Decomposable and Template Polymers: Fundamentals and Applications

Polymers can be used as temporary place holders in the fabrication of embedded air gaps in a variety of electronic devices. Embedded air cavities can provide the lowest dielectric constant and loss for electrical insulation, mechanical compliance in devices where low-force deformations are desirable, and can temporarily protect movable parts during processing. Several families of polymers have been used as sacrificial, templating polymers including polycarbonates, polyimides, epoxy, and bis-benzocyclobutene (BCB). The methods of air-gap fabrication are discussed. Finally, the use of photoactive compounds in the patterning of the sacrificial polymers is reviewed. [DOI: 10.1115/1.4033000]

Keywords: sacrificial polymer, ceiling temperature, photoactive compound

Introduction

Polymeric materials which serve as temporary place holders can be used to fabricate a variety of electrical and mechanical devices. Polymers which decompose into small molecular weight products are especially useful if the reaction products can permeate through solid encapsulation layers because embedded gas cavities or air gaps can be fabricated. Triggering the polymer degradation mechanism by thermal, chemical, or optical means provides a pathway for fabrication of unique devices where the air cavity is created at a particular point in the fabrication sequence. Triggering also provides a way to control the polymer decomposition temperature so that a variety of structural materials can be used in the device without any harm to the other materials.

In this review, some of the air-cavity application areas will be reviewed followed by examples of fabricated structures and devices. The mechanism and processing of different kinds of decomposable or sacrificial polymers are divided into those which are thermodynamically stable at room temperature and those which have a low ceiling temperature and are not stable at room temperature. The review is concluded with comments and future considerations.

Gases, including air, have a very low relative dielectric constant at atmospheric pressure because of the presence of low density of atoms or molecules compared to solids. Thus, embedded air cavities can be a means of lowering the dielectric constant of insulators used in electronic devices including integrated circuits (ICs) and their packages. The advancement of IC performance is intimately tied to the scaling of transistor dimensions to smaller sizes. Smaller transistors consume less energy and power, per binary transition, and can change between on and off states more rapidly (i.e., operate at higher frequency). However, smaller transistor dimensions have created electrical and mechanical problems for many technology advances, including the introduction of copper (in place of aluminum) and low-k dielectric interconnects (in place of silicon dioxide), especially for long interconnects. The situation becomes more desperate as the technology advances. Table 1 shows the increasing time constant in recent technology generations and increasing wiring density with time. Lowering the dielectric constant of the insulator has been very difficult because of process integration issues. Advanced polymers have replaced epoxy in some off-chip packaging applications.

Table 1: Summary of specific performance metrics for several past and future generations of transistors for high-performance microprocessors to demonstrate some of the problems with interconnects [1]. The data was taken from early and later versions of the International Technology Roadmap for Semiconductors (ITRS). Not all values were reported in early versions of the ITRS. Shrinkage of the gate length to less than 10 nm decreases the transistor switching time. It also lowers the energy per transition because the transistor gate has a smaller area and the gate insulator is thinner. The faster switching time allows the clock speed to increase, as shown in Table 1. The clock speed will be increasing from 600 MHz to almost 7 GHz in 2019. This scaling of transistors to smaller dimensions is the basis for Moore’s law and the year-over-year improvements in electronic devices. However, only transistor performance benefits from smaller dimensions. Since the wire dimensions must also shrink with transistor scaling, the interconnect metrics become worse. If we view the wires as a simple series resistance (R) and capacitance (C), then the application of a potential step, V, to the RC circuit results in the flow of current, i, with respect to time, t, as shown in the following equation [2]:

\[ i = \frac{V}{R} e^{-t/RC} \] (1)

Although it is more accurate to also consider the inductance of the wire, this example serves to show the direction and magnitude of the changes in wire performance. The exponentially decreasing current shrinks to 1/e of its initial value (37%) in the time \( t = RC \) and to 5% of its initial value at \( t = 3RC \). Thus, \( t = RC \) is often recognized as a characteristic time constant for short wires.

The time constant for interconnect rises with each technology node, as shown in Table 1. The RC delay has become a very serious concern in recent technology generations and is the subject of many technology advances, including the introduction of copper (in place of aluminum) and low-k dielectric interconnects (in place of silicon dioxide), especially for long interconnect. The situation becomes more desperate as the technology advances.
same wiring level) and interlevel contributions (the insulator between the wires on different wiring layers). Figure 1 shows a schematic cross section of interconnects with an intralevel insulator (marked by the symbol “T”) between metal lines (shaded regions) (Fig. 1(a)), and an interlevel insulator (T) between a metal line and a ground plane (Fig. 1(b)), respectively. To illustrate the dependence of capacitance on the physical dimensions, the time constant τ for a series RC circuit can be represented by Eq. (2) for intralevel capacitance (Fig. 1(a)) and Eq. (3) for interlevel capacitance (Fig. 1(b)) (ignoring fringing fields) [2]:

\[ \tau = \frac{1}{\rho \varepsilon} \left[ \frac{1}{WTHL^2} \right] \]  
\[ \tau = \frac{1}{\rho \varepsilon} \left[ \frac{1}{HTL^2} \right] \]  

In Eqs. (2) and (3), \( \rho \) is the resistivity of the metal, \( \varepsilon \) is the dielectric constant of the insulator between the metal wires and the ground plane, \( H \) is the metal height, \( W \) is the width, and \( L \) is the length of the wire (not shown in Fig. 1). The insulator thickness, \( T \), is different in the intralevel case (Fig. 1(a)) and interlevel case (Fig. 1(b)). In both cases, one can easily see the advantages of using metals with lower resistivity (\( \rho \)) and insulators with lower dielectric constant (\( \varepsilon \)). The intralevel capacitance is the dominant contributor to the overall RC delay for on-chip applications, Fig. 1(a). One can also see the desirability of using wider metals (increase \( H \)) and thicker insulators (increase \( T \)). However, the spatial dimensions of wires must match the dimensions of the transistors (especially for the short wires directly on the transistors, i.e., local interconnects) and the processes used to fabricate wires limit the dimensional choices and shapes. It is difficult to fabricate wires substantially taller than they are wide.

The metal resistivity has already been optimized with the integration of copper, which has lowered the resistivity to essentially its lowest value. While silver has a lower resistivity, it has reliability problems due to the electrochemical formation of silver dendrites which cause electrical shorts. Thus, for any particular wire geometry, the primary materials-related advances in interconnect delay are tied to lowering the intralevel dielectric constant to its minimum possible value. The incorporation of air (or a gas) in place of an intralevel solid is the ultimate limit for low-capacitance interconnects.

The dielectric constant of on-chip insulators has been reduced by using dielectrics with less polarity, such as fluorinated materials, and by lowering their density, such as by using porous materials. However, the maximum benefit of incorporating air into the dielectric material is achieved by replacing as much of the solid dielectric with an air gap. Several methods have been developed for fabricating intralevel air gaps using temporary place holders and/or selective deposition. Sputter-deposited carbon has been used as the sacrificial place holder following by high-temperature oxidation via air permeating through an overcoat dielectric [3]. Partial intralevel air gaps have also been formed by altering the deposition condition of a gap-fill dielectric [4,5]. A 0.3 μm intralevel air gap using a single damascene process has been fabricated by utilizing a sacrificial polymer as the spatial place holder for the air cavity [6–9]. Figure 2 shows a cross section of a series of copper lines on silicon with air gaps formed between the copper lines (i.e., dark regions are air gaps) [6,7]. The width of the air cavities between the copper lines is about 0.3 μm. In this work, the sacrificial polymer was a PNB-based polymer. Silicon dioxide was used as the interlevel dielectric through which the PNB products permeated to form the intralevel air cavity. Metalization was done by electroplating copper using the superfilling process after the dielectrics were patterned. The air cavity was formed by sacrificial polymer decomposition during copper annealing at 400–450°C resulting in a fully enclosed intralevel air cavity. An additional process step allowed the air cavity to be extended into the interlevel dielectric which significantly decreased the effective intralevel dielectric constant by more than 50% with SiO2 or epoxy dielectrics because it reduced the fringing electric field in the interlevel dielectric [9]. The use of a porous interlevel dielectric with an intralevel air gap can further lower the dielectric constant as well as assist in the removal of the sacrificial material [4].

The need for low-latency connections extends to the chip substrate and printed circuit board (PCB) onto which the packaged ICs are mounted. However, the use of organic dielectrics, especially FR4 epoxy materials, limits the process temperature to
about 250 °C. Spencer et al. demonstrated a process for fabricating buried interlevel air cavities on PCBs [10]. A polycarbonate-based sacrificial polymer was patterned on top of the copper conductor lines etched on copper-clad FR4. The polycarbonate sacrificial polymer was decomposed during curing of the overcoat polymer. It was also found that the copper metallization could be used to selectively pattern the polycarbonate sacrificial polymer. Trace amounts of Cu(I) impurities were found to shift the decomposition temperature of the polycarbonate polymer to higher temperatures enabling a self-aligned patterning process for sacrificial polymer. The capacitance of the PCB signal lines was reduced by more than 40% and the loss was reduced by more than 85% with air isolation.

Fig. 3 Scanning electron microscopy (SEM) images of mechanically compliant I/O structures: (a) an array and (b) a close-up view of S-shaped compliant metal leads. (Adapted from Ref. [14].) (c) A close-up view of a compressible embedded air gap.

Fig. 4 SEM images of (a) a single fully packaged microresonator and (b) its cross section. (Reprinted with permission from Joseph et al. [18]. Copyright 2007 by IEEE.)

Packages for future, high-performance IC packages are especially challenged because of the simultaneous demand for a reduction in energy per bit and an increase in signal speed. Kumar et al. modeled the performance gains of embedded air cavities in organic IC packages [11]. They found that the optimal bandwidth density (bits per second/interconnect width) with an air-cavity interposer could be increased by as much as 70X compared to an organic PCB.

The low dielectric constant advantages of embedded air cavities are widely recognized. Several other strategic uses of air cavities have been explored. The need for interconnect with short path lengths applies to all wiring levels including chip input/output (I/O) connections and substrates. One way to shorten the chip-to-chip path length is to reduce the number of layers of packaging and place I/Os very close to each other on a substrate. Close-packed, direct solder attachment of ICs onto a high-density substrate has cost, performance, size, and weight benefits; however, it creates mechanical stresses during chip assembly and in-service thermal cycling due to the mismatch in coefficient of thermal expansion (CTE) between the silicon die (CTE = 3 ppm/°C) and FR4 or other organic substrates and PCBs (CTE about 17 ppm/°C). Bakir et al. demonstrated the fabrication of mechanically compressible air gaps which can provide strategic stress relief points [12]. Figure 3(a) shows a mechanically compliant I/O built onto a test chip with 12,000x–y–z compliant leads per cm² [12–15]. An individual connection (magnification of Fig. 3(a)) is shown in Fig. 3(b). The electrical contact goes from the chip surface to top of the compressible region. Figure 3(c) shows a cutaway of one of the compressive regions where the embedded air cavity is visible. When a force is applied to the top of the bubblelike compressive region, Fig. 3(b), the dome-shaped compressive region deforms. The addition of embedded air gaps into the I/O provides vertical compliance (z-axis) needed for wafer level testing and mating to nonplanar boards. Air gaps also serve to lower the dielectric constant of the I/O connections. The use of a low-elasticity modulus polymer encapsulating the air gap forms a structure capable of elastically deforming in all three dimensions. The mechanical compliance of the I/O can be easily adjusted by careful selection of the overcoat and design of the size and shape of the air cavity. A similar air cavity, dome-shaped structure fabricated with a sacrificial polymer was developed by Ostrowicki et al. for mechanical characterization of interfacial adhesion [16]. A permanent magnet was mounted on top of the air cavity and a controlled force was applied to the structure which could be calibrated and correlated to the adhesion strength of the metal under the magnet.

The processes and materials developed for making embedded air cavities have been used in a low-cost packaging scheme for microelectromechanical systems (MEMS) [17–19]. MEMS devices such as microresonators, gyroscopes, and accelerometers have movable parts which respond to external forces. Packaging of these MEMS devices has been problematic and expensive because traditional IC packaging methods, such as low-cost lead-frame packaging, cannot be used due to possible damage to the exposed, movable MEMS component. A process for packaging MEMS devices has been developed based on first encasing the movable MEMS component in a sacrificial polymer followed by overcoating with suitable dielectric. Decomposition of the sacrificial polymer at elevated temperature releases the movable MEMS component, and the overcoat protects the component during packaging, as shown in Fig. 4 [18]. Thus, the released device is housed in a protective overcoat. The MEMS device can then be handled and packaged like an IC using epoxy encapsulated lead-frame
packaging or epoxy overmolded chip-on-substrate packaging. This approach is applicable to both surface and bulk micromachined devices. The frequency response of silicon-on-insulator beam microresonators was found to remain unchanged by the packaging process [18]. The Q-factor of a microgyroscope was also shown to be unaffected by the packaging process [17]. Hermetic packaging of MEMS devices can be envisioned where a metal layer is deposited on the polymer overcoat while the device is under vacuum following polymer decomposition.

The embedding of air gaps and channels into ICs and packages has been used for fluid pathways for improved heat transfer. The transfer of heat from cooling high-performance ICs has reached a critical level. Air cooling is no longer adequate for densely packed, high-power ICs. Liquids are needed to increase the heat transfer coefficient between the solid (IC) and the coolant (liquid). Thus, delivery and distribution of a liquid through the package and on the IC can be facilitated by the incorporation of air channels [20]. Liquids or gases can be flowed through the channels to deliver a coolant for open- or closed-cycle cooling methods. In other areas, microchannels formed with sacrificial polymer and a silicon dioxide overcoat were used as the flow channel for a microfuel cell integrated onto a silicon substrate [21]. The fuel cell electrodes were formed by sputtering platinum and platinum/ruthenium onto the silicon dioxide overcoat.

Optical interconnects are a potential solution to some of the interconnect bottlenecks, especially clock distribution. Air-cladding can be an enabling technology for guided wave optical interconnects. A high refractive index mismatch between the core and cladding of an optical waveguide will allow high optical confinement, especially for waveguides with sharp bends. Figure 5 shows a series of waveguides with air-cladding fabricated on silicon using a sacrificial templating approach [22]. Thus, optical waveguides could be routed like wires (sharp vertical and horizontal bends).

Finally, the ability to decompose the sacrificial polymer at or near room temperature is opens up interesting new device ideas. Polymers used in packaging and encapsulation can be made to disappear when not needed. This could lower the amount of material put in the landfills and more responsibly dispose of the electronic components. In a more aggressive line of thinking, decomposition of the electronic device can be made to occur on command so as to prevent reverse engineering of materials or discovery of the device’s very existence. This can lead to devices which disappear when triggered. The trigger can be electronic, optical, or chemical.

In summary, embedded air cavities have four key features which make them useful in microelectronic systems including ultralow dielectric constant, high compressibility provided to air-gap structures, ultralow refractive index, and pathway for fluidic uses. The primary considerations for selection of materials and applications include the following. First, the sacrificial polymer needs to conform to the processing and stability temperature of the device. Epoxy-based devices like printed wiring boards (PWBs) are cured at about 180 °C and can only withstand temperature just over 200 °C. Polycarbonates fit very well within this temperature window. Ceramic and glass materials can withstand higher temperatures allowing the use of PNB.

**High Ceiling Temperature Polymers**

When the polymer is at its ceiling temperature, the rate of polymerization is equal to the rate of depolymerization. At temperatures above the ceiling temperature, the material is thermodynamically stable in the polymer state. At temperatures below the ceiling temperature, depolymerization dominates. Thermodynamically stable polymers at room temperature (i.e., those with a high ceiling temperature) have been used in the sacrificial polymer templating process. The basic function of a sacrificial polymer is to provide a temporary space holder for microcavity creation. Thermally decomposable sacrificial polymers decompose into small and volatile molecules upon heating to higher temperature. The decomposition temperature is an important parameter for the polymer because it must be matched to the deposition and processing of the overcoat material and must be compatible with the other materials present.

**Types of Polymers.** A number of polymer families have been found to be useful in the templating process. PNBs and polycarbonates are the two main families of sacrificial polymers with thermal decomposition temperatures around 350–400 °C and 100–300 °C, respectively. The general chemical structures of PNBs and polycarbonates are shown in Fig. 6.

PNB can be functionalized with a variety of substituents to enhance its usefulness as a sacrificial polymer. Wedlake et al. investigated the decomposition mechanism of four different PNB-functionalized polymers: methyl, butyl, hexyl, and triethoxysilyl-butyl copolymer [23]. Dynamic and isothermal thermogravimetric analyses were used to show that PNB was decomposed by a first-order degradation reaction mechanism with an activation energy of 229.6 ± 12.5 kJ/mol. The decomposition mechanism occurred through a backbone, free-radical scission mechanism. Cleavage of the polymer at the linkages between the PNB bicyclic rings produced volatile monomer and oligomer fragments. The degradation of PNB took place via a depopagation and transfer reaction process. Initially, the depopagation pathway is dominant, but with increasing conversion, intra- and intermolecular hydrogen transfer reactions become more important.

A photosensitive version of PNB was developed for sacrificial polymer templating applications [24–26]. Copolymers of butyl norbornene and pendant alkyl-substituted norbornene were made photosensitive by the use of a free-radical generator, benzoin ethyl ether. Exposure of the free radical generator catalyzed cross-linking of the unsaturated side-groups on the PNB backbone. The resulting negative-tone, sacrificial polymers had...
and surface energy is 42.9 mJ/cm². Recently, the dielectric (30/C14 BCB, SU-8, metals, SiO₂, spin-on glass, and SiNx [27,28].

The rate of PNB degradation was characterized and fitted to an Arrhenius kinetic model [26]. The kinetic model was used to design heating profiles for the decomposition of PNB to maintain a constant rate of decomposition, such as 1% per minute. It was found that the pressure buildup due to polymer decomposition could result in overcoat failure when the decomposition rate was too rapid. By maintaining a constant polymer decomposition rate (e.g., 1–2% per minute), gas permeation through the overcoat was fast enough to mitigate overcoat fracture caused by internal pressure buildup.

The high-temperature decomposition requirement for PNB-based polymers limits the overcoat material selection and narrows the subsequent processing step conditions. Polycarbonate-type low-temperature decomposable polymers offer lower temperature process conditions, which translate into process compatibility with a wider range of substrates and overcoat materials. Low-temperature decomposable polymers are well suited for applications ranging from PWB and boardlike applications, to IC, MEMS and on-chip applications. Sacrificial polymer can be used on both hybrid substrates (e.g., FR-4, BT, Duroid) and inorganic substrates (Si, SiO₂, SiNₓ, and GaAs). They can be encapsulated with a wide variety of overcoat materials such as Avatrel, polycarbonates, BCB, SU-8, metals, SiO₂, spin-on glass, and SiNₓ [27,28].

Polycarbonates are ideal thermally decomposable sacrificial polymers mainly owing to their favorable decomposition range (200–300°C) and nearly residue-free decomposition in both inert (N₂ or Ar) and oxygen-rich environments [27,29]. Various types of polycarbonates have been studied including poly(ethylene carbonate), poly(propylene carbonate) (PPC), poly(butylene carbonate) (PBC), poly(cyclohexene carbonate) (PCHC), poly(norbornene carbonate) (PNC), and poly(cyclohexyl propylene carbonate) (PCPC) [20,27,30]. PCPC is a random copolymer of PPC and PCHC [31]. The chemical structures of the polycarbonates are shown in Fig. 7.

PPC is the most widely used and commercially available aliphatic polycarbonate. PPC is an alternating copolymer of propylene oxide and CO₂ usually synthesized in the presence of heterogeneous or homogeneous catalysts, such as diethyl zinc, zinc glutarate (commonly used), aluminum tetraphenylporphyrin complexes, Cr(III) salen complexes, and Co(III) salen complexes [30,32–34]. PPC is a thermoplastic with a glass transition temperature (Tg) between 25°C and 46°C [32] and a decomposition temperature between 200°C and 300°C [30,32–34]. The properties of PPC include density of 1.26 g/cm³, refractive index of 1.463, and tensile strength of 7–30 MPa. The tensile modulus of PPC with Tg of 40°C is 700–1400 MPa whereas the modulus of lower Tg PPC (30°C) is 200–1000 MPa. The elongation at break is 600–1200%, and surface energy is 42.9 mJ/cm². Recently, the dielectric constant and loss tangent of PPC were measured in our group as 3.253 ± 0.040 and 0.0237 ± 0.0002, respectively, based on ASTM standard D150-11 d where ± terms represent one standard deviation in measurements done on 22 different test structures on the same substrate. PPC is soluble in acetone, N-methyl-2-pyrrolidone (NMP), anisole, propylene glycol methyl ether acetate, gamma-butyrolactone (GBL), propylene carbonate, and methyl-ene chloride. PPC swells in cyclohexane and ethyl acetate. It is insoluble in mesitylene, isopropanol, toluene, and xylenes [31].

**Decomposition Mechanism.** The key enabling property behind PPC’s utilization as sacrificial polymer in air-gap applications in microelectronics is its thermal decomposition. Thermal decomposition of PPC takes place in two mechanisms, i.e., chain unzipping and chain scission. Chain scission occurs through a decarboxylation reaction in the PPC backbone and leads to formation of CO₂ and alkene moieties [32]. Chain scission has a higher activation energy than chain unzipping and, therefore, takes place at a higher temperature. On the other hand, chain unzipping occurs at a lower temperature since the activation energy is less due to a more thermodynamically stable cyclic propylene carbonate product. Owing to reactive terminal hydroxyl groups, chain unzipping can take place in two intramolecular backbiting reactions, namely, alkoxide backbiting and carbonate backbiting. In alkoxide backbiting, highly nucleophilic terminal alkoxide or alcohol groups can attack a relatively nonpolar carbonyl carbon atom in the polymer chain. In carbonate backbiting, a relatively less nucleophilic carbonate group at the chain end attacks the electrophilic carbon in the polymer chain. According to density functional theory calculations, it was found that the carbonate backbiting has a lower activation energy [35]. However, others found (through computational chemistry) that the free energy barrier in carbonate backbiting is higher than that of alkoxide backbiting [36].

The kinetics of PPC decomposition has been assessed using thermogravimetric analysis (TGA). It is advantageous to capture the temperature–time decomposition profile of the polymer decomposition so that the rate of decomposition can be estimated at any temperature. Also, mathematically capturing the decomposition profile allows the user to design heating profiles for polymer decomposition where a set decomposition rate (e.g., 2% per minute) is desired to prevent a rapid pressure buildup.

In thermogravimetry, the change in sample mass due to degradation is measured either against temperature with a specified heating rate (non-isothermal mode) or against time at a specified temperature (isothermal mode) in a specific gaseous environment using a sensitive balance. The TGA data can be analyzed using various methods. As a common feature, all of these methods are based on the disappearance rate expressed in the following equation [37]:

$$\frac{dz}{dt} = k_f(z)$$

(4)

In Eq. (4), z is the fractional decomposition (i.e., the ratio of weight of the polymer decomposed to the initial weight of the polymer), f(z) is a temperature-independent function of z, and k is the Arrhenius-type reaction rate constant given by [37]

$$k(T) = A \cdot \exp\left(\frac{-E_a}{RT}\right)$$

(5)

In Eq. (5), A is the frequency factor, Eₓ is the activation energy for decomposition, R is the universal gas constant, and T is the absolute temperature. If we substitute Eq. (5) in Eq. (4), the resulting equation becomes

$$\frac{dz}{dt} = A \cdot \exp\left(\frac{-E_a}{RT}\right) f(z)$$

(6)
The TGA data analysis methods differ in the handling of Eq. (6), which can be analyzed either in its current differential form or in its integrated form. For most solid-state degradation reactions (solid → solid + gas), the f(x) term is assumed to be
\[ f(x) = (1 - x)^n \]
where \( n \) is the reaction order [38]. Among the many methods available in the literature [37,39,40], the most common ones are as Kissinger method [38], Ozawa–Flynn–Wall method [41], Coats–Redfern method [42], Phadnis–Desphande method [43], and Chang’s method [44]. The current ASTM standard for determining decomposition kinetics using thermogravimetry (ASTM E1641-15) utilizes the Ozawa–Flynn–Wall method [45]. The advantage of Ozawa–Flynn–Wall method is that it requires no prior knowledge of reaction order.

The Ozawa–Flynn–Wall method can be explained as follows. If a constant heating rate \( \beta = dT/dt \) is accepted in a dynamic TGA, Eq. (6) can be rewritten as [37]
\[
\frac{dx}{dt} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right)f(x)
\]  
(7)

After separation of variables, rearranging and integrating Eq. (7) can be rewritten as
\[
g(x) = \int_{x_i}^{x_f} \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_i}^{T_f} \exp\left(-\frac{E_a}{RT}\right)dT
\]  
(8)

In Eq. (8), the subscripts \( i \) and \( f \) stand for initial and final conditions, respectively, and \( g(x) \) is an integral function of fractional decomposition, \( x \). Varying \( x \), the \( g(x) \) function can follow either a sigmoidal or deceleration curve, for which various expressions are available in the literature [39]. The \( g(x) \) term is constant for a particular fractional decomposition. Previously, Liu et al. found that the PP pyrolysis follows a sigmoidal behavior, based on a single-stage, random nucleation and growth process (where \( g(x) \) equals to \( -\ln(1 - x)^n \) and \( x \) can be 1/2, 1/3, or 1/4) [39]. The \( T_f \) term can be approximated as 0 K since the rate of decomposition is very low at that temperature and \( x_i = 0 \) [41].

If we define \( x = E_a/RT \), and the right-hand side of Eq. (8) can be written as [37]
\[
g(x) = \frac{A}{\beta} \int_{T_i}^{T_f} \exp\left(-\frac{E_a}{RT}\right)dT = \frac{AE_a}{\beta R} p(x)
\]  
(9)

Taking the logarithm of both sides in Eq. (9) results in the following equation:
\[
\log \beta = \log \frac{AE_a}{g(x)R} + \log p(x)
\]  
(10)

In Eq. (10), the \( p(x) \) function can be estimated by using Doyle’s approximation [39,46] provided \( 20 \leq x \leq 60 \), as shown in the following equation:
\[
\log p(x) = -2.315 - 0.4567x
\]  
(11)

Substitution of Eq. (11) into Eq. (10) results in the following equation:
\[
\log \beta = \log \frac{AE_a}{g(x)R} - 2.315 - \frac{0.4567E_a}{RT}
\]  
(12)

In order to calculate the kinetic parameters using the Ozawa–Flynn–Wall method, dynamic TGA data at different fractional decomposition levels (e.g., 5%, 10%, 15%, and 20%) are obtained using four or more different heating rates ranging between 1 K/min and 10 K/min [45]. According to Eq. (12), \( \log \beta \) should change linearly with respect to \( 1/T \). Hence, an estimate of the activation energy of decomposition, \( E_a \), can be obtained by linear fit to the set of \( \log \beta \) versus \( 1/T \) plots generated at different fractional decomposition levels. After \( E_a \) is obtained, the preexponential factor, \( A \), can be evaluated from Eq. (9) with a proper choice of \( g(x) \). Using the Ozawa–Flynn–Wall method, Liu et al. calculated the activation energy for PPC decomposition in inert \( N_2 \) atmosphere as 94.42 kJ/mol [39]. The reaction order can be calculated using Eq. (6) with use of \( f(x) = (1 - x)^n \) previously. Kohl et al. used the Ozawa–Flynn–Wall to calculate the activation energy and utilized Eq. (6) to estimate the reaction order for PPC decomposition from the dynamic thermogravimetric data obtained in oxidative (ambient) and inert atmospheres. Activation energy and reaction order were found to be 92.7 ± 3.4 kJ/mol and 2.28 ± 0.37, respectively, in inert atmosphere, and 152.7 ± 18.4 kJ/mol and 1.71 ± 0.37, respectively, in ambient atmosphere (where ± values represent a 95% confidence interval) [47].

The decomposition kinetics of PPC is partly determined by its structural purity. Alternating copolymerization should ideally insert propylene oxide and \( CO_2 \) moieties into the PPC backbone in a tandem fashion; however, the alternation is not always perfect. Nonideal consecutive insertion of propylene oxide moieties (i.e., epoxide homopolymerization) results in ether linkages in the PPC backbone [33,34]. Thus, the resulting polymerization product can include polyether content, which is undesirable. Polyether acts as a plasticizer, decreasing PPC’s glass transition temperature, similar to the effect of cyclic propylene carbonate by-product in PPC synthesis [32,33]. It also hinders acid-catalyzed PPC decomposition by forming alcohols after reacting with acid, thus preventing acid regeneration. The polyether content in PPC backbone can be analyzed by 1H-NMR. The molar concentration of polyether linkages in commercially available PPC is generally less than 10% and can be as low as 1% [29]. High-purity PPC leads to residues of less than 1% of the original film thickness. Another factor influencing PPC decomposition kinetics is the regioregularity of PPC. The methyl groups of propylene can be in the up or down position with respect to the central axis of PPC backbone, creating head or tail forms, respectively. The head-to-head (HH), tail-to-tail (TT), and head-to-tail (HT) forms of PPC are shown in Fig. 8. Unlike the HH and TT forms, the regioregular HT form can be exclusively present. Increasing the fraction of HT units corresponds to higher glass transition temperature, higher

\[ \text{Fig. 8 Regiochemistry of PPC: (a) head-to-head (HH), (b) tail-to-tail (TT), and (c) head-to-tail (HT) forms} \]
mechanical strength, and higher decomposition temperatures, whereas HH and TT forms slow down the decomposition process. The relative molar concentrations of HT, HH, and TT forms can be quantified by $^{13}$C NMR measurements. A thorough NMR analysis of PPC can be found in Refs. [29,48–50].

The residual solvent content can also affect the thermal degradation kinetics of solvent-cast PPC films. Previously, Spencer et al. showed that PPC films cast from methyl chloride, anisole, and acetone have lower decomposition temperatures, whereas PPC films cast from GBL, trichloromethane, and cyclohexanone have higher decomposition temperatures, compared to neat, as-received PPC. Although no obvious trend for change in decomposition temperature was observed as a function of dipole moments, heats of vaporization, and boiling points of probed solvents, end-capping was speculated as a potential reason for the obtained results [37].

In a recent study, Phillips et al. investigated the thermal stability of PPC to widen the process window for various applications [51]. It was shown that each of the two decomposition mechanisms, chain unzipping and random chain scission, can be either catalyzed to occur at a lower temperature (e.g., 5 wt. % loss at 70°C) or stabilized so that the onset decomposition temperature rises (e.g., 260°C). Chain scission can be catalyzed by the addition of photoacid generators (PAGs) that release a strong protonic acid that will attack the backbone of PPC. It is noted that the presence of PAGs can increase the amount of residue after decomposition because of the nonvolatile salt they produce. Unzipping can be catalyzed by the addition of photobase generators (PBGs) that release an amine to facilitate backbiting decomposition pathways of PPC. PPC can also be thermally-stabilized by inhibiting both degradation mechanisms. Chain unzipping occurs through reactive free hydroxyl groups at the end of polymer chains. Reacting electrophilic organic compounds with the free hydroxyl end groups can kinetically stabilize the polymer referred to as end-capping. Many reports have shown this thermal stability shift with PPC with a variety of compounds [52–54]. It was found in Ref. [51] that the structure of the endcap can affect the degree of stabilization. An organic additive such as citric acid was suggested to stabilize PPC from chain scission through complex interactions with the carbonyl groups that form the backbone of the polymer. Small amounts of citric acid (less than 1 pphr) were used to stabilize solvent-cast PPC films that left minimal to no residue after full decomposition of polymer. Inhibiting both unzipping through endcapping and chain scission from addition of citric acid showed the highest thermal stability for PPC.

**Patterning Methods.** The PPC decomposition can be acid catalyzed where the acid can be mixed into the PPC formulation or the acid can be generated in situ, as with a PAG. The two most common PAGs reported in the literature for use in combination with polycarbonates are diaryliodonium or triarylsulphonium salts [20]. Upon ultraviolet (UV) irradiation, the salt undergoes a photocatalysis reaction and generates an in situ Brønsted acid. 4-Methylphenyl[4-(1-methylpropyl)phenyl]iodonium tetrakis(pentafluorophenyl)borate (commercial name Rhodorsil-FABA) is one of a widely used PAGs for PPC decomposition, Fig. 9. The general acid generation mechanism of PAGs with cations similar to that of Rhodorsil-FABA is demonstrated in Fig. 10. The proton from the generated acid protonates the polymer and forms an active site to initiate chain scission. Upon activation, the organic cation part dissociates into two radicals, namely, an aryl radical and an aryliodonium radical. The aryliodonium radical then reacts with a proton donor (residual solvent or PAG itself). This creates a proton that pairs with the complex anion of the PAG to form a strong monoprotic acid. Since the PAG activation can be induced photolytically or thermally, the PAG can act as a PAG as well as a latent thermal-acid generator. The organic cation of PAG is responsible for UV absorption, solubility in solution, and thermal stability. The bulky complex anion determines the vapor pressure of PAG and serves as a conjugate base of a strong acid [27,55].

The protonic acid produced upon PAG activation catalyzes the PPC decomposition, lowering PPC’s decomposition temperature compared to that of acid-free (neat) PPC (100–180°C versus 200–300°C), as shown in Fig. 11. The thermal degradation temperature of neat PPC (i.e., no PAG added, as received) occurs around 200°C, whereas the photo-induced and thermally induced acid-catalyzed decomposition temperatures are about 100°C and 180°C, respectively (50 wt. % loss temperature is often reported) [19,31]. The catalytic activity is due to acid regeneration after each subsequent PPC decomposition cycle [31,37,56]. Jayachandran et al. used mass spectrometry with electron impact ionization to detect the evolved species during PPC depolymerization and product evolution at 110°C and 300°C and constructed a mechanism scheme for acid-catalyzed PPC decomposition in the presence of a diphenyliodonium-type PAG, 4-methylphenyl[4-(1-methylpropyl)phenyl]iodonium tetrakis(pentafluorophenyl) borate. According to the reaction scheme shown in Fig. 12, the proton from the generated acid protonates the carbonyl oxygen in the PPC backbone and creates polar transition states which lead to formation of unstable intermediates that degrade into acetone, propylene carbonate, CO$_2$, ethylene oxide, propylene oxide, and ethylene carbonate [20]. The lowering of the PPC decomposition temperature by photo-induced acid catalysis can be used for photopatterning PPC films. The exposed PPC can be selectively removed by a low-temperature thermal treatment, i.e., dry-developing.

**Fig. 9 Chemical structure of PAG Rhodorsil-FABA**

**Fig. 10 Photolytic/thermolytic decomposition mechanism of diphenyliodonium-type PAGs. (Adapted from Ref. [56].)**
Similar to PAGs, PBGs can also be used to photopattern polycarbonate, although the subject is not as well studied and PBGs are not as common as PAGs. PBGs can also be photolytically or thermally induced to degrade PPC films. In the base-catalyzed PPC degradation process, a nucleophilic attack by a strong base of the electrophilic carbonyl carbon of PPC can generate alkoxides, which can lead to formation of propylene carbonate product [57,58]. A new class of tetraphenylborate-based PBGs has been shown to be very effective. One such PBG is a bicyclic guanidine base, 1,5,7-triazabicyclo[4.4.0]dec-5-ene tetraphenylborate (referred to as TBD•HBPh4) [59]. Upon exposure to UV light, the tetraphenylborate ion rearranges and abstracts a proton from the protonated TBD to release TBD as a strong base. These PBGs have been reported to have a 1% weight loss above 240°C as opposed to most PAGs showing substantial weight loss around 150–180°C [20,58]. The thermal stability of the PBG may widen the process window for photosensitive PPC films in air-gap creation applications.

The patterning of sacrificial polymers can be achieved mainly by two methods depending on the photosensitivity of sacrificial polymer, i.e., direct photopatterning if PPC is photosensitive (i.e., PAG is mixed into PPC solution) or patterning by reactive-ion etching (RIE) if the sacrificial polymer is not photosensitive (i.e., no PAG is mixed into PPC solution). The two processes are shown in Fig. 13. The process flow can be explained on silicon substrates (step i in Fig. 13) using Cyclotene 4026-46 (BCB) as the overcoat and pattern-transfer material. The RIE process starts with coating the substrate with a nonphotosensitive PPC solution by spin-coating (<35–40 wt. % PPC in GBL). The PPC film is usually soft-baked at 100°C for 5–10 mins on a hotplate (step ii in Fig. 13(a)). A thin layer of photosensitive dielectric, such as BCB, can be spin-cast and photopatterned on the sacrificial polymer layer (step iii in Fig. 13(a)). The thin layer of BCB can be cast from a solution prepared by diluting the BCB solution with an appropriate solvent (e.g., mesitylene for Cyclotene 4026-46). Photopatterning BCB is performed by exposure to 365 nm radiation to the desired dose, postexposure baked on a hotplate at 60–75°C, depending on the thickness, and solvent developing in 1,3,5-triisopropylbenzene [60]. This BCB film is used as a pattern-transfer layer in subsequent RIE step (step iv in Fig. 13(a)) for patterning the PPC layer. The etch rate of BCB is significantly less than the etch rate of PPC in an O2 plasma. The etch selectivity is about 1:36 (BCB:PPC) in an O2 plasma (100 sccm O2 flow rate at 300 mTorr and 25°C with 250 W alternating current power) [29]. The patterned PPC was encased by a thick, spin-coated layer of BCB. The BCB overcoat layer can be photopatterned, if needed. A blanket exposure using 365 nm UV radiation and postexposure bake was used to initiate the BCB cross-linking (step v in Fig. 13(a)). A final thermal treatment in a N2-purged convection oven simultaneously cured the BCB and decomposed the PPC creating an internal air-gap structure (step vi in Fig. 13(a)).

The direct photopatterning process uses a photosensitive PPC solution with
process [29]. The first step was at a lower temperature to achieve coat layers can be achieved using a two-step thermal treatment previously, Uzunlar et al. found that air gaps with intact BCB over-superstructure without significant PPC decomposition (at about sufficient BCB curing to provide mechanical strength to air-gap... (steps i and ii in Fig. 13(b)), photonsensitive PPC was directly photopatterned with 248 nm UV radiation to activate the Rhodorsil-FABA PAG, followed by dry-developing (step iii in Fig. 13(b)). The sample was then overcoated with a thick BCB layer, exposed to UV radiation and postexposure baked to initiate cross-linking in BCB (step iv in Fig. 13(b)). A final thermal treatment was used to create air gaps (step v in Fig. 13(b)), as in the RIE process. Previously, Uzunlar et al. found that air gaps with intact BCB overcoat layers can be achieved using a two-step thermal treatment process [29]. The first step was at a lower temperature to achieve sufficient BCB curing to provide mechanical strength to air-gap superstructure without significant PPC decomposition (at about 180°C). The second thermal step was at a higher temperature where PPC decomposes at a more substantial rate (at about 240°C), and the air-gap forming process is complete. Comparing the two process flows shown in Fig. 13, the direct photopatterning is simpler due to a smaller number of processing steps. However, the photopatterning has an intrinsic disadvantage because of the presence of the PAG which can leave a salt residue after air-gap formation. Also, the lateral diffusion of the acid may distort the desired pattern. The lateral acid diffusion can be accounted for by resizing the exposure pattern [61].

An additional patterning method for PPC was found through the thermal stabilization of photosensitive PPC films on copper surfaces. Spencer et al. previously showed that photosensitive PPC films with Rhodorsil-FABA PAG cast on fresh Cu surfaces had a higher thermal decomposition temperatures by about 50°C compared to the same PPC film on a non-Cu surface. The copper surface effect was found with both UV-exposed and non-UV-exposed films, as shown in Fig. 14 [28]. Energy-dispersive X-ray spectroscopy measurements showed that the Cu was oxidized, dissolved, and diffused throughout the PPC film during soft-baking and postexposure baking steps. Oxygen from the air was the oxidizing agent for copper oxidation [62]. The experimentally measured amount of Cu ions in the PPC film was about 21 ions per polymer chain, each of which contained about 2100 monomers [28]. Uzunlar et al. showed that the improved thermal stability on copper surfaces is unique to PPC films with PAGs containing iodonium-based cations, rather than PAGs with noniodonium-based cations (i.e., sulfonium-based cations) [63]. It was also shown that the thermal stability effect involved the iodonium cation. When the copper oxidized, it was complexed by the iodide from the PAG is in the Cu(I) oxidation state, thus destroying the PAG [64]. The PAG-loaded PPC not in contact with the copper surface decomposed at a lower temperature than the copper-exposed PPC. It is because the PAG can thermally generate an acid which catalyzes the PPC decomposition in the former case. The use of PPC’s improved thermal stability on Cu surfaces is demonstrated in Fig. 15. In step (a), a copper line on a silicon substrate is first treated with a mild acidic solution to remove native oxide on copper. In step (b), a PPC/Rhodorsil-FABA PAG film is spin-cast and soft-baked at ca. 100°C for 5 mins. The copper oxidation, dissolution, and diffusion creates a Cu-rich PPC layer inside the PPC film, as depicted in step (c). In step (d), the PPC film is UV exposed to activate PAG for acid creation. The copper-rich PPC remains undecomposed due to destruction of the PAG from the Cu(1)—I interaction. The Cu-rich PPC layer stays undecomposed after postexposure baking at 100°C for 3 mins, as shown in step (e). Previously, Rajarathinam et al. used the Cu interaction to fabricate half-coaxial transmission lines on silicon [65]. Patterning through the Cu interaction was used to self-planarize PPC inside dielectric trenches on copper-sputtered silicon substrates and for creating self-centered polymeric structures on Cu-clad through-silicon vias [61,66].

An alternative method to pattern sacrificial polymers is imprint lithography. In imprint lithography, a mold or stamp with protrusion-like features is pressed onto an imprint resist (preferably a thermoplastic polymer) at a temperature above the resist’s glass transition temperature to create contrast patterns. As the imprint resist cools, the mold can be removed from the sample. The relief pattern generated in the imprint resist can be transferred to the entire resist layer in the compressed area and/or to underlying...
layers using anisotropic etching methods, such as RIE or wet etching. Another option is metallization of patterned regions followed by removal of resist (lift-off process) [67]. Previously, Rajarathinam et al. used a semicircular mold made out of reflowed solder and Avatrel 2000P imprint resist to create half-coaxial and coaxial air-clad transmission lines by using photosensitive PPC as a temporary etch mask [65]. The patterned PNB layer was electroplated with copper and filled with photosensitive PPC. The self-patterning interaction between the Cu layer on the walls of the semicircular trench and the photosensitive PPC inside the trench was used to achieve a planar PPC surface along the horizontal Avatrel 2000P layer. A thin layer of epoxy-functionalized cross-linkable hybrid dielectric material polyhedral oligomeric silsesquioxane (POSS) was used to suspend a Cu signal line on top of the semicircular trench after thermal decomposition of the photosensitive PPC. Finally, a sample with semicircular patterns was bonded to the sample holding the signal line, and a copper-shielded coaxial transmission line with encapsulated air-dielectric was obtained. Li et al. created 100 nm wide fluidic channels by patterning the PNB sacrificial polymer using imprint lithography [68]. First, an imprint resist was spin-coated onto PNB layer. A lift-off process was used to deposit Cr metal on the imprint resist, and the resulting metal pattern was utilized as an etch mask during RIE to pattern the PNB. The patterned PNB was encapsulated by plasma-enhanced chemical vapor deposition of SiO₂. Imprint lithography is a low-cost, high-throughput, and simple patterning method that is applicable to sacrificial polymer patterning [67].

**Issue of Residue Formation.** A potentially important issue with PPC is the residue remaining after thermal decomposition. The polyether content can lead to residue as well as impurities such as from the PAG. As previously mentioned, polyether can block the decomposition mechanism by reacting with the acid and producing alcohols, thus hindering acid regeneration needed for a catalytic PPC decomposition. Catalyst residues coming from PPC synthesis can be left as solid residues on surfaces after PPC decomposition. The residual catalyst can also alter the thermal stability of PPC. Thermal stability is improved if metal ion coordination occurs between the metal and carbonyl groups on PPC backbone [69,70], or the thermal stability can be diminished during synthesis since a Lewis acid and water can generate carbon dioxide or hydroxyl chain ends which promote the unzipping reaction [33,71]. The residual salt from the use of PAGs can also contribute to the residue because the vapor pressure of the salt is negligible. Uzunlar et al. characterized the chemical composition of the residue from both nonphotosensitive PPC films and photosensitive PPC films using X-ray photoelectron spectroscopy [29]. The nonphotosensitive PPC residue was found to have a large concentration of oxygen-containing carbon functionalities, indicating that the residue is mainly undecomposed PPC. On the other hand, the photosensitive PPC residue was shown to have a large amount of C-C functionalities along with C-F functionalities. Additionally, two shake-up peaks were observed in the photosensitive PPC residue due to \( \pi - \pi^* \) transition in the aromatic rings from the anion part of the PAG. These findings show that the residue from photosensitive PPC mainly originated from the PAG.

The residue is potentially harmful to the surfaces in transmission line and MEMS packaging applications, thus the residue should be minimized. In transmission line applications, the residue can contribute to parasitic capacitance and loss. In MEMS packaging applications, the residue can create unintended damping which can shift the resonant spectra (resonant frequency and quality factor) to lower values. For minimum residue, the PPC should have low contents of polyether and residual catalyst. The polyether content cannot be removed post-synthesis because it is part of the PPC backbone [29]. However, the residual catalyst can be removed by purification [34,69,72–75]. The most common PPC purification method involves dissolution of PPC in an organic solvent such as acetone or GBL, filtering through a fine filter paper, and precipitation using a nonsolvent such as methanol or isopropanol followed by vacuum drying [34,69,76].

The residue created by PAG-loaded PPC can be minimized by using a two-layer photosensitive/nonphotosensitive PPC film instead of a single-layer photosensitive film. Previously, the PAG residue was lowered by implementing a two-layer PPC film that includes a thin layer of PAG-loaded PPC layer on top of a non-PAG-loaded PPC layer [77]. Uzunlar et al. compared combinations of two-layer PPC films and found that the reliable air gaps with less PAG residue can be obtained if a photosensitive PPC layer is the bottom layer of the two-layer PPC structure [29].

**Overcoat Materials.** The overcoat material is an important part of the process in the air-gap structures created by polymeric materials. The requirements for overcoat materials can be summarized as follows. The overcoat material should provide adequate mechanical stability to the air-gap structure; otherwise, the air gap can collapse or expand due to the pressure of the gas created from the decomposing PPC. To provide mechanical stability to the overcoat, thermostet polymers which can cross-link upon curing are generally used, such as polyimides, Avatrel, BCB, and POSS. Ideally, a sufficient degree of cross-linking should be achieved before the sacrificial polymer decomposes. The glass transition temperature of the overcoat material should be higher than the decomposition temperature of the sacrificial polymer to prevent reflow of the overcoat. The overcoat material should be permeable to the decomposition products of the sacrificial polymer; otherwise, the decomposition products stay trapped inside the air gap. The overcoat polymer should be chemically compatible with the sacrificial polymer. The casting solvent of the overcoat polymer should not dissolve the sacrificial polymer because it could distort the air-cavity shape. In cases where the sacrificial polymer is soluble in the overcoat solvent, a barrier layer (e.g., SiO₂) can be added to prevent mixing [78]. Table 2 shows a list of overcoat materials, the overcoat solvent, and solvent interference.

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**Fig. 15 Process summary of maskless patterning of PPC on copper lines.** The cross section build up process shows (a) a copper line on a substrate which is coated with PPC dissolved in solvent which is heated on a hotplate to ca. 100 °C, (b) evaporating solvent and dissolving copper from the line surface and edges into PPC, where (c) copper diffuses into PPC to form a copper-rich layer, which (d) continues to take up copper and does not decompose when the film is UV exposed, (e) leaving a copper-rich PPC layer encapsulating the line. (Reprinted with permission from Spencer et al. [28]. Copyright 2011 by Springer International Publishing AG.)
with various sacrificial polymers [78]. It also shows when silicon dioxide glass is needed to separate incompatible overcoats from the sacrificial polymer.

The reliability of polymer-based air-gap structures can be ensured by structural design considerations, such as the geometry and the mechanical properties of the overcoat material. The mechanical stability of a circular or square overcoat membrane can be analyzed using an analytical bulge equation given in the following equation [79]:

$$P = \frac{Ch\sigma_0}{a^2} + \frac{4h^3Et}{3a^4(1-\nu^2)}$$  \hspace{0.5cm} (13)

In Eq. (13), $P$ is the applied pressure on the overcoat membrane, $h$ is the vertical deflection of the membrane, $t$ is the membrane thickness, $\sigma_0$ is the residual stress in the membrane, $a$ is the radius or half of the side length of the membrane, $E$ is the elasticity modulus of the membrane material, and $\nu$ is the Poisson’s ratio of the membrane material. $C$ is a geometry-dependent term which equals to 3.393 for circular membranes and 2 for square membranes [79]. In the bulge equation, the first term represents the pressure balanced by the stress in the overcoat, and the second term represents the pressure balanced by deflection of the overcoat. Previously, Saha et al. showed that the mechanical stability of air gap produced by POSS overcoats with a metal coating on top comes from the deflection term [19]. Uzunlar et al. showed that a BCB-encased air gap has mechanical stability due to the tensile stress in the BCB film [29].

The air-gap structures encapsulated by the overcoat polymers are not hermetic due to the permeability of the overcoat. In applications where hermetic packages are required, the internal cavity can be sealed (inert gas or vacuum) by performing the thermal decomposition of sacrificial polymer inside a heated vacuum chamber, followed by metal deposition on the overcoat while the sample is still inside the gas-filled or vacuum chamber. Previously, Saha et al. showed hermetic packaging using air gaps for MEMS packaging applications [19].

### Low Ceiling Temperature Polymers

High-temperature decompositions can limit the materials that can be used during processing, restricting the use to highly thermally stable structures. Low-temperature degradations can be helpful for creating channels and features with low energy requirements or allowing depolymerization of a polymer shell for drug delivery. One method of achieving low-temperature degradations is through the use of thermodynamically unstable polymers.

#### Polymerization

Polymerizable polymers whose ceiling temperature is below room temperature are considered low ceiling temperature polymers. Polymers that are thermodynamically unstable take advantage of a polymer’s ceiling temperature. Ceiling temperature is the temperature at which polymer propagation and depolymerization are in equilibrium, as shown in the generic polymer propagation/depolymerization reaction: $[M] + [M] = [M_{n+1}]$. Above the ceiling temperature, no polymer can be formed. Below the ceiling temperature, polymer can be formed. A polymer that is thermodynamically unstable has a low ceiling temperature. Ceiling temperatures for various monomers are given in Table 3. As the concentration of monomer decreases, the ceiling temperature of the polymerization also decreases. While most of the ceiling temperatures shown are not useful for a thermodynamically unstable polymer at room temperature, low ceiling temperature polymers ($T_c < 70^\circ$C) offer the use of moderate to low temperatures to dry-pattern features or cavities [80,81].

After polymerization at temperatures below the ceiling temperature, the polymer can be kinetically stabilized by endcapping. The resulting polymer is a thermodynamically unstable solid that can be heated well above the ceiling temperature. Poly($\alpha$-methyl

### Table 2 The sacrificial polymers (Unity 2207P, Unity 2507P, Unity 3807P, and Unity 4411) and dielectric overcoat materials compatibility chart [78]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dielectric overcoat material</th>
<th>Overcoat solvent</th>
<th>Unity 2207P</th>
<th>Unity 2507P</th>
<th>Unity 3807P</th>
<th>Unity 4411</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Avatrel EPM™</td>
<td>Mesitylene</td>
<td>G</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>2</td>
<td>Avatrel 2090P™</td>
<td>Mesitylene</td>
<td>G</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>Sumiresin Excel CRC-8650</td>
<td>GBL</td>
<td>G</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>PI-2611</td>
<td>NMP</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>G</td>
</tr>
<tr>
<td>5</td>
<td>PI-2734</td>
<td>NMP</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>G</td>
</tr>
<tr>
<td>6</td>
<td>Dow Corning PI</td>
<td>NMP</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>SU-8 2025</td>
<td>GBL</td>
<td>G</td>
<td>B</td>
<td>B</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>Cyclotene 3022-63</td>
<td>Mesitylene</td>
<td>G</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>9</td>
<td>Photoneece DL-1000</td>
<td>GBL</td>
<td>G</td>
<td>G</td>
<td>G</td>
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</tr>
<tr>
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<td>Photoneece PWDC-1000</td>
<td>GBL</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
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<td>Mesitylene</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>12</td>
<td>SiO$_2$ + Avatrel 2090P™</td>
<td>Mesitylene</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>13</td>
<td>SiO$_2$ + Sumiresin CRC-8650</td>
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<td>G</td>
<td>G</td>
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<tr>
<td>14</td>
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<tr>
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<td>SiO$_2$ + Dow Corning PI</td>
<td>NMP</td>
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<tr>
<td>17</td>
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<td>G</td>
<td>G</td>
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</tr>
<tr>
<td>18</td>
<td>SiO$_2$ + Cyclotene 3022-63</td>
<td>Mesitylene</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>19</td>
<td>SiO$_2$ + Photoneece DL-1000</td>
<td>GBL</td>
<td>G</td>
<td>G</td>
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<td>G</td>
</tr>
<tr>
<td>20</td>
<td>SiO$_2$ + Photoneece PWDC-1000</td>
<td>GBL</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
</tbody>
</table>

#### Note
G = compatible and air channels can be formed, B = incompatible and not work, NMP = N-methyl-2-pyrrolidone, and GBL = gamma-butyrolactone. Unity 2207P contains poly(propylene carbonate), Unity 2507P contains poly(cyclohexene carbonate), Unity 3807P contains poly(norbornene carbonate), and Unity 4411 contains polynorbornene [78].

### Table 3 Ceiling temperatures for various monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Ceiling temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate</td>
<td>200</td>
</tr>
<tr>
<td>Styrene</td>
<td>400</td>
</tr>
<tr>
<td>$\alpha$-methyl styrene</td>
<td>61</td>
</tr>
<tr>
<td>Phthalaldehyde</td>
<td>−42</td>
</tr>
<tr>
<td>Ethyl glyoxylate</td>
<td>37</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>119</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>−39</td>
</tr>
</tbody>
</table>

Ceiling temperature is reported for pure monomer [80,114,123].
Polycarbamates recently revived thermodynamically unstable polymers by providing a valuable application. Sagi et al. synthesized a polycarbamate that when triggered, produced amplification of a fluorescent signal [83]. The polycarbamate undergoes depolymerization from head to tail once the endcap is removed through a \( \beta \)-elimination by a protein. The authors termed this type of material a self-immolative polymer due to the nature of the depopagation mechanism. Depolymerization rates of polycarbonates can be decreased by increasing molecular weight [92]. Another scheme changed the carbamate backbone by adding electron-donating groups which caused two orders of magnitude faster depolymerization [93].

Polyaldehydes with different monomer structures have been synthesized with moderate success. Low molecular weight aldehyde monomers (i.e., acetaldehyde, propionaldehyde, butyaldehyde) tend to create highly crystalline polymers that are insoluble in most common organic solvents [94–98]. This insolubility limited applications when polyaldehydes were first observed [99]. As larger monomers were attempted, solubility was achievable.

Polyphthalaldehyde was one of the first chemically amplified resists where the amplification is derived from the complete, cata- lytic depolymerization of an entire polymer chain [100]. In recent years, phthalaldehyde has garnered increased interest due to the ease of synthesis and new controllability of the end groups [101]. Several studies have looked at the kinetics and reaction conditions to achieve reproducible and high-quality polyphthalaldehyde [101–104]. Figure 16 shows a typical phthalaldehyde synthesis. The reaction temperature is by necessity well below the ceiling temperature of the polymer, \(-42^\circ\text{C}\). The resulting polymer is thermally stable up to \(120^\circ\text{C}\), but upon attack of either end groups or the polymer backbone will depolymerize at temperatures above its ceiling temperature [101].

Due to this increased interest and ease of synthesis, polyphthalaldehyde has recently been used in many unique applications. Polyphthalaldehyde’s first use as a chemically amplified resist is still being explored with focus on altering the endcap to slightly alter the trigger necessary to initiate depolymerization [105,106]. Thick films of polyphthalaldehyde have been used in an emerging field of transient electronics or electronics that change over time in response to environmental stimuli [107,108].

A polyphthalaldehyde block copolymer with polystyrene was synthesized to create nanochannels. The polyphthalaldehyde blocks phase segregated in a predominantly polystyrene matrix. Trifluoroacetic acid was then used to selectively remove the polyphthalaldehyde creating nanochannels for fluids in a spin-coated polymer film [109]. A polyphthalaldehyde block copolymer with poly(alkylene oxide) was used in a similar way to create hollow nanocapsules [105]. Wood et al. used polyphthalaldehyde as a sacrificial material to transfer graphene onto a silicon dioxide substrate through low-temperature thermal decomposition [110].

Ethyl glyoxylate is another aldehyde that has been captured in a thermodynamically unstable polymer [111–114]. Similar to phthalaldehyde, ethyl glyoxylate can be polymerized below its ceiling temperature, \(-20^\circ\text{C}\), and used as a self-immolative polymer. Unique to poly(ethyl glyoxylate) are the depolymerization modes. The polymer degradation involves both chain scission and ester hydrolysis, unlike the unzipping typical of polyaldehydes [114,115].

The thermal properties of polyaldehydes can also be controlled by varying the macrostructure. Moore et al. developed the use of a cationic synthesis to achieve more thermally stable macrocyclic polyaldehydes when compared to the linear counterparts [111,112]. The 50 wt. \% thermal decomposition temperature for ethyl glyoxylate was increased by \(80^\circ\text{C}\) from the linear to the macrocyclic structures [112].

Phthalaldehyde with chlorine substituted in the fourth and fifth positions on the phenyl ring also shifts the decomposition temperature. In addition to the thermal decomposition temperature increase, the stability at ambient conditions of the homopolymer is increased [103]. The added stability allowed targeted degradation of different layers of similar polymer based on the endcap triggers. Layers of poly(4,5-dichlorophthalaldehyde) in a multilayer structure were selectively depolymerized by exposure to different triggering agents [104].

Poly(olefin sulfone)s constitute a broad class of polymers that, by changing the olefin structure, can have significant variation in the thermal stability of the polymer. Numerous studies have been performed to understand the effect of olefin structure on the polymerization, degradation, and vapor development of the polymer [90,118–122]. Bowden and Thompson performed significant characterization on a series of olefin monomers and the application of the polymers to EUV resists [118,119,121]. An increased cooling temperature corresponds to slower vapor development due to the limitations of polysulfone depopagation. As the chain depolymerizes, the olefin sulfone backbone can encounter secondary reactions that terminate the depopagation, slowing the vapor development by maintaining an undesirable solid polymer phase [118]. Recent studies have focused on the application of poly(olefin sulfone)s to photocatalyzed depolymerization [120,122]. The benefit of poly(olefin sulfone)s for photo-depolymerization is direct irradiation will cause the amplified response, eliminating the need for photosensitive additives [120].

Summary and Conclusions

The phase change or decomposition of polymers has been used in a variety of ways to produce air cavities and structures with ultralow dielectric constant, mechanical compliance, or releasable layers. The use of air cavities in electronic devices lowers the energy dissipated and improves the interconnect speed. Process integration remains a challenge because the temperature of...
decomposition has to match the existing process temperature or new process conditions must be developed. It is desirable to have the polymer decompose at a specific temperature rather than over a wide temperature range. It is desirable to have the sacrificial polymer remains stable as other materials are being processed, then decompose at a specific temperature within a designated process window. Progress has been made at catalyzing the polymer decomposition or stabilizing the polymer so that target temperatures can be achieved. However, rapid polymer decomposition can produce high pressure inside encapsulated regions. The pressure buildup due to rapid decomposition can be mitigated by controlled temperature ramping. Nevertheless, a careful matching of the polymer decomposition temperature to the temperature window of the other materials can facilitate integration.

Low temperature polymers have been shown to expand the decomposition temperature range to values at or below room temperature. Room temperature decomposition can be catalyzed by chemical exposure or radiation events. Potential applications include environmentally conscious disposal of materials and the triggered destruction of devices.

Photoactivation of the polymer decomposition process has led to processing advances via direct polymer patterning. Photoactivation is also useful for the selective decomposition of the sacrificial polymer.

The polymer decomposition products are especially important because they must permeate through dense overcoat materials to form embedded air cavities. The chemical and physical properties of the cavity superstructure are important and should be matched to the sacrificial polymer so that precise physical structures can be formed. It can be challenging to select materials for the air cavity superstructure which do not distort or interfere with the sacrificial polymer.

Although progress has been made to understand the degradation mechanisms and expand the choice of usable polymers, many questions remain. In particular, the purity of the sacrificial polymer and control over the formation of undesired solid residue can be important for particular applications. The applications of this technology can be expanded by greater control over the polymer type, temperature of polymer decomposition, purity of the materials, and methods of catalysis and stabilization of the polymer.

References

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