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(54) **Title:** SEAMLESS ROLL-TO-ROLL NANO-IMPRINTING

(57) **Abstract:** A seamless shim for roll-to-roll or roll-to-plate nanoimprint lithography may be obtained by (a) providing a relief master, which is a nanostructured surface comprising a specific area with a pattern, which does not contain any optically detectable seam, (b) providing a cylindrical substrate whose outer surface is smaller than the specific surface area on the relief master, (c) applying a radiation curable coating on the nanostructured surface and/or the cylindrical substrate to a wet film thickness ranging from 50 nm to 1.8 micrometer, preferably up to 1.0 micrometer, (d) transferring the pattern of the specific surface area on the relief master to the cylindrical substrate by applying electromagnetic radiation or heat to the curable coating in the contact area between the nanostructured surface of the relief master and the cylindrical substrate's surface, characterized in that the contact area is moved over a length, which exceeds the cylindrical substrate's circumference, and the dosage of electromagnetic radiation applied at one contact does not effect full cure of the coating. The shim thus obtained allows for the cost efficient preparation of large scaled nanopatterned substrates, e.g. transparent films, without visually detectable defects.



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Seamless Roll-to-Roll Nano-Imprinting

Description

- 5 The present invention provides a method for the preparation of a seamless nanostructured cylindrical surface (seamless shim) by transfer from a suitable relief plate into a thin coating film on the cylindrical surface, to a cylindrical shim obtainable by said method, and to a method for seamless nanoimprinting using said shim.
- 10 Nano imprint lithography (NIL) fabrication methods have use in a wide variety of technological applications, including nano-scale fabrication for solar cells, LEDs, integrated circuits, MEMs devices, information displays, and more.
- 15 Roll-to-roll and roll-to-plate lithography methods typically use cylindrically shaped masks (e.g. molds, stamps, photomasks, etc.) to transfer desired patterns onto rigid or flexible substrates. A desired pattern can be transferred onto a substrate using, for example, imprinting methods (e.g. nanoimprint lithography (NIL)), the selective transfer of materials (e.g. micro- or nano-contact printing, decal transfer lithography, etc.), or exposure methods (e.g. optical contact lithography, near field lithography, etc.). Some
- 20 types of such cylindrical masks use polymers or metals as patterned layers laminated on a cylinder's outer surface. Unfortunately, lamination of a layer onto a cylindrical surface creates a seam line where the edges of the lamination layer meet. This can result in an undesirable image feature at the seam when the pattern is repeatedly transferred to a substrate by using the cylindrical mask.
- 25 Patterned substrates and structured coatings have attractive properties for a variety of applications, including architectural glass, information displays, solar panels, and more. For example, nanostructured coatings can provide desirable antireflection characteristics for architectural glass; improvements in efficiency can be achieved for current applications in areas such as solar cells and LEDs, and in next generation data storage
- 30 devices.
- 35 Current methods of patterning substrates, including methods such as direct laser writing or electron beam lithography, photolithography, interference lithography, and other methods, are often too costly for practical use in the manufacture of patterned substrates or structured coatings in applications requiring larger areas, especially those having areas of 200 cm² or more.
- 40 As such, there is a need in the art for large area patterned layers and low cost methods of manufacturing the same. It is within this context, that a need for the present invention arises.

Pressing a surface relief into a substrate under heat and pressure (embossing, e.g. thermal NIL) or pressing a surface relief into a radiation curable liquid layer and applying radiation for hardening the liquid (casting, e.g. UV NIL), results in a transfer or replication of the surface relief on the substrate. A surface relief is a structure, image, or representation of a three-dimensional (3D) relief, holographic image, diffractive pattern, non-diffractive pattern, or surface texture. A substrate is a material that can receive a surface relief, such as a continuous web of film(s), foil(s), coated film(s), coated foil(s), or coated paper or board, or glass or coated glass, or metal or coated metal. The substrate may be untreated or pre-treated, e.g. by plasma, metalizing, vacuum coating, atomic layer deposition, or the like as desired. The original surface relief typically consists of glass, silicon wafer, metal, or plastic material with a structured surface, also known as metal, glass, silicon or plastic shim (hereafter "shim"). The shim is used to transfer the surface relief onto the substrate.

Typically, a cylindrical shim is created by wrapping a structured flat sheet around a large cylindrical roller (hereafter "cylindrical base"), and attaching (mounting) it using adhesives and/or fasteners. The cylindrical base, with the shim mounted thereon, is mounted into an embossing or casting or coating (or printing) assembly, wherein an impression or replication of the surface relief is transferred from the shim onto the substrate during the embossing or casting or coating (or printing) process.

The structured substrate thus resulting is generally accumulated on large rolls, which can be cut into smaller rolls or sheets as desired for a variety of uses such as antireflection films for solar cells, outcoupling films for LED displays, integrated circuits, microelectromechanical systems (MEMs devices), optical films e.g. for information displays, and more. The roll or sheets of embossed or cast substrate also can be printed, coated, metalized and/or laminated to plastic films, glass, metal or other surfaces to create functional surfaces or films with distinct patterns, textures, angle dependent light interaction properties, or images.

While using shims on cylindrical bases is an effective method in producing embossed or cast substrates, there are currently several disadvantages to using these shims. First, shims are time consuming and expensive to prepare. In addition, wrapping a flat shim around a cylindrical base leaves a void or line where the side edges of the shim meet. Furthermore in some cases, there may be more than one flat shim required to cover the surface of the cylindrical base. When more than one shim is present, not only is a joint line present where the ends of the shims meet when encircling the cylindrical base, but there are also join lines evident where the two or more shims abut one another along the width of the cylindrical base. Consequentially, with each revolution of the cylindrical base, an impression of the join line(s) is transferred into the substrate along with the surface relief. These join lines are often referred to as repeats, interruptions, or seams (hereafter collectively referred to

as “seam(s)”) that are visible on the substrate. With multiple shims per cylindrical base, there can be an increasing number of seams. The multiple seams create a “parquet” effect on the embossed or cast substrate, not unlike multiple tiles on a floor.

- 5 Seams present in the final substrate obtained e.g. by such embossing, casting or coating method are difficult to eliminate in the final product. Seams are particularly noticeable in continuous transparent or translucent substrates such as optical films on glass or plastic and are highly undesirable.

10 Therefore in order to ensure that seams do not appear as flaws or defects in an end product, when cutting the embossed or cast substrate, downstream converters are forced to work around the seams which inevitably creates a great deal of material scrap and complicates the processing, or it is even impossible to eliminate the seams, e.g. in case that the surface of the final product is larger than the surface area of the cylindrical base.

15 Efforts have been made to make seamless shims by imprinting the surface relief directly onto a photoresist material on the cylindrical base itself (WO2013/165915, EP1649969, CN103448351, WO2006/078918). However these proposed processes only shift the problem of generating a seamless shim structure to the employed imprinting master template. Another method involves writing or etching a surface relief directly
20 onto the cylindrical base e.g. by direct laser writing or electron beam writing (EP1837202, WO2005/053115). However direct forming or etching of nanostructures on a cylindrical base is very time consuming and requires expensive equipment. Another method proposes the use of a stretchable sleeve with a seamless surface relief
25 which is slid over the cylindrical base (WO2011/097483, WO2002/20255). However, seamless nanostructured surface reliefs on a stretchable sleeve are extremely difficult to prepare. Yet another method proposes transferring the nanostructured relief from a plate to a large cylinder via a small transfer cylinder (CN103399460), but remains silent on how seams thus can be avoided.

30 Accordingly, there is a need for cylindrical base with surface relief structures having no seams (seamless shim). Desirably, such seamless shim is formed using a fast and cost efficient process resulting in a precisely controlled and durable surface relief structure. In addition to fabricating a mask (shim) having a seamless nanostructured layer, it
35 would be desirable to fabricate layers with “smooth” surfaces (i.e. surfaces, which do not contain any structures other than those desired for subsequent replication steps) that are durable and uniform for use in subsequent lithography fabrication methods.

40 It is an object of the present invention to provide a process for making a relief pattern on a cylindrical substrate (i.e. a process for making a cylindrical shim) without optically detectable line (seam). The term „optically detectable“ herein generally denotes a length of a discontinuity (incoherence in the pattern transferred onto the cylindrical

shim), which is of about the same length as the pattern's period length in the direction parallel to the shim's circumference, and thus does not contain a seam, which would be visually detectable. Importantly, the process of the invention also avoids discontinuities in direction perpendicular to the shim's circumference (i.e. no visual "step" on the surface of the cylindrical substrate). Avoiding such discontinuities is important to reduce or remove undesired light scattering, which could be visible or detectable by the naked eye, and thus is in the following noted as "optically seamless" or "without optically detectable seam". Particularly, the first aspect of the present invention thus relates to a cylindrical substrate (cylindrical shim) having a surface relief embossed or cast or etched therein, which does not contain such optically detectable seam and may be used as a print roll e.g. for nanoimprint lithography, and a method for making the same.

According to a first aspect of the present invention, the object is solved by a process for preparing a cylindrical substrate, which comprises:

- (a) providing a relief master, which is a nanostructured surface comprising a specific area, which does not contain any optically detectable seam and is generally characterized by the product of a length l and a width w standing rectangular to each other (i.e. $l \cdot w$),
- (b) providing a cylindrical substrate whose circumference is smaller than the length l of the relief master (or even its outer surface is smaller than the specific surface area on the relief master), i.e. typically $d \cdot \pi < l$ (with d standing for the cylinder's diameter and $d \cdot \pi$ standing for the cylindrical substrate's circumference),
- (c) applying a radiation curable coating on the nanostructured surface and/or the cylindrical substrate,
- (d) transferring the pattern of the specific surface area on the relief master to the cylindrical substrate by applying electromagnetic radiation to the curable coating in the contact area between the nanostructured surface of the relief master and the cylindrical substrate's surface, characterized in that the contact area is moved over a length, which exceeds the cylindrical substrate's circumference, and the dosage of electromagnetic radiation applied at one contact does not effect full cure of the coating.

The shim thus obtained allows for the cost efficient preparation of large scaled nano-patterned substrates, e.g. transparent films, without visually detectable defects.

- Figure 1 shows an example of the present process at the end of the transfer step (d) for the case, wherein the pattern is transferred from the flat nanostructured surface of the relief master (101) onto a rotated and cylindrical substrate coated with a liquid curable film (120, drawn in white; arrow 105 indicating the rotational direction) while being irradiated with UV light through the relief master (101): The relief master's nanostructured surface (101) transfers the pattern onto the UV coating (110, 120) on the surface of the rotating cylindrical substrate (100) while being irradiated with UV light through the nanostructured surface (101). Irradiation converts the liquid coating (120, white)

into a solid gel (110, grey). At the completion of one round, the remaining uncured section of the coating (120, white) meets the section already partly cured (110, grey) and patterned at the beginning of step (d); due to the gel-like state of the coating (110, grey; see more details described for step d further below), the second imprint by the relief master reshapes the already patterned coating again with transfer of the pattern, such that any discontinuity (seam) in the final pattern on the cylinder (i.e. after removal of the relief master) may arise only from the renewed patterning, in particular the height difference ("step", typically in the junction of previously uncured (120, white) and previously cured (110, grey) coating) remains considerably smaller than the original coating thickness, i.e. generally below 500 nm, preferably below 300 nm, especially below 100 nm; and the only discontinuity resulting is of the magnitude of the original pattern or less.

Preferred conditions for steps (a) and (b):

Preferably, the nanostructured surface (relief master) employed in the above step (a) is substantially flat; it may be based on a plate (e.g. flat glass or quartz) or may be flexible (e.g. polymer film). The material of the relief master preferably provides sufficient transparency for UV light in order to apply the necessary dosage of UV light to the NIL material during step (d).

The length l of the relief master advantageously is at least 2% longer than the circumference of the cylindrical substrate (hereinafter also recalled as cylinder), and may suffice for several rotations of the cylinder. In one variant of the present process, the relief master thus is a flat sheet of a certain length l , which may be from the range $1.02 d \cdot \pi$ to $5 d \cdot \pi$. In another variant of the present process, the relief master thus is a film, which is contacted with the cylindrical substrate in the manner of a rotary press. In both cases, the contact area typically moves over 1.02 up to 5 cylinder rotations or more.

The pattern of the nanostructures may comprise rectangular, trapezoidal, triangular and/or round shapes, it may be parquet-like or preferably in form of gridlines. Preferred are rectangular structures. The ratio of peak surface : total surface of the relief master (duty cycle) often is from the range 0.1 to about 0.9. Overlays of different patterns, such as crossed gridlines, are possible as well. The nanostructured surface thus comprises trenches and ridges or peaks, usually as part of a repeating pattern. Period of the nanostructures (i.e. the distance, or average distance, between adjacent peaks in direction parallel to the cylinder's circumference; on relief master as well as in the structures transferred to the cylinder) is typically from the range 0.1 to 10 micrometer; depth of the structures is typically from the range 50 to 1000 nm, especially 100 to 800 nm. The pattern generally does not comprise microlenses, since this generally would

require larger shapes (i.e. periods of about 10 to 100 micrometer, thickness of several micrometer).

5 The cylindrical substrate is generally a cylinder of length up to 3200 mm, preferred cylinders have a length of about 50 to 1500 mm. The cylinder is generally of circular cross section, and smooth surface as usually required for nanoimprint lithography. The cylinder's diameter is often from the range 20 to 1000 mm, typically 30 to 800 mm.

10 In a preferred variant of the present process, the cylindrical substrate has an electrically conducting surface in order to facilitate later production steps such as electroplating; in one embodiment, such conducting surface is metal such as nickel. This variant implies that the irradiation in present step (d) is effected through the relief master, which thus needs to be sufficiently transparent for the electromagnetic radiation applied.

15 Preferred conditions for step (c):

Coating materials generally are known materials used for radiation curable coatings, i.e. materials which are partially or fully cured by irradiation. Typical are coating systems for curing with ultraviolet radiation; such UV-curable systems often contain a photoinitiator, the systems are often based on oligomeric urethane acrylates, or oligomeric urethane acrylates in combination with other oligomers or monomers. Fluorinated oligomers or monomers may advantageously be used. The UV curable systems may also be hybrid systems containing an inorganic resin component such as a silane or siloxane and an organic part such as a acrylate or methacrylate. The UV curable system
20 may also contain cationically curable monomers or oligomers such as epoxides or oxetanes or it may contain thiol groups which can undergo a thiol-ene crosslinking reaction. Corresponding systems are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A18, pages 451-453, or in Nanoimprint Technology, Eds. J. Taniguchi, H. Ito, J. Mizuno, T. Saito, John Wiley & Sons, 2013, 1st Edition,
25 pages 115-136.
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Advantageously, dual cure systems may be employed as the radiation curable coating. Such systems are fully cured only after application of two different kinds of measures, for example

- 35
- by subsequent irradiation with two different wavelengths of UV radiation (which may be facilitated by addition of two different classes of photoinitiators with sensitivity for these wavelengths), or
 - by irradiation with electron beams and subsequently with UV radiation, or vice versa, or
- 40
- where the first curing step is effected by heat, and final cure by UV or electron irradiation, or vice versa.

Components of the radiation curable systems usually contain ethylenic double bonds or strained heterocyclic structures capable to react on irradiation with UV light in presence of a photoinitiator or with an electron beam. Curing by heat is typically effected by exposure to temperatures from the range 50 - 200°C.

5

In order to meet various differently functional demands of the soft UV-NIL process, applied coating materials should possess a number of desirable properties such as physical rigidity for high resolution, flexibility for intimate conformal contact, low surface energy for high quality demolding, high UV transparency for fast curing resist, low viscosity for easy and fast filling into the nano-cavities or features of a master at low pressure to achieve a high resolution mold, small curing-induced shrinkage for dimension accuracy and stability, and chemical inertness for mold durability, as well as thermal stability, easy material processing and high pattern transfer fidelity, etc. A proper balance between the mold rigidity required for patterning a very fine and dense structure and the flexibility may be established for a conformal contact with the substrate.

Especially preferred are coating materials designed for nanoimprint lithography (NIL), some of which are characterized by especially high dimensional accuracy of the structures formed and/or the ability to get completely displaced during the structuring step where required. Examples for such NIL resist materials (non-exhaustive) are

Ormocomp UV curable hybrid polymer based on ormocer (organically modified ceramics) by micro resist technology GmbH, Berlin;

Ormoclear series UV curable hybrid polymer based on ormocer (organically modified ceramics) by micro resist technology GmbH, Berlin;

Ormstamp UV curable hybrid polymer based on ormocer (organically modified ceramics) by micro resist technology GmbH, Berlin;

mr-UVCur21 series, UV curable, micro resist technology GmbH, Berlin;

mr-XNIL26 series, a UV curable photoresist with high content of fluorinated components, micro resist technology GmbH, Berlin;

mr-NIL 6000E series, combined thermal and UV cure, micro resist technology GmbH, Berlin;

mr-UVCur06 series, UV curable, micro resist technology GmbH, Berlin;

Amonil series, UV curable organic-inorganic composite material, AMO GmbH;

UV curable mixtures of acryloyl morpholine with a photoinitiator (GENOCURE LTM) as disclosed by Auner et al., Organic Electronics 10, 1466 (2009);

Norland Optical adhesive 81 (UV curable polyurethane based resist containing mercapto-ester components);

XNRX-2000 series, UV curable, Nanonex Corp.;

NXR-1000 series, thermal cure, Nanonex Corp.;

mr-I 7000R series, thermal cure organic thermoplast based resist, micro resist technology GmbH, Berlin;

- mr-I 8000R series, thermal cure organic thermoplast based resist with fluorinated additive, micro resist technology GmbH, Berlin;
SIPOL series, thermal cure silicon containing resist, micro resist technology GmbH, Berlin;
- 5 mr-I T85 series, thermal cure resist based on cyclo-olefin-copolymer, micro resist technology GmbH, Berlin;
mr-I 9000M series, thermal cure organic thermoset resin, micro resist technology GmbH, Berlin;
mr-I PMMA series, thermal cure, micro resist technology GmbH, Berlin;
- 10 PAK-01, UV curable resist from Toyo Gosei Co.;
LUMOGEN OVD Primer 301, BASF;
HQ40-0005, BASF Coatings GmbH;
HQ40-0106, BASF Coatings GmbH.

- 15 Application of such coatings under various conditions is disclosed e.g. in John et al., Nanotechnology 24, 505307 (2013); Gilles et al., Microelectronic Engineering 86, 661 (2009); or in the technical literature relating to the respective resist technology.

20 The curable coating is applied in step (c) to a wet film thickness generally ranging from 50 nm to 1.8 micrometer, typically from 50 nm to 1.0 micrometer, preferably from 0.1 to 0.8 micrometer. This thickness includes the filling of trenches, in case that the radiation curable coating is applied on the nanostructured surface.

25 A first partial cure, for increasing the viscosity of the coating film or for transferring the liquid coating film into the state of a solid gel as described in more detail below for step (d), may be effected in step (c) after applying the radiation curable coating film onto the nanostructured surface and/or the cylindrical substrate. Depending on the curing system chosen, such first partial cure may be effected by applying one of the curing methods described above.

30 Advantageously, the nanostructured surface is covered with a surface active agent or a release agent, typically selected from fluorinated release agents, silicone release agents and silane systems (example: perfluorochlorooctyl-trichlorosilane), typically in form of a thin layer (e.g. 1 to 100 nanometer). The agent serves to reduce adhesion

35 between the nanostructured surface and the radiation curable coating material, and thus to provide good separation of said surface from the coating after transfer of the pattern. It may be a radiation reactive agent, as for example 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxyundecyl acrylate. The surface active agent may further modify surface interactions between coating material

40 and template and thus help to reduce defects during replication. Advantageously, a nanoimprint system already containing the release agent (within its bulk volume) may be used (see, for example, materials disclosed by Takei and Sekiguchi, Appl. Sci. 2,

24-34 (2012); doi:10.3390/app2010024). For improving the adhesion on the shim, an adhesion promoter may be applied (such as mr-APS1, recommended e.g. for NIL resist mr-UVCur21 from micro resist technology GmbH, Berlin).

5 Preferred conditions for step d:

The pattern is transferred in step (d) to finally cover the whole circumference of the cylindrical substrate; this is achieved by moving the contact area between the nanostructured surface and said substrate over the whole circumference of the substrate, e.g. by simultaneously rotating the cylindrical substrate with moving of the surface, or by rolling the substrate over said surface.

Typically, moving of the contact area over the length exceeding the cylindrical substrate's circumference is effected by a rotating movement of the cylindrical substrate (100), as shown in Fig. 1. The cylindrical substrate thus may either be stationary, with movement of the relief master (101), or may be rolled over the relief master with keeping the latter in place. Typically, the contact between cylindrical substrate and the relief master is improved by applying a small or large pressing force, as commonly done in the field of nanoimprint lithography; dependent on the NIL material used, the pressure is typically from the range 0.1 to about 100 bar, preferably a low pressure is applied such as from the range 0.5 to 10 bar and a corresponding NIL material is chosen.

Temperature at transfer is generally chosen to comply with the requirements of the coating material (NIL resist) applied.

The pattern thus transferred onto the coating on the cylinder comprises a pattern with trenches and ridges/peaks; the depth of the pattern thus transferred is about the same as the one given by the relief master, where the term "depth" is to be understood as the height difference between trenches and ridges/peaks. The relief master providing a depth of the structures typically from the range 50 to 1000 nm, especially 100 to 800 nm, thus results in a pattern imprinted on the cylinder, whose structural dimensions are about identical in case that the coating thickness applied in step (c) allows such dimensions. Transfer of the pattern in step (d) causes a certain displacement of imprinting material, such displaced material primarily filling trenches in the patterned surface of the relief master. The depth of the pattern thus imprinted into the coating on the cylinder is preferably at least 50% of the coating thickness; advantageously, the depth is such that the remaining coating thickness in the trenches obtained on the cylinder's surface is only 20 % or less of the thickness at the ridges/peaks; thus, thickness of the coating applied in step (c) typically is smaller than the maximum depth of structures in the relief master; depending on the type of structure transferred (i.e. more peaks than trenches in the master surface [high duty cycle], or vice versa), the thickness of the coating applied in step (c) may be considerably smaller than the maximum depth of

structures in the relief master. Examples of preferred ratios (thickness of the coating applied in step (c) : maximum depth of structures in the relief master) are 0.9 or less, especially 0.1 to 0.8. Example: A wet film thickness on the cylinder of 50 nm requires a depth of structures in the relief master of duty cycle 0.5 of at least 50 nm to obtain a
5 depth of at least 50% of the coating on the cylinder, or at least 100 nm to effect the desired displacement of most NIL material in the trenches.

In order to facilitate optional further steps for converting the pattern on the cylinder, as explained further below, a low remaining coating thickness, or a complete displacement
10 of the original coating film by the formation of the trenches, thus creating voids between the ridges or peaks, is of advantage, especially where an electrically conducting surface of the cylindrical substrate can thus be laid open. Consequently, the original wet film coating thickness applied in step (c) advantageously matches with the amount of coating material required to form, in step (d), the pattern on the cylinder. Still, displacement of NIL material during the transfer step and rotation of the cylinder often
15 results in the formation of a bulge of NIL material in front of the contact area (such bulge of uncured NIL material is hereinbelow also referred to as "excess coating material"). Since curing is effected in the contact area (also denoted as contact zone) and/or in short distance behind it, any displaced bulge material remains in uncured state; it is removed after completion of the transfer step or even during the transfer step by rinsing
20 (e.g. contacting in a bath) with a suitable solvent, which removes the uncured NIL material but leaves the cured or partly cured NIL material unaffected. Suitable solvents advantageously are selected from solvents recommended for the NIL material chosen; typically, such solvents are poly or unpolar solvents such as hydrocarbons, esters, amides, ketones, aldehydes, alcohols, ethers.
25

The coating applied in step c is generally from the range 50 to 1800 nm, typically from the range 50 to 1000 nm, especially 100 to 800 nm.

30 After the contact between cylindrical substrate and the relief master, the coating adheres to the cylindrical surface. Since the dosage of electromagnetic radiation or heat applied at one contact is less than the dosage required for full cure of the coating, only a partial cure of the coating is effected during the first contact between relief master and the cylinder.

35 The partial curing is generally achieved during or immediately after the transfer of the pattern (i.e. in the contact one or closely behind it) by applying radiation or heat through the relief master. Preferred is the application of UV radiation. For this purpose, the beam of the radiation source is preferably focused by means of a mask (for example a grey tone mask made of Cr metal). The curing zone, where the coating is exposed to
40 the radiation or heat, may exceed the contact zone, but is preferably limited to the contact zone or is even smaller than the contact zone. Thus, one preferred variant of step

(d) comprises applying electromagnetic radiation by projection lithography through a grey tone mask. In a further preferred embodiment, step (d) comprises applying electromagnetic radiation by projection lithography through the grey tone mask only in the section where the flat nanostructured surface of step (a) is substantially parallel to the surface of the cylindrical substrate of (b).

Transparency for the radiation is ensured by choosing suitable materials known in the art, e.g. quartz or suitable polymer sheets or films such as ethylene tetrafluoroethylene (ETFE) for the case of UV-radiation.

If not transferred into the gel-like state in step (c) as noted above, passing the contact area with application of electromagnetic radiation exposes the coating to a certain dosage of radiation ("one pass dosage"), and preferably transfers the radiation curable coating into the state of a solid gel, which adheres to the cylindrical substrate.

The state of a "solid gel" is, within the context of the present invention, to be understood as a solid retaining the structure transferred by the nanostructured surface (i.e. the negative structure of the relief master), but remaining shapeable under pressure, such as pressure applied by renewed contact with the relief master.

The completely cured state is typically reached after applying 2 to 10 of such "one pass dosages" in case that a coating material is chosen, which can be fully cured by the radiation applied during contact between relief master and cylinder in step (d). Such dosages for final hardening of the structured coating on the cylinder may be applied during subsequent contacts with the curing zone. Preferably, the completely cured state may be effected in a subsequent step, e.g. with application of thermal cure or radiation cure using another radiation or higher radiation dosage than applied during the transfer step.

Preferred is a process of the invention wherein the coating material applied in step (c) is curable by UV light only, or is curable by a combination of UV light and heat, and wherein the partial cure in step (d) is effected by irradiation with UV light.

The electromagnetic radiation thus preferably is UV light, and the radiation curable coating typically is a UV curable coating. Cure of the UV curable coating (UV lacquer) during the transfer step may be accomplished in analogy to methods described in WO 12/176126. The UV coating may also be pre-cured to increase viscosity before transfer (as described before for step c), followed by final cure during or immediately after the transfer step, e.g. using two different types of photoinitiators in accordance to methods described e.g. in EP-A-1837202, see especially sections [0046] to [0050]. Preferred curing wavelengths are, for example, from the short wavelength range 220 – 300 nm,

especially 240 – 270 nm, and/or from the long wavelength range 340 – 400 nm, especially 350 – 380 nm.

5 In order to prevent reflection on the surface of the device structure (e.g. the relief master) transmitting the radiation to the coating to be cured, a liquid is advantageously introduced between light source and device structure, which matches the refraction indices of the source cover and the transmitting structure (index matching). The liquid further may facilitate the movement of the transmitting structure over the radiation source (reduction of friction).

10 The seamline in the thus patterned cured coating (110) can thus be minimized to be no longer visibly detectable. The cylindrical substrate thus obtainable, carrying the pattern on the surface of the cured coating layer (110), thus provides a master for optically seamless imprinting the original pattern from the nanostructured surface.

15 In a preferred embodiment of the first aspect, the cylindrical substrate of step (b) has an electrically conductive outer surface and the process comprises further steps
(f) applying an electroplating process to the cylindrical substrate to deposit metal in the voids exposing the electrically conductive outer surface, and subsequently
20 (g) removing the remaining cured coating from the surface of the cylindrical substrate.

Optionally, before the above step (f), the following step (e) may be carried out, especially in cases where no voids had been created between the ridges or peaks of the structure created in the foregoing steps to uncover the electrically conducting surface, and a coating of certain thickness is remaining in these trenches:

25 (e) partially removing the nanostructured coating on the cylindrical substrate obtained in step (d) by reactive ion etching, thus uncovering the electrically conductive outer surface and creating voids.

30 Since some advantageous coating materials are available for nanoimprinting, which are designed to create such voids (such as mr-UVCur06, or some other systems listed above), step (e) is not always necessary.

35 The following examples illustrate the invention.

Wherever noted, room temperature depicts a temperature from the range 18-23°C; over night denotes a time period in the range 12-16 hours. Percentages and ratios in the examples and elsewhere are by weight, if not indicated otherwise.

40 Abbreviations:

RIE reactive ion etching

UV ultraviolett, typically referring to electromagnetic radiation from the wavelength range from about 200 up to 400 nm (UV light)

NIL material coating material designed for nanoimprint lithography

5 Example Nanoimprint lithography and electroplating:

The UV-curable nano imprint coating (for example mr-UVcur21 from micro resist) is put on the cylindrical substrate, for example by printing it on with a second rotating cylinder. The film thickness of the NIL photoresist is adjusted by a doctor blade (thickness
10 e.g. 400 nm), under which the cylindrical substrate is rotated.

Once the coating has the required uniform thickness around the cylindrical substrate, the cylindrical substrate is rolled over the flat nanostructured surface of the relief master (rectangular grating, e.g. depth 500 nm and period 450 nm), as described in step d), to transfer the nanostructure onto the cylinder, and illuminated by UV-light. The UV
15 light may be broad band UV illumination, or preferably narrow band i-line illumination around 365nm, for better process control. Typical powers are 20-30 W/cm² for broad band illumination, or 5-15 W/cm² in case of i-line illumination. The curing process then takes between 0.1 and 5 s, depending on the lamp and the precise material used. After illumination, there is a residual layer of mr-UVcur21 at the base of the nanostructure that requires removal, which is performed by anisotropic plasma etching with oxygen/CHF₃, an etch pressure of 45 mTorr (i.e. 6 kPa), RIE power of 75 W; oxygen flow
20 of 15 sccm and CHF₃ flow of 60 sccm is used to remove the residual layer and expose the underlying metal. A nickel layer is then built up in the exposed metal regions using electroplating as explained below.

25 The Ni electroplating is done with a pulse and pulse reverse plating processes. This technique increases Ni layer density, eliminates pores and increases hardness of very thin Ni layers. The electrical pulse frequency is typically between 20-900 Hz and the ratio between cathodic/anodic pulse current density typically ranges from 0.1 to 1.5. A typical electrolyte is Nickel Sulfamate with a Ni concentration of 1-1.5 mol/l (typically 1.27 mol/l) and a working temperature from the range 40-45°C. Depending on the growth speed, current densities of 0.002-0.2 A/dm² are commonly used resulting in plating durations between a few 10s and a few hours. Lower current densities lead to nearly perfect layers and small local height variations with very uniform properties, however at the expense of productivity. The distance between anode
35 and cathode is typically between 2 and 15cm.

In a specific embodiment, pulse reverse plating is carried out using a pulse frequency of 80 Hz; anodic/cathodic pulse density: equal.

40 Electrolyte: 1.26 mol/l nickelsulfamate in distilled water.

Bath temperature: 42°C.

Current density: 0.015 A/dm².

Distance between anode and cathode: 10 cm.

Electrode material: Pt (alternatively possible: Ir-covered Pt).

Plating controller: Computer controlled pulse reverse power supply system from Plating Electronic (Power Pulse pe86 CB 3HE).

5

In a further aspect, present invention provides a method for optically seamless nanoimprinting, which makes use of the seamless shim provided in accordance with the first aspect of the present invention. This method is especially advantageous for the nanostructuring of large surfaces, such as large format films useful inter alia for appli-

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cation in glazing, architectural façade elements or windows.

Claims

1. Process for preparing a cylindrical substrate having an optically seamless surface relief, which process comprises the steps
 - 5 (a) providing a relief master, which is a nanostructured surface comprising a specific area with a pattern, which specific surface area is characterized in that it does not contain any optically detectable seam,
 - (b) providing a cylindrical substrate whose outer surface is smaller than the specific surface area on the relief master, and preferably comprises an electrically conductive
10 outer surface,
 - (c) applying a radiation curable coating containing ethylenic double bonds and/or a photoinitiator on the nanostructured surface and/or the cylindrical substrate to a wet film thickness ranging from 50 nm to 1.8 micrometer, preferably up to 1.0 micrometer,
 - (d) transferring the pattern of the specific surface area on the relief master to the
15 cylindrical substrate by applying electromagnetic radiation and/or heat through the relief master to the curable coating in the contact area between the nanostructured surface of the relief master and the cylindrical substrate's surface, characterized in that the contact area is moved over a length, which exceeds the cylindrical substrate's circumference, and the dosage of electromagnetic radiation and/or heat applied at one contact
20 does not effect full cure of the coating.
2. Process of claim 1, wherein the relief master provided in step (a) comprises a specific area of length l and width w rectangular to each other,
and the cylindrical substrate provided in step (b) is of a diameter d such that the product $d \cdot \pi$ is smaller than the relief master specific area's length l .
25
3. Process according to any of claims 1 to 2, wherein the relief master is flexible, such as a polymer film which is contacted with the cylindrical substrate in step (d) in the manner of a rotary press.
30
4. Process according to any of claims 1 to 3, wherein the partial cure in step (d) is effected by irradiation with UV light or electron beams, and wherein the beam of the radiation source is focused by means of a mask, for example a grey tone mask made of Cr metal.
35
5. Process according to any of claims 1 to 4, wherein step (d) is followed by an additional rinsing step to remove excess coating material.
6. Process according to any of claims 1 to 5, wherein the pattern provided in step (a) is
40 transferred from the seamless nanostructured surface of the relief master (101) by contact onto a rotated and cylindrical substrate coated with a curable film (120) while being irradiated with UV light through the relief master (101), where the curable film (120) is

in liquid state or has been pre-cured to obtain a gel-like state, characterized in that the dosage of irradiation applied in step (d) converts the liquid or gel-like coating (120) into a solid gel (110), and the rotation of the cylindrical substrate with contact to the seamless nanostructured surface of the relief master (101) is continued for more than one
5 round.

7. Process according to any of claims 1 to 6, wherein the pattern of the nanostructured surface provided in step (a) has a period from the range 0.1 to 10 micrometer and a depth from the range 50 to 1000 nm.
10

8. Process according to any of claims 1 to 7, wherein the coating applied in step (c) is a dual cure system requiring for complete cure either 2 or more types of electromagnetic radiation or electromagnetic radiation and heat, where the electromagnetic radiation in each case preferably is ultraviolet radiation.
15

9. Process according to any of claims 1 to 8, wherein the thickness of the radiation curable coating applied in step (c) is smaller, especially 90% or less, of the depth of the pattern in the relief master.

20 10. Process according to any of claims 1 to 9, wherein the cylindrical substrate provided in step (b) comprises an electrically conductive outer surface, and wherein the pattern transferred in step (d) of said process comprises voids partly uncovering said electrically conductive outer surface, and/or wherein a further step
(e) partially removing the nanostructured coating on the cylindrical substrate obtained in step (d) by reactive ion etching, thus uncovering the electrically conductive
25 outer surface and creating voids in the coating
is conducted.

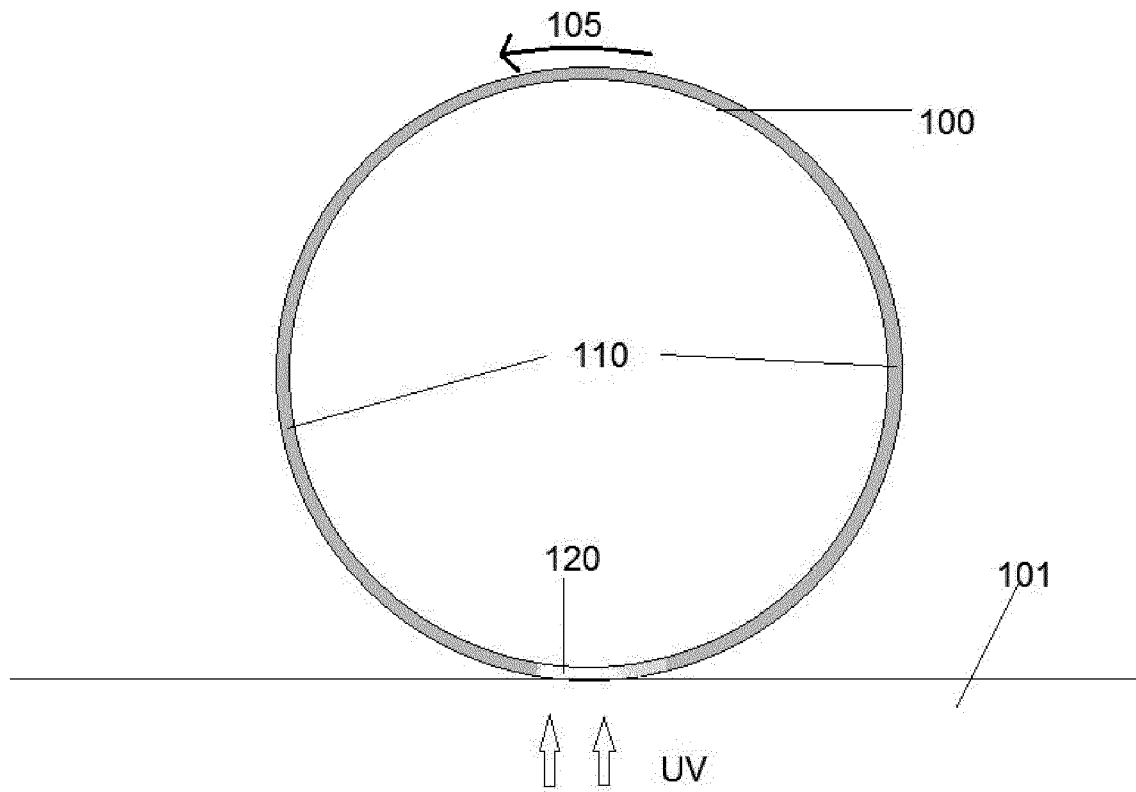
11. Process of claim 10, which comprises the further steps
30 (f) applying an electroplating process to the cylindrical substrate to deposit metal in the voids uncovering the electrically conductive outer surface of the cylindrical substrate, and
(g) removing the remaining cured coating from the surface of the cylindrical substrate.
35

12. Cylindrical shim, especially comprising an electrically conducting surface such as a metal surface, which carries the coating material structured in step (d), obtainable according to any of the foregoing claims.

40 13. Cylindrical shim according to claim 12 of cylinder of length 100 to 3200 mm and diameter from the range 20 to 1000 mm.

14. Method for seamless roll-to-roll or roll-to-plate nanoimprinting, which method comprises structuring the surface of a suitable substrate, which substrate is preferably a transparent polymer film or a coated glass, by contacting said surface with the cylindrical shim according to claim 12 or 13; or comprises preparing a structured cylindrical
- 5 substrate in accordance with the process of any of claims 1 to 11 and structuring the surface of a suitable substrate, which substrate is preferably a transparent polymer film or a coated glass, by contacting said surface with the structured cylindrical substrate thus obtained.
- 10 15. Substrate, which is preferably a transparent polymer film or a coated glass, having a nanostructured surface obtainable according to the method of claim 14.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/069853

A. CLASSIFICATION OF SUBJECT MATTER
INV. G03F7/00 G03F7/24
ADD.

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)
G03F B29C B82Y

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

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X	CN 103 399 460 A (QINGDAO BONA PHOTOELECTRIC EQUIPMENT CO LTD) 20 November 2013 (2013-11-20) paragraphs [0027] - [0029], [0053] - [0057]; claim 1; figures 3,4 -----	15
Y	EP 0 237 574 A1 (KITAMURA ATSUSHI [JP]) 23 September 1987 (1987-09-23) page 6, line 25 - page 8, line 17; claims 4-6; examples 3-5 page 22, line 23 - page 23, line 5; examples 3-5 -----	1,2,8,14
X	----- -/--	12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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