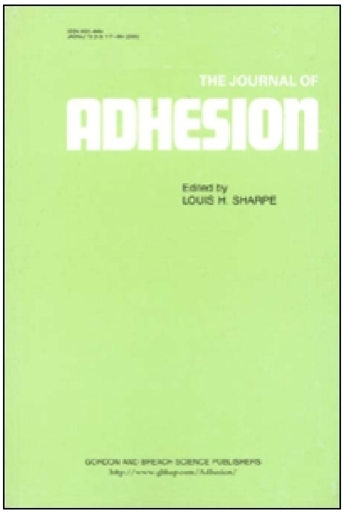

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Interfacial Chemistry of Langmuir-Blodgett Deposited Polyimide Films on Si (100)*

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Using the Langmuir-Blodgett (LB) technique, ultrathin films of the octadecylammonium salt of polyamic acid (PACS) on (100) oriented silicon wafers with one, three and five monolayers were prepared. The imidization of the films was investigated with x-ray photoelectron spectroscopy (XPS) during a stepwise heating procedure in vacuum. Significant differences in the XPS spectra indicate an incomplete polymerization of the films as a function of film thickness. It is believed that the chemical interaction at the interface between Si substrate and PACS is responsible for the incomplete polymerization of the LB film in direct contact with the substrate. From ellipsometric measurements the absolute thickness of a PACS and a polyimide layer has been determined to be 1.7 nm and 0.6 nm, respectively. These measurements allow us to determine the electron mean free path for the Si2p electrons ($E_k = 1153$ eV) of $\lambda = 4.2 \pm 0.1$ nm through these films.

KEY WORDS Langmuir-Blodgett deposited polyimide films; Si (100); interfacial chemistry; x-ray photoelectron spectroscopy; ellipsometry; electron mean free path.

1 INTRODUCTION

The favorable dielectric properties and high thermal stability of polyimides make them important polymers for application in solid state electronic technology.[1] However, reliable adhesion between the polymer and the substrate remains of major concern with polyimides. In this paper we describe x-ray photoelectron spectroscopy (XPS) measurements of polyimide (PI) films prepared by heating Langmuir-Blodgett deposited PI precursor films (PACS) on clean Si wafers under UHV conditions. The precursors were deposited by the LB technique as 1, 3 and 5 LB layer samples on the clean Si wafers, thus enabling us to determine the interaction of the

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polymer with the substrate as a function of polymer thickness.

The most widespread PI is formed by the reaction of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA).[2] PI/metal interfacial configurations are necessarily dependent on the way in which the interface is formed. The methods of PI preparation on a bulk substrate surface include 1) spin coating of the polyamic acid (PAA) precursor dissolved in a polar solvent (N-methyl-2-pyrrolidone, NMP) onto the substrate with subsequent curing and PI formation, and 2) codeposition of the polyimide constituents pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) from the vapor phase at a controlled temperature and polymerization of the adsorbed film.[3] In the vapor-deposited films the precursor molecules PMDA and ODA react in the adsorbate phase to form a carboxylate-amine salt complex and polyamic acid, their relative concentration depending on the PMDA/ODA ratio in the condensate.[4] At 373 K, the excess component is desorbed and the film consists of polyamic acid. XPS and IR data of PI/Ag and PI/Cu interfaces prepared by curing the vapor-deposited polyamic acid film reveal partial fragmentation of the ODA and PMDA molecules in the adsorbate phase providing unoccupied valences as linkage sites for the actual PI chains.[5] Consequently, the imidization reaction at the interface is in part incomplete. Under the conditions just described it does not yield PI at the interface in the exact stoichiometry expected. A similar situation is encountered in the PI/Si system described in this article.

Ultrathin spin coated polyamic acid (dissolved in NMP) films with an estimated thickness of $d \approx 2.5$ nm and the resulting polyimide films on nickel, nickel oxide, chromium, and native silicon oxide surfaces were studied by Iacona *et al.*[6] Whereas strong reactions of the carboxylic acid groups in PAA were found on Ni, NiO_x and Cr to prevent imidization in the interface, the absence of chemical interactions was concluded for PAA and PI on the native oxide on silicon.[6] Adhesion of PMDA/ODA polyimide onto an amorphous bulk SiO_2 surface was studied by Oh *et al.* experimentally[7] and, using the acid-base concept, by Buchwalter in a hypothetical study of polymer interaction with metal/metal oxide surfaces.[8] From her estimate of the acid-base interaction between the polyimide and the SiO_2 surface, Buchwalter concluded that polyimide only adheres *via* dispersion forces onto the SiO_2 substrate.[8] Although this conclusion would be in agreement with the results of Iacona *et al.*,[6] the adhesion strength measurements for PI on SiO_2[7] gave values similar to those obtained for a PI/Al_2O_3 interface which was predicted to exhibit strong adhesion based on the acid-base properties of the two materials.[8] The reason for this distinct discrepancy between the experimental measurements and the adhesion strength prediction from the acid-base properties has not been resolved. A possible explanation is that defects in the SiO_2 surface containing silicon in lower oxidation states facilitates a strong interfacial reaction. In this respect, we refer to the XPS results of Kowalczyk *et al.*,[9] who observed a strong reaction between vapor-deposited polyamic acid and a clean Si (111) surface. An interesting observation in this respect was reported by Perry *et al.*[10] who studied adsorption of PMDA on a clean and on an oxidized Si (100) surface. On the clean Si (100) surface PMDA was found to adsorb dissociatively through the formation of bidentate bridging and chelating carboxylate species. Oxide growth preferentially blocked formation of the chelating species, whereas the bridging carboxylate species persisted even on thicker oxide layers.

A reasonable alternative to the aforementioned preparation methods for polyimide films is the LB technique.[11–13] This preparation technique involves the layer-for-layer deposition of the precursor (the ammonium salt or ester of polyamic acid) which results in well defined ultrathin films. The deposition occurs with relative ease under atmospheric conditions. However, contamination in air is a concern for the time span between film deposition and probe transfer in the UHV chamber for future analysis. A detailed comparison of the interfacial chemistry of polyimide films prepared by different techniques is given in Reference 11.

In this article we report XPS and ellipsometry results of 1, 3 and 5 LB PACS films on a Si (100) surface obtained after heating from 293 to 573 K in 50 K steps under UHV conditions. Our main interest is in the chemistry of adhesion between the two materials, the correlation between the degree of polymerization and precursor film thickness, and the thickness of the layers. The results as a whole are compared with the more popular PI preparation methods described above.

2 EXPERIMENTAL

Preparation of the LB films started with a cleaning procedure of the silicon wafers followed by hydrophobic deposition of the PACS onto the wafer in a Langmuir trough. Cleaning of the silicon (100) wafers included the following steps: After ultrasonic treatment in an alkaline surfactant solution for 15 min, the wafers were placed for one hour in a mixture of one part hydrogen peroxide (40%) and four parts concentrated sulfuric acid. To achieve a hydrophobic surface, the silicon substrate was dipped for 10 sec into hydrofluoric acid (10%), which was buffered by ammonium fluoride. Between the different steps the wafers were thoroughly rinsed by purified water (Milli-Q-system). The contact angle against water before film deposition was 75°–80° confirming a hydrophobic surface.

For synthesis of the polyamic acid salt commercially available anhydrides and amines were used without further purification. 5.3 mmol pyromellitic acid dianhydride (99%; Aldrich Chemie GmbH&Co KG, Steinheim, Germany) were dissolved in 20 ml N-methyl-pyrrolidone under a weak flow of nitrogen and heated to 423 K. After recooling to room temperature 5 mmol of 4,4′-oxydianiline (99%; Aldrich) in 20 ml of solvent and three drops of tributylamine were added. The mixture was stirred overnight. Purification was done by repeated precipitations from NMP with methanol or isopropanol. The polymer was dried in vacuum at room temperature. The yield was 73%. The polyamic acid amine salt was formed in NMP solution by adding the stoichiometric amount of octadecylamine (99%; Aldrich). For further details see Reference 14.

Hydrophobic deposition of the LB films was performed in the following way: Solutions of PACS in a concentration of about 1 mg/ml solvent (one part dimethylacetamide (DMA) and nine parts chloroform) were spread onto a pure water subphase kept at 288 K. The Milli-Q-water had a conductivity of 18 MΩ cm. The films were compressed in a film balance (Lauda Langmuir trough FW 1) to the deposition pressure of 25 mN/m. Subsequent transfer onto the silicon wafer was achieved by dipping the wafer attached to a film-lift (Lauda FL 1) at a deposition speed of 4 mm/min for the up and down stroke. An IR analysis of the starting

PACS solution indicates that about 10% of the polyamic acid is already imidized.

Experiments were carried out in a Leybold Heraeus standard UHV system for surface analysis equipped with a Mg K_α radiation source and a monochromatized Al K_α source for x-ray photoelectron spectroscopy (XPS). The total pressure during experiments in the analysis chamber was about 5×10^{-9} mbar. A mechanically driven sample holder rod enabled sample transfer into the analysis chamber. The sample was then mechanically moved onto a manipulator equipped with a resistive heating facility and PT100 thermal resistant wire to monitor temperature externally. Heating during experiments was controlled manually and scans were started after the desired temperature was reached. The spectra were recorded with a modified Leybold Heraeus EA11 hemispherical electron energy analyzer equipped with a multichannel detector. Experimental resolution was measured to be 1.2 eV for the Mg K_α source and 0.84 eV for the monochromatized Al K_α source, respectively. The data were analyzed by peak deconvolution applying a fixed Gaussian/Lorenzian ratio and FWHM for a specified core level signal. The background was fitted using a nonlinear model function proportional to the integral of the unscattered or elastically scattered particles (Shirley background).

The film thicknesses were measured with a manual zero ellipsometer with a He-Ne light source (632.8 nm). The incidence angle of the light beam (1.5 mm diameter) was 70°. In evaluating the thickness it was assumed that the organic films are non-absorbing ($k=0$) and isotropic. For the silicon substrate $n=3.87$ and $k=0.14$ were used, which compare well with values found in the literature.[15] The refractive indices measured for the PACS and PI films were $n=1.62$ and $n=1.71$, respectively.[14]

3 RESULTS

3.1 Chemical Composition of the Films

The imidization reaction leading to polymer formation was followed *in situ* with x-ray photoelectron spectroscopy. Figure 1a shows the schematic reaction pathway. Heating PACS molecules to $T>473$ K in vacuum leads to imidization, ideally resulting in the desorption of water and primary alkylamine and the collapse of the initially stacked LB-films of polyamic acid (Fig. 1b) when polyimide is formed.

In Figure 2 we display the C1s spectra for the 1, 3 and 5 layer deposits recorded at 293 K, 423 K, and 573 K. The 1 LB film is only shown for $T\leq523$ K since the data points at higher temperatures were obscured by experimental problems. The 293 K spectra are dominated by a C1s emission around 285.5 eV binding energy, which arises predominantly from photoemission from the alkyl chains. The shoulder on the low binding energy side is due to phenyl carbon atoms in polyamic acid; the low intensity feature at 289.5 eV is due to the acidic and amide carbonyl groups. The spectra of vapor-deposited and dissolved polyamic acid have been discussed in the literature.[3,16,17] The data shown in Figure 2 are consistent with polyamic acid, considering the strong alkyl chain emission. A deconvolution of the PACS XPS spectra was not attempted due to the ambiguities in assigning specific electron binding energies for the different carbon species present in the prepolymer.

Heating the PACS layers leads to spectral changes indicative for desorption of

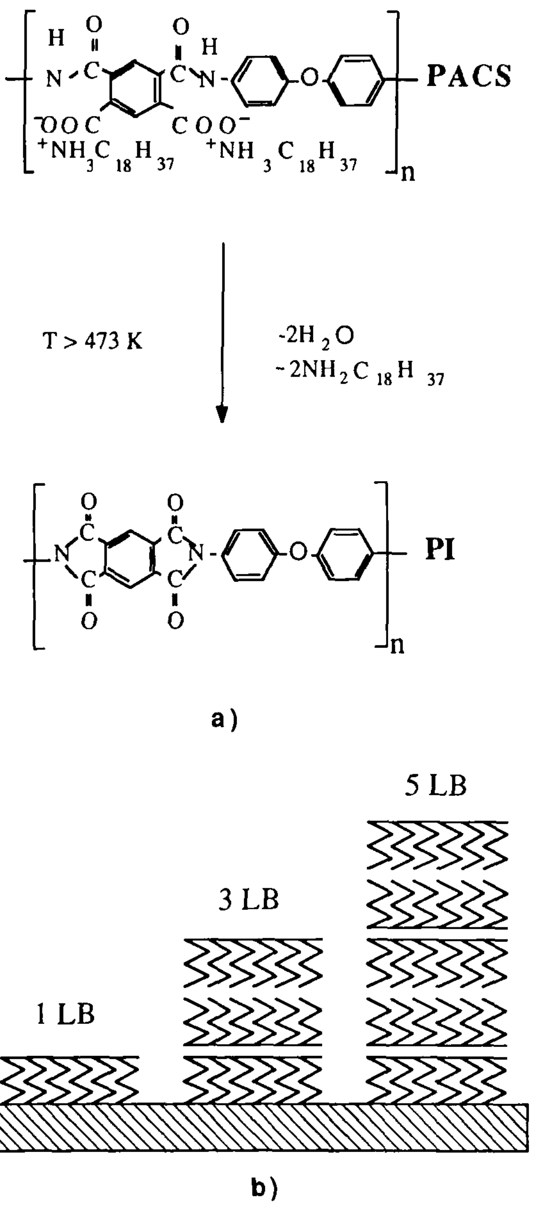

FIGURE 1 a) Schematic representation of the imidization reaction at T>473 K of PACS to polyimide. b) Model of 1, 3 and 5 LB layers of PACS deposited on the substrate.

the alkyl chains and for the 3 and 5 layers at temperatures around 473 K for imidization.[16,17] Imidization is most evident in the pronounced increase in the carbonyl C1s intensity indicating the conversion of the carboxylic acid salt (having a carbonyl C1s binding energy at around 288 eV)[17] into the imide carbonyl group. We note at this point that for the one-layer film the carbonyl intensity does hardly increase, *i.e.* the

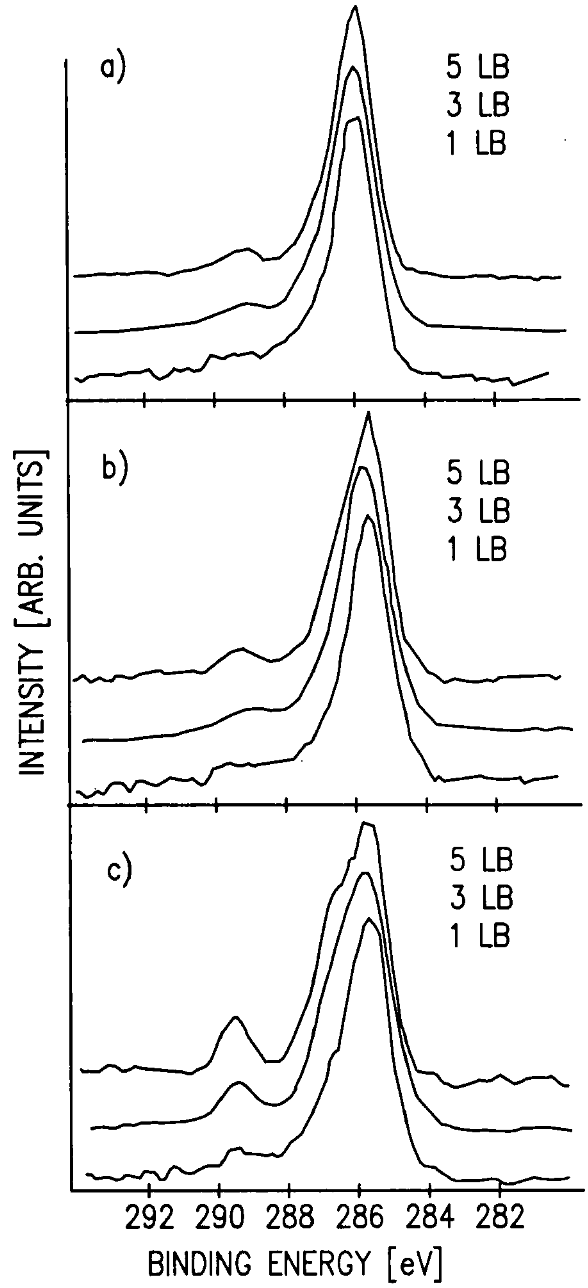

FIGURE 2 C1s spectra recorded at a) 293 K, b) 423 K and c) 523 for 1 LB and 573 K for 3 and 5 LB of 1, 3 and 5 LB polymer layers on Si (100).

imide ring closure is obviously strongly inhibited. As discussed below, the presence of a not completely imidized layer at the interface does also partly explain the deviation in spectral appearance for the 3 and 5 layer deposits from the characteristic C1s spectrum of polyimide.

Figure 3 shows the N1s spectra of the 1- and 5-layer deposits as a function of temperature. Signals for amide nitrogen and imide nitrogen in polyamic acid and polyimide and for ammonium-type nitrogen occur at 400.4 eV, 400.8 eV and 401.9

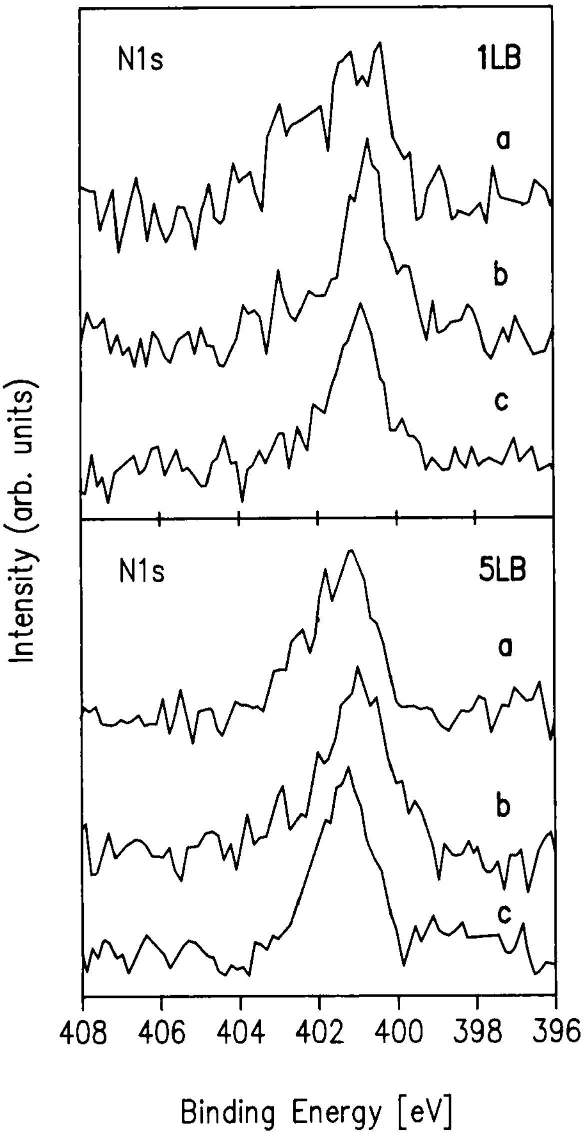

FIGURE 3 N1s spectra of 1 and 5 LB layers at a) 293 K, b) 423 K and c) 523 K.

eV, respectively.[17] In our spectra the presence of protonated nitrogen from the ammonium salt and a N1s feature arising from the polyamic acid amide nitrogen can be distinguished in the spectra recorded at room temperature. In agreement with the observed alkyl chain desorption at 373–473 K observed in the C1s spectra, the ammonium species signal disappears in the same temperature range. A closer look at the C-total:N ratio, however, shows clearly an ammonium ion deficit at room temperature in the 1- and in particular for the 5-layer LB film. An ammonium ion deficit is also apparent from the N1s spectra (theory, $N:N^+ = 1:1$; exp., $N:N^+ = 2:1$). Ammonia or octadecylamine molecules obviously escape upon sample transfer into the UHV chamber or during the XPS analysis.

The amide nitrogen binding energy shifts as expected by ~0.5 eV to higher binding energy upon annealing from 423 to 523 K in the 5 LB film, but such a shift is not obvious from the 1 LB deposit. The absence or suppression of imidization in the 1 LB layer seen in the N1s data corroborate the C1s spectra, where a strong deficit of imide carbonyl groups is observed. The relatively more stoichiometric $N^+:N$ ratio in the 1 LB film at room temperature as compared with the 5-layer film and suppression of imidization is indicative of a strong chemical interaction of PACS with the substrate in the interface. The effect of the substrate on the PACS molecules is evident also from the fact that for the 3- and 5-layer deposits not in direct contact with the silicon surface, ammonium nitrogen is released to a much higher degree from the films at room temperature. This chemical interaction between PACS and the substrate surface obviously prevails when the octadecylamine is released during heat treatment.

A qualitative evaluation of alkyl chain desorption and imidization can be obtained from a deconvolution of the C1s spectra. In polyamic acid and polyimide four different carbon species are distinguished in the XPS data: Phenyl carbon atom in the ODA part not attached to oxygen or nitrogen (C1), PMDA phenyl carbon atoms (C2), ODA phenyl carbon attached to nitrogen or oxygen (C3) and carbonyl or carboxylic acid carbon (C4).[16]

The C2 and C3 carbon species are not distinguishable in our XPS spectra and are therefore assumed to be contained in one spectral envelope in the deconvolution procedure. With imidization, the absolute and relative energy position of the different carbon species changes. In order to determine the binding energies and peak widths for the imidized films we subtracted the 523 K 1-layer C1s spectrum from the 523 K 5-layer C1s spectrum. This difference spectrum was used as an input to deconvolute also the spectra for the lower temperatures. Since our primary interest here is to evaluate alkyl carbon desorption, which has the same binding energy as C1 in polyimide, and thus is reflected in the decrease of C1s intensity, this procedure is justified. The difference spectrum was calculated taking into account that in the 5 LB film the C1s signal intensity of the first LB layer (closest to the substrate) decreases when passing through the overlaying LB layers. This attenuation can be estimated, using the Si2p substrate signal intensities of the 1 and 5 LB film, because both lines lie at comparable kinetic energies (1202.0 eV for C1s, 1386.0 eV for Si2p using Al K_α radiation, respectively) so that the mean free paths do not differ very much. Using this estimate we obtained an attenuation factor of 0.7 ± 0.05 for the 1 LB layer spectrum. The same value for the attenuation factor is derived from the calculation of film thicknesses described in Section 3.2. Hence, the difference spectrum is calculated as I(diff) = I(5 LB) − 0.7 × I(1 LB). The resultant difference spectrum is shown in Figure 4 together with the structural formula for polyimide. In comparison with the 5-layer spectrum, the 5 − 1 difference spectrum resembles much more closely a polyimide C1s spectrum. However, whereas in stoichiometric polyimide the C1 : (C2 + C3) : C4 ratio is 8 : 10 : 4, the respective result is 14.1 : 10 : 3.3 (normalized to 10 C2 + C3 carbon atoms) for the 5–1 spectrum, indicating a surplus of C1 and deficit of carbonyl carbon (C4). We note that a deficit of carbonyl carbon with respect to the expected stoichiometry is always observed for polyimide.[16,17]

A reasonable fit for the 523 K difference spectrum reveals the following positions of the carbon species: C1 at 285.5 eV, (C2 + C3) at 286.7 eV and C4 at 289.5 eV. The C1s data for all temperatures were fitted with these binding energy separations for C1, (C2 + C3), and C4 and a constant FWHM for these three peaks of 1.2 eV

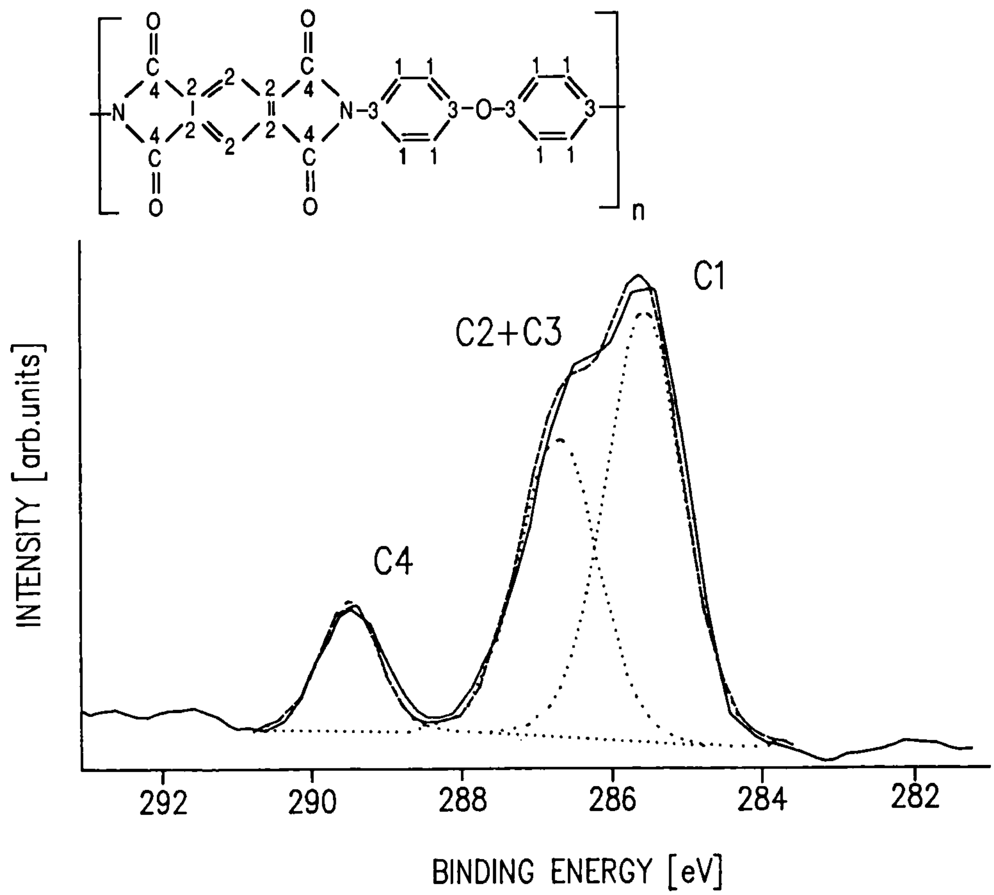

FIGURE 4 C1s difference spectrum of 5 − 1 LB layers, of the annealed PACS films at 523 K. The inset gives our notation for the different carbon species in polyimide.

as determined from Figure 4. We note that this procedure will not give reliable stoichiometric values, in particular for temperatures below imidization, because the C1 : (C2 + C3) deconvolution results are not unique due to the overlays of the peaks. Somewhat more reliable values for the absolute stoichiometry are expected for the C1 : C4 ratio, because these spectral features are well separated. However, the deconvolution facilitates a comparison between the 1, 3 and 5 layer deposits with respect to their relative compositions.

The C1 : (C2 + C3) and C1 : C4 ratios from 293 to 573 K (to 523 for 1 LB) obtained upon fitting the carbon 1s signals are depicted in Figure 5 a,b. Also inserted in

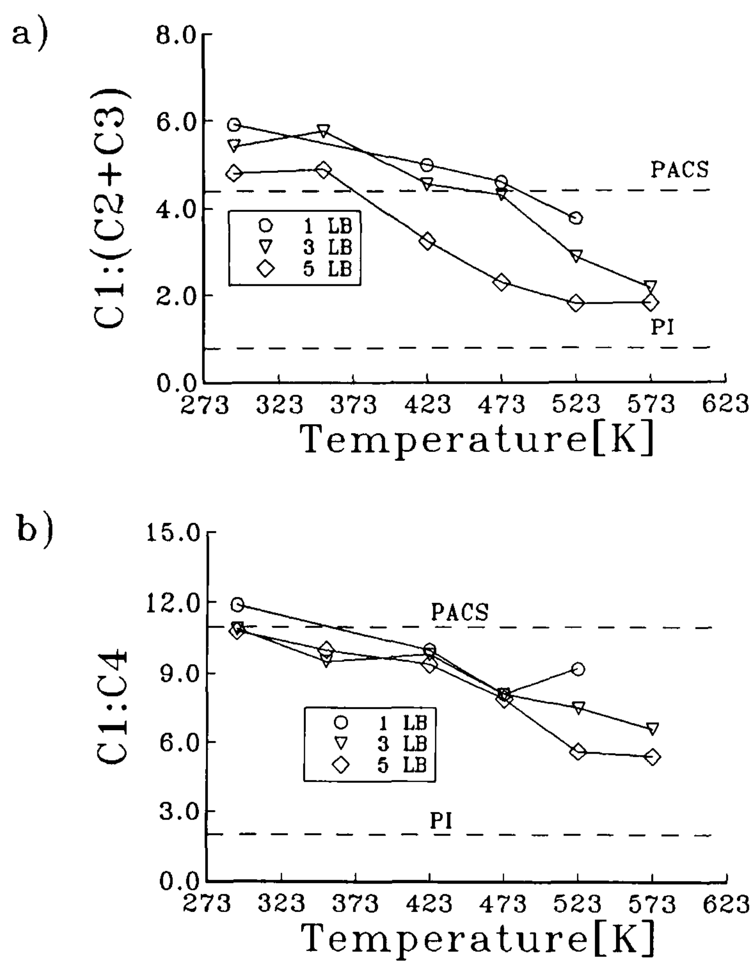

FIGURE 5 a) C1 : (C2 + C3) ratios of the absolute intensities in the temperature range of 293 K to 523 K for 1 LB film and to 573 K for 3 and 5 LB films. Stoichiometric C1 : (C2 + C3) ratios for PACS and PI are 4.4 and 0.8, respectively.

b) C1 : C4 ratios of absolute intensities from 293 K to 523 for 1 LB and to 573 K for 3 and 5 LB. Stoichiometric C1 : C4 ratios for PACS and PI are 11 and 2, respectively.

Figure 5a are the stoichiometric values for the C1 : (C2 + C3) ratio for PACS (44 : 10) and PI (8 : 10). Obviously, the ratios determined with the deconvolution procedure used systematically give a too-high C1 : (C2 + C3) ratio. However, the decrease in the ratio at $353 \leq T \leq 573$ K for the three films studied correlates with desorption of alkyl chain carbon. Comparing the ratios for the 5, 3 and 1 layer films we note a consistent trend to higher C1 : (C2 + C3) values with decreasing thickness. This corroborates the N1s spectra, where the intensity ascribed to protonated amine groups is most prominent for 1 monolayer. If the N^+ intensity directly reflects the relative concentration of octadecylamine molecules, the 5-layer N1s spectrum would indicate that 50% of the C1s alkyl carbon has desorbed in the room temperature sample. This clearly is excluded for the C1 : (C2 + C3) ratio at 293 K plotted in Figure 5a. Therefore, we conclude that the amine groups can be eliminated, leaving alkyl carbon chains in the films. Elimination of amino groups could be facilitated by reaction with air borne contaminants (*e.g.* H_2O) while the films are exposed to the ambient prior to insertion into the UHV chamber. The relative excess of octadecylamine entities in the 1 LB film as compared with the 5 LB film then, supposedly, is due to a reaction and stabilization of the amino group with the silicon surface.

Taking the C1 : C4 (carbonyl carbon) ratio into account in Figure 5b reveals a decreasing CO deficit for the imidized films in the direction of increasing film thickness. At room temperature an approximately stoichiometric ratio for the C1 : C4 ratio is determined which, however, is fortuitous considering the discussion above. However, with the depletion of alkyl carbon and the increase in the imide carbonyl carbon peak at 289.5 eV, the ratio becomes more reliable in terms of absolute stoichiometry supporting the qualitative result of Figure 2, that the final films still contain alkyl carbon chains and show a deficit of carbonyl carbon. This observation is evidence for a chemical interaction at the substrate surface blocking alkyl chain desorption and imide ring closure.

The films studied are not sufficiently dense to exclude oxidation of the silicon surface during exposure to the ambient. Figure 6 shows the Si2p peak at 293 K of a 3 LB PACS film exposed to air in a desiccator for several days (a) and a silicon wafer prior to deposition (b), *i.e.*, after the Si wafer cleaning procedure described above (samples are not identical). Note the SiO_x signal at 103.9 eV in Figure 6a which we observed regardless of film thickness prior to annealing in vacuum. An immediate result thereof is the ambiguity encountered upon interpretation of the O1s signals, which are not shown for this reason. Briefly, the O1s signals are consistent with the presence of carbonyl, carboxyl, ether and, foremost for the 1 LB film, SiO_x groups. Strict peak assignment was not attempted as the total oxygen excess encountered due to substrate oxygen contamination in each film exceeded at least 50% of the stoichiometric value for the films expected between 293 K and 523 K.

Considering the overall stoichiometry, deposition should lead to total C : N : O ratios comparable with the stoichiometric ratio of PACS, 58 : 4 : 6. This C : N : O ratio is not found experimentally due to excess substrate oxygen present in all examined films and ammonium nitrogen deficiency in the LB films prior to annealing. The total C : N : O ratios (corrected for thin films[16]) for the 1, 3 and 5 LB-films after imidization at 523 K are 44 : 2 : 55; 27 : 2 : 14 and 28 : 2 : 14, respectively. In comparison with a stoichiometric PI film (22 : 2 : 5), we find an oxygen surplus due to the substrate

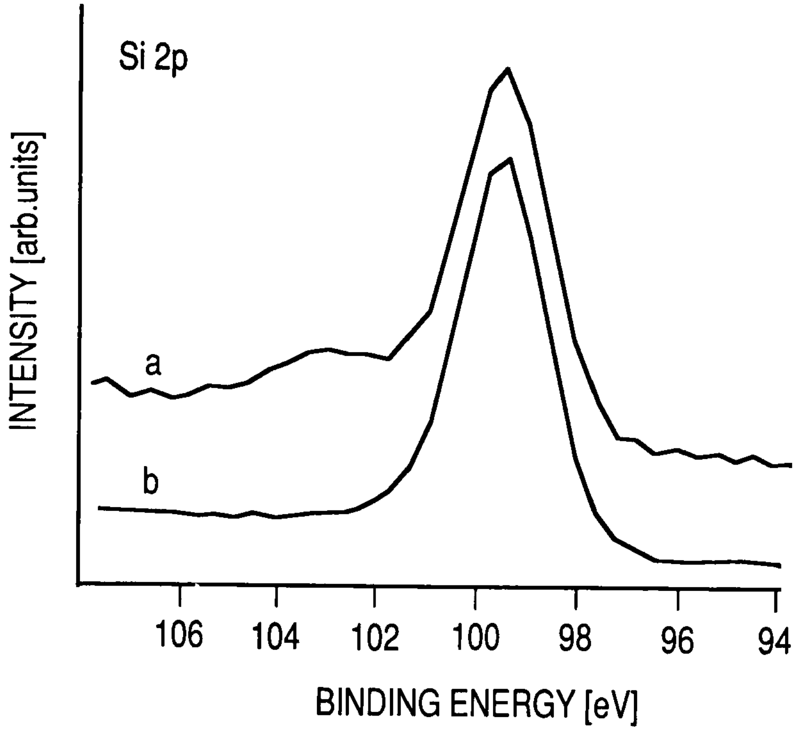

FIGURE 6 Si2p spectra taken at room temperature: a) 3LB-deposited Si wafer after insertion into the vacuum chamber, b) Si wafer after cleaning procedure as described in text.

oxygen in addition to excess total carbon even in the well-imidized 5 LB film. Carbon excess is caused by incomplete alkyl carbon desorption as a result of a chemical interaction at the substrate surface and, possibly, alkyl chain entanglement preventing desorption within the thicker 5 LB film. From our data we cannot exclude a further possibility, that free radical reactions in the octadecylamine moiety lead to reactions forming chemical grafts or interpenetrating networks in the polyimide films.

3.2 Thickness of the PACS and PI Films

The attenuation of the Si2p signal can be used to calculate the thickness of the adsorbate films. To simplify our analysis we regarded the LB-films as being homogeneous and of uniform thickness. This assumption is justified for the PACS deposits, but not necessarily correct for the imidized films as shown below. As will be presented elsewhere, orientational changes of the polymer chains during imidization are found in Near Edge X-ray Absorption Fine Structure (NEXAFS) experiments. These orientational changes could also lead to an inhomogeneous film thickness, which would invalidate the assumption of homogeneity for the imidized films.

Photoelectrons originating from the Si substrate can suffer inelastic losses resulting in an exponential intensity decrease by the adsorbate. Comparing the Si2p intensities of a clean Si wafer with a covered wafer the overlayer thickness can be estimated using

$$I = I_0 \exp(-d/\lambda) \qquad \textbf{(1)}$$

where d is the film thickness, λ the electron mean free path in the adsorbed overlayer, I the Si2p intensity of an adsorbate covered and I_0 the intensity of the clean wafer, respectively. I and I_0 are determined experimentally, whereas the value for λ is always ambiguous if not determined experimentally because it is a function of both electron energy and material. However, if the absolute value for λ is not available, one can derive relative thicknesses since for a fixed energy λ is constant and the relative thickness is expressed in units of λ, *i.e.*, $d_r = d/\lambda$ **(2)**. Hence, d_r is dimensionless and proportional to the absolute film thickness. Comparing films with a different number of LB layers, the difference in film thickness Δd_r can be calculated from $\Delta d_r = \Delta d/\lambda$ **(3)**.

XPS spectra of the 1 and 5 LB films were taken using a monochromized Al K_α source, whereas the 3 LB film was measured with a nonmonochromatized Mg K_α source. For the latter excitation energy a spectrum of a clean Si wafer was also available, which allowed us to determine an absolute film thickness for the 3 LB film. No such data were available for the Al excitation energy so we were constrained to calculation of changes in film thickness for the 1 and 5 LB films according to (3).

In an independent experiment, the thickness of PACS and the resulting polyimide films (however, cured in only a poor vacuum) of 1, 3 and 5 layers were measured ellipsometrically.[14] In Figure 7 we show the film thicknesses as a function of the number of layers. The data points lie on straight lines. That the line for the imidized films does not go through the origin can be explained by an increase in oxide thickness during imidization. From the data displayed in Figure 7 we derive a thickness of 1.7 ± 0.1 nm for a PACS film at 293 K and, by subtracting the increase in substrate oxide increase during imidization, of 0.6 ± 0.1 nm for a PI layer imidized at 523 K. These absolute thicknesses allow us to calculate a value of λ for the 3 LB PACS and PI layers from the attenuation of the Si2p signal according to eq. (1). We find $\lambda = 4.16$ nm and $\lambda = 4.28$ nm from the attenuation of the Si2p emission by the 3 LB PACS film and 3 LB PI film, respectively. Thus, we use $\lambda = 4.2 \pm 0.1$ nm for the Si2p electrons with a kinetic energy $E_{kin} = 1153$ eV (Mg K_α excitation) in the following evaluation of the data. From measurements on polyparaxylylene and other organic materials a considerably smaller value of $\lambda = 2.2 \pm 0.3$ nm would be expected.[18,19] However, the value reported by Anderson and Swalen[20] of $\lambda \sim 4.5$ nm for Langmuir-Blodgett deposited cadmium arachidate films is in good agreement with our measurements.

Assuming a proportional increase in film thickness for the deposited PACS films at room temperature, explicitly a ratio of 1:3:5, the thickness of the 1 and 5 layer PACS films can be calculated and the decrease of thickness as a function of heating temperature for all three films can be plotted in one diagram. The result is shown in Figure 8. The left scale denotes d_r and the right scale gives an estimation of the absolute film thickness using $\lambda = 4.2$ nm. All three curves show their largest drop

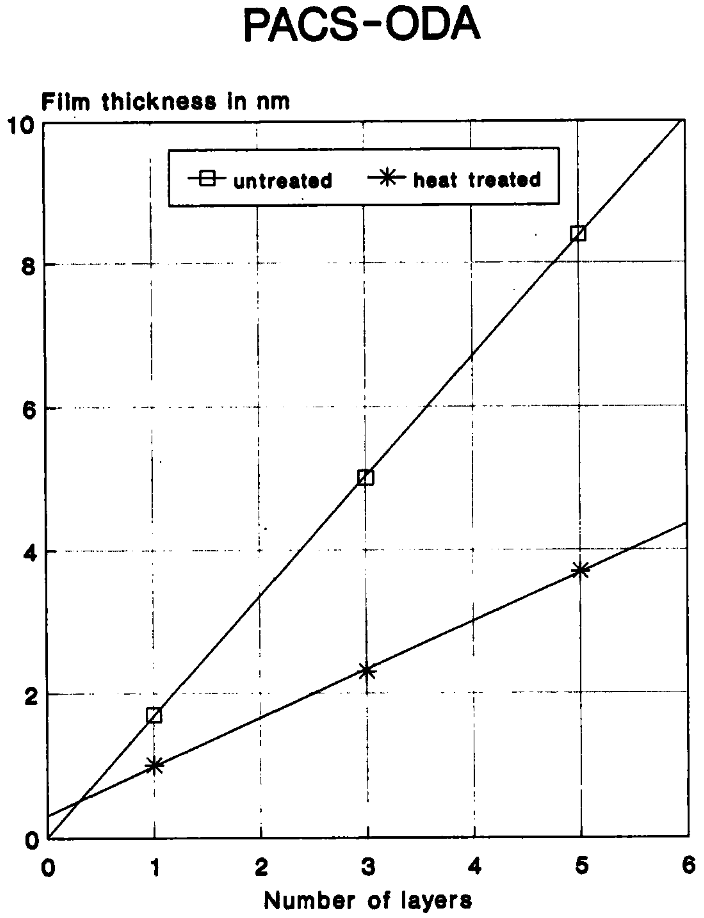

FIGURE 7 Film thickness of PACS and PI as a function of the number of layers determined by ellipsometry.

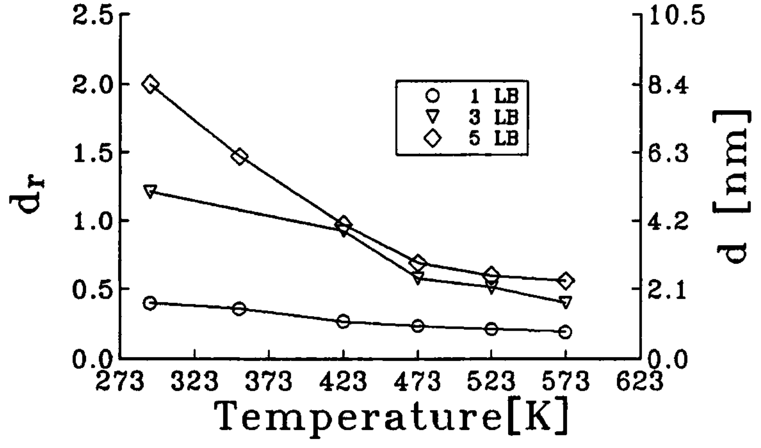

FIGURE 8 Change of film thickness for the LB films during the heating process. See text for details.

prior to 473 K. Above this temperature there is no drastic change which we understand as being the immediate result of the termination of the alkyl chain desorption process at this point. The thickness for the imidized 1, 3, and 5 PI layers are 0.67 nm, 1.77 nm and 2.40 nm, respectively.

4 DISCUSSION

The results obtained in this study demonstrate convincingly the presence of chemical bonds between the polyimide and the silicon substrate through the lack of imide ring closure in the interfacial polymer layer. This result is in contrast to the observations of Iacona *et al.*[6] for spun on polyimide films on native silicon oxide surfaces. This difference can be explained by the fact that in our experiments the oxide layers were removed from the silicon substrates in order to facilitate a hydrophobic deposition. The clean silicon surface is expected to react much stronger than a silicon oxide suface with the carboxylic acid groups in PAA when the ammonium-carboxylate bond is cleaved either during deposition or during curing in vacuum. For the nature of the chemical interaction between polymer and silicon surface it is reasonable to postulate carboxylate-type bonds, which have been suggested by Kowalczyk and Jordan-Sweet[9] for vapor-deposited polyamic acid on Si (100) and have been shown to exist for vapor-deposited polyamic acid on polycrystalline silver surfaces.[5,11,17]

The octadecylammonium salt of polyamic acid resembles, in terms of complexation of the acid carboxyl groups, the chemistry of solventless polyamic acid where, based on XPS[12] and FTIR[4] measurements, the presence of amine carboxylate type bonds between polyamic acid and excess and/or terminal oxydianiline molecules was observed. Only at temperatures around 373 K is excess oxydianiline desorbed and polyamic acid is the predominant adsorbate species which then provides the reaction sites for interface bonding. In the present study at about the same temperature ($T \geq 373$ K) a distinct loss of the octadecylamine molecule is observed. At the interface, carboxylate bonding to the substrate dominates ring closure, thus preventing polyimide formation.[17] The carbonyl deficit found in the 5 – 1 LB difference spectra cannot be taken as a measure for a chemical interaction of the subsequent layers with the substrate, since a carbonyl deficit is also found (but not understood) in thick polyimide films.

The absolute values for the thickness of the PACS films determined in the ellipsometric and XPS measurements are considerably too small to account for alkyl chains standing perpendicular to the substrate surface as schematically shown in Figure 1b. As the alkyl groups are linked to the PMDA chains *via* an ionic bond, however, any orientation of the chain is allowed, so that we suggest a model where the alkyl chains have a random orientation with respect to the polymer backbone. This randomness is not surprising, considering the relatively large spatial separation between the alkyl groups which eliminates an ordering effect due to lateral alkyl-alkyl interactions. Whether this disorder is present in the compressed PACS phase in the LB trough, or is a result of the film transfer process, has to be determined in further experiments. However, the disorder in the adsorbate phase can cause an interaction of the carboxylate groups of polyamic acid with the substrate, thus leading to a mono- or bidentate bond between the polyamic acid polymer and the Si (100) surface. Formation of such an ionic bond between polymer precursor and substrate surface is believed to be the reason for the inhibition of imide ring closure upon annealing in the polymer/substrate interface.

Apparently, the alkyl chain disorder in the transferred PACS layers does not prevent a layer-by-layer polyimide film formation. The resultant polyimide film thickness scale with 1:3:5 perfectly in the ellipsometry experiments, but in the XPS experiments a decrease in layer thickness with increasing film thickness is observed. This discrepancy between the two techniques could be due to the sensitivity of the photoemission intensity to defects in the film. For discontinuous or inhomogeneous overlayers the attenuation of the signal is less than from a homogeneous overlayer, suggesting a thinner overlayer. However, a change in orientation of the polymer molecules as a function of thickness could also change the XPS attenuation per monolayer. NEXAFS results show a random orientation of the phenyl rings in the 1 LB film of polyimide on a Si (100) substrate, changing to a preferential orientation of the phenyl rings parallel to the substrate plane with increasing thickness.[13,21] Further experiments are necessary to identify the difference in layer thickness with increasing film thickness between the two techniques.

An unexpected observation relates to the persistence of alkyl carbon chains being still present in the polymer film after annealing to 573 K in vacuum. Since this is also observed for the thicker layers, it can not be attributed to a direct interaction of the aliphatic hydrocarbon chains with the silicon surface but must be due to an entrapment of the alkyl chains in the polymer network. Whether higher annealing temperatures lead to quantitative desorption of alkyl carbon chains needs to be tested in further studies.

5 SUMMARY

Ultrathin polyimide films on Si (100) were prepared by Langmuir-Blodgett deposition of the octadecylammonium salt of polyamic acid (PACS) and subsequent annealing in vacuum to facilitate alkyl carbon desorption and imidization. From our results it follows that the first PACS layer adheres *via* (presumably mono- or bidentate) chemical bonds to the substrate and thus is not converted to polyimide upon heating. For 3 and 5 layer deposits of PACS polyimide formation is detected by XPS, although alkyl carbon chain entanglement in the polymer network is still present after vacuum annealing at 573 K for 15 min.

The PACS films are not sufficiently dense to exclude oxidation of the silicon substrate during exposure to ambient conditions. The interfacial chemistry of adhesion between the polyimide and the silicon substrate is qualitatively identical to the chemistry of vapor-deposited polyamic acid on silicon[9] or silver surfaces.[17] The Langmuir-Blodgett technique, however, has the advantage that the polymer precursor can be deposited in a controlled layer-by-layer fashion, thus allowing one to study chemical effects as a function of film thickness. From ellipsometric measurements the absolute thickness of PACS and polyimide layers have been determined to be 1.7 nm and 0.6 nm, respectively. These measurements also allow us to determine the electron mean free path for the Si2p electrons ($E_k = 1153$ eV) of $\lambda = 4.2 \pm 0.1$ nm in PACS and PI films on Si (100). However, the thickness of the PACS layers is not consistent with a deposition mode where the alkyl chains are effective "spacers" between the polyamic acid molecules, but indicate that the alkyl carbon chains are randomly oriented. This conclusion is supported by NEXAFS results published elsewhere.[13,21]

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References

1. *Polyimides-Synthesis, Characterization and Application,* Vols. 1 (1982), 2 (1984), K. L. Mittal, Ed. (Plenum, New York).
2. M. I. Bessenov, M. M. Koton, V. V. Kudryavtsev and L. A. Laius, Polyimides, *Thermally Stable Polymers* (Consultants Bureau, New York 1987).
3. J. R. Salem, F. O. Sequeda, J. Duran, W. Y. Lee, and R. M. Yang, *J. Vac. Sci. Technol.*, **A4,** 369 (1986).
4. C. Hahn, T. Strunskus, D. Frankel and M. Grunze, *J. Electron Spectros. Rel. Phenomena,* **54/55,** 1123 (1990).
5. M. Grunze, R. Lamb, *Surf. Sci.*, **204,** 183–212 (1988).
6. F. Iacona, M. Garilli, G. Marletta, O. Puglisi and S. Pignataro, *J. Mater. Res.*, **6,** 861 (1991).
7. T. S. Oh, L. P. Buchwalter and J. Kim, *J. Adhesion Sci. Technol.*, **4,** 303 (1990).
8. L. P. Buchwalter, *J. Adhesion Sci. Technol.*, **1,** 341 (1987).
9. S. Kowalczyk und J. Jordan-Sweet, *Chemistry of Materials,* **1,** 592 (1989).
10. S. S. Perry and A. Campion, *Surf. Sci.*, **259,** 207–214 (1991).
11. M. Grunze, A. Killinger, C. Mainka, C. Hahn, T. Strunskus, *Proceedings of the 2nd Symposium on Metallized Plastics: Fundamental and Applied Aspects,* Electrochemical Society Meeting in Montreal, May 1990, K. L. Mittal, Ed., in press.
12. K. B. Blodgett, I. Langmuir, *Phys. Rev.*, **51,** 964 (1937).
13. M. Grunze, G. Hähner, M. Kinzler, A. Killinger, C. Mainka, W. Meyer, A. Ortega-Villamil, Ch. Wöll and W. Schrepp, in *Haftung bei Verbundwerkstoffen und Werkstoffverbunden,* W. Brockmann, Ed. (DGM Informationsgesellschaft, Oberursel, 1989), p. 11.
14. W. Schrepp and U. Licht, *Thin Solid Films,* to be published.
15. R. M. A. Azzam, N. R. Bashara, *Ellipsometry and Polarized Light* (North Holland Publ., 1979), pp. 425, 479.
16. R. N. Lamb, M. Grunze, C. W. Kong, W. N. Unertl, *Langmuir,* **4,** 249 (1988).
17. T. Strunskus, M. Grunze, and S. Gnanarajan, "Solventless Polyamic Acid," in *Metallization of Polymers,* E. Sacher, J. J. Pireaux and S. Kowalczyk, Eds. *ACS Symposium Series* **440,** 353 (1990).
18. M. P. Seah, W. A. Dench, *Surf. Interface Anal.* **1,** 2 (1979).
19. A. Dilks, "X-Ray Photoelectron Spectroscopy for the Investigation of Polymeric Materials," in *Electron Spectroscopy: Theory, Techniques, and Applications,* Vol. 4, C. R. Brundle, A. D. Baker, Eds. (Academic Press, NY, 1981), pp. 276–359.
20. H. P. Anderson, J. D. Swalen, *J. Adhesion,* **9,** 197 (1978).
21. G. Hähner, Ch. Wöll, C. Thümmler, A. Killinger, M. Grunze, to be published.