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Growth of ODPA–APB polyimide films using molecular beam deposition, and their characterization

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We report the first growth of polyimide ODPA–APB films by the molecular beam deposition (MBD) technique and characterize these films using X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. MBD is a dry, ultra-high vacuum technique based on the co-deposition of monomers from two different sources, followed by a thermally induced polycondensation reaction to form polyimide. This technique is an alternative to standard wet processing techniques involving the use of solvents. As-deposited films consist largely of low-molecular-weight species. Heat-treated films are chemically indistinguishable from thermally cured, spin-coated films. Different heat treatment conditions are compared.

(Keywords: polyimide films; vapour deposition; molecular beam)

INTRODUCTION

Polyimide (PI) is an important dielectric material for microelectronic applications[1–3]. Its useful properties include low dielectric constant and good thermal stability[4,5]. The standard method of preparing thin films of polyimide in microelectronic applications is that of spin casting poly(amic acid) (PAA) from solution, subsequently followed by thermal curing to induce imidization[6].

An alternative, dry deposition process, is molecular beam deposition (MBD). In this technique the constituent monomers are co-deposited on a substrate using two molecular beams, one for each monomer. The as-deposited films are then heat-treated to produce PI. The elimination of solvents from the film deposition process impedes the PAA–metal substrate reactions that occur during the thermal curing step of the spin coating process[7]. Such reactions lead to the formation of metal oxide particles in PI, which may adversely affect the properties of the polymer[3]. Another difference between the two film forming processes is that PI films formed on patterned surfaces by the spin coating method have a planarizing effect while MBD PI films conform to the shape of the substrate pattern[8].

A vapour deposition technique for PI film growth was first studied by Salem *et al.*[9] and Iijima *et al.*[10]. Shortly after, this technique was further developed for the production of ultrathin films in ultra-high vacuum (UHV), for *in situ* interfacial chemistry studies[11–16] and for studies on the role of solvents in interfacial reactions[7]. A study of the key growth parameters for the preparation of uniform, high quality, relatively thick PI films by MBD has been presented previously[8]. These investigations have primarily dealt with poly(4,4′-oxydiphenylenepyromellitimide) (PMDA–ODA), deposited from the monomers pyromellitic dianhydride (PMDA) and oxydianiline (ODA).

The main goal of this work is to investigate the applicability of this technique to another polyimide, which is produced by the polycondensation reaction of oxydiphthalic dianhydride (ODPA) (or 1,3-bis-(3,4-dicarboxyphenoxy) benzene) and 1,3-bis-(3-aminophenoxy) benzene (APB) (*Figure 1*). The ODPA–APB polyimide has good adhesive properties due to the flexibility of the molecule[17].

EXPERIMENTAL

Sample preparation using MBD

A cold wall deposition system dedicated to polyimide film growth was employed for these studies. This system and the film growth technique have been described previously[8]. The sources, one for ODPA and one for APB, were cylindrical quartz containers with a capacity of 2.8 cm^3, supported in a Macor^{TM} block. The charges were ODPA monomer (purity 99%, Occidental Chemical Corporation) and APB monomer (purity 99%, National Starch). The sources were heated resistively to produce a

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sufficient vapour pressure for each monomer. The flux of each molecular beam was independently monitored by quartz crystal thickness monitors, one for each source. Each monitor was controlled by an Inficon IC6000 deposition controller. Two Lambda LLS-5008 programmable power supplies, each controlled by the output voltage of the corresponding deposition controller, provided the required electric power to the sources, so that the deposition rate of each monomer was kept constant throughout the deposition, despite changes in the total surface area of the monomer powder during deposition (both monomers sublime). The top, substrate flange was isolatable with a pneumatic gate valve which was used as a shutter. A rotatable substrate holder, magnetically coupled to an electric motor, was employed to achieve uniform distribution of the deposited monomers, and thickness uniformity of the film. The source to substrate distance was 35 cm. The substrate was kept at room temperature during growth and the total deposition rate was usually 0.4 nm s^{-1}. Typical pressure during growth – for the deposition rate employed – was approximately 5×10^{-6} torr.

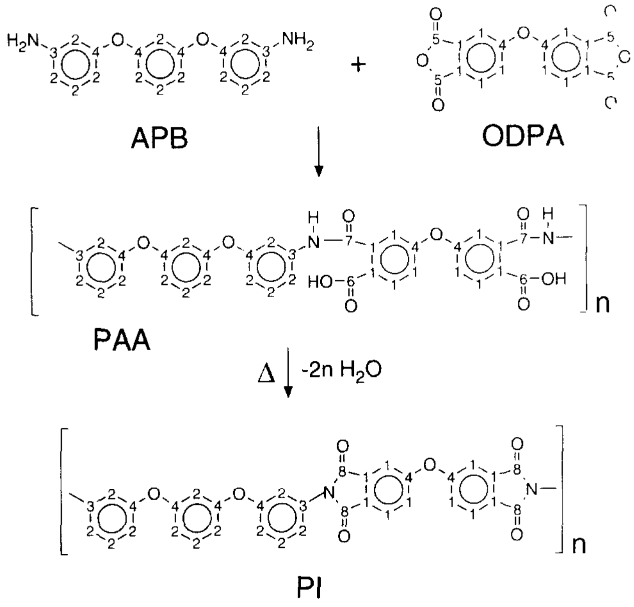

Figure 1 Schematic of the molecular structure of monomers ODPA and APB and their reaction to form poly(amic acid) and after heating polyimide. The labels on C atoms are used for X.p.s. peak assignment

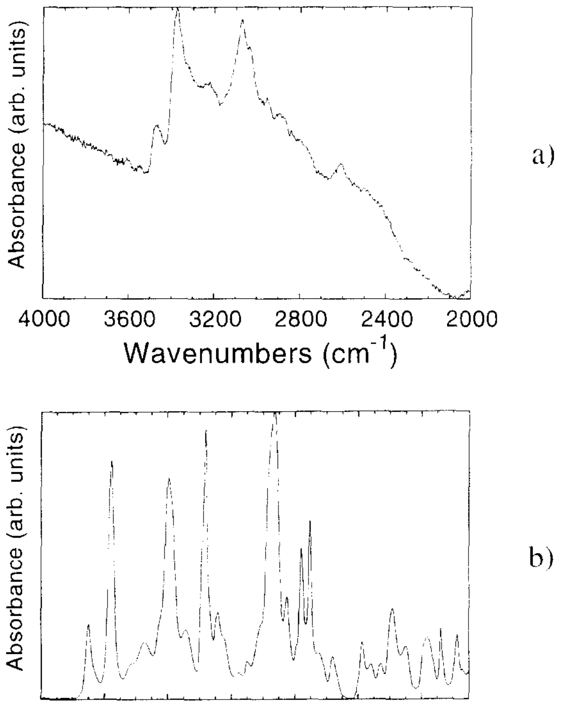

Figure 2 (a) and (b) Two regions of the transmittance i.r. spectrum of a MBD ODPA–APB film, as-deposited on a NaCl disc substrate

As-deposited films were annealed to induce imidization. Annealing was performed *ex situ*, either in an oven purged with nitrogen using a cure schedule (30 min at 150°C, 30 min at 230°C, 30 min at 300°C and 1 h at 400°C, named c-cure), or in a UHV chamber with a base pressure of 5×10^{-10} torr, at 320°C for 10 min.

The substrates used were NaCl discs for transmittance i.r. characterization, Si for X.p.s. characterization, and polycrystalline Cr on Si for external reflectance i.r. characterization.

Analytical techniques and instrumentation

We have characterized MBD ODPA–APB PI films with a number of analytical techniques including transmittance infra-red (i.r.) spectroscopy, external reflectance i.r. spectroscopy (e.r.i.r.), X-ray photoelectron spectroscopy (X.p.s.), optical microscopy, scanning electron microscopy (SEM) and ellipsometry.

Transmittance (i.r.) spectra were obtained using a Nicolet model 740 FTIR spectrometer equipped with an MCT-A detector. The resolution of the spectra obtained from the monomers was 2 cm^{-1}. All other spectra had a resolution of 4 cm^{-1}.

E.r.i.r. spectra were obtained using a Nicolet model 510 FTIR spectrometer equipped with an MCT-B detector at a resolution of 4 cm^{-1}.

X.p.s. spectra of MBD films were recorded on a Surface Science Instruments 301 spectrometer using Al $K\alpha$ radiation and a hemispherical electron energy analyser. The beam spot size was 150 μm. The experimental energy resolution of the spectrometer, measured as the full width at half maximum (*FWHM*) of Au $4f_{7/2}$, was 0.66 eV. The X.p.s. spectra of a spin-coated film were obtained on a Perkin–Elmer PHI 5500 ESCA system, using monochromated Al $K\alpha$ radiation and a hemispherical electron energy analyser. No flood gun was used for charge compensation. In the case of the MBD films, which had thicknesses <100 nm there were no charging effects observed. The spin-coated film was thicker (about 1 μm) and charging resulted in a peak shift of 3.1 eV shift towards higher binding energies. Curve fitting was done with the ESCA TOOLS software package, and the software provided with the spectrometers.

SEM micrographs were obtained using an ISI DS-130S scanning electron microscope in the secondary electron mode. An Olympus AH-2 metallographic microscope was used to obtain optical micrographs.

A Waferscan ellipsometer was used for thickness and index of refraction measurements, complemented by a Tencor profilometer.

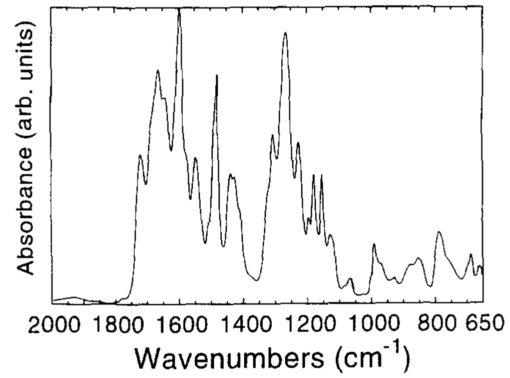

Figure 3 Transmittance i.r. spectrum of a spin-coated film of ODPA–APB poly(amic acid) on KBr disc substrate, heated to 80°C for 30 min

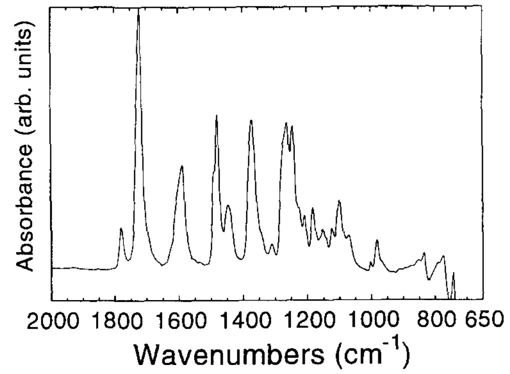

Figure 4 Transmittance i.r. spectrum of an MBD ODPA–APB film on NaCl disc substrate, annealed at 150°C for 1.75 h in N_2 atmosphere

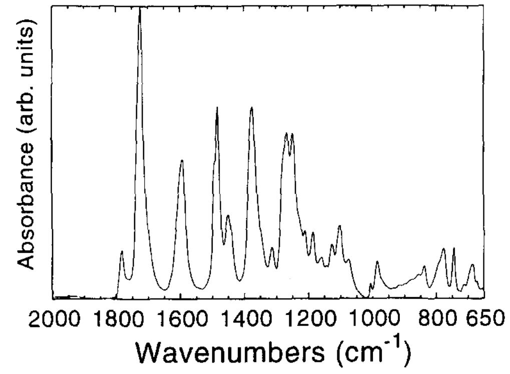

Figure 5 Transmittance i.r. spectrum of a c-cured, MBD ODPA–APB polyimide film on NaCl disc substrate

RESULTS AND DISCUSSION

Characterization

Film morphology. Good thickness uniformity was obtained as indicated by ellipsometry. Thickness variation was <2% across the surface of a 57 mm (2.25 in) Si wafer. Smooth film surfaces were also obtained, as judged by featureless scanning electron micrographs. As in the case of PMDA–ODA PI[8], the crucial growth parameter for producing smooth and continuous films was the deposition rate ratio of the two monomers, which had to be controlled to achieve a 1:1 stoichiometric ratio. Large excess of either of the monomers produced rough film surfaces due to evaporation of the excess monomer during curing.

I.r. spectra. *Figure 2* shows the transmittance i.r. spectrum of an MBD ODPA–APB film recorded a few minutes after deposition (as-deposited). From this spectrum we can conclude that as-deposited films are either a mixture of unreacted monomers and polymer chains, or consist of dimers or other oligomers of ODPA–APB. In the latter case it is the end groups of anhydride and amine, respectively, that are responsible for the monomer peaks. The assignment of the i.r. peaks for each monomer, the as-deposited phase and the cured polyimide film has been carried out in detail elsewhere[18]. The presence of the anhydride moieties is manifested by the symmetric and antisymmetric anhydride carbonyl peaks at 1848 and 1777 cm^{-1}, respectively. The primary amine stretching bands that appear from 3500 to 3200 cm^{-1} substantiate the presence of the other monomer, APB, or amine end groups. Here it should be noted that in the case of co-deposition of APB with ODPA there are intermolecular interactions between APB molecules occurring via hydrogen bonding through primary amine groups, which could indicate a phase separation of APB, or at least the existence of APB dimers. Evidence for this interaction is provided by the peak at 3220 cm^{-1}. There is experimental evidence that the product of the reaction of stoichiometrically deposited monomers of PMDA and ODA in MBD films, up to room temperature, is dimers and oligomers and no evidence of hydrogen bonding between amine moieties was found[18]. In the present case there is evidence for such bonding. However, it could be assumed that these amine moieties are actually ends of ODPA–APB dimers or larger

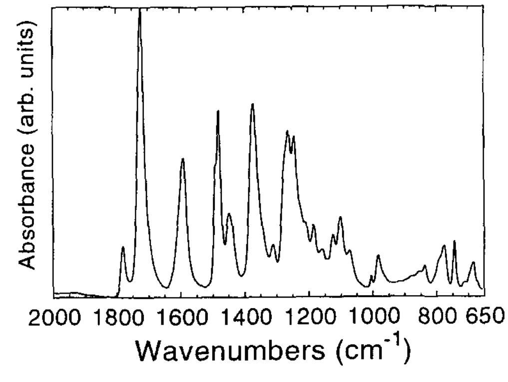

Figure 6 Transmittance i.r. spectrum of a c-cured, spin-coated ODPA–APB polyimide film on KBr disc substrate

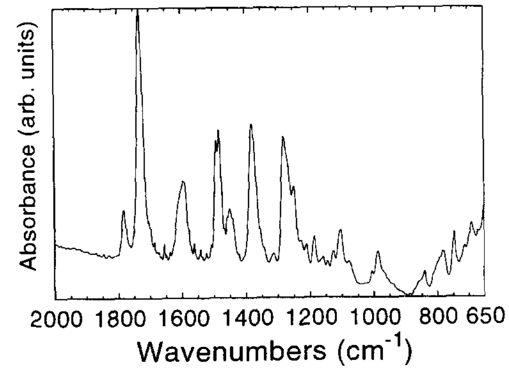

Figure 7 E.r.i.r. spectrum of a c-cured, MBD ODPA–APB polyimide film on a Cr-coated Si wafer

oligomers in which case bonding is facilitated by the flexibility of the molecules. Quantitative measurements are required for the clarification of this point.

The peak at 1671 cm^{-1}, which is due to amide carbonyl stretching (amide I band), is a proof that amidization reaction has taken place. The peaks at 1712 and 1540 cm^{-1} which are attributed to the amic acid carbonyl stretching and the amide II band (NH bending mode), respectively, further support the above conclusion.

Figure 3 shows the transmittance i.r. spectrum of a spin-coated ODPA–APB poly(amic acid) film on a KBr disc, after heating for 30 min at 80°C. We do not see unreacted monomers present in this film. We observe the amic acid carbonyl stretching (1717 cm^{-1}), the amide carbonyl stretching band (amide I at 1665 cm^{-1}) and the NH bending peak (amide II at 1545 cm^{-1}).

Figures 4 to *7* show the i.r. spectra of imidized films of ODPA–APB. *Figure 4* shows the transmittance i.r. spectrum of an MBD film on NaCl, after annealing at 150°C for 1.75 h under nitrogen. *Figure 5* shows the spectrum of a film from the same deposition run after annealing with a c-cure schedule in N_2, and having a thickness of 240 nm after imidization. For comparison purposes, *Figure 6* shows a spin-coated film of ODPA–APB after c-cure. *Figure 7* shows the e.r.i.r. spectrum obtained at 45° angle, from an MBD ODPA–APB film on Cr, which was imidized with a c-cure schedule in N_2 and had a thickness of 47 nm after imidization. The four spectra look very similar. Symmetric and antisymmetric imide carbonyl stretching peaks appear at 1779 and 1721 cm^{-1}, respectively, and the characteristic C–N stretching mode of the imide ring appears as a sharp intense band at 1372 cm^{-1} (ref. 19). The features characteristic of monomer and amide vibrations have vanished, evidence that the film has been completely imidized.

An interesting observation is that the ratio of the symmetric to antisymmetric imide carbonyl stretching is the same in transmittance i.r. and e.r.i.r. The vibrational dipole moments of these modes lie in the plane of the imide ring, which is coplanar to the neighbouring phenyl ring. This is a reasonable approximation for ODPA–APB polyimide, because in the case of PMDA–ODA polyimide the benzene ring and the two imide rings of the pyromellitimide moiety are coplanar[20]. The phenyl ring and the two five-membered anhydride rings of the PMDA molecule are approximately coplanar (the angle between the plane through the atoms of the benzene ring and the plane through each of the five-membered rings is 1°)[21]. We therefore postulate that there is no preferred orientation of the plane of the ODPA phenyl rings of the polyimide chain parallel to the substrate. If there was, then the intensity of both imide carbonyl stretching peaks would vanish in e.r.i.r. configuration. This proposal is also supported by conformational calculations[22] for the monomer ODPA, which show that there is rotational freedom around the C–O bonds of the ether linkage connecting the phthalimide rings, and a conformational energy minimum when the sum of the angles of rotation of the phthalimide ring planes around the C–O axes of the ether bond is 90°. The conformational energy is close to this minimum for a fairly wide range around 90°, but angles below 40 are considered as energetically forbidden[22]. Hence, two neighbouring phthalimide moieties cannot be coplanar and thus they cannot be parallel to the substrate simultaneously.

In the repeat unit of the ODPA–APB PI, there are three ether linkages that allow for large rotation angles without a remarkable increase in the conformational energy. This indicates that the structure of the polymer cannot have a significant degree of ordering. In ref. 23 a polyimide resulting from the monomers ODPA and *para*-phenylenediamine (*p*-PDA) was used to study the effect of the ether linkage of the dianhydride on the order of the resulting polyimide. It was concluded that such a linkage leads to a structure with a lower degree of order relative to the structures obtained from rigid dianhydride molecules (e.g. PMDA), even when ODPA–*p*-PDA films were drawn in the poly(amic acid) state to induce order. In the case of ODPA–APB, the two additional ether linkages present in the repeat unit will enhance the above result, and it is therefore expected that this PI has a disordered structure.

X.p.s. spectra. X.p.s. spectra of MBD ODPA–APB films were recorded in the as-deposited state, after c-cure in nitrogen atmosphere, and after curing at 320°C for 10 min in a UHV chamber with a base pressure of 5×10^{-10} torr. The film thickness of the samples was below 100 nm so that charging effects were minimized[15]. The X.p.s. spectrum of a c-cured, spin-coated ODPA–APB film was also recorded.

Figure 8a shows the C 1s spectrum of a c-cured, spin-coated ODPA–APB film, as recorded. *Figure 8b* shows the same spectrum after shifting the binding energy axis by 3.1 eV relative to the spectrum, performing a Shirley

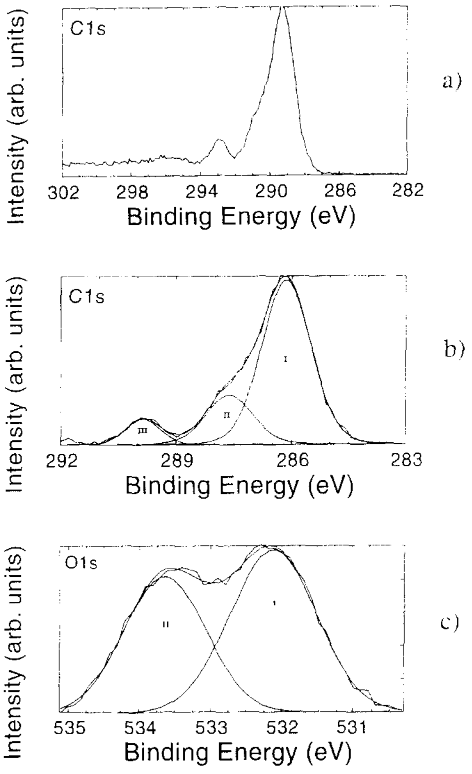

Figure 8 (a) As-recorded C 1s X.p.s. spectrum of a spin-coated ODPA–APB polyimide film. (b) The same spectrum after shifting, background subtraction and curve fitting. (c) O 1s X.p.s. spectrum of the same film

Table 1 Results of the curve fit to the experimental C 1s lineshape of c-cured, spin-coated ODPA–APB polyimide

Component	Binding energy (eV)	*FWHM* (eV)	Experimental (% of total area)	Theoretical (% of total no. of C atoms)
I	286.1	1.52	70.92	64.71
II	287.6	1.41	21.11	23.53
III	289.9	1.04	7.97	11.76

background subtraction, which takes into account the scattering of low energy electrons, and curve fitting.

The C 1s spectrum (*Figure 8b*) is fitted with three components. Component III at 289.9 eV is assigned to the imide carbonyl C atoms (labelled 8 in *Figure 1*), according to results of calculations in the case of PMDA–ODA and model compounds[24] which show that these atoms have the highest shifts to higher energy levels, and in agreement with previous experimental results[15,25]. Component I at 286.1 eV is assigned to the aromatic C atoms not bonded to oxygen or nitrogen (labelled 1 and 2). Component II is assigned to aromatic C atoms joined to oxygen or nitrogen (labelled 4 and 3 respectively). The broad peak at the high energy side of *Figure 8a* is due to π–π^* 'shake-up' transitions[26]. The FWHM of components I and II is somewhat larger than expected (*Table 1*). We attributed this to different binding energy (BE) shifts that result from the different chemical environments of the various aromatic C atoms. The BE shifts due to the attachment of four carbonyl groups (PMDA) or two carbonyl groups (n-phenylphthalimide) on a phenyl ring are 1 and 0.5 eV, respectively[15,24,25]. There is no published information on the relative shift produced by the attachment of two carbonyl groups and an O atom on one phenyl ring, which is the case of C atoms labelled 1 in *Figure 1*, but according to our assignment this shift should be between 0.5 and 1 eV. Component II is broad because of the different shifts produced due to attachment of O and N respectively on an aromatic C. The differences in BE shifts resulting from C atoms assigned to the same peak component (I or II) are below or close to the net energy resolution of the spectrometer and thus not producing a distinctive shoulder or asymmetry in the C 1s lineshape attributable to them. Curve fits of the experimental lineshape with an extra peak component inserted between components I and II did not improve noticeably the already high quality of the fit.

The theoretical percentage of the total for each of the C atom groups assigned to components I, II and III is displayed in the last column of *Table 1*. There is a general agreement between the experimental and theoretical values for components I and II, but there is a 32% deficiency of carbonyl C. When we take account of the 'shake-up' peak and distribute its intensity to components I, II and III proportionally to the number of C atoms assigned to each component, we still find a carbonyl C deficiency of 27%. Such a deficiency has been observed in PMDA–ODA PI[25,27]. Bagus *et al.*[28] performed self-consisted field calculations to describe the positions and relative intensities of the main C 1s and O 1s peaks of the X.p.s. spectrum of PMDA and the agreement with experiment was very good when localized 1 s holes were assumed. They concluded that the losses of intensity to the 'shake-up' and 'shake-off' satellites for the different, inequivalent C and O atoms are different, so that the intensity ratios of the main peaks do not reflect directly the stoichiometry of these atoms. The missing intensity in the experimental results can be accounted for by considering the complete photoemission process (multi-electron effects, relaxation, etc.)[15,28]. Meyer *et al.*[29] have discussed the apparent carbonyl deficiency in detail for PMDA–ODA PI, and they too have concluded that the carbonyl C and O deficiency is not due to a chemical effect but due to a difference in the 'shake-up' and 'shake-off' intensity distributions from the different carbon and oxygen species in that polyimide.

Figure 8c shows the O 1s spectrum of a c-cured, spin-coated ODPA–APB PI film fitted with two peak components at 532.1 and 533.6 eV. The former is assigned to carbonyl oxygen and the latter to ether oxygen as in the case of PMDA–ODA[14,30,31]. The ratio of the areas of these peaks is very close to the stoichiometric ratio of carbonyl oxygen and ether oxygen of ODPA–APB PI (3 : 3.8 *versus* 3 : 4, respectively, or 5% carbonyl O deficiency). This observation

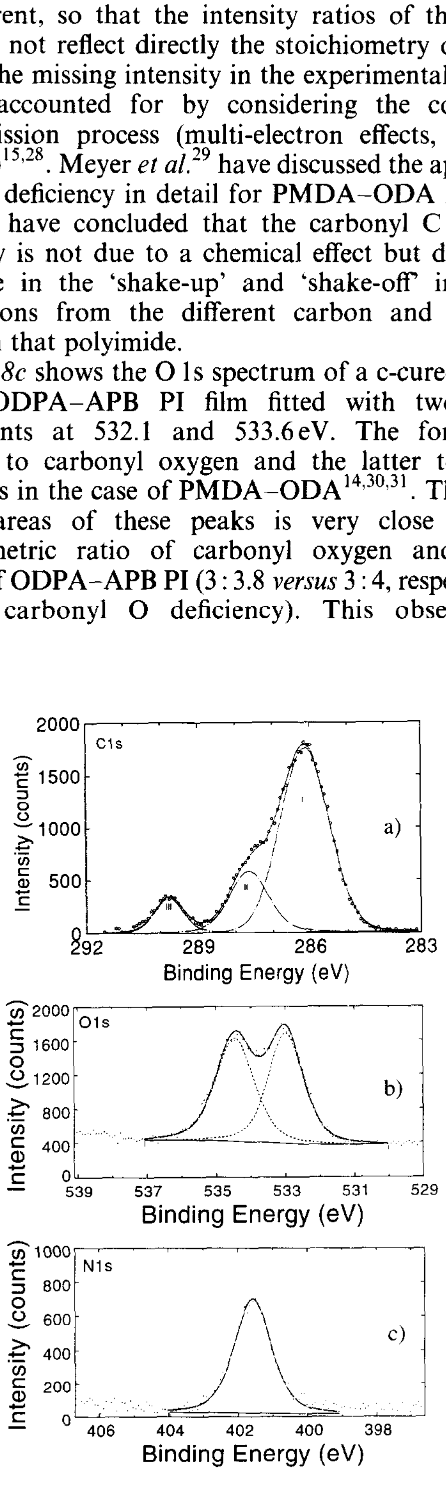

Figure 9 (a) C 1s, (b) O 1s and (c) N 1s X.p.s. spectra of a c-cured MBD ODPA–APB film

Table 2 Results of the curve fit to the experimental C 1s lineshape of c-cured, MBD ODPA–APB polyimide

Component	Binding energy (eV)	*FWHM* (eV)	Experimental (% of total area)	Theoretical (% of total no. of C atoms)
I	286.1	1.53	70.71	64.71
II	287.6	1.23	20.32	23.53
III	289.8	0.92	8.97	11.76

Table 3 Results of the curve fit to the experimental C 1s lineshape of UHV-cured, MBD ODPA–APB polyimide

Component	Binding energy (eV)	*FWHM* (eV)	Experimental (% of total area)	Theoretical (% of total no. of C atoms)
I	286.3	1.41	68.52	64.71
II	287.7	1.32	22.75	23.53
III	290.0	0.83	8.74	11.76

reinforces the argument that there is no real deficiency of carbonyl moieties; it is the apparent intensity assigned to carbonyl carbons that is smaller than expected from stoichiometry.

Figure 9 shows the C 1s, and O 1s and N 1s spectra of a c-cured, MBD ODPA–APB film. In the C 1s spectrum (*Figure 9a*) three components are resolved after curve fitting, centred at 286.2, 287.6 and 289.8 eV. The assignments are the same as for the spin-coated ODPA–APB PI film components I, II and III respectively. *Table 2* shows the position, *FWHM* and experimental and theoretical concentration assigned to each component, for the curve fit to the experimental C 1s lineshape of c-cured, MBD ODPA–APB polyimide. In general the experimental intensities are similar to those of the spin-coated sample. There is a slight increase in indicated carbonyl C concentration but still the apparent carbonyl deficiency is high (23%). In the O 1s spectrum (*Figure 9b*) two components are resolved from the curve fit: one at 533.0 eV and the other at 534.5 eV. The first can be assigned to the carbonyl oxygen and the second to the ether oxygen as in the case of the spin-coated film. The ratio of the components is approximately 1 : 1 instead of the calculated stoichiometric 3 : 4, so that the carbonyl O apparent deficiency is 24%. The N 1s spectrum (*Figure 9c*) consists of a single symmetric peak, corresponding to two chemically equivalent nitrogen atoms. There is no shoulder in the lower binding energy side of the peak,

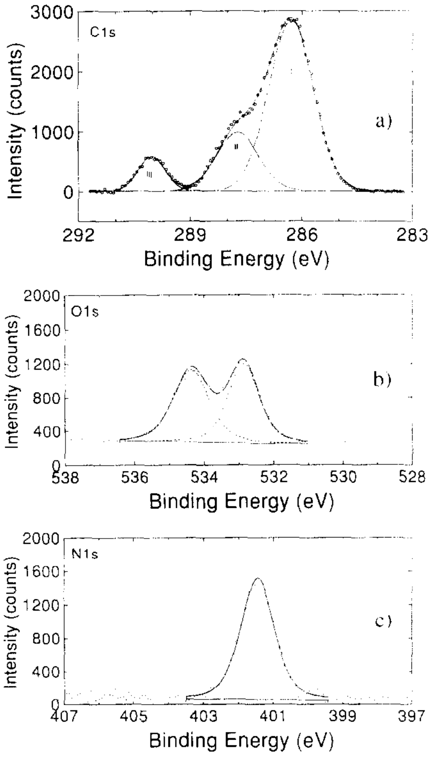

Figure 10 (a) C 1s, (b) O 1s and (c) N 1s X.p.s. spectra of an MBD ODPA–APB film annealed in UHV at 320°C for 10 min

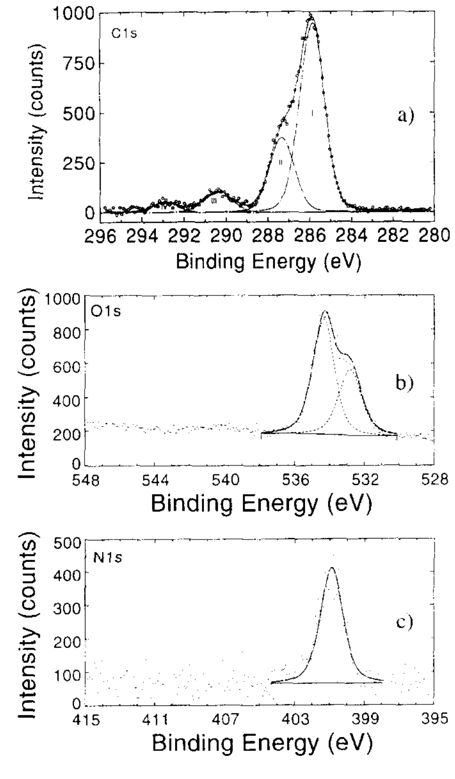

Figure 11 (a) C 1s, (b) O 1s and (c) N 1s X.p.s. spectra of an as-deposited MBD ODPA–APB film

Table 4 Results of the curve fit to the experimental C 1s lineshape of as-deposited MBD ODPA–APB

Component	Binding energy (eV)	*FWHM* (eV)	Experimental (% of total area)	Theoretical (% of total no. of C atoms)
I	285.9	1.38	65.68	64.71
II	287.3	1.40	26.19	23.53
III	290.4	1.59	8.13	11.76
IV	292.8	1.43	–	–

which would indicate the existence of isoimide or other moieties containing double-bonded nitrogen[32].

In *Figure 10* we see the C 1s, O 1s and N 1s spectra of a UHV-cured ODPA–APB PI film. They are all very similar to the corresponding spectra of the c-cured films described previously. *Table 3* shows the results of the curve fit to the C 1s spectrum.

Figure 11 shows the C 1s, O 1s and N 1s spectra of the as-deposited film. In the C 1s spectrum (*Figure 11a*) the broad peak at the highest energy side, centred at 292.8 eV, is due to 'shake-up' transitions related to the various kinds of C atoms of the molecule. At 290.4 eV there is another peak corresponding to carbonyl C atoms labelled 5, 6 and 7 in *Figure 1*. The *FWHM* of this peak is more than 60% larger than the *FWHM* of the corresponding peak of imidized films because it includes contributions from anhydride, carboxylic acid and amid carbonyl groups. As shown from the Fourier transform infra-red (*FT*i.r.) results, the as-deposited film is a mixture of monomers and oligomers. The rest of the peaks are assigned as in the case of the cured films. *Table 4* shows the results of the curve fit to the C 1s spectrum. The integrated intensity of the 'shake-up' feature has been excluded from the calculation of the fractions of the total integrated intensity (area under peaks) assigned to each of the other three components of the fit. We observe a 31% apparent deficiency in carbonyl C.

The O 1s spectrum (*Figure 11b*) exhibits two unequal peaks: the larger one at 534.4 eV includes contributions from ether oxygen and hydroxyl oxygen atoms and constitutes 61.8% of the total intensity; the other one, appearing at 532.9 eV, is due to the carbonyl oxygen atoms and constitutes 38.2% of the total intensity. The assignment is analogous to the PMDA–ODA case[14]. In stoichiometric PAA the first peak should have 55.6% of the total intensity and the second 44.4%. However, we cannot conclude that this is an indication of carbonyl deficiency because there are contributions to the first peak from the O atom of unreacted anhydride rings, which exist in the as-deposited film, as shown in the i.r. characterization section.

The N 1s spectrum (*Figure 11c*) exhibits only one peak at 400.2 eV, corresponding to amide nitrogen. Contributions from unreacted APB are not apparent, although in *Figure 2a* the presence of unreacted primary amine groups is clearly indicated.

Discussion

Cured films of the MBD PI have the same chemical structure as the spin-coated films. This is apparent from the identical *FT*i.r. and X.p.s. spectra from films prepared using both preparation methods. However, there is a big difference in the as-deposited, uncured films. In the MBD films there are a lot of unreacted anhydride and amine groups, as evident from the i.r. spectrum (*Figure 2*) and the carbonyl C 1s region of the X.p.s. spectrum (*Figure 11*) of as-deposited ODPA–APB, while in the spin-coated films there is no evidence of such unreacted moieties, which shows that the polymerization reaction is complete (*Figure 3*).

The thickness of the films, as-deposited and after three different annealing treatments, has been measured using ellipsometry. An as-deposited film of ODPA–APB on a 76 mm (3 in) Si wafer was cut in several pieces and each subjected to different annealing treatments. One sample was c-cured, another was cured in UHV for 10 min at 320°C, and a third one was first c-cured and then cured in UHV for 10 min at 320°C. The thickness of the as-deposited film was 89 nm and the refractive index 1.65. The c-cured film had a thickness of 78 nm and the refractive index was 1.66. The film that was only UHV-cured lost more than 50% of its original thickness. After curing its thickness was measured to be 43.1 nm and the refractive index was 1.66. The film surface was found to be much rougher than in the case of the c-cured film using atomic force microscopy[18,33].

This thickness reduction cannot be accounted for by the loss of water due to polycondensation during imidization. The mechanism involved is directly linked to the presence of unreacted monomers or other low-molecular-weight (*MW*) species in the as-deposited state of the films. The longer a molecule is, the lower its equilibrium vapour pressure. Polymerization and desorption of low *MW* species may occur simultaneously and be competing processes. At a very fast temperature ramp rate, there is less time available for these species to react with each other and produce larger molecules, thus a larger portion of them desorbs, relative to the case of a slower temperature ramp rate. At atmospheric pressure, under N_2, monomers reacted before the temperature was high enough for desorption of low *MW* species. It is possible that an equilibrium partial pressure of these molecules developed in the oven chamber during annealing, suppressing desorption. In the c-cure schedule the first step is at 150°C for 30 min. The *FT*i.r. results (*Figure 4*) show that annealing at the same temperature in nitrogen for 1.75 h was sufficient to not only transform the as-deposited film to poly(amic acid) but also to imidize it. Hence, under atmospheric pressure, at 150°C the low *MW* species do not desorb significantly and the polymerization reaction is completed. In the UHV annealing process, there was no intermediate annealing step at 150°C, and the temperature was raised to 320°C with a fast temperature ramp.

The previous points are reinforced by the thickness measurement of the sample that was first c-cured and then UHV-cured at 320°C for 10 min. It was found to be 77.2 nm thick and the refractive index was 1.66. There was practically no further loss of thickness in UHV compared with the c-cured film.

CONCLUSIONS

The MBD technique was successfully used to grow PI films from ODPA and APB for the first time. Ultrathin to thick films with high thickness uniformity can be produced. As-deposited films contain large amounts of low *MW* species. Thermal imidization starts below 150°C. Curing in a nitrogen atmosphere with a stepped cure sequence produces higher quality films than curing in UHV using a fast temperature ramp rate. The i.r. and X.p.s. results demonstrate that cured MBD films are chemically indistinguishable from spun films. ODPA–APB polyimide has a disordered structure.

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REFERENCES

1 Wilson, A. M. in 'Polyimides: Synthesis, Characterization, and Applications' (Ed. K. L. Mittal), Vol. 2, Plenum Press, New York, 1984, p. 715

2 Jensen, R. J., Cummings, J. P. and Vora, H. *IEEE Trans., Comp. Hybrids Manufact. Technol. CHMT* 1984, 7, 384

3 Feger, C. and Feger, C. in 'Multichip Module Technologies and Alternatives' (Eds D. A. Doane and P. D. Franzon), Van Nostrand Reinhold, New York, 1993

4 Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V. and Laius, L. 'Polyimides', Consultants Bureau, New York, 1987

5 Wilson, D., Stenzenberger, H. D. and Hergenrother, P. M. 'Polyimides', Chapman and Hall, New York, 1990

6 Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* 1976, **11**, 161

7 Kowalczyk, S. P., Kim, Y. -H., Walker, G. F. and Kim, J. *Appl. Phys. Lett.* 1988, **52**, 375

8 Kowalczyk, S. P., Dimitrakopoulos, C. D. and Molis, S. *Mater. Res. Soc. Symp. Proc.* 1991, **227**, 55

9 Salem, J. R., Sequeda, F. O., Duran, J., Lee, W. Y. and Yang, R. M. *J. Vac. Sci. Technol. A* 1986, **4**, 369

10 Iijima, M., Takahashi, Y., Inagawa, K. and Itoh, A. *J. Vac. Soc. Jpn* 1985, **28**, 437 (in Japanese)

11 Grunze, M. and Lamb, R. N. *J. Vac. Sci. Technol. A* 1987, **5**, 1695

12 Lamb, R. N., Baxter, J., Grunze, M., Kong, C. W. and Unertl, W. N. *Langmuir* 1988 **4**, 249

13 Mack, R. G., Grossman, E. and Unertl, W. N. *J. Vac. Sci. Technol. A* 1990, **8** 3827

14 Kowalczyk, S. P. and Jordan-Sweet, J. L. *Chem. Mater.* 1989, **1**, 592

15 Kowalczyk, S. P. in 'Metallization of Polymers' (Eds E. Sacher, J.-J. Pireaux and S. P. Kowalczyk), ACS Symp. Ser. 440, American Chemical Society, Washington, DC, 1990, p. 10

16 Kowalczyk, S. P., Stafstrom, S., Bredas, J. L., Salaneck, W. R. and Jordan-Sweet, J. L. *Phys. Rev. B* 1990, **41**, 1645

17 Lee, K. W., Walker, G. F. and Viehbeck, A. *Polym. Prepr.* 1993, **34**(2), 298

18 Dimitrakopoulos, C. D. *PhD Thesis*, Columbia University, New York, 1993

19 Ishida, H., Wellinghoff, S. T., Baer, E. and Koenig, J. L. *Macromolecules* 1980, **13**, 826

20 Wachsman, E. D. and Frank, G. W. *Polymer* 1988, **29**, 1191

21 Aravamudhan, S, Haeberlen, U., Irngartinger, H. and Krieger, C. *Molecular Phys.* 1979, **38**, 241

22 Milevskaya, I. S., Baklagina, Y. G. Sidorovich, A. V., Korzhavin, L. N. and Lukasheva, N. V. *Zhurnal Strukturnoi Khimii* 1981, **22**, 42. English translation: *J. Struct. Chem.* 1981, **22**, 345

23 Gudkov, V. A., Chistyakov, I. G., Chumakova, S. P., Baklagina, Y. G. and Sidorovich, A. V. *Kristallografiya* 1983, **28**, 752. English translation: *Sov. Phys. Crystallogr.* 1983, **28**, 445

24 Silverman, B. D., Sanda, P. N., Ho, P. S. and Rossi, A. R. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 2857

25 Leary, H. J. Jr and Campbell, D. S. in 'Photon, Electron and Ion Probes of Polymer Structure and Properties' (Eds D. W. Dwight, H. R Thomas and T. J. Fabish), ACS Symp. Ser. 162, American Chemical Society, Washington, DC, 1981, p. 420

26 Clarck, D. T., Adams, D. B., Dilks, A., Peeling, J. and Thomas, H. R. *J. Electron Spectrosc.* 1976, **8**, 51

27 Silverman, B. D., Bartha, J. W., Clabes, J. G., Ho, P. S. and Rossi, A. R. *J. Polym. Sci., Part A* 1986, **24**, 3325

28 Bagus, P. S., Coolbaugh, D., Kowalczyk, S. P., Pacchioni, G. and Parmigiani, F. *J. Electron Spectrosc. Relat. Phenom.* 1990, **51**, 69

29 Meyer, W., Grunze, M., Lamb, R., Ortega-Vilamil, A., Schrepp, W. and Braun, W. *Surface Sci.* 1992, **273**, 205

30 Buchwalter, P. L. and Baise, A. I. in 'Polyimides: Synthesis, Characterization, and Applications' (Ed. K. L. Mittal), Plenum Press, New York, 1984

31 Haight, R., White, R. C., Silverman, B. D. and Ho, P. S. *J. Vac. Sci. Technol. A* 1988, **6**, 2188

32 Strunskus, T., Grunze, M. and Gnanarajan, S. in 'Metallization of Polymers' (Eds E. Sacher, J.-J. Pireaux and S. P. Kowalczyk), ACS Symp. Ser. 440, American Chemical Society, Washington, DC, 1990, p. 353

33 Dimitrakopoulos, C. D. and Kowalczyk, S. P. 'Atomic force microscopy of polyimide surfaces' paper to be published