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## (54) Title: FLEXIBLE AND TUNABLE ANTI-REFLECTION SKIN

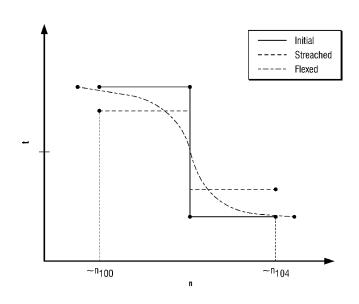


FIG. 2

(57) Abstract: Free-standing, flexible articles (skins) are disclosed which are substantially transparent to a range of electromagnetic frequencies and impart Anti-reflection (AR) characteristics when used as an optical interface between two media, devices or structures. Comprising of a monolayer, or multi-layers, of ductile, or elastic, materials which have appropriate refractive index profiles to perform the AR function. Further comprising of structures, materials and optical designs which can substantially retain their mechanical integrity and AR performance when the skin, or one, or both, interfaced media or substrates are non-planar or stretched, flexed or otherwise alter their shape or position during deployment and, or subsequent use. Methods of tuning the AR characteristics of the skins through stretching, flexing or otherwise changing the orientation, or shape of the skins, during deployment, or use, are also provided.



#### FLEXIBLE AND TUNABLE ANTI-REFLECTION SKIN

#### FIELD OF INVENTION

[0001] The present invention relates to the structure and functionality of a free-standing or self-supporting anti-reflection (AR) skin, which is flexible and tunable. The skin can provide an interface between different media whereupon it performs an analogous function to a deposited AR coating. Illustrative targeted applications include non-planar, mobile or adaptive-shape devices or structures.

#### **BACKGROUND**

Specular Reflection of Light at Interfaces

**[0002]** From optics theory, when incident light of wavelength (lambda), intensity (I) and angle of incidence (theta) encounters an interface between two media with different refractive indices ( $n_1$  and  $n_2$ ), it is partially reflected and partially transmitted. Phenomena such as absorption and, or diffuse reflection (scattering) may also be evident.

[0003] The intensity of the specular reflected light depends on both the wavelength and angle of incidence. The wavelength dependence correlates with refractive index, while the angular dependence may be described by Fresnel Reflection. The reflection coefficient (R) of light at a non-conducting interface between two media can be approximated by;

$$R(\text{theta}) = R_0 + (1-R_0) (1-\cos(\text{theta}))^5 \dots (1)$$

Where, R<sub>0</sub> is the reflection at normal incidence (theta=0) and is given by,

$$R_0 = ((n_2-n_1)/(n_2+n_1))^2 -----(2)$$

[0004] If the interface includes an optical component, or device, this reflection may result in significant system inefficiency. For example, more than 30% of normally incident, light can be reflected from the surface of a bare c-Si (n~3.5) photovoltaic

(PV) device in air (n~1) leading to a reduction in energy harvesting potential. The technology of anti-reflection (AR) coatings has been developed to address analogous issues for transmitting (e.g. windows and lenses) or active (e.g. LEDs and PV cells) optical devices. For transmitting devices, reflections from both the top and bottom interfaces are relevant to performance.

### AR Coatings

[0005] AR coatings are typically deposited directly on the surface of an optical component or device in order to reduce the reflectance of incident light of desired wavelength(s) and thus improve the net system efficiency of the optical component. A wide range of deposition methods have been used and a number of different AR coating structures are commonly employed including:

[0006] Index Profiled AR coatings: Single-step, multi-step and graded index approaches have been used. Although, the introduction of an intermediate layer(s), with a refractive index lying between the two primary media, results in reflections at each added interface, the net reflectance can be lower. For a single-step AR coating, an intermediate material with a geometric mean index of (n<sub>1</sub>.n<sub>2</sub>)<sup>1/2</sup> gives the lowest theoretical reflection. Multi-layers with incremental index steps can also be employed or continuously graded index layers which do not have intermediate reflective interfaces. The main challenge for multi-step and graded approaches is the availability of suitable materials to bridge the primary index gap, which are often between air (n~1) and glass (n~1.5) or semiconductor (n>3) elements. Ideally, the coatings and their structure should not introduce significant additional losses (e.g. from absorption or scattering) which can offset the benefits of reducing the reflection.

[0007] Interference Based AR Coatings: Single and multi-step interference coatings can be designed which produce out-of phase reflections from intermediate interfaces. These reflections can destructively interfere and null the primary reflection from the first interface. For a single layer coating, ~1/4 wavelength thick, with a mean geometric index, the center wavelength reflection is theoretically zero. Multi-layer interference solutions typically employ precision stacks of thin, alternating low (e.g. SiO<sub>2</sub>) and

high index (e.g.TiO<sub>2</sub>) layers. Such a multi layer approach can produce broadband performance over a range of wavelengths. However, interference layers are commonly made from brittle materials which limit their usefulness as will be described below.

[0008] Nano-structured or Nano-particulate AR Coatings: These AR coatings are typically implemented by the deposition, imprinting or etching of sub-optical (e.g < 100 nm) particles, or structures. With this dimensionality, the resulting coatings can have effective refractive indices determined by the air/material porosity, and may thus provide a better index match to air than traditional dense coatings. Examples include deposited single-layer meso-porous silica nano-particles and bio-inspired "Moth-eye" structures. By grading the porosity through the coating, for example using protruding cone nano-structures, the effective index can be graded through the coating. Surface nano-structures can also impart wide-angle performance.

[0009] Composite AR Coatings: Examples of composite AR coatings for broadband or wide-angle performance include (i) sequentially deposited layers with stepped refractive indices made by adjusting the loading of high-index dielectric nanoparticles in low index resins and (ii) nano-structured layers on top of multi-layer interference structures.

### **SUMMARY**

[0010] Conventional AR coating technology has limited applicability in certain situations including when there is flexing or stretching of the coating or the underlying device or structure. In addition to commonly inadequate mechanical robustness, as noted above, AR coating flexing or stretching can also result in dimensional and refractive index changes which are challenging for optical design. These issues are exacerbated for devices, or structures, which alter shape or dimension in use (e.g. wearable devices)

[0011] Conventional AR coating technology also has limited applicability when used for large area devices, or arrays, which are non-planar and present variable

orientations to incident light. Such issues are also evident for devices on mobile platforms (e.g. cars, ships or planes) on which the relative orientation may vary because of the platform shape and during operation.

[0012] In accordance with a first aspect, the invention features a free-standing film (skin) which is flexible, stretchable and can optically interface between two media, one of which can be air. The skin is transparent to, and can, by virtue of its refractive index profile, act as an AR element which substantial reduces the reflection of electromagnetic radiation of a given range of wavelength that occurs at the interface between the media in the absence of the skin. Furthermore, the skin is distinguished from conventional AR technology in that it is specifically designed to be mechanically durable and to retain AR performance when stretched or flexed. In this regard the materials, structure and optical design are selected, or engineered, such that critical values of dimension, refractive index or other essential characteristics for AR performance are not surpassed during deformation.

[0013] A variety of flexible and transparent base materials including fluoro-polymers and standard engineering and design methods may be employed to achieve the desired AR characteristics. The latter includes single or multi-layer structures, doped, composite and nano-structured layers or surfaces. The AR characteristics are appropriate for a wide range of devices which are not satisfactorily addressed by conventional AR technology.

[0014] In accordance with a second aspect, the invention, features wide angle performance, which makes the skin more appropriate for use on non-planar or mobile platforms, which can present variable angles to incident light and are thus more susceptible to variation in reflections.

[0015] Wide-angle performance may be achieved through surface nano-structuring. The flexibility and formability of the skin can also facilitate deployment on contoured or irregular media surfaces or devices.

[0016] In accordance with a third aspect, the invention features a skin with sufficient ductility or elasticity to be used on structures or devices which can change shape during deployment or use.

[0017] Examples of such applications include inflatable structures and wearable devices.

[0018] In accordance with a fourth aspect, the invention features tunable AR characteristics which are achieved by actively stretching or flexing the skin. In this case the structure and AR design of the skin is engineered to have a level of sensitivity to controlled deformation. This approach can be used to provide the ability to optimize performance for different wavelengths of light, filtering of incident or emitted light from an underlying device, optical identification or tagging of reflective camouflage applications.

[0019] Embodiments of the present invention, summarized above and discussed in greater detail below, can be understood by reference to the illustrative embodiments of the invention depicted in the appended drawings. It is to be noted, however, that the appended drawings illustrate only some embodiments of the invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

### **BRIEF DESCRIPTION OF DRAWINGS**

[0020] Figure 1(a) shows an exemplary cross section of an AR skin with a single functional layer and optional top and bottom layers designed to serve as an interface between media 100 and 104.

[0021] Figures 1(b) and 1(c) show the AR skin of figure 1(a) when being axially stretched and flexed, respectively.

[0022] Figure 2 shows exemplary index (n) vs. thickness (t) profiles corresponding to the skin shown in Figures 1 (a), (b) and (c).

[0023] Figure 3(a) shows an exemplary cross section of a nano-structured layer with a protruding cone structure.

[0024] Figures 3(b) and 3(c) show the nano-structured layer of Figure 3(a) when being axially stretched or flexed, respectively.

[0025] Figure 4 shows index (n) vs. thickness (t) profiles corresponding to the skin in Figures 3 (a), (b) and (c).

## **DETAILED DESCRIPTION**

[0026] In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of exemplary embodiments or other examples described herein. However, it will be understood that these embodiments and examples may be practiced without the specific details. In other instances, well-known methods, procedures, components and circuits have not been described in detail, so as not to obscure the following description. Further, the embodiments disclosed are for exemplary purposes only and other embodiments may be employed in lieu of, or in combination with, the embodiments disclosed.

## Structure:

[0027] The Anti-Reflective (AR) articles described herein are discrete (i.e., free-standing or self-supporting) films or skins which are resilient to significant mechanical or functional degradation or failure when stretched and, or flexed in the course of deployment or use. They are preferably comprised of ductile materials, if a single deployment is sufficient, or elastic materials if repeated or continuous bi-directional modification is required during use. In cases where the skin is comprised of multiple-layers the physical properties of the constituent layers should be sufficiently similar to maintain the integrity of the skin under conditions of use without mechanical or functional degradation. Examples of suitable skin materials include standard polymeric materials which meet the requirements of the given application.

[0028] The skins should also comprise appropriate materials or surfaces to facilitate interfacing with the two media which are being interfaced. Such interfacing may be achieved in a number of conventional ways by structural, chemical, thermal, mechanical, electrical or other means and may include optional surface layers or materials to assist the interfacing process. Examples of such surface layers include layers comprised of standard adhesives.

[0029] The skins may have any of a number of transverse structures which enable their AR performance. They may be comprised of mono-layers, which have constant, graded or varied refractive index. They may be comprised of a multi-layer where the layers have an engineered progression of refractive index. They may include nano-structured or nano-composite layers or surfaces which can provide a wider range of engineered refractive index profiles than dense or single material layers. It may also be appropriate to employ AR skin which includes an interference stack of materials although such structures may have a narrower operational range when subject to flexing and stretching.

[0030] Figure 1(a) depicts an exemplary cross section of an AR skin with a single functional layer 102 and optional top and bottom layers 101 and 103, designed to serve as an interface between media 100 and 104. Figure 1(b) & 1(c) refer to the same cross section when axially stretched and flexed, respectively. Multi-layer, or multi-step, structures may be considered to behave as the combinations of single layer structures with additive effects.

[0031] Figure 2, depicts exemplary index (n) vs. thickness (t) profiles corresponding to the skin in Figures 1 (a), (b) and (c). For this illustration the material layers are considered to be substantially compliant when stretched. When flexed, there can be stretching of the top surface and compression of the bottom surface, which result in dimensional, density and refractive index changes from top to bottom.

[0032] Figure 3(a) depicts an exemplary cross section of a nano-structured layer, with a protruding cone structure. Figures 3(b) and 3(c) depict the same layer when axially stretched or flexed, respectively.

[0033] Figure 4 depicts exemplary index (n) vs. thickness (t) profiles corresponding to the skin in Figures 3 (a), (b) and (c). The structure has an initial graded index profile due to the porosity, the gradient of which increases with axial stretching. Under flexing can be an asymmetric top to bottom change in the periodicity, density and index.

## AR Functionality:

[0034] The flexible AR skin should be sufficiently transparent to function in the desired range of electromagnetic frequencies which may be in the ultra-violet, visible or infra red regions of the spectrum.

[0035] In some embodiments, the thickness and refractive index of respective layers in the flexible AR skin should be in a range that any changes in these parameters induced by stretching or flexing during deployment or use will be insufficient to substantially degrade the AR characteristics of the skin from its performance before deformation.

[0036] Materials with suitable properties include various polymers which are appropriately, transparent and elastic, or ductile. Depending on the optical structure employed they should also be suitable for chemical, or structural, modifiable to provide index variations, for patterning, or loading with a high index particles, including nano-particles. Examples include polymers which are polyethelene or polypropylene or fluoro-polymers such as ETFE and PVDF and modifications thereof which have an accessible range of refractive index which can be tailored between those of air through glass to semiconductors by various means which will be described below.

[0037] By way of example, in some embodiments the flexible AR skin structures may be employed for air-to-air (where the skin itself may function as a window), air-to-glass (for passive optical components) and air-to-semiconductor (for active photonic components) interfaces. Of course, the flexible AR skin structures may used as an interface between other media as well.

[0038] One embodiment of a flexible AR skin for use as an air-to-air interface may comprise a monolithic ETFE skin with top and bottom surfaces both being nanostructured. The nano-structuring would be designed either to provide a step index profile with an outer layer structure having a refractive index close to the geometric mean (~1.14) between air and ETFE (~1.3), or more preferably, a graded index profile on each face. The thickness, or depth, of the skin and the nano-structuring should be sufficient for mechanical integrity. Also, the dimension and/or the periodicity of the nano-structuring should be appropriate to sustain the AR performance over the range of stretching and, or flexing that the skin will encounter in use. The nano-texturing may also enhance the wide angle performance of the skin.

[0039] One embodiment of a flexible AR skin for use as an air-to-glass interface may comprise a monolithic ETFE skin. Since the refractive index of ETFE (~1.3) is greater than the geometric mean (1.22) of the air-to-glass interface, nano-structuring of the outer layer of the skin may be beneficial for AR performance. Additionally, a graded, or step-index multi-layer AR structure which is less reflective may be engineered by diffusion or other doping of the ETFE with an index increasing dopant from the "glass" interface. For multi-layer solutions different levels or types of doping can be implemented in individual batches of the polymer or precursors followed by the sequential deposition of layers during the fabrication of the skin.

[0040] Air-to-semi-conductor AR skin implementations are challenging, in so far as the index difference between the media is large and standard polymer material options. For example, the geometric mean index for air and c-Si is ~1.88. In one embodiment, a multi-layer, composite skin is formed from sequential layers of a polymer, for example ETFE, which are loaded with increasing levels of high

refractive index nano-particles towards the semi-conductor interface. The level of loading, nano-particle dimensions and distribution, and the nature and refractive index of the materials, may be engineered to maintain stretchability, flexibility and transparency of the composite. Candidate materials for the nano-particles, with reflactive indices in the range of 2.5-3.5, include refractory oxides (e.g. TiO2) and transparent chalcogenides (S, Se, Te) of Zn, or Cd.

[0041] An example for a AR skin for use on an unencapsulated c-Si PV cell or module, could include a ETFE polymer material of about 5-10 micron thickness substantially >10% loaded with TiO<sub>2</sub> nano-particles at the interface with the cell and optional multi-layers with a top layer comprising of conically structured ETFE interfacing to air. This top layer also providing wide angle performance to accommodate deployment of the device under varying angles of illumination.

#### Substrates and Platforms:

[0042] Many preferred embodiments of the invention are directed to addressing AR functionality, for applications involving non-planar, flexible, mobile and shape-changing substrates or platforms

[0043] A preferred embodiment for a non-planar, and flexible, substrate is the application of an AR skin to flexible PV devices including large area arrays. In such an application the AR skin should accommodate and perform during any flexing of the PV device, for example on it's deployment on a contoured structure or platform. Furthermore, since the reflectivity and performance of such a PV device is markedly dependent on orientation to incident solar radiation, an AR skin which is designed for wide angle performance, e.g. the incorporation of a nano-structured surface layer in the AR skin can be extremely beneficial.

[0044] Preferred embodiments for mobile platforms including cars, ships and planes, can likewise include non-planar surfaces (e.g. a car top or fuselage) as well as the variations in the relative angle of incidence from a defined source during operation. As above embodiments which include wide-angle AR performance are preferred.

[0045] Preferred embodiments, for platforms which change shape during use, including inflatable or wearable platforms require both a high resilience of AR performance to stretching or flexing and wide angle performance. It is also critical that the AR skin be elastic to allow for continued usage.

#### Tunability:

[0046] In contrast to the above examples, which are centered on the substantially invariant performance of an AR skin when deployed on various platform and devices, another range of preferred embodiments centers on the ability to tune or adjust the intensity and, or wavelength of reflectivity of an AR skin. Such preferred embodiments may involve sensitizing the AR skin designs in terms of tailoring thickness and optical characteristics to be near some critical point for changing AR performance by stretching, flexing or otherwise changing the shape of a skin within a range which is accessible by the influence of an external stimulus, which could include a mechanical, thermal or electrical means of controlled flexing or stretching of the skin. For example by inflation, or by activating a piezo-electric element to induce stretching to reduce the index and/or layer thickness below a critical value.

[0047] In the simplest case a preferred embodiment could be used to tune the skin for optimized AR performance at a given wavelength. Another preferred embodiment is for reducing transmission intensity by increasing reflectivity, for example in order to prevent saturation of sensory devices. Another preferred embodiment is to adjust the wavelength, intensity or modulation of reflected light for optical tagging or camouflage applications.

#### **CLAIMS**

What is claimed is:

1. A self-supporting anti-reflective (AR) film or skin to be disposed between first and second media, comprising:

at least one layer at least partially transparent to optical energy at one or more optical wavelengths, the at least one layer being substantially flexible and/or stretchable and having a refractive index profile which imparts anti-reflection (AR) behavior for incident light when used as an optical interface between the first and second media; and

wherein the AR behavior is retained when the at least one layer is flexed and/or stretched.

- 2. The self-supporting AR film or skin of claim 1, wherein the at least one layer includes a plurality of layers formed from different materials, each of the layers having common physical and mechanical properties.
- 3. The self-supporting AR film or skin of claim 1, wherein the refractive index profile of the layer is tunable by chemical modification, structural modification, variable porosity, composite blending or loading of a base material.
- 4. The self-supporting AR film or skin of claim 1, further comprising at least one bond for bonding the at least one layer to at least one of the media.
- 5. The self-supporting AR film or skin of claim 1, wherein one or both of the media is air or vacuum.
- 6. The self-supporting AR film or skin of claim 1, wherein one or both of the media is an optical component or device.
- 7. The self-supporting AR film or skin of claim 6, wherein the optical component includes a plurality of devices.
- 8. The self-supporting AR film or skin of claim 6, wherein the optical component is flexible and/or stretchable.

9. The self-supporting AR film or skin of claim 1, wherein one or both media have surfaces that are planar, non-planar or irregular.

- 10. The self-supporting AR film or skin of claim 1, wherein the at least one layer is a single layer having a refractive index approximately equal to the geometric mean of the first and second media.
- 11. The self-supporting AR film or skin of claim 1, wherein the at least one layer is a single layer skin having a graded refractive index matched with the first and second media for providing AR functionality.
- 12. The self-supporting AR film or skin of claim 1, wherein the at least one layer includes a plurality of layers having progressively stepped refractive indices, an outermost of the layers being index matched to each of the first and second media for providing AR functionality.
- 13. The self-supporting AR film or skin of claim 1, wherein the at least one layer includes an interference stack with alternating refractive index layers.
- 14. The self-supporting AR film or skin of claim 13, wherein the interference stack is configured to impart broadband AR performance over a range of wavelengths of incident light.
- 15. The self-supporting AR film or skin of claim 1, wherein the at least one layer is nano-structured.
- 16. The self-supporting AR film or skin of claim 15, wherein the nano-structured layer is a surface layer.
- 17. The self-supporting AR film or skin of claim 16, wherein the nano-structured layer is configured to impart wide angle AR performance over a range incident angles between 0 to +,-  $90^{\circ}$ .
- 18. The self-supporting AR film or skin of claim 6, wherein the optical device is a photovoltaic cell or array of photovoltaic cells.
- 19. The self-supporting AR film or skin of claim 18, wherein the photovoltaic cell or array of photovoltaic cells is flexible.

20. The self-supporting AR film or skin of claim 1, wherein the first media is, or is disposed on, a mobile platform.

- 21. The self-supporting AR film or skin of claim 20, wherein the mobile platform is selected from the group consisting of a car, ship, plane and spacecraft.
- 22. The self-supporting AR film or skin of claim 20, wherein the mobile platform is a person or animal.
- 23. The self-supporting AR film or skin of claim 1, wherein the first media is a structure which alters shape in use.
- 24. The self-supporting AR film or skin of claim 23, wherein the structure is inflatable and/or deflatable.
- 25. The self-supporting AR film or skin of claim 23, wherein the structure is a wearable article.
- 26. The self-supporting AR film or skin of claim 1, wherein the AR behavior is tunable by flexing and/or stretching the at least one layer.
- 27. The self-supporting AR film or skin of claim 26, wherein the flexing and/or stretching is activated by a mechanical, electrical or thermal stimulus.
- 28. The self-supporting AR film or skin of claim 26, wherein the tuning can be selectively localized across the at least one layer.
- 29. The self-supporting AR film or skin of claim 26, wherein the tuning is used for optimizing the AR behavior at a given range of wavelengths and/or angles of incidence.
- 30. The self-supporting AR film or skin of claim 26, wherein the tuning is settable, periodic or continuously variable.

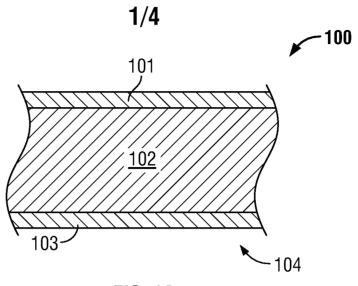


FIG. 1A

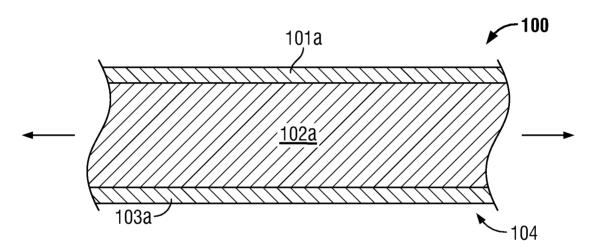


FIG. 1B

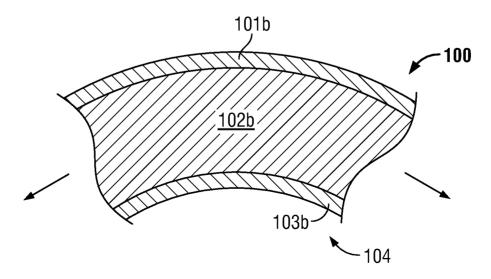
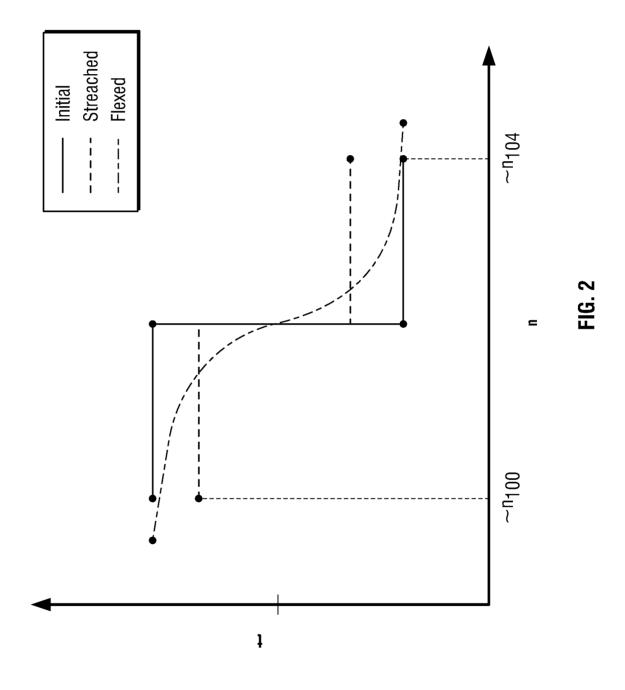


FIG. 1C



3/4

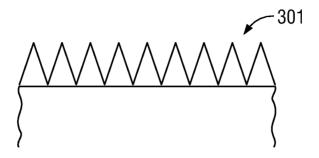


FIG. 3A

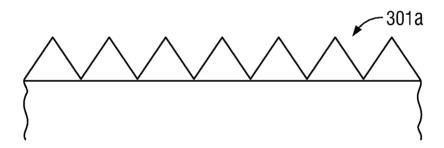


FIG. 3B

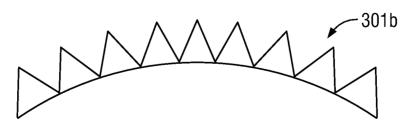
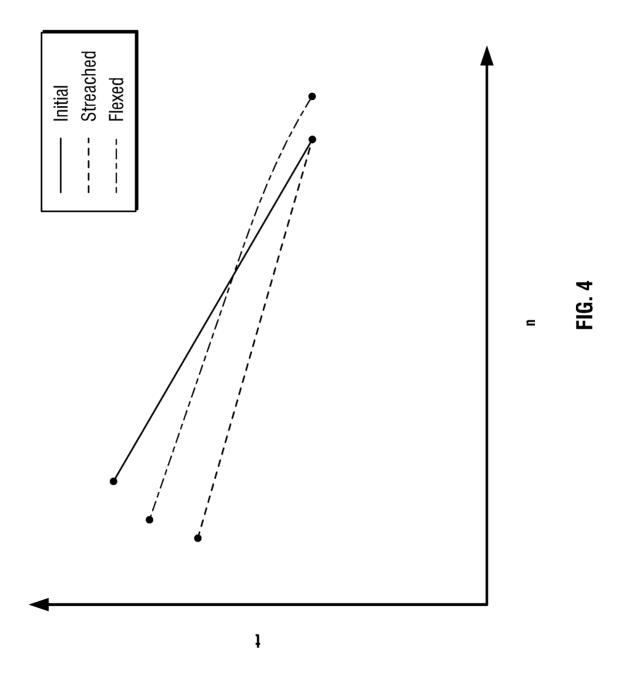


FIG. 3C



#### INTERNATIONAL SEARCH REPORT

International application No PCT/IIS2015 / 045310

PCT/US2015/045319 A. CLASSIFICATION OF SUBJECT MATTER INV. G02B1/11 G02B1/111 G02B1/118 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) G<sub>0</sub>2B 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) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. χ US 2013/004711 A1 (DOI SEITARO [JP] ET AL) 1-11, 15-30 3 January 2013 (2013-01-03) paragraphs [0012], [0013], [0084], [0085] 1-9, χ EP 0 945 254 A1 (AGFA GEVAERT NV [BE]; 12 - 14INNOVATIVE SPUTTERING TECH [BE]) 29 September 1999 (1999-09-29) paragraphs [0012], [0023], [0032] Χ US 5 783 049 A (BRIGHT CLARK I [US] ET AL) 1-4,6,7,21 July 1998 (1998-07-21) 9,13,14 column 11, lines 42-43; claims 7,8 -/--

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European Patent Office, P.B. 5818 Patentlaan 2	,				
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