

Atomic layer deposition of polyimide thin films

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The atomic layer deposition (ALD) of different polyimide thin films has been studied. We have demonstrated self-limiting ALD deposition of PMDA–DAH, PMDA–EDA, PMDA–ODA and PMDA–PDA thin films at 160 °C. The maximum deposition rate of 5.8 Å cycle⁻¹ was obtained for the PMDA–DAH process. Although the deposition rate was high at 160 °C, a sudden decrease was observed when the temperature was increased. Regardless of the process studied, no film growth was obtained at 200 °C or above. Deposited polyimide films were analysed by FTIR, AFM and TOF-ERDA. According to the FTIR measurements, imide bonds were formed already in as-deposited films indicating polyimide formation without any additional thermal treatment.

Introduction

Polyimide thin films are interesting materials due to their resistance to high temperatures, mechanical stress and a variety of chemicals. For example, they have been considered for use in microelectronics as insulating materials for interlayer dielectric materials^{1–4} or as the gate dielectric in all-organic thin film transistors.⁵

The most common way to produce polyimide thin films is based on the liquid phase reaction between selected dianhydrides and diamines. Polyamic acid is thus formed and is then used for the coating of substrates by various methods, including spin coating and dipping. Finally thermal annealings are used to remove solvents and transform polyamic acid to polyimide.

In addition to traditional wet chemical polymer manufacturing processes, different gas phase methods have also been applied. The most often used method, vapor deposition polymerisation (VDP), is based on the evaporation of the monomers and controlling the film properties by changing the evaporation rates.^{6–8} Optimisation of the VDP process often requires a strict control of the evaporation temperatures to avoid crack formation during the post-deposition imidisation. Typically these as-grown films by the VDP method consist of mixed dianhydride and diamine, which are converted to polyimide by thermal treatments usually below 300 °C. VDP produces polyimide films with better thickness control and conformality compared to the liquid phase methods. It is capable of processing films with a thickness from tens of nanometres up to a several hundreds of microns. The most critical factor in VDP is the optimisation of the imidisation process, since an excessive heating rate and unstoichiometric films will lead to increased stress and subsequent cracking of the film.⁹

Atomic layer deposition (ALD) is a variant of the chemical vapor deposition (CVD)

technique. In ALD, the thin film is deposited by alternating, saturating pulses of the precursor gases separated by inert gas purging.¹⁰ Typically ALD has been utilized for the deposition of inorganic compounds where metal precursors have been either halides, alkoxides, β -diketonate chelates or organometallic compounds.^{11,12} The second precursor has been either an oxygen, nitrogen or sulfur source, when oxides, nitrides or sulfides are deposited, respectively.

In practice, due to steric hindrances, one reaction cycle usually produces only a distinct fraction of a monolayer, giving a deposition rate typically less than a few Ångstroms per deposition cycle. Self-limiting and surface terminating growth of ALD enables processing of high-quality thin films on large area substrates even onto deep trenches, and thus ALD has gained increasing attention in the microelectronics industry.

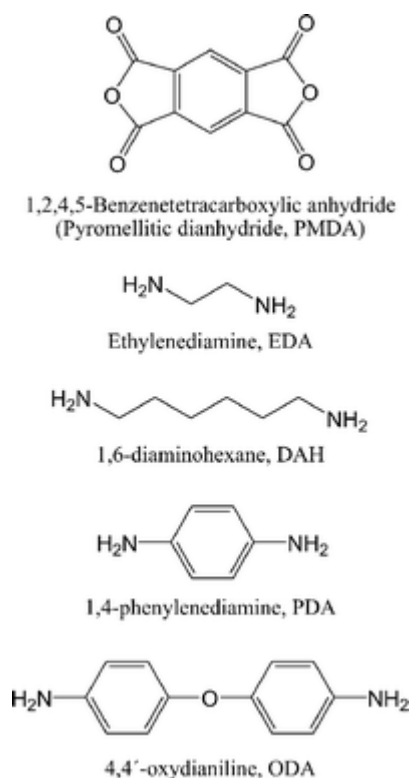
For inorganic compounds the deposition temperatures of ALD are typically in the range 200–500 °C although some processes enable near room temperature growth. The deposition of organic compounds by ALD has not been extensively studied. Previously a variant of ALD, namely molecular layer deposition (MLD), has been studied for the growth of the PMDA–DNB and PMDA–ODA thin films at 50–80 °C (PMDA = 1,2,3,5-benzenetetracarboxylic anhydride, DNB = 2,4-diaminonitrobenzene, ODA = 4,4'-oxydianiline).¹³ These, about 10 nm thick, films were deposited at a reduced pressure of 5×10^{-8} Torr. It was observed, however, that in the case of PMDA–DNB the desorption of DNB from the PMDA surface destroys self-limiting growth.

Self-limiting ALD-type reactions between APTMS, PMDA and DAH (APTMS = γ -aminopropyltrimethoxysilane, DAH = 1,6-diaminohexane) have been previously studied¹⁴ on high surface area silica bulk powders. In these studies an oxidised silicon surface was first treated with the APTMS in order to achieve an $-\text{NH}_2$ terminated surface where PMDA can anchor. In this type of deposition experiment only a few pulsing cycles were used since pulsing and purging times of precursors are often several hours.

In this paper we report the atomic layer deposition of different polyimide thin films by using PMDA as a second reactant and report the effect of different diamines on the film growth.

Experimental

Commercial γ -aminopropyltrimethoxysilane, pyromellitic dianhydride (1,2,3,5-benzenetetracarboxylic anhydride), 1,6-diaminohexane, 4,4'-oxydianiline, 1,4-phenylenediamine (PDA), ethylenediamine (EDA) were used as precursors. Their volatility was either obtained from available literature data or checked by simultaneous TG/DTA (thermogravimetry/differential thermal analysis) in a Seiko SSC 5200 thermobalance. 2 mbar pressure and nitrogen (99.999%) carrier gas were used in order to simulate the ALD deposition conditions.¹⁵



Scheme 1 Precursors used for ALD of polyimides.

Polyimide thin films were deposited in a commercial flow-type hot-wall ALD reactor (F-120 by ASM Microchemistry Ltd) using PMDA as a precursor. The second precursor was a diamine, being either EDA, DAH, PDA or ODA, which were evaporated at 25, 40, 100 or 150 °C, respectively. All precursors were evaporated from open glass crucibles, except for EDA which was evaporated using an external reservoir held at room temperature. Nitrogen (>99.999%, Schmidlin UHPN 3000 N₂ generator) was used as a carrier and purging gas. Thin film depositions were carried out under a 2–3 mbar pressure onto (100) oriented silicon and soda lime glass substrates measuring 10 × 5 cm². All substrates were cleaned ultrasonically in ethanol and water before use. The deposition rate of polyimide thin films was studied as a function of the deposition temperature at 160–200 °C.

Reflectance and transmittance spectra were measured in a Hitachi U-2000 double beam spectrophotometer. The obtained reflectance data were used for calculating thicknesses of the deposited films using the method described by Ylilammi and Ranta-aho.¹⁶

Crystallinity of the deposited films was determined by X-ray diffraction using Cu K α radiation in a Philips MPD 1880 diffractometer. Bonding information for the films was obtained from Fourier transform infrared (FTIR) spectra. The transmission spectra of the films were obtained using a Nicolet Magna-750 Fourier transform infrared spectrometer equipped with a deuterated-triglycine-sulfate (DTGS) detector. FTIR measurements were exploited for the deposited samples in order to verify the imide bond formation during an ALD cycle. Polyimide–silicon structures were analysed by transmittance measurements and the silicon substrate contribution was removed by subtracting the spectra measured from clean silicon wafer alone.

Surface morphology was studied by a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode. Samples were measured with a scanning frequency of 0.5–1 Hz. Several wide scans (5–10 μ m) were performed from different parts of samples to check the uniformity of the sample. Final images were measured from a scanning area of 2 × 2 μ m. Roughness values were calculated as root mean square (rms) values. Adhesion of the deposited films was evaluated with the adhesive tape test.

Composition of selected films was analysed by time-of-flight elastic recoil detection analysis

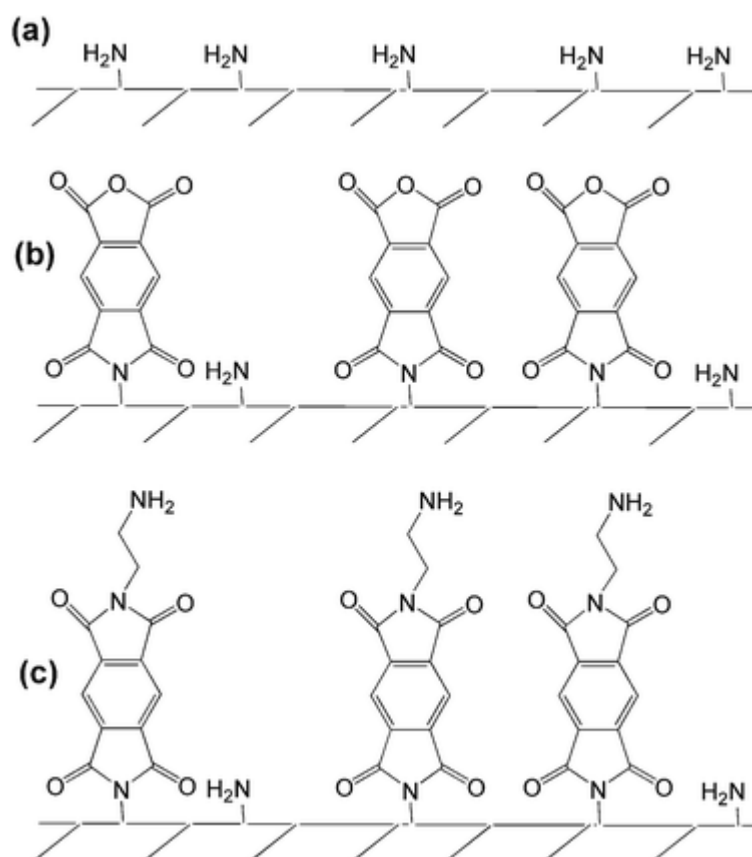
(TOF-ERDA). For these TOF-ERDA studies, a 16 MeV $^{63}\text{Cu}^{7+}$ ion beam was used, samples were measured at 19° tilt and the recoils were detected at 38° with respect to the incoming beam.¹⁷ For heavy recoils, energy spectra were obtained from the TOF signals and hydrogen spectra from the charged particle detector with 100% detection efficiency. Film homogeneity was confirmed by means of converting elemental energy spectra to depth profiles. The average film composition was, however, calculated directly from the number of detected recoils per element in order to avoid the effect of possibly erroneous ion stopping powers. As polymer films are sensitive to the ion bombardment, extra care was taken when elemental yields were extrapolated to the beginning of the measurement.

Selected thin film samples were heat-treated in a rapid thermal annealing (RTA) furnace PEO 601 (ATV Technologie GmbH, Germany). The annealing was carried out in a nitrogen atmosphere for 10 min at temperatures between 200 and 350 °C.

Results and discussion

ALD growth of polyimide thin films

Previously reported¹⁸ modification of the initial surface by APTMS–H₂O prior to polyimide deposition was first tested in the thin film depositions. The polyimide deposition rate was studied as a function of the deposition temperature using sufficiently long precursor pulsing times to obtain complete surface saturation. Deposition temperatures were kept below 250 °C to prevent thermal decomposition of the precursors. Before polyimide deposition, 10 cycles of APTMS–H₂O were applied to the surface. For initial experiments the pulse time of PMDA was 3.0 s while the diamine pulse time was kept constant at 2.0 s. Purge times of 1.5–3.0 s between the reactive pulses were used but this had no effect on the growth rate. However, it appears that –NH₂ termination by APTMS–H₂O was not necessarily needed for the growth initiation, since the same deposition rate was also obtained without this treatment. It suggests that growth also starts from the –OH terminated surface. Adhesion of these films was quite good according to the tape test, since no peeling was observed with the polyimide films deposited onto bare Si or onto the APTMS–H₂O-treated substrates. Therefore, during the following experiments polyimide depositions were carried out onto untreated Si and soda lime glass substrates.



Scheme 2 Suggested ALD sequence for PMDA-EDA polyimide formation depicting starting surface (a), surface after PMDA pulse (b) and surface after EDA pulse (c).

The deposition rate of polyimide films was greatly dependent on the precursor selection as well as the deposition temperature. Because the evaporation temperature for PMDA is around $150\text{ }^\circ\text{C}$, the lowest temperature for ALD was selected to be $160\text{ }^\circ\text{C}$ in order to avoid precursor condensation. A distinct plateau in the growth rate was not observed (Fig. 1) while the deposition rate decreased with the increasing temperature.

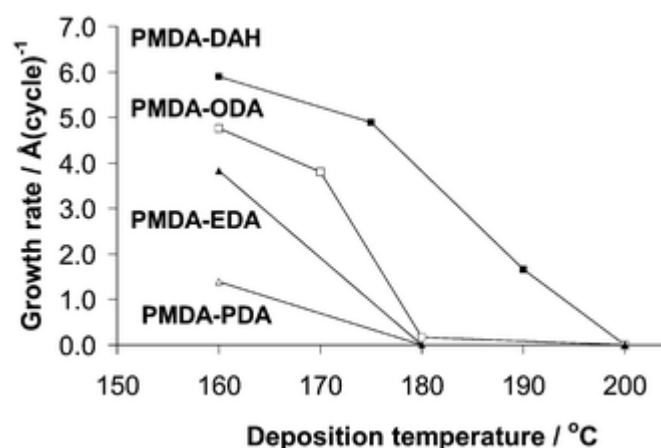


Fig. 1 Growth rate of polyimide thin film as a function of the deposition temperature.

A maximum growth rate of $5.8\text{ Å}(\text{cycle})^{-1}$ was measured for the PMDA-DAH process at $160\text{ }^\circ\text{C}$. If other diamines were used, the deposition rate was lower, being 4.9 , 3.9 and $1.4\text{ Å}(\text{cycle})^{-1}$ for the PMDA-ODA, PMDA-EDA and PMDA-PDA processes, respectively. If the deposition

temperature was increased a sudden drop in the growth rate was observed regardless of the precursors used. No ALD growth was observed above 180 °C except for PMDA–DAH, which gave the deposition rate of 1.7 Å cycle⁻¹ at 190 °C. A sudden decrease in the deposition rate is most likely due to the low sticking coefficient or monomeric precursor desorption at elevated temperatures. It may be noted that the deposition rate is significantly higher than in the conventional ALD processes for inorganic materials where the deposition rate is typically significantly less than a monolayer being rarely over 1.5 Å cycle⁻¹ due to the bulky ligands that cause steric hindrances.¹¹ Instead of depositing a single layer of atoms, here PMDA and diamine units are deposited yielding a high growth rate. Furthermore, one monolayer of deposited film consists of one PMDA and one diamine unit. If the deposition rate of polyimide thin films is expressed as monolayers formed (ML) per deposition cycle it can be seen that for both linear diamine precursors, *i.e.* PMDA–DAH and PMDA–EDA processes, the deposition rate is 0.4 ML cycle⁻¹ at 160 °C which is quite comparable with values for the deposition of inorganic materials. Furthermore, if aromatic diamines, *i.e.* ODA or PDA, were used as precursors, deposition rates were only 0.3 and 0.1 ML cycle⁻¹, respectively. One possible suggestion for the lower deposition rate of PMDA–ODA and PMDA–PDA is steric effects of the more bulky diamine precursors. Previously in the PMDA–ODA depositions by MLD a deposition rate of about 6.7 Å cycle⁻¹ has been reported, which represents a deposition rate of 0.45 ML cycle⁻¹.¹³

ALD-type growth was verified by increasing pulsing times of the reactive precursors (Fig. 2). At the same time the purging time between reactive pulses was increased in order to avoid pulse overlapping. Uniform films were obtained when the PMDA precursor pulsing time was 1.5–7.0 s indicating an ALD-type film growth. For the PMDA–DAH process a constant deposition rate of 5.8 Å cycle⁻¹ was obtained at 160 °C all along the length of the 10 cm long substrate. Regardless of the pulsing time the deposited films were smooth with thickness variation of less than 5%. Self-limiting growth was verified also for PMDA with the other diamines at 160 °C.

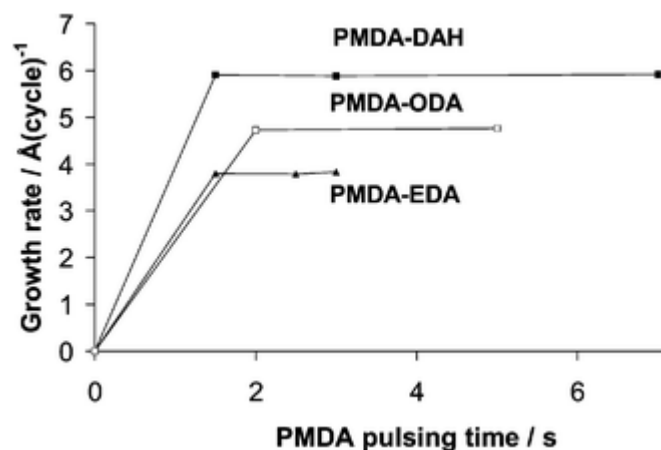


Fig. 2 Film growth rate at 160 °C as a function of PMDA pulse times using DAH, ODA or EDA as a second precursor.

In a similar manner, pulsing times of diamines were studied (Fig. 3). For example, DAH pulse times of 1.0–5.0 s resulted in uniform films throughout the substrate area of 5 × 10 cm².

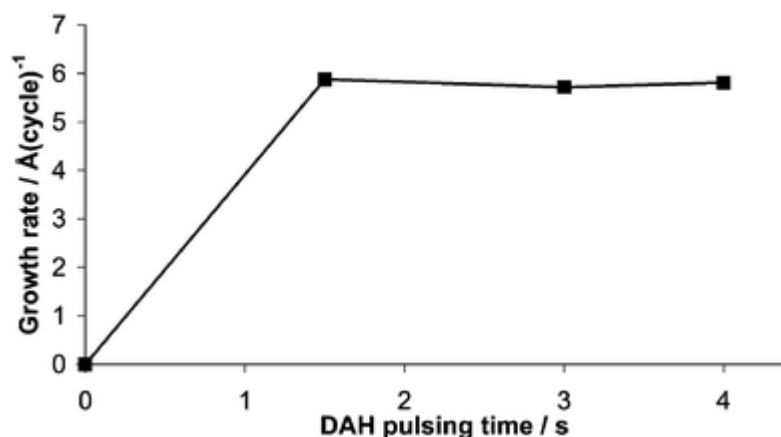


Fig. 3 PMDA–DAH film growth rate as a function of DAH pulse time. Deposition temperature was 160 °C.

Although the deposition rate observed is quite large, the film thickness could be controlled by the number of deposition cycles and therefore an ALD-type linear dependency of film thickness on the number of deposition cycles was observed (Fig. 4).

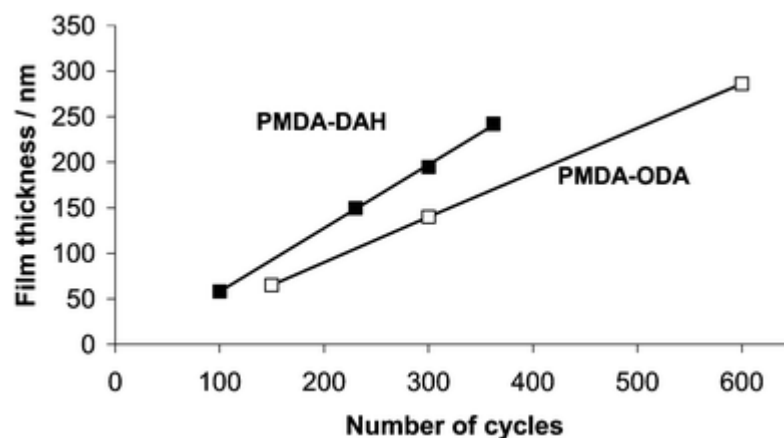


Fig. 4 Thickness of polyimide films as a function of the number of deposition cycles at 160 °C. Solid squares represent depositions carried out using PMDA and DAH as precursors. Open squares correspond to depositions carried out by the PMDA–ODA process.

The reaction between pyromellitic dianhydride and different diamines is a polycondensation reaction where water is formed. Since the reactive pulse separation in ALD is essential to avoid CVD-type reactions, we studied the effect of purging times between reactive pulses in more detail. In addition, it has been reported that the desorption of diamine precursors was observed in some cases at around 50 °C.¹³ It was observed that even 7 s purging times after reactive pulses did not affect the deposition rate of thin film. One possible explanation for this may be the higher deposition temperature where reactions between carbonyl-oxy-carbonyl and amine should be more facile.

Film composition

The presence of ring closure in the PMDA–ODA films is often followed by monitoring the intensity of the peaks at 1860 and 1806 cm⁻¹ originating from the unreacted anhydride.⁶ In the ALD-deposited polyimide films no traces of peaks originating from the unreacted precursors

were observed (Fig. 5). Typically incomplete imidisation is seen either as the presence of isoimide or amide bonds. In general, isoimide bond formation, *i.e.* amine reaction with the carbonyl of PMDA can be seen in the IR spectra of the PMDA–ODA films as the isoimide C–N stretch at 1399 and 1709 cm^{-1} , whereas amine bonds can be seen as the carbonyl vibration of polyamic acid around 1650 cm^{-1} .⁷ In the ALD-prepared PMDA–DAH films a small peak originating from the amide bond at 1665 cm^{-1} were observed in as-deposited films.

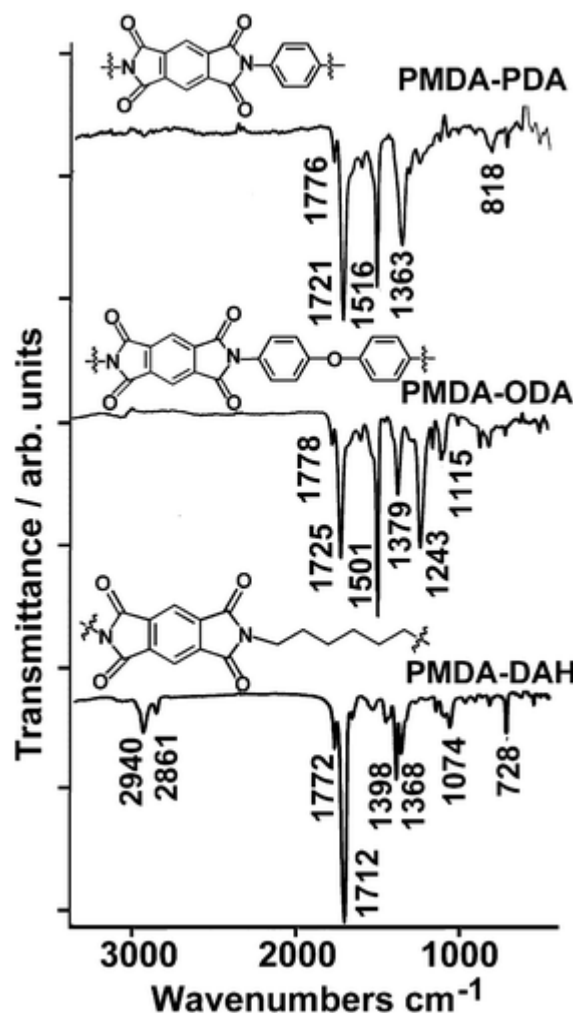


Fig. 5 FTIR spectra of different polymer films deposited at 160 °C onto a Si (100) substrate.

The degree of the imidisation in the PMDA–ODA films has been typically calculated by using the aromatic C=C bond peak at 1500 cm^{-1} as an internal reference and measuring the height and area of the characteristic imine peak at 1380 cm^{-1} . In this method, aromatic ring absorption is considered constant while the imide bond is formed.^{19,20} In the as-deposited PMDA–ODA films the ratio between imide and aromatic peak height was calculated to be 0.3 which increased to 0.45 after annealing at 300 °C. Further increase was not observed if the annealing temperature was increased. If the peak ratio at 400 °C is considered to correspond to 100% imidisation, as-deposited films had an imidisation rate of about 60–65%. This is quite close to the values obtained for the VDP-fabricated PMDA–ODA films after thermal treatment at 350 °C.⁷ For the other polyimide thin films a similar calculation would yield incomparable results, since there are no reference peaks originating from the aromatic ring of ODA.

The composition of selected PMDA–DAH films was analysed by TOF-ERDA. The composition of these films was uniform throughout the thickness of the film (Fig. 6). According to TOF-ERDA, the composition of the PMDA-DAH film was 43 ± 2 at% hydrogen, 39 ± 2 at% carbon, 6.4 ± 0.5 at% nitrogen and 10.9 ± 1.0 at% oxygen being in good agreement with the stoichiometry of the repeating monomeric unit $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$.

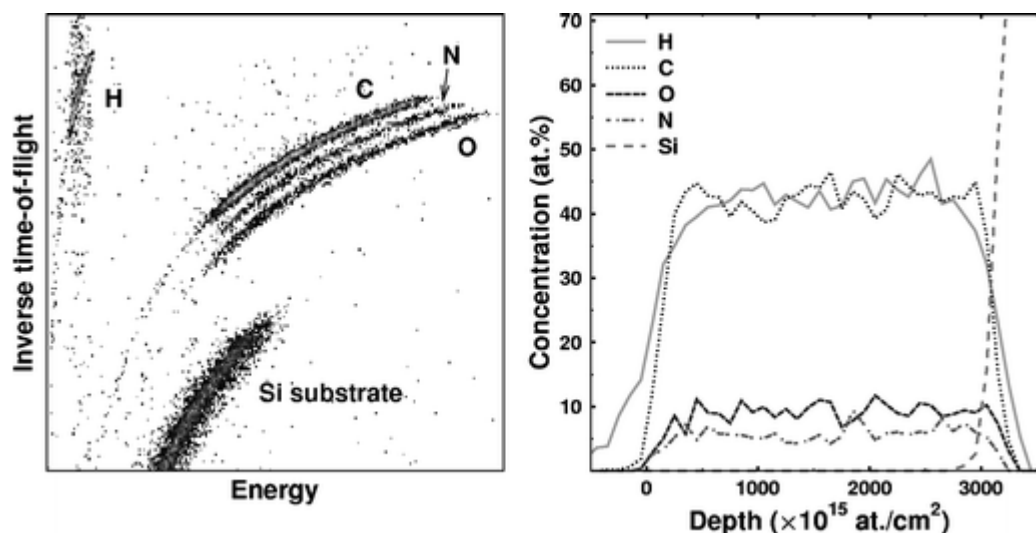


Fig. 6 An raw energy vs. inverse time-of-flight histogram for a 350 nm thick PMA–DAH film (left) measured using 16 MeV $^{63}\text{Cu}^{7+}$ incident ions (depth increases from upper right corner towards bottom left corner) and the corresponding elemental depth profiles (right).

According to the XRD measurements, the deposited films were amorphous regardless of the precursor combination used. This is quite typical for inorganic films deposited by ALD at low temperatures, although crystalline polyimide films have been often obtained after thermal imidisation.²¹ Annealing of the PMDA–DAH and PMDA–ODA thin films was studied at 200–400 °C. According to the XRD measurements both films remained amorphous even after RTA treatment at 400 °C.

Surface morphology of ALD-deposited polyimide films was studied by AFM. Images were collected from 50–350 nm thick polymer films grown at 160 °C. Generally as-deposited films were uniform and no cracks were observed. The dependence of surface roughness on different types of polymer film was not notable. Regardless of the film thickness, the roughness of PMDA–DAH and PMDA–ODA films was around 0.3–0.9 nm and 0.6–0.8 nm, respectively. Only a small increase in the roughness as a function of thickness was detected on films grown on silicon. As a representative example, the AFM image of a PMDA–DAH film grown at 160 °C is presented in Fig. 7.

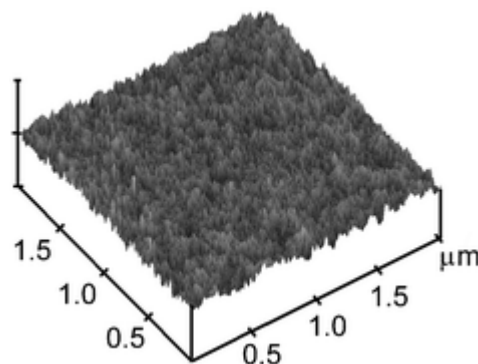


Fig. 7 AFM image of a 170 nm thick PMA–DAH film deposited at 160 °C. The rms value of the sample was 0.3 nm. Depth scale: 5 nm from black to white.

Solubility of the deposited polyimide thin films was studied by immersing the as-deposited

and annealed samples into concentrated H_2SO_4 at 25 °C. It was observed that all ALD-deposited films were readily soluble in H_2SO_4 . Typically, increased solubility of the polyimide films is an indication of the low molecular weight of the films or the low degree of the crosslinking of the chains.⁸

Conclusions

We have demonstrated the deposition of different polyimide thin films by ALD using PMDA as an acid anhydride and a variety of diamines, including EDA, DAH, PDA or ODA, as the second precursor. Due to the evaporation temperature of PMDA, the lowest deposition temperature was 160 °C where the self-limiting growth was verified for all of these processes. In addition, the maximum deposition rate was observed at 160 °C but it radically decreased when the deposition temperature was increased, indicating probable desorption of the precursors. Regardless of the precursor combination used, no growth was observed at 200 °C or above. The maximum deposition rate was obtained for the PMDA–DAH process, being 5.8 Å cycle⁻¹ at 160 °C. This deposition rate is much higher than observed for typical ALD processes, which is due to the different deposition mechanism compared to conventional ALD of inorganic materials.

According to the TOF-ERDA analysis uniform composition through the thickness of the deposited polyimide films was observed. In addition, correct stoichiometry of the PMDA–DAH films was confirmed by TOF-ERDA.

The deposited films were smooth and uniform with a thickness variation of less than 5% over the substrate area of 5 × 10 cm². According to the AFM measurements roughness of the measured films was small, being less than 1 nm regardless of the polyimide film studied.

Imide bond formation with only traces of isoimide bonds as well as without unreacted precursors was observed by FTIR for all the polyimides studied. Together with the self-limiting growth nature this indicates a true ALD growth of the polyimide thin films.

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Footnote

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