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.
Properties and Adhesion of Polyimides in Microelectronic Devices

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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 laminate 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.

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 stability. Polyimides are 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 trends 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 experiments 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 tetra-carboxylic 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. 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 dianime, e.g. poly [N,N']- (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 macro-molecules themselves [3].

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 dianime portion of the polymer. The thermal expansion coefficients can be controlled by the chemical composition of the dianhydride from 4 x 10^-7 to 5.7 x 10^-5K^-1 /10/, hence matching the thermal expansion-coefficient of quartz glass (4 x 10^-5K^-1), ceramics, metals, and on the higher end those of ordinary organic polymers as interlayer dielectric in MOS structures. Possible models for the correlation between thermal expansion and chemical structure are dis-cussed by Numata et al. [10]. Numata et al. [10] also describes the use of low thermal expansion coefficient polyimides as interlayer dielectric in flexible printed circuit boards. The matched thermal expansion coefficient of the dielectric polyimide film to the metallization layers and 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 poly-pyromellitimides have been investigated and it was observed that the high temperature conductivity (T>230°C) correlates with the ionization potential and electron affini-ties of the donor (dianime) and electron acceptor (dianhydride) units in the chain. The electric 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 dielectric constant of typically ε~3.0-3.8, dielectric breakdown strengths of 100-200 mV/m, and a specific volume resistance of ~10^12 Ω cm. The parameters remain nearly independent of frequency and temperature up to ~200°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 H2O 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 (SiO2) 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 adhesional or cohesive failure of the laminar structure are not well understood. Basically, in order to determine 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, Sn, Zn, and V should react with the ambient 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 interaction at the interface between the polymer. Clabes et al. /14/ compared their XPS data for submonolayer coverages of Cr on PI with chemical and electron spectroscopic techniques. 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 carbonyl oxygen atoms and the carbonyl oxygen atom in the PMDA part of the polymer. Clabes et al. interpret their data by postulating a model involving two parallel PI-chains by charge donation into the LUMO of the PMDA part of the PI macromolecules. A coordination with two adjacent ligands bonding to different monomer units 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 chemistry of metals deposited onto cured polyimida, 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 and then ultra high vacuum conditions onto the polyimide films and their chemical interaction was followed by x-ray photodetection 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 was published in 1984 by Chou and Tang /13/. They studied monolayers and submonolayers of Cr, Ni, Cu and Ag on freshly cleaned (T=350°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, Sn, Zn, and V should react with the ambient oxygen in polyimide.

2) Chemical interactions in polyimide/metal interfaces

Experiments to determine the chemical interaction between polyimide and metals have concentrated on poly [M,N,N'(phenyloxophenyl)-pyromellitimide (PMDA-ODA) and related model compounds. The two methods to prepare PMDA-ODA polyimide films are spin coating (SC) and vapor deposition polymerisation (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,N'-dimethylformamide (DMF). The interfacial chemistry and adhesion is directly influenced by the way in which the interface is formed. Therefore, variations in the preparation of the polyimide and metal film will lead to different interfacial interactions with different physicochemical properties.

In the following the results obtained for the interfacial
transfer complex where the most stable coordination site for copper is above the phenyl ring, analogous to a metal–arene complex. The chemical shifts in the Cls, OIs, and N1s spectra upon chromium deposition can be explained by a model that involves formation of covalent or ionic bonds. Support for this model also comes from the fact that the changes in the polyimide Cls, OIs, and N1s spectra are qualitatively the same both whether chromium or copper is deposited, since chemical intuition would strongly argue against covalent bond formation with copper. Haig 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 Hack et al. /22/ the interaction is stronger with vapor deposited FI surfaces than with the FI surfaces prepared by spin coating. Another bonding configuration where the copper interacts with the ODA part of the FI polymer was proposed by Sanda et al. /26/. 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 FI/copper interfaces formed by (1) 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 interaction between polyamic acid and copper (II) as compared to copper atoms or clusters interacting with cured polyimide. The difference in interface chemistry was evident across sectional TEM micrographs. 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 polyamic acid interface prepared by spin coating of polyamic acid and subsequent imidization, cuprous oxide (Cu2O) particles were found in the polymeric matrix.

That copper oxide particles are distributed over a thickness of ~500 nm was recently reported by Dell et al. /24/ for spun on polyimide films on copper. In their XPS and IR-Reflection Absorption measurements /24/ they attributed 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 particle formation in the polyimide film 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 polymeric 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 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 facilitated by the solvent weld formed at the interface.

In commercially produced polyimide (Kapton®) /copper laminates poor adhesion is typically caused by cohesive failure in the polymer foil. As shown by a detailed XPS/IR/SEM study by Dorn et al. /29/ a thin surface layer of the polyimide foil facilitates the interface bond to the metalization layer, possibly via the adhesion promoters added to the polymer. This adhesion layer is a self-assembled metal-oxide interphase, i.e. an adhesion between metal and polymer is stronger than cohesion in the polymer itself. If or to what extent 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 shear resistance, parallel plate capacitance measurements, FTIR and x-ray photoelectron spectroscopy. 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 polymeric 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 polymeric matrix.

For spectroscopic methods to be applied to analyze the polymer/substrate interface the polymer films have to be
sufficiently thin. To prepare sufficiently thin polymer films by spin coating was only successful in a few cases. Russel /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 Kowalsky 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>10μm). Application of UHV surface studies to such films was first described in reference /32/.

A detailed study of monomer adsorption (PMDA and ODA) interaction with clean silver surfaces /33/ showed that both molecules undergo partial fragmentation upon room temperature adsorption. Spectroscopic analysis (IRAS, NEXAFS) of vapor deposited polyamic acid indicates that the reactive sites for the interaction with a silver substrate, as well as for vapor deposition, are the anhydride oxygen atoms, establishing the importance of the anhydride group in the molecule /37/. Evaporated gold atoms and clusters preferentially bond via an electron from the metal to one of the oxygen atoms present in the molecule /37/. The interaction with a bulk silver surface is believed to involve silver carboxylate formation. A silver carboxylate bond, either 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/. This silver-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 oxynitride layers 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.

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 polymeric 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. The 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>10μm) the polyimide layers on films are oriented parallel to the surface plane. Such an orientation of the polymeric chains with respect to the metal is confirmed by XPS and IR Reflection absorption experiments for vapor deposited polyimide films (d>10μm) on copper /36/. At present it is not known at what distance away from the metal interface this transition takes place. It is similar to a parallel orientation relative to substrate plane of the polymer chains occurs, but it is tempting to speculate that both an orientation 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 at the interface 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-
mains a challenge for future research.

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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.

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