(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 September 2014 (25.09.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/153336 A1

(51) International Patent Classification:
C08J 7/18 (2006.01) *C08L 79/08* (2006.01)
C08J 5/18 (2006.01) *C08J 3/28* (2006.01)
C08G 73/10 (2006.01)

(21) International Application Number:
PCT/US2014/031015

(22) International Filing Date:
18 March 2014 (18.03.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/986,012 22 March 2013 (22.03.2013) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: METHOD OF CURING THERMOPLASTICS WITH MICROWAVE ENERGY

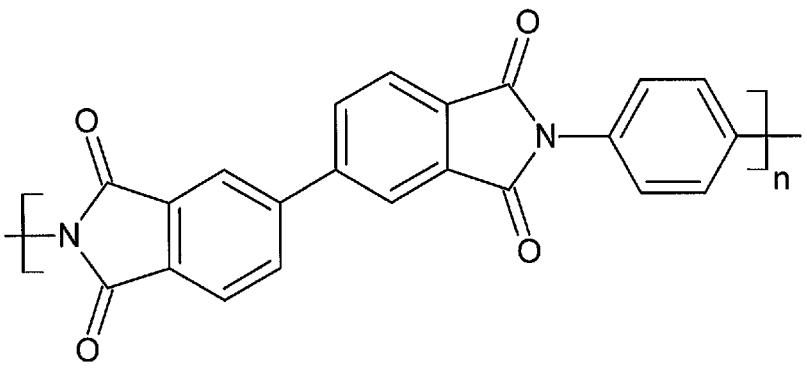

FIGURE 1

(57) Abstract: A method for densifying thermoplastics, particularly polyimides, for use in conjunction with electronic circuits while producing improved physical properties and a high degree of crystallinity, involves variable frequency microwave (VFM) processing at temperatures typically 100°C below the glass transition temperature or lower, for times of about 50 to 100 minutes. It is particularly applicable to polymers based on BPDA-PPD, but may also be generally applied to other intentionally designed polyimide structures with the same features. The invention enables the creation of layered structures involving integrated circuits with small feature sizes and overcoatings of polymers with high T_g and other desirable properties.

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METHOD OF CURING THERMOPLASTICS WITH MICROWAVE ENERGY

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

[0002] The invention pertains to apparatus and methods for densifying thermoplastic polymers, and more particularly to methods for creating dense thermoplastic films with improved crystallinity on selected substrates.

[0003] Description of Related Art

[0004] Polyimides are attractive materials for the microelectronics industry because of their excellent mechanical, electrical, and chemical properties. The process time for conventional thermal curing typically ranges from 4 to 6 hours; slow temperature ramp rates and extended hold times at various temperatures are needed to allow for slow reaction rates, outgassing of reaction by-products and solvent, and orientation of polymer chains. Reducing the processing time required to cure these polymers would increase throughput and reduce overall production costs.

[0005] Polyamic acid based polyimides such as 3, 3', 4, 4'-biphenyltetracarboxylic acid dianhydride (BPDA) with p-phenylenediamine (PPD) are desirable for electronic packaging applications where a low residual stress dielectric is essential. Many of the unique properties of this polymer are attributed to the rigid nature of its backbone and the high degree of orientation that occurs during cure. This orientation is critical to achieving the low coefficient of thermal expansion (CTE), creating a low stress film.

[0006] One obvious shortcoming of this type of polymer system is the high cure temperature (typically 350°C), which precludes its use in many advanced semiconductor systems, where the small feature size and correspondingly reduced diffusion distances severely limit the thermal budget available for the various process

steps. For instance, a recent paper reported desirable properties of this polymer system, Table 1, but all of the films reported had been processed at 310-350°C, whether by conventional oven curing, rapid hotplate curing, or microwave curing [K. D. Farnsworth et al., Variable Frequency Microwave Curing of 3,3′,4,4′-Biphenyltetracarboxylic acid dianhydride / P-Phenylenediamine (BPDA/PPD), *Intl. Journal of Microcircuits and Electronic Packaging* 23:162-71 (2002)]. Although the VFM cure was significantly faster, cure temperature was unchanged, and cure temperatures in this range are well beyond the allowable maximum temperature for many applications of interest. The difficulty in applying these polymer systems to demanding electronic applications can be seen by the fact that the commercial version of BPDA/PPD has been available for more than thirty years, and yet had very limited use.

[0007] Table 1 Typical Cured PI 2611 Properties by Prior Art Methods

Method	**Thermal Cure**	**Hotplate**	**VFM**
Property			
Final cure temperature, °C	350	350	350
Total cure time, s	18,000	3600	1200
Residual stress, MPa on [100] Si	6	35.3	4.2
CTE, ppm/°C	3	6.6	3.8
Tensile strength, GPa	>0.374	>0.0841	>0.361
Dielectric constant at 10 kHz	3.06	3.09	3.34
Loss tangent at 10 kHz	0.0032	0.00426	0.0033
Birefringence	0.2249	-	0.2237
Degree of cure	100%	87-108%	82-102%
Degradation temperature, °C	539	-	540

[0008] Objects and Advantages

[0009] Objects of the present invention include the following: providing an improved method for densifying thermoplastic films; providing a method for densifying

thermoplastic films on semiconductor substrates; providing a method for coating a semiconductor wafer with a thermoplastic film having improved properties; providing a low-temperature process for making a thermoplastic film with improved crystallinity; and, providing a method for creating a polyimide film with controlled orientation on a selected substrate. These and other objects and advantages of the invention will become apparent from consideration of the following specification, read in conjunction with the drawings.

SUMMARY OF THE INVENTION

[0010] According to one aspect of the invention, a method for densifying a thermoplastic film comprises:

depositing the thermoplastic in soluble form onto a selected substrate;

soft baking the film to remove residual solvent; and,

curing the film by VFM for 20 to 120 minutes at a temperature no higher than 100°C below the glass transition temperature, T_g, of said thermoplastic.

[0011] According to another aspect of the invention, a method for making a microelectronic device comprises:

preparing a semiconductor wafer with an integrated circuit thereon;

depositing a thermoplastic film in soluble form onto the semiconductor wafer;

soft baking the film to remove residual solvent; and,

curing the film by VFM for 20 to 120 minutes at a temperature no higher than 100°C below the glass transition temperature, T_g, of the thermoplastic.

[0012] According to another aspect of the invention, an electronic device comprises:

a semiconductor having a functional integrated circuit thereon; and,

a substantially dense thermoplastic coating thereon, said coating having a T_g in the range of 300-400°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings accompanying and forming part of this specification are included to depict certain aspects of the invention. A clearer conception of the invention, and of the components and operation of systems provided with the invention, will become more readily apparent by referring to the exemplary, and therefore non-limiting embodiments illustrated in the drawing figures, wherein like numerals (if they occur in more than one view) designate the same elements. The features in the drawings are not necessarily drawn to scale.

[0014] Figure 1 is a schematic diagram of the structure of BPDA-PPD.

[0015] Figure 2 illustrates the modulus of BPDA-PPD films cured under various conditions.

[0016] Figure 3 illustrates the hardness of BPDA-PPD films cured under the same conditions as in Figure 2.

[0017] Figure 4 illustrates the % imidization of BPDA-PPD cured at 200°C by VFM for various times.

[0018] Figure 5 illustrates the kinked chain characteristic of the polyimide PMDA-ODA.

[0019] Figure 6 illustrates some alternative classes of molecules that can provide a di-functional polyamic acid section for a linear polyimide.

[0020] Figure 7 illustrates some alternative classes of molecules that can provide di-functional amines for a polyimide.

DETAILED DESCRIPTION OF THE INVENTION

[0021] In general terms, the invention provides a method for densifying thermoplastics, particularly polyimides, at sufficiently low temperature to be used in conjunction with

electronic circuits while producing improved physical properties and a high degree of crystallinity. It is particularly applicable to polymers based on BPDA-PPD, but it will become apparent in the disclosure that follows that the method may be generally applied to other intentionally designed polyimide structures with the same features.

[0022] The polymer BPDA-PPD, 3,3′,4,4′- Biphenyltetracarboxylic acid dianhydride / P-Phenylenediamine, is a polyamic acid based polyimide manufactured by HD Microsystems (250 Cheesequake Road, Parlin, NJ 00859-1241) and sold under the product designation PI 2611. At high temperatures (> 200°C), the material undergoes a conversion from its soluble, polyamic acid form, as received from HD Microsystems, to an insoluble, fully imidized polymer. Many of the unique properties of the polymer are attributed to the rigid nature of its backbone and the high degree of orientation, which occurs during cure.

[0023] The unusually linear BPDA-PPD, FIG. 1, when cured by conventional oven methods at the recommended 350°C, displays an increase in orientation and crystallinity as evidenced by an increase in modulus, decrease in coefficient of thermal expansion, and infrared (FTIR) peak shifts [J.C. Coburn, M.T. Pottiger, and C.A. Pryde, "Structure Development in Polyimide Films", Mat. Res. Soc. Symp. Proc., Vol. 308, 475-87 (1993)]. These high levels of orientation/crystallization are achieved with cure temperatures between 250°C and 350°C with convection heating are seen in Table 2. Curing at temperatures from 350-400°C, which is above the T_g (340°C), actually decreases the CTE and increases the modulus which results in a sharp increase in residual stress σ in the film. This is actually attributed to a loss of in-plane orientation of the rings to the surface. Curing typical non-linear polyimides like BTDA/ODA/MPD, Table 3, above the T_g does not affect the residual stress because they are not aligned to the surface.

[0024] Table 2 Properties of BPDA-PPD vs. cure temperature (data from Coburn et al. 1993).

cure temp. (°C)	Δn	$n_{average}$	$E_{Young's}$ (GPa)	$\alpha_{in\text{-}plane}$ (μm/m°C)	σ (MPa)
BPDA//PPD (Tg=340)					
250	0.1826	1.7641	7.1 ± 0.2	3 ± 1	-
300	0.1960	1.7714	7.2 ± 0.2	3 ± 1	2 ± 1
350	0.1979	1.7637	7.3 ± 0.2	3 ± 1	2 ± 1
400	0.2186	1.7771	8.2 ± 0.2	5 ± 1	10 ± 1

[0025] Table 3 Properties of BPDA-ODA-MPD vs. cure temperature.

BTDA//ODA/MPD (Tg=320)					
250	0.0122	1.6840	3.3 ± 0.2	45 ± 1	-
300	0.0100	1.6859	3.2 ± 0.2	46 ± 1	25 ± 2
350	0.0104	1.6861	3.3 ± 0.2	46 ± 1	41 ± 2
400	0.0102	1.6867	3.3 ± 0.2	46 ± 1	41 ± 2

[0026] Applicant began a series of studies to determine if microwave curing could be carried out at substantially lower temperatures, in order to process materials such as BPDA-PPD in a range that would be useful for integrated circuit applications. Experiments were done using a MicroCure™ 2100 VFM (Lambda Technologies, Morrisville, NC) with a sweep frequency range of 5.65-7.0 GHz, sweep rate of 0.1 seconds, and 200W power. As will be shown in the examples that follow, the results were not only surprising, but indeed counter-intuitive from the viewpoint of conventional polymer theories.

EXAMPLE

[0027] Films of PI 2611 were VFM cured at 175 and 200°C for times ranging from 5 to 120 minutes. The resin was spun onto a silicon wafer at 4000 rpm to achieve a 7 μm thick film which was subsequently soft-baked at 130°C for two minutes to remove residual solvent before the cure. FIG.

2 shows the Young's modulus of these samples compared to oven-cured samples (350 and 400°C). A surprising observation is that there is a jump in modulus after 60 minutes of curing at 200°C, at which point the modulus is actually higher than that of material cured in a conventional oven. Note: modulus was measured by nanoindentation methods on thickness of 100-200 nm in order to minimize substrate effects.

EXAMPLE

[0028] FIG. 3 presents the hardness of the BPDA-PPD films described in the previous example. Again, one can see a sharp increase at a cure time of about 60 minutes, at which point the hardness is comparable to that produced by a 350°C oven cure.

EXAMPLE

[0029] FIG. 4 presents the per cent imidization as a function of time at 200°C by VFM cure, as measured by FTIR. One can see that imidization is about 80% complete after 20 minutes, and essentially complete after 60 minutes, with minor changes from 60 to 120 minutes.

[0030] When BPDA-PPD is fully cured (T_g=350°C) by microwaves (VFM) at only 200°C, the increase in extent of cure from 90-100% and orientation occurs at a sharp transition between 60 and 75 minutes into the process as shown by modulus, FIG. 2, hardness, FIG. 3, and FTIR, FIG. 4. This orientation occurs unexpectedly as a sharp phase transition in time with MW but the modulus does not increase to the higher level seen with convection oven curing while the CTE remains at 3.1 ppm/°C. This represents an even lower residual stress level while never being heated above the T_g. As a result, the VFM curing of BPDA/PPD films on silicon wafers shows no additional warpage.

[0031] This high orientation represents a tighter alignment of the polymer chains which is analogous to the highly oriented "rod-like" packing of liquid crystal phases. The electronic nature of this particular thermoplastic structure results from unusually well aligned sp^2 orbitals in the aromatic rings and the heterocyclic imide rings along this very linear and rigid structure as shown in Figure 1. The more common structure of commercially available polyimides, by contrast, is more kinked and flexible as shown in the structure of the common polyimide in Kapton® film, PMDA-ODA, FIG. 5.

[0032] The morphologically isotropic PMDA-ODA has an out-of-plane CTE that is only 1.2 times the in-plane CTE whereas an oriented BPDA-PPD is anisotropic with a ratio 25 times higher in-plane. This anisotropic and low CTE closely matches that of silicon (3 ppm/°C) which allows polymer films coated on silicon wafers to have practically no induced stress after cooling. This is very important to the electronics industry that is increasing the use of stacked thin silicon wafers coated with polyimide dielectric films to provide very high density functionality. The current mismatch of CTE between polymer dielectric films (~60 ppm/°C) and silicon wafers typically creates 300-800 μm of warpage in 300 mm diameter wafers. This has been an intractable problem because the conventional oven cure temperatures of 350-400°C cure of BPDA-PPD is far beyond the practical limits of wafer processing for an electronics industry seeking cure temperatures below 250°C compatible with advanced devices and packaging structures. For example, some advanced memory devices such as polymer or ceramic RAM devices are made inoperable at temperatures much above 250°C. The capability to create highly oriented low CTE polymide films at a cure temperature of only 200°C with microwaves is a significant technical breakthrough.

[0033] Polyimide films have been the organic dielectric of choice for decades in the microelectronic industry because of the materials' high thermal, chemical, and mechanical stability to temperatures above 300°C. Recent progress in electronic device technologies has often created a sensitivity to high temperature processes above 250°. This limitation has forced the industry to search for other chemical classes such as polybenzoxazoles and epoxies that have cure temperatures below 250°C. In all cases,

these substitutes for polyimides have compromised stability and dielectric properties or reduced manufacturing robustness. Polyimides incompletely cured by conventional ovens at temperatures below 300°C have unacceptable chemical and dielectric properties for microelectronic devices.

[0034] The capability to create highly oriented, low CTE polyimide films at temperatures as low as 200°C allows the inclusion of a robust polyimide film cure in most of the packaging process flows which are predominately at or below 250°C to avoid the decomposition of commonly used epoxy adhesives in die attach, die encapsulation, molding, die underfill, and die stacking applications.

[0035] In addition, the difference between a low microwave cure temperature below T_g and the highest temperature seen by any of the other process steps used in the packaging or assembly is now 50°C or less. This low temperature range excursion nearly eliminates the strong effects of time and temperature on modulus and CTE found with conventional oven curing as described by M.T. Pottiger and J.C. Coburn, "Modeling Stresses in Polyimide Films", Mat. Res. Soc. Symp. Proc., Vol 308, 527-534 (1993).

[0036] With the uniform microwave excitation of the critical reactive dipoles throughout the bulk of the material, the cure reaction (imidization/cyclization) of polyimide chains becomes highly efficient while maintaining much lower temperature (200°C) in bulk. Low temperature curing of polymers has been demonstrated in various systems. As the reaction approaches completion (nearly 90% as shown in FIG. 4), the rigidity of the chains becomes higher and the chains become less mobile. The continued effect of microwave energy in rotating dipoles (primarily carbonyls at this point) assists the orientation/crystalization of these rigid rods into lower energy stacking sites. An analogy can be seen in the synchronous crystallization (freezing) point of small water molecules in the very last degree before 0°C. This synchrony is not seen with the standard convection heating of polymers because that process involves the random collision of chains by collisions with others which disrupts order almost as much as enhances it, thus requiring higher temperatures.

[0037] Applicants have shown that microwave induced orientation at surprisingly low temperatures is possible with the linear structure of BTDA-PPD. Based on this observation Applicants expect that this phenomenon can be extended to other intentionally designed polyimide structures with the same features.

EXAMPLE

[0038] The design of other polymers to exploit the inventive process may combine a di-functional polyamic acid section as suggested by the general classes of FIG. 6 and di-functional amines with R1 and R2 as suggested in FIG. 7. There are many other possibilities that would produce, when cured, a linear, conjugated, and rigid polyimide films with high orientation probability.

[0039] It has also been shown [Y. Kuramoto, *Chemical Oscillations, Waves, and Turbulence.* Springer, Berlin (1984)] that sudden phase transitions in chemistry and biology can occur with interactions between molecules at a critical level of distribution. The microwave induced interactions of polarizable polymer chains that are moving at reduced rates near the end of cure, could become more effectively synchronized and highly oriented if the distribution of the lengths of these chains was narrower.

EXAMPLE

[0040] Since the observed orientation or crystallization of BTDA-PPD appears to be sharply synchronous in the manner of a phase transition (see FFIGs. 2-4) it should be possible to induce high levels of orientation in other polyimides and other thermoplastics in MW radiation by reducing the chain length distribution in the starting materials. Reducing the polydispersity index (PDI) of a thermoplastic can be done by either using separation techniques such as size exclusion chromatography or by

limiting the initial formation of the thermoplastic endcap reaction in the formation of starting materials. By these methods it should be possible to enhance the mechanical properties of a much wider selection of polyimides as well as other thermoplastics such as polyolefins, polyvinyls, polycarbonates, and acrylonitriles that would benefit from adjustable hardness and CTE. This selective design capability is clearly not possible by the use of standard thermal curing technologies.

[0041] Based on the foregoing examples and discussion, it will be appreciated that there is a range of process variables that will yield acceptable results and that optimal parameters may vary from one particular application to another. The skilled artisan can easily optimize the process for a particular system through routine experimentation. For the BPDA-PPD system, Applicants prefer to process in the range of temperatures from 175-225°C for about 20-120 minutes. For custom-designed polymer formulations, such as those discussed in connection with FIGs. 6 and 7, it will be appreciated that T_g values will likely vary somewhat, but in many cases will lie in the range of about 300-400°C. For these systems, by analogy to BPDA-PPD, Applicants prefer that microwave processing be carried out at a temperature no higher than about 100°C below Tg for a particular formulation. The upper limit on desirable processing temperature will also be dictated to some degree by the end use. For electronic devices, the industry in general prefers to stay below about 250°C, and in many cases below 200°C, if possible.

[0042] It will be clear to the skilled artisan that the invention allows one to fabricate structures that have heretofore been impossible to build. Specifically, one can build up a composite structure in which a functional silicon integrated circuit with an upper temperature limit of 250°C or less is coated with a dense layer of thermoplastic having a T_g of 350°C or more. The integrated circuit may comprise features in the range of 100 to 15 nm. By all prior art methods, the processing temperatures needed to densify such polymers would destroy the functionality of the underlying circuit elements.

[0043] It will be understood that VFM processing is an inherently flexible method, in which the skilled artisan may select a particular frequency range, sweep rate, etc., based on such variables as the size and shape of the cavity and workpiece, type of substrate, etc. It is well known that sweeping the frequency across some selected bandwidth (typically ±5% or ±10% of a center frequency not only improves uniformity, but prevents arcing and other damaging effects to electronic components in the workpiece. Thus, Applicants prefer to sweep the frequency over a bandwidth of at least ±5% of the center frequency and more preferably ±10%.

We claim:

1. A method for densifying a thermoplastic film comprising:

depositing said thermoplastic in soluble form onto a selected substrate;

soft baking said film to remove residual solvent; and,

curing said film by VFM for 20 to 120 minutes at a temperature no higher than 100°C below the glass transition temperature, T_g, of said thermoplastic.

2. The method of claim 1 wherein said thermoplastic comprises a polyimide having a di-functional polyamic acid section and a di-functional amine section, and said polyimide has a T_g in the range of 300-400°C.

3. The method of claim 2 wherein said polyimide comprises BPDA-PPD and said VFM curing is carried out at a temperature of about 175-225°C.

4. The method of claim 1 wherein said VFM curing comprises applying microwave power in a sweeping manner over a bandwidth of at least $\pm$5% of a selected center frequency.

5. The method of claim 1 wherein said substrate comprises a semiconductor wafer having integrated circuits thereon.

6. The method of claim 1 wherein said thermoplastic comprises a polymer selected from the group consisting of: polyimides, polyolefins, polyvinyls, polycarbonates, and acrylonitriles.

7. The method of claim 6 further comprising the step of reducing the polydispersity index (PDI) of said thermoplastic.

8. The method of claim 7 wherein said PDI is reduced by a method selected from the group consisting of: using separation techniques including size exclusion

chromatography; and by limiting the initial formation of the thermoplastic endcap reaction in the formation of starting materials for said thermoplastic.

9. A method for making a microelectronic device comprising:

preparing a semiconductor wafer with an integrated circuit thereon;

depositing a thermoplastic film in soluble form onto said semiconductor wafer;

soft baking said film to remove residual solvent; and,

curing said film by VFM for 20 to 120 minutes at a temperature no higher than 100°C below the glass transition temperature, T_g, of said thermoplastic.

10. The method of claim 9 wherein said thermoplastic comprises a polyimide having a di-functional polyamic acid section and a di-functional amine section, and said polyimide has a T_g in the range of 300-400°C.

11. The method of claim 10 wherein said polyimide comprises BPDA-PPD and said VFM curing is carried out at a temperature of about 175-225°C.

12. The method of claim 9 wherein said VFM curing comprises applying microwave power in a sweeping manner over a bandwidth of at least $\pm$5% of a selected center frequency.

13. The method of claim 9 wherein said integrated circuit comprises functional circuit features in the range from 100 to 10 nm in width and said thermoplastic has a T_g in the range of 300-400°C.

14. An electronic device comprising:

a semiconductor having a functional integrated circuit thereon; and,

a substantially dense thermoplastic coating thereon, said coating having a T_g in the range of 300-400°C.

15. The device of claim 14 wherein said integrated circuit comprises functional circuit features in the range from 100 to 10 nm in width.

16. The device of claim 14 wherein said thermoplastic comprises a polymer selected from the group consisting of: polyimides, polyolefins, polyvinyls, polycarbonates, and acrylonitriles.

17. The device of claim 16 wherein said thermoplastic comprises a polyimide having a di-functional polyamic acid section and a di-functional amine section.

18. The device of claim 17 wherein said polyimide comprises BPDA-PPD.

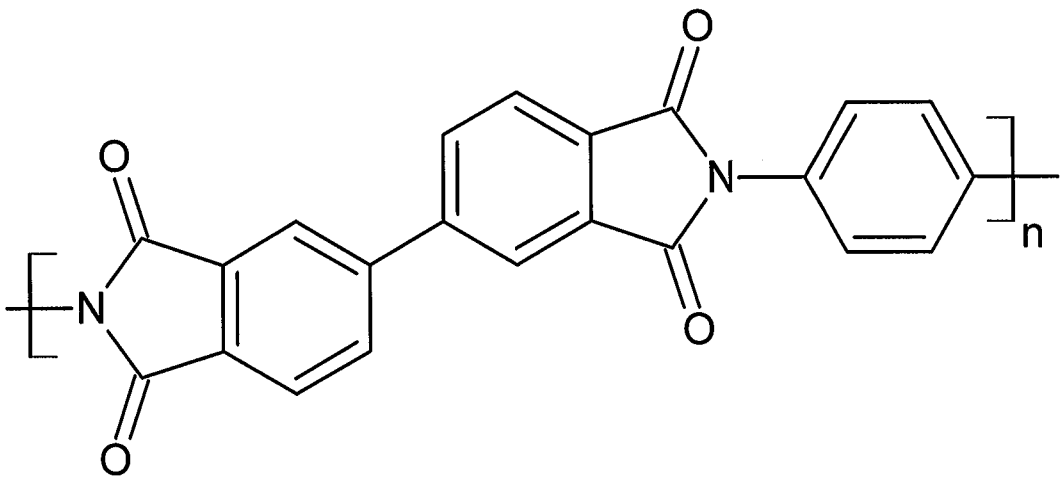

FIGURE 1

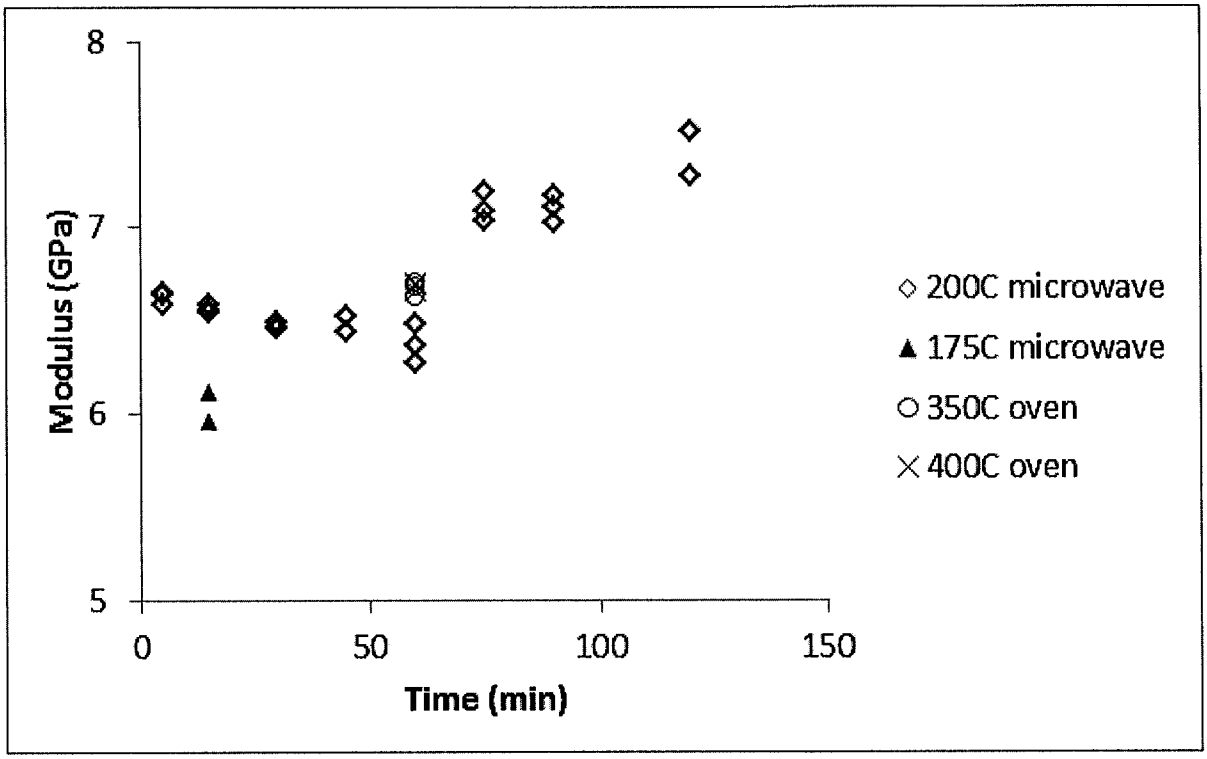
8
7
6
5
Modulus (GPa)
0
50
100
150
Time (min)
◇ 200C microwave
▲ 175C microwave
○ 350C oven
× 400C oven

FIGURE 2

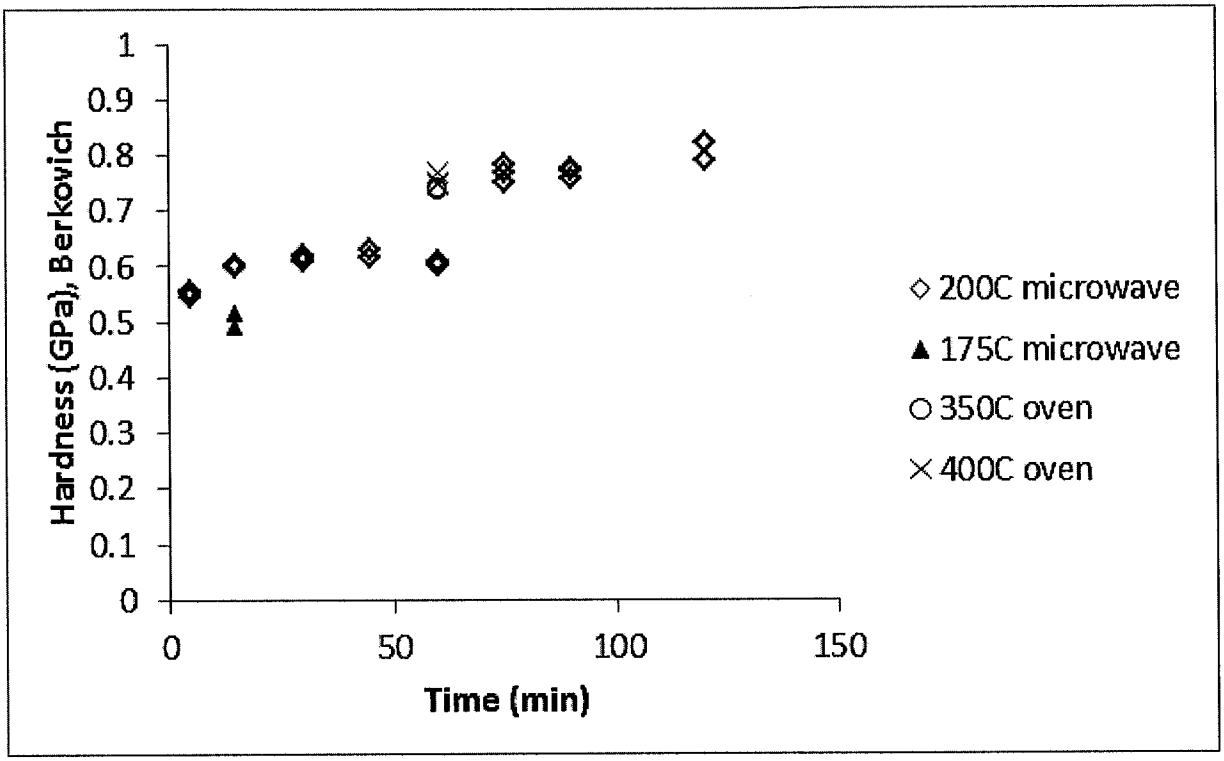
Hardness (GPa), Berkowich
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
Time (min)
◇ 200C microwave
▲ 175C microwave
○ 350C oven
× 400C oven

FIGURE 3

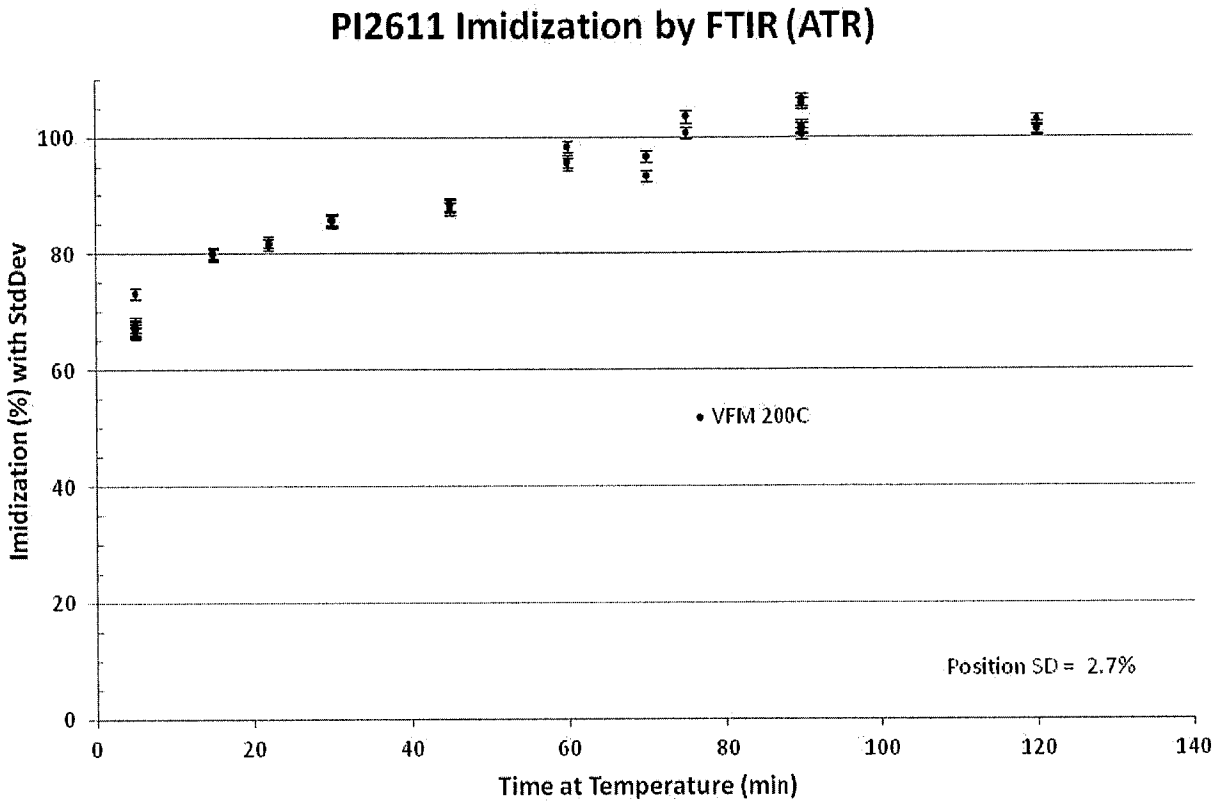
PI2611 Imidization by FTIR (ATR)
Imidization (%) with StdDev
100
80
60
40
20
0
0
20
40
60
80
100
120
140
Time at Temperature (min)
• VFM 200C
Position SD = 2.7%

FIGURE 4

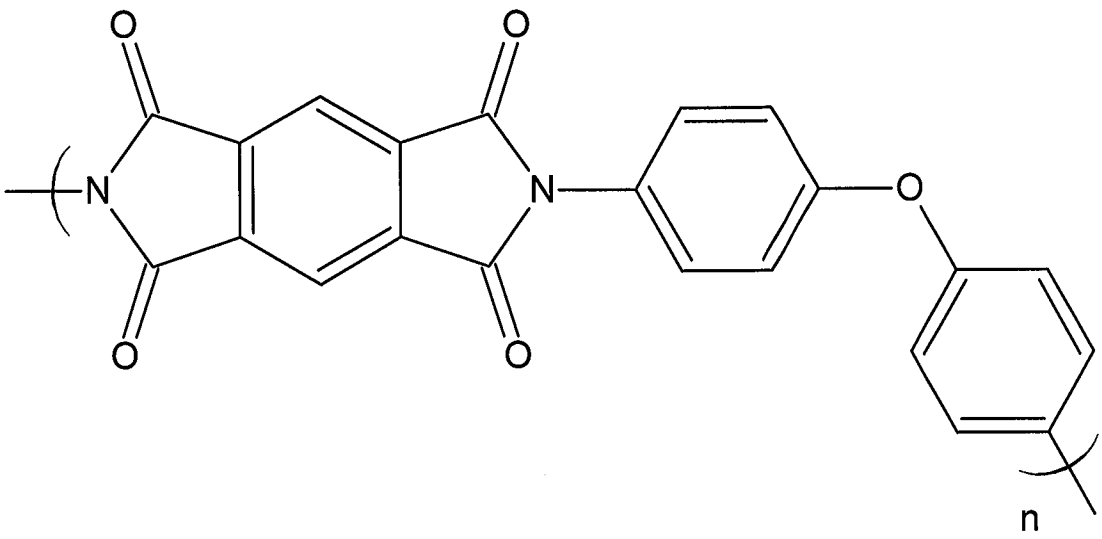

FIGURE 5

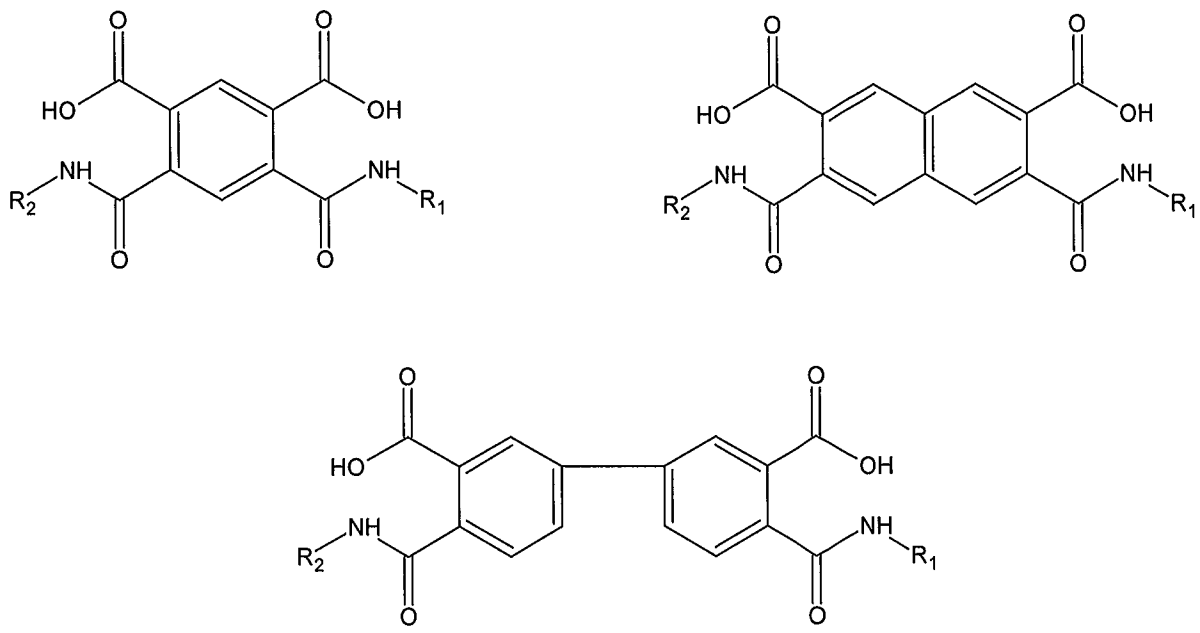

FIGURE 6

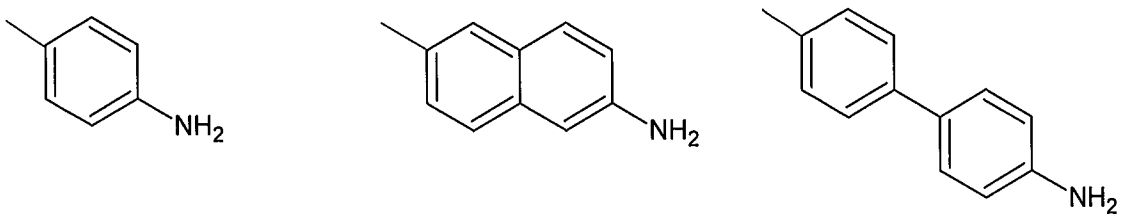

FIGURE 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/031015

A. CLASSIFICATION OF SUBJECT MATTER

C08J 7/18(2006.01)i, C08J 5/18(2006.01)i, C08G 73/10(2006.01)i, C08L 79/08(2006.01)i, C08J 3/28(2006.01)i, C08F 6/10(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J 7/18; B05D 5/12; H01L 21/4763; H01L 21/336; B05D 3/06; C08F 2/46; C08G 69/26; C08J 5/18; C08G 73/10; C08L 79/08; C08J 3/28; C08F 6/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: polyimide film, curing, microwave, VFM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MATSUTANI, H. et al., 'Low Temperature Curing of Polyimide Precursors by Variable Frequency Microwave', Journal of Photopolymer Science and Technology. 2005, Vol. 18, No. 2, pages 327-332 See abstract; pages 328-330; and figure 1.	1-18
A	US 7557035 B1 (RYAN, E. T. et al.) 07 July 2009 See abstract; column 9, line 42-column 10, line 21; and claims 1, 8.	1-18
A	US 2012-0100649 A1 (KIM, Y-M. et al.) 26 April 2012 See abstract; paragraphs [0027], [0028]; and claims 1-10.	1-18
A	US 5879756 A (FATHI, Z. et al.) 09 March 1999 See abstract; claim 1; and figure 1.	1-18
A	US 5317081 A (GELORME, J. D. et al.) 31 May 1994 See abstract; column 8, lines 1-30; and claim 1.	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 August 2014 (21.08.2014)	**21 August 2014 (21.08.2014)**

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Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/031015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7557035 B1	07/07/2009	None	
US 2012-0100649 A1	26/04/2012	KR 10-2012-0041568 A	02/05/2012
US 5879756 A	09/03/1999	AT 243078 T	15/07/2003
		AU 1998-83297 A	14/04/1998
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		DE 69722946 T2	19/05/2004
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		US 5738915 A	14/04/1998
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US 5317081 A	31/05/1994	EP 0465858 A1	15/01/1992
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		JP 02755340 B2	20/05/1998
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