

AD-A238 204



REPORT DOCUMENTATION PAGE

2

1a. SECURITY CLASSIFICATION AUTHORITY N/A		1b. RESTRICTIVE MARKINGS N/A	
2a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N00014-89-J-1314-18		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION LASST University of Maine	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Branch Office Chicago	
6c. ADDRESS (City, State, and ZIP Code) Sawyer Research Center Orono, ME 04469		7b. ADDRESS (City, State, and ZIP Code) 536 S. Clark Street Chicago, IL 60605	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research--Chemistry Program	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-89-J-1314	
8c. ADDRESS (City, State, and ZIP Code) 800 W. Quincy Street Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Properties and Adhesion of Polyimides in Microelectronic Devices			
12. PERSONAL AUTHOR(S) M. Grunze			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 1/6/90 TO 31/5/91	14. DATE OF REPORT (Year, Month, Day) 15 May 1991	15. PAGE COUNT 10
16. SUPPLEMENTARY NOTATION In: Advanced Materials and Processes, Eds.: H. E. Exner and V. Schumacher, Proceedings of EUROMAT '89, Nov. 22-24, 1989 Aachen, Germany, Vol. 2 (1990) p. 871.			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Polyimides, Metals, Interfacial Chemistry, Adhesion	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			

This paper gives a summary on the properties of polyimide films used in microelectronic devices and on recent research efforts to understand the adhesion between polyimides and inorganic materials. One of the major concerns in the application of polyimides is the integrity and reliability of the laminar structures. Surface sensitive spectroscopies have been recently applied to identify the nature of the chemical bond for metals evaporated onto cured polyimide surfaces and for spun-on and subsequently imidized polyamic acid films on metal surfaces. Depending on the preparation of the interface, e.g. metal on polymer or polymer on bulk metal, different phenomena are observed.

91-05008



20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL William V. Unertl		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL	

91 7 15 001

in: "Advanced Materials and Processes"

Proceedings of EUROMAT '89, 1989

Aachen(FRG), Vol. 2, p. 871-880

Properties and Adhesion of Polyimides in Microelectronic Devices

M. Grunze, Lehrstuhl für Angewandte Physikalische Chemie am Physikalisch-Chemischen Institut, Universität Heidelberg, F.R.G.

Abstract

This paper gives a summary on the properties of polyimide films used in microelectronic devices and on recent research efforts to understand the adhesion between polyimides and inorganic materials. One of the major concerns in the application of polyimides is the integrity and reliability of the laminar structures. Surface sensitive spectroscopies have been recently applied to identify the nature of the chemical bond for metals evaporated onto cured polyimide surfaces and for spin-on and subsequently imidized polyamic acid films on metal surfaces. Depending on the preparation of the interface, e.g. metal on polymer or polymer on bulk metal, different phenomena are observed.

Introduction

The widespread use of polyimides (PI) is a result of their unique properties which can be tailored to fulfill or to provide a compromise for specific requirements. Aromatic linear polyimides in particular are a class of organic polymers with favourable mechanical and dielectric properties for applications in electronic devices which can easily be processed into planar films. Originally polyimides were introduced in Japan as an interlevel dielectric for multilevel metal transistors /1/. Today they are used routinely in VLSI devices as multilevel dielectric insulation /2-4/. There are also several other applications which emerged in the last 10-15 years. Because of their high absorption coefficient for α -particles they are used as protective coatings in charge sensitive memory devices, their mechanical properties and high temperature stability is utilized in composite materials for aerospace uses /5/, and they are tested as high temperature adhesives /6/ as well as lubricants in spacecraft applications /7/. More recent application of some polyimides take advantage of their crystallinity which makes them applicable as orienting layers for LCD devices, or, when crystallization is reduced by adjustment of the curing procedure, as light guide materials /8/.

However, reliable adhesion, particular in humid environments, remains to be a major issue of concern in the application of PI's. Only recently spectroscopic results on polyimide/metal interfaces have become available which can shed some light on the chemical and physical parameters determining the adhesive bond between polyimide and metallic, oxidic, or semiconducting substrates. These experi-

ments will be summarized in the second part of this paper.

1) Preparation and Properties of Aromatic Polyimides

Aromatic polyimides can be prepared by a condensation reaction of an aromatic tetracarboxylic dianhydride and an aromatic diamine. In the two-step reaction a soluble polyamic acid is formed which can be converted to polyimide by thermal or chemical loss of water. To date nearly every aromatic and aliphatic function in the dianhydride or diamine has been studied allowing to vary the chemical and physical properties of the polymer over a wide range. A comprehensive compilation of the relationship between chemical stability, thermal stability, optical, electrical and mechanical properties as a function of chemical structure can be found in the monograph "Polyimides: Thermally Stable Polymers" by M.I. Bessonov et al. /9/. Polyimides with rigid rod-like structures (e.g. p-phenylene pyromellitimide, show the highest thermal stability, followed by polyimides of rigid cyclic structures of the ladder type and those containing single "hinge" atoms between the phenyl rings in the diamine, e.g. poly [N,N']-(p-phenoxyphe-nyl)-pyromellitimide (PMDA/ODA). The thermal stability of the polymers is primarily determined by their intermolecular interactions and not by the flexibility of the macromolecules themselves /9/.

The physical reason for the high flexibility of polyimides is a high degree of freedom of rotation of the phenylene rings around internal atomic "hinges" in the diamine portion of the polymer. The thermal expansion coefficients can be controlled by the chemical composition from 4×10^{-7} to $5.7 \times 10^{-5} \text{K}^{-1}$ /10/, hence matching the thermal expansion-coefficient of quartz glass ($4 \times 10^{-7} \text{K}^{-1}$), ceramics, metals and on the higher end those of ordinary organic polymers. Possible models for the correlation between thermal expansion and chemical structure are discussed by Numata et al. /10/. Numata et al. /10/ also describe the use of low thermal expansion coefficient polyimides as interlayer dielectric in VLSI's and flexible printed circuit boards. The matched thermal expansion coefficient of the dielectric polyimide film to the metallization layers or inorganic substrates in the laminar structure is essential because the device has to withstand the anneal temperature and further thermal cycling, e.g. in soldering processes.

The dark and photoelectric conductivity of various polyarylether polyimides have been investigated and it was observed that the high temperature conductivity ($T > 230^\circ \text{C}$) correlates with the ionisation potential and electron affinities of the electron donor (diamine) and electron acceptor (dianhydride) units in the chain. The electrical conductivity increases sharply upon illumination with visible

light by about a factor of 100 at room temperature /9/. In terms of dielectric properties, aromatic polyimides are classified as medium frequency dielectrics with a dielectric constant of typically $\epsilon=3.0-3.8$, dielectric breakdown strengths of 100-200 mV/m, and a specific volume resistance of $\sim 10^{18} \Omega \text{ cm}$. The parameters remain nearly independent of frequency and temperature up to $\sim 200^\circ\text{C}$ thus making them an ideal choice for a dielectric in heat resistant electrical insulating laminar structures.

Exposure to moisture at elevated temperature leads to water absorption in the polyimide film /11,12/. As discussed by Wilson /11/, water absorption (up to 1.5 H_2O molecules per repeat unit) is believed to hydrolyse polyimide to polyamic acid. Subsequent annealing up to 450°C in nitrogen for 30 minutes removes the water. Water absorption leads to a tensile stress in the polymer film which can cause delamination, in particular in cases where the film is not coupled to the substrate (SiO_2) by an adhesion promoter, e.g. organosilanes /11/. In order to avoid moisture induced degradation, polyimide films used as passivation coatings are typically covered with another plastic passivant /11/ as a moisture barrier.

Although the macroscopic behavior of polyimide films degraded by moisture exposure has been well established, the chemical changes occurring in the interface leading to adhesive or cohesive failure of the laminar structure are not well understood. Basically, in order to describe the failure mechanism, the chemical interactions and the structural properties of the intact interface need to be known. The present understanding of the chemical and physical interactions between polyimide and inorganic films is summarized in the following paragraphs.

2) Chemical interactions in polyimide/metal interfaces

Experiments to determine the chemical interaction between polyimide and metals have concentrated on poly [N,N'-(phenoxyphenyl)-pyromellitimide (PMDA-ODA) and related model compounds]. The two methods to prepare PMDA-ODA polyimide films are spin coating (SC) and vapor deposition polymerization (VDP). They differ in the way the film precursor (polyamic acid) is applied to the substrate. VDP is a solventless technique in which the monomers PMDA and ODA are codeposited by evaporation onto the substrate where they react at room temperature to polyamic acid. Spin coating (SC) requires that the polymer precursor polyamic acid is applied in a polar solvent, typically N-methyl pyrrolidone (NMP). The interfacial chemistry and adhesion is directly influenced by the way in which the interface is formed. Therefore, variations in the preparation of the polymer and/or metal film will lead to polyimide/metal interfaces with different physicochemical properties.

In the following the results obtained for the interfacial

chemistry of metals deposited onto cured polyimide, spin coated polyimide on metals and silicon, and for vapor deposited polyimide films on silver and copper surfaces will be outlined.

a. Metals deposited onto cured polyimide surfaces

The polyimide substrates were prepared by spin coating polyamic acid onto a substrate followed by solvent extraction, imidization and curing at temperatures exceeding 250°C . The metals were evaporated at room temperature under ultra high vacuum conditions onto the polyimide films and their chemical interaction was followed by x-ray photoelectron spectroscopy /13-16, 18-20, 22/, x-ray absorption fine structure (NEXAFS) measurements /14/, high resolution electron loss spectroscopy (HREELS) /17/ and recently also scanning electron tunneling microscopy /22/.

The first systematic XPS study on the interaction of evaporated metals with polyimide surfaces were published in 1984 by Chou and Tang /13/. They studied monolayers and submonolayers of Cr, Ni, Cu and Ag on freshly cured ($T=350^\circ\text{C}$, 30 min) polyimide substrates. They concluded that Cr and Ni react with the pendant oxygen in the substrate, whereas Cu and Ag are not forming chemical bonds. They also presented a simple thermodynamic model to predict whether a given metal will form a chemical bond with the polymer during metallization at room temperature. According to this model Al, Mg, Mn, Sn, Ti and V should react with the pendant oxygen in polyimide.

Later experiments indicated that Cr /14/, Ti /15,16/ Al /17,18/ react with polyimide surfaces at coverages around and exceeding one monolayer under polymer bond cleavage and formation of metal oxides, carbides and nitrides. In the case of Cr /14,19/ and Al /18/ spectroscopic data suggest that the initial interaction between metal and polymer involves a charge transfer with the PMDA part of the polymer. Clabes et al. /14/ compared their XPS data for submonolayer coverages of Cr on PI with chemical and electrochemical reduced polyimide films. Reduction of PI involves electron transfer into the lowest unoccupied orbital (LUMO) of the PI which, according to calculations performed by Haight et al. /19/, has its highest amplitude on the carbonyl carbon next nearest phenyl carbon atoms and the carbonyl oxygen atom in the PMDA part of the polymer. Clabes et al. interpret their data by postulating that the Cr atom initially interacts with two carbonyl oxygen atoms of two parallel PI-chains by charge donation into the LUMO of the PMDA parts of the PI macromolecules. A coordination with two adjacent ligands belonging to different monomer unit thus allows the chromium to reach the stable Cr^{2+} configuration, which, according to Clabes et al., is not possible through interaction with a single PMDA unit.

Supported by their "ab initio" calculations Haight et al. /19/ interpret their XPS data by a chromium/PMDA charge

transfer complex where the most stable coordination site for the Cr-atom is above the phenyl ring, analogous to a metal- π arene complex. The chemical shifts in the Cls, Ols and Nls spectra upon chromium deposition can be explained by theoretical calculation based on this model without invoking formation of covalent or ionic bonds. Support for this model also comes from the fact that the changes in the polyimide Cls, Ols, and Nls spectra are qualitatively the same irrespective whether chromium or copper is deposited, since chemical intuition would strongly argue against covalent bond formation with copper. Haight et al. also interpret the spectra taken for chromium coverages exceeding one monolayer without involving bond breaking in the polymer or compound formation.

However, recent experiments on copper deposition on polyimide films prepared by spin coating /21/ and by vapor deposition /22/ suggest that copper interacts via the imide part of the molecule and by chemical attack of the carbonyl groups. According to Mack et al. /22/ the interaction is stronger with vapor deposited PI surfaces than with the PI surfaces prepared by spin coating. Another bonding configuration where the copper interacts with the ODA part of the PI polymer was proposed by Sanda et al. /20/. Which of the models presented to describe the initial interaction between chromium and copper and polyimide surfaces remains open at this stage.

b. Interfacial chemistry of polyimide films on inorganic substrates

Polyimide on bulk copper and copper on polyimide is, despite the controversial models proposed for the chemical interaction, a well studied model system to demonstrate the differences in interfacial chemistry as a function of preparation method. In the following we will summarize the results for the PI/copper interfaces formed by (i) copper deposition on cured polyimide and (ii) spin coating of the polymer precursor polyamic acid (PAA) onto a copper film.

Kim and coworkers /23/ measured the adhesion strength by 90° peel tests for (i) and (ii). They found, that in case (ii) adhesion is significantly enhanced as compared to copper deposited onto cured polyimide (i) and they attributed this to the difference in interfacial chemistry, i.e. chemical reaction between polyamic acid and bulk copper (ii) as compared to copper atoms or clusters interacting with cured polyimide. The difference in interface chemistry was evident in cross sectional TEM observations /23/. In the case of a sputter deposited copper film on a cured polyimide film, a sharp boundary was observed, whereas in the case of a polyimide/copper interface prepared by spin coating polyamic acid and subsequent imidization, cuprous oxide (Cu_2O) particles were found in the polymer matrix.

That copper oxide particles are distributed over a thickness of ~500 nm was recently reported by Burrell et al. /24/ for spun on polyimide films on copper. In their XPS and IR-Reflection Absorption measurements /24/ they at-

tributed the observed degradation and chemical modification of the thick polyimide films to copper oxide particle formation /24/.

Contrary to the observations made by Kim et al. /23/ on spun-on polyimide films, Kowalczyk et al. /25/ found no copper oxide particles in the polymer matrix in polyimide films produced by vapor deposition (VD). However, if prior to imidization a drop of the solvent N-methylpyrrolidone is applied to a vapor deposited polyamic acid film, copper oxide particle formation in the polymer matrix can be observed by TEM /25/. The results of Kowalczyk et al. clearly show that the solvent provides mobility for the copper ions formed at the interface to diffuse into the polymer matrix and eventually react to cuprous oxide. Results on vapor deposited polyimide films on copper revealed that it is not possible to produce polyimide films of thickness less than 1 nm /26,27/. According to Kowalczyk et al. /28/ this is due to incomplete imidization at the interface caused by carboxylate formation, whereas we believe /27/ that this is a consequence of fragmentation and loss of functional groups of the PMDA and ODA molecules in the interface. Both, the strong initial reaction of PMDA and ODA or of PAA with the copper surface, can provide an explanation for the dissolution of the copper surface and eventual cuprous oxide formation in the polymer matrix facilitated by the solvent.

In commercially produced polyimide (Kapton®) /copper laminate poor adhesion is typically caused by cohesive failure in the polymer foil. As shown by a detailed XPS/IR/SEM study by Horn et al. /29/ a thin surface layer of the polyimide foil facilitates the interface bond to the metallization layer, possibly via the adhesion promoters added to the polymer. Delamination leaves a thin polymer film on the metal, i.e. an adhesion between metal and polymer is stronger than cohesion in the polymer itself. If or to which extend copper cluster migration into the polymer as described above could cause cohesive failure is not known at present.

Relatively thick polyamic acid films were spun onto copper substrate by D.Y. Shih et al. /30/. They followed the imidization and curing by sheet resistance, parallel plate capacitance measurements, FTIR and x-ray photoemission. Evidence for the interaction of copper with polyamic acid and for copper oxidation and degradation controlled by the supply of oxygen to the interface was obtained from FTIR and cross-sectional TEM micrographs. Shih et al. reported that the amount of cuprous oxide found in the polymer matrix was significantly less when curing was performed in a reducing gas atmosphere as compared to nitrogen or vacuum curing. They concluded that Cu-ions are dissolved in the polyamic acid solvent layer in the initial curing stage and subsequently diffuse into the polymer matrix.

For spectroscopic methods to be applied to analyze the polymer/substrate interface the polymer films have to be

The results for PAA on a Si (111)7x7 surface show a highly complex pattern, which can be explained by more than one geometric adsorption site, more than one functional group being involved in the bond formation, or a stepwise interaction pathway /28/. It is clear, however, that covalent bonds to the silicon substrate are formed in the polyamic acid state. No results have been published so far for curing experiments of vapor deposited polyamic acid films on silicon.

The results summarized above refer to studies related to the interfacial bond between polyimide films and the inorganic substrates. Typically delamination between polyimide and the substrate is, however, not caused by adhesive failure, but rather cohesive failure in the polymer itself. Although the effect of adhesion promoters (typically aminosilanes) in the formation of a strong interface bond have not been studied by spectroscopic techniques for polyimide laminar structures, it is informative to recall the results obtained for a structural transition of the polymer between a polymer/metal interface and the polymer bulk.

XPS and IR data on silver led to the conclusion that at the surface the polymer chains are oriented away from the surface plane. This geometry is induced by the chemical bond to the surface /33,36/. (Small angle x-ray scattering data by Russel /38/, however, proof that for thick polyimide films ($d \sim 75\mu\text{m}$) the polyimide polymer chains in spun-on films are oriented parallel to the surface plane. Such an orientation of the polymer chains with respect to the substrate was confirmed by IR absorption reflection studies for vapor deposited polyimide films ($d > 10\text{nm}$) on copper /36/. At present it is not known at what distance away from the surface a transition between a nearly perpendicular to a parallel orientation relative to substrate plane of the polymer chains occurs, but it is tempting to speculate that such an orientational change in the polymer is related to the locus of failure in the case of cohesive delamination.

Conclusion

With their high temperature stability and easy processibility polyimide based polymers became an integral component in microelectronic device technology. Problems associated with adhesion in laminar structures have been mainly overcome by a careful control of process conditions, yet our understanding of the interfacial chemistry is still rudimentary and controversial. The application of spectroscopic techniques to identify the chemical composition and bonding at the interface has been established and is now routinely used in basic and applied research efforts. However, delamination typically occurs by cohesive failure in the polymer. To identify the locus and chemical and/or physical mechanism of cohesive failure re-

sufficiently thin. To prepare sufficiently thin polymer films by spin coating was only successful in a few cases. Russat /31/ reported results where polyamic acid dissolved in NMP was spun onto gold resulting in polyimide film thicknesses ranging between 1.3 to 2.9 nm after imidization and curing. However, the interfacial reaction on gold could not be unambiguously established /31/.

Deposition of polyamic acid by coevaporation of the anhydride (PMDA) and the diamine (ODA) can provide sufficiently thin polyamic acid and, after curing, polyimide films to study the interfacial reaction with x-ray photoelectron spectroscopy /26-28, 32-37/, near edge x-ray absorption fine structure (NEXAFS) /28/ and infrared reflection absorption spectroscopy (IRAS) /36/. This vapor deposition preparation method to study the interfacial reactions has been applied by our group for copper /26,27/, silver /32-34/ and gold /37/ substrates and by Kowalczyk for Cu, Cr and Si surfaces /28/. The first description of the vapor phase preparation of polyimide films was given by Salem et al. /39/ for thick PI films ($d \leq 10\mu\text{m}$). Application of UHV surface studies to such films was first described in reference /32/.

A detailed study of monomer adsorption (PMDA and ODA) in interaction with clean silver surfaces /33/ showed that both molecules undergo partial fragmentation upon room temperature adsorption. Spectroscopic analysis of vapor deposited polyamic acid indicates that the reactive sites for the interaction with a silver substrate, as well as for vapor deposited gold atoms and clusters, are the amino carboxylic acid groups in the molecule /37/. Evaporated gold atoms and clusters preferentially interact via an electron transfer from the metal to the amino acid part of the molecule /37/. The interaction with a bulk silver surface is believed to involve silver carboxylate formation. A silver carboxylate bonding, either in a monodentate or bidentate configuration, is derived from the XPS and IR reflection absorption experiments for the ultra-thin polyimide films obtained after curing the polyamic acid layers /33,37/. Such a salt-like ionic surface bond explains the sensitivity towards humidity, i.e. it suggests that hydrolysis of the interface bond is a likely cause for adhesive failure.

There are strong similarities in the XPS and NEXAFS data for the case of PAA vapor deposited onto Cr surfaces and Cr evaporated onto cured polyimide surfaces /28/ suggesting that the same reactions occur in these differently prepared laminar structures. With the highly reactive chromium surfaces the formation of carbide, nitride and oxide species when the PAA/Cr interface is annealed was concluded from the XPS data. However, as discussed above, the XPS data for small and higher chromium coverages on cured polyimides are ambiguous with respect to charge transfer or covalent bond formation and fragmentation of the polymer.

mains a challenge for future research.

Acknowledgements:

Financial support for some of the author's work summarized here was obtained from the Office of Naval Research and IBM. Stimulating discussions with S. Kowalczyk, W.N. Unertl and R.N. Lamb are gratefully acknowledged.

Note added in proof:

An excellent overview on the adhesion of polyimides to metal and ceramic surfaces including a summary on adhesion theories and adhesion measurements, by L.P. Buchwalter, came to the attention of the author. This review will appear in the Journal of Adhesion Science and Technology.

References

- /1/ K. Sato, S. Harada, A. Saito, T. Kimura, T. Okubo, K. Mukai, IEEE Trans. on Parts, Hybrids/Packaging, PHP-9, No. 3, (1983) 175
- /2/ K.L. Mittal, ed. "Polyimides-Synthesis, Characterisation and Application", Vol 1 and 2, Plenum Press, New York (1984)
- /3/ R. Jaccodine, K.A. Jackson, R.C. Sundahl eds. "Electronic Packaging Materials Science III", Materials Research Society Symposium Proceedings, Vol 108, (1988)
- /4/ D.P. Seraphim, R. Lasky, Che-Yu Lin, eds.: "Principles of Electronic Packaging" McGraw Hill, New York (1989)
- /5/ L.M. Poveromo, in ref /2/, p. 1003
- /6/ A.K. St.Clair, T.L. St.Clair, in ref. /2/, p. 977
- /7/ R.L. Fusaro, in ref. /2/, p. 1053
- /8/ R. Reuter, H. Franke, C. Feger, Applied Optics, Vol. 27 (1988), 4565
- /9/ M.I. Bessonov, M.M. Koton, V.V. Kudryatsev and L.A. Lailus, "Polyimides - Thermally Stable Polymers", Consultants Bureau, New York and London (1987)
- /10/ S. Numata, T. Miwa, Y. Misawa, D. Makino, J. Imaizumi and N. Kinjo, in ref./3/, p. 113
- /11/ A.M. Wilson, in ref /2/, p. 715
- /12/ G. Samuelson and S. Lytle, in ref /2/, p. 751
- /13/ N.J. Chou and C.H. Tang, J.Vac.Sci. Technol. A2 (1984) 751
- /14/ J.G. Clabes, M.J. Goldberg, A. Viehbeck, C.A. Kovac, J.Vac.Sci.Technol. A6 (1988) 985
- /15/ F.S. Okuchi and S.C. Freilich, J.Vac.Sci.Technol.A4 (1984) 1039
- /16/ W.N. Unertl, private communication
- /17/ J.J. Pireaux, M. Vermeersch, N. Degosserie, C. Grégoire, Y. Novis, M. Chetail, and R. Candano in "Adhesion and Friction" ed.

- M Grunze and H.J. Kreuzer, Springer Series in Surface Sciences, Vol. 17 (1989) 53
- /18/ L.J. Aranasoska, S.G. Anderson, H.M. Meyer, Z. Lir and J.H. Weaver, J.Vac.Sci.Technol. A5, (1987) 3325
- /19/ R. Haight, R.C. White, B.D. Silverman and P.S. Ho, J.Vac.Sci.Technol. A6(4) (1988) 2188
- /20/ P.N. Sarda, J.W. Bartha, J.G. Clabes, J.L. Jordan, C. Feger, B.D. Silverman and P.S. Ho, J.Vac.Sci.Technol A4 (1986) 1035
- /21/ D.S. Dunn and J.L. Grant, J.Vac.Sci.Technol. A7 (1989) 253
- /22/ R.G. Mack, E. Grossman and W.N. Unertl, J.Vac.Sci.Technol, in press.
- /23/ Y.H. Kim, G.F. Walker, J. Kim and J. Park, J. Adhesion Sci. Techn. 1 (1987) 331
- /24/ M.C. Burrell, P.J. Codella, J.A. Fontana, J.J. Cheva, M.D. MacConnell, J.Vac.Sci. Technol. A7 (1989) 53
- /25/ S.P. Kowalczyk, Y.H. Kim, G.F. Walker, J. Kim, Appl. Phys. Lett. 52 (1988) 375
- /26/ M. Grunze, J.P. Baxter, C.W. Kong, R.N. Lamb, W.N. Unertl, and C.R. Brundie, "Vapor phase growth of Polyimide Films", AVS National Symposium, Topical Conference "Deposition and Growth: Limits for Microelectronics" Anaheim, Ca., Nov. 1987
- /27/ R.N. Lamb, M. Grunze, J. Baxter, C.W. Kong and W.N. Unertl, in ref /7/, p. 35
- /28/ S.P. Kowalczyk
- /29/ K. Horn, A.M. Bradshaw, K. Doblhofer, S. Krause, G. Weinberg, Z. Fresenius Anal. Chem, Vol 333, (1989), 590
- /30/ D.Y. Shih, J. Parasczak, N. Klymko, R. Flitsch, S. Nunes, J. Lewis, C. Yang, C. Cataldo, R. McGouey, W. Graham, R. Serino, E. Galligan, J.Vac.Sci.Technol A7 (3) (1989) 1402
- /31/ J. Russat, Surface and Interface Analysis, Vol. 11 (1988) 414
- /32/ M. Grunze and R.N. Lamb, Chem. Phys. Lett. (1987) 133
- /33/ M. Grunze and R.N. Lamb, Surf. Sci, 204 (1988) 183
- /34/ M. Grunze and R.N. Lamb, J.Vac.Soc.Technol A5 (1987) 1685
- /35/ R.N. Lamb, J. Baxter, M. Grunze, C.W. Kong and W.N. Unertl, Langmuir 4 (1988) 249
- /36/ M. Grunze, W.N. Unertl, S. Gnanarajan and J. French, Mat. Res. Soc. Symp. Proc. Vol. 108 (1988) 189
- /37/ T. Strunskus, M. Grunze, S. Gnanarajan, Proceedings of the International Symposium on the metallization of Polymers, Montreal, 1989, in press
- /38/ T.P. Russell, Journal of Polymer Science; Polymer Physics Edition, Vol. 22 (1984) 1105
- /39/ J.R. Salem, R.O. Ojeda, J. Duran, W.Y. Lee and R.M. Yang, J. Vac. Sci Technol A 4 (1986) 369

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

David Taylor Research Center (1)
Dr. Eugene C. Fischer
Annapolis, MD 21402-5067

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Defense Technical Information Center (2)
Building 5, Cameron Station (high quality)
Alexandria, VA 22314

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering
Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067