

RESEARCH ARTICLE

Residue analysis of thermally depolymerized phthalaldehyde-based polymer thin films

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Abstract

In this study, thermolysis of poly(phthalaldehyde), pPHA, was investigated, and the nonvolatile residues produced were characterized by bulk and surface analyses to provide insight into its use as a resist material for thermal scanning probe lithography. A temperature of 300°C for a short time was required to remove nearly all of the residue produced from pPHA depolymerization. X-ray photoelectron spectroscopy (XPS) was used to quantify the trace amount of hydrocarbon residue after thermolysis. Time-of-flight secondary ion mass spectrometry (SIMS) results show that the residue is largely PHA monomers and oligomers, but also include hydrocarbon char. Differences in molecular weight and composition of the residue as a function of copolymer composition were investigated to give insight into designing new thermal resist materials.

KEYWORDS

poly(phthalaldehyde), polymer thin film, residue analysis

1 | INTRODUCTION

Poly(phthalaldehyde) (pPHA) was originally investigated for applications in semiconductor manufacturing in the 1980s when Ito and Willson first explored using the polymer as a chemically amplified resist material for optical lithography. Pragmatic considerations of shelf life and deposition of volatile monomers onto exposure and metrology tools prevented its commercialization.^{1,2} More recently, pPHA has become one of the choice resist systems for thermal scanning probe lithography due to its ability to cleanly degrade and vaporize in response to heat.^{3,4} The patterning process involves bringing a heated probe tip, at a temperature up to ~1000°C, in contact with the resist for 1 to 100 μs to vaporize the polymer to form a topographical pattern. The ability to directly pattern features on nanometer length scales without the need for photomasks or vacuum systems makes this a promising technology to rapidly prototype and manufacture structures for applications in sensors, imprint molds, and other nanodevices.^{4–6} The clean degradation of pPHA is due to the fact that it is a metastable polymer that can spontaneously depolymerize to its

constituent monomers at ambient conditions in response to specific stimuli. When using heat as a stimulus, the monomers can rapidly vaporize leaving nearly pristine substrates. The rapid depolymerization of pPHA its copolymers is due to its low ceiling temperature (T_c), ca. –35°C for pPHA.^{7,8} At temperatures above T_c , the polymer is thermodynamically driven to depolymerize but can exist in a metastable state as long as there are no reactive chain ends. These metastable polymers can undergo thermally induced chain scission to introduce reactive chain ends at temperatures higher than T_c , such as >100°C.^{9,10} Once a backbone bond is broken above T_c and reactive chain ends are formed, the polymer can rapidly depolymerize from the solid state into volatile, low-molecular-weight products.

Although pPHA has been used for thermal probe lithography applications for over a decade, there is no study that examines the residue composition and amount that form after thermolysis of thin films.⁴ Recently, Moore et al proposed that pPHA thermolysis followed a single electron transfer induced depolymerization to cleanly form *o*-phthalaldehyde monomer,⁹ however, their residue analysis focused on bulk polymer samples and did not explore the non-monomeric residues formed on the substrate surface. Identifying and quantifying the thin-film residues that form on a substrate is

Anthony Engler and Chi Kin Lo contributed equally to this study.

important for semiconductor processing applications, especially for small critical dimensions, where trace amounts of residue could account for a substantial volume at the length scales considered or could alter the physical and electrical properties of surfaces. A residue study could also lead to insight into the sources of probe-tip contamination in thermal probe lithography, an ongoing challenge to the field.⁴

In this study, the residue generated from pPHA and its copolymer with propanal (PA) depolymerization was investigated through the use of bulk and surface analysis techniques including X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (SIMS) as means to quantify the composition and amount of the residue. The trends with film thickness, thermal processing conditions, polymer molecular weight, and copolymer composition were quantified to provide insight into designing new resist systems for thermal patterning applications.

2 | EXPERIMENTAL METHODS

Unless otherwise stated, all chemicals were obtained from commercial suppliers and used as-received without further purification. Anhydrous dichloromethane was purchased from EMD Millipore. *o*-Phthalaldehyde, >99.7%, was purchased from TCI. Propanal, anhydrous 99% bis(2-methoxyethyl) ether (diglyme), and boron trifluoride diethyl etherate, ca. 48% BF₃, were purchased from Acros Organics. Pyridine, 99%, was purchased from Alfa Aesar. Propanal was distilled over calcium hydride under an inert atmosphere before use. Polymers used in this study were synthesized according to previously reported methods.¹⁰ Formulations were prepared by dissolving polymer in diglyme on a roller mixer until homogeneous, and then passed through a 0.2 μ m syringe filter into a clean vial. Fresh formulations were prepared before each set of experiments.

Polymer number average molecular weight (M_n) and molar mass dispersity (\bar{D}) were measured on a gel permeation chromatography (GPC) system composed of Shimadzu GPC units utilizing a refractive index detector and a Shodex column (KF-805L) with HPLC grade tetrahydrofuran (1 ml/min flow rate at 30°C) as the eluent. The GPC was calibrated using a series of linear, monodisperse polystyrene standards from Shodex.

The composition of the copolymers was determined by integration of the acetal proton peaks in ¹H NMR spectra obtained using a Bruker Avance III 400 MHz tool. Samples were analyzed in deuterated chloroform (CDCl₃). Infrared spectra were collected using a Nicolet iN10 MS infrared imaging microscope. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 under 40 ml/min flow of N₂ or ambient air.

Unless otherwise stated, all substrate and thin film preparations took place in a laboratory cleanroom. Crystalline silicon and silicon-germanium (SiGe) wafers were provided by Lam Research Corporation. SiGe wafers had 50 nm of SiGe at a 1:3 ratio of Si-to-Ge, on top of crystalline silicon. All substrates were cleaned immediately before use by washing the substrate for 2 min in an aqueous 1:50 HF

solution, followed by rinsing with deionized water and drying under a pressurized stream of nitrogen gas.

Polymer thin films were deposited on freshly cleaned wafers by spincoating from diglyme solutions. There was about 30 s between wafer cleaning and spincoating where the film was exposed to ambient air in a laminar flow hood. The film thickness was measured on a Woollam M-2000 ellipsometer using a Cauchy model for wavelengths >380 nm. Attempts at imaging the neat polymer films with a scanning electron microscope resulted in immediate polymer depolymerization due to the high-energy electrons. Some thin film treatments took place in a nitrogen-filled glovebox operating at <80 ppm O₂ and <1 ppm H₂O. Samples were heated at specific time and temperature conditions on top of a hotplate to thermally decompose the polymer films. The samples were transported and stored in plastic wafer boxes or sealed plastic bags that had been flushed with nitrogen gas in order to minimize atmospheric contamination.

After polymer decomposition, substrates were analyzed using XPS using a Thermo Scientific K-alpha XPS system and by time-of-flight SIMS using a SIMS 5-300 instrument (IONTOF GmbH, Münster, Germany). The XPS had an Al/K source gun with a 400 μ m spot size and ion beam energy of 200 eV for survey scans (1 eV per step) and 50 eV for elemental scans (0.1 eV per step) for 15 s steps. Some samples were ion milled in situ to provide depth profiling information by XPS. Each etch step was carried out with 500 eV argon ions at 1 mA/mm² for 5 s. SIMS spectra were collected using a Bi₃⁺⁺ liquid metal ion gun as the primary ion source at 25 kV at a 45° angle. Pulsed primary positive ions were rastered across the substrate surface with a scan area of 500 μ m². An electron flood gun was used for charge compensation.

3 | RESULTS AND DISCUSSION

Several polyaldehyde polymers were synthesized throughout this study to test how different variables affect residue formation after thermolysis. The polymers were synthesized via a cationic polymerization mechanism, which has been shown to produce polymers with long shelf-life.^{10,11} Table 1 shows the properties of the polymers used in this study.

The investigations began by comparing the XPS analysis of the substrate surface to determine the atmospheric impurities and adventitious carbon content.¹²⁻¹⁴ Silicon and SiGe wafers have native

TABLE 1 Synthetic details of polyaldehydes used in this study

Sample	Propanal Content (mol%) ^a	M_n (kg/mol) ^b	\bar{D} ^b
H1	0	278	2.1
H2	0	140	2.3
H3	0	78	2.3
P1	20	18	2.2

^aDetermined by peak integrations on ¹H-NMR spectra.

^bDetermined by GPC.

oxides in addition to adventitious carbon on the surface and polymer depolymerization may contribute hydrocarbon residue.^{15,16} The first experiments used the high-molecular-weight homopolymer, H1 from Table 1, coated on a SiGe substrate (70 and 400 nm thick), along with an uncoated control wafer. After spin-coating, one set of samples was placed in a nitrogen-filled glovebox to avoid exposure to atmospheric oxygen and water. The second set of samples was placed in a closed container with an open beaker of water to provide a higher local humidity. After aging in their local environments for 5 days, the thin films were removed by dissolving the polymer with copious amounts of anhydrous dichloromethane (DCM) inside a glovebox. DCM cleaning was chosen as a control process because it would not contribute to the XPS oxygen content and interfere with the polymer related oxygen content after thermolysis of the polymer films. Samples were immediately transported to the XPS tool after treatment for analysis to prevent unnecessary exposure to ambient atmosphere.

Table 2 shows the surface composition of the aged samples after polymer film dissolution in DCM. The samples stored in an inert atmosphere (i.e., glovebox) showed no oxygen, within the sensitivity of XPS, and high levels of germanium and silicon. High-resolution scans of the Ge3d and Si2p peaks were performed and are shown in Figure 1A,B. Data from all samples are provided in Figures S1 and S2 in Data S1. The samples that had 400 nm of polymer showed negligible amounts of GeO₂ and SiO₂ signal. Carbon was present at 22 to 25 at% of the total elemental composition for each sample, which is likely due to adventitious contamination from the glovebox or solvent wash because residual polymer would also contain an oxygen signal. Samples that were aged in air showed signs of substrate oxidation, as given by the high levels of oxygen present. Deconvolution of the high-resolution scans for Ge3d and Si2p peaks showed that significant portions of germanium and silicon on the bare wafer control existed as GeO₂ and SiO₂, respectively. Samples aged with pPHA thin films showed a lower level of oxidation, Figure 1C,D. It is noted that the extent of oxidation was minimally affected by the thickness of the film. Carbon signals from the samples aged in air are similar to those for samples aged in a glovebox. The lower carbon content on the uncoated, air sample was likely due to the larger presence of oxide skewing the relative percentages.

The thermal treatment was optimized before quantifying the surface residue from polymer thermolysis. TGA was used to quantify the polymer weight loss as a function of temperature as a guide to the

thermal processing. Sample H1 was heated at 1 to 50°C/min in a nitrogen ambient to determine how the heating rate affects the residue from polymer depolymerization and vaporization, Figure 2A. The onset temperature for thermal degradation (T_{onset}) increased from 124 to 153°C as the heating rate was increased from 1 to 50°C/min. The increase in T_{onset} with heating rate is due to the shorter time spent at each temperature when the scan rate was fast and is a commonly observed phenomenon of polymers on TGA.¹⁷ The temperature where the mass was observed to drop to zero wt% remaining (T_{clear}) also increased with an increase in heating rate from 221 to 298°C.

The head space atmosphere during sample heating was changed from nitrogen to ambient air to see what affect it would have on the TGA profiles and residue formation. Samples were heated at 10°C/min and isothermally held at 150°C, for 90 min before continuing the heating ramp to show the effect of soak time at high temperature. Figure 2B shows a slightly lower T_{onset} when the sample was heated in nitrogen compared to air, and the residual residue was significantly different. The air sample mass decreased to <1 wt% over a 90 min isothermal time period at 150°C. The mass approached zero during the final temperature ramp with $T_{\text{clear}} = 253^\circ\text{C}$. The sample in N₂ ended the isothermal period with 2 wt% mass with $T_{\text{clear}} = 270^\circ\text{C}$. It is unlikely that the small residue at the end of the TGA experiments is residual monomer because all the monomers have a significant vapor pressure at the temperature. Used. The higher residue amount observed in the nitrogen atmosphere is attributed to pyrolysis of the polymer depolymerization products and formation of higher mass, less-volatile products. Although thermal probe lithography tools are capable of much faster heating rates than the TGA used in these experiments, these results provide valuable information with respect to minimum required patterning temperatures and residue differences in response to different atmospheres.

A larger starting mass of polymer was used to study the residue produced to increase amount available for analysis. Bulk polymer powder, 2.5 g, was placed on top of a heated silicon substrate on a hotplate at 200 or 300°C for 5 min. Polymer powder was used in these experiments to eliminate the solvent casting step so that the possibility of residual solvent participating in the residue-forming reaction was not possible. After the thermal treatment, DCM was used to dissolve and collect the residue on the silicon substrates. The DCM solution containing the residue was dried and then taken up in

TABLE 2 XPS surface compositions of SiGe substrates after aging for 5 days and removing pPHA thin films by DCM

Aging condition	pPHA thickness (nm)	Ge3d (at%)	GeO ₂ (at%)	Si2p (at%)	SiO ₂ (at%)	O1s (at%)	C1s (at%)
Glovebox	0	61.7	ND	15	ND	ND	23.3
Glovebox	70	60.6	ND	14.6	ND	ND	24.8
Glovebox	400	63.1	ND	14.9	ND	ND	22.0
Air	0	46.7	6.3	10.3	3.1	14.7	18.9
Air	70	47.9	4.7	11.9	2.2	9.2	24.1
Air	400	46.6	4.4	10.6	1.9	9.5	27.0

Abbreviation: ND, Not detected.

FIGURE 1 High-resolution XPS scans, peak fits, and deconvolutions from SiGe substrates aged 5 days with 400 nm of pPHA followed by solvent cleaning: (A) Ge3d peak and (B) Si2p peak from glovebox sample, and (C) Ge3d peak and (D) Si2p peak from air sample

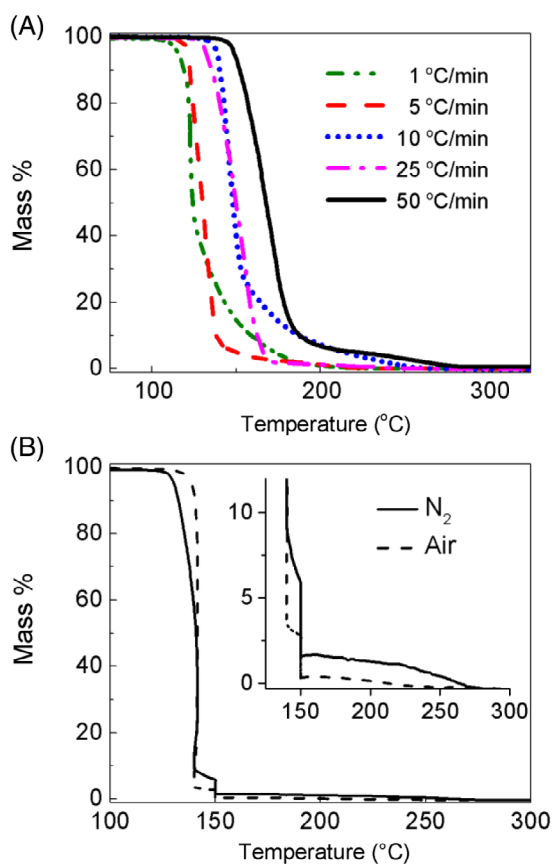
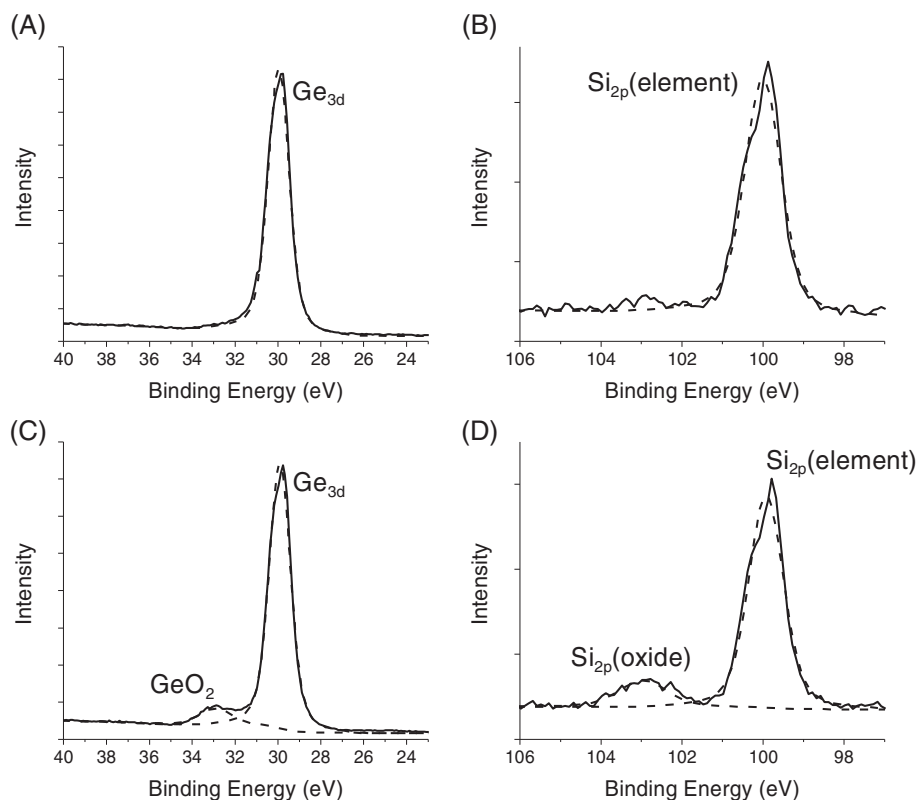


FIGURE 2 pPHA TGA traces of (A) dynamic temperature ramp in N_2 atmosphere for heating rates of 1, 5, 10, 25, and 50 °C/min, and (B) a comparison of heating under ambient air versus nitrogen atmospheres at 10 °C/min with a 90 min isothermal hold at 150 °C

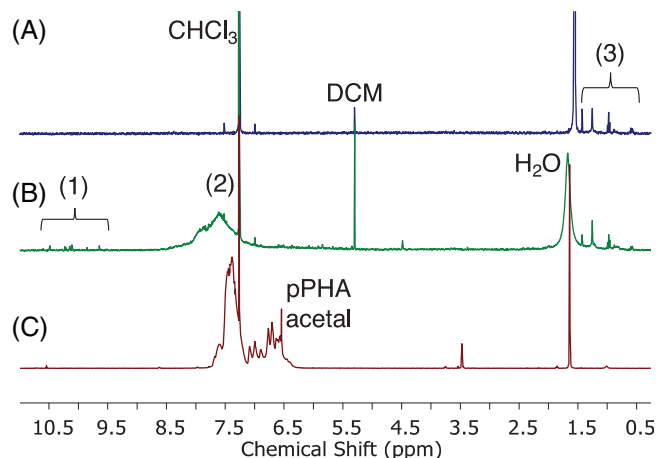


FIGURE 3 1H -NMR spectra (400 MHz, $CDCl_3$) of the residues collected from samples decomposed for 5 min at (A) 300 °C and (B) 200 °C in a cleanroom environment, and (C) pristine pPHA as a reference

$CDCl_3$ for 1H -NMR analysis. Figure 3 shows the stacked spectra from the two samples (i.e., 200 and 300 °C decomposition) and reference pPHA sample. The peaks at 5.32 and 7.26 ppm are attributed to residual DCM and chloroform, respectively. The spectrum from the sample decomposed at 200 °C has several peaks in the range of $\delta = 9.5$ to 11 ppm, designated by the (1) label, typical of aldehyde protons. This indicates that the side reactions form non-monomeric by-products because unreacted monomer would only have a single peak at 10.52 ppm.⁷ This sample also had a broad peak centered at 7.59 ppm,

labeled (2), representative of aryl hydrogens, and a broad peak at 1.56 ppm that is likely due to water impurities complexing other species in solution. A few smaller peaks are also observed in the range of $\delta = 0.5$ to 1.5 ppm, labeled (3), and are attributed to hydrocarbons. No characteristic peaks of the pPHA acetal protons, $\delta = 6.5$ to 7.1 ppm, were observed. The peaks at $\delta = 0.5$ to 1.5 ppm are the only ones observable for the sample decomposed at 300°C, which was largely insoluble black dust showing that only char type material was produced.

The residue formed on the silicon substrate from the bulk polymer decomposition was analyzed using an infrared imaging microscope to measure the IR spectra, Figure 4, to gain insight into the chemical species formed during thermolysis. Similar to the previous NMR results, the sample exposed to 300°C had only limited spectral features with strong peaks at 2922 and 2853 cm^{-1} , indicative of alkyl C—H_x stretching, and minor peaks at 1450 and 780 cm^{-1} , indicative of aromatic C=C stretching and aromatic C—H bending, respectively. The sample decomposed at 200°C had similar peaks representative of aromatic and aliphatic species, but also had significant O—H stretching at 3450 cm^{-1} and carbonyl stretching at 1717 cm^{-1} , corroborating the NMR solution data. Based on the TGA and residue characterization findings, decomposing the polymer films at 300°C is needed to remove a majority of the aldehyde-type residue to leave behind a near pristine substrate with only a trace of hydrocarbon residue.

XPS was used to examine the amount and atomic composition of the residue formed after the thin film thermolysis. The surface oxide on silicon and SiGe was HF cleaned followed by a hotplate bake at 400°C for 10 min to remove adventitious carbon. Samples were immediately coated after the bake with pPHA (70 nm and 400 nm thicknesses). A blank was also cleaned and heated as a control. Thermolysis of the films was carried out by placing the wafers on a 300°C hotplate for 5 min in a cleanroom atmosphere. Visually, the films appeared to instantly depolymerize and vaporize at the hotplate temperature. However, the wafers were heated for a full 5 min to ensure more complete residue removal. Unlike the bulk powder decompositions that left visible remains, these samples produced mirror-like surfaces with no visible char formation on any of the substrates. Once completed, all samples were immediately transported to the XPS tool for analysis. Table 3 shows the surface composition of the substrates after thermolysis. The oxide formed during the wafer heating prior to polymer deposition accounts for the high oxygen signals at 38 to 42 at%. The uncoated wafer controls showed 4.0 and 4.8 at% carbon for the SiGe and Si substrates, respectively. It is noted

that the pPHA-coated films showed only a minimal addition of carbon on the surface. The four coated samples had carbon content ranging from 4.9 to 5.9 at%. Samples with decomposed 400 nm thick films showed only slightly higher carbon signals after decomposition confirming that the carbon residue was from the polymer decomposition, which agrees from the bulk powder degradation study. Longer heat

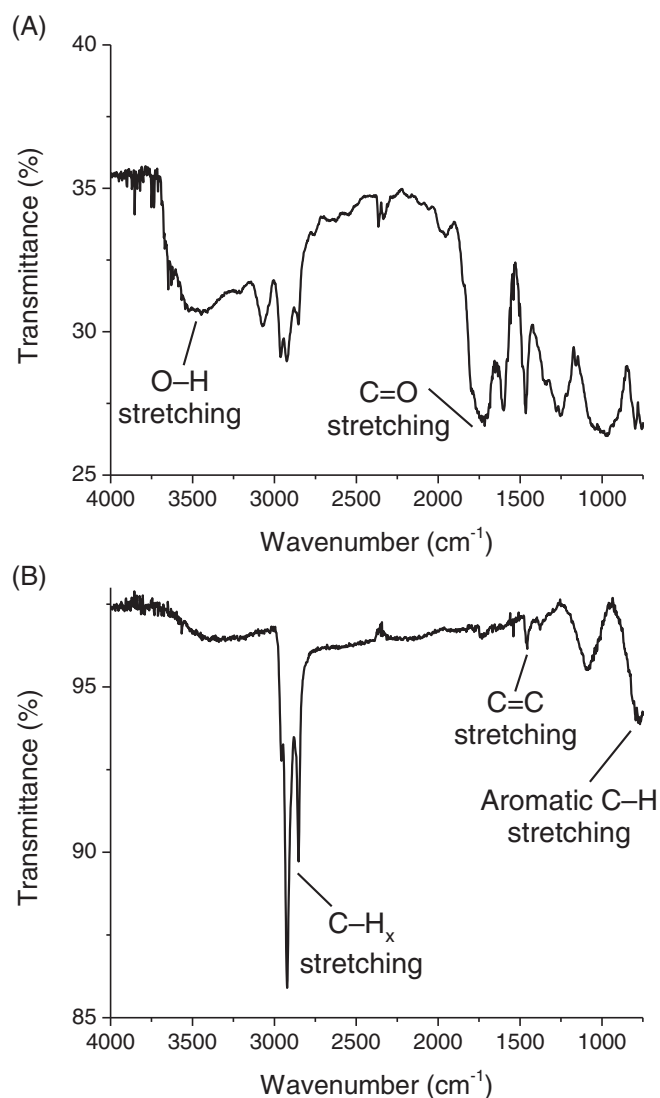


FIGURE 4 IR spectra of the insoluble residues left behind on the Si substrate after thermolysis at (A) 200°C and (B) 300°C in a cleanroom environment

Substrate	p(PHA) thickness (nm)	Ge (at%)	Si (at%)	O (at%)	C (at%)
Si	0	-	56.8	38.4	4.8
Si	70	-	56.9	37.5	5.6
Si	400	-	57.2	37.1	5.7
SiGe	0	38.8	15.6	41.6	4.0
SiGe	70	39.1	15.2	40.8	4.9
SiGe	400	39.3	15.1	39.7	5.9

TABLE 3 XPS surface compositions of SiGe and Si substrates after thermolysis of pPHA thin films at 300°C for 5 min in ambient atmosphere

treatments at higher temperatures may lower the nonvolatile residue formed on the substrate.

The residue formed from the thin polymer films was analyzed by depth profile using Ar-ion sputtering and XPS. Figure 5 shows representative high-resolution scans of the C1s peak before and after 10 etch steps for the bare silicon control and silicon wafer with decomposed polymer (400 nm film). See Figure S3 in Data S1 for depth profiling spectra for all samples. The red curve shows the scan before wafer Ar-ion sputtering with stronger signals around 285 eV from C—C bonds and a small shoulder at 287 eV that is likely due to C—O bonds.¹⁸ After the first 5 s etch step, the C1s signal falls below the sensitivity limit of the XPS instrument. The absence of measurable residue was confirmed by ellipsometry, which consistently showed <1 nm of material on the substrate after thermolysis. Overall, these

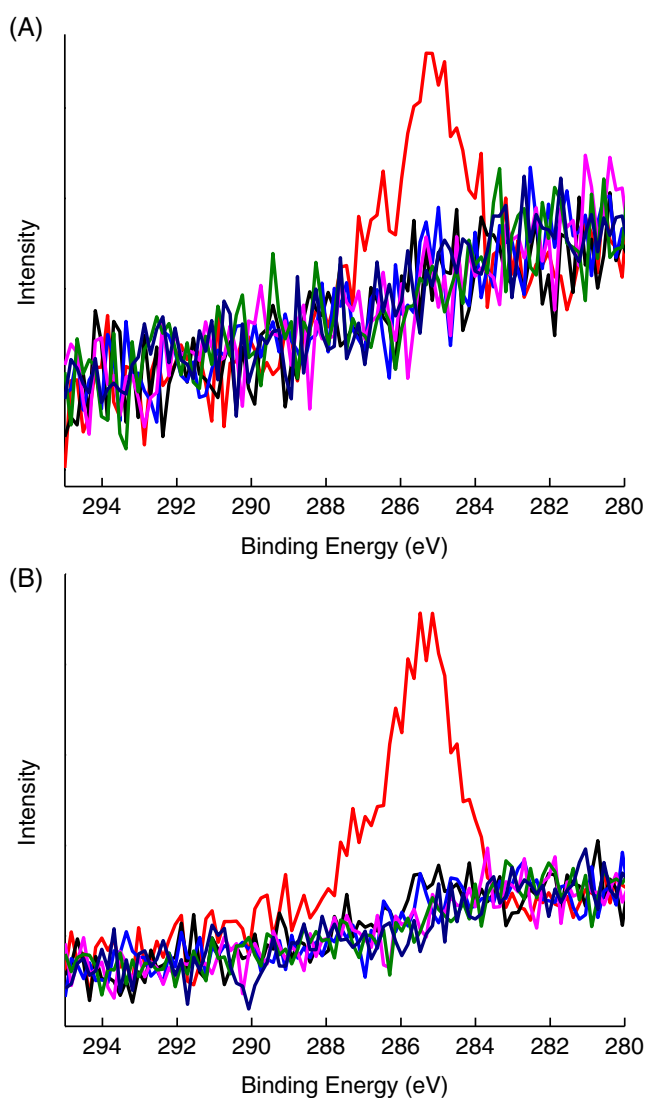


FIGURE 5 High-resolution XPS scans of the C1s peak after a series of Ar-ion etch steps to evaluate the depth profiling of the carbon residues after thermolysis at 300°C for 5 min of the (A) uncoated Si control and (B) 400 nm pPHA on Si. Red curve is the signal before any etching and subsequent curves show the C1s signal to fall below the sensitivity limit

XPS result show that pPHA depolymerization and vaporization produced little or no residue.

SIMS was used to investigate the atomic mass of the residue on the wafers after thermolysis.¹⁹ As an initial control, a 400 nm thick film of pristine pPHA was analyzed prior to heating and is shown in Figure 6A. The mass to charge ratio (m/z) range of 0 to 200 showed the highest intensity signals, with the molecular ion peak at 133 due to phthalaldehyde monomer ($M = 134.03$ g/mol) minus one hydrogen atom. Several other peaks in this region were attributed to other phthalaldehyde fragments including m/z of 118 (phthalaldehyde minus oxygen), 77 (C_6H_5), and 29 (CHO). Phthalaldehyde oligomers were observed from the dimer, m/z of 267, up to the hexamer, m/z of 803. Some oligomer species were also observed complexed with cations, given the peaks at m/z of 409 and 559 that correspond to trimer + lithium and tetramer + sodium, respectively. The sodium and lithium were unintentional impurities introduced from the use of glassware and chemicals.

After thermolysis at 300°C for 5 min, Figure 6B, silicon (m/z of 28) dominated the spectrum. Monomer fragment peaks similar to those for pPHA were observed with higher intensity than the monomer peak itself, most notably m/z of 77 corresponding to benzene (C_6H_5). Other residue-related species were also identified, such as toluene, indene, and naphthalene. Oligomer fragments up to tetramers appeared at low intensity. Signals from $m/z > 600$ were practically undetected. An experiment run concurrently with samples heated to 200°C (see Figure S4 in Data S1) supports the previous spectroscopy findings that this temperature leaves behind some PHA-related residue. Specifically, there was roughly an order of magnitude increase in the signals coming from PHA-related products, which dwarfed the silicon signal, compared to the 300°C heated sample. Tetramers and pentamers complexed with sodium were also observed. The enhanced stability of these cation-oligomer complexations require a higher temperature to volatilize. It is noted that a peak at 278 m/z was observed that is likely from plasticizer contaminants (dibutyl phthalate) from the plastic containers used for sample storage and transportation.^{20,21}

The effect of increasing the soak time at 300°C was investigated, Figure 6C. The time was increased from 5 to 60 min. Bare silicon and a substrate washed with the casting solvent diglyme were used as controls. The two control samples showed very similar spectra. Both pPHA samples showed higher levels of residue, with the 60 min sample showing a slight reduction in the higher m/z values. The results show that only a short heating time is needed to remove a majority of residue and extended heating time does not have a significant effect on the amount of residue. Thermolysis experiments (5 min, 300°C) were performed on pPHA samples of increasing polymer molecular weight, Figure 6D. The results suggest there may be a weak correlation to forming higher mass residue with starting polymer molecular weight.

The depolymerization and volatilization of phthalaldehyde copolymers were investigated to see the effect of volatile comonomers on product removal.^{10,22} A propanal copolymer, p(PHA-PA) sample P1, was compared to pPHA at the previously used thermolysis conditions, 5 min at 300°C. The SIMS analysis of the substrates after heating the 100 nm thick polymer samples is shown in Figure 7. See Figure S5 in

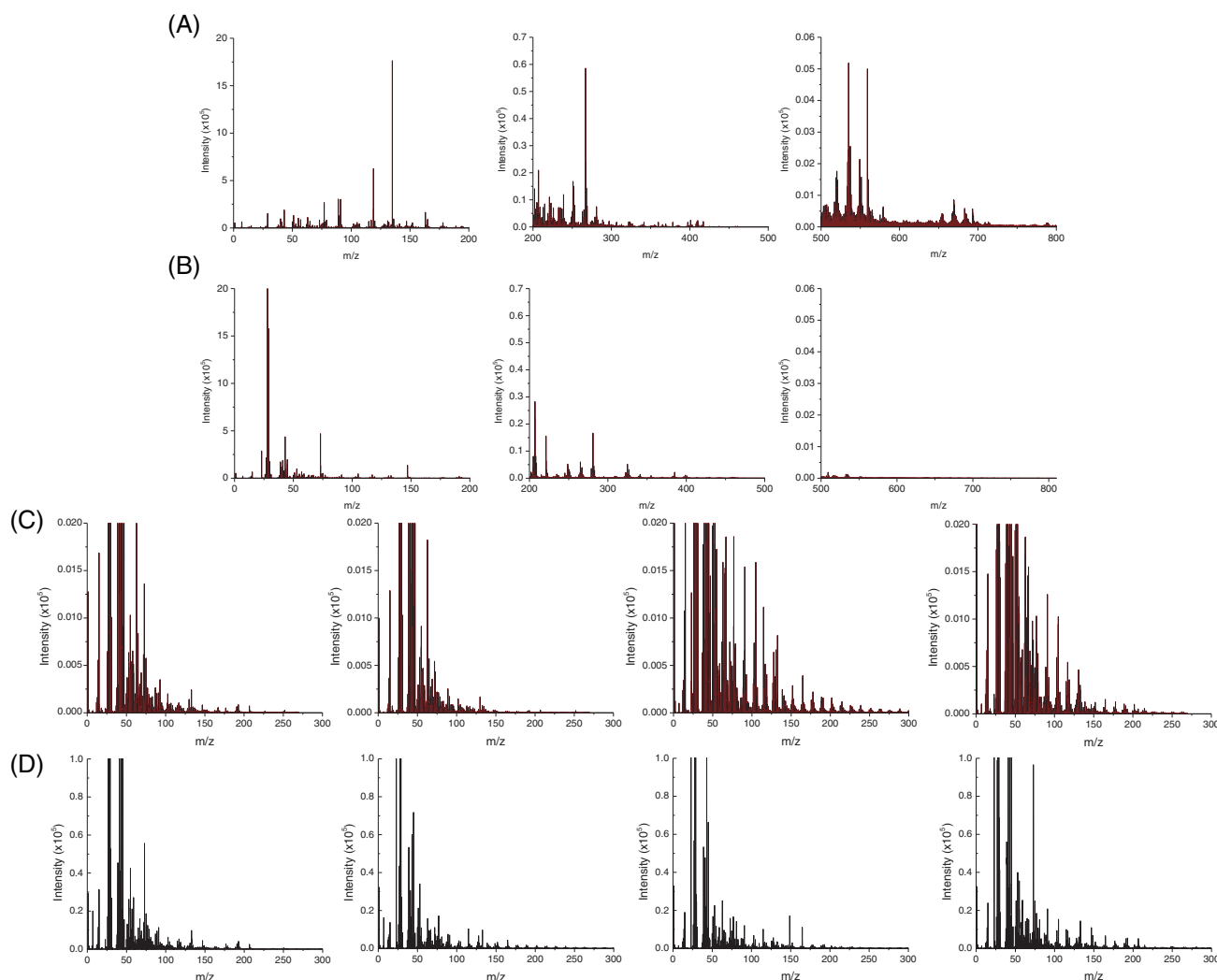


FIGURE 6 SIMS analysis of (A) pPHA thin film at varying intensities and m/z ranges; (B) residues of 100 nm pPHA film after thermolysis at 300°C for 5 min at varying intensities and m/z ranges; (C) effect of length of time at 300°C on residue formation for samples (left to right) bare Si, diglyme washed Si, 100 nm pPHA after thermolysis at 300°C for 5 min, and 60 min; (D) effect of pPHA molecular weight on residue formation of 100 nm thin films (left to right) bare Si, 78, 140, and 278 kg/mol

Data S1 for the bare Si and diglyme washed controls. The homopolymer sample showed higher intensity peaks for residue in the $m/z < 300$ range, but both samples had similar residue species forming (i.e., same m/z). The only significant, new peak from the copolymer sample was at m/z of 279 due to the (PHA + PA + PA + CHO) oligomer fragment.

4 | CONCLUSIONS

A variety of bulk and surface analysis techniques were used to characterize the residue that formed during the thermal processing of phthalaldehyde-based, polymer thin films. Thermal analysis was used to identify processing windows, namely short times at 300°C, that can vaporize nearly all the polymer residues. There was a trace of high-molecular-weight residue when the experiment was performed at

lower temperature. Thermolysis in an inert atmosphere was found to leave slightly more nonvolatile residue than thermolysis in ambient air, presumably through a pyrolysis-based mechanism that promotes char formation. XPS was used to identify the carbonaceous residue are left behind after thermolysis of thin films on silicon and SiGe substrates. Spectroscopic analysis of degraded bulk polymer powders showed that a majority of the residue is composed of aromatic and aliphatic groups. Results were confirmed through the SIMS analysis to identify some of the residue species by mass. The residue was largely oligo/monomeric in nature with some char forming during the processing.

Material parameters were modified to examine how the resist properties would change the residue profile. Higher molecular weight polymers have a slightly negative effect on the formation of high-molecular-weight residue. Copolymers that incorporate higher volatility comonomers, such as propanal, leave less high-molecular-weight residue. Overall, these results support the use of these material as a

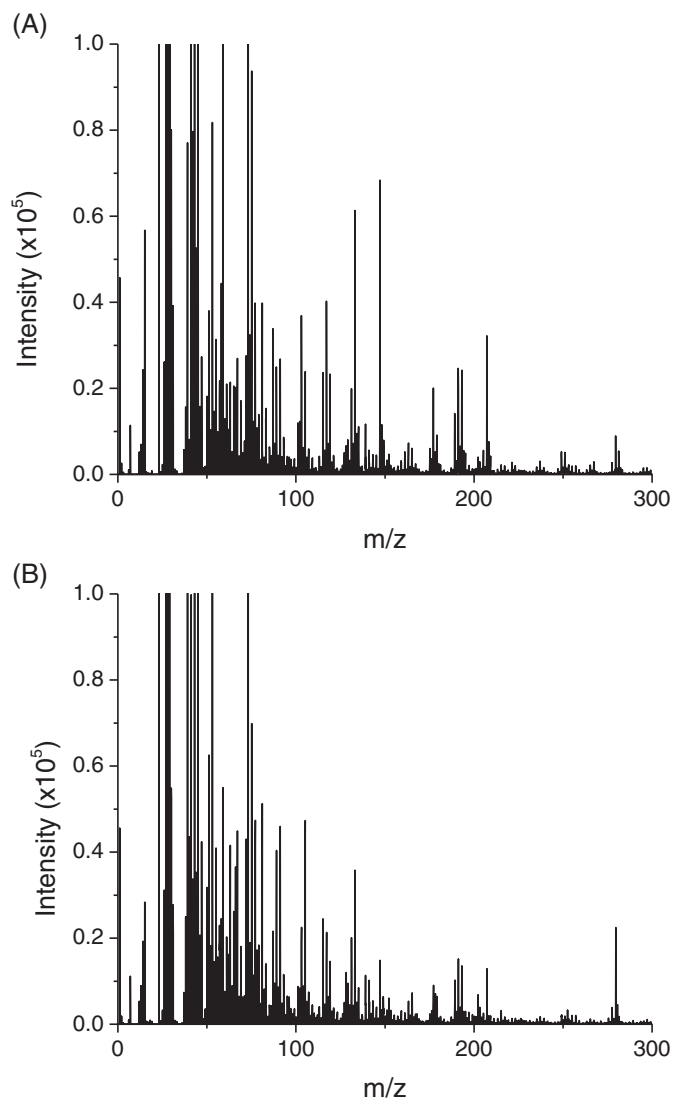


FIGURE 7 SIMS analysis after thermolysis for 5 min at 300°C for (A) 100 nm pPHA and (B) 100 nm p(PHA-PA)

thermal resist and provide insight into the residue formed during thermolysis, which is important for semiconductor processing and avoiding probe-tip contamination in thermal probe lithography. Future work will be directed toward applying these resists in thermal probe lithography tools to investigate residue characteristics under actual processing conditions and heating rates.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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