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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 June 2019 (27.06.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/123019 A2

(51) International Patent Classification:
Not classified

(21) International Application Number:
PCT/IB2018/001623

(22) International Filing Date:
18 December 2018 (18.12.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/708,613 18 December 2017 (18.12.2017) US

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

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

Published:
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: A METHOD FOR THE SYNTHESIS OF FLEXIBLE MULTIFUNCTIONAL HIGH-VOIDAGE ULTRATHIN PE MEMBRANES

(57) **Abstract:** A method of manufacturing a polyethylene membrane can comprise: stretching a polyethylene film in a first direction during a first stretching; attaching a plurality of rods on side edges of the polyethylene film; attaching a tape on the polyethylene film; stretching the polyethylene film having the rods attached thereto in a second direction during a second stretching; and annealing the polyethylene film after the second stretching. The second direction can be a transverse direction of the first direction, and the first stretching and the second stretching can be performed at the same (or higher) temperature and the same stretching speed as each other.

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DESCRIPTION

A METHOD FOR THE SYNTHESIS OF FLEXIBLE MULTIFUNCTIONAL HIGH-VOIDAGE ULTRATHIN PE MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Application Serial No. 62/708,613, filed December 18, 2017, which is hereby incorporated by reference in its entirety including any tables, figures, or drawings.

BACKGROUND

Free-standing polymer ultra-thin film is extremely difficult to prepare and to handle due to its (1) high surface energy and micro-scale effect along thickness direction, and (2) the usually weak mechanical integrity for ultra-thin or thin polymer films. However, conventional methods to prepare the ultra-thin film including spin coating, dip coating, self-assembly and electro-spinning will either need a substrate or an intermediate support, or they are extremely vulnerable when handled, while also having poor results on mechanical property tests by direct tensile experiments. Also, the resultant structures are usually in the form of being dense and non-porous. i.e., there are no current commercially available products could be simultaneous 1) freestanding (the integrity of the material could stably exist without a substrate or a supporting layer); 2) porous (consisting of the void-form structures that could connect through the thickness direction); and 3) ultrathin (homogeneous and has an average thickness less than 100 nm).

BRIEF SUMMARY

Embodiments of the subject invention provide novel and advantageous ultrathin polyethylene (PE) membranes that comprise biaxially oriented polymer chains with a thickness of about or less than 100 nm.

Embodiments of the subject invention also provide novel and advantageous methods of manufacturing ultrathin PE membranes that comprise a first hot stretching and a second hot stretching in a transverse direction, thereby providing a film that has a super-high mechanical strength biaxially and that is ultra-thin. The method can include (1) modified gel film extrusion and (2) a new specially designed hot stretching along with post-stretching annealing to prepare ultra-thin ultra-high molecular weight polyethylene (UHMWPE) films. The low entanglement polymer gel extrusion is carried out by extruding swelling polymer solutions at solid contents low enough to ensure maximum drawability in the stretching process. A main advantage of the resultant films of this method is that they have super-high mechanical strength biaxially while simultaneously being ultra-thin.

In an embodiment of the subject invention, a polyethylene membrane can comprise biaxially oriented polymer chains, wherein a total thickness of the polyethylene membrane is less than 100 nm.

In another embodiment of the subject invention, a method of manufacturing a polyethylene membrane can comprise: stretching a polyethylene film in a first direction during a first stretching; and stretching the polyethylene film in a second direction during a second stretching, wherein the second direction is a transverse direction of the first direction.

In yet another embodiment of the subject invention, a method of manufacturing a polyethylene membrane can comprise: stretching a polyethylene film in a first direction during a first stretching; attaching a tape on the polyethylene film; stretching the polyethylene film in a second direction during a second stretching, and annealing the polyethylene film after the second stretching, wherein the second direction is a transverse direction of the first direction, and wherein the first stretching and the second stretching are performed at a same temperature or a higher temperature and a same stretching speed as each other.

In yet another embodiment of the subject invention, a method of manufacturing a polyethylene can comprise: stretching a polyethylene film simultaneously in two orthogonal directions at either the same or different speed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a first hot stretching and its transverse shrinking of an ultrathin PE membrane according to an embodiment of the subject invention.

Figure 2 shows a second hot stretching of an ultrathin PE membrane according to an embodiment of the subject invention.

Figure 3 shows a method to constrain membranes during hot stretching, schematic illustration of polytetrafluoroethylene (PTFE) tapes installed on PE films.

Figure 4 shows a schematic model of light interference on a film and a wafer.

Figure 5 shows a utilization of fringe (destructive phase interaction) shift due to a film, to calculate thickness.

Figure 6 shows a theoretical basis for the calculation of the thickness of an ultrathin PE membrane according to an embodiment of the subject invention.

Figure 7 shows Optical profiler results

Figure 8 shows a UV-vis Photospectrometer transmittance result of an ultra-thin UHMWPE film compared with a glass slide according to an embodiment of the subject invention.

Figure 9 shows a demonstration of high optical transparancy and free-standing ability of an ETHMWPE ultra thin film according to an embodiment of the subject invention.

DETAILED DESCRIPTION

Embodiments of the subject invention provide novel and advantageous ultrathin PE membranes that comprise biaxially oriented polymer chains and have a total thickness of less than 100 nm. Embodiments of the subject invention also provide novel and advantageous methods of manufacturing ultrathin PE membranes that comprise a first hot stretching and a second hot stretching in a transverse direction, thereby providing a film that has a super-high mechanical strength biaxially and that is ultra-thin.

In an embodiment, a method of manufacturing an ultrathin PE membrane comprises biaxial hot stretching, in particular, a first hot stretching and a second hot stretching in a transverse direction of that of the first hot stretching. A first direction of the first hot stretching can be across a second direction of the second hot stretching, and in certain embodiments the first direction can be perpendicular to the second direction.

Figure 1 shows a first hot stretching and its transverse shrinking of an ultrathin PE membrane according to an embodiment of the subject invention. Referring to Figure 1, a PE film **100** is stretched in a first direction of the PE film **100** during a first hot stretching. The PE film **100** can be a gel type film. After the first hot stretching, no post-stretching annealing needs be conducted. In addition, transverse constraining can be done by the installed PTFE tape **300** at edges of the PE film **100.** The final transverse shrinkage rate can be measured to be 10%, as shown in Figure 1. The first hot stretching is performed at a temperature of 100-130 °C and the stretching ratio can be between 10 and 180 times at a speed of 100-10000 %/min. In a specific embodiment, the first hot stretching can be performed at a temperature of 120 °C, and gauge length can be extended from 10 mm to 200 mm at a speed of 500%/min after 10 minutes of conditioning.

Figure 2 shows a second hot stretching of an ultrathin PE membrane according to an embodiment of the subject invention. Referring to Figure 2, the PE film **100** is stretched in a second direction of the PE film **100** during a second hot stretching, wherein the second direction of the PE film **100** is transverse to the first direction of the PE film **100**. That is, the PE film **100** is stretched in the first direction during the first hot stretching and then stretched in the second direction during the second hot stretching. The gauge length, temperature, and stretching speed during the second hot stretching can be the same as those of the first hot stretching or the temperature can be higher than the first hot stretching. While there is no post-stretching annealing after the first hot stretching, a post-stretching annealing can be performed right after the second hot stretching; for example, a post-stretching annealing can be performed at a temperature of 100-145 °C (e.g., for 5-15 minutes).

Transverse shrinking can become significant during the second hot stretching and yield rate may not be 20% during the second hot stretching. To overcome the serious transverse shrinking during the second hot stretching and reduce failure possibilities, the PTFE tape **300** can be used similar to the first hot stretching of Figure 1. As a result, the transverse shrinking is significantly reduced. The shrinking rate is less than 5% after stretching and post-stretching annealing.

Figure 3 shows a method to constrain membranes during hot stretching, including schematic illustration of PTFE tapes installed on PE films. In addition, the PTFE tape **300** can be replaced by other elastic tapes. PTFE tapes can be replaced by other elastomers such as polydimethylsiloxane (PDMS).

Methods of embodiments of the subject invention can comprise (1) modified gel film extrusion and (2) a new specially designed hot stretching along with post-stretching annealing to prepare ultra-thin ETFMWPE films. The resultant films (*i.e.*, ultrathin PE membranes) have super-high mechanical strength biaxially while simultaneously being ultra-thin (e.g., thickness of about or less than 100 nm). The maximum stress of the film reaches up to 1000 MPa, which is over two times stronger than stainless steel. The ductility of the film reaches up to 100%. By taking the density difference between polyethylene and steel and porosity of the film into consideration, the specific strength of EIHMWPE ultra-thin film is over twenty times higher than that of stainless steel. In addition, the ultra-thin film also has many other advantages, such as being waterproof, gas-permeable, and extremely transparent (ETV-vis transmission at 200 nm can be higher than 50%, while at 1100 nm the transmittance is around 98.5%).

Methods of embodiments of the subject invention provide preparation of an ultra-thin film made of ultra-high molecular weight polyethylene, and the resulting ultrathin film can include the following technical features:

(1) ultra-thin thickness below 100 nanometers;

(2) free-standing (i.e., it can be handled without any substrate);

(3) biaxially oriented, which means its polymer chain orientation is isotropic/or anisotropic if desired in a two-dimensional plane perpendicular to the thickness direction;

(4) highly porous, with a pore diameter of 5 - 100 nm;

(5) maximum stress of 1000 MPa and a Young's Modulus of between 500 MPa to 10,000 MPa.

In many embodiments, the ultrathin PE membrane has a thickness of less than 100 nm while being a free-standing film. The thin thickness of the ultrathin PE membrane can be measured by light interference *{i.e.,* optical profiler). The thickness of EIHMWPE thin/ultra-thin films can be determined by light interference and ETV-vis spectrometry synergistically. Figure 4 shows a schematic model of light interference on a film and a wafer, and Figure 5 shows utilization of fringe shift due to the film to calculate thickness. Referring to Figures 4 and 5, the film is disposed on the wafer, and the thickness is calculated using light interference based on the top-surface altitude difference between films and the silicon wafer underneath.

Figure 6 shows a theoretical basis for the calculation of the thickness of an ultrathin PE membrane according to an embodiment of the subject invention. Referring to Figures 4-6, for destructive phase interaction, the light path difference is:

$$\delta = \frac{(2k+1)}{2}\lambda ,$$

where δ is the light path difference, k is a natural number, and λ is the wavelength of incident light that used. There are two similar triangles: one is formed by the fringes shift distance l_{Shift} and film thickness /?; and the other is the distance between two neighboring fringes /, and the light path difference.

The assumptions for the calculation are as follows.

(1) The shift of fringes is only I st order, i.e., the shift distance could be:

$$l_{shift} = nl + l' ,$$

where $l_{sh,fi}$ is the actual shift distance between a fringe on the film and its original fringe on the wafer, and n is a natural number. Here, it is taken as $l_{sh,fi} = l'$; later the equation is revisited and used to verify the assumption.

(2) The used wavelength is 532 nm. The measurement uses narrow band green light for the measurement. For green light, 532 nm is taken as its wavelength, and afterwards the validity of this assumption is checked.

Thus, for neighboring destructive fringes, the light path difference is (&=l):

$$\delta = \frac{\lambda}{2} = \frac{532\ [nm]}{2} = 266.3\ [nm]$$

$$\tan\Theta = \frac{\delta}{l} = \frac{h}{l'}$$

$$h = l'\frac{\delta}{l} = \frac{24\ [\mu m] \cdot 266.3\ [nm]}{136.2\ [\mu m]} = 46.9\ [nm]$$

In addition, the assumptions for inspections are as follows. If it is not a first order shift, the thickness is thus almost doubled or even tripled, according to the number of order shifted, but the system is designed to apply a theta sweep to determine the thickness itself by adjusting the distance between the sample and the light source. The system measured result is an AFM-analogous form, and the height difference between a film and a wafer can be read on each point. This is the advantage, while the disadvantage is that the overall thickness of the film cannot be calculated precisely.

Figure 7 shows machine-generated interference results of an ultra-thin film according to an embodiment of the subject invention. Referring to Figure 7, the machine-generated result serves as a double confirmation to check the order of magnitude of the thickness. That is, the recovered roughness of the film by the machine is demonstrated in Figure 7. The average height difference is around 50 nm, suggesting that assumption (1) above is valid.

Figure 8 shows a UV-vis photospectrometer transmittance result of an ultra-thin UHMWPE film according to an embodiment of the subject invention, and Figure 9 shows a demonstration of the transmittance and free-standing ability of an UHMWPE ultra thin film according to an embodiment of the subject invention. Referring to Figures 8 and 9, the methods of embodiments of the subject invention provide ultrathin PE membranes that are free-standing, ultrathin, and transparent.

The subject invention includes, but is not limited to, the following exemplified embodiments.

Embodiment 1. A polyethylene membrane, comprising:

a plurality of biaxially oriented polymer chains,

wherein a thickness of the polyethylene membrane is 100 nanometers (nm) or less (or about 100 nm or less).

Embodiment 2. The polyethylene membrane according to embodiment 1, wherein orientations of the polymer chains are isotropic in a two-dimensional plane perpendicular to a direction of the thickness of the polyethylene membrane.

Embodiment 3. The polyethylene membrane according to embodiment 1, wherein orientations of the polymer chains can exhibit preferentially higher orientation in one of the plane direction perpendicular to a direction of the thickness of the polyethylene membrane.

Embodiment 4. The polyethylene membrane according to any of embodiments 1-3, wherein the polyethylene membrane comprises a plurality of pores with a pore diameter in a range of 5 nm to 100 nm.

Embodiment 5. The polyethylene membrane according to any of embodiments 1-4, wherein the polyethylene membrane is a free-standing film.

Embodiment 6. The polyethylene membrane according to any of embodiments 1-5, wherein the polyethylene membrane has a maximum stress of at least 300 mega-Pascal (MPa).

Embodiment 7. The polyethylene membrane according to any of embodiments 1-6, wherein the polyethylene membrane has a Young’s Modulus of at least 500 MPa.

Embodiment 8. The polyethylene membrane according to any of embodiments 1-7, wherein the polyethylene membrane has a ETV-vis transmittance of at least 50% with respect to 200 nm wavelength light.

Embodiment 9. The polyethylene membrane according to any of embodiments 1-8, wherein the polyethylene membrane has a UV-vis transmittance of at least 95% with respect to 1100 nm wavelength light.

Embodiment 10. A method of manufacturing a polyethylene membrane, the method comprising:

stretching a polyethylene film in a first direction during a first stretching; and

stretching the polyethylene film in a second direction during a second stretching, wherein the second direction is a transverse direction of the first direction.

Embodiment 11. The method according to embodiment 10, further comprising performing a post-stretching annealing of the polyethylene film after the second stretching.

Embodiment 12. The method according to any of embodiments 10-11, further comprising, after the first stretching and before the second stretching, attaching a plurality of elastic films on side edges of the polyethylene film, including attaching a first elastic film on a first side edge of the polyethylene film and a second elastic film on a second side edge of the polyethylene film.

Embodiment 13. The method according to embodiment 12, wherein the plurality of elastic films are made of an elastomer including for example one of polytetrafluoroethylene (PTFE) or polydimethylsiloxane (PDMS) or the like.

Embodiment 14. The method according to any of embodiments 10-13, further comprising, after the first stretching and before the second stretching, attaching a tape on the polyethylene film.

Embodiment 15. The method according to any of embodiments 10-14, further comprising, before the first stretching, attaching a tape on the polyethylene film.

Embodiment 16. The method according to any of embodiments 10-15, wherein the first stretching is performed at a temperature of 100-130 °C.

Embodiment 17. The method according to any of embodiments 10-16, wherein the polyethylene film is stretched in the first direction such that the stretching ratio of the polyethylene film is between 10 and 180 times at a speed of l00-l0000%/min.

Embodiment 18. The method according to any of embodiments 10-16, wherein, during the first stretching, a gauge length of the polyethylene film is extended from 10 mm to 200 mm at a speed of 500%/min after 10 minutes of conditioning.

Embodiment 19. The method according to any of embodiments 10-18, wherein the second stretching is performed at a same temperature as or higher temperature than the first stretching.

Embodiment 20. The method according to any of embodiments 10-19, wherein the second stretching is performed at a same stretching speed as the first stretching.

Embodiment 21. The method according to any of embodiments 11-20, wherein the post-stretching annealing is performed at a temperature of 100-145 °C for 5-15 minutes.

Embodiment 22. The method according to any of embodiments 10-21, wherein the second stretching is performed after the first stretching without any annealing performed before the second stretching.

Embodiment 23. The method according to any of embodiments 10-22, wherein the first stretching and the second stretching are performed simultaneously biaxially.

Embodiment 24. A method of manufacturing a polyethylene membrane, the method comprising:

stretching a polyethylene film in a first direction during a first stretching;

attaching a plurality of elastic films on side edges of the polyethylene film, including attaching a first film on a first side edge of the polyethylene film and a second film on a second side edge of the polyethylene film;

stretching the polyethylene film, having the plurality of elastic films attached thereto, in a second direction during a second stretching; and

annealing the polyethylene film after the second stretching,

wherein the second direction is a transverse direction of the first direction,

wherein the second stretching is performed at a same (or higher) temperature as (or than) the first stretching, and

wherein the second stretching is performed at a same stretching speed as the first stretching.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

CLAIMS

What is claimed is:

1. A polyethylene membrane, comprising:
a plurality of biaxially oriented polymer chains,
wherein a thickness of the polyethylene membrane is 100 nanometers (nm) or less.

2. The polyethylene membrane according to claim 1, wherein orientations of the polymer chains are isotropic in a two-dimensional plane perpendicular to a direction of the thickness of the polyethylene membrane.

3. The polyethylene membrane according to claim 1, wherein preferred orientations of the polymer chains in a two-dimensional plane perpendicular to a direction of the thickness of the polyethylene membrane.

4. The polyethylene membrane according to claim 1, wherein the polyethylene membrane comprises a plurality of pores with a pore diameter in a range of 5 nm to 100 nm.

5. The polyethylene membrane according to claim 1, wherein the polyethylene membrane is a free-standing film.

6. The polyethylene membrane according to claim 1, wherein the polyethylene membrane has a maximum stress of at least 300 mega-Pascal (MPa).

7. The polyethylene membrane according to claim 1, wherein the polyethylene membrane has a Young’s Modulus of at least 500 MPa.

8. The polyethylene membrane according to claim 1, wherein the polyethylene membrane has a UV-vis transmission of at least 50% with respect to 200 nm wavelength light and at least 95% with respect to 1100 nm wavelength light.

9. A method of manufacturing a polyethylene membrane, the method comprising:

stretching a polyethylene film in a first direction during a first stretching; and

stretching the polyethylene film in a second direction during a second stretching,

wherein the second direction is a transverse direction of the first direction.

10. The method according to claim 9, further comprising performing a post-stretching annealing of the polyethylene film after the second stretching.

11. The method according to claim 10, further comprising, after the first stretching and before the second stretching, attaching a plurality of elastic films on side edges of the polyethylene film, including attaching a first elastic film on a first side edge of the polyethylene film and a second elastic film on a second side edge of the polyethylene film.

12. The method according to claim 11, wherein the plurality of elastic films are made of an elastomer including at least one of a polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS).

13. The method according to claim 11, further comprising, after the first stretching and before the second stretching, attaching a tape on the polyethylene film.

14. The method according to claim 10, further comprising, before the first stretching, attaching a tape on the polyethylene film.

15. The method according to claim 10, wherein the first stretching is performed at a temperature of 100-130 °C.

16. The method according to claim 10, wherein the polyethylene film is stretched in the first direction such that the stretching ratio is between 10 and 180 times at a speed of l00-l0000%/min.

17. The method according to claim 10, wherein, during the first stretching, a gauge length of the polyethylene film is extended from 10 mm to 200 mm at a speed of 500%/min after 10 minutes of conditioning.

18. The method according to claim 10, wherein the second stretching is performed at a same temperature as or higher temperature than the first stretching, and wherein the second stretching is performed at a same stretching speed as the first stretching.

19. The method according to claim 10, wherein the post-stretching annealing is performed at a temperature of 100-145 °C for 5-15 minutes.

20. The method according to claim 9, wherein the second stretching is performed after the first stretching without any annealing performed before the second stretching.

21. The method according to claim 9, wherein the first stretching and the second stretching are performed simultaneously biaxially.

22. A method of manufacturing a polyethylene membrane, the method comprising:

stretching a polyethylene film in a first direction during a first stretching;

attaching a plurality of elastic films on side edges of the polyethylene film, including attaching a first elastic film on a first side edge of the polyethylene film and a second elastic film on a second side edge of the polyethylene film;

stretching the polyethylene film, having the plurality of elastic films attached thereto, in a second direction during a second stretching; and

annealing the polyethylene film after the second stretching,

wherein the second direction is a transverse direction of the first direction,

wherein the second stretching is performed at a same temperature as the first stretching, and

wherein the second stretching is performed at a same stretching speed as the first stretching.

FIGURE 1

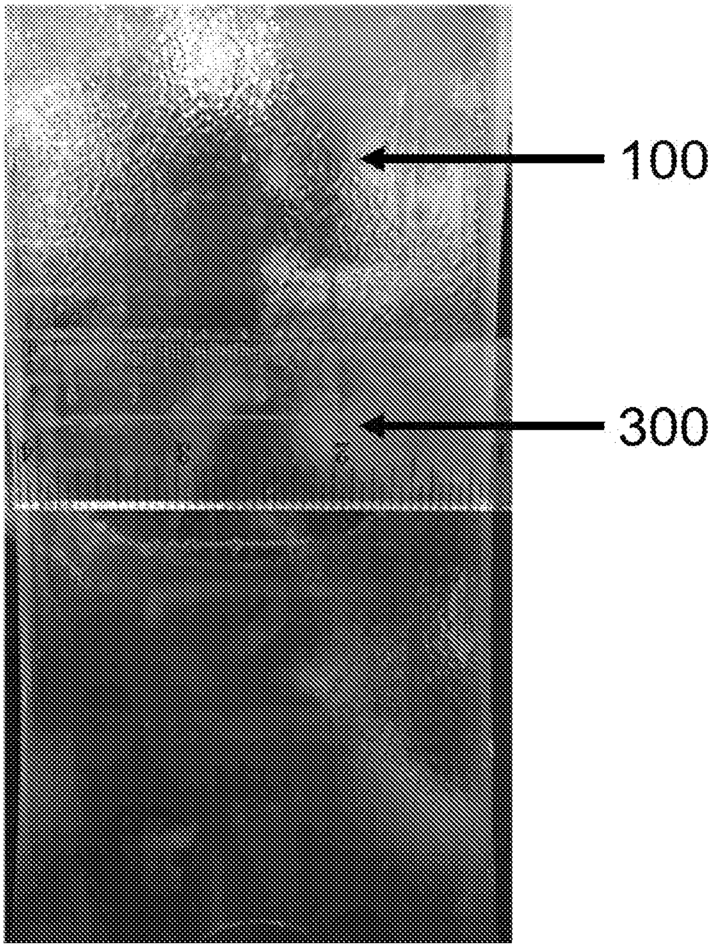

FIGURE 2

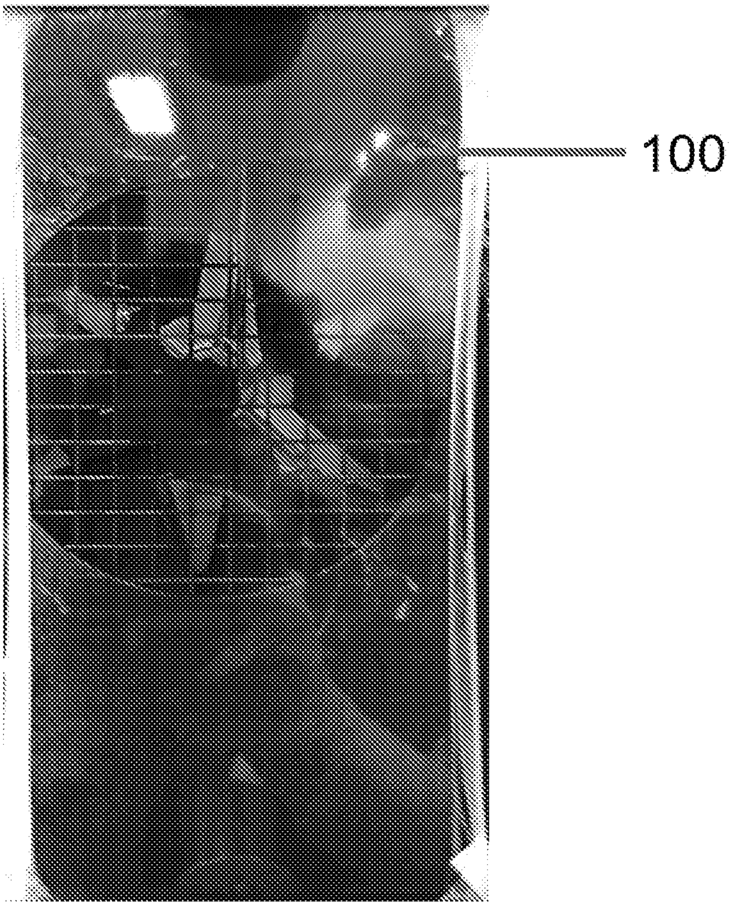

FIGURE 3

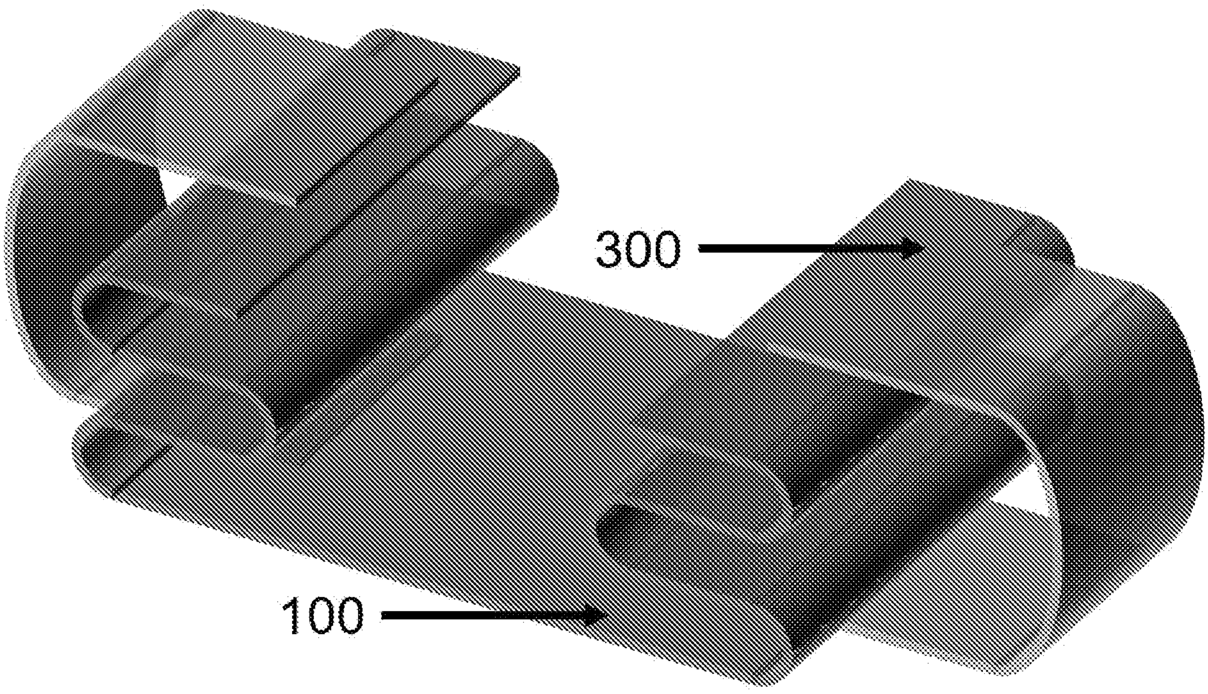

FIGURE 4

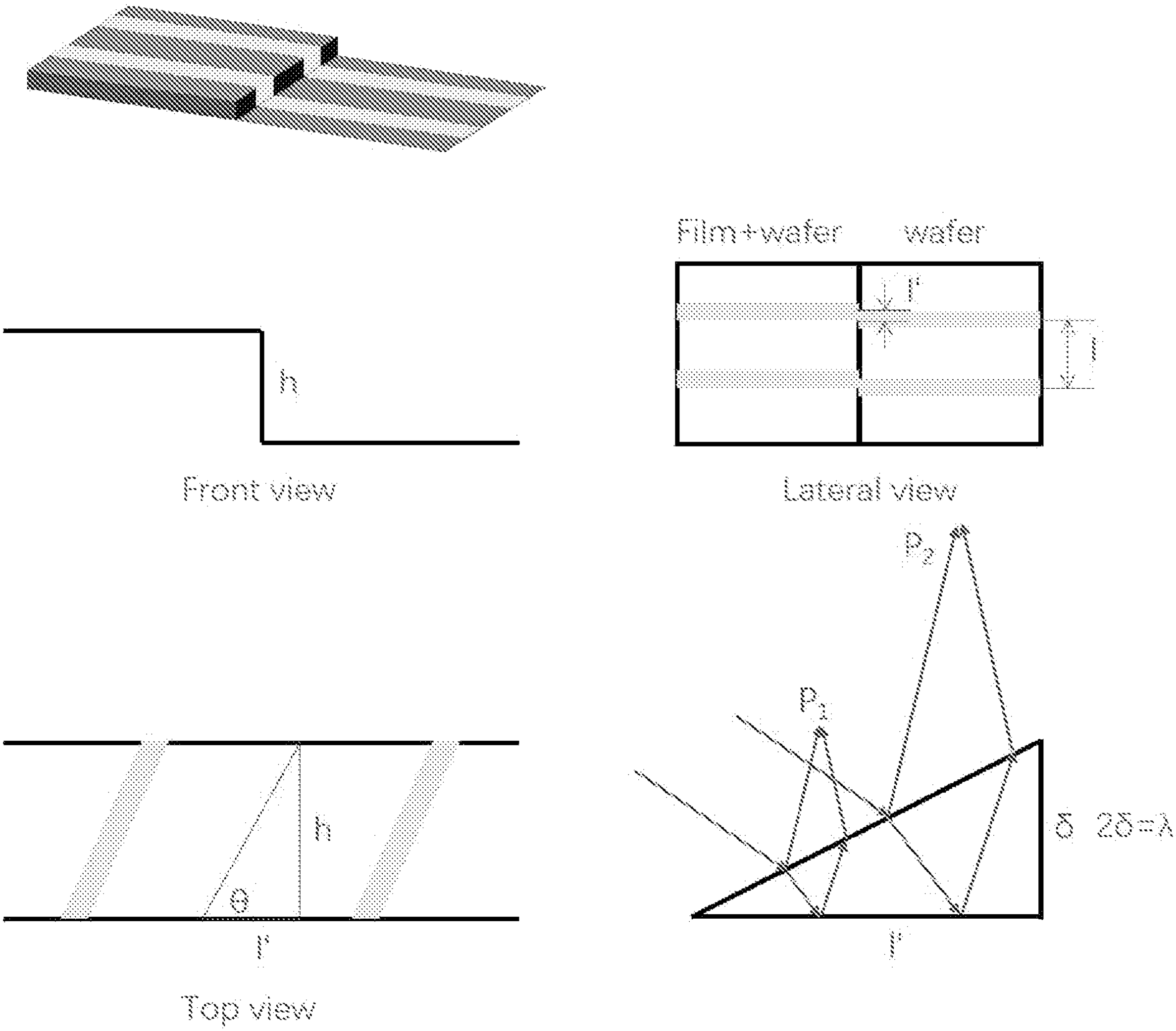
Film+wafer
wafer
l'
l
h
Front view
Lateral view
P2
P1
δ 2δ=λ
h
θ
l'
l'
Top view

FIGURE 5

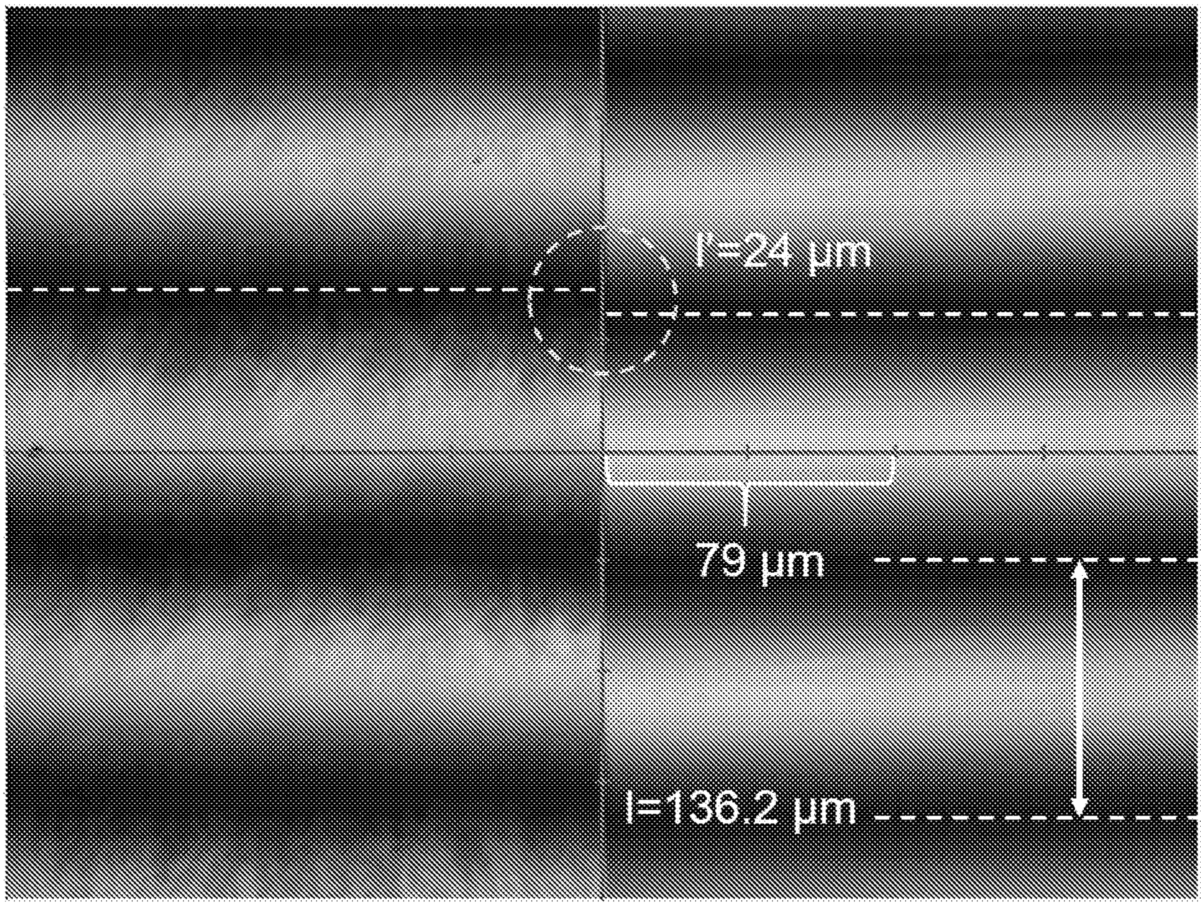

FIGURE 6

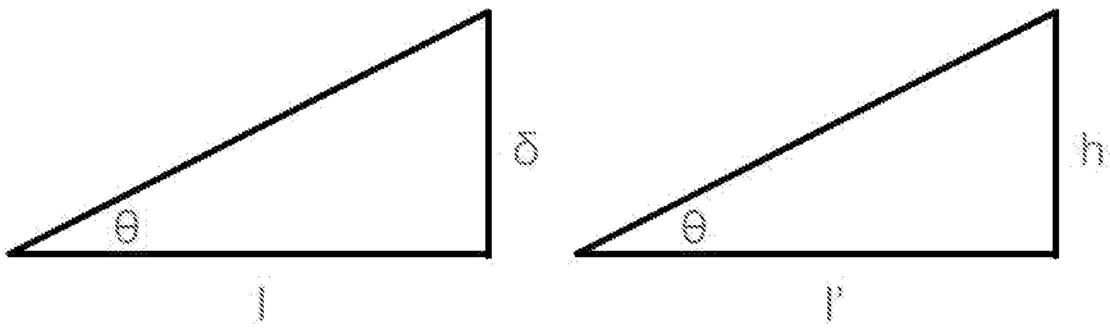

FIGURE 7

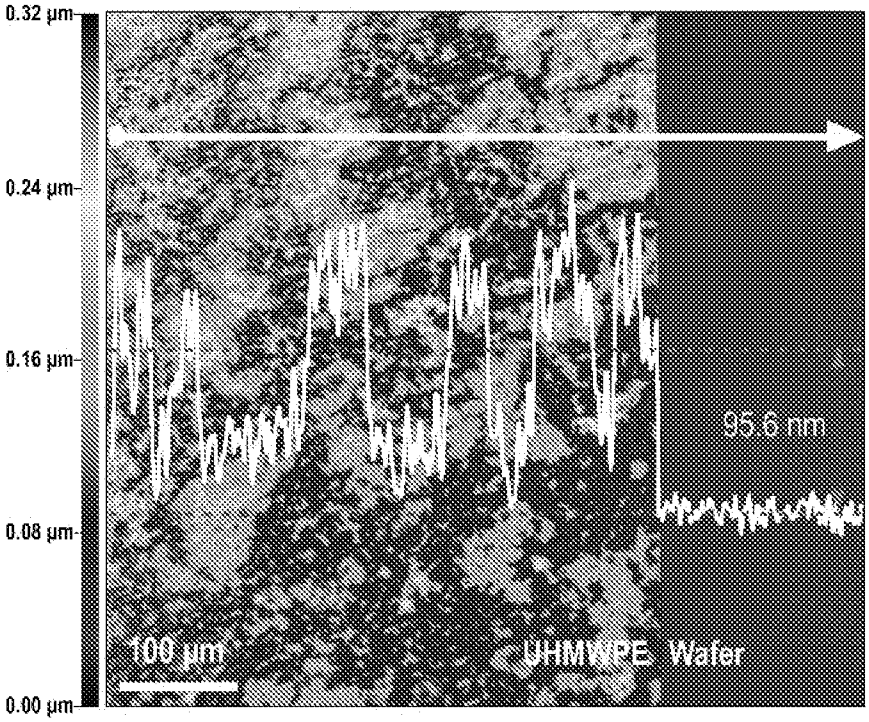

FIGURE 8

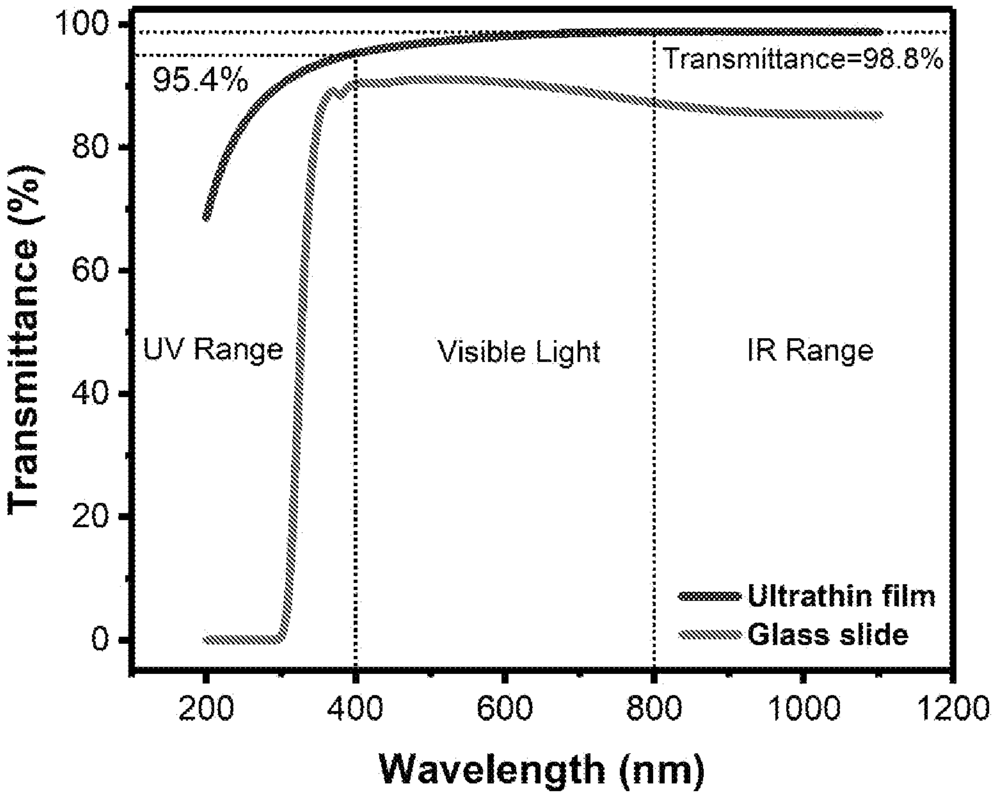
100
80
60
40
20
0
Transmittance (%)
95.4%
Transmittance=98.8%
UV Range
Visible Light
IR Range
Ultrathin film
Glass slide
200
400
600
800
1000
1200
Wavelength (nm)

FIGURE 9