

METHOD AND APPARATUS FOR FORMING STRUCTURES ON A RESIN

Technical Field

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The present invention generally relates to a method and apparatus for performing nanoimprinting on a resin substrate.

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Background

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Ultra-violet (UV) roll-to-roll nanoimprinting technology is a known technique for producing nano-sized patterned features on a resin supported on a polymer substrate such as polyethylene terephthalate (PET), which has seen commercial applications in the manufacture of semi-conductor devices, e.g., transistors, microchips and MEMS devices.

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In particular, in roll-to-roll nanoimprinting processes, adhesion between resin and substrate plays a crucial role because it is a contact patterning technique, i.e., where the patterning tool (such as a mold) comes into contact with the resin while it is supported by the polymer substrate.

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In this regard, one common technical problem associated with conventional roll-to-roll nanoimprinting methods is that the resin, after being contacted with a mold during an imprinting step, continues to adhere to the mold even after the imprinting step. This may cause the resin to peel off from the polymer substrate, rather than from the mold, during a subsequent separation step. This may result in damage to the patterned features on the resin and render the resin unusable for further applications. More importantly, the mold will need to be

dismounted from the imprinting apparatus and cleaned to remove the resin adhered thereon, resulting in unnecessary downtime of the imprinting process.

5 Furthermore, the patterned features are usually of a low aspect ratio (e.g., about 0.5 to about 3.0). Therefore, if the resin fails, it generally fails at the interface between the resin and the polymer substrate, where the cohesive strength of the assembly is the
10 weakest.

 In order to prevent cohesive failure at the interface between resin and polymer substrate, a number of strategies have been proposed to reduce the resin adhesion to the mold and to increase resin adhesion to
15 the polymer substrate. One such approach relates to the application of anti-stick coatings on the mold. However, anti-stick coatings typically suffer from limited lifetimes and tend to degrade over the imprint cycles. Another approach relates to the application of an
20 adhesion promoter film between resin and polymer substrate. However, adhesion promoters can be costly especially when there is a need to apply them over large surface areas as is typically required for roll-to-roll nanoimprinting processes.

25 Yet another approach to solve the cohesive failure problem resides in the use of low surface energy molds, such as molds composed of fluoropolymer material. One drawback associated with this approach is that fluoropolymer materials tend to be soft and thus suffer
30 from creep resulting from cyclic loading over thousands of imprint cycles.

 Accordingly, none of the currently proposed and adopted approaches are viable for scale-up production of an imprinted resin using a roll-to-roll nanoimprinting

method. Therefore, there is a need to provide a method for roll-to-roll nanoimprinting that would overcome or at least ameliorate the technical problems described above.

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Summary

In a first aspect, there is provided a method for forming a structure on a resin substrate, the method comprising the steps of: (a) contacting a mold having a defined surface pattern with an ultra-violet (UV) curable resin substrate supported on an photodegradable, amorphous polymer substrate, said defined surface pattern forming a structure on the UV curable resin substrate; (b) curing the UV curable resin supported on the amorphous polymer substrate by exposing said UV curable resin to UV radiation; and (c) separating the cured resin from the mold. In one embodiment, the method may be for performing roll-to-roll nanoimprinting.

In this regard, it has been surprisingly found that by supporting the UV curable resin on a substantially photodegradable, amorphous polymer substrate, significant improvements in adhesion between the resin and the polymer substrate can be achieved. Advantageously, the improved adhesion prevents the cured resin from sticking to the mold after the contacting step (a) and/or curing step (b). Hence, the cured resin supported on the amorphous polymer substrate may be readily decoupled from the mold without causing damage to the formed structures on the resin. The disclosed method also does not need to be periodically interrupted just so that the mold can be dismounted and cleaned to remove resin that may have adhered to the mold's surface.

Without wishing to be bound by theory, it is being postulated that the amorphous polymer has more free

volume, a more open structure, is more permeable to the UV curable resin, and demonstrates greater propensity to physisorb the resin. In particular, the amorphous nature of the polymer substrate improves adhesion because it
5 does not possess the closely packed chains of a crystalline polymer, which would otherwise act as a barrier to the diffusion of other molecules, such as pre-polymer oligomers or other polymer chains and thus prevent formation of entanglements extending through the
10 crystalline structure of the polymer.

Additionally, amorphous polymers will generally present more potential sites for reaction with other polymer chains and/or photoinitiators, because amorphous polymer chains do not stack. On the other hand, the
15 closely packed chains of crystalline polymers may prevent access of photoinitiators to the reactive groups in the polymer chains and inhibit photodegradation.

Compared to a crystalline or semi-crystalline polymer, the disordered polymer chains of the amorphous polymer more readily diffuse into the polymer structure
20 of the adjacent resin, and vice versa. Accordingly, the amorphous nature of the polymer substrate may serve to promote formation of entanglements between its random, disordered polymer chains and the polymer chains of the
25 curable resin at the polymer / resin interface. The formation of entanglements and increased diffusion are both crucial for the adhesion of the amorphous polymer substrate to the curable resin.

Additionally, in one embodiment, the
30 photodegradable, amorphous polymer substrate is selected be a chemically unstable polymer substrate containing unstable bond conformations, such as but not limited to, C-C bonds, C-O bonds, C-S bonds, C-N bonds, C-Cl bonds, or C-Br bonds. These bonds are inherently unstable and

may be attacked by photons or resin photoinitiators to form polymerization sites within the polymer itself. Advantageously, this allows the polymer to readily form covalent bonds with the resin at the resin / polymer substrate interface, leading to improved adhesion.

In a second aspect, there is provided an apparatus for forming a structure on a resin substrate, comprising: (a) a moveable mold having a defined surface pattern, said mold being configured to contact a layer of UV curable resin supported on an amorphous, photodegradable polymer substrate layer, said resin being movable relative to said mold; (b) compressing means configured to engage said mold to thereby sandwich said resin and polymer substrate layer therebetween, thereby forming a structure on said resin; (c) an UV source arranged to irradiate the UV curable resin; and (d) a decoupling means to decouple the cured resin from the mold.

In one embodiment, the disclosed apparatus may be an apparatus for roll-to-roll nanoimprinting.

The technical benefits of the disclosed apparatus are as disclosed above for the method of the first aspect.

In a third aspect, there is provided a composite comprising a cured resin supported on an amorphous polymer substrate layer, said composite being produced by a method as disclosed above, or by an apparatus as disclosed above.

Definitions

The following words and terms used herein shall have the meaning indicated:

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where

necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are
5 intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations,
10 typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated
15 value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an
20 inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a
25 range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies
30 regardless of the breadth of the range.

Disclosure of Optional Embodiments

Exemplary, non-limiting embodiments of a method for forming a structure on a resin according to the first aspect will now be disclosed.

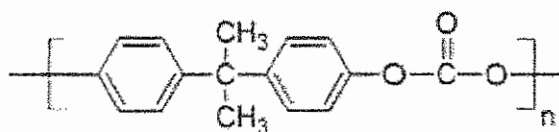
In one embodiment, there is disclosed a method for forming a structure on a resin substrate, the method comprising the steps of: (a) contacting a mold having a defined surface pattern with an ultra-violet (UV) curable resin substrate supported on an amorphous, photodegradable polymer substrate, said defined surface pattern forming a structure on the UV curable resin substrate; (b) curing the UV curable resin supported on the amorphous polymer substrate by exposing said UV curable resin to UV radiation; and (c) separating the cured resin from the mold.

The structure formed on the resin may be an imprint. The imprint may be a microimprint or a nanoimprint. In one embodiment, the imprint is a nanoimprint. In one embodiment, the amorphous polymer may be selected from the group consisting of amorphous polycarbonates, amorphous polyacrylates, amorphous polyethylene naphthalate, and co-polymers thereof.

The amorphous polymer may comprise aromatic groups in its polymer structure. The aromatic groups may be selected from phenyl groups, pyridine groups, pyrazine groups, imidazole groups, thiophene groups, pyrrole groups, furan groups, benzannulated analogs and mixtures thereof.

In one embodiment, the polymer substrate may comprise polycarbonate (PC). In yet another embodiment, the polymer substrate may consist essentially of

polycarbonate. A non-limiting, exemplary polycarbonate may be represented by the general formula (I) below;



Formula (I)

wherein n may be any integer greater than 2.

In one embodiment, polycarbonate is selected as it is fully amorphous, flexible, transparent and is not semi-crystalline. The amorphous nature may be attributed at a molecular level to the bulky methyl groups on the main polymer chain, which are disposed between two phenyl groups, thereby preventing pi-stacking of the phenyl groups between neighboring polymer chains.

In another embodiment, the polymer substrate may be selected to be a polymer that is at least partially degradable by UV radiation. In one embodiment, the UV degradable polymer is polycarbonate. It has been found that polycarbonate is capable of absorbing electromagnetic ("EM") radiation in the wavelength of from about 200 nm to about 400 nm, with particularly strong absorbance of EM radiation below 300 nm. Advantageously, free radicals generated from the photodegradation of the polymer substrate may participate in the polymerization reaction within the curable resin during the curing step, thus allowing the polymer substrate to form covalent bonds with the polymerizing resin. Advantageously, the formation of covalent bonds greatly enhances the adhesion between the polycarbonate and the curing resin.

Further advantageously, as polycarbonate is comprised of a random network of polymer chains with randomly oriented aromatic groups, it is able to more efficiently absorb UV radiation for generating radicals.

Specifically, the random orientation of aromatic groups in polycarbonate causes more efficient absorption of randomly polarized UV photons, allowing for uniform dispersion of free radicals capable of generating photodegradative reactions throughout the polycarbonate substrate. In contrast, crystalline polymers such as PET exhibit preferential orientation of aromatic groups in their crystalline regions, which can only absorb UV photons of a certain polarization, thereby reducing absorption efficiency.

In another embodiment, the amorphous polymer substrate may be selected to be one having aromatic groups that demonstrate strong absorbance of the UV photons, particularly in the range of 280 nm to 350 nm. Advantageously, after absorption, polymer chain scissioning follows with the formation of free radicals at the ends of the scissioned chains. These radicals may polymer with the resin molecules and form a cross-linked, covalently bonded, and heavily entangled network at the resin / polymer substrate interface.

In the disclosed method, the contacting step (a) and curing step (b) may be performed concurrently under pressure. In one embodiment, the pressure for imprinting and UV curing may be from about 600 kPa to about 1,000 kPa. In one embodiment, the mold and the resin supported on the amorphous substrate may be pressed together under pressure of about 800 kPa, for example, by means of pressure rollers. Performing the contacting step under pressure may also be useful in squeezing out air bubbles between the mold and the resin and may also work to partially planarize the resin, thus spreading the resin more uniformly across the polymer substrate.

In the disclosed method, the mold may be selected to be composed of a reflective material. In one embodiment,

the selected reflective material is one capable of reflecting at least 80% of normal-incident radiation below 400 nm in wavelength.

5 A reflective mold is useful because UV photons which have passed through the resin/polymer substrate assembly without being absorbed at the resin/polymer interface can be reflected through the resin/polymer substrate assembly again. This increases the likelihood of photons being absorbed by the polymer substrate and consequently
10 increase the number of free radicals generated. The method may further comprise using a UV source that is installed with a reflector to enable multiple reflections through the resin / polymer substrate interface. This would further enhance radical formation and further
15 improve the adhesion at the resin / polymer substrate interface.

The reflective material may comprise a transition metal. In one embodiment, the mold used in the disclosed method may comprise Nickel (Ni). In one embodiment, the
20 mold may consist substantially of Ni. Advantageously, nickel molds are tough and resistant to defect accumulation. Nickel molds can also be flexible when provided in thin sheet form. Additionally, Ni is a highly reflective material and which would facilitate UV
25 absorption by the resin / polymer substrate assembly.

In another embodiment, the reflective material may comprise of alloys of Ni, e.g., Ni-Co alloys.

The UV curable resin may comprise a curable polymer precursor that is capable of forming cross-linkages upon
30 exposure to UV radiation. The polymer precursor may be selected from the group consisting of vinyl precursors, acrylic precursors, epoxy precursors, epoxysilicone, polydimethylsilicone, photocurable silsesquioxane or

mixtures thereof. The polymer precursor may be in liquid form, having a viscosity of less than 15 Pa.s.

The UV curable resin may be selected to be one where it is capable of diffusing into the polymer substrate network and to form polymerization sites within the polymer substrate. Accordingly, the polymer precursor should be selected to be capable of forming entanglements with the polymer substrate and covalent bonds with the polymer substrate. The polymer precursors may be of low molecular weight to facilitate diffusion into the polymer substrate. In one embodiment, the polymer precursors have a molecular weight of less than 10,000.

The polymer precursors may be provided with photoinitiators that are capable of starting polymerization reactions between the polymer precursors as well as to attack the unstable bonds in the polymer substrate to form radical polymerization sites on the polymer substrate.

In one embodiment, the mold is substantially free of an anti-stick coating. That is, the disclosed method may exclude a step of applying an anti-stick coating to the mold.

In one embodiment, the polymer substrate is substantially free of an adhesion promoter. That is, the disclosed method may also exclude a step of applying an adhesion promoter to the polymer substrate.

The defined surface pattern on the mold may be configured to impart micro-sized or nano-sized structures on the imprinted resin. The micro-sized or nano-sized structures may be substantially comprised of polymerized resin that has been cured by UV radiation.

During the curing step (b), UV radiation having a wavelength of from about 200 nm to 400 nm may be directed at the mold and/or the resin supported on the amorphous polymer substrate. In one embodiment, the UV radiation
5 may have a wavelength of from about 200 nm to 350 nm, from about 200 nm to about 300 nm, or from 200 nm to about 250 nm. In one embodiment, the UV radiation has a wavelength range of from 280 nm to 350 nm. The curing step (b) may comprise exposing the resin to UV radiation
10 while it is in contact with the mold. The curing step (b) may also comprise irradiating parts of the resin that has already undergone compression by the mold. The UV radiation employed during curing step (b) may comprise an energy range of from about 3.0 eV to about 6.2 eV. In
15 another embodiment, the UV radiation may have an energy range of about 2.5 eV to about 5.0 eV (or about 200 - 500 nm)

The method as described herein may be performed continuously, wherein a moving belt (or "web") of polymer
20 substrate (with resin deposited thereon) is continuously being fed to the mold for imprinting and thereafter decoupled from the mold after an imprint is formed. The continuous method may be capable of fabricating micro- or nano-sized features at a speed of 1 mms^{-1} .

25 The moving belt of polymer substrate may be fed towards the mold at a speed between 0.1 ms^{-1} to 10 ms^{-1} . As can be appreciated, this is just an exemplary range and the actual speed can be varied depending on the size of the apparatus, the circumference of the mold used, the
30 intended output speed of the imprinted structures.

In one embodiment, curing step (b) may be undertaken for a time period ranging from 2 to 3 minutes to 1 second or lesser. In one embodiment, the curing duration may be

selected from 200s, 190s, 180s, 170s, 160s, 150s, 140s, 130s, 120s, 110s, 100s, 90s, 80s, 70s, 60s, 50s, 40s, 30s, 20s, 10s, 5s, 1s, 0.5s or lesser. The curing duration may be dependent on the speed at which the polymer substrate and resin are fed towards the mold.

In another embodiment, the resin may be dispensed onto the surface of the mold and later contacted with the polymer substrate when the mold is contacted with the substrate.

The disclosed method may further comprise a step of depositing the UV curable resin on the amorphous polymer substrate prior to the contacting step (a). This deposition step may comprise depositing the UV curable polymer precursor on the polymer substrate. The deposition step may comprise ink jetting, spraying or contacting the moving belt with rollers that have been immersed in the polymer precursor solution.

Exemplary, non-limiting embodiments of an apparatus for forming a structure according to the second aspect will now be disclosed.

In one embodiment, there is provided an apparatus for forming a structure on a resin substrate, comprising: (a) a moveable mold having a defined surface pattern, said mold being configured to contact a layer of UV curable resin supported on an amorphous, photodegradable polymer substrate layer, said resin being movable relative to said mold; (b) compressing means configured to engage said mold to thereby sandwich said resin and polymer substrate layer therebetween, thereby forming a structure on said resin; (c) an UV source arranged to irradiate the UV curable resin; and (d) a decoupling means to decouple the cured resin from the mold.

In one embodiment, the apparatus may be suited to perform roll-to-roll nano-imprinting.

The amorphous polymer substrate may be as such described above.

5 The moveable mold may be a rotatable mold. The rotatable mold may be configured to move the resin along its circumference as it rotates. In one embodiment, the mold is a rotatably-mounted roller that is configured to engage the resin supported on the amorphous substrate to
10 thereby move the resin / polymer substrate assembly along its circumference via rotary motion.

 The decoupling means may comprise one or more demolding rollers. The demolding rollers may be configured to engage the polymer substrate layer to
15 thereby decouple the resin from the mold.

 The mold may comprise a reflective material capable of reflecting at least 80% of normal-incident radiation having wavelengths of less than 400 nm. The reflective material may be a transition metal. In one embodiment,
20 the mold comprises Nickel.

 The compressing means of the disclosed apparatus may comprise rollers configured to engage the mold to apply a compressive force on said resin. The mold and mechanical rollers may be arranged to sandwich the resin and polymer
25 substrate assembly therebetween, to thereby apply a compressive force to the assembly. The mold may also comprise a patterned surface that is brought into contact with the resin in order to impart an imprint on the resin surface. The applied force may be sufficient to imprint
30 the resin and thereby form micro-scale or nano-scale structures on the resin surface.

The UV source may be selected from a fluorescent lamp, arc lamp, gas-discharge lamp, light-emitting diode array, laser or a combination of two or more of the above. In one embodiment, the UV source may be a mercury
5 short-arc lamp with a rated power of at least 100 W.

In one embodiment, the UV source may be disposed within the mold such that the UV radiation would be transmitted through the resin before passing through the polymer substrate.

10 In another embodiment, the UV source may be located external to the mold in order to irradiate the mold, resin and polymer substrate at an incident angle of from 0° to about 90°. More than one external UV source may be provided to provide UV radiation at various incident
15 angles to the resin / polymer substrate assembly. The UV source may be arranged to irradiate the resin / polymer substrate assembly that is being compressed or has been compressed by the pressurizing means. The UV source may be configured to emit UV radiation having a wavelength of
20 about 200 nm to about 400 nm.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed
25 embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

30 Fig. 1 is a schematic diagram of an apparatus for performing roll-to-roll nanoimprinting according to an embodiment.

Fig. 2 is a close-up schematic diagram of the apparatus of Fig. 1.

Fig. 3 is a graph showing the UV-Vis emission spectra of two UV sources that can be used in the apparatus shown in Fig. 1.

Fig. 4 is a representative transmission spectra for a 100 μm thick sheet of polycarbonate.

Fig. 5a is a schematic diagram of a manufacturing process for fabricating UV cured polymer working molds. Fig. 5b is a method for forming bit patterned hard disk media.

Fig. 6 is a scanning electron microscope (SEM) image at 30,000 x magnification of an imprinted polycarbonate substrate web having 50 nm linewidth data tracks made according to Example 1 below.

Fig. 7 is an angled cross-sectional SEM image at 30,000 x magnification of the imprinted polycarbonate substrate web of Fig. 6.

Fig. 8a is a SEM image at 2,700 x magnification of DVD tracks replicated in UV curable resin on a polycarbonate web made according to Example 2 below. Fig. 8b is the cross-section view of the resin of Fig. 8a.

Detailed Description of Drawings

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Referring to Fig. 1, there is shown a schematic diagram of an apparatus 100 for forming a structure on a resin substrate. The apparatus 100 is suitable for performing roll-to-roll nanoimprinting. The apparatus comprises: (a) a movable mold 2 having a defined surface pattern 4, the mold 2 being configured to contact a layer

of UV curable resin 6 supported on an amorphous, photodegradable polymer substrate layer 8, said resin 6 being movable relative to the mold 2; (b) compressing means in the form of pressure rollers 10 configured to engage said mold 2 to thereby sandwich said resin 6 and polymer substrate layer 8 therebetween, thereby forming an imprint 12 on said resin 6; (c) an UV source 14 arranged to irradiate the UV curable resin 6 in contact with said mold 2 to thereby cure the UV curable resin 6; and (d) a decoupling means in the form of a demolding roller 16 configured to decouple the cured resin 18 from the mold 2.

The UV curable resin 6 is dispensed onto the polymer substrate layer 8 by a dispense unit 20 and is smoothened out by a doctor blade 22 such that the height or thickness of the UV curable resin 6 on the polymer substrate layer 8 is substantially consistent throughout the length of the UV curable resin 6.

Fig. 2 is a close-up schematic diagram of the apparatus of Fig. 1. Here, like features are defined by like reference numerals but with a prime symbol (''). Here, the mold 2' is made up of a highly reflective metal such as nickel and the UV source 14' includes a reflector. By having a reflective nickel mold 2' and a UV source reflector 14', multiple reflections can occur through the interface 24 between the UV curable resin 6' and the polymer substrate layer 8'. UV photons can be reflected through the polymer substrate layer 8' multiple times, which will assist in increasing the absorption of UV photons at the interface 24. Free radicals generated from photodegradation of the polymer substrate layer 8' can participate in the polymerization reaction within the UV curable resin 6', allowing the polymer in the polymer

substrate layer 8' to form covalent bonds with the polymerizing UV curable resin 6' so as to greatly enhance adhesion between the polymer substrate layer 8' and the UV curable resin 6' at the interface 24.

5 In an alternate embodiment (not shown), multiple UV sources 14' can be oriented almost parallel to the polymer substrate layer 8' so as to increase the propagation distance through the polymer substrate layer 8'.

10 The UV source 14 used in Fig. 1 may be a mercury vapour arc lamp having one of the UV-Vis emission spectra as shown in Fig. 3. Fig. 3 shows the UV-Vis emission spectra of a S2000 mercury arc lamp and a S1000 mercury arc lamp.

15 As shown, there is a strong emission peak from about 280 nm to 350 nm. This emission is sufficiently energetic to excite the phenyl groups of the amorphous polymer such as polycarbonate in the polymer substrate layer. The excitation of the phenyl groups in the
20 polycarbonate contributes to the better adhesion characteristics of the polycarbonate. This is demonstrated in Fig. 4 which shows the representative transmission spectrum for a 100 μ m thick sheet of polycarbonate. As can be seen Fig. 4, the polycarbonate
25 sheet begins to absorb at around 400 nm wavelength light and strongly absorbs below 300 nm wavelength light. The aromatic groups in polycarbonate are able to absorb light or UV photons efficiently in the 250 to 350 nm regime. Due to the random orientation of the aromatic groups
30 within the polycarbonate, more efficient absorption of the randomly polarized UV photons can take place to allow for uniform dispersion of free radical generating photodegradative reactions to take place. Following

absorption, polymer chain scissioning often follows, along with the formation of free radicals at the ends of the scissioned chains. These free radicals can start a polymerization reaction with the resin monomers to form a cross-linked, covalently bound, and heavily entangled network at the polymer/resin interface. Hence, it is preferable for the amorphous polymer to be one which is strongly aromatic so that it can be used in conjunction with a UV source with strong emission on the absorption edge of the polymer.

Fig. 5a is a schematic diagram of a manufacturing process 200 for fabricating UV cured polymer working molds using the apparatus of Fig. 1. Specifically, Fig. 5a shows one possible application of a cured resin formed from the disclosed method or apparatus. In particular, the cured resin is hardy enough such that it may be used as a mold itself for subsequent imprinting processes.

An exemplary subsequent imprinting process using the cured resin as a mold is shown in Fig. 5b, wherein a working mold (made from Fig. 5a) is used to form an imprint on a layer of photoresist which is supported on a magnetic layer (CoCrPt) and an aluminum blank base layer. This form of imprinting is typically performed during the manufacture a hard disk platter. The batch process shown in Fig. 5b may be a thermal hot embossing method or another UV nanoimprint process with a UV curable resin.

Advantageously, the disclosed method and apparatus may be used to mass-produce disposable polymer molds via the roll-to-roll process. These disposable molds can be used to perform subsequent lithography in batch mode lithography (thermal or UV nanoimprint). Importantly, as these molds may be produced at a sufficiently low cost,

they may be discarded after use or recycled for future use.

Examples

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Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

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Example 1

The apparatus of Fig. 1 was used in this example to form imprints of 50 nm linewidth data tracks on a 200 μ m thick polycarbonate substrate layer. The polycarbonate was obtained from Solves Innovative Technology Pte Ltd, Singapore. The polycarbonate substrate is formed through a melt extrusion process to form a reel of plastic web, which is then fed to the apparatus of Fig. 1 as polymer substrate 8.

The apparatus 100 comprises a movable mold 2 in the form of a nickel mold having a defined surface pattern 4 in the form of sub-50 nm data tracks. The nickel mold was fabricated by replicating a 2.5" hard disk master mold containing the sub-50 nm data tracks onto the nickel mold by electroplating. The nickel mold was fabricated to be approximately 100 μ m thick so that it remains flexible and can be mounted onto a cylindrical roller.

Several commercially available UV acrylic resins may be used as the UV curable resin 6 as all these acrylic resins exhibit similar behavior. Exemplary commercial resins are procured under the Trademarks YNIL-R2-1, from Young Chang Chemical Co., mr-UVCur21SF from Micro Resist

Technology GmbH, or MAR-02 from Beulah Company. The UV curable resin 6 was dispensed by the dispense unit 20 onto the amorphous polymer substrate layer 8 made up of polycarbonate having a thickness of 200 μm and the height of the UV curable resin 6 on the polycarbonate layer was made consistent by the doctor blade 22. It is to be noted that the nickel mold was bare with no anti-stick coating and the polycarbonate layer was also bare with no adhesion promoter. Oxygen plasma treatment was not carried out on the polycarbonate. The thickness of the dispensed UV curable resin 6 varies with a number of factors, e.g., the resin viscosity, dispensing speed, movement speed of the polymer substrate 8 towards mold 2. Typically, the thickness of the dispensed UV curable resin 6 is about 200 nm to 2 microns.

As the UV curable resin 6 and polycarbonate layer moved along the circumference of the nickel mold, the nickel mold, UV curable resin 6 and polycarbonate layer were sandwiched together under a pressure of about 400 kPa by the pressure rollers 10. The pressure rollers 10 work to squeeze out air bubbles from between the nickel mold and the UV curable resin 6 and also work to partially planarize the UV curable resin 6 so as to spread the UV curable resin 6 more uniformly across the polycarbonate layer.

After passing through the pressure rollers 10, the UV curable resin 6 is cured by an UV source 14 in the form of a 100 Watt UV lamp in which the UV light is guided by fiber optic cables to illuminate the UV curable resin. The fiber optic light guides prevent excessive heating of the UV curable resin 6 and the polycarbonate layer by separating the UV lamp from the UV curable resin 6 and the polycarbonate layer. The curing of the UV

curable resin takes place at room temperature. The UV curable resin solidified during curing through radical polymerization to form the cured resin 18. The cured resin 18 is then decoupled (demolded) from the nickel mold after passing through the decoupling means in the form of a demolding roller 16. The cured resin 18 had imprints on its surface which were complementary to the surface pattern 4 of the nickel mold.

Alternatively, the UV curable resin 6 can be deposited directly onto the nickel mold instead of being dispensed onto the polycarbonate layer.

The rotation of the Ni mold 2 corresponds to the speed which the amorphous substrate layer 8 is being fed towards the mold. In this particular embodiment, the speed may be varied from 0.1 meters per minute to about 10 meters per minute. It can be appreciated that the speed is dependent on other factors like size of the apparatus and circumference of the mold and is not intended to form a limitation on the present disclosure.

The duration of the curing step may be from about 2 to 3 minutes to less than 1 second, depending on the speed of rotation of the mold.

Fig. 6 shows the imprints on the polycarbonate substrate layer. The imprints were of 50 nm linewidth, 100 nm pitch, which were complementary to the surface pattern on the nickel mold. Hence, the surface pattern on the nickel mold could be replicated on the cured resin 18 effectively.

Fig. 7 is an angled cross-sectional SEM image at 30,000 x magnification of the imprinted polycarbonate substrate layer of Fig. 6. The residual layer, which refers to the layer of cured resin beneath the imprinted features, has a thickness of slightly less than 1 μm

(approximately 600 nm to 800 nm thick, with $\pm$ 100 nm variation across the sample area).

From Fig. 7, some particle defects and defects shaped like small holes are visible. The particles were likely deposited due to handling outside the cleanroom while the small holes shaped defects were likely due to trapped air bubbles that did not fully dissolve during the imprint process. These defects could be dealt with by introducing a helium shroud just prior to the UV curable resin making contact with the nickel mold. The helium bubbles will dissolve much more easily into the resin leaving a defect-free result. These images demonstrate the feasibility of fabricating working molds.

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Example 2

The apparatus of Fig. 1 based on the method described in Example 1 was used to form an imprint pattern of about 200 nm to 1 μ m long concentric dots on a UV curable resin supported by a polycarbonate layer. The same UV curable resin, polycarbonate and imprinting conditions are used in this Example. The imprinted resin can be used as a DVD or DVD-ROMs. Fig. 8a is a SEM image at 2,700 x magnification of the DVD tracks replicated in the UV curable resin on a polycarbonate layer. Fig. 8b is the cross-section view of the resin of Fig. 8a showing the residual layer thickness of the resin as well as the relief profile of the imprinted dots.

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Applications

In the disclosed method and apparatus, the cured resin may be adhered to the polymer layer and may be demolded easily from the mold. Due to its enhanced adhesion to the polymer layer, the cured resin may not peel off easily from the polymer layer. Due to the ease of demolding from the mold, the mold can be continuously used without having any operational downtimes associated with peeling off the resin from the mold, unlike in prior art imprinting.

The disclosed method and apparatus may not require any treatment of the mold and hence, may not require the application of an anti-stick coating onto the mold. Further, it may not be necessary to apply an adhesion promoter film between the UV curable resin and polymer substrate. Hence, the cost of imprinting can be reduced since it is not necessary to factor in the costs of the anti-stick coating or adhesion promoter film or both. The improved economics will make a big difference in terms of industrial adoption of the present method and apparatus, particularly in applications such as patterned media, optical films and coatings (anti-reflection particularly), and biological applications (anti-fouling surfaces).

The disclosed method and apparatus may not require the use of molds composed of fluoropolymer material, which are known to be soft and thus suffer from creep resulting from cyclic loading over thousands of imprint cycles.

The disclosed method and apparatus can be used to make working molds for subsequent lithography. UV crosslinked resins are sufficiently hard and stiff due to its large Young's modulus and hence can be used as a mold material, in particular, as a rigid patterned surface

layer for imprinting a resist layer on another substrate. Bonding this crosslinked resin layer with a flexible and conformal polymer substrate layer creates the best of both worlds, that is, rigidity at the interface with the
5 resist layer to be patterned and overall conformality due to the polymer layer. The latter can be adjusted in thickness to be more or less stiff as required for the given application. Due to the enhanced adhesion between the polymer substrate layer and the UV resin, working
10 molds with adequate cohesive strength to survive subsequent lithographic operations can be manufactured.

The disclosed method and apparatus can be used to manufacture hard disk as well as other patterned media formats such as DVD.

15 The disclosed method and apparatus can be used to form optical coatings and films, optical components (photonic crystals, waveguides, etc), wire grid polarizers, displays, biological applications (anti-fouling surfaces), and chemistry (supported catalysis).

20 It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such
25 modifications and adaptations come within the scope of the appended claims.

Claims

1. A method for forming a structure on a resin substrate, the method comprising the steps of:
- 5 (a) contacting a mold having a defined surface pattern with an ultra-violet (UV) curable resin substrate supported on an amorphous, photodegradable polymer substrate, said defined surface pattern forming a structure on the UV curable resin substrate;
- 10 (b) curing the UV curable resin supported on the amorphous polymer substrate by exposing said UV curable resin to UV radiation; and
- (c) separating the cured resin from the mold.
- 15 2. The method according to claim 1, where said structure is an imprint.
3. The method according to claim 2, wherein said imprint is a nanoimprint.
- 20 4. The method according to any one of claims 1 to 3, wherein said photodegradable polymer substrate is capable of generating free radicals upon absorbing UV radiation.
- 25 5. The method according to any one of claims 1 to 4, wherein said polymer substrate comprises polycarbonate.

6. The method according to any preceding claim, wherein said contacting step (a) and curing step (b) is performed concurrently under pressure.
- 5 7. The method according to claim 6, wherein said pressure may be from 600 kPa to 1,000 kPa.
8. The method according to any preceding claim, wherein said mold is selected to be composed of a reflective
10 material.
9. The method according to claim 8, wherein said reflective material comprises a transition metal.
- 15 10. The method according to any one of the preceding claims, wherein said mold is substantially free of an anti-stick coating.
11. The method according to any one of the preceding
20 claims, wherein said polymer substrate is substantially free of an adhesion promoter.
12. The method according to any one of the preceding
25 claims, wherein the UV radiation is selected to have a wavelength of from 200 nm to 400 nm.
13. The method according to any one of the preceding claims, wherein said polymer substrate comprises aromatic groups selected from the group consisting of: phenyl
30 groups, pyridine groups, pyrazine groups, imidazole

groups, thiophene groups, pyrrole groups, furan groups, benzannulated analogs and mixtures thereof.

14. The method according to claim 13, wherein said
5 aromatic group is selected to absorb UV photons having a wavelength of 280 nm to 350 nm.

15. The method according to any one of the preceding claims, wherein curing step (b) comprises exposing said
10 resin to UV radiation when the resin is contacted with said mold.

16. An apparatus for forming a structure on a resin substrate, comprising:

15 (a) a moveable mold having a defined surface pattern, said mold being configured to contact a layer of UV curable resin supported on an amorphous, photodegradable polymer substrate layer, said resin being movable relative to said mold;

20 (b) compressing means configured to engage said mold to thereby sandwich said resin and polymer substrate layer therebetween, thereby forming a structure on said resin;

(c) an UV source arranged to irradiate the UV
25 curable resin; and

(d) a decoupling means to decouple the cured resin from the mold.

17. The apparatus of claim 16, wherein said moveable
30 mold is a rotatable mold.

18. The apparatus of claim 17, wherein said rotatable mold is configured to move said resin along its circumference.
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19. The apparatus of any one of claims 16 to 18, wherein said decoupling means comprises one or more demolding rollers.
- 10 20. The apparatus of claim 19, wherein said demolding roller is configured to engage the polymer substrate layer to thereby decouple the resin from the mold.
- 15 21. The apparatus of any one of claims 16 to 20, wherein said polymer substrate layer comprises polycarbonate.
22. The apparatus of any one of claims 16 to 21, wherein said mold comprises a reflective material.
- 20 23. The apparatus of claim 22, wherein said reflective material comprises a transition metal.
- 25 24. The apparatus of any one of claims 16 to 23, wherein said compressing means comprise rollers configured to engage said mold to apply a compressive force on said resin.
- 30 25. The apparatus of any one of claims 16 to 24, wherein said UV source is configured to emit UV radiation having a wavelength of about 200 nm to about 400 nm.

26. A composite comprising a cured resin supported on an amorphous polymer substrate layer, said composite being produced by a method as claimed in any one of claims 1 to 5 15, or by an apparatus as claimed in any one of claims 16 to 25.