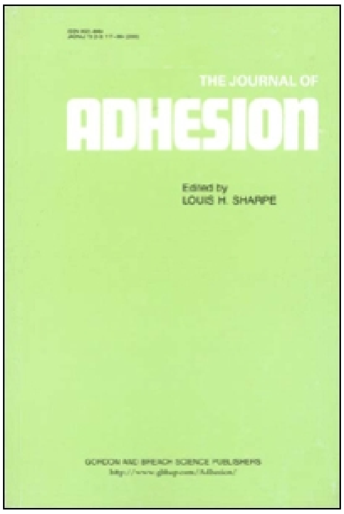

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

New Experimental Approaches for the Study of Polymer/Metal Interphases

M. Grunze[a]; M. Buck[a]; Ch. Dressler[a]; M. Langpape[a]
[a] Lehrstuhl für Angewandte Physikalische Chemie, Universität Heidelberg, Heidelberg, Germany

To cite this Article Grunze, M. , Buck, M. , Dressler, Ch. and Langpape, M.(1994) 'New Experimental Approaches for the Study of Polymer/Metal Interphases', The Journal of Adhesion, 45: 1, 227 — 243
To link to this Article: DOI: 10.1080/00218469408026640
URL: http://dx.doi.org/10.1080/00218469408026640

J. Adhesion, 1994, Vol. 45, pp. 227–243
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

New Experimental Approaches for the Study of Polymer / Metal Interphases*

M. GRUNZE, M. BUCK, CH. DRESSLER AND M. LANGPAPE

Lehrstuhl für Angewandte Physikalische Chemie, Universität Heidelberg, INF 253, W-6900 Heidelberg, Germany

(Received March 23, 1993; in final form July 30, 1993)

In this short review we present recent experiments which can be used to infer the structural parameters of ultrathin polyimide and polyamide acid films as a function of distance from the substrate surface. The polyimide films are prepared by the Langmuir-Blodgett technique in a layer-by-layer fashion, and the orientation of the pyromellitic imide unit in the polyimide macromolecules is determined as a function of film thickness by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. Subsequent delamination experiments on these Langmuir-Blodgett (LG) deposited polyimide films reveal that the locus of failure does not occur in a "weak boundary-layer" adjacent to the silicon substrate as expected from delamination experiments with macroscopically thick films.

As a non-destructive method to study the orientation of polymer molecules during film growth, second harmonic generation (SHG) experiments on the deposition of polyamide acid (PAA) on gold and silver surfaces will be briefly described. In this particular case, the experiments reveal an influence on the interfacial chemical bond on the film structure up to a total thickness of 60–100 mm.

KEY WORDS polyimide; polyamide acid; NEXAFS; XPS; Langmuir-Blodgett films; monolayers; interphase structure; interfacial chemical bond; molecular orientation; PMDA; ODA; silicon; gold; silver; weak boundary layer; second harmonic generation.

1. INTRODUCTION

The stability of a polymer/substrate laminate structure depends on two criteria: a strong *interfacial* bond between the macromolecule and the substrate surface atoms, and the *cohesive* strength of the polymer and the inorganic substrate in the inter*phase*, *i.e.* the region between the inorganic substrate and the organic bulk. This interphase can be chemically different from the bulk phase, as for instance in epoxy/galvanised steel coupons exposed to environmental tests,[1-3] but this case will not be considered here. As will be discussed in this communication, even when there is no chemical difference between the interphase and the bulk polymer, the interphase does not necessarily have the same structure since it is affected by the presence of, and the interaction with, the inter*face*. This is, in particular,

---

*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21-26, 1993.

expected in cases of strong interfacial bonding since the chemical bond between polymer and substrate is directional and, hence, forces the polymer chains into an orientation which is most likely inconsistent with the polymer bulk structure.

There are examples in the literature which support this hypothesis. When strong interfacial bonds are formed between a polymer and a solid substrate, delamination frequently occurs in a "weak" boundary layer. For example Oh, Buchwalter and Kim[4] studied the peel strengths of polyimides (PI) on SiO_2, Al_2O_3 and MgO and related these measurements to XPS and SEM results on the delaminated surfaces. In all cases a cohesive delamination was observed to occur predominantly in a "weak boundary layer" with a locus of failure extending to about 20Å into the polyimide film.[5] However, to what extent the "weak boundary layer" is caused by chemical effects or by a transition between the interphase orientation and bulk orientation could not be determined due to the lack of suitable probes for the molecular orientation in the interphase.

Oh and coworkers[4] were able to correlate the macroscopic fracture behaviour with the adhesion strength measured in peel experiments. Strong interfacial adhesion of polyimides showed a discontinuous stick-slip behaviour due to non-uniform bonding characteristics during the debonding process. This behaviour was not observed with low adhesion strength samples, such as for the ester-derived pyromellitic dianhydride (PMDA)/4,4′-oxidianiline (ODA) PI/MgO interphases. Since for both types of delaminated surfaces a polymer residue was observed on the substrate surface, the interphase bond between the two materials was clearly strong, but whether there was a structure transition between the interphase and the bulk of the polymer on the substrates could not be determined.

In this article we present first results of delamination experiments performed on ultrathin Si(100)/PI/Cr laminates in an attempt to correlate them with structural information obtained on identically-prepared samples by NEXAFS experiments.

Whereas the NEXAFS and the delamination experiments are conducted on the samples after their preparation, SHG offers the exciting possibility to study structure formation *in situ* and in real time when the film is formed. We will present here our SHG experiments on the deposition of PMDA/ODA polyamide acid and PMDA/DAPS (diaminodiphenyldisulfide) polyamide acid vapour deposited onto gold and silver surfaces. As demonstrated, the interfacial chemistry during the film formation process is clearly detected and the SHG signal as a function of thickness reflects the orientation of the polyamide acid molecules in the film. A brief summary on the results of model calculations to explain the measured data is given.

We will not review the results on the interfacial chemistry between polyimide and solid surfaces; the reader is referred to recent reviews on this subject.[6,7]

2. MOLECULAR ORIENTATION IN LANGMUIR-BLODGETT DEPOSITED POLYIMIDE FILMS

In the past, investigations have focused on the in-plane orientation of PMDA/ODA polyimide macromolecules in the bulk[8] and at the vacuum/polymer interface.[9] In the bulk, a slight rotation of the repeat unit around the oxygen atom in the deiphenylether moiety of the molecules results in a nonplanar conformation of the polymer chain, which changes locally at the vacuum interface into a more planar zigzag conformation and, hence, leads to a higher degree of crystallinity at the polymer surface.

The orientation of the polymer molecule as a function of distance from a solid interface can be determined by preparing films of defined thickness in a layer-by-layer-fashion using the Langmuir-Blodgett technique. The first studies on polyimide films prepared by the Langmuir-Blodgett technique were reported by Kakimoto *et al.*[10] Chemically-imidized monolayers of polyimide were prepared on HOPG graphite and SiO_2 surfaces by Sotobayashi and coworkers.[11-13] NEXAFS results on HOPG indicated that the two polymer sub-units (PMDA and ODA) are coplanar and oriented with their molecular planes parallel to the surface. The Cls NEXAFS data for a monolayer of PMDA/ODA polyimide on SiO_2[13] show the expected spectrum for an intact polyimide macromolecule but revealed no definite information on the orientation with respect to the surface plane. This implies that the arene rings of PMDA and ODA have either a different but fixed orientation relative to the surface *or* that the orientation is random.

The situation is different when a chemical reaction occurs between the polymer precursor and the substrate. Langmuir-Blodgett deposited polyamide acid films on Si(100)[14,15] and on polycrystalline gold and silver surfaces[16] have been studied recently in our group. 1, 3 and 5 layers of the octadecylammonium salt (on Si(100)) and the dimethyldodecylammonium salt (on Au and Ag) of polyamide acid were prepared on the substrates and subsequently analyzed by X-ray photoelectron spectroscopy and NEXAFS. NEXAFS measurements revealed that there is no preferential orientation of the phenyl rings on Au and Ag in the *polyamide acid* macromolecules with respect to the surface plane.[14] Loss of the alkylamine moities in the films during the curing procedure leads to free acid groups in the polymer backbone. Evidence was found in the XPS data that the free acid groups in the monolayer films react with the silicon and the silver surfaces, in the case of silver possibly under formation of carboxylate type complexes, as observed for vapour-deposited[17-19] and spun-on films.[20,21] On gold substrates, changes in the XPS spectra as a function of thickness indicated a dispersive interaction between PAA and the metal surface.[16]

The thermally-imidized Langmuir-Blodgett deposited polyimide films on gold and silver surfaces showed a different preferential orientation of the polymer chain on the two substrates.[22] From the NEXAFS data it was concluded that the polymer *chains* in both cases are oriented parallel to the surface. The O1s→π^* resonance was used as a searchlight to infer the orientation of the pyromellitic imide moiety in the polyimide unit, since it is polarized perpendicular to the imide ring plane. For the monolayer on gold the pyromellitic imide units are, on average, oriented parallel to the surface as evident from the absence of the O1s→π^* intensity in the normal incidence spectrum. For the 3-layer LB films, inclined orientation of the pyromellitic imide moities by about 35° with respect to the surface plane is found. The orientation of the pyromellitic imide unit of the 5-layer LB film approaches the one measured for vapour-deposited films, where an orientation of the pyromellitic imide moiety of 45° with respect to the surface plane is observed.

On silver, the O1s NEXAFS data showed that in a monolayer film the PMDA unit is tilted with respect to the surface plane due to the chemical bond at the interface. However, for the 3-layer LB films the average orientation is close to the one observed for the same film thickness on the gold surface (35°) and approaches the bulk orientation (as compared with vapour-deposited film) with increasing thickness. These measurements show that the nature of interaction in the interface determines the orientation of the molecules in contact with the metal, but they also reveal that the intermolecular forces can be strong enough to induce a bulk-like orientation within a film thickness of a few monolayers.

On Si(100), an even stronger reaction than on silver leads to *disordered* monolayer films as concluded from the NEXAFS data.[15,22] A preferential orientation of the pyromellitic imide unit with respect to the surface plane, although with a high degree of disorder, is only detected when the film thickness exceeds three monolayers.

A comparison of the NEXAFS results on the chemically-inert graphite and silicon oxide surfaces with those on polycrystalline silver and clean Si(100) surfaces suggests that for a high degree of order a weak interaction between the polymer and the metal is required. For the monolayers on gold, graphite and silicon oxide no evidence for a chemical interaction between polymer and substrate was found, whereas for the more reactive substrates covalent or ionic bond formation prevents full imidization and ring closure in the interphase and, hence, leads to an orientation of the polymer chains different from that observed on the inert substrates.

3. DELAMINATION EXPERIMENTS ON LANGMUIR-BLODGETT DEPOSITED POLYIMIDE FILMS

One monolayer of Langmuir-Blodgett deposited polyimide has a thickness of 0.6 nm as measured by ellipsometry.[15] Hence, the interphase on Au, Ag and Si(100), found to be structurally different from the bulk polymer, extends over at least 3 nm. The most striking differences as compared with the bulk structure is observed on clean Si(100) because of the strong chemical interaction at the interface. In order to determine whether the structural transition between the interphase and the bulk of the polymer can be associated with the "weak boundary layer," we performed preliminary 90° peel tests on Langmuir-Blodgett deposited polyimide layers.[23]

In order to carry out the delamination experiments, a laminar structure has to be made with these ultrathin films. Several methods to contact the surface of the LB deposited polyimide films were tested. One method was to attach a solid metal foil *via* an epoxy adhesive (Si/PI/epoxy/metal). Although this resulted in a stable bond, XPS spectra recorded on the delaminated surface of the PI/epoxy/metal side revealed a pronounced deficit in nitrogen as compared with stoichiometric polyimide, suggesting that the epoxy adhesive chemically reacted with the polyimide and thus led to a chemically-modified interphase. Since this chemically-modified polyimide layer might comprise an artificial "weak boundary layer," these results are not considered further.

In another set of experiments we evaporated 50 nm of Cr followed by 50 nm of Cu onto the polyimide surface and subsequently increased the copper thickness by electroplating (Si/PI/Cr/Cu). As an alternative to plating copper onto the evaporated Cr films, we bonded a metal foil to Cr with an adhesive (Si/PI/Cr/epoxy/metal). These preparations led to delaminated surfaces giving XPS spectra which are representative for the chemical composition of the polyimide at the respective thickness of delamination, and were used to determine the locus of failure by measuring the attenuation of the Si2p XPS substrate intensities. The calibration of film thickness *versus* Si2p signal intensity was obtained from a stepped Langmuir-Blodgett polyimide film, in which the film thickness was varied between 1–33 monolayers. No thickness calibrations for the opposite chromium film side were attempted, due to the frequent disruption of the film structure during delamination, exposing the metal film.

In Figure 1 we show the Si2p X-ray photoelectron *micrograph* of a delaminated polyimide film of 15 nm thickness (25 layers) obtained with the imaging photoelectron microscope (ESCASCOPE, Fisons Instruments).[1,2] The image shows streaks of high silicon signal intensity, corresponding to a low carbon signal in corresponding C1s micrographs, indicating that delamination is not homogeneous, but can be described by a stick-slip behaviour caused by stress relaxation in the film during delamination. Consistent with a fracture mechanism, where the stretched polyimide film breaks at its rupture limit and catastrophic failure occurs, the forces measured during the 90° peel test on a sample varied around 20 g/mm, with peak values at around 35 g/mm. As described by Oh *et al.*[4] for polyimide films in the

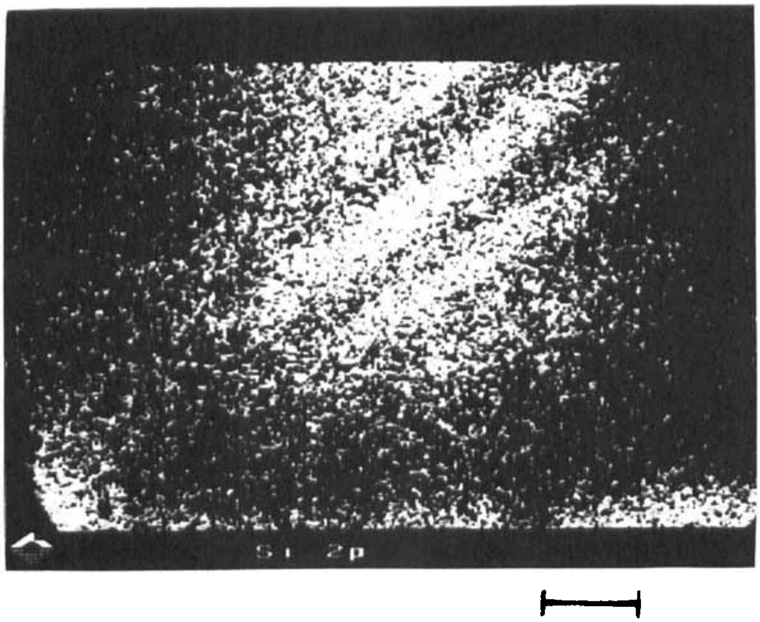

FIGURE 1 X-ray photoelectron microscopy images of the Silicon (100) side of a delaminated 25-layer Langmuir-Blodgett deposited polyimide film. Bright areas correspond to a higher Si2p photoelectron yield.

micrometer thickness range, strong interfacial bonds result in a discontinuous stick-slip behaviour and produce a corrugated surface topography. In the measurements of Oh *et al.*[4] the peel strength measured during delamination was about twice as high for the Langmuir-Blodgett films studied here. The width of the ripples caused by stick-slip delamination of the thick films were in the 2–5 μm range, whereas in our experiments their width is more in the 20–50 μm range. However, the qualitative similarity between our and Oh's data suggests that some of the mechanical concepts applied to the description of the delamination process of macroscopic coupons are also valid for film thicknesses expressed in molecular monolayers.

When small spot XPS spectra are recorded to estimate the thickness of the polyimide layers on the two complementary sides of the delaminated coupons, they will differ around an average thickness. Hence, we decided to record wide area spectra (field of view 800 μm × 800 μm) rather than small spot spectra in order to evaluate an average locus of failure by the attenuation of the Si2p substrate signal. Still, the non-homogeneous residual film thickness causes a wide scatter around an average locus of failure (see below).

Figure 2 shows the wide scan spectra of, a) a 25-layer polyimide film on clean Si(100), b) the delaminated interface on the silicon side of the sample, and c) the delaminated interface on the Cr side of the sample. 25 layers of polyimide correspond to a thickness of approx. 15 nm, *i.e.* much thicker than the electron mean free path of λ=4.2 nm[15] for the Si2p electrons through polyimide. Hence, the small Si signal in Figure 2a is due to inhomogeneities in the LB film. The spectrum of the delaminated film in Figure 2b from the silicon side is used to estimate the average thickness of the remaining polyimide film and, as described above, to determine the locus of failure. That both Cr and Cu are detected on the opposite side indicates that some of the film structure was destroyed in the peel process.

From the detailed spectra of the 15-monolayer and 23-monolayer films, as well as for some of the 25-layer films, we find that the delamination occurs in a distinct boundary layer close to the Si(100) surface. In these cases, the C1s spectra are marginally different from the two complementary delaminated sides. In Figure 3 we show the C1s spectra for, a) the 25-monolayer LB film (the asymmetric shape of the C1s at 284 eV band is due to incomplete desorption of alkyl amine chains in the polymer matrix),[15] b) the delaminated polyimide side attached to chromium and c) the delaminated polyimide side on the Si(100) interface where failure occurred at an estimated absolute thickness of 3–7 monolayers. As indicated by the peak around 285.5 eV, some carboxylate groups remain in the film, *e.g.* imidization was not complete. Spectrum c) compared with spectrum b) reveals an absolute higher C1s intensity, consistent with a thicker polyimide residue on the chromium side, and a somewhat different stoichiometry between the different carbon species. An assignment of the different carbon species in Langmuir-Blodgett deposited polyimide films has been given by us in Ref. 15. The spectral differences in Figure 3, however, are not strong enough to warrant a more detailed discussion. We would like to emphasize that in no case did we observe adhesion failure at the interface; delamination always occurred in the inter*phase*.

The O1s data for the same samples as shown in Figure 3 are displayed in Figure 4. While the data in Figure 4a are consistent with polyimide,[15,16] the low bind-

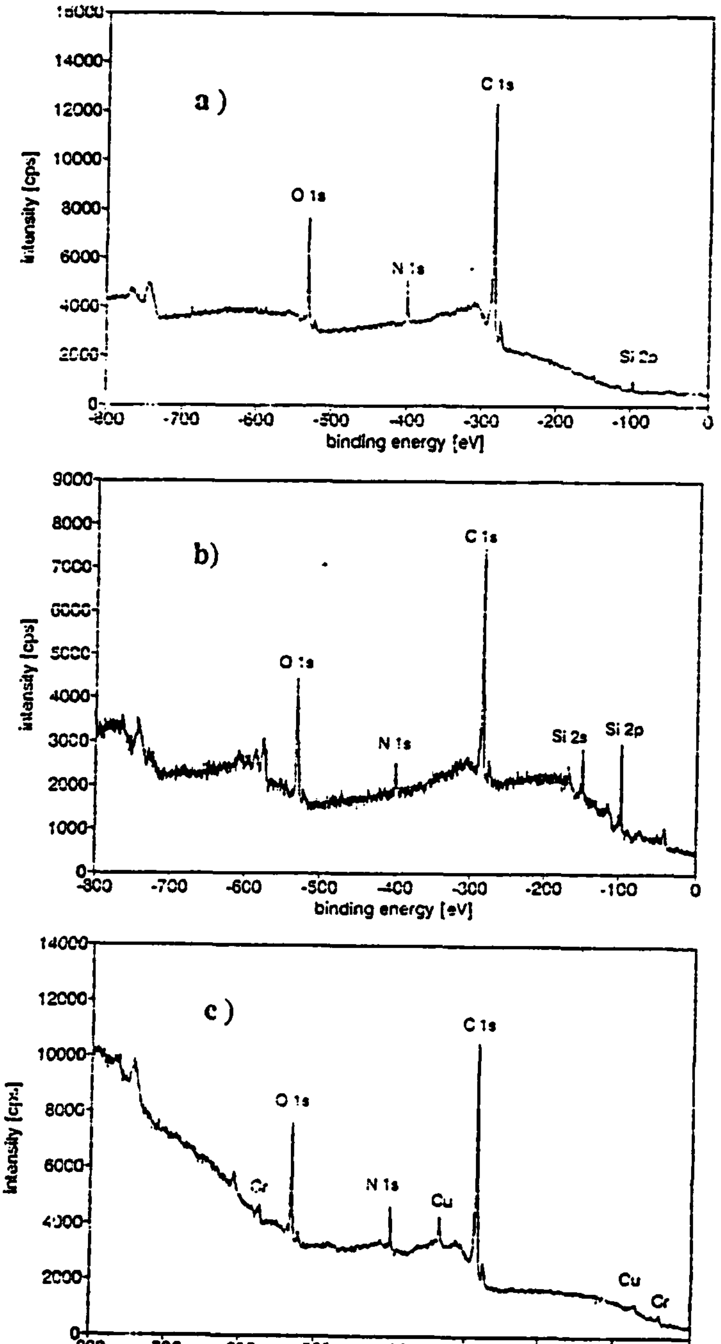

FIGURE 2 Wide survey X-ray photoelectron spectra of the: a) 25-layer Langmuir-Blodgett deposited polyimide film; b) polyimide residues on the delaminated Si(100) side; c) polyimide residues on the delaminated Cr/epoxy/metal side.

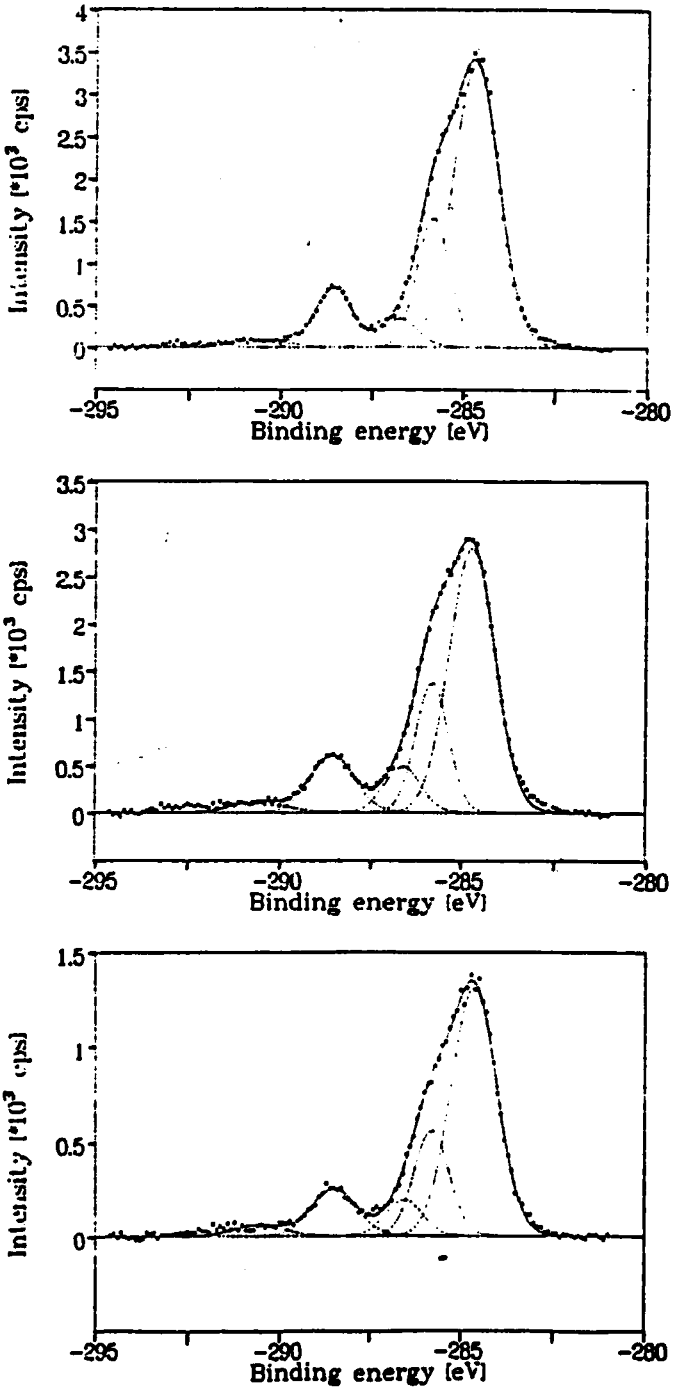

FIGURE 3 C1s spectra of a 25-layer Langmuir-Blodgett deposited polyimide film (Shirley background subtracted) for the: a) polyimide film prior to delamination; b) delaminated Cr side; c) delaminated Si(100) side.

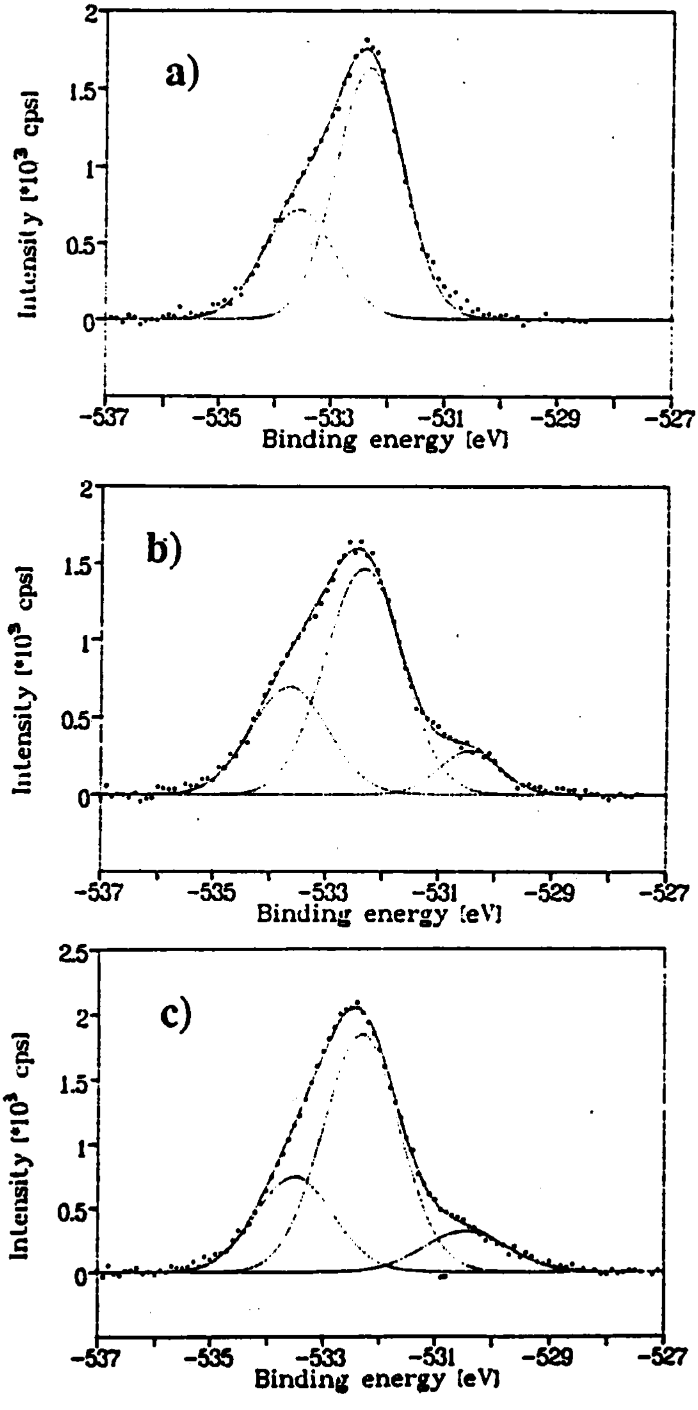

FIGURE 4 O1s spectra of a 25-layer Langmuir-Blodgett deposited polyimide film (Shirley background subtracted) for the: a) polyimide film prior to delamination; b) delaminated Cr side; c) delaminated Si(100) side.

ing energy band in the spectra taken on the silicon and chromium side of the film indicate the presence of oxide oxygen. A similar oxide O1s intensity was not only observed on the thinnest samples studied, but also on some, but not all, thicker specimens. On the silicon side of the substrate, the oxide oxygen corresponds to the Si2p SiO_2 signal at 104 eV binding energy, and its intensity is consistent with the estimated average locus of failure in the film. On the chromium side, we interpret the presence of oxide oxygen as indicative of a disrupted film structure due to the delamination process exposing the metallization. Alternatively, the presence of an oxide O1s (together with the small Cr signal observed) peak could indicate that failure occurs at a chromium diffusion boundary in the film which, however, would imply that adhesion at the chromium/polyimide interface is weaker than at the SiO_2/polyimide interface. This interpretation is unlikely in view of the results reported on chromium/polyimide interfaces.[6,7]

The average locus of the cohesive failure line expressed in monolayers for some representative samples is plotted in Figure 5 as a function of total film thickness. Note that a discontinuous film structure, as well as a mechanical destruction of the laminate, will result in an underestimate of the film thickness remaining on the

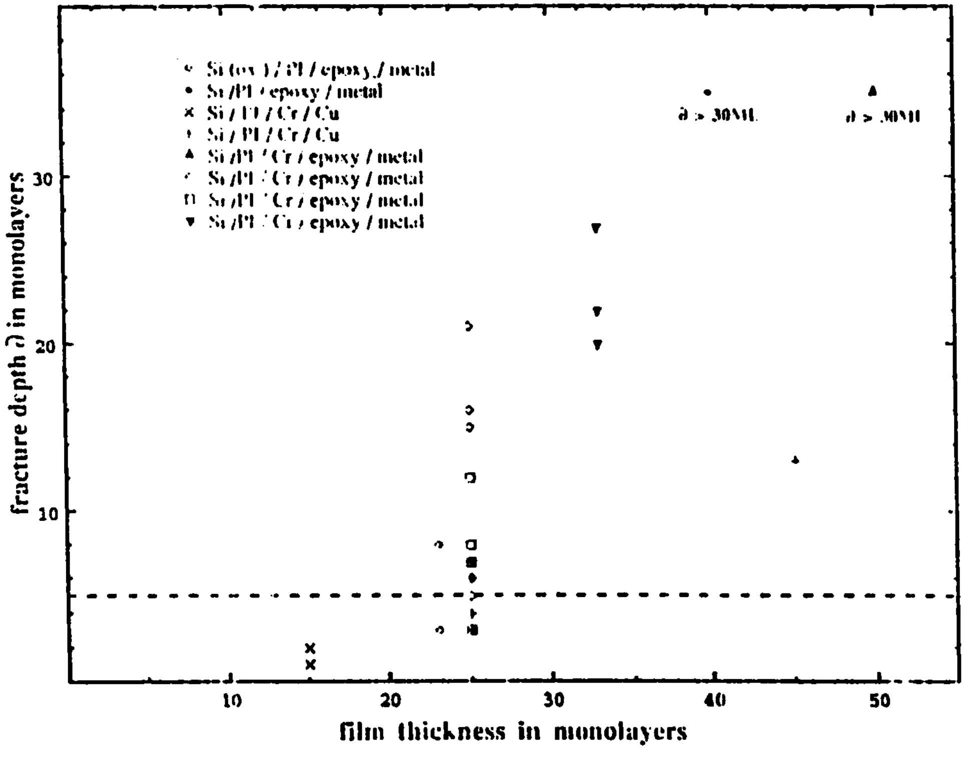

FIGURE 5 Fracture depth of the Langmuir-Blodgett deposited polyimide laminates as a function of total film thickness. The dashed line (at 5 monolayers) corresponds to the approximate thickness of the structurally and chemically distorted interphase on Si(100). Different symbols refer to different samples. Several data points for a particular sample refer to measurements on different spots on the delaminated surfaces.

silicon substrate. However, we observe a systematic trend in our measurements: the locus of failure depends on the thickness of the laminate, *i.e.* the thicker the films, the further away from the Si(100) surface failure occurs. We can not determine from our data whether fracture occurs at a constant depth in the film with respect to the chromium side, or if the depth also varies as for the silicon side of the laminates. Due to the limited depth resolution of XPS to measure the remaining film thickness, this question has to be addressed in further studies using other means of film thickness measurements.

The fact that the fracture depth, with respect to the silicon substrate surface films, progresses into the bulk of the polymer with increasing film thickness suggests that the mechanical properties of the laminate and possibly the details of our delamination experiment influence the result. A correlation between peel strength and film thickness is commonly observed in delamination experiments on much thicker polyimide films (μm).[4]

For a quantitative correlation between the structural properties of the interphase and the cohesive strength a more sophisticated experimental set-up than presently available to us is needed. As an important finding, however, we would like to point out again that the observation of "ripples" on the delaminated Si(100) surfaces indicates that a discontinuous stick-slip behaviour is also occurring in the delamination of ultrathin polymer films.

4. ADSORPTION AND STRUCTURE OF POLYAMIDE ACID FILMS STUDIED BY OPTICAL SECOND HARMONIC GENERATION

When substrate surfaces are to be coated with a polyimide film, the initial interaction occurs in the polyamide acid state of the polymer. Due to the experimental difficulties in preparing ultrathin films of polyamide acid, only very few results have been published on the interfacial chemistry between dissolved polyamide acid and bulk metal substrates. For vapour-deposited polyamide acid films an identification of the interfacial chemistry is possible, because the vapour deposition technique offers the advantage of being able to clean or purposely modify substrate surfaces under well-defined conditions and to analyze them by surface-sensitive techniques prior to deposition of the polymer precursor.

In the vapour phase deposition technique the dianhydride (pyromellitic dianhydride, PMDA) and the diamine (4,4′-oxidianiline/ODA) are codeposited onto a substrate where they react to form polyamide acid. The transformation to polyimide is obtained by subsequent heating to temperatures up to or exceeding 515 K. Hahn *et al.*[24] showed that at room temperature the PMDA/ODA codeposited layers consist predominantly of an amine carboxylate salt of polyamide acid. Recent results by Strunskus further indicate that in the vapour-deposited films the average repeat unit length is only n=1.5.[25] In the vapour-deposited films, imidization to polyimide (as evidenced by imide ring closure) starts above 410 K. After heating to 515 K the films are completely imidized and give infrared and X-ray photoelectron spectra characteristic of a stoichiometric polyimide film.

It is reasonable to assume that the molecular orientation of polyamide acid in the interphase will determine also to some extent the physical properties of the interphase after imidization. Hence, an *in situ* and real time analysis of the growing polymer film could, after a sufficient database is established, help to predict the properties of the polyimide/substrate interphase. As will be demonstrated below, second harmonic generation (SHG) offers the potential possibility to do so.

Before discussing the SHG experiments on the growth of polyamide acid films on metallic substrates, some basic principles on the origin of SHG have to be discussed. Due to the lack of space, only a strongly simplified description can be given. The equations presented are based on the electric dipole approximation. Details about theoretical aspects of SHG for interface analysis are found in the literature.[26–28] Due to the nonlinear interaction of a laser field E(ω) incident on a substrate, a polarization

$$P_i(2\omega)=\chi_{ijk}E_j(\omega)\,E_k(\omega) \tag{1}$$

is induced which oscillates at twice the incident frequency. The nonlinear susceptibility χ_{ijk} is a third rank tensor and represents the material properties. The polarisation is the source of the second harmonic radiation and can be viewed as an ensemble of coherently driven antennas emitting the frequency-doubled light in a well-defined direction. An important consequence of Eq. (1) is that the bulk of amorphous substances or materials possessing inversion symmetry does not generate any SHG signal. Only at interfaces where the inversion symmetry is broken is a SHG signal produced. However, in systems lacking inversion symmetry a bulk second harmonic signal is generated, too.

The systems under study here are a composite of a metallic substrate and an evaporated polymer film. The intensity of the second harmonic light consists of a sum of three contributions and can be written as:

$$I_{SHG}\sim|(\chi_{sub}+\chi_{int})E(\omega,z=0)^2+\int \chi_f(z)E(\omega,z)^2 f(E(2\omega,z))^2 e^{i\Delta kz}dz|^2. \tag{2}$$

The Cartesian coordinate system has been chosen such that its origin lies in the surface plane and the positive z-axis points away from the substrate in the normal direction. For simplicity the tensor notation has been omitted. χ_{sub} describes the second-order optical properties of the bare substrate and χ_{int} refers to the change of the electronic properties of the substrate surface due to its chemical interaction with the evaporated molecules. In other words, this term reflects the interface formation and the corresponding contribution to the SHG signal should level off when the interface formation is completed. The SHG signal generated by the polymer film is given by the integral. From the above arguments it follows that, if the film growth yielded randomly-oriented molecules, the third term of Eq. (2) would vanish and, therefore, one would be unable to monitor the growth of the polymer layer. In contrast, if the molecules showed a preferential orientation a continuously-changing SHG signal with increasing film thickness would be observed. The detailed development of the signal with film thickness is determined by several facts. One is given by the behaviour of χ_f as a function of distance from the substrate and reflects the structural properties of the film. Since we deal with a three-layer system, interference effects, in analogy to linear optics, have to be taken into account. This is reflected by the variation of the fundamental and second harmonic electric fields along the surface normal. Thirdly, the dispersion of the polymer film has to be considered. This is taken into account by the exponential term of Eq. (2) which contains the phase vector difference of the fundamental and second-harmonic fields. A comprehensive model has also to address absorption of the SHG light in the polymer film. A detailed discussion of these issues which is based on the work of Bloembergen and Pershan[26] on second harmonic generation of a nonlinear plane parallel plate is beyond the scope of this article and will be presented in a forthcoming publication.[29] In terms of a mathematical description only the most simple case which is based on three assumptions can be considered here. If disperson and interference effects are negligible, and if the susceptibility χ_f of the film is independent of the distance from the substrate, Eq. (2) can be simplified to

$$I_{SHG} \sim |\chi_{sub}(2)+\chi_{int}^{(2)}+\chi_f^{(2)} z|^2 E(\omega)^2. \tag{3}$$

In cases where molecules interact strongly with the substrate a distinct signal change should be observable in the very early stages of deposition. As already pointed out above, the change of the SHG signal due to processes at the interfaces should saturate when the first monolayer is completed. The subsequent film growth is then expected to yield a continuously-increasing SHG signal which depends quadratically on the film thickness.

The experiments were carried out in a high vacuum chamber. The monomers evaporated from two Knudsen cells condense on the substrate where they react to form polyamide acid. Polycrystalline gold and silver films were used as substrates. Pyromellitic dianhydride (PMDA) and 4,4′-diaminodiphenylether (ODA) or 4,4′-diaminodiphenyldisulfide (DAPS) served as chemicals. The deposition was carried out with the substrate at ambient temperature. The correlation between deposition time and film thickness was accomplished by calibration with a quartz microbalance. The SHG signal was monitored in reflection at a frequency of 532 nm. Both fundamental and analyzed second harmonic were p-polarized. More experimental details are found in Refs. 29 and 30.

The result of such a CVD experiment is shown in Figure 6a for the codeposition of PMDA and ODA on silver. For the following discussion the SHG curve might be divided into three regions. The first one is the silver/polymer interface. No interface reaction is detected by SHG for this system. At first glance this is surprising since PMDA is expected to react with Ag forming a bidentate.[17,19] This strong reaction should be easily reflected in a distinct change of the SHG signal. However, in our case the evaporated silver films had been exposed to the atmosphere prior to the deposition. The surface is covered with oxygen and organic contaminants leading possibly to a weaker bonding between deposit and substrate or, alternatively, the displacement of contaminants and bond formation with the polymer precursors does not lead to a measurable change in the electronic properties of the silver surface. In cases where ODA/PMDA were evaporated onto freshly sputtered Ag a pronounced change of the SHG signal is observed right at the beginning of the deposition.

The second range extends up to 70 nm and can be described by a quadratic

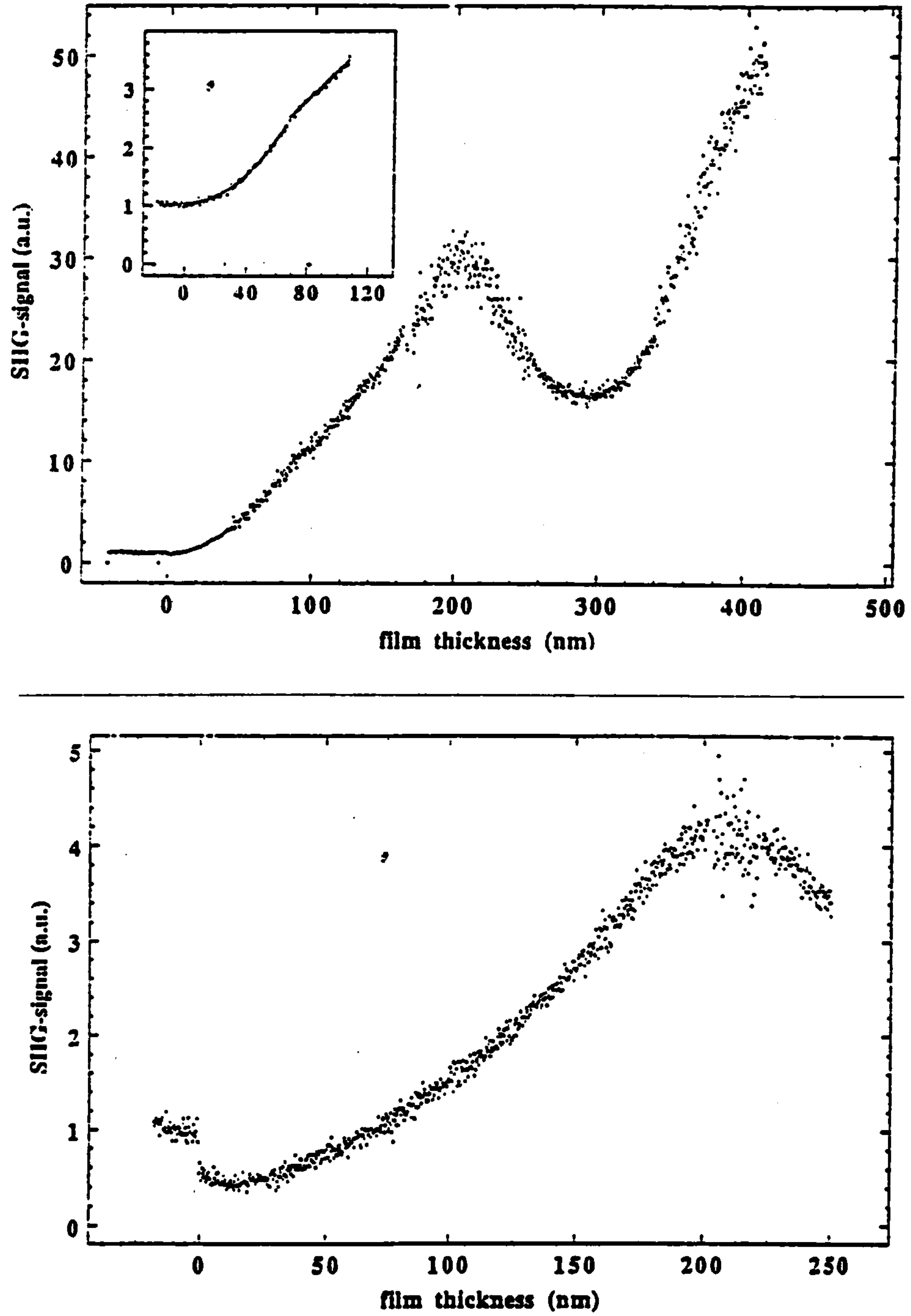

FIGURE 6 SHG signal as a function of total film thickness for: a) PMDA/ODA polyamide acid on Ag (inset shows enlarged thin film region); b) PMDA/DAPS polyamide acid on Au.

dependence of the SHG signal on the film thickness in agreement with Eq. (3). As outlined above, this indicates that the growing film cannot be randomly oriented but must have a preferential orientation.

The third range beyond 70 nm shows a pronounced deviation from the quadratic behaviour. The SHG intensity alternates between maxima and minima. In this region interference effects come into play and the assumptions made in the derivation of Eq. (3) no longer hold. The structural information is contained in the detailed shape of the SHG curve.

A different behaviour is observed for DAPS/PMDA deposited on gold. As Figure 6b illustrates, a sudden drop of the SHG signal right at the beginning of the deposition is observed, indicating clearly the interface formation. The interfacial bond is formed by the DAPS. Besides its role as one of the polymer constituents, it serves as the link between the substrate and the polymer film via dissociation of the disulfide bond and formation of a 4-aminophenyl thiol-Au complex. The adsorption chemistry of DAPS is the same as for thiols and disulfides which have been investigated extensively by a variety of techniques[31,32] including SHG.[33] The subsequent film growth yields qualitatively the same shape of the SHG curve as for ODA/PMDA on Ag. However, the rather sudden change in the slope of the SHG signal shown in the inset of Figure 6a is not observed for DAPS/PMDA on gold. We ascribe this observation to different structures present in the polymer films. For PMDA/ODA on Ag we propose that the film structure adjacent to the interface deviates from the bulk structure of the polymer film and is determined by the nature of the interaction between polyamide acid and the metal at the interface. Therefore, a structural transition is expected going from the near-interface interphase layer to larger thickness. The influence of the interfacial chemistry on the structure of the interphase layer is supported by experiments where PMDA/ODA is evaporated on gold. The corresponding SHG signal shows a linear increase until the same interference effects as described above become prominent.

The optical experiments on polymer film growth show that SHG is a valuable technique for *in situ* film formation studies. Three different regions can be observed by SHG. Firstly, the interface formation which takes place instantaneously at the beginning of the codeposition of the monomers. Subsequently, an interphase layer extending up to a thickness of several tens of nanometers grows whose structure is determined by the interfacial chemistry. Finally, the bulk properties of the films are expressed by the SHG signal from thicker layers. The general shape of the second harmonic signal in this regime is independent of the substrate and the chemical constituents.

Applying a three-layer model for the generation of second harmonic light and approximating the susceptibility tensor by a one-dimensional tensor, the general shape of the SHG signal as a function of film thickness can be calculated. We find that the orientation of the one-dimensional susceptibility tensor in the model calculation has a drastic effect on the initial slope of the SHG signal and changes as a function of film thickness. Both a quadratic and linear dependence of the SHG intensity on film thickness can be simulated. This result implies that the structure in the interphase, as determined by the interfacial chemistry, is reflected in the different shapes of the SHG curves. Also, the rather sudden change from a quadratic to a linear film thickness dependence, as shown in the inset of Figure 6, indicates a structural transition rather than a continuous change in orientation of the polyamide acid units. In order to understand the long-range order established in the interphase of these polyamide acid layers we have to realise that the vapour-deposited polyamide acid has no polymeric character, but is better represented by polyamide acid units of approximately the size of 1–2 repeat units.[25] Those polyamide acid molecules can easily crystallize and have the long-range order which is reflected in the SHG signal.

5. SUMMARY

The in-plane orientation of the pyromellitic imide unit in the Langmuir-Blodgett deposited polyimide films on polycrystalline gold, silver and Si(100) has been studied in a layer-by-layer fashion using NEXAFS. It was found that the orientation of the pyromellitic imide unit in the *interphase* depends on the nature of the interaction at the *interface*. Ordered monolayers are observed on gold, where only an electrostatic or dispersion interaction between the two materials take place. On silver, the formation of carboxylate-type bonds induces an inclined orientation of the pyromellitic imide unit. However, at a thickness of 3 monolayers the orientation on gold and silver is almost identical, but not yet consistent with the bulk structure determined for vapour-deposited polyimide films. On Si(100), a strong interfacial reaction leads to strongly-disordered films within a thickness of at least 3 monolayers and to a different molecular orientation in the 5-layer film as compared with the metal substrates.

Delamination experiments on polyimide layers of thickness ranging between 15–50 monolayers revealed only for the thinnest films (up to 25 monolayers) a locus of failure at the chemically and structurally distinct interfacial layer in contact with the Si(100) substrate. For the thicker polyimide films we found that the locus of failure progresses with film thickness into the bulk of the films. The laminated Si(100) surfaces studied by X-ray photoelectron microscopy revealed the occurrence of a discontinuous stick-slip behaviour characteristic for the debonding process. More sophisticated methods are needed to study quantitatively crack propagation and the micromechanics of delamination in the ultrathin Langmuir-Blodgett films.

We finally presented second harmonic generation results for polyamide acid film growth on silver and gold surfaces. The interfacial chemistry (physical *versus* covalent or ionic interaction) is clearly seen in the SHG signal when deposition is started. A different behaviour in SHG intensity as a function of thickness was observed on the different substrates and also depending on whether 4,4′-diaminophenylether or 4,4′-diaminodiphenyldisulfide was used as the diamino compound in the vapour deposition process. First model calculations show that the shape of the SHG signal as a function of thickness is sensitivity dependent on the orientation of the susceptibility tensor in the polyamide acid molecules. Hence, second harmonic generation offers the possibility to study interfacial chemistry and structure in the interface during film growth in real time.

Acknowledgements

The work described here was supported in part by the BMFT under grant #01BM206/3 and by the DFG (Gr 625/13-1).

We thank Wolfgang Schrepp (BASF) for providing us with and helping us in the preparation of the Langmuir-Blodgett deposited polyimide films and we thank Thomas Strunskus, Georg Hähner and Christolf Wöll for helpful discussions.

References

1. M. Kinzler, M. Grunze, N. Blank, H. Schenkel and I. Scheffler, *J. Vac. Sci. Technol.* **A10**(4), 2691–2697 (1992).
2. M. Kinzler, M. Grunze, N. Blank, H. Schenkel and I. Scheffler, *J. Adhesion,* (1993), to be published.
3. F. Gailland, D. Vercheve, H. Hocquaux and M. Romand, *J. Adhesion,* to be published.
4. T. S. Oh, L. P. Buchwalter and J. Kim in *Acid-Base Interactions,* K. L. Mittal and H. R. Anderson, Eds. (VSP, Amsterdam, 1991), p. 287.
5. L. P. Buchwalter and J. Greenblatt, *J. Adhesion* **19,** 257 (1986).
6. M. Grunze, A. Killinger, C. Thümmler, C. Hahn and T. Strunskus, "Comparison between the interfacial chemistry of metallized polyimides and polyimide films on bulk metal substrates," in K. L. Mittal, Ed. (1991), pp. 165–177.
7. M. Grunze and T. Strunskus, in "Chemical and Structural Studies of Polyimide/Metal Interfaces," in , S. P. Kowalczyk, Ed. (Marcel Dekker, New York, in press).
8. T. P. Russell, *J. Polym. Sci., Phys. Ed.* **22,** 1105 (1984).
9. B. J. Factor, T. P. Russell and M. F. Toney, *Phys. Rev. Lett* **66,** 1181 (1991).
10. M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto and T. Hino, *Chem. Lett.* 823, (1986).
11. H. Sotobayashi, D. Schilling and D. Tesche, *Langmuir* **6,** 1246 (1990).
12. T. Schedel-Niedrig, H. Sotobayashi, A. Ortega-Vilamil and A. M. Bradshaw, *Surf. Sci.* **247,** 83 (1991).
13. T. Schedel-Niedrig, M. Keil, H. Sotobayashi, T. Schilling, B. Tesche and A. M. Bradshaw *Ber. Bunsengesellschaft* **95(11),** 1385 (1991).
14. M. Grunze, G. Hähner, M. Kinzler, A. Killinger, Ch. Mainka, W. Meyer, A. Ortega-Vilamil, Ch. Wöll and W. Schrepp, in *Berichtsband zum Symposium "Haftung bei Verbundwerkstoffen und Werkstoffverbunden,"* W. Brockmann, Ed. (Konstanz (FRG), 1990), p. 11.
15. A. Killinger, Ch. Thümmler, M. Grunze and W. Schrepp, *J. Adhesion* **36,** 229–245 (1992).
16. W. Meyer, M. Grunze, R. N. Lamb, A. Ortega-Vilamil, W. Schrepp and W. Braun, *Surf. Sci.* **273,** 205 (1992).
17. M. Grunze and R. N. Lamb, *Surf. Sci.* **204,** 183 (1988).
18. T. Strunskus, M. Grunze and S. Gnanarajan in *Metallization of Polymers,* E. Sacher, J. J. Pireaux and S. Kowalczyk, Eds., *ACS Symposium Series* **440,** 353 (1990).
19. S. S. Perry and A. Campion, *Surf. Sci. Lett.* **234,** L275, (1990).
20. J. T. Young, W. H. Tsai and F. J. Boerio, *Macromolecules* **25,** 887 (1992).
21. W. H. Tsai and F. J. Boerio, *Polym. Preprints* **32**(3), 312 (1991).
22. M. Grunze, G. Hähner, Ch. Wöll, *Surface and Interface Analy.* **20,** 393 (1993).
23. Where is No. 23??
24. C. Hahn, T. Strunskus, D. Frankel, M. Grunze, *J. Electron Spectr.* **54/55,** 1123 (1990).
25. T. Strunskus, Ph.D. Thesis, University of Heidelberg, (1993), to be published.
26. N. Bloembergen, P. S. Pershan, *Phys. Rev.* **128,** 606 (1962).
27. P. Guyot-Sionnest, Y. R. Shen, *Phys. Rev. B* **38,** 7985 (1988) and references therein.
28. V. Mizrahi, J. E. Sipe, *J. Opt. Soc. Am.* **B5,** 660 (1988).
29. C. Dressler, M. Buck, F. Träger and M. Grunze, to be published.
30. M. Grunze and M. Buck in *Surface Science: Principles and Applications,* Springer Proc. Phys., Vol 73, R. F. Howe, R. N. Lamb and K. Wandelt, Eds. (Springer, Berlin, 1992), p. 67.
31. L. H. Dubois, R. G. Nuzzo, *Ann. Rev. Phys. Chem.* **43,** 437 (1992).
32. G. Hähner, *J. Vac. Sci. Technol.* **A10,** 2758 (1992).
33. M. Buck, F. Eisert, J. Fischer, M. Grunze, F. Träger, *Appl. Phys.* **A53,** 552 (1991); M. Buck, M. Grunze, F. Eisert, J. Fischer and F. Träger, *J. Vac. Sci. Technol.* **A10,** 926 (1992).