissolved by the solvent so that a solution results.
- The polymer carrier should not complex with palladium ions on mixing with the palladium salt.
- The polymer carrier should allow palladium ions, palladium atoms, or both to diffuse within a solid matrix of the polymer carrier during activation.
- The polymer carrier should be identical to, similar to, or compatible with the substrate upon solidification so that good adhesion is created between the substrate and the solid matrix of the polymer carrier.

For organic polymer substrate material, numerous polymers, including monomers and oligomers, can be suitable carriers. A polyamic-acid carrier can be used with solvents such as 1-methyl-2-pyrrolidinone. For example, a solution of 34.6% by weight polyamic acid, 62.35% by weight 1-methyl-2-pyrrolidinone, 0.925% by weight palladium acetate, 2.1% by weight concentrated ammonia hydroxide, and 0.025% by weight FC 430 (a fluoroaliphatic polymeric ester surfactant from 3M Corporation) forms a suitable catalyst solution. A polyamic-acid carrier becomes polyimide once polymerized or cured, and therefore is especially suitable for use with polyimide substrate materials. Skybond 3300 (24-28% polymer content, 10,000-20,000 cps viscosity), from Summit Precision Polymers Corporation, is an example of a suitable polyamic acid.

A polyvinyl butyral carrier can be used with a solvent such as a mixture of 4-methyl-2-pentanol and n-butanol. For example, a solution of 4.9% by weight polyvinyl butyral, 1.45% by weight palladium chloride, 30.0% by weight 4-methyl-2-pentanol, and the remainder n-butanol forms a suitable catalyst solution.

5 A polyvinyl chloride latex resin carrier can be used with water as a solvent. Aqueous solutions can be less environmentally hazardous than organic solvent-based solutions. For example, a solution of 18.2% by weight polyvinyl chloride latex resin, 3.3% by weight butyl cellosolve, 3.4% by weight palladium acetate, 7.5% by weight concentrated ammonium hydroxide, 5.4% by weight polyurethane resin (such as the ACRY SOL RM-8W thickening agent marketed by Rohm and
10 Haas), 4.5% by weight Triton-X 100 (a polyethylene glycol-based surfactant marketed by Aldrich), and the remainder water forms a suitable catalyst formulation. Both the polyvinyl butyral carrier and the polyvinyl chloride latex carrier can be cured at low temperatures (approximately 150°C to 190°C). Accordingly, they are suitable for use with substrates such as polyester and epoxy-based polymers that cannot withstand the high temperatures needed for curing a polyamic-acid carrier.

15 The catalyst solution is applied to a surface of the substrate. Dipping, spraying, slide coating, slot coating, roll coating, Meyer-rod coating, gravure coating, and draw-down processes known to those skilled in the art can coat an entire surface of the substrate. Full coating can result in full metallization of the substrate surface, or selective metallization if irradiation is selective. Alternatively, processes such as screen printing, flexographic printing, plotting, ink-jet printing,
20 and gravure printing can apply catalyst solution to only selected portions of the substrate surface. The substrate surface will be metallized only where the catalyst solution was applied and subsequently irradiated.

Processing such as heating the substrate can reduce the concentration of solvent in the catalyst solution on the substrate surface. Solvent removal can dry the catalyst coating and allow
25 easier handling and storage. A properly dried catalyst layer on a substrate can be stored for many years before activation. For example, a polyamic-acid catalyst solution on a polyimide substrate can be dried by heating it for 15 minutes to 60 minutes at temperatures of 50°C to 100°C. For

ease of handling, the majority of the solvent should be removed. Excessive drying temperatures should be avoided because they can trap solvent beneath thick polymer carrier surface skins. Generally, heating to at least one third the boiling temperature of the solvent until at least half the solvent is removed is desirable; heating until 90% of the solvent is removed is preferred.

5 Electromagnetic radiation supplied to the substrate and catalyst coating activates the palladium catalyst. Irradiative activation accomplishes several important tasks:

- It produces catalytic metallic palladium clusters by reducing the palladium ion to palladium metal and by diffusion of palladium metal to form clusters by nucleation and growth.
- It polymerizes or otherwise cures the polymer carrier in the catalyst coating to foster
10 cohesive strength within the cured carrier.
- It fosters interdiffusion of molecules between the substrate and the polymer carrier, causing enhanced adhesion between the substrate and the cured polymer carrier.

Lithographic techniques known to those skilled in the art can be used to selectively irradiate portions of the coated substrate. For a Skybond 3300 catalyst solution, irradiation with ultraviolet
15 light, having a wavelength from 300 nm to 390 nm (310 nm to 350 nm preferred) with a total energy flux of over 15.0 joules per square centimeter can activate the catalyst layer. The specific wavelength and total energy flux required can be dependent on the choice of catalyst; wavelengths and energy fluxes sufficient to form palladium clusters averaging at least about 5nm can result in satisfactory plating.

20 After irradiative activation, any one of a plurality of electroless plating processes can deposit metal on the substrate. Electroless plating processes are known to those skilled in the art. See, e.g., *Electroless Plating: Fundamentals and Applications*, edited by G. O. Mallory and J. B. Hajdu, 1990. Commercial copper plating baths, for example Shipley Cuposit 328, are suitable for use with the present invention (Shipley Cuposit 328 bath conditions: 3 g/L suspended
25 copper, 7.5 g/L formaldehyde, 23°C operating temperature, 10.2 bath pH). Other metals such as gold, silver, and nickel can also be deposited. In electroless plating, reducing agents such as formaldehyde are oxidized to produce electrons. Metal ions in the plating bath consume the

electrons and are reduced to metal. The reduction chemical reaction proceeds in the presence of a catalyst such as palladium metal or palladium metal clusters. Palladium metal clusters greater than 5 nm in average size are effective as catalysts in electroless plating processes.

5 Heating the substrate after electroless plating can significantly increase adhesion of the metallization to the substrate. In general, long exposure to temperatures sufficient to soften the substrate (i.e., above the glass transition temperature of the substrate) and cure the polymer carrier is desirable. The heating must not melt the substrate, but long exposure to sufficient temperatures promotes adhesion between the substrate and the polymer carrier. For example, a substrate can be heated for at least one hour at 80°C to 200°C (two hours at 170°C preferred)

10 Heating can also remove moisture at the polymer-metal interface that reduces bonding strength. Heating can also cause oxidation of metal at the polymer-metal interface, which can increase bonding strength and thereby improve adhesion. Additional heating can also help further cure the polymer carrier.

Existing electroless plating processes can normally deposit metal up to a few microns thick in a reasonable time. A new commercial copper bath, Circuposit 71 Full Build Electroless Copper,

15 marketed by Shipley, can deposit 25 microns of copper in ten hours. It has also been reported that 25 micron thick copper can be deposited using commercial baths in eight to fourteen hours. See, e.g., "Electroless Plating: Fundamentals and Applications," Chapter 13, edited by Mallory and Hajdu, 1990.

20 Alternatively, electrolytic plating can be used to deposit additional metal to the desired thickness on the seed metal layer formed by electroless plating. Electrolytic plating is more efficient (has a higher plating rate) than electroless plating. Electrolytic plating processes comprise applying an electric current through a copper anode to provide electrons needed in the reduction chemical reaction at the cathode and are known to those skilled in the art. See, e.g.,

25 Electroplating (a chapter in Comprehensive Treatise of Electrochemistry Vol. 2, Bockris, Conway, Yeager, and White, Plenum Press, NY 1981); Fundamentals of Metal Deposition (Raub and Muller, Elsevier, Amsterdam, 1967). Commercial electrolytic plating solutions, for example the

LeaRonol Glean Copper PC Plating Bath, can be used to increase the metal thickness from the seed metal layer deposited by electroless plating (LeaRonol Glean Copper PC Plating Bath composition: 12 oz./gal. copper sulfate, 25 oz./gal. sulfuric acid, 70 ppm chloride, 0.5% Copper Glean PC additive; process conditions: air agitation, 30 amps/square foot cathode current density, 5 phosphorized copper anode).

The following non-limiting examples further illustrate the invention.

EXAMPLE 1

This example demonstrated that ultraviolet light or electromagnetic waves can be employed to activate or generate palladium clusters that are necessary to catalyze the substrate surface for electroless plating in fine-line patterned metallization applications. A Skybond 3300 polyamic acid (purchased from Summit Precision Polymers in Fort Lee, NJ) catalyst solution was coated onto a 10 2.75 inch x 6 inch, 5 mil thick Kapton sheet substrate uniformly using a GARDCO size 20 metering rod (or draw-down bar; available from GARDCO Company). After coating, the sample was immediately transferred to a low-temperature oven and dried at 80°C for 30 minutes. After 15 drying, the sample was placed on top of a 5.75 inch x 4.875 inch and 0.125 inch thick Soda Lime Float glass. A Mylar circuit pattern mask was placed on top of the sample. A 5.75 inch x 4.875 inch and 0.125 inch thick Soda Lime Float glass was then placed on top of the Mylar mask. Next, the glass-sample-mask-glass sandwich was placed outdoor in the direct New Mexico sunlight (starting at 9:15 A.M.) while simultaneously activating a DYNACHEM model 500 20 UV Integrating Radiometer. The sample was irradiated with direct sunlight for 6 hours (from 9:15 A.M. to 3:15 P.M.) and the Radiometer registered a total energy flux of 22.4 joules per square cm (or J/cm²). The UV-activated sample was then placed vertically into a Shipley Cuposit 328 electroless copper bath and plated at room temperature (23°C) for 30 minutes. The plated sample was rinsed with water and dried by blowing nitrogen gas on it. It was observed that copper 25 was plated uniformly on the unmasked areas to yield a circuit pattern with 2 mil (50 microns) metal lines and 2 mil spacing between lines. Adhesion was tested by applying common

transparent tape, with pressure, to the metallized areas. Peeling the tape produced no apparent metal separations from the substrate.

EXAMPLE 2

This example demonstrated the relationship between catalyst activation and the wavelength of ultraviolet (UV) light or electromagnetic waves employed. A 5.5 inch x 4.5 inch, 5 mil thick Kapton substrate was coated with the Skybond polyamic acid catalyst solution using a GARDCO size 20 metering rod, and dried at 80°C for 30 minutes (as in Example 1). The sample was then placed on top of one piece of 5.75 inch x 4.875 inch and 0.125 inch thick Soda Lime Float glass. Filters, which pass only selected wavelengths of light, were placed on the top surface of the sample and then the filter-covered sample was subjected to UV radiation. Various filter and wavelength combinations were tested. The sample, along with the filters sitting on the top surface being irradiated, was placed outdoors (starting at 9 A.M.) for eight hours. The UV-activated sample was then placed vertically into a Shipley Cuposit 328 electroless copper bath and plated at room temperature (23°C) for 30 minutes. The results obtained are summarized in Figure 2. In the figure, "Wavelength" refers to the wavelength of light passed through the filter and to the substrate.

EXAMPLE 3

This example demonstrated how the total energy flux impinging on the catalyst layer affects the catalytic activity and thus plating quality. Seven dried catalyst samples were prepared the same way as in Examples 1 & 2. All seven samples were placed outdoors in direct sunlight for catalyst activation. The activation process was terminated at 30 minute intervals by taking one sample off UV radiation at a time and recording the total energy flux then indicated by a Radiometer. The UV-activated samples were then placed vertically into a Shipley Cuposit 328 electroless copper bath and plated at room temperature (23°C) for 30 minutes. The results obtained are summarized in Figure 3. The plating quality for samples with total energy flux greater than about 24.7 Joules per square centimeter were about the same.

The particular sizes and equipment discussed above are cited merely to illustrate particular embodiments of the invention. It is contemplated that the use of the invention may involve

components having different sizes and characteristics. It is intended that the scope of the invention be defined by the claims appended hereto.

ABSTRACT OF THE DISCLOSURE

An improved additive process for metallization of substrates is described whereby a catalyst solution is applied to a surface of a substrate. Metallic catalytic clusters can be formed in the catalyst solution on the substrate surface by irradiating the substrate. Electroless plating can
5 then deposit metal onto the portion of the substrate surface having metallic clusters. Additional metallization thickness can be obtained by electrolytically plating the substrate surface after the electroless plating step.

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Figure 1e

Figure 1f

Length of UV activation (hours)	Total energy flux (J/cm ²)	Plating quality
2.0	11.4	no plating
2.5	15.0	no plating
3.0	19.5	poor plating
3.5	24.7	good plating
4.5	27.5	good plating
5.0	34.0	good plating
5.5	35.0	good plating

Figure 3

Wavelength	Plating Quality
>780 nm	no plating
>700 nm	no plating
> 630 nm	no plating
520 nm	no plating
440 nm	no plating
400 nm	no plating
>390 nm	no plating
350 nm	poor plating
330 nm	good plating
326.1 nm	good plating
310 nm	poor plating
300 nm	no plating
266.5 nm	no plating
254 nm	no plating
220 nm	no plating

Figure 2

Effects of Processing Parameters on Microstructures of Palladium Catalysts as an Intermediate Layer in Polymeric Metallization

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Preface

This paper is submitted as the written requirement for the senior individual project. This requirement was completed at Sandia National Laboratories in Albuquerque, New Mexico, under the supervision of Ken S. Chen of the Engineering Sciences Center. I would like to thank the staff at Sandia National Laboratories for the opportunity to work in the facility. Also, I would like to thank Dominique Foley Wilson (an alumnus of Kalamazoo College) for facilitating this opportunity.

ABSTRACT

Sandia National Laboratories has developed a unique palladium-catalyzed thermally activated metallization process¹. In this process a palladium-catalyst layer is created in which metallic palladium clusters are embedded in polymer matrix that has identical or similar chemical make-up to the nonconductive substrate. The process involves coating and drying the catalyst solution, thermal activation of the metal catalyst clusters and curing of the polymeric carrier. A seed layer of copper is then deposited via electroless plating. The final step involves electrolytic plating to raise the metal thickness. By introducing the intermediate palladium catalyst layer, adhesion is promoted between the metallic copper and nonconductive substrates. Polymeric substrate metallization has widespread defense and industrial applications including: circuit boards, electromagnetic shielding, antennas, and heat spreaders².

The catalytic activity of the clusters is strongly dependent on the size and distribution of their microstructures, which in turn is dependent on the conditions of activation. Activation is a process in which palladium ions are reduced to their metallic state and enlarged into clusters via thermal heating. In this study effects of activation conditions (time and temperature) on the microstructures were examined using transmission electron microscopy. It was found that the size of palladium clusters depended more on the dried catalyst layer thickness (which in turn depends on activation conditions) at temperatures above 250 °C. It was also found that a minimum of 4 nm in size (on average) was required for palladium clusters to sufficiently catalyze a desired uniform copper coating. Effects on catalytic activity were studied by electroless plating; whether or not plating occurred, uniformity of metal coverage, and thickness of the coating. It was found that electroless bath make-up influenced the copper coating thickness more so than palladium cluster size. Size of palladium microstructures effected uniformity of coverage and adhesion.

¹ Chen, K.S., Morgan, W.P., Zich, J.L. *Process for Metallization of a Substrate* United States Patent Application filed on April 29, 1997.

² Karas, B. et al. *J. Adhesion Sci. Technol.* 1992, 6, No. 5, 557-567.

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INTRODUCTION

Metallization

History. Metallization in this thesis refers to the process of depositing a layer of metal coating onto a nonconductive substrate. The substrate of interest in this study is a polymer: specifically polyimide. Metallization of nonconductive substrates has long been of interest to humankind, and archeological studies have dated evidence to Egyptian times. Although the metallization process still remains unknown, the artifacts that remain are metallized wood and terra cotta. The next known example of metallization occurred in the early 1800s when an alchemist was accredited with successfully plating the inside of a test tube with metallic silver in an experiment involving the reduction of an aldehyde. Since then metallization of non-metals- ranging from graphite to animals and human corpses- have been reported¹.

Modern Applications. Today, many practical uses exist for metallization of nonconductive substrates. Electromagnetic shielding, reflectors, conductors for electric current, and aerospace applications are just some of the metallization techniques used that involve polymeric substrates². Consumer applications include heat spreaders in coffeepots. Polymeric metallization is particularly important in microelectronics in the production of circuit boards. Sandia National Laboratories has interests in polymeric metallization for defense and industrial applications.

Metallization Techniques- *Vacuum Deposition.* Existing metallization technologies are numerous. Each has benefits and drawbacks specific to the method at hand. Current methods include vacuum deposition, metal foil/adhesive lamination, and direct metallization. In vacuum deposition, the target metal is physically vaporized or sputtered and deposited in its atomic form directly onto a substrate while the system is under high vacuum (the system pressure is as low as 10^{-6} torr)³. Although this method is fast and reproducible, its need for specialized and sophisticated equipment makes the technology capital intensive. The operational expense of maintaining the high-vacuum condition during metallization is also a problem. Additionally, a subtractive etching process is required to obtain an appropriate metal pattern. Etching utilizes harsh and toxic chemicals that require special handling and disposal; thus, it is extremely environmentally unfriendly.

Metallization Techniques- *Metal Foil/Adhesive Lamination.* In metal foil/adhesive lamination an intermediate adhesive layer is used to bond the metal coating to the polymeric substrate. This adhesive is normally an epoxy or acrylic-based polymer. A metal foil is laminated onto a polymeric base film using a press at an applied pressure and elevated temperature⁴. This technique has often been the method of choice for wiring boards and flex circuits because the conductive layer is readily obtained on the surface of the nonconductive material. The substrate shape is limited, however, to sheet films because the lamination process is normally carried out on a laminating press. The materials are expensive, and require a thick metal sheet to facilitate proper web handling.

Finally, the low molecular weight adhesive can become a weak link between the metal coating and the polymer substrate under high temperatures and high humidities.

Metallization Techniques- Direct Metallization. Direct metallization via electroless plating is a new technique of growing interest. Sandia National Laboratories is working to improve a process that incorporates an intermediate catalyst layer that bonds well to both the polymeric substrate and the metallic coating. The substrate surface can be catalyzed in two ways: 1) by chemically reducing Pd^{2+} ions to Pd^0 by e.g., SnCl_2 (as in conventional electroless plating processes), and 2) by thermally activating, or reducing, the palladium ions to metallic palladium (as in the thermal metallization process being developed at Sandia). The catalyst layer, initially, (i.e. when first deposited) is a palladium salt dispersed in a polyamic acid solution. Upon heating, the polyamic acid is converted to a polyimide in a process known as imidization:

The substrate is normally a polyimide or equivalent polymer, so bonding is greatly enhanced due to the similarity in chemical make-up. Palladium ions are reduced to metallic palladium in the heating process, which in turn, can catalyze the copper reduction chemical reaction in the subsequent electroless plating process. The catalyst layer can bond well to the metal coating because it shares electrons with the metallic palladium⁵. Sandia's metallization process consists of three basic steps: 1) the catalyst solution is coated onto the substrate; 2) heating: the drying step is a low temperature heating to drive off solvents (and avoid the detrimental effect of skinning which traps solvents which results in extremely poor plating and adhesion), and the subsequent high temperature heating of the activation step initiates the reduction reaction of palladium ions to its metallic or atomic state (its catalytic form), and also converts the polyamic acid carrier to polyimide; 3) metal is deposited by electroless plating. Copper is the metal of choice because it offers several advantages: it has a high electrical conductivity over chromium or nickel, high ductility over aluminum, and it is relatively inexpensive compared to gold⁶.

It is known that good plating in the electroless bath correlates to successful activation. It has been hypothesized that a minimum of 5 nm is needed of the palladium microstructures in order for plating to occur⁵. If the clusters are too large, the copper plates too rapidly and blistering occurs. If the clusters are too small, plating does not occur at all or is spotty.

Objectives

The goal of this research was to understand how process conditions affect the microstructure of catalytic palladium clusters. Effects of activation conditions (time and temperature) on the microstructures of the palladium clusters and plating quality were examined using high resolution transmission electron microscopy (TEM). Effects on the catalytic activity were studied by electroless plating: whether or not plating occurs and uniformity of metal coverage. Finally, the interface between the palladium clusters and copper coating was examined via chemical analysis by transmission electron microscopy.

Transmission Electron Microscopy

Imaging. When resolution is needed, electron microscopes are necessary for investigation of tiny particles. Its basis utilizes an electron beam to produce enlarged images on an nonhomogeneous magnetic field⁷. A magnetic field created by a tungsten hairpin heated to incandescence replaces the glass lens used in conjunction with a light wave in an optical microscope. The sample in an electron microscope must be so thin that it is transparent to electrons (i.e. allows electrons to pass straight through the thin sample). Bulky samples are usually unresolvable due to excessive diffraction.

Preparation of samples consists of microtoming; transparent slices are cut with a diamond knife and placed on a grid for transport into the microscope. Magnification occurs by multiplication of individual enlargements of a series of lenses, as in light optics. The magnified image is visible on the fluorescent final image screen or, when the screen is lifted, is recorded on the photographic plate. The condenser lens focuses the divergent

beam of electrons directly onto the sample. The sampling area is normally only 3 – 5 μm in diameter⁷.

Chemical Analysis. When an electron beam strikes a sample, many interactions occur, which create a number of different signals. A direct beam that cleanly penetrates the sample and passes through it produces an image. Scattered electrons that have passed through the sample can be elastic or inelastic, but neither is incorporated into the image. Backscattering, secondary electrons, auger electrons and x-rays are products of interactions with the surface. Chemical analysis via transmission electron microscopy uses x-ray emission to identify atoms in a sample. Atoms, when struck by electrons, yield x-ray photons, which are specific only to that atom. The electron beam ionizes the atom, ejecting an electron to an excited state or removing it from the atom altogether. Stabilization of this excited state can occur by emission of an x-ray photon as the electron relaxes to the next lowest energy state. The potential energy difference between two shells is equal in energy to the x-ray photon⁸. Chemical analysis in this project was used to confirm the presence of the elements palladium and copper in activated and electroless-plated samples.

EXPERIMENTAL METHODS

General

The 1-methyl-2-pyrrolidone (NMP, C_5H_9NO) used was HPLC grade, 99+ %, purchased from Sigma Chemical. The polyamic acid (Sky Bond 705), viscous and amber in color, was purchased from Monsanto. The palladium acetate $[Pd(OAc)_2]$ solid was dark reddish brown and crystalline, and bought from Akron. The ammonium hydroxide was 99+ % concentrated purchased from Sigma Chemical. The substrate used was 5-mil thick Kapton marketed by DuPont. The mechanical stirrer was a Fischer Scientific Dyna-Mix.

Three deposition techniques were employed: 1) pen plotting driven by the plotting program "hvpeelc10.plt," which plotted 1/8" x 8" strips using a Numeridex fine 0.3 mm fiber tip pen; 2) pen plotting driven by the program called "jillsqr.plt," which plotted 1" squares using a Numeridex stainless liquid ink point pen (unless otherwise noted); 3) drawdown bar coating, wire gauge sizes from 5- 30. Coating by the drawdown bar was inconsistent in uniformity and was discontinued early in the research. The catalyst plotting was carried out using a 7475A Hewlett Packard Plotter. All ovens used were Blue M ovens unless otherwise noted. The microtome was a Bausch & Lomb microtome machine. The transmission electron microscope was a Philips 300 kV electron microscope.

1 % Catalyst Solution

The protocol followed was a standard operating procedure (SOP) for Sandia National Laboratories⁹. 0.92 g Pd(OAc)₂ was slowly added to 2.13 g NH₄OH in a vial and agitated with a magnetic stirrer. The mixture was stirred for 20 minutes, or until all Pd(OAc)₂ dissolved. 94.85 g of a pre-mixed solution of Sky Bond/NMP was weighed out into a plastic container. The mixture was formulated on October 10, 1996 using 301 g NMP in 172.5 g Sky Bond 705. The container was connected to a mechanical stirrer and turned on "high." The Pd(OAc)₂/ NH₄OH mixture was added drop-wise via syringe. Once added, the mixture was stirred for approximately 15 hours. A mixture of 0.30 g FC-430 surfactant in 2.23 g NMP was added while being stirred with a magnetic stir bar. The catalyst solution was stored at room temperature.

Electroless Plating

The bath used in this study was a Shipley Cuposit 328 plating bath. The conditions for the bath were as follows: 3 g/L suspended copper, 7.5 g/L formaldehyde, 23 °C operation temperature, 10.2 pH bath. The plating bath was constructed and maintained by Thomas Gilligan, a student intern at Sandia National Laboratories (Org 1471).

TEM Microtoming

A 0.5 x 1 mm piece of activated sample was cut and inserted into a small plastic tube. 12.5 g Epon 828 epoxy resin was mixed with 1.5 g diethanolamine hardener, and

heated until colorless. The mixture was poured into the plastic tube until full. The sample was heated at 80 °C for at least 8 hours in a Fischer Scientific IsoTemp Oven, model 615F. The plastic tube was removed after cooling and the sample was inserted into the microtomer equipped with a DuPont diamond knife at 4 ° relative to horizontal.

Transparent slices were cut (thickness control set at "2") containing the epoxy resin and sample. Commercial TEM grids of 200 copper or titanium mesh were used to pick up the samples and transport them into the transmission electron microscope. Sample imaging and chemical analysis with the microscope were performed by Thomas Headley of Sandia National Laboratories (Org 1822).

Caution

Polyamic acid is corrosive and appropriate protection should be worn. Concentrated NH₄OH causes immediate, irreparable damage if contact with eyes occurs. Respiratory arrest may occur if large amounts of its gaseous fumes are inhaled. Safety glasses or shields should be worn at all times while using in a well-ventilated hood.

RESULTS AND DISCUSSION

Process Conditions

The process conditions for activation of the palladium catalyst solution are composed of two parts: the drying conditions and activation conditions, each with variable times and temperatures. The drying conditions were fixed at 80 °C for 30 minutes because preliminary deviations from this accepted condition did not significantly improve the catalyst performance. The activation conditions were varied according to Table I, testing both time and temperature. The method of deposition used was the pen plotter, program "jillsqr.plt." All samples were deposited using this program.

Table I: Activation conditions tested

Set Number	Activation Times (min)	Activation Temperature (°C)
1	60, 30, 15, 10, 5, 2, 1, 0.5	320
2	60, 30, 15, 10, 5, 2, 1, 0.5	300
3	60, 30, 15, 10, 5, 2, 1, 0.5	280
4	120, 60, 30, 15, 10, 5, 2, 1, 0.5	260
5	120, 60, 30, 15, 10, 5, 2	250

Objectives

Four main goals were outlined in order to further the understanding of the catalyst and the occurrence of activation: 1) fixed temperature while changing activation time to

observe growth patterns of the palladium clusters; 2) fixed time while changing temperature to compare cluster sizes and the effects of temperature; 3) conditions for various times and temperatures at which satisfactory plating occurs to determine minimum cluster size necessary for plating; 4) thickness testing of copper layer after one hour electroless plating to observe how cluster size affects plating thickness. The goals were met by preparing the designated samples and using transmission electron microscopy to image the clusters.

Objective 1: Study of growth patterns. It was expected that a longer activation time at an elevated temperature would increase cluster size. Another assumption made was that the wet catalyst layer would be uniform after deposition, and the subsequent dry catalyst layer would also be uniform, although slightly less thick (the assumption was that at increased activation times and temperatures, the dry catalyst layer would decrease in thickness; this was based on previous studies conducted by Ken S. Chen of Sandia National Laboratories (Org 9111)). Uniformity here is defined as spacial continuity within the strip and that plotting is reproducible from on strip to the other.

Throughout this paper the catalyst layer thickness measurements refer to the dry catalyst layer. The thickness of the dry catalyst layer was assumed to be uniform, but was found to fluctuate and so a direct correlation could not be made between temperature and cluster size. Table II lists the samples, cluster sizes, and the corresponding dry catalyst layer thickness. Upon first inspection it would appear that cluster size is not affected in a rational manner when time of activation is varied at fixed temperature. Notice however, that the catalyst layer thickness directly determines the cluster size at these elevated

temperatures (Figure 1). The dried catalyst layer thickness does not seem to depend on activation temperature as was originally suspected. This is most likely due to the differences in deposition methods from the previous studies which showed the correlation.

Table II: Fixed temperature study to show effects of time on size of palladium microstructures.

Temperature (°C)	Time (min)	Catalyst Layer Thickness (nm)	Pd Cluster Size (nm)
320	30	60(± 18)	8(± 2)
	15	24(± 3)	3.0(± 6)
	10	39.6(± 4)	4(± 1)
	5	25(± 1)	3.2(± 1)
300	30	39(± 4)	4(± 1)
	15	32(± 6)	5.0(± 1)
	10	51(± 3)	7.1(± 2)

Figure 1: Growth patterns for temperatures 320 °C and 300 °C, varying times from 30 – 5 minutes (order is according to increasing thickness, not time or temperature).

Objective 2: Comparison of cluster sizes. Importance of activation temperature on palladium cluster sizes was shown through fixed time tests. The time was fixed at 30 minutes while activation temperature was varied. Table III shows the five temperatures tested and the corresponding catalyst layer thickness and cluster size.

Table III: Comparison of cluster sizes as function of temperature at fixed time of 30 minutes.

Time (min)	Temperature (°C)	Catalyst Layer Thickness (nm)	Cluster Size (nm)
30	320*	60(±18)	8(±2)
	300*	39(±4)	4(±1)
	280	32(±4)	5.2(±1)
	260	18(±3)	3.2(±8)
	250	120(±39)	3.3(±6)

*Micrographs shown in appendix A.

For all but one of the temperatures it appears obvious that cluster size is more dependent on catalyst layer thickness than actual activation temperature, until a critical temperature of 250 °C is reached (Figure 2).

Figure 2: Time is fixed at 30 minutes, growth of palladium clusters is dependent on temperature below 260 °C.

Note: There was some experimental error in the thickness measurement of the sample at 250 °C. This was because of the angle at which the sample was viewed in the microscope. The sample was cut so that the electron beam focused straight down the interface. As the thickness of the slice increases, the probability of surface undulation increases and so the image that appears may not be a true representation. Even at 0 ° tilt, the sample can appear thicker than actual due to this bending. In such a case, the sample is tilted to an angle of minimum thickness to compensate for this error.

The results of this test were also used to determine a minimum cluster size required for satisfactory plating. All samples were plated in the electroless bath.

However, at temperatures 250 °C and 260 °C (30 minutes activation time) the plating was not uniform and was slightly spotty. All other temperatures showed uniform plating. Therefore it was concluded that 4 nm (on average) was minimum cluster size necessary to plate satisfactorily (Figure 3).

Figure 3: Minimum cluster size necessary for successful copper plating.

Objective 3: Critical conditions required for satisfactory plating. Using the series of tests in Table I, a “Scotch Tape Test” was done to determine the minimum conditions that plating would occur with a satisfactory adhesion. “Critical condition” can be described as the lowest time at a fixed temperature that plating occurs and passes the scotch tape test. Those conditions were imaged and their cluster sizes measured in order to determine the conditions required for satisfactory plating (Table IV). Even though all samples passed the scotch tape test, the experiments tested at 250 °C and 260 °C did not show clean uniform copper plating; therefore these temperatures were undesirable.

Table IV: Critical conditions required for satisfactory plating with sufficient adhesion.

Temperature (°C)	Time (min)	Catalyst Layer Thickness (nm)	Cluster Size (nm)
320	10	39.6(4)	4(1)
300	10	51(3)	7.1(2)
280	60	18(1)	2.5(6)
260	120	52(4)	3.2(9)

At these critical activation conditions a trend is apparent showing that cluster size increases linearly with activation temperature. There seems to be little affect to catalyst layer thickness at these temperatures (Figure 4). Additionally, Figure 4 shows that at lower temperatures, a longer activation time is required to produce large clusters.

Figure 4: General trend of increasing cluster sizes with increasing temperature at critical activation conditions required for satisfactory plating.

Objective 4: Thickness measurements after electroless plating. The most sophisticated thickness-measuring instrument in the lab had a maximum precision of 0.043 mil. After one hour of electroless plating, the copper layer was still less than 0.043 mil, so alternative measuring methods were sought. TEM imaging was used to measure the copper layer thickness. In addition to the measurement, it was possible to study the palladium clusters at the interface of the copper coating. In some instances the palladium clusters were visible, but in others they were not. Table V shows the conditions that were used to measure electroless plating thickness. A second experiment in this investigation was to determine if cluster size had an effect on copper plating thickness.

Table V: Activation conditions at which electroless plating thickness was measured.

Temp (°C)	Time (min)	Cluster Size (nm)	Electroless Plating Thickness (nm)
320	15	3.0(±6)	630 (±19)
	10	4(±1)	688(±6)
	5	3.2(±1)	600(±48)
300	30	4(±1)	720(±27)
	15	5.0(±1)	950(±16)
	10	7.1(±2)	560(±26)

Because of the inconsistency in copper thickness, it was concluded that the copper layer was not linked directly to the cluster size, but rather to the bath make-up, specifically the concentration of oxidizing agent present and copper ions in solution (Figure 5). In other words, it was not possible to determine the effects of palladium cluster size on copper

plating thickness since uncertainty due to the plating bath was significant. Even though the variation in uniformity was ~400 nm the reproducibility is crucial in circuit board manufacture. Any discontinuities in uniformity of the surface could result in an interception of current flow.

Figure 5: Samples after electroless plating for one hour and the resulting plating thickness.

Chemical Analysis

Chemical analysis confirmed whether or not palladium was still present after electroless plating. Additionally, areas under the palladium clusters were probed to determine if copper had diffused through the catalyst layer. Four samples were examined: two activation conditions, each before and after electroless plating. The conditions tested were 320 °C at 15 minutes and 300 °C at 30 minutes (and listed as A

plated, 2 not plated, D plated, 5 not plated, respectively). The elements found are listed in Table VI. Note that, although the beam was extremely fine tuned to the point of interest, some scattering did occur which gave false signals. A false signal is highlighted wherever suspected.

Table VI: Elements detected in samples via chemical analysis

Element	Sample(s)
Carbon (C)	A, 2, D, 5
Oxygen (O)	A, 2, D, 5
Palladium (Pd)	A, 2, D, 5
Titanium (Ti)	A, D
Copper (Cu)	A, 2, D, 5
Silicon (Si)	A, D, 5
Sodium (Na)	A, D
Chlorine (Cl)	A, D
Calcium (Ca)	A, D
Zinc(Zn)	A
Sulfur (S)	A

Carbon and oxygen were present in high amounts due to the Kapton and epoxy. Because of the size of the palladium particles, it was impossible to narrow the beam directly onto a single particle. Therefore, a series of particles grouped closely together were examined. As a result, carbon and oxygen from the polymeric substrate were always present in large

considerably less in intensity than copper and so were considered minor and attributed to water.

Figure 6: Example of TEM image and points that were probed for chemical analysis.

Sample 2, 320 °C/15 minutes. This sample was the only one of the four examined that did not contain any unexpected artifacts. Only in areas where the beam hit the palladium particles directly was the metal detected. Examples of areas similar to those probed during chemical analysis are shown in Figure 7. Copper was present in extremely small amounts, but was attributed to the microscope. Many areas were probed with similar results.

amounts even when focusing on a metallic area. The Titanium present in samples A and D was indicative of the grid on which the sample rested, i.e. a false signal due to spreading. Samples 2 and 5 were placed on copper grids, which accounted for some of the copper that was present. In all samples, copper was present due to an artifact inside the microscope. All other metals were quantified as being present only in minor amounts compared to copper. Small amounts of sodium were found, attributable to the copper electroless bath; sodium hydroxide was used to adjust pH. The elements chlorine, calcium, silicon, and sulfur were accounted for as artifacts from water (water was used to support the transparent slices after cutting). It was suspected the metal ions present in water had a small electrostatic attraction to the metals on the surface of the sample, but further investigation will be necessary for confirmation. Zinc may be present in water, but is highly unlikely. It is unknown and cannot be speculated why zinc was present. Because it was present in only one of the four samples, and in very trace amounts, it was not considered to be part of the system. Palladium was found in all samples when probed for the metal, as was expected. It was necessary to confirm the presence of palladium on samples that were electroless plated because the clusters were not visible in all cases.

Sample A, 320 °C/15 minutes and one hour electroless plating. Areas of the sample that were probed were predominantly near the interface of copper and palladium. In this sample, the palladium particles were much more difficult to identify near the copper coating. Figure 6 shows some representative areas probed like those during chemical analysis. Palladium was found only in areas where the clusters were explicitly visible. Chlorine was found present in a variety of places, but in variable amounts, yet all were

Figure 7: TEM micrograph of activated sample at 320 °C/15 minutes. Similar points to those probed during chemical analysis are designated.

Sample D, 300 °C/30 minutes and one hour electroless plating. Many areas of the sample were probed for elemental analysis. Representative areas are shown in Figure 8. The corresponding graphs showing the elements found are in appendix E. This example confirms the diffusion of copper past the palladium clusters down to the polymeric substrate (charts 10 – 12). This was not evident in all samples.

Because it was not evident in all samples, it is suspected that diffusion occurs only at higher temperatures; further study should be conducted for confirmation. If it is the case, that copper is diffusing past the layer of palladium clusters, it is suspected that adhesion would be at a maximum.

Figure 8: Example of TEM image for conditions 300 °C/30 minutes and points of probing for chemical analysis.

Sample 5, 300 °C/30 minutes. The basis for probing the complementary sample after activation was to identify any artifacts consistently present between samples. Silicon was the only element found consistently in both samples labeled "D" and "5".

Representative areas are shown in Figure 9. Consistently, where no clusters were visibly present, palladium levels were trace and assumed to be from scattering.

Figure 9: TEM micrograph of representative areas probed via chemical analysis.

A representative sample of clusters has been shown for clarification within the text. See the appropriate appendices for further detail on the physical appearance of the clusters.

CONCLUSION

From objective 1 (fixed temperature, changing time conditions) TEM confirmed a general trend of increasing temperature corresponding to an increase in palladium clusters size. It was also discovered that the deposition method of pen plotting was not as uniform as originally thought. Because of the nonuniformity, a direct correlation could not be made relating an increase in activation time and temperature to a decrease in dry catalyst layer as was seen in previous studies. TEM micrographs of samples confirmed the uniformity problem.

The results from objective 2 (fixed time, changing temperature) showed that temperature was not an important factor until the temperature of 250 °C was reached. At all temperatures above 250 °C, the micrographs showed a trend relying more on the dried catalyst layer thickness than on temperature.

It was found from the third objective (critical conditions), temperature and time were more crucial to palladium cluster size than catalyst layer thickness. For uniform copper plating to occur, the palladium clusters must be a minimum of 4 nm in size on average.

Finally from the fourth objective (thickness testing of copper coating), TEM chemical analysis confirmed that palladium was still present in elemental form after coating the sample with copper. Additionally, the thickness of copper coating was more dependent on the chemical make-up of the bath and not the specific conditions of activation and cluster size as originally suspected.

FUTURE WORK

Future work includes improving catalyst-solution deposition uniformity, so a definite trend can be determined that specifically correlates activation conditions to cluster size. Because the pen used in pen plotter was specifically designed for ink, it is suspected that the difference in viscosity between ink and the catalyst solution contributed to the uniformity problem. A pen that is capable of dispensing higher viscosity liquids (perhaps to the level of liquid glue) would dispense a much more uniform layer of catalyst solution. Or, a machine could be designed to evenly coat the catalyst layer as in a spray mechanism. However, construction of this machine would be very costly, so alternative, less expensive measures should be studied first.

In studying the copper thickness, an alternative measuring device should be considered. Although TEM is accurate, it is extremely time consuming to prepare a sample, and can be quite expensive. A more sophisticated measuring device other than the one originally tried would be an essential attribute to the research so that uniformity throughout the sample could be assessed.

An important component not considered in this research, but equally significant to metallization, is studying the effects of palladium acetate in the catalyst solution on platability; particularly in determining the critical palladium acetate concentration below which plating would not occur. Using a less concentrated sample would be much more cost effective.

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Adhesion Aspect of Polymeric Substrate Metallization:

**A Study of the Effects of the Polyamic-Acid Imidization Extent on the Adhesion
between Copper and Polyimide Substrate***

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University of New Mexico
Project Report
for
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*This work was performed at Sandia National Laboratories under the supervision of Ken S. Chen. This project is one aspect of a collaborative effort at Sandia to develop a low cost polymeric-substrate metallization process.

ABSTRACT

Metallization of polymeric substrates is an important technology that has widespread applications: e.g. flex circuits, printed wiring boards, and multichip modules. Irrespective of the purpose of the metal coating, it must adhere well to the underlying substrate. So the need to understand the factors which influence metal-polymer adhesion and the way to attain adhesion is highly desired. Experiments carried out in this study make of Sandia's thermally-activated, palladium-catalyzed metallization process in examining the effects of the polyamic-acid imidization extent on the overall adhesion between the copper and polyimide substrate. Specifically, the effects of palladium catalyst activation time (i.e. 1 hr, 2 hr, and 4 hr) at an isothermal curing of 320°C was studied. The overall adhesive or peel strength between the copper coating and Kapton (polyimide) film was quantified using the IPC-TM-650 technique. The Fourier Transform Infrared (FTIR) Spectroscopy was used to determine the extent of polyamic-acid imidization. Peel strength measurements show significant variability in adhesion. Preliminary IR spectra analyses indicate that the extent of imidization does affect adhesion: IR spectra show that where high adhesive peel strength was measured, full conversion of the polyamic-acid to polyimide had occurred; and in areas of low adhesive peel strength, complete imidization had not occurred.

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INTRODUCTION

The idea of depositing a layer of metal coating onto a non-conductive substrate has been around for a long time. Although the details of its origin remain unknown, the history of metallizing non-conductive materials can be traced, through archaeological evidence, even as far back as to the time of the Egyptians (Goldie 1968). Metallized wood and terra cotta made by the Egyptians using unknown methods have been found in which metallization was used primarily for sheathing purposes. In modern times, the applications of metallized nonconductive substrates, particularly polymeric substrates, are prevalent in daily life: e.g. protective coating, electromagnetic shielding, reflectors, conductors for electric current, etc. (cf., e.g. Mittal 1989, Karas et. al. 1992). Most recently, electroplated aluminum on polyimide has also been reportedly employed in micromachine fabrication (Frazier 1994). Polymeric substrate metallization particularly plays a major role in the field of microelectronics where insulators are metallized for interconnection and other functional purposes as mentioned above. Plastics are also metallized to provide electromagnetic shielding on parts which have complex geometries and are difficult and expensive to manufacture from metals such as steel. For example, in the case of radar and communication horns and antennas, fabricating these devices from polymeric materials, e.g. using stereolithography, with the desired geometry and then metallizing the parts significantly reduces manufacturing turn-around time and is more economical.

Copper Metal Coatings and Polyimide Insulating Substrates

The metal layer on the polymeric substrate serves various purposes depending on the application: e.g. conductor, reflector, and/or protective coating. Copper is the popular choice of metal conductor in interconnect applications because of its low resistivity and mechanical stability and reliability (see, e.g. Harper et. al. 1994, Qian et. al. 1991, and Bhansali and Sood 1995). The copper metal is what this study focuses on. On the other hand, polyimide is widely employed as insulating substrates because of its good mechanical properties, dimensional stability, and low dielectric constant (see, e.g. Harper et. al. 1994). According to Bhansali and Sood (1995), various polyimides are extensively used in the microelectronics industry and in micro-machine fabrication as a patterning material and interlayer dielectric because of their ease of patternization and chemical stability once fully cured. Earlier, Jones et. al. (1975) had reported that partially fluorinated polyimides possess great potential for long term service in highly oxidative environments at temperatures up to 700°C. However, the drawback of polyimide is that it is an expensive material in comparison with other polymeric substrates such as FR4 and this disadvantage has researchers investigating such alternatives. FR4 is a composite material which is made by impregnating a solid glass fiber matrix by an epoxy resin (produced, e.g. by the reaction tetrabromobisphenol A and epichlorohydrin) (cf. Miller and Laberge 1989). Also, polyimide has a relatively smooth surface which has led to problems in getting the copper to adhere well onto the surface. To overcome this adhesion problem, many researchers are looking into and have found that surface modification techniques do improve adhesion. Inagaki et. al. (1996) used graft polymerization to form an island-sea type structure at the surface of Kapton (a

polyimide film marketed by Du Pont) film. They claimed that by the graft polymerization, the adhesive peel strength between the Kapton film and copper was increased by a factor of about three.

Metallization Technologies

There are various techniques employed for metallizing polymeric substrates, including conventional and emerging processes (i.e., those currently under research): vacuum deposition, metal foil/adhesive lamination, electroless plating, cast to foil, and direct metallization. Vacuum deposition refers to processes in which metal is deposited directly onto a substrate under high vacuum. Many different variations of this technique exist, including physical (e.g. electron beam and sputtering) and chemical deposition (e.g. chemical vapor deposition). Vacuum deposition has been traditionally employed for fast, reproducible metal deposition (see, e.g. Queau et. al. 1994, Anetsberger 1992, and Pollack and Jacques 1992). However, this technology is capital intensive due to its high vacuum operating conditions. As commented by Stoffel et. al. (1996), metal foil/adhesive lamination is a widely used technique in which a metal foil is laminated onto a base film using an adhesive layer. This process is performed using a lamination press at an elevated temperature. The disadvantage of this method is the use of thick metal foils and its ineptness for three-dimensional complex substrates. As defined by Mallory (1990), electroless plating is a chemical means of plating metallic substrates without utilizing an external source of electric current; and it is a process that continuously deposits metal from an aqueous medium. There are several steps crucial to the overall process: surface treatment, catalyzing, and electroless plating (c.f. Bindra and White 1990). A catalytic seeding step is used to chemically sensitize, usually in a $\text{PdCl}_2/\text{SnCl}_2$ solution, the substrate surface. In the solution, Pd^{2+} is reduced to yield catalytic Pd^0 , or metallic palladium. Electroless plating is favored by manufacturers because of the precision in copper thickness which may be obtained. However, this method requires numerous wet processing steps and adhesion between metal coating and polymeric substrate may be less than desired; moreover, bath maintenance (so as to prevent the bath from crashing) is time-consuming and can be costly. Cast to foil is an emerging technology in which a liquid solution of polyamic-acid is cast onto the surface of a copper foil (cf. Pollack and Jacques, 1992). The entire composition is then heated to a temperature high enough that will evaporate the solvent and imidize the polyamic-acid. The polyamic-acid is a precursor to polyimide; and this process forms a polyimide or amide modified polyimide film. This technology has produced well adhered copper on polyimide films without utilizing an adhesive layer. The disadvantages of this technology is the limit on copper thickness that may be used and the high temperatures at which copper is annealed. Direct metallization is a relatively new method, which can be used to deposit a metal coating directly onto plastic substrates without have to deposit the seed-layer metal via electroless plating technique. According to Stamp et. al., a "conductivator" metal such as palladium in colloidal or semi-colloidal form is used as a catalyst coating to produce a conductive polymer film, fixed and adhering to the nonconductive areas of the substrate. Although the issue of adhesion has not been addressed, the technology's ability to effectively eliminate the need for electroless plating has stimulated much interest.

Adhesion Issues and Problems

Clearly there are needs and means for putting metal on polymeric substrates. However, metal and polymer are inherently incompatible (which is due to their chemical dissimilarities) and poor adhesion has been a great adversity which continues to challenge researchers in the field of polymeric-substrate metallization. According to Sacher (1990), it is the issue of generating good adhesion between the polymer substrate and the metal coating that remains largely unresolved. As reviewed by Mittal (1976), several theories have evolved to explain the adhesion between the metal/polymer interface. They can be classified as chemical, physical, or mixed physical-chemical in nature. Today, the chemical mechanism is favored because adhesion is clearly observed in association with the occurrence of chemical reaction (see Kim 1987 and 1988). So the need to understand the factors which influence metal-polymer adhesion and the way to attain adhesion is highly desired.

This report presents preliminary results of a mini-project in which the adhesion aspect of polymeric substrate metallization is studied. My study aims to develop a quantitative understanding of how the extent of polyamic-acid imidization affects the overall adhesion between copper and polyimide substrate using Sandia's additive metallization process. The IPC-TM-650 technique was used to measure the adhesive peel strength between the layers; and the Fourier Transform Infrared (FTIR) spectroscopy was used to determine the extent of imidization.

NATURE OF WORK

In this project the effects of the extent of polyamic-acid imidization on the overall adhesion between copper and polyimide substrate is studied. Figure 1 shows the polyamic-acid imidization reaction which forms polyimide.

Figure 1. Starting materials and reaction products for polyimide synthesis

There are several factors that play important roles in determining the extent of imidization: e.g. catalyst layer thickness, activation temperature, activation time, and polyamic-acid concentration. This project focuses on investigating the correlation between activation time at isothermal curing and imidization conditions; extent of imidization is believed to be directly related to adhesive strength.

There are various techniques employed for metallizing polymeric substrates. Processes such as Sandia's thermally-activated palladium-catalyzed metallization process usually involve three steps: catalyzing the substrate surface, electroless plating to deposit the seed layer, and electrolytic plating to build the metal thickness. In using these processes, obtaining a strong bond between the metal and polymeric substrate is strongly desired. There are three regions which contribute to the overall bonding or adhesion between the metal coating and the polymeric substrate (see Figure 2): 1) adhesion between the polymeric substrate and the catalyst layer, which consists of metallic palladium clusters embedded in a "cured" polymer matrix (strong adhesion at this interface can be achieved because the polymer substrate and polymer matrix in the catalyst layer is usually identical or at least similar in chemical nature); 2) adhesion between the metal coating and the catalyst layer, which contains catalytic metallic palladium clusters on its surface (strong adhesion at this interface can be realized because the metal coating and the metallic palladium clusters share electrons - a key mechanism by which good adhesion can be created); and 3) cohesion within the catalyst layer. Preliminary research previously conducted at Sandia National Laboratories showed that failure tended to occur within the catalyst layer (i.e. cohesive failure) when copper coating was peeled off the Kapton substrate. It was concluded that the key to achieve good bonding between the copper coating deposit and the polyimide substrate is to create strong cohesion for polymer in the catalyst layer.

Figure 2. Structure of a metallized sample using Sandia's thermally-activated palladium-catalyzed metallization process

A research team led by Dr. Ken S. Chen at Sandia National Laboratories has developed an activation process to create a semi-metallic catalyst layer that consists of metal palladium and possibly palladium oxides embedded in a "cured" polymer (e.g. polyamic-acid) matrix (Chen et. al. 1996). This semi-metallic catalyst layer enables strong adhesion between the substrate and the catalyst layer: the polymer binder in the catalyst layer bonds well to the nonmetallic polymeric substrate and the metallic Pd clusters in the catalyst layer bond well to the metal coating.

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a characterization technique and was used to study the extent of polyamic-acid imidization. Infrared (IR) spectroscopy is the study of the interaction of infrared radiation with matter (c.f. Smith, 1996). All objects in the universe at temperatures above absolute zero give off IR. When IR interacts with matter it can be absorbed, causing chemical bonds in the material to vibrate. Since functional groups tend to absorb IR in the same wavenumber range, there is a correlation between wavenumbers at which a molecule absorbs IR and its structure. This correlation allows the structure of unknown molecules to be identified from the molecule's IR spectrum. The width of the IR band gives information about the strength and nature of the molecular interactions.

The basis of all quantitative analyses in FTIR is Beer's law, which relates concentration to absorbance:

$$A = \epsilon l c$$

where A is absorbance, ϵ is absorptivity (for a given molecule and wavenumber, ϵ is a fundamental physical property of the molecule), l is pathlength, and c is concentration. Thus, IR spectra also allow the concentration of a molecule in a sample to be identified.

The feasibility of using FTIR spectroscopy to investigate the curing of polyamic-acid has been demonstrated by many researchers (see, e.g. Ginsburg and Susko 1984, Navarre 1984, Numata et. al. 1984, and Jordan and Iroh 1996). Ginsburg and Susko (1984) report using this technique to follow the progress of imidization by monitoring the changes in the imide peak at 1780 cm^{-1} with the aromatic peak at 1012 cm^{-1} . They found that the percent imidization is greatest at high temperatures, long cure time, and in thick film regions. Navarre (1984) quantified the curing of polyimides by taking the ratio of the 1778 to 720 cm^{-1} absorption bands. Numata et. al. (1984) report using an infrared spectrometer to quantify percent imidization and found that when the polyamic-acids were heated rapidly, there was a strong positive correlation between imidization reaction and temperature. Jordan and Iroh (1996) followed the progress of imidization by monitoring the increase in the imide absorption band at 1780 and 1380 cm^{-1} . They report that the commencement of imidization occurs at shorter aging times at higher temperatures than at lower temperatures. At higher aging temperatures, they observed extensive imidization.

EXPERIMENTAL

Pd-Catalyst Solution Formulation

The catalyst was prepared following the standard operational procedure for Pd-catalyst solution preparation.¹ The polyamic-acid solution used was pre-mixed and comprised of Sky Bond in NMP (1-methyl-2-pyrrolidinone) solvent.

Catalyst Deposition on Polyimide Substrate and Curing

The catalyst ink solution was deposited onto the polyimide film using the 7475A Hewlett-Packard Plotter. The dimensions of the pattern printed on the polyimide film was 4" x 11". The pattern consists of 10 catalyst strips which are 1/8" wide. A reduced strip pattern is shown in Figure 4.

Figure 4. Catalyst strips which were printed onto polyimide film. This pattern allowed for adhesive strength measurements to be made.

The polymeric substrate used was 5-mil thick Kapton (a polyimide film substrate marketed by DuPont). Blue M air-circulated ovens were used for curing the samples. The temperatures in the ovens were maintained by Pro-star, a microprocessor-based programmer/controller. The oven was preheated to the required temperature for 15 min prior to sample insertion.

Electroless Plating Bath

The Shipley Cuposit 328 was used as the makeup for the electroless plating bath. Periodic maintenance of the bath was made by using titration correction methods. Plating in the bath was performed at room temperature without agitation.

Electrolytic Plating Bath

The LeaRonald Acid Copper Plating Solution and the Copper Gleam PC electrolytic plating bath were employed in order to raise the copper thickness on the metallized samples. A plating rate of 5.5 Amp/ft² was used.

¹ The exact catalyst formulation is not disclosed here due to pending patent application. However, as a source of reference, the interested readers can refer to the patent by Tokas, Shaltout, and Chen (1994).

Metallizing Steps in Sample Preparation

The sample metallization protocol for fabricating adhesiveless laminates combines the Sandia's thermally-activated, palladium-catalyzed metallization process with an after-plating heating step (C. E. Baumgartner and L. R. Scott, 1995). The catalyst ink solution was prepared and the solution was left stirring vigorously for approximately 24 hours. Such intense mixing was to ensure thorough distribution of the Pd⁰ in the polyamic-acid and to prevent the solution from coagulating and polymerizing. The catalyst ink was printed in a strip pattern onto the Kapton film.

The coated sample was heated at 80°C for 30 min. in order to remove the solvent from the catalyst solution. The sample was then isothermally cured at 320°C for a period of time (i.e. 1 hr, 2 hr, or 4 hr). The sample was placed vertically into the electroless copper plating bath where it remained for an hour. To drive out moisture, a post heating followed where the sample was heated at 150°C for two hours. The sample was then placed on a copper board and submerged into the electrolytic plating bath for three hours. The sample was subjected to a final post heating at 175°C for two hours in order to drive out any remaining moisture.

Peel Strength Measurements

In performing the adhesive peel strength measurements, only five of the ten strips (every other strip) were peeled. Data was collected at a sampling rate of 5 pts/sec. The strips were peeled at a constant rate of 2 in/min.

IR Spectroscopy

The IR spectra specimens were prepared by manually slicing a small thin layer of the aged sample (i.e. the catalyst layer) and subsequently pressing the sample between two salt windows. The samples were analyzed using the Nicolet 800 Sx FTIR spectrometer and the microscope attachment in transmission mode. The salt window was used as the background; and this background spectrum was subtracted from the sample spectra. No baseline correction was performed.

RESULTS AND DISCUSSION

Adhesive Peel Strength Measurements

The adhesive peel strength measurement results are shown in Table I.

Table I. Adhesive Peel Strength Measurements

Sample	Activation Time (hr) @ 320°C	Average Peel Strength (lb _f /in)	Maximum Peel Strength (lb _f /in)
R1	1.0	3.89	4.17
R2	1.0	3.88	4.06
R3	1.0	4.43	5.57
R4	1.0	4.67	5.76
R5	1.2	3.07	3.18
R6	2.0	1.92	2.70
R7	2.0	6.38	8.25
R8	2.0	3.00	3.92
R9	4.0	1.32	1.96
R10	4.0	6.28	9.21

The results show that there is variability from sample to sample which were prepared in the same manner and activated for the same amount of time. Within some samples, there are also significant differences in average adhesive peel strength from strip to strip. For example, one sample which was activated at four hours had average strip peel strengths which varied anywhere from 3.5 to 9.2 lb_f/in (see Appendix A for individual strip average peel strengths). To study the variability of adhesive peel strength within a strip, the peel strengths (lb_f/in) were plotted versus displacement (in) along the copper strips. Figure 5 through 7 are representative of the types of variability observed within a strip. Figure 5 shows a strip on a two hour activated sample with an average peel strength of 5.23 lb_f/in. This plot shows that the peel strength was erratic throughout the entire strip. Figure 6 shows a strip on a four hour activated sample with an average peel strength of 1.64 lb_f/in. This strip had notably low peel strengths on the edges. Figure 7 shows a strip on a two hour activated sample with an average peel strength of 8.25 lb_f/in. This strip had a relatively consistent peel strength throughout the entire strip.

A noted observation of the catalyst layer between the peeled copper deposit and the Kapton substrate is that there is a clear substance, or no substance, where poor adhesion was measured and a yellow substance where good adhesion was measured. It is hypothesized that the yellow substance signifies complete imidization (i.e. the polyamic-acid has been converted to polyimide).

Figure 5. Peel strength versus displacement plot of a copper strip (2 hr activated with average peel strength of 5.23 lbf/in)

Figure 6. Peel strength versus displacement plot of a copper strip (4 hr activated with average peel strength of 1.64 lbf/in)

Figure 7. Peel strength versus displacement plot of a copper strip (2 hr activated with average peel strength of 8.25 lbf/in)

Chemical Analyses using IR Spectroscopy

Infrared spectroscopy was used to characterize the catalyst material between the peeled copper deposit and the Kapton film. By characterizing the material where good and poor peel strengths are observed, the extent of imidization can be determined and correlated to adhesive peel strength. Kapton, which is a fully cured polyimide, was used as the "standard" with which the catalyst material was compared. The IR spectrum of Kapton film is shown in Figure 8. The Kapton spectrum shows peaks above 3000 cm^{-1} which are due to O-H, N-H, and C-H bands from aromatic rings (see, e.g. Nakanishi and Solomon, 1977). Figure 9 shows a spectrum of a clear region, where poor adhesive peel strength was measured, compared with the Kapton spectrum. The bands above 3000 cm^{-1} are indiscernible for the clear region spectrum; and while all of the polyimide characteristic peaks below 1800 cm^{-1} are present, the absorbance is lower. These differences suggest that the material is different from the polyimide or that the polyamic-acid did not fully imidize. Figure 10 shows a spectrum of a yellow material, where good adhesive peel strength was measured, compared with the Kapton spectrum. All of the polyimide bands are present in the yellow region spectrum, and most of the peaks coincide exactly with the Kapton spectrum. These similarities indicate that this yellow material is unchanged polyimide or fully imidized polyamic-acid.

Limited data has been collected using the IR spectroscopy and more analyses are needed before any conclusions may be made. However, preliminary results do suggest that the extent of imidization of the polyamic-acid is related to the adhesive strength between the coat coating and the Kapton film.

FUTURE DIRECTIONS

Preliminary Scanning Electron Microscopy (SEM) analyses were performed on a one hour activated sample (not metallized) in order to determine the thickness of the catalyst layer. These analyses show that the Pd^0 is not uniformly dispersed throughout the surface of the Kapton film. Insufficient or absence of Pd^0 would have an adverse effect on the adhesion; and accordingly, there is a need to understand why there is a non-uniform layer of Pd^0 on the surface of the Kapton substrate. Due to the limited data collected, more samples should be prepared and additional analyses performed. Also, since there is always some error involved with reading IR spectra, other characterization techniques should be investigated.

One of the larger goal in metallization technologies is to maximize adhesion between the metal coating and polymeric film. Thus, a correlation, if any exists, should be determined between the extent of polyamic-acid imidization and the adhesive peel strength of copper coating to polyimide substrate. Then, all of the factors which affect imidization should be studied: e.g. activation time, activation temperature, catalyst layer thickness, and polyamic-acid concentration.

IR Spectrum of Kapton (Polyimide) Substrate

Figure 8. IR spectrum of Kapton (polyimide) substrate

IR Spectra Comparison of a Clear Region with Kapton Substrate

Figure 9. IR spectra comparison of a clear region with Kapton substrate

IR Spectra Comparison of a Yellow Region with Kapton Substrate

Figure 10. IR spectra comparison of a yellow region with Kapton substrate

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APPENDIX A

Individual Strip Average Peel Strength Data

R1 - 1.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.417	0.886	0.626	4.170
#3	0.488	0.858	0.617	4.111
#5	0.388	0.733	0.543	3.620
#7	0.437	0.821	0.549	3.659
#9	0.423	0.906	0.582	3.883
Mean	0.431	0.841	0.583	3.889
S.D.	0.037	0.068	0.038	0.252
C.V.	8.549	8.108	6.475	6.475
Minimum	0.388	0.733	0.543	3.620
Maximum	0.488	0.906	0.626	4.170

R2 - 1.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.460	0.836	0.602	4.013
#3	0.347	0.842	0.589	3.929
#5	0.409	0.863	0.610	4.064
#7	0.322	1.013	0.608	4.051
#9	0.367	0.701	0.504	3.359
Mean	0.381	0.851	0.583	3.883
S.D.	0.055	0.111	0.045	0.298
C.V.	14.310	13.016	7.667	7.667
Minimum	0.322	0.701	0.504	3.359
Maximum	0.460	1.013	0.610	4.064

R3 - 1.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.243	1.034	0.572	4.087
#3	0.306	0.940	0.629	4.493
#5	0.567	1.061	0.780	5.569
#7	0.334	0.951	0.539	3.850
#9	0.382	1.156	0.579	4.134
Mean	0.366	1.028	0.620	4.427
S.D.	0.123	0.088	0.095	0.679
C.V.	33.590	8.590	15.332	15.332
Minimum	0.243	0.940	0.539	3.850
Maximum	0.567	1.156	0.780	5.569

R4 - 1.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#2	0.441	0.919	0.604	3.772
#4	0.365	1.073	0.556	3.914
#6	0.455	0.976	0.669	4.714
#8	0.511	1.024	0.734	5.169
#10	0.586	1.140	0.818	5.757
Mean	0.472	1.026	0.676	4.665
S.D.	0.083	0.085	0.104	0.838
C.V.	17.500	8.307	15.363	17.970
Minimum	0.365	0.919	0.556	3.772
Maximum	0.586	1.140	0.818	5.757

R5 - 1.2 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.255	0.686	0.476	3.175
#3	0.284	0.696	0.470	3.132
#5	0.221	0.645	0.456	3.037
#7	0.261	0.788	0.448	2.987
#9	0.296	0.672	0.451	3.004
Mean	0.264	0.697	0.460	3.067
S.D.	0.029	0.054	0.012	0.083
C.V.	10.996	7.796	2.693	2.693
Minimum	0.221	0.645	0.448	2.987
Maximum	0.296	0.788	0.476	3.175

R6 - 2.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.090	0.441	0.174	1.157
#3	0.203	0.469	0.377	2.511
#5	0.389	0.516	0.406	2.704
#7	0.280	0.473	0.383	2.555
#9	0.026	0.635	0.101	0.671
Mean	0.198	0.507	0.238	1.920
S.D.	0.145	0.077	0.141	0.937
C.V.	73.569	15.135	48.793	48.793
Minimum	0.026	0.441	0.101	0.671
Maximum	0.389	0.635	0.406	2.704

R7 - 2.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#2	0.194	1.310	0.836	5.226
#4	0.205	1.305	0.778	4.862
#6	0.199	1.477	0.996	6.224
#8	0.879	1.652	1.174	7.336
#10	1.044	1.713	1.321	8.253
Mean	0.504	1.491	1.021	6.380
S.D.	0.421	0.189	0.227	1.421
C.V.	83.617	12.667	22.278	22.278
Minimum	0.194	1.305	0.778	4.862
Maximum	1.044	1.713	1.321	8.253

R8 - 2.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.145	1.283	0.626	3.915
#3	0.080	1.242	0.333	2.082
#5	0.079	1.101	0.366	2.288
#7	0.036	1.308	0.464	2.898
#9	0.082	1.393	0.608	3.801
Mean	0.084	1.265	0.479	2.997
S.D.	0.039	0.107	0.135	0.842
C.V.	46.209	8.473	28.104	28.104
Minimum	0.036	1.101	0.333	2.082
Maximum	0.145	1.393	0.626	3.915

R9 - 4.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#3	0.039	0.089	0.059	0.393
#4	0.065	0.365	0.145	0.968
#5	0.068	0.405	0.246	1.637
#7	0.183	0.498	0.294	1.960
#9	0.147	0.418	0.248	1.653
Mean	0.100	0.355	0.198	1.322
S.D.	0.061	0.156	0.095	0.633
C.V.	61.063	43.970	47.898	47.898
Minimum	0.039	0.089	0.059	0.393
Maximum	0.183	0.498	0.294	1.960

R10 - 4.0 hr

	Minimum Peeling Load (lbf)	Maximum Peeling Load (lbf)	Average Peeling Load (lbf)	Average Peeling Strength (lbf/in)
#1	0.405	0.883	0.531	3.538
#3	0.541	1.062	0.771	5.143
#5	0.623	1.031	0.855	5.698
#7	0.791	1.505	1.168	7.788
#9	0.933	1.794	1.381	9.206
Mean	0.659	1.255	0.941	6.275
S.D.	0.207	0.380	0.335	2.235
C.V.	31.492	30.306	35.624	35.624
Minimum	0.405	0.883	0.531	3.538
Maximum	0.933	1.794	1.381	9.206

Literature Survey: Metallization of Polymeric Substrates

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INTRODUCTION

The idea of depositing a layer of metal coating onto a non-conductive substrate has been around for a long time. Although the details of its origin remain unknown, the history of metallizing non-conductive materials can be traced, through archaeological evidence, even as far back as to the time of the Egyptians (Goldie 1968). Metallized wood and terra cotta made by the Egyptians using unknown methods have been found in which metallization was used primary for sheathing purposes. In modern times, the applications of metallized nonconductive substrates, particularly polymeric substrates, are widespread in daily life: e.g. protective coating, electromagnetic shielding, reflectors, conductors for electric current, etc. (cf., e.g. Mittal 1989, Karas et. al. 1992). Most recently, electroplated aluminum on polyimide has also been reportedly employed in micromachine fabrication (Frazier 1994). Polymeric substrate metallization particularly plays a major role in the field of microelectronics where insulators are metallized for interconnection and other functional purposes as mentioned above. Plastics are also metallized to provide electromagnetic shielding on parts which have complex geometries and are difficult and expensive to manufacture from metals such as steel. For example, in the case of radar and communication horns and antennas, fabricating these devices from polymeric materials, e.g. using stereolithography, with the desired geometry and then metallizing the parts significantly reduces manufacturing turn-around time and is more economical.

The metal layer on the polymeric substrate serves various purposes depending on the application: e.g. conductor, reflector, and/or protective coating. Copper is the popular choice of metal conductor in interconnect applications because of its low resistivity and mechanical stability and reliability (see, e.g. Harper et. al. 1994, Qian et. al. 1991, and Bhansali and Sood 1995). The copper metal is what this survey focuses on. On the other hand, polyimide is widely employed as insulating substrates because of its good mechanical properties, dimensional stability, and having a low dielectric constant (see, e.g. Harper et. al. 1994). According to Bhansali and Sood (1995), various polyimides are extensively used in the microelectronics industry and in micro-machine fabrication as a patterning material and interlayer dielectric because of their ease of patternization and chemical stability once fully cured. Earlier, Jones et. al. (1975) had reported that partially fluorinated polyimides possess great potential for long term service in highly oxidative environments at temperatures up to 700°C. However, the drawback of polyimide is that it is an expensive material in comparison with other polymeric substrates such as FR4 and this disadvantage has researchers investigating such alternatives. FR4 is a composite material which is made by impregnating a solid glass fiber matrix by an epoxy resin (produced, e.g. by the reaction tetrabromobisphenol A and epichlorohydrin) (cf. Miller and Laberge 1989). Also, polyimide has a relatively smooth surface which has led to problems in getting the copper to adhere well onto the surface. To overcome this adhesion problem, many researchers are looking into and have found that surface modification techniques do improve adhesion. Inagaki et. al. (1996) used graft polymerization to form an

island-sea type structure at the surface of Kapton (a polyimide film marketed by Du Pont) film. They claimed that by the graft polymerization, the adhesive peel strength between the Kapton film and copper was increased by a factor of about three.

Clearly there are needs for putting metal on polymeric substrates. However, metal and polymer are inherently incompatible (which is due to their chemical dissimilarities) and poor adhesion has been a great adversity which continues to challenge researchers in the field of polymeric-substrate metallization. According to Sacher 1990, it is the issue of generating good adhesion between the polymer substrate and the metal coating that remains largely unresolved. As reviewed by Mittal (1976), several theories have evolved to explain the adhesion between the metal/polymer interface. They can be classified as chemical, physical, or mixed physical-chemical in nature. Today, the chemical mechanism is favored because adhesion is clearly observed in association with the occurrence of chemical reaction (see Kim 1987 and 1988).

The following survey selectively reviews the key literature pertaining to conventional processes and current research in the area of metallization of polymeric substrates, including discussion on vacuum deposition, metal foil/adhesive lamination, electroless plating, cast to foil, and direct metallization techniques.

EXISTING METALLIZATION TECHNOLOGIES

Vacuum Deposition

Vacuum deposition refers to processes in which metal is deposited directly onto a substrate under high vacuum, usually the pressure is on the order of 10^{-6} torr. According to Queau et. al. (1994) (also see, e.g. Anetsberger 1992 and Pollack and Jacques 1992), many different variations of this technique exist and they are the most widely used methods for fast, reproducible metal deposition. Such means include physical, such as electron beam and sputtering, and chemical deposition, such as chemical vapor deposition. These methods use expensive and specialized equipment (including the vacuum chamber and pumps), in most cases are not selective, and require etching processes for patterned metallization.

As discussed by Pollack and Jacques (1992) and Wan et. al. (1991), copper is vaporized in a vacuum chamber and is deposited on a polymeric film substrate in the physical vapor deposition method. They claimed that this process is usually fast, but the copper thicknesses is limited to about $2\mu\text{m}$; normally, further thicknesses can be raised by electrolytic plating. In sputtering operations, the film is placed in a large vacuum chamber which contains a copper cathode. This cathode is bombarded with positive ions to cause small particles of the charged copper to impinge on the polymeric film substrate. Wan et. al. (1991) has found that in some cases, copper adhesion is poor, and a base metal of chrome or nickel may be applied first in order to improve adhesion. Vacuum deposited copper to fully cured polyimide has almost no adhesion strength (less than 0.3 lb/in) (cf. Kim et. al. 1987).

Metal Foil/Adhesive Lamination

As commented by Stoffel et. al. (1996), metal foil/adhesive lamination is a widely used technique in which a metal foil is laminated onto a base film using an adhesive layer. Commercially avail-

able films such as Kapton or Upilex (a polyimide film developed in Japan and marketed by ICI) can be used as the polymeric substrate support. These polymeric film substrates are first coated with an epoxy or acrylic based adhesive. They are then laminated onto the metal foil in a lamination press by applying pressure at an elevated temperature.

According to Sun et. al. (1989), this technique has been widely employed in the fabrication of printed wiring boards and flex circuits because of its simplicity to obtain a conductive layer on the surface of nonconducting materials. In the manufacturing of interlevel dielectrics in multiple layer components, much higher yield for this process is possible because of the advantage of the parallel preparation of the individual layers which allows for their inspection before lamination (cf. Stoffel et. al. 1996). One of the disadvantages of this process is that it has limits on the shape of a substrate and metal film thickness that can be used.

Nevertheless, there has been continued interest in this area. Chen et. al. (1994) has improved on previous process by increasing the adhesion between polyimide/copper laminate and decreasing the high radius of curvature of the laminate which results from the coating shrinkage after cooling (the polyimide/metal laminate for tape automated bonding involves an application of polyamic acid onto a metallic foil and then thermal imidization). They found that the thermal expansion coefficient of the polyimide must nearly equal that of the copper to prevent curling. A curl-free polyimide/copper laminate of 9.0 lb/in using 60% 6-amino-2-(p-aminophenyl)-benzimidazole (BIA) and 40% oxydianiline (ODA) as diamines had been reportedly made by Chen et. al. (1994).

The counter-part to adhesive laminates is adhesiveless copper clad laminates. In this relatively new family of laminates, copper is bonded to the polyimide film without adhesives (see Pollock and Jacques 1992). Compared to its adhesive-based predecessor, adhesiveless laminates provide a thinner circuit, greater flexibility and better thermal conductivity. Advantages of adhesiveless base laminates is thinner circuit without an adhesion layer and elimination of mismatched characteristics of the adhesives to copper and film. The next three metallization technologies discussed are members of the adhesiveless laminate family.

Electroless Plating

The term "electroless plating" was first coined by Abner Brenner in 1947. He originally used it to describe a method of plating metallic substrates with nickel or cobalt alloys without utilizing an external source of electrical current. Mallory (1990) expanded on the original meaning and defined the contemporary version of this term as any process that continuously deposits metal from an aqueous medium. However, this definition by Mallory (1990) is not quite precise.

Due to its large number of applications and current employment in the manufacture of printed circuit boards, the electroless copper wet process (chemical reduction) has been studied by many researchers (see, e.g. Rantell and Holtman 1976, Bindra and White 1990, Stone 1990, and Queau et. al. 1994). This process is characterized by the selective reduction of metal ions only at the surface of a catalytic substrate immersed in an aqueous solution of some metal ions with continued deposition onto the substrate through the catalytic action of the deposit itself.

Several steps, each crucial to the overall process, are involved in electroless deposition: surface

treatment, catalyzing, and electroless plating. The process begins with a surface treatment of the substrate (cleaning, conditioning, and etching). The catalytic seeding step follows in which the substrate surface is chemically sensitized, usually in a $\text{PdCl}_2/\text{SnCl}_2$ solution. In the solution, Pd^{2+} is reduced to yield catalytic Pd^0 , or metallic palladium. The copper is then continuously plated onto the palladium-catalyzed substrate surface to the desired thickness. With this class of electroless plating, etching is required for patterned metallization.

As discussed by Stone (1990) and Bindra and White (1990), a typical electroless copper plating solution contains a source of metal ions, a reducing agent (formaldehyde), a complexant (alkaline hydroxide), chelating agents (quadrol and EDTA), and stabilizers. For the catalysts, palladium and tin are the most commonly utilized metals. Two catalyzing or seeding processes exist (a two step process, as opposed to the single step mentioned above, in which the polymer substrate is immersed first in a solution of SnCl_2 , followed by immersion into a separate solution of PdCl_2); Rantell and Holtzman (1976) discussed these different processes in which they examined the theories of the colloidal and complex nature of the catalyst solution.

There are several issues concerned with the traditional electroless copper process. For one, this process in most cases uses formaldehyde, a suspected carcinogen, as the reducing agent. Also, as Stone (1990) has found, this process is inherently unstable and requires much maintenance. Stabilizing additives and periodic bath analyses are required to keep the copper in solution and to prevent the bath from crashing. In the alkaline electroless medium, environmentally undesirable complexing agents, such as EDTA, are used to prevent copper precipitation. Another issue is the high water consumption which comes with the large number of chemical processes and rinsing procedures. In response to these concerns, alternative processes which eliminate the use of formaldehyde and EDTA have been developed (see Dietz 1995 and Nakahara 1992). However, in all cases, patterned metallization still requires the costly and environmentally unfriendly etching process.

The unlimited ability of the electroless process to produce metal film thicknesses exceeding a few micrometers and to metallize three-dimensional complex substrates outweigh the above discussed disadvantages and have captured the interest of many researchers (see Krause and Speckhard 1991, Baumgartner 1992, Karas et. al. 1992, and Baumgarnter and Scott 1995). An issue that has been under much study is the weak adhesion between the copper and polymeric substrate. As discussed by Baumgartner (1992), one approach to increasing the adhesive bond at the metal/polymer interface is through surface modification. The idea behind surface modification is to alter the morphology of the surface, either by mechanically abrading or chemically modifying the surface so that better interfacial bonding between the metal and polymer surface may be obtained due to the increased roughness of the surface (cf. Baumgartner 1992). Baumgartner (1992) found that the level of adhesion is dependent on the extent of surface modification. In later work, Baumgartner and Scott (1995) studied the effects of various chemical pretreatments of the polymeric surface, before employing electroless plating, on the level of adhesion. They found that in all cases, adhesion was improved with the pretreatments.

Another way researchers have found of improving the level of adhesion obtained from electroless process is by limiting the amount of moisture present at the metal/polymer interface. A detailed study on an electrochemical process for depositing copper films on polyimide substrates was car-

ried out by Krause and Speckhard (1991). Using an aqueous chemical process, Krause and Speckhard produced metal films which were highly adhered to the polymer substrate (5.6 to 7.8 lb/in in peel strength) under dry conditions. However, they found that this adhesion decreases drastically under high humidity conditions and dropped as low as or below 0.6 lb/in, but they could not explain this occurrence. In a later work, Baumgartner (1992) observed that the rate at which adhesion develops increases as relative humidity decreases and found that there is a complete lack of adhesion development at high-humidity ambients. These observations led him to believe that the elimination of interfacial water is necessary for adhesion development. Baumgartner and Scott (1995) extended on this work and investigated the effects of post-curing on the level of adhesion obtained by the electroless process. Following metallization, they heated the samples to drive interfacial dehydration and promote chemical bond formation. Using surface modification and subjecting the samples through a series of thermal cycles, combined with post-electroless heating, they produced metal layers which were well adhered to polyimide. They obtained a maximum adhesive peel strength for copper of 10.1 lb/in.

EMERGING METALLIZATION TECHNOLOGIES

Cast to Foil

Cast to foil is a metallization method in which a liquid solution of polyamic acid is casted onto the surface of a copper foil (cf. Pollack and Jacques, 1992). The entire composition is then heated to a temperature high enough that will evaporate the solvent and imidize the polyamic acid. This process forms a polyimide or amide modified polyimide film. Stoffel et. al. (1996) have made well adhered multilayer polyimide structures by building one layer on top of another. Thus subsequent layers can be made by sequentially spincasting poly(amic acid) precursor, imidizing and patterning individual layers.

Prior to the work of Stoffel et. al. (1996), Kim et. al. (1987) had used this technology to produce polyimide films on copper. They measured adhesive peel strength of about 4 lb/in between the copper foil and polyimide; and they found this value to decrease with an increase in polyimide thickness. Their spectroscopy studies revealed copper-rich particles which formed as a result of reaction of polyamic acid with copper during thermal curing. They attributed the strong chemical bonding across the copper/polyimide interface, which results in high peel strength, to this occurrence.

While adhesion is considered good, Pollack and Jacques (1992) has found that this metallization technique is limited to copper that are 1 oz thick or more. Although thinner copper is available, it is more difficult to handle and, as a result, may be too costly. The copper is annealed at very high temperatures and as a result, makes devices produced this way difficult to handle without damage to the copper. Etching is required for patterned metallization. Additionally, as Stoffel et. al. (1996) has pointed out, preparing films from the precursor material as in this method is more expensive than using the commercially available polyimide films (see discussion on the adhesive lamination process above).

Direct Metallization

Direct metallization is a process of depositing a metal coating directly onto plastic substrates without having to deposit the seed-layer metal via the electroless plating technique. This technology first appeared in 1963 when Radovski patented a process for the direct metallization of nonconductive substrates. He used a "conductivator" metal such as palladium in colloidal or semi-colloidal form (cf. Stamp et. al. 1995) as a catalyst coating to produce a conductive polymer film, fixed and adhering to the nonconductive areas of the substrate. He found that the electrical conductivity of the catalytic film, though much less than that of metals, is sufficient for direct electrolytic plating. However, it was not until several years later that the first commercial application of this process emerged in the form of vertical panel plating. As reported by Metzger et. al. (1997) and Dietz (1995), this process was developed in the mid-1980s as an environmentally safe alternative to the electroless process. The main advantage of this process over electroless plating is the labor and equipment savings and reduced laboratory requirements. However, there has been mixed reports from fabricators who have implemented this process according to Crum (1995). Positive reports have claimed that the process has reduced their cycle time and lowered processing costs significantly without the costly wastewater treatment. Negative reports claim otherwise and state that the process offers poor reliability in multilayer applications, offer little reduction in cycle time, and little or no difference in costs.

It is the vision of effectively producing well adhered metal on polymeric substrates without the above mentioned problems of electroless plating that has kept interest in the area of direct metallization high. Reddy et. al. (1992) has taken advantage of the extraordinary affinity of poly-(amine-quinone) polymers towards metals to develop a generic method for metallizing plastics without electroless plating or specialized equipment. In this process, the polymer is applied onto the substrate and the metal or alloy powder is sprinkled over the tacky polymer. Upon curing, they have found that this metal/polymer system is well adhered and, to some degree, electrically conductive.

In their patents, Conrad and Sutcliffe (1994) and Stamp et. al. (1995) claimed to have devised processes for depositing metal on nonconductive polymeric substrates via electrolytic plating. These processes eliminate the need for electroless plating and use suspended noble metal colloids in a polymer matrix to render the substrate surface conductive. These processes are full coverage metallization and imaging (i.e. patterned metallization) requires etching processes.

CONCLUDING REMARKS

The different metallization methods and their main advantages and disadvantages have been discussed. Vacuum deposition has been traditionally employed for fast, reproducible metal deposition. The major drawback to this method is the high-vacuum operation condition required, which makes it a relatively expensive technology. The wide use of metal foil/adhesive lamination methods can be attributed to its simplicity in obtaining a conductive layer on polymeric substrates. The disadvantages of this method is the use of thick metal foils and its ineptness for three-dimensional complex substrates. Electroless plating is favored by manufacturers because of the precision in copper thicknesses which may be obtained. However, this method requires numerous wet processing steps and adhesion between metal coating and polymeric substrate may be less than desired; moreover, bath maintenance (so as to prevent bath crashing) is time-consuming and can be costly. Cast to foil is an emerging technology which has produced well adhered copper on polyimide films without utilizing an adhesive layer. The disadvantages of this technology is the

limit on copper thicknesses that may be used and the high temperatures at which copper is annealed. Direct metallization is a relatively new method, which can be used to deposit metal on plastic substrates using only electrolytic plating. Although the issue of adhesion has not been addressed, the technology's ability to effectively eliminate the need for electroless plating has stimulated much interest. This process, and those mentioned above with the exception of vacuum deposition where a mask is used, requires etching for patterned metallization.

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