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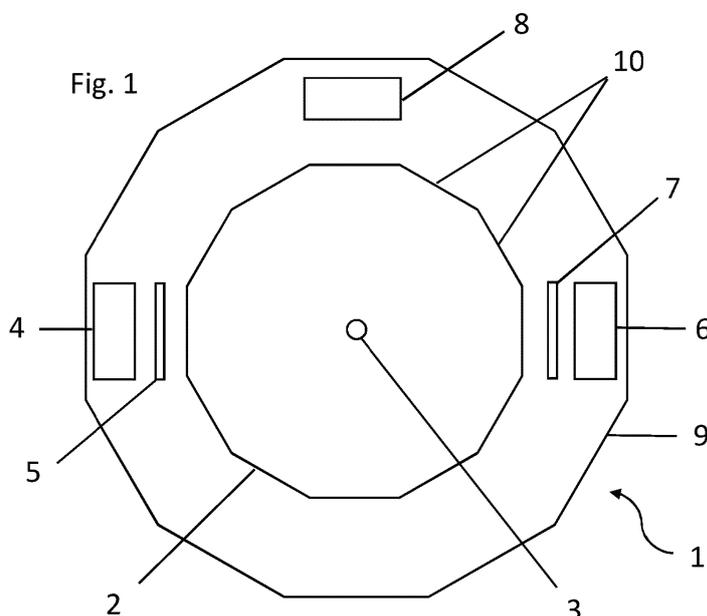
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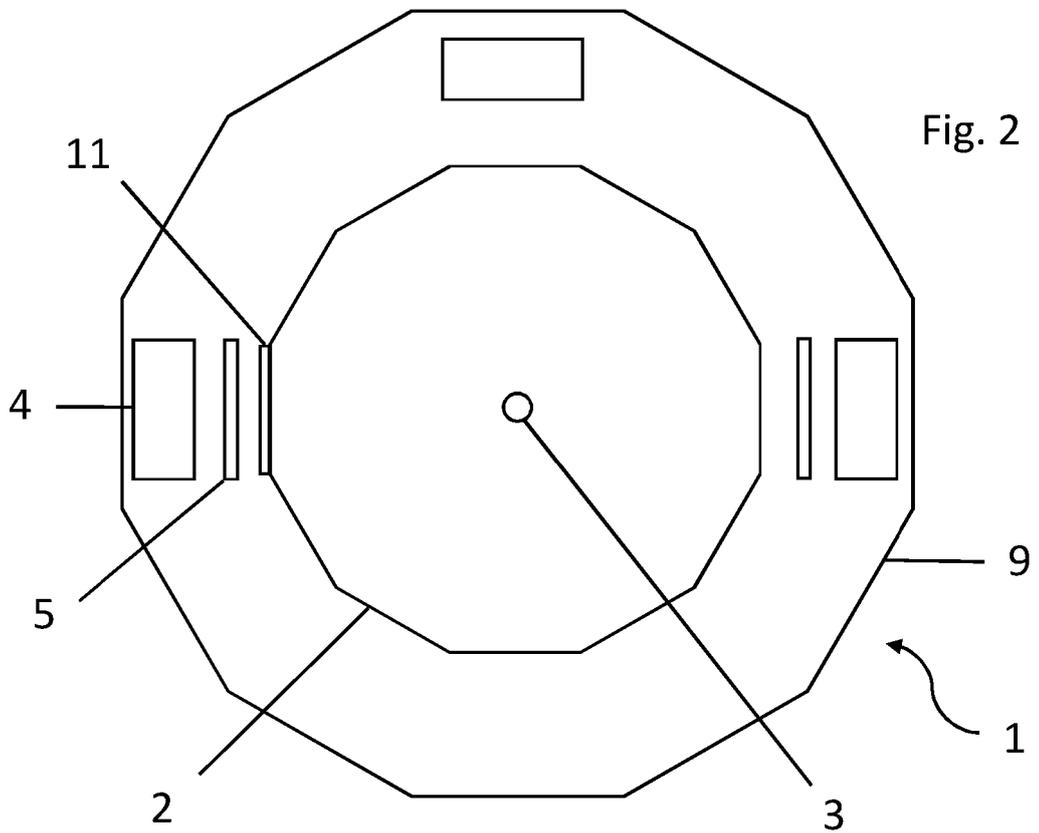
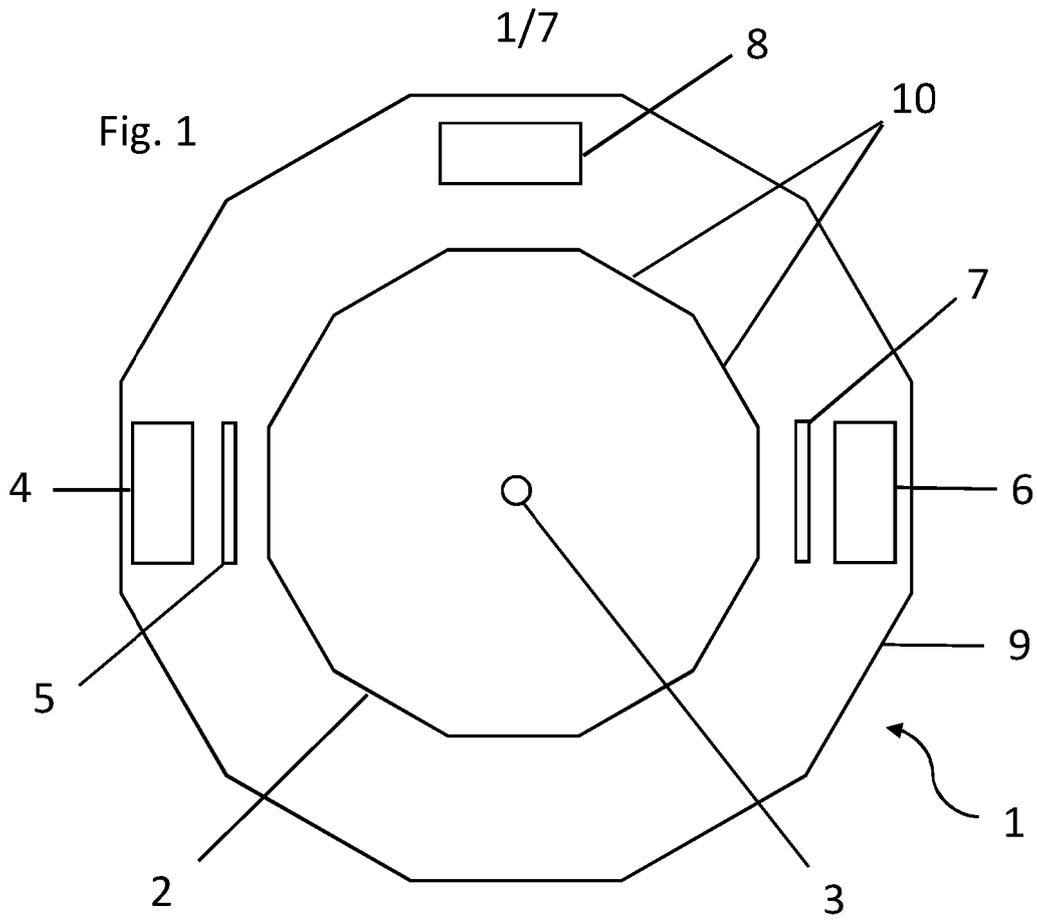
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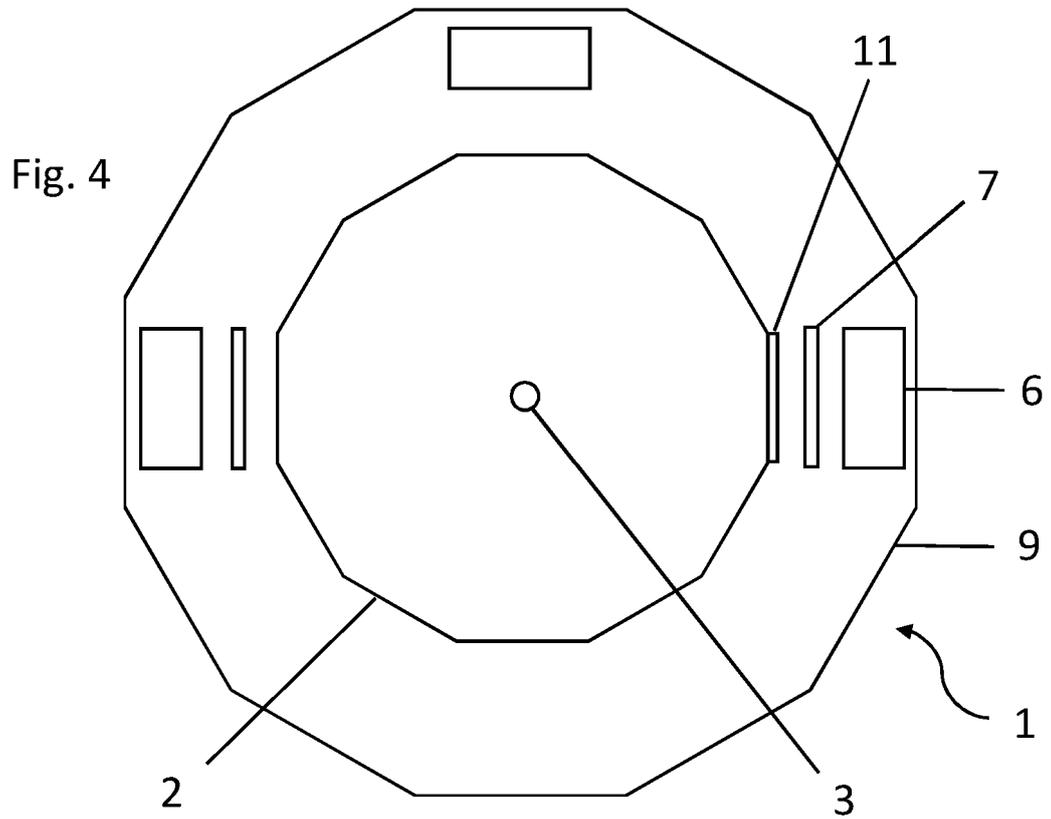
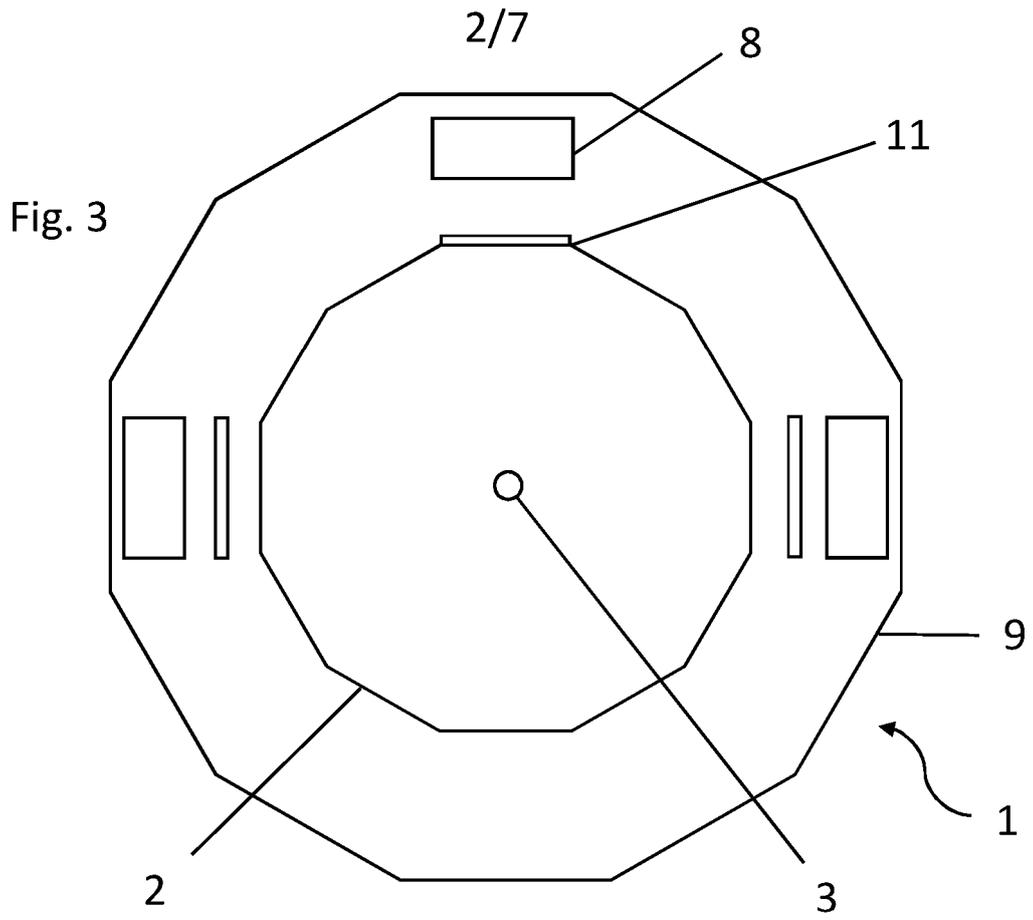
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Other: EPODOC, WPI, XPESP, XPSRNG, Patent
Fulltext

(54) Title of the Invention: **Apparatus and methods for depositing durable optical coatings**
Abstract Title: **Apparatus and methods for depositing germanium carbide coatings by magnetron sputtering**

(57) An apparatus 1 for depositing germanium and carbon onto one or more substrates comprises a vacuum chamber, at least one moveable mount 2, a first magnetron sputtering device 4 configured to sputter germanium from a first sputtering target 5 comprising germanium, thereby defining a germanium sputtering zone, and a second magnetron sputtering device 6 configured to sputter carbon from a second sputtering target 7, thereby defining a carbon sputtering zone. The apparatus preferably comprises at least one deposition sensor (12a, 12b figure 5) configured to measure a parameter indicative of the amount of germanium or carbon or both deposited onto a sensing surface. The sensor may comprise a quartz microbalance. The apparatus may further comprise at least one plasma processing device 8 defining a plasma treatment zone. The at least one mount is preferably a drum 2 rotatable about a longitudinal axis 3 thereof. A method of depositing germanium and carbon using the apparatus of the invention comprises moving the one or more substrates through the germanium sputtering zone and moving the one or more substrates through the carbon sputtering zone.







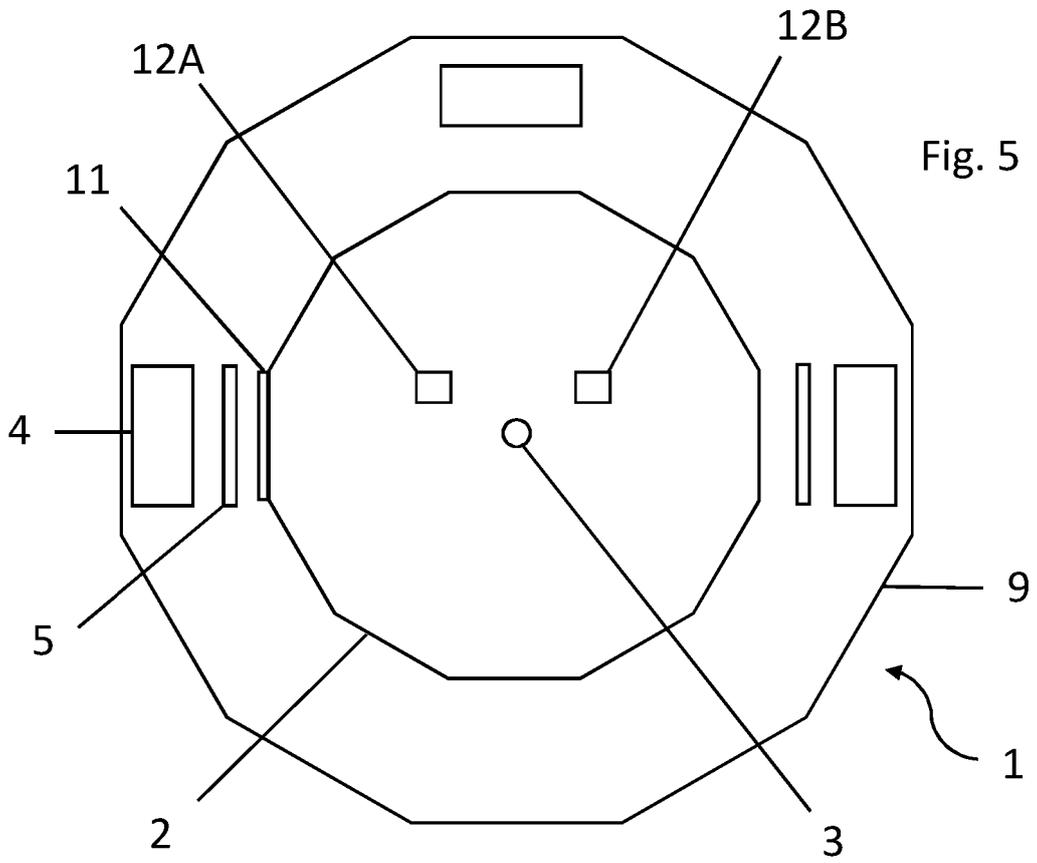


Fig. 5

Test	Method	Specification
Adhesion	Scotch Tape Test (snap tape removal)	Mil_C_48497A para 4.5.3.1
Humidity	24hrs , 50°C, 95 % RH (achieved > 7 days)	Mil_C_48497A para 4.5.3.2
Severe Abrasion	50 strokes (achieved > 100 strokes)	Mil_C_48497A para 4.5.5.1
Sand wiper test	Requirement 10,000 (achieved > 30,000)	TS1888 para 5.4.3
Salt Spray	Requirement 24hrs (achieved > 200 hrs)	Mil_C_675C para 4.5.9

Fig. 6

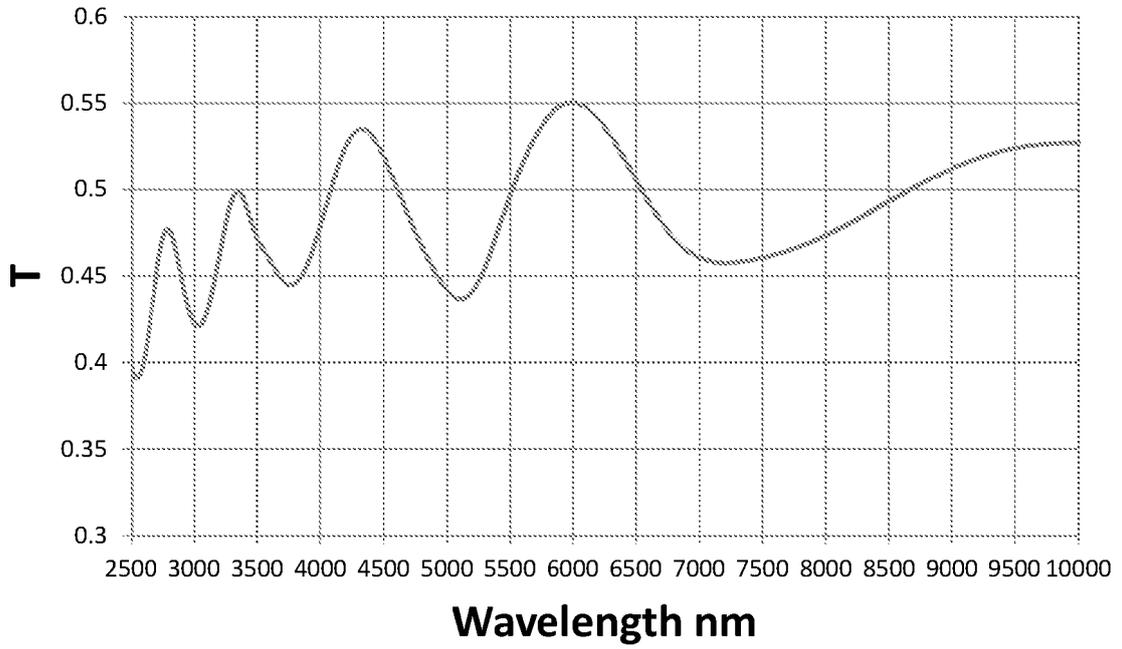


Fig. 7

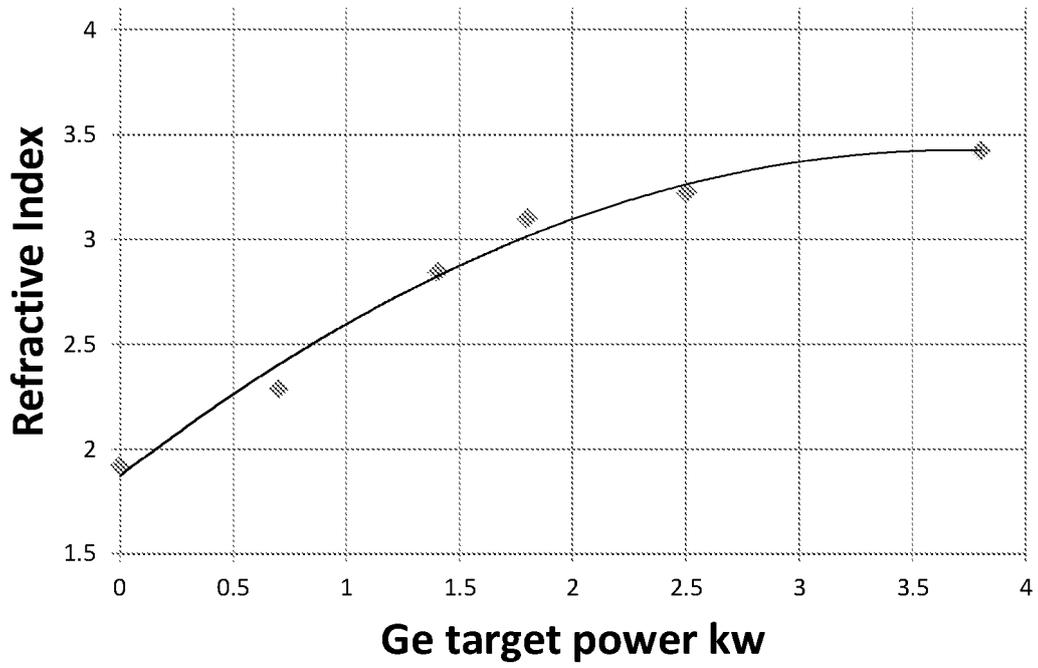


Fig. 8

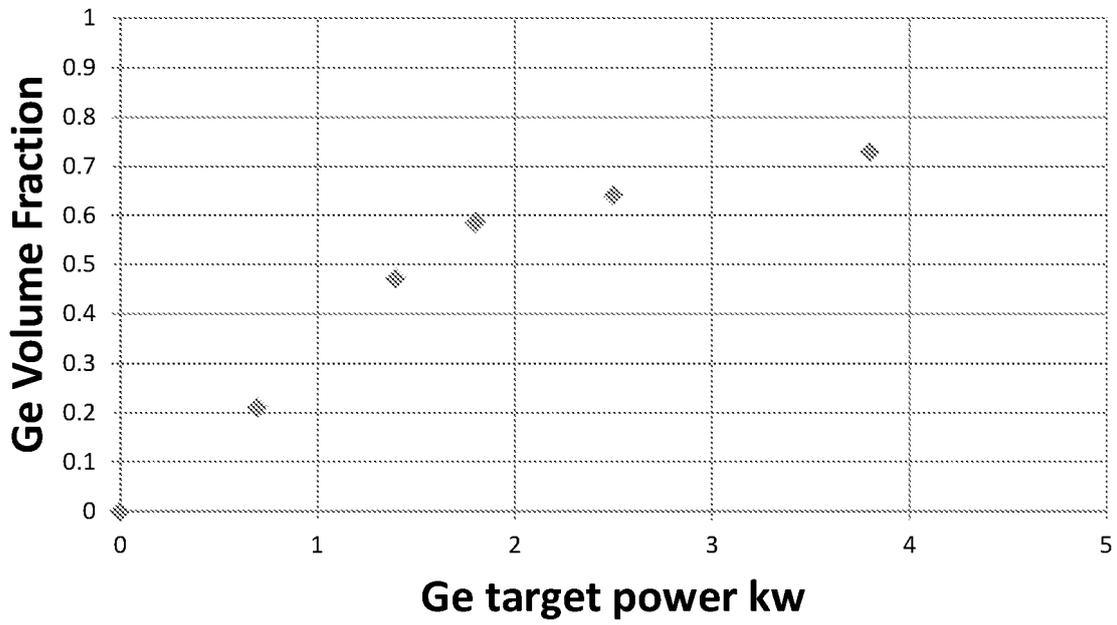


Fig. 9

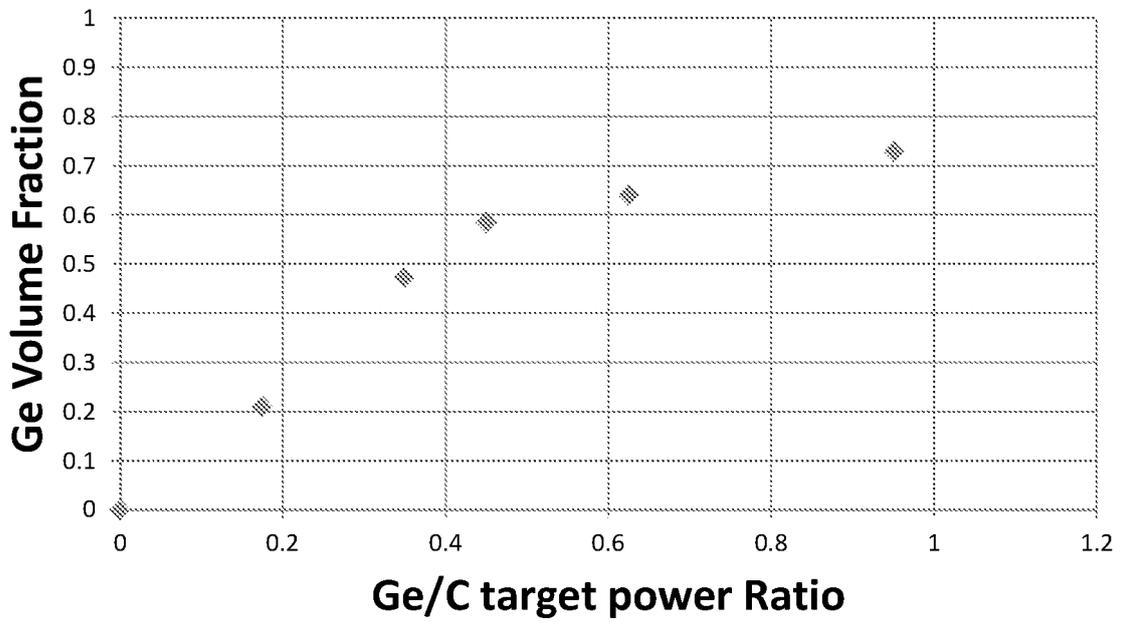


Fig. 10

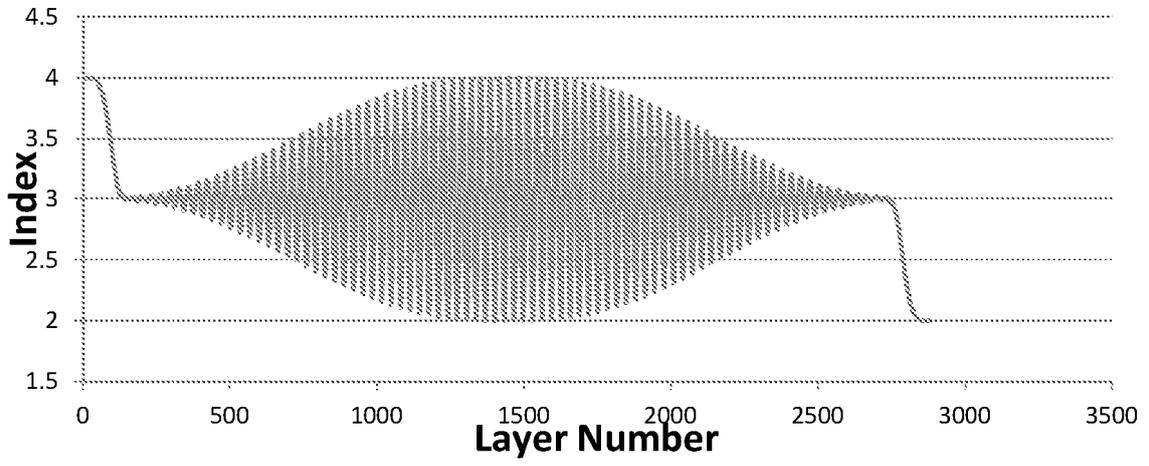


Fig. 11

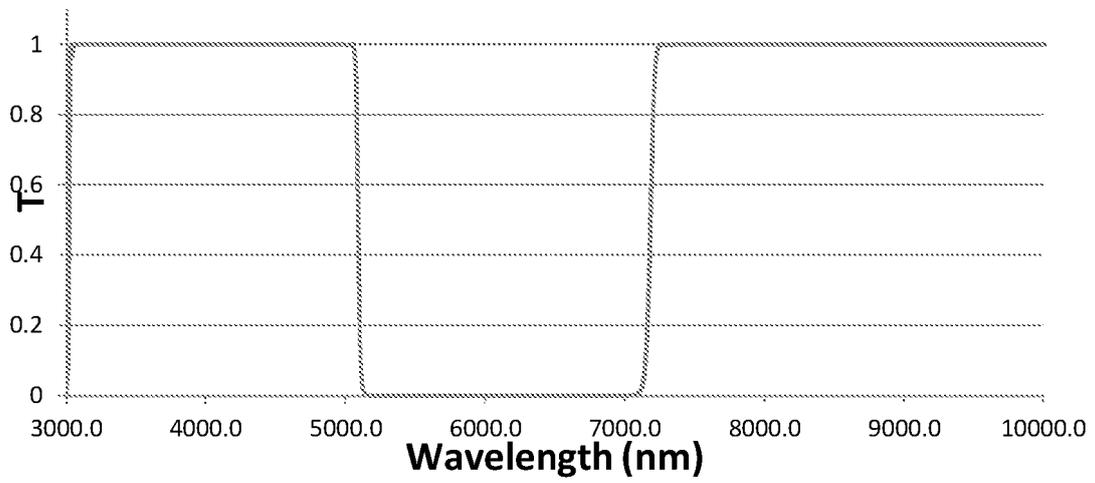


Fig. 12

1 APPARATUS AND METHODS FOR DEPOSITING DURABLE OPTICAL COATINGS

2

3 Field of the invention

4

5 The invention relates to apparatus and methods for depositing germanium and
6 carbon onto one or more substrates.

7

8 Background to the invention

9

10 Infra-red (IR) light detectors typically require external optical windows through which
11 IR light may be transmitted. IR-transmissive windows are currently made from
12 materials such as zinc sulphide, germanium and mouldable chalcogenide glass.
13 These materials have the required optical property of transmitting IR light. However,
14 these materials generally exhibit inadequate mechanical properties, such as poor rain
15 or sand erosion resistance, and typically suffer from surface scratching or wear after
16 only light abrasion. IR windows made from such materials are therefore only suitable
17 for use in relatively benign environments and in particular are not suitable for use in
18 harsh environments.

19

20 The mechanical properties of IR windows made from materials such as zinc sulphide,
21 germanium or mouldable chalcogenide glass can be improved by applying a hard,
22 stiff and transparent external protective coating. Hard coatings, such as diamond-like
23 carbon (DLC) or germanium carbide ($\text{Ge}_x\text{C}_{1-x}$), are typically deposited onto IR
24 windows using plasma enhanced chemical vapour deposition (PECVD) at elevated

1 temperatures (e.g. about 300°C). PECVD is an expensive, low-throughput method,
2 and the elevated temperatures required are incompatible with low-cost chalcogenide
3 glass window materials in particular. PECVD-deposited coatings typically exhibit
4 high residual stresses.

5

6 Germanium carbide is a promising hard coating for IR windows, but it is difficult to
7 deposit at low temperatures using known methods.

8

9 Accordingly, there is a need for new methods of depositing hard coatings like
10 germanium carbide having higher throughputs while retaining precise control over
11 coating optical properties. In particular, there is a need for methods of depositing
12 such hard coatings at room temperature so as to be compatible with chalcogenide
13 glass IR windows. There is also a need for methods of depositing rugate-structured
14 hard coatings, in which the refractive index of the coating varies continuously through
15 the thickness of the coating.

16

17 Summary of the invention

18

19 A first aspect of the invention provides apparatus for depositing germanium (Ge) and
20 carbon (C) onto one or more substrates. The apparatus comprises a vacuum
21 chamber, at least first and second magnetron sputtering devices and at least one
22 movable mount for supporting the one or more substrates within the vacuum
23 chamber. The first magnetron sputtering device is configured to sputter (i.e. in use)
24 germanium towards the at least one mount from a first sputtering target comprising
25 germanium, thereby defining a germanium sputtering zone within the vacuum
26 chamber. The second magnetron sputtering device is configured to sputter (i.e. in
27 use) carbon towards the at least one mount from a second sputtering target
28 comprising carbon, thereby defining a carbon sputtering zone within the vacuum
29 chamber. The at least one mount and the at least first and second magnetron
30 sputtering devices (i.e. typically including the first and second sputtering targets) are
31 arranged such that, when each substrate is moved through the germanium sputtering
32 zone on the at least one movable mount, germanium is deposited on the said
33 substrate, and when each substrate is moved through the carbon sputtering zone on
34 the at least one movable mount, carbon is deposited on the said substrate.

35

36 The first sputtering target typically comprises predominantly germanium. The first
37 sputtering target may consist entirely of germanium. The skilled person will

1 understand that the term 'germanium' does not necessarily refer to 100% pure
2 germanium. The first sputtering target may comprise (e.g. consist of) at least 99.0%
3 pure germanium, or more preferably at least 99.5% pure germanium, or more
4 preferably at least 99.9% pure germanium, or more preferably at least 99.99% pure
5 germanium or more preferably at least 99.999% pure germanium. The first sputtering
6 target may comprise (e.g. consist of) germanium tiles bonded (using, for example,
7 indium) to a copper backing.

8

9 The second sputtering target typically comprises predominantly carbon. The second
10 sputtering target may consist entirely of carbon. The skilled person will understand
11 that the term 'carbon' does not necessarily refer to 100% pure carbon. The second
12 sputtering target may comprise (e.g. consist of) at least 99.0% pure carbon, or more
13 preferably at least 99.5% pure carbon, or more preferably at least 99.9% pure carbon,
14 or more preferably at least 99.99% pure carbon, or more preferably at least 99.999%
15 pure carbon. The second sputtering target may comprise (e.g. consist of) carbon in
16 the form of graphite.

17

18 The apparatus is typically apparatus for depositing a thin film comprising both
19 germanium and carbon onto the one or more substrates, that is to say a thin film
20 comprising both germanium and carbon atoms. A thin film typically has a thickness
21 (i.e. in a direction substantially perpendicular to the surface of the substrate on which
22 it is formed) of a few nanometers or a few microns, e.g. typically not more than 100
23 microns.

24

25 Thin films comprising germanium and carbon typically transmit infrared light across a
26 broad band of wavelengths and are therefore suitable for use as hard coatings for IR
27 windows. Germanium and carbon may also both be sputtered at low temperatures,
28 e.g. room temperature. Sputtering of germanium and carbon is therefore compatible
29 with the deposition of hard coatings onto, for example, chalcogenide glass
30 substrates. Sputtering at low temperatures also typically results in thin films having
31 low residual stresses (of the order of 100 MPa). Thin films deposited by other
32 methods, such as PECVD, typically exhibit high residual stresses (of the order of 1
33 GPa), most likely due to the high deposition temperatures required. Because the
34 residual stresses achieved using low-temperature sputtering are low, the inventors
35 have found that the maximum thickness (and thus hardness) of coatings comprising
36 germanium and carbon which can be deposited using the apparatus of this first

1 aspect of the invention is significantly higher than the thickness (and thus hardness)
2 achievable when coatings are deposited using PECVD.

3

4 It may be that the apparatus is apparatus for depositing one or more layers of
5 germanium and one or more layers of carbon onto the one or more substrates. It
6 may be that the apparatus is apparatus for depositing one or more monolayers of
7 germanium and one or more monolayers of carbon onto the one or more substrates,
8 wherein a monolayer is one atom thick.

9

10 It may be that the apparatus is apparatus for depositing a multi-layered structure onto
11 the one or more substrates, the multi-layered structure comprising one or more layers
12 of germanium and one or more layers of carbon. The multi-layered structure may
13 comprise a plurality of layers of germanium and a plurality of layers of carbon. Each
14 layer of germanium may comprise (e.g. be formed from) one or more monolayers of
15 germanium. Each layer of carbon may comprise (e.g. be formed from) one or more
16 monolayers of carbon. The multi-layered structure may comprise alternating layers of
17 germanium and carbon. Each alternating layer of germanium and carbon may have
18 the same thickness. Alternatively, different layers of germanium and carbon may
19 have different thicknesses.

20

21 It may be that the apparatus is apparatus for depositing germanium carbide ($\text{Ge}_x\text{C}_{1-x}$)
22 onto the one or more substrates. It may be that the apparatus is apparatus for
23 depositing amorphous germanium carbide ($\text{Ge}_x\text{C}_{1-x}$) onto the one or more substrates.

24

25 It may be that the apparatus is apparatus for depositing a multi-layered structure onto
26 the one or more substrates, the multi-layered structure comprising one or more layers
27 of $\text{Ge}_x\text{C}_{1-x}$ and one or more layers of $\text{Ge}_y\text{C}_{1-y}$, wherein x and y have different values.
28 The multi-layered structure may comprise a plurality of layers of $\text{Ge}_x\text{C}_{1-x}$ and a
29 plurality of layers of $\text{Ge}_y\text{C}_{1-y}$. Each layer of $\text{Ge}_x\text{C}_{1-x}$ may comprise (e.g. be formed
30 from) one or more monolayers of $\text{Ge}_x\text{C}_{1-x}$. Each layer of $\text{Ge}_y\text{C}_{1-y}$ may comprise (e.g.
31 be formed from) one or more monolayers of $\text{Ge}_y\text{C}_{1-y}$. The multi-layered structure may
32 comprise alternating layers of $\text{Ge}_x\text{C}_{1-x}$ and $\text{Ge}_y\text{C}_{1-y}$. Each alternating layer of $\text{Ge}_x\text{C}_{1-x}$
33 and $\text{Ge}_y\text{C}_{1-y}$ may have the same thickness. Alternatively, different layers of $\text{Ge}_x\text{C}_{1-x}$
34 and $\text{Ge}_y\text{C}_{1-y}$ may have different thicknesses.

35

36 The refractive index of germanium carbide typically depends on the stoichiometric
37 ratio of germanium to carbon. The greater the concentration of germanium, the

1 typically greater the refractive index. A multi-layered structure comprising alternating
2 layers of $\text{Ge}_x\text{C}_{1-x}$ and $\text{Ge}_y\text{C}_{1-y}$, wherein x and y have different values, therefore
3 typically has a refractive index which varies (e.g. alternates between at least two
4 different values) spatially along a direction substantially perpendicular to the surface
5 of the one or more substrates onto which the structure is deposited.

6

7 It may be that the apparatus is apparatus for depositing a rugate structure onto the
8 one or more substrates. In the rugate structure the composition (e.g. the
9 concentrations of germanium and carbon) varies continuously along the direction
10 substantially perpendicular to the surface of the one or more substrates onto which
11 the structure is deposited. Accordingly, the refractive index typically varies
12 continuously along the direction substantially perpendicular to the surface of the one
13 or more substrates onto which the structure is deposited. Continuous variation in
14 composition also reduces discrete boundaries between regions of different
15 composition within the rugate structure, increasing the mechanical strength of the
16 rugate structure (since any discrete boundaries can act as weak points).

17

18 It may be that the apparatus is apparatus for depositing a solid solution comprising
19 germanium and carbon onto the one or more substrates, for example a solid solution
20 of carbon in germanium and/or a solid solution of germanium in carbon.

21

22 It may be that the apparatus is apparatus for depositing an anti-reflection coating
23 comprising germanium and carbon onto the one or more substrates. The one or
24 more substrates may be one or more infra-red transmissive windows. The anti-
25 reflection coating is therefore typically an infra-red transmissive anti-reflection
26 coating. The anti-reflection coating may transmit infra-red light having wavelengths in
27 the range $3\ \mu\text{m}$ to $12\ \mu\text{m}$. The anti-reflection coating may transmit infra-red light
28 having wavelengths in the range $3\ \mu\text{m}$ to $5\ \mu\text{m}$ and/or in the range $8\ \mu\text{m}$ to $12\ \mu\text{m}$.

29

30 The anti-reflection coating is typically an abrasion-resistant anti-reflection coating.

31

32 The at least one mount and the at least first and second magnetron sputtering
33 devices (i.e. typically including the first and second sputtering targets) may be
34 arranged such that, when each substrate is moved through the germanium sputtering
35 zone on the at least one movable mount, a layer (e.g. comprising one or more
36 monolayers, for example a single monolayer) of germanium is deposited onto the
37 said substrate.

1

2 The at least one mount and the at least first and second magnetron sputtering
3 devices (i.e. typically including the first and second sputtering targets) may be
4 arranged such that, when each substrate is moved through the carbon sputtering
5 zone on the at least one movable mount, a layer (e.g. comprising one or more
6 monolayers, for example a single monolayer) of carbon is deposited onto the said
7 substrate.

8

9 The skilled person will understand that by a magnetron sputtering device we mean
10 apparatus adapted for carrying out magnetron sputtering of a sputtering target.
11 Sputtering involves the ejection of particles (e.g. atoms) from a solid sputtering target
12 on bombardment of the said target by energetic particles such as gas ions. In a
13 magnetron sputtering device, an electric field is applied between the target and the
14 substrate onto which material is to be sputtered such that the target functions as a
15 cathode. A plasma is ignited in an inert gas (such as argon) adjacent to the target.
16 An array of magnets (e.g. typically permanent magnets) is arranged around the target
17 to generate a magnetic field which confines the inert gas plasma close to the surface
18 of the target. The electric field accelerates gas ions from the plasma into the surface
19 of the target, resulting in the ejection of uncharged particles from the target, which are
20 subsequently deposited onto the substrate.

21

22 At least a portion of the first magnetron sputtering device may be located within the
23 vacuum chamber. For example, the first sputtering target may be located within the
24 vacuum chamber. Alternatively, at least a portion of the first magnetron sputtering
25 device may be provided in fluid communication with the interior of the vacuum
26 chamber such that material (e.g. sputtered germanium) may be transported between
27 the first magnetron sputtering device and the interior of the vacuum chamber (e.g.
28 germanium may be sputtered from the first sputtering target into the vacuum
29 chamber).

30

31 At least a portion of the second magnetron sputtering device may be located within
32 the vacuum chamber. For example, the second sputtering target may be located
33 within the vacuum chamber. Alternatively, at least a portion of the second magnetron
34 sputtering device may be provided in fluid communication with the interior of the
35 vacuum chamber such that material (e.g. sputtered carbon) may be transported
36 between the second magnetron sputtering device and the interior of the vacuum

1 chamber (e.g. carbon may be sputtered from the second sputtering target into the
2 vacuum chamber).

3

4 The first magnetron sputtering device may be a planar magnetron sputtering device,
5 that is to say the magnetron sputtering device may be configured to generate a (e.g.
6 substantially) planar sputtering plasma adjacent to the first sputtering target (i.e. the
7 plasma may be (e.g. substantially) confined to one plane). The first magnetron
8 sputtering device may be a rectangular (e.g. linear) magnetron sputtering device, that
9 is to say the magnetron sputtering device may be configured to generate a (e.g.
10 substantially) rectangular sputtering plasma adjacent to the first sputtering target (i.e.
11 the plasma may be confined in a plane to a (e.g. substantially) rectangular shape).

12

13 The first magnetron sputtering device may be a direct current (DC) magnetron
14 sputtering device. In a DC magnetron sputtering device, the electric field is
15 generated between the sputtering target and the one or more substrates using a DC
16 power source. DC magnetron sputtering is most suitable for sputtering electrically
17 conductive metal targets. Conventional DC magnetron sputtering is less suitable for
18 sputtering dielectric targets where charge build-up on the target due to deposition of
19 plasma ions can lead to excessive arcing in the plasma and poisoning of the target.

20

21 Alternatively, the first magnetron sputtering device may be a radio frequency (RF)
22 magnetron sputtering device. In an RF magnetron sputtering device, the electric field
23 is generated between the sputtering target and the one or more substrates using a
24 radio-frequency alternating current (AC) power source. RF magnetron sputtering is
25 suitable for sputtering both metal targets and dielectric targets as plasma ion charges
26 are not able to build up on the target due to the oscillating electric field.

27

28 It may be that the first magnetron sputtering device is a pulsed DC magnetron
29 sputtering device, that is to say a DC magnetron sputtering device configured such
30 that the DC electric field is repeatedly pulsed (i.e. switched on and off), or such that
31 the magnitude and polarity of the electric field is varied (e.g. switched), typically at a
32 frequency of between 10 kHz to 350 kHz. Pulsing of the DC electric field repeatedly
33 removes inert gas ions from the surface of the target. Pulsed DC magnetron
34 sputtering is therefore suitable for sputtering both metal and dielectric targets.

35

36 The second magnetron sputtering device may be a planar magnetron sputtering
37 device. The second magnetron sputtering device may be a rectangular (e.g. linear)

1 magnetron sputtering device. The second magnetron sputtering device may be a
2 direct current (DC) magnetron sputtering device. The second magnetron sputtering
3 device may be a radio frequency (RF) magnetron sputtering device. It may be that
4 the second magnetron sputtering device is a pulsed DC magnetron sputtering device.

5
6 The apparatus is not typically a Closed Field Magnetron (CFM) apparatus. CFM
7 apparatus typically comprises two or more unbalanced magnetron sputtering devices
8 arranged such that neighbouring devices have opposite magnetic polarity.
9 Unbalanced magnetron sputtering devices are devices in which the magnetic field is
10 shaped to permit expansion of plasma away from the target towards the substrate,
11 increasing bombardment of the substrate with plasma ions. In CFM apparatus,
12 magnetic field lines link neighbouring magnetron sputtering devices and thereby trap
13 plasma around the vacuum chamber. It is typically difficult to control the
14 stoichiometry of deposited thin films using CFM apparatus. It is therefore not
15 possible to deposit, for example, rugate structures using CFM apparatus.

16
17 Accordingly, the at least first and second magnetron sputtering devices are not
18 typically magnetically linked, i.e. they are not typically linked to one another by
19 magnetic field lines which extend between the said at least first and second
20 magnetron sputtering devices. Plasma generated by the first magnetron sputtering
21 device (i.e. the plasma used to sputter germanium from the first sputtering target) is
22 typically confined to the germanium sputtering zone and plasma generated by the
23 second magnetron sputtering device (i.e. the plasma used to sputter carbon from the
24 second sputtering target) is typically confined to the carbon sputtering zone.

25
26 The apparatus typically comprises means for moving (e.g. an actuator configured to
27 move) the at least one mount such that the one or more substrates supported by the
28 said at least one mount are moved (e.g. sequentially and/or repeatedly) through the
29 germanium and/or carbon sputtering zones. For example, it may be that the
30 apparatus comprises means for moving (e.g. an actuator configured to move) at least
31 a portion of the at least one mount through the germanium and/or carbon sputtering
32 zones.

33
34 The at least one mount may be rotatable. The apparatus may comprise means for
35 rotating (e.g. an actuator configured to rotate) the at least one mount such that the
36 one or more substrates supported by the said at least one mount are moved (e.g.
37 sequentially and/or repeatedly) through the germanium and/or carbon sputtering

1 zones. For example, it may be that the apparatus comprises means for rotating (e.g.
2 an actuator configured to rotate) the at least one mount such that at least a portion of
3 the at least one mount moves through the germanium and/or carbon sputtering
4 zones.

5

6 The at least one mount may be rotatable about a (e.g. substantially) horizontal axis.
7 The at least one mount may be rotatable about an axle extending along the said (e.g.
8 horizontal) axis.

9

10 The at least one mount may be a drum. The drum may be (e.g. substantially)
11 prismatic (e.g. cylindrical). The drum may take the shape of a convex regular
12 polygonal prism. The drum may be rotatable about a longitudinal axis thereof (e.g.
13 an axle extending along said longitudinal axis). The drum is typically configured to
14 support the one or more substrates. For example, one or more externally facing walls
15 of the drum may be configured to support the one or more substrates.

16

17 It may be that the drum is configured to support one substrate. It may be that one
18 externally facing wall of the drum is configured to support the said one substrate.

19

20 It may be that the drum is configured to support two or more substrates. It may be
21 that one externally facing wall of the drum is configured to support the said two or
22 more substrates. Alternatively, it may be that two or more externally facing walls of
23 the drum are configured to support the two or more substrates. It may be that each of
24 the two or more externally facing walls of the drum is configured to support a single
25 corresponding substrate of the one or more substrates.

26

27 The apparatus may comprise one or more baffles configured to confine sputtered
28 material within (e.g. each of) the germanium and/or carbon sputtering zones. At least
29 one of the one or more baffles may be located adjacent to the first magnetron
30 sputtering device. At least one of the one or more baffles may be located adjacent to
31 the second magnetron sputtering device. The one or more baffles may extend away
32 from the first and/or second magnetron sputtering devices into the vacuum chamber
33 towards the mount. The one or more baffles may extend away from one or more
34 interior walls of the vacuum chamber towards the mount. The one or more baffles
35 may define external boundaries (e.g. walls) of the germanium and/or carbon
36 sputtering zones. The one or more baffles may restrict (e.g. prevent) sputtered
37 material from escaping from the germanium and/or carbon sputtering zones into the

1 rest of the vacuum chamber. The one or more baffles may restrict (e.g. prevent)
2 particles (e.g. atoms, ions, molecules or molecular fragments) from entering the
3 germanium and/or carbon sputtering zones from the rest of the vacuum chamber.

4

5 The germanium sputtering zone and the carbon sputtering zone do not typically
6 overlap. The germanium sputtering zone and the carbon sputtering zone are typically
7 spaced apart from one another within the vacuum chamber.

8

9 The first and second magnetron sputtering devices (e.g. the first sputtering target and
10 the second sputtering target) may be located (e.g. diametrically) opposite one
11 another. The first and second magnetron sputtering devices (e.g. the first sputtering
12 target and the second sputtering target) may be located on (e.g. diametrically)
13 opposing sides of the vacuum chamber.

14

15 The apparatus may comprise at least one plasma processing device. The at least
16 one plasma processing device typically comprises a source of plasma. The source of
17 plasma typically comprises a source of gas (i.e. a source of gas atoms and/or
18 molecules) and means for igniting a plasma within the gas. The gas may be an inert
19 gas (such as argon (Ar)). The at least one plasma processing device may be a
20 microwave plasma device, that is to say that the means for igniting the plasma may
21 comprise a source of microwave radiation.

22

23 The at least one plasma processing device may be configured (e.g. arranged) to
24 direct the plasma towards the at least one mount, thereby defining a plasma
25 treatment zone within the vacuum chamber. The means for moving (e.g. the actuator
26 configured to move) the at least one mount, or the means for rotating (e.g. the
27 actuator configured to rotate) the at least one mount, may be configured to move (i.e.
28 in use) the one or more substrates through the plasma treatment zone.

29

30 Gas ions may be deposited on the one or more substrates moved through the plasma
31 treatment zone. Gas ions may react with the one or more substrates moved through
32 the plasma treatment zone. Gas ions may react with one or more layers of material
33 located on the one or more substrates moved through the plasma treatment zone.

34

35 Plasma treatment typically enhances durability of the material (i.e. the germanium
36 and carbon) deposited onto the one or more substrates.

37

1 It may be that the gas supplied by the plasma processing device comprises hydrogen
2 and that the plasma processing device directs hydrogen ions towards the mount,
3 thereby defining a plasma hydrogenation zone within the vacuum chamber. It may
4 be that movement of the one or more substrates through the plasma hydrogenation
5 zone results in hydrogenation of one or more layers of material located on the said
6 one or more substrates.

7

8 The means for moving (e.g. the actuator configured to move) the at least one mount,
9 or the means for rotating (e.g. the actuator configured to rotate) the at least one
10 mount, may be configured to move (i.e. in use) the one or more substrates
11 sequentially through the germanium sputtering zone and the plasma treatment zone
12 (e.g. the plasma hydrogenation zone). The means for moving (e.g. the actuator
13 configured to move) the at least one mount, or the means for rotating (e.g. the
14 actuator configured to rotate) the at least one mount, may be configured to move the
15 one or more substrates sequentially through the carbon sputtering zone and the
16 plasma treatment zone (e.g. the plasma hydrogenation zone). The means for
17 moving (e.g. the actuator configured to move) the at least one mount, or the means
18 for rotating (e.g. the actuator configured to rotate) the at least one mount, may be
19 configured to move the one or more substrates sequentially through the germanium
20 sputtering zone, the carbon sputtering zone and the plasma treatment zone (e.g. the
21 plasma hydrogenation zone).

22

23 Plasma-assisted hydrogenation allows substantially higher hydrogenation rates to be
24 achieved than hydrogenation by other methods. Hydrogenation typically reduces the
25 number of dangling bonds in the deposited material, thereby reducing optical
26 absorption. Hydrogen plasma can also be used to clean the first and second target
27 surfaces during deposition, thereby reducing the level of dust on the target surfaces
28 and resultant contamination of the one or more substrates. Hydrogen plasma can be
29 used to pre-clean the one or more substrates prior to deposition of the thin film
30 comprising germanium and carbon.

31

32 The one or more substrates may be one or more glass substrates. The one or more
33 substrates may be one or more borosilicate glass substrates (e.g. formed from BK7
34 glass). The one or more substrates may be one or more zinc sulphide substrates.
35 The one or more substrates may be one or more germanium substrates. The one or
36 more substrates may be one or more chalcogenide substrates (e.g. formed from
37 chalcogenide glass such as germanium-sulphide (Ge-S) glass).

1

2 The apparatus may comprise at least one deposition sensor.

3

4 The at least one deposition sensor may be configured (e.g. calibrated) to measure a
5 parameter indicative of the amount of material deposited onto a sensing surface of
6 the said deposition sensor. Additionally or alternatively, the at least one deposition
7 sensor may be configured (e.g. calibrated) to measure a parameter indicative of the
8 rate at which material is deposited onto the sensing surface of the said deposition
9 sensor.

10

11 The at least one deposition sensor may be configured (e.g. calibrated) to measure a
12 parameter indicative of the amount of germanium and/or carbon (i.e. germanium
13 and/or carbon sputtered from the first and/or second sputtering targets) which is
14 deposited onto the said sensing surface. The at least one deposition sensor may be
15 configured (e.g. calibrated) to measure a parameter indicative of the rate at which
16 germanium and/or carbon (i.e. germanium and/or carbon sputtered from the first
17 and/or second sputtering targets) is deposited onto the said sensing surface.

18

19 The at least one deposition sensor may be configured (e.g. calibrated) to measure a
20 parameter indicative of the amount of material which is deposited onto the one or
21 more substrates. The at least one deposition sensor may be configured (e.g.
22 calibrated) to measure a parameter indicative of the rate at which material is
23 deposited onto the one or more substrates.

24

25 The at least one deposition sensor may be configured (e.g. calibrated) to measure a
26 parameter indicative of the amount of germanium and/or carbon (i.e. germanium
27 and/or carbon sputtered from the first and/or second sputtering targets) which is
28 deposited onto the said sensing surface. The at least one deposition sensor may be
29 configured (e.g. calibrated) to measure a parameter indicative of the rate at which
30 germanium and/or carbon (i.e. germanium and/or carbon sputtered from the first
31 and/or second sputtering targets) is deposited onto the said sensing surface.

32

33 The apparatus may comprise a controller configured to receive measurements of the
34 said parameter (i.e. the parameter indicative of the amount of material (e.g.
35 germanium and/or carbon) deposited or the rate at which material (e.g. germanium
36 and/or carbon) is deposited onto a sensing surface and/or the parameter indicative of
37 the amount of material (e.g. germanium and/or carbon) deposited or the rate at which

1 material (e.g. germanium and/or carbon) is deposited onto the one or more
2 substrates) from the at least one deposition sensor. The controller may be configured
3 to cause a change in the movement of the at least one movable mount responsive to
4 the received measurements. The controller may be configured to cause a change in
5 the speed of the movement of the at least one movable mount responsive to the
6 received measurements. The controller may be configured to cause a change in the
7 speed of rotation of the at least one movable mount responsive to the received
8 measurements. The controller may be configured to cause a change in the intensity
9 of sputtering at the first magnetron sputtering device and/or the second magnetron
10 sputtering device responsive to the received measurements. The controller may be
11 configured to cause a change in the amount of power supplied to the first magnetron
12 sputtering device and/or the second magnetron sputtering device responsive to the
13 said received measurements. The controller may be configured to switch the first
14 and/or second magnetron sputtering devices on or off responsive to the received
15 measurements.

16

17 The apparatus may comprise a first deposition sensor and a second deposition
18 sensor. The first deposition sensor may be configured to measure a first parameter
19 indicative of the amount of germanium (and/or the rate at which germanium is)
20 deposited onto a sensing surface of the said first deposition sensor from the first
21 magnetron sputtering device and/or the amount of germanium (and/or the rate at
22 which germanium is) deposited onto the one or more substrates. The second
23 deposition sensor may be configured to measure a second parameter indicative of
24 the amount of carbon (and/or the rate at which carbon is) deposited onto a sensing
25 surface of the said second deposition sensor from the second magnetron sputtering
26 device and/or the amount of carbon (and/or the rate at which carbon is) deposited
27 onto the one or more substrates. The apparatus may comprise a controller
28 configured to receive measurements of the first parameter from the first deposition
29 sensor and measurements of the second parameter from the second deposition
30 sensor. The controller may be configured to cause a change in the movement of the
31 at least one movable mount (e.g. the speed of the movement of the at least one
32 movable mount, for example the speed of rotation of the at least one movable mount)
33 and/or the intensity of sputtering at the first magnetron sputtering device and/or the
34 second magnetron sputtering device (e.g. the amount of power supplied to the first
35 magnetron sputtering device and/or the second magnetron sputtering device)
36 responsive to the said received measurements of the first parameter and/or the
37 second parameter.

1

2 For example, in use, the first magnetron sputtering device may be used to deposit
3 germanium onto the one or more substrates moved through the germanium
4 sputtering zone and the second magnetron sputtering device may be switched off.

5 As the one or more substrates are moved repeatedly through the germanium
6 sputtering zone, a layer of germanium may be deposited onto the said one or more
7 substrates one or more monolayers at a time. Germanium may also be deposited
8 onto the sensing surface of the first deposition sensor, but only when germanium is
9 deposited onto the one or more substrates. The first deposition sensor may measure
10 a parameter indicative of the amount of germanium deposited onto the sensing
11 surface (and/or the rate of deposition of germanium onto the sensing surface), the
12 said parameter also being indicative of the amount of material deposited onto the one
13 or more substrates (and/or the rate of deposition of germanium onto the one or more
14 substrates). The controller may receive the parameter measured by the first
15 deposition sensor and thereby calculate the thickness of the layer of germanium
16 which has been deposited onto the one or more substrates. When the calculated
17 thickness reaches a predefined desired germanium layer thickness, the controller
18 may switch off the first magnetron sputtering device and switch on the second
19 magnetron sputtering device. As the one or more substrates are moved repeatedly
20 through the carbon sputtering zone, a layer of carbon may be deposited onto the
21 layer of germanium already deposited on the one or more substrates. Carbon may
22 also be deposited onto the sensing surface of the second deposition sensor, but only
23 when carbon is deposited onto the one or more substrates. The second deposition
24 sensor may measure a parameter indicative of the amount of carbon deposited onto
25 the sensing surface (and/or the rate of deposition of carbon onto the sensing
26 surface), the said parameter also being indicative of the amount of carbon deposited
27 onto the one or more substrates (and/or the rate of deposition of carbon onto the one
28 or more substrates). The controller may receive the parameter measured by the
29 second deposition sensor and thereby calculate the thickness of the layer of carbon
30 which has been deposited onto the one or more substrates. When the calculated
31 thickness reaches a predefined desired carbon layer thickness, the controller may
32 switch off the second magnetron sputtering device. The process may be repeated to
33 build up alternating layers of germanium and carbon on the one or more substrates
34 with accurately controlled thicknesses.

35

36 In alternative uses, both the first and second magnetron sputtering devices may be
37 switched on and the one or more substrates may be repeatedly and sequentially

1 moved through the germanium and carbon sputtering zones. As the one or more
2 substrates are moved through the germanium sputtering zone, germanium may be
3 deposited onto the one or more substrates and onto the sensing surface of the first
4 deposition sensor. As the one or more substrates are moved through the carbon
5 sputtering zone, carbon may be deposited onto the one or more substrates and onto
6 the sensing surface of the second deposition sensor. The amount of germanium
7 and/or carbon deposited onto the one or more substrates each time the said one or
8 more substrates pass through the germanium and/or carbon sputtering zones is
9 typically dependent on the speed of movement of the one or more substrates and the
10 power supplied to the first and/or second magnetron sputtering devices. The
11 controller may therefore vary the speed of movement of the one or more substrates,
12 or the power supplied to the first and/or second magnetron sputtering devices,
13 responsive to parameters measured by the first and/or second deposition sensors, to
14 control the quantity of germanium and/or carbon deposited onto the one or more
15 substrates during each pass through the germanium and/or carbon sputtering zones.
16 Accordingly, germanium carbide ($\text{Ge}_x\text{C}_{1-x}$) or a solid solution of germanium in carbon
17 or carbon in germanium may be deposited with fine stoichiometric control. Since the
18 speed of movement or the power supplied to the first and/or second magnetron
19 sputtering devices can be varied during the deposition process, thin films may be
20 deposited in which the composition (e.g. the concentration of carbon and/or
21 germanium) varies, such as along a direction perpendicular to the surface of the one
22 or more substrates onto which the material is deposited. Rugate thin films may
23 therefore be deposited.

24

25 The apparatus may comprise two or more deposition sensors (e.g. three depositions
26 sensors) per magnetron sputtering device. Use of two or more (e.g. three) deposition
27 sensors per magnetron sputtering device results in a more accurate determination of
28 the amount of material deposited and/or the rate of deposition of material, and allows
29 the apparatus to continue functioning even if one or more deposition sensors fail
30 during use.

31

32 The at least one deposition sensor (e.g. the first and/or second deposition sensors)
33 may (e.g. each) comprise a microbalance (e.g. a quartz crystal microbalance). The
34 microbalance (e.g. the quartz crystal microbalance) is typically configured to measure
35 a parameter indicative of the resonant frequency of an acoustic resonator (e.g. a
36 quartz crystal resonator). The resonant frequency of the acoustic resonator (e.g. the
37 quartz crystal resonator) typically depends sensitively on the mass of the said

1 acoustic resonator (e.g. the quartz crystal resonator). Accordingly, small changes in
2 mass of the acoustic resonator (e.g. the quartz crystal resonator) due to deposition of
3 material onto the said acoustic resonator (e.g. onto the quartz crystal resonator)
4 which result in changes to the resonant frequency are typically measured by the
5 microbalance. The time dependence of the resonant frequency measured by the
6 microbalance is typically indicative of the rate of deposition of material onto the
7 acoustic resonator (e.g. onto the quartz crystal resonator).

8

9 The at least one deposition sensor may be calibrated by measuring a change in the
10 resonant frequency of the acoustic resonator (e.g. the quartz crystal resonator) as
11 single layers (i.e. monolayers) of carbon and/or germanium are deposited onto the
12 sensing surface (i.e. onto the quartz crystal). The at least one deposition sensor may
13 be calibrated by measuring a change in the resonant frequency of the acoustic
14 resonator (e.g. the quartz crystal resonator) as symmetric multilayers of carbon and
15 germanium are deposited onto the sensing surface (i.e. onto the quartz crystal).
16 Symmetric multilayers have spectral characteristics which are sensitive to an
17 imbalance in high- and low-refractive index materials, allowing the amount of material
18 deposited to be determined accurately using spectroscopic techniques, which is then
19 used to calibrate the at least one deposition sensor.

20

21 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
22 may be static. The at least one deposition sensor (e.g. the first and/or second
23 deposition sensor) may be (e.g. fixedly) mounted within the vacuum chamber. The at
24 least one deposition sensor (e.g. the first and/or second deposition sensor) may form
25 part of the first and/or second magnetron sputtering devices.

26

27 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
28 may be attached to (e.g. fixedly attached to) the movable mount. The at least one
29 deposition sensor (e.g. the first and/or second deposition sensor) may move with the
30 movable mount.

31

32 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
33 may be mounted within the drum. One or more apertures may be provided in the
34 drum. The one or more apertures may be located directly between the at least one
35 deposition sensor (e.g. the first and/or second deposition sensor) and the first and/or
36 second magnetron sputtering devices, such that (i.e. some of the) material sputtered
37 by the first and/or second magnetron sputtering devices reaches and is deposited on

1 the at least one deposition sensor (e.g. the first and/or second deposition sensor), i.e.
2 the one or more apertures are located on a direct line of sight between the at least
3 one deposition sensor (e.g. the first and/or second deposition sensor) and the first
4 and/or second magnetron sputtering devices. The one or more apertures may extend
5 around a circumference of the drum. Alternatively, the one or more apertures may be
6 spaced out around the circumference of the drum (i.e. such that there is solid material
7 forming the drum between each aperture). It may be that the drum is prismatic and
8 comprises a plurality of external faces onto which the one or more substrates may be
9 mounted, and that the one or more apertures are located around the drum on
10 alternate external faces. It may be that, as the drum rotates, (i.e. some of the)
11 material sputtered by the first and/or second magnetron sputtering devices reaches
12 and is deposited onto the at least one deposition sensor (e.g. the first and/or second
13 deposition sensor) when the one or more apertures are provided directly between the
14 at least one deposition sensor (e.g. the first and/or second deposition sensor) and the
15 first and/or second magnetron sputtering devices, and that material sputtered by the
16 first and/or second magnetron sputtering devices is prevented from being deposited
17 onto the at least one deposition sensor (e.g. the first and/or second deposition
18 sensor) when the one or more apertures rotated out of alignment with the first and/or
19 second magnetron sputtering devices.

20

21 It may be that a first sputtering mask is located between the first sputtering target and
22 the at least one mount.

23

24 The first sputtering mask may be configured (e.g. shaped) such that (i.e. in use),
25 when each substrate is moved through the germanium sputtering zone on the at least
26 one movable mount, a layer of germanium having a uniform thickness is deposited on
27 each said substrate. The skilled person will understand that a layer of material
28 having a uniform thickness means that the thickness of the layer of material is
29 substantially constant across the said layer.

30

31 The first sputtering mask may be configured (e.g. shaped) such that (i.e. in use),
32 when each substrate is moved through the germanium sputtering zone on the at least
33 one movable mount, a layer of germanium having a non-uniform thickness is
34 deposited on each said substrate. The skilled person will understand that a layer of
35 material having a non-uniform thickness means that the thickness of the layer of
36 material varies spatially (i.e. with location) across the said layer.

37

1 It may be that a second sputtering mask is located between the second sputtering
2 target and the at least one mount. The second sputtering mask may be configured
3 (e.g. shaped) such that (i.e. in use), when each substrate is moved through the
4 carbon sputtering zone on the at least one movable mount, a layer of carbon having a
5 uniform thickness is deposited on each said substrate. The second sputtering mask
6 may be configured (e.g. shaped) such that (i.e. in use), when each substrate is
7 moved through the carbon sputtering zone on the at least one movable mount, a
8 layer of carbon having a non-uniform thickness is deposited on each said substrate.

9
10 A second aspect of the invention provides a method for depositing germanium (Ge)
11 and carbon (C) onto one or more substrates. The method comprises: at least one
12 first magnetron sputtering device sputtering germanium from a first sputtering target
13 comprising germanium to thereby define a germanium sputtering zone within a
14 vacuum chamber; at least one mount moving the one or more substrates through the
15 germanium sputtering zone so that germanium is deposited on each said substrate;
16 at least one second magnetron sputtering device sputtering carbon from a second
17 sputtering target comprising carbon to thereby define a carbon sputtering zone within
18 the vacuum chamber; the at least one mount moving the one or more substrates
19 through the carbon sputtering zone so that carbon is deposited on each said
20 substrate.

21
22 The method is typically a method for depositing a thin film comprising both
23 germanium and carbon onto the one or more substrates, that is to say a thin film
24 comprising both germanium and carbon atoms.

25
26 It may be that the method is a method for depositing one or more layers of
27 germanium and one or more layers of carbon onto the one or more substrates. It
28 may be that the method is a method for depositing one or more monolayers of
29 germanium and one or more monolayers of carbon onto the one or more substrates,
30 wherein a monolayer is one atom thick.

31
32 It may be that the method is a method for depositing a multi-layered structure onto
33 the one or more substrates, the multi-layered structure comprising one or more layers
34 of germanium and one or more layers of carbon. The multi-layered structure may
35 comprise a plurality of layers of germanium and a plurality of layers of carbon. Each
36 layer of germanium may comprise (e.g. be formed from) one or more monolayers of
37 germanium. Each layer of carbon may comprise (e.g. be formed from) one or more

1 monolayers of carbon. The multi-layered structure may comprise alternating layers of
2 germanium and carbon. Each alternating layer of germanium and carbon may have
3 the same thickness. Alternatively, different layers of germanium and carbon may
4 have different thicknesses.

5

6 It may be that the method is a method for depositing germanium carbide ($\text{Ge}_x\text{C}_{1-x}$)
7 onto the one or more substrates. It may be that the method is a method for
8 depositing amorphous germanium carbide ($\text{Ge}_x\text{C}_{1-x}$) onto the one or more substrates.
9 It may be that the method is a method for depositing a multi-layered structure onto
10 the one or more substrates, the multi-layered structure comprising one or more layers
11 of $\text{Ge}_x\text{C}_{1-x}$ and one or more layers of $\text{Ge}_y\text{C}_{1-y}$, wherein x and y have different values.

12

13 It may be that the method is a method for depositing a rugate structure onto the one
14 or more substrates. In the rugate structure the composition (e.g. the concentrations
15 of germanium and carbon) varies continuously along the direction substantially
16 perpendicular to the surface of the one or more substrates onto which the structure is
17 deposited. Accordingly, the refractive index typically varies continuously along the
18 direction substantially perpendicular to the surface of the one or more substrates onto
19 which the structure is deposited.

20

21 It may be that the apparatus is apparatus for depositing a solid solution comprising
22 germanium and carbon onto the one or more substrates, for example a solid solution
23 of carbon in germanium and/or a solid solution of germanium in carbon.

24

25 The at least one mount and the at least first and second magnetron sputtering
26 devices (i.e. typically including the first and second sputtering targets) may be
27 arranged such that the at least one mount moving each substrate through the
28 germanium sputtering zone results in (i.e. causes) a layer (e.g. comprising one or
29 more monolayers, for example a single monolayer) of germanium to be deposited
30 onto the said substrate.

31

32 The at least one mount and the at least first and second magnetron sputtering
33 devices (i.e. typically including the first and second sputtering targets) may be
34 arranged such that the at least one mount moving each substrate through the carbon
35 sputtering zone results in (i.e. causes) a layer (e.g. comprising one or more
36 monolayers, for example a single monolayer) of carbon to be deposited onto the said
37 substrate.

1
2 The method may comprise providing at least a portion of the first magnetron
3 sputtering device within the vacuum chamber. For example, the method may
4 comprise providing the first sputtering target within the vacuum chamber.
5 Alternatively, the method may comprise providing at least a portion of the first
6 magnetron sputtering device in fluid communication with the interior of the vacuum
7 chamber such that material (e.g. sputtered germanium) may be transported between
8 the first magnetron sputtering device and the interior of the vacuum chamber (e.g.
9 germanium may be sputtered from the first sputtering target into the vacuum
10 chamber).

11
12 The method may comprise providing at least a portion of the second magnetron
13 sputtering device within the vacuum chamber. For example, the method may
14 comprise providing the second sputtering target within the vacuum chamber.
15 Alternatively, the method may comprise providing at least a portion of the second
16 magnetron sputtering device in fluid communication with the interior of the vacuum
17 chamber such that material (e.g. sputtered carbon) may be transported between the
18 second magnetron sputtering device and the interior of the vacuum chamber (e.g.
19 carbon may be sputtered from the second sputtering target into the vacuum
20 chamber).

21
22 The first magnetron sputtering device may be a planar magnetron sputtering device.
23 The first magnetron sputtering device may be a rectangular (e.g. linear) magnetron
24 sputtering device. The first magnetron sputtering device may be a direct current (DC)
25 magnetron sputtering device. The first magnetron sputtering device may be a radio
26 frequency (RF) magnetron sputtering device. It may be that the first magnetron
27 sputtering device is a pulsed DC magnetron sputtering device.

28
29 The second magnetron sputtering device may be a planar magnetron sputtering
30 device. The second magnetron sputtering device may be a rectangular (e.g. linear)
31 magnetron sputtering device. The second magnetron sputtering device may be a
32 direct current (DC) magnetron sputtering device. The second magnetron sputtering
33 device may be a radio frequency (RF) magnetron sputtering device. It may be that
34 the second magnetron sputtering device is a pulsed DC magnetron sputtering device.

35

1 The at least one mount may be rotatable. The method may comprise rotating the at
2 least one mount and thereby moving the one or more substrates (i.e. supported by
3 the said at least one mount) through the germanium and/or carbon sputtering zones.

4

5 The method may comprise rotating the at least one mount about a (e.g. substantially)
6 horizontal axis. The method may comprise rotating the at least one mount about an
7 axle extending along the said (e.g. horizontal) axis.

8

9 The at least one mount may be a drum. The drum may be (e.g. substantially)
10 prismatic (e.g. cylindrical). The drum may take the shape of a convex regular
11 polygonal prism. The drum may be rotatable about a longitudinal axis thereof (e.g.
12 an axle extending along said longitudinal axis). The drum is typically configured to
13 support the one or more substrates. For example, one or more externally facing walls
14 of the drum may be configured to support the one or more substrates.

15

16 It may be that the drum is configured to support one substrate. It may be that one
17 externally facing wall of the drum is configured to support the said one substrate.

18

19 It may be that the drum is configured to support two or more substrates. It may be
20 that one externally facing wall of the drum is configured to support the said two or
21 more substrates. Alternatively, it may be that two or more externally facing walls of
22 the drum are configured to support the two or more substrates. It may be that each of
23 the two or more externally facing walls of the drum is configured to support a single
24 corresponding substrate of the one or more substrates.

25

26 The method may comprise confining sputtered material within (e.g. each of) the
27 germanium and/or carbon sputtering zones (for example, by way of one or more
28 baffles). At least one of the one or more baffles may be located adjacent to the first
29 magnetron sputtering device. At least one of the one or more baffles may be located
30 adjacent to the second magnetron sputtering device. The one or more baffles may
31 extend away from the first and/or second magnetron sputtering devices into the
32 vacuum chamber towards the mount. The one or more baffles may extend away
33 from one or more interior walls of the vacuum chamber towards the mount. The one
34 or more baffles may define external boundaries (e.g. walls) of the germanium and/or
35 carbon sputtering zones. The method may comprise restricting (e.g. preventing)
36 sputtered material from escaping from the germanium and/or carbon sputtering zones
37 into the rest of the vacuum chamber. The method may comprise restricting (e.g.

1 preventing) particles (e.g. atoms, ions, molecules or molecular fragments) from
2 entering the germanium and/or carbon sputtering zones from the rest of the vacuum
3 chamber.

4

5 The germanium sputtering zone and the carbon sputtering zone do not typically
6 overlap. The germanium sputtering zone and the carbon sputtering zone are typically
7 spaced apart from one another within the vacuum chamber.

8

9 The method may comprise exposing the one or more substrates to plasma. The
10 method may comprise at least one plasma processing device exposing the one or
11 more substrates to plasma. The at least one plasma processing device typically
12 comprises a source of plasma. The source of plasma typically comprises a source of
13 gas (i.e. a source of gas atoms and/or molecules) and means for igniting a plasma
14 within the gas. The gas may be an inert gas (such as argon (Ar)). The at least one
15 plasma processing device may be a microwave plasma device, that is to say that the
16 means for igniting the plasma may comprise a source of microwave radiation.

17

18 The method may comprise (i.e. the at least one plasma processing device) directing
19 plasma towards the at least one mount, thereby defining a plasma treatment zone
20 within the vacuum chamber. The method may comprise moving the one or more
21 substrates (e.g. the at least one mount moving the one or more substrates) through
22 the plasma treatment zone.

23

24 Gas ions may be deposited on one or more substrates moved through the plasma
25 treatment zone. Gas ions may react with one or more substrates moved through the
26 plasma treatment zone. Gas ions may react with one or more layers of material
27 located on the one or more substrates moved through the plasma treatment zone.

28

29 Plasma treatment typically enhances durability of the germanium and carbon
30 deposited onto the one or more substrates.

31

32 It may be that the gas supplied by the at least one plasma processing device
33 comprises hydrogen and that the method comprises the at least one plasma
34 processing device directing hydrogen ions towards the mount, thereby defining a
35 plasma hydrogenation zone within the vacuum chamber. It may be that the method
36 comprises moving the one or more substrates (e.g. the at least one mount moving the
37 one or more substrates) through the plasma hydrogenation zone. Movement of the

1 one or more substrates through the plasma hydrogenation zone typically results in
2 hydrogenation of one or more layers of material located on the said one or more
3 substrates.

4

5 The method may comprise moving the one or more substrates (e.g. the at least one
6 mount moving the one or more substrates) sequentially through the germanium
7 sputtering zone and the plasma treatment zone (e.g. the plasma hydrogenation
8 zone). The method may comprise moving the one or more substrates (e.g. the at
9 least one mount moving the one or more substrates) sequentially the carbon
10 sputtering zone and through the plasma treatment zone (e.g. the plasma
11 hydrogenation zone). The method may comprise moving the one or more substrates
12 (e.g. the at least one mount moving the one or more substrates) sequentially through
13 the germanium sputtering zone, the carbon sputtering zone and the plasma treatment
14 zone (e.g. the plasma hydrogenation zone).

15

16 The method may comprise at least one deposition sensor measuring a parameter
17 indicative of the amount of material deposited onto a sensing surface of the said
18 deposition sensor. The method may comprise at least one deposition sensor
19 measuring a parameter indicative of the rate at which material is deposited onto a
20 sensing surface of the said deposition sensor.

21

22 The method may comprise the at least one deposition sensor measuring a parameter
23 indicative of the amount of germanium and/or carbon (i.e. germanium and/or carbon
24 sputtered from the first and/or second sputtering targets) deposited onto the said
25 sensing surface. The method may comprise the at least one deposition sensor
26 measuring a parameter indicative of the rate at which germanium and/or carbon (i.e.
27 germanium and/or carbon sputtered from the first and/or second sputtering targets) is
28 deposited onto the said sensing surface.

29

30 The method may comprise the at least one deposition sensor measuring a parameter
31 indicative of the amount of material deposited onto the one or more substrates. The
32 method may comprise the at least one deposition sensor measuring a parameter
33 indicative of the rate at which material is deposited onto the one or more substrates.

34

35 The method may comprise the at least one deposition sensor measuring a parameter
36 indicative of the amount of germanium and/or carbon (i.e. germanium and/or carbon
37 sputtered from the first and/or second sputtering targets) deposited onto the one or

1 more substrates. The method may comprise the at least one deposition sensor
2 measuring a parameter indicative of the rate at which germanium and/or carbon (i.e.
3 germanium and/or carbon sputtered from the first and/or second sputtering targets) is
4 deposited onto the one or more substrates.

5

6 The method may comprise a controller receiving measurements of the said
7 parameter (i.e. the parameter indicative of the amount of material (e.g. germanium
8 and/or carbon) deposited and/or the rate at which material (e.g. germanium and/or
9 carbon) is deposited onto a sensing surface and/or the one or more substrates) from
10 the at least one deposition sensor. The method may comprise the controller causing
11 a change in the movement of the at least one movable mount responsive to the
12 received measurements. The method may comprise the controller causing a change
13 in the speed of the movement of the at least one movable mount responsive to the
14 received measurements. The method may comprise the controller causing a change
15 in the speed of rotation of the at least one movable mount responsive to the received
16 measurements. The method may comprise the controller causing a change in the
17 intensity of sputtering at the first magnetron sputtering device and/or the second
18 magnetron sputtering device responsive to the received measurements. The method
19 may comprise the controller causing a change in the amount of power supplied to the
20 first magnetron sputtering device and/or the second magnetron sputtering device
21 responsive to the said received measurements. The method may comprise the
22 controller switching the first and/or second magnetron sputtering devices on or off
23 responsive to the received measurements.

24

25 The method may comprise a first deposition sensor measuring a first parameter
26 indicative of the amount of germanium deposited (and/or the rate at which
27 germanium is deposited) onto a sensing surface of the said first deposition sensor
28 from the first magnetron sputtering device and/or the amount of germanium deposited
29 (and/or the rate at which germanium is deposited) onto the one or more substrates.
30 The method may comprise a second deposition sensor measuring a second
31 parameter indicative of the amount of carbon deposited (and/or the rate at which
32 carbon is deposited) onto a sensing surface of the said second deposition sensor
33 from the second magnetron sputtering device and/or the amount of carbon deposited
34 (and/or the rate at which carbon is deposited) onto the one or more substrates. The
35 method may comprise a controller receiving measurements of the first parameter
36 from the first deposition sensor and measurements of the second parameter from the
37 second deposition sensor. The method may comprise the controller causing a

1 change in the movement of the at least one movable mount (e.g. the speed of the
2 movement of the at least one movable mount, for example the speed of rotation of
3 the at least one movable mount) and/or the intensity of sputtering at the first
4 magnetron sputtering device and/or the second magnetron sputtering device (e.g. the
5 amount of power supplied to the first magnetron sputtering device and/or the second
6 magnetron sputtering device) responsive to the said received measurements of the
7 first parameter and/or the second parameter.

8

9 The at least one deposition sensor (e.g. the first and/or second deposition sensors)
10 may (e.g. each) comprise a microbalance (e.g. a quartz crystal microbalance). The
11 method may comprise the microbalance (e.g. the quartz crystal microbalance)
12 measuring a parameter indicative of the resonant frequency of an acoustic resonator
13 (e.g. a quartz crystal resonator).

14

15 The method may comprise calibrating the at least one deposition sensor (e.g. the
16 microbalance). Calibrating the at least one deposition sensor may comprise
17 measuring a change in the resonant frequency of the acoustic resonator (e.g. the
18 quartz crystal resonator) as single layers (i.e. monolayers) of carbon and/or
19 germanium are deposited onto the sensing surface (i.e. onto the quartz crystal).
20 Calibrating the at least one deposition sensor may comprise measuring a change in
21 the resonant frequency of the acoustic resonator (e.g. the quartz crystal resonator) as
22 symmetric multilayers of carbon and germanium are deposited onto the sensing
23 surface (i.e. onto the quartz crystal).

24

25 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
26 may be static (i.e. the position of the at least one deposition sensor may be fixed).
27 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
28 may be (e.g. fixedly) mounted within the vacuum chamber. The at least one
29 deposition sensor (e.g. the first and/or second deposition sensor) may form part of
30 the first and/or second magnetron sputtering devices.

31

32 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
33 may be attached to (e.g. fixedly attached to) the movable mount. The at least one
34 deposition sensor (e.g. the first and/or second deposition sensor) may move with the
35 movable mount.

36

1 The at least one deposition sensor (e.g. the first and/or second deposition sensor)
2 may be mounted within the drum. One or more apertures may be provided in the
3 drum. The one or more apertures may be located directly between the at least one
4 deposition sensor (e.g. the first and/or second deposition sensor) and the first and/or
5 second magnetron sputtering devices, such that (i.e. some of the) material sputtered
6 by the first and/or second magnetron sputtering devices reaches and is deposited on
7 the at least one deposition sensor (e.g. the first and/or second deposition sensor), i.e.
8 the one or more apertures are located on a direct line of sight between the at least
9 one deposition sensor (e.g. the first and/or second deposition sensor) and the first
10 and/or second magnetron sputtering devices. The one or more apertures may extend
11 around a circumference of the drum. Alternatively, the one or more apertures may be
12 spaced out around the circumference of the drum (i.e. such that there is solid material
13 forming the drum between each aperture). It may be that the drum is prismatic and
14 comprises a plurality of external faces onto which the one or more substrates may be
15 mounted, and that the one or more apertures are located around the drum on
16 alternate external faces. It may be that, as the drum rotates, (i.e. some of the)
17 material sputtered by the first and/or second magnetron sputtering devices reaches
18 and is deposited onto the at least one deposition sensor (e.g. the first and/or second
19 deposition sensor) when the one or more apertures are provided directly between the
20 at least one deposition sensor (e.g. the first and/or second deposition sensor) and the
21 first and/or second magnetron sputtering devices, and that material sputtered by the
22 first and/or second magnetron sputtering devices is prevented from being deposited
23 onto the at least one deposition sensor (e.g. the first and/or second deposition
24 sensor) when the one or more apertures rotates out of alignment with the first and/or
25 second magnetron sputtering devices.

26

27 The method may comprise providing a first sputtering mask between the first
28 sputtering target and the at least one mount.

29

30 The first sputtering mask may be configured (e.g. shaped) such that (i.e. in use),
31 when each substrate is moved through the germanium sputtering zone on the at least
32 one movable mount, a layer of germanium having a uniform thickness is deposited on
33 each said substrate.

34

35 The first sputtering mask may be configured (e.g. shaped) such that (i.e. in use),
36 when each substrate is moved through the germanium sputtering zone on the at least

1 one movable mount, a layer of germanium having a non-uniform thickness is
2 deposited on each said substrate.

3

4 The method may comprise providing a second sputtering mask between the second
5 sputtering target and the at least one mount. The second sputtering mask may be
6 configured (e.g. shaped) such that (i.e. in use), when each substrate is moved
7 through the carbon sputtering zone on the at least one movable mount, a layer of
8 carbon having a uniform thickness is deposited on each said substrate. The second
9 sputtering mask may be configured (e.g. shaped) such that (i.e. in use), when each
10 substrate is moved through the carbon sputtering zone on the at least one movable
11 mount, a layer of carbon having a non-uniform thickness is deposited on each said
12 substrate.

13

14 The one or more substrates may be one or more glass substrates. The one or more
15 substrates may be one or more borosilicate glass substrates (e.g. formed from BK7
16 glass). The one or more substrates may be one or more zinc sulphide substrates.
17 The one or more substrates may be one or more germanium substrates. The one or
18 more substrates may be one or more chalcogenide substrates (e.g. formed from
19 chalcogenide glass such as germanium-sulphide (Ge-S) glass).

20

21 The method is typically carried out at room temperature.

22

23 A third aspect of the invention provides an optical device comprising a substrate and
24 a thin film, comprising germanium and carbon, deposited thereon by a method
25 according to the second aspect of the invention.

26

27 The thin film may comprise one or more layers (e.g. one or more monolayers) of
28 germanium and one or more layers (e.g. one or more monolayers) of carbon. The
29 thin film may have a multi-layered structure comprising a plurality of layers (e.g.
30 monolayers) of germanium and a plurality of layers (e.g. monolayers) of carbon. The
31 multi-layered structure may comprise alternating layers (e.g. monolayers) of
32 germanium and carbon.

33

34 The thin film may comprise germanium carbide ($\text{Ge}_x\text{C}_{1-x}$) (e.g. amorphous germanium
35 carbide ($\text{Ge}_x\text{C}_{1-x}$)). The thin film may comprise a multi-layered structure comprising
36 one or more layers (e.g. one or more monolayers) of $\text{Ge}_x\text{C}_{1-x}$ and one or more layers
37 (e.g. one or more monolayers) of $\text{Ge}_y\text{C}_{1-y}$, wherein x and y have different values.

1

2 The thin film may have a rugate structure comprising germanium and carbon, i.e. a
3 structure in which the composition (e.g. the concentrations of germanium and carbon)
4 varies continuously along a direction substantially perpendicular to the surface of the
5 substrate onto which the thin film is deposited.

6

7 It may be that the substrate comprises an infra-red transmissive optical region (e.g.
8 an infra-red transmissive optical window).

9

10 The substrate (e.g. the infra-red transmissive optical region) may comprise (e.g. be
11 formed from) one or more of the following: borosilicate (e.g. borosilicate glass, for
12 example BK7 glass), zinc sulphide, germanium, chalcogenide (e.g. chalcogenide
13 glass, for example germanium-sulphide (Ge-S) glass).

14

15 Optional and preferred features of any one aspect of the invention may be features of
16 any other aspect of the invention.

17

18 Description of the Drawings

19

20 An example embodiment of the present invention will now be illustrated with
21 reference to the following Figures in which:

22

23 Figure 1 shows a schematic cross section through apparatus for depositing
24 germanium and carbon;

25

26 Figure 2 shows the deposition apparatus of Figure 1 with a substrate positioned in
27 front of a first pulsed DC magnetron sputtering source provided with a germanium
28 target;

29

30 Figure 3 shows the deposition apparatus of Figure 1 with the substrate positioned in
31 front of a microwave plasma source;

32

33 Figure 4 shows the deposition apparatus of Figure 1 with a substrate positioned in
34 front of a second pulsed DC magnetron sputtering source provided with a carbon
35 target;

36

1 Figure 5 shows the deposition apparatus of Figure 1 provided with first and second
2 quartz crystal microbalance deposition rate sensors;

3

4 Figure 6 is a table of test results for a 1 μm thick film of stoichiometric germanium
5 carbide as deposited on germanium, zinc selenide and chalcogenide substrates;

6

7 Figure 7 shows the optical transmission as a function of wavelength of incident light
8 for a 2.46 μm thick layer of germanium carbide having a germanium volume fraction
9 of 0.567 deposited on a germanium substrate;

10

11 Figure 8 shows the refractive index measured using infra-red light at 3 μm for six
12 different germanium carbide films deposited using different germanium target
13 powers;

14

15 Figure 9 shows the volume fraction of germanium in each deposited film shown in
16 Figure 8;

17

18 Figure 10 shows the same data as figure 9 plotted as a function of the ratio of the
19 germanium target power to the carbon target power;

20

21 Figure 11 shows the variation in refractive index as a function of layer number in a
22 germanium carbide rugate structure rugate filter; and

23

24 Figure 12 shows the transmission of the rugate structure of Figure 11 as a function of
25 wavelength of incident light.

26

27 Detailed Description of an Example Embodiment

28

29 Figure 1 shows schematically deposition apparatus 1 for depositing a thin film
30 comprising germanium and carbon. The apparatus 1 includes a rotatable drum
31 mount 2 mounted on a substantially horizontal axle 3, first and second pulsed DC
32 magnetron sputtering sources 4 and 6, each provided with respective sputtering
33 masks 5 and 7, and a microwave plasma source 8, all provided within a vacuum
34 chamber 9. The drum mount 2 has the shape of a dodecagonal prism, the axle 3
35 extending along the longitudinal axis of the prism and each external prism face 10
36 comprising a bracket for receiving a deposition substrate.

37

1 The first pulsed DC magnetron sputtering source 4 is set up such that, when turned
2 on, it generates and confines a substantially rectangular, planar plasma adjacent to a
3 germanium target, to thereby sputter germanium atoms towards the drum. The
4 second pulsed DC magnetron sputtering source 6 is also set up such that, when
5 turned on, it generates and confines a substantially rectangular, planar plasma
6 adjacent to a carbon target, to thereby sputter carbon atoms towards the drum. The
7 microwave plasma source 8 is supplied with a flow of hydrogen gas to generate a
8 flow of hydrogen ions towards the drum.

9

10 In use, a substrate 11 (such as a chalcogenide glass substrate) is mounted on one of
11 the flat external surfaces of the drum and the drum is rotated continuously about the
12 axle 3 at a speed of 60 rpm. The vacuum chamber is evacuated and backfilled with
13 argon or another inert gas. The first pulsed DC magnetron sputtering source 4 is
14 switched on, as is the microwave plasma source 8. As shown in Figure 2, the
15 substrate 11 is first rotated past the first sputtering source 4, which sputters
16 germanium atoms towards the drum. A portion of the sputtered material is blocked
17 by the sputtering mask 5 but the remainder of the sputtered material is able to pass
18 through the sputtering mask 5 to deposit one or two monolayers of germanium onto
19 the substrate.

20

21 As shown in Figure 3, the substrate is subsequently rotated past the microwave
22 plasma source 8. As the substrate passes the microwave plasma source, high-
23 energy hydrogen ions are directed onto the substrate. Exposure to hydrogen plasma
24 enhances the durability of the deposited germanium layer through densification.
25 Exposure to hydrogen plasma also passivates and reduces the number of dangling
26 bonds on the exposed surface of the deposited germanium.

27

28 Each time the substrate passes the first sputtering source 4, a few more monolayers
29 of germanium are deposited onto the existing layers of germanium. Each time the
30 substrate passes the plasma source 8, these monolayers of germanium are exposed
31 to the hydrogen plasma. Over repeated passes of the substrate past the first
32 sputtering source and the plasma source, the thickness of a layer of germanium is
33 built up a few monolayers at a time until a desired thickness is achieved.

34

35 At this point the first sputtering source 4 is switched off and the second sputtering
36 source 6 is switched on. As the substrate is rotated past the second sputtering
37 source, a portion of the sputtered material is blocked by the sputtering mask 7 but the

1 remainder of the sputtered material is able to pass through the sputtering mask 7 to
2 deposit one or two monolayers of carbon on top of the layer of germanium. The
3 substrate is subsequently rotated past the plasma source which exposes the carbon
4 layer to hydrogen plasma. Exposure to hydrogen plasma enhances the durability of
5 the deposited carbon layer through densification. Exposure to hydrogen plasma also
6 passivates and reduces the number of dangling bonds on the exposed surface of the
7 deposited carbon. Over repeated passes of the substrate past the second sputtering
8 source and the plasma source, the thickness of a layer of carbon is built up a few
9 monolayers at a time until a desired thickness is achieved.

10

11 As rotation of the drum continues, the first and second sputtering sources are
12 repeatedly switched on and off to deposit alternating layers of germanium and carbon
13 onto the substrate.

14

15 The rotational speed of the drum is such that only one or two monolayers of material
16 are deposited during each pass through each of the germanium and carbon
17 sputtering zones, which provides precise control over the layer thicknesses and the
18 composition of the resultant thin film.

19

20 Even more precise control over the thin film stoichiometry and structure can be
21 achieved through use of first and second quartz crystal microbalances 12A and 12B.
22 As shown in Figure 5, the quartz crystal microbalances 12A and 12B are mounted
23 onto a rear wall of the vacuum chamber within the drum 2. The microbalances are
24 fixed in position and do not rotate with the drum. An aperture is provided in the drum
25 and is positioned adjacent to the substrate such that, when the substrate moves in
26 front of the first sputtering source 4, sputtered germanium is able to pass through the
27 aperture in the drum and reach the first quartz crystal microbalance 12A, and when
28 the substrate moves in front of the second sputtering source 6, sputtered carbon is
29 able to pass through the aperture in the drum and reach the second quartz crystal
30 microbalance 12B. The first and second quartz crystal microbalances each have a
31 sensing surface and are configured to measure the amount of material deposited
32 onto the said sensing surface. The first and second quartz crystal microbalances
33 output signals dependent on the measured amounts of deposited material, which are
34 received by a controller (not shown). The controller is connected to both the first and
35 second sputtering devices and to an actuator which drives rotation of the drum 2.
36 The controller is programmed to adjust the power supply to each of the first and
37 second sputtering devices (including, for example, switching each of the first and

1 second sputtering devices on or off) and/or to adjust the speed of rotation of the drum
2 responsive to the measured amounts of deposited material. By controlling the power
3 supplied to each sputtering device and the speed of rotation of the drum, the amount
4 of material deposited onto the substrate as it passes through each sputtering zone
5 can be controlled with monolayer precision. This permits the stoichiometry of the
6 deposited thin film to be controlled very accurately.

7

8 The apparatus may be used to deposit layered structures comprising germanium and
9 carbon, for example where each individual layer comprises a few monolayers of
10 germanium or carbon respectively. The power supplied to each of the sputtering
11 devices and the speed of rotation of the drum may be selected such that the
12 thickness of each layer of germanium and carbon are similar. Alternatively, the
13 power supplied to each of the sputtering devices and the speed of rotation of the
14 drum can be controlled so as to deposit a thin film in which the composition (e.g. the
15 concentration of germanium and/or carbon) varies continuously along a direction
16 normal to the substrate surface, such as a rugate structure where the resultant
17 refractive index of thin film also varies continuously along the normal direction.

18

19 In practice, one or more substrates may be mounted to each external, planar face of
20 the drum, permitting a plurality of layered structures to be deposited at the same time.
21 This significantly increases throughput compared to existing deposition technologies.
22 The polygonal drum permits a high surface area of substrate to be coated for a given
23 vacuum chamber volume.

24

25 An aperture may be provided in the drum adjacent to each substrate such that the
26 deposition rates of germanium and carbon may be measured by the first and second
27 quartz microbalances located within the drum. Alternatively, a single circumferential
28 aperture may extend around the drum adjacent to each substrate.

29

30 The sputtering masks 5 and 7 are typically selected dependent on the desired spatial
31 variation in thickness of the deposited layers. For example, sputtering masks can be
32 designed to ensure a uniform thickness of deposited material. Alternatively,
33 sputtering masks can be designed to ensure a non-uniform thickness of deposited
34 material (such as a thickness which is uniform along a first direction in the plane of
35 the substrate but non-uniform in a second direction in said plane of the substrate).

36

1 Figure 6 shows the results of testing the properties of a 1 μm thick film of
2 stoichiometric germanium carbide deposited on germanium, zinc selenide and
3 chalcogenide substrates using the apparatus described hereinabove. In each case
4 the film was tested for adhesion, humidity and severe abrasion properties using the
5 US Military Test Standard Mil_C_48497A, for salt spray resistance using the US
6 Military Test Standard Mil_C_675C para 4.5.9, and for the sand wiper test according
7 to the UK Military Test Standard TS1888 para 5.4.3. These tests are designed to
8 simulate the typical environments to which optical coatings may be subjected in
9 military applications. The germanium carbide film passed each standardised test.

10

11 Figure 7 shows the results of testing the optical transmission of a single layer of
12 germanium carbide, having a germanium volume fraction of 0.567 and a thickness of
13 2.46 μm , deposited on a germanium substrate using the apparatus described
14 hereinabove. The transmission is seen to oscillate as a function of wavelength of
15 incident light. The refractive index of this film was found to be 3.058 at a wavelength
16 of 5000 nm.

17

18 Figure 8 shows the refractive index measured using infra-red light at 3 μm for six
19 different germanium carbide films deposited using different germanium target
20 powers. As the power supplied to the germanium target increases, the volume
21 fraction of germanium in the deposited film increases and therefore so does the
22 refractive index. The variation in germanium volume fraction as calculated using a
23 Bruggeman model with the refractive index data of Figure 8 as the input is shown in
24 Figure 9. Figure 10 shows the same data plotted as a function of the ratio of the
25 germanium target power to the carbon target power.

26

27 Because the refractive index of the deposited film depends sensitively on the volume
28 fractions of germanium and carbon, rugate structures having alternating refractive
29 indices can be deposited by continuously varying the power supplied to the
30 germanium and carbon targets (and thus continuously varying the germanium and
31 carbon volume fractions in the deposited films) during deposition. For example,
32 Figure 11 shows the variation in refractive index which was achieved in a germanium
33 carbide rugate structure in which the volume fraction of germanium was varied from 0
34 to 1 and back again 90 times during deposition. The variation in the deposited
35 volume fraction was given by the following quintic function:

36

37

$$f(x) = 10x^3 - 15x^4 + 6x^5,$$

1

2 apodised using an exponential function.

3

4 Each volume fraction cycle involved the deposition of 32 layers of material, each
5 layer having a different composition. The physical thickness of each layer was
6 different and was chosen such that the optical thickness of each layer was the same.

7 The refractive index observed oscillates 90 times from 2 (equivalent to the refractive
8 index of pure carbon) to 4 (equivalent to the refractive index of pure germanium).

9 The average refractive index of the rugate structure is 3. This finely-structure rugate
10 film can be used as a rugate filter; Figure 12 shows the transmission of the rugate
11 structure as a function of wavelength of incident light. The structure blocks light
12 having wavelengths between approximately 5000 nm and 7200 nm. This rejection
13 bandwidth can be turned by varying the refractive index range of the rugate structure.
14 A narrower index range results in a narrower rejection bandwidth.

15

16 Further variations and modifications may be made within the scope of the invention
17 herein disclosed.

18

1 Claims

2

- 3 1. Apparatus for depositing germanium and carbon onto one or more
4 substrates, the apparatus comprising a vacuum chamber, at least first and
5 second magnetron sputtering devices and at least one movable mount for
6 supporting the one or more substrates within the vacuum chamber, the
7 first magnetron sputtering device being configured to sputter germanium
8 towards the at least one mount from a first sputtering target comprising
9 germanium, thereby defining a germanium sputtering zone within the
10 vacuum chamber, the second magnetron sputtering device being
11 configured to sputter carbon towards the at least one mount from a
12 second sputtering target comprising carbon, thereby defining a carbon
13 sputtering zone within the vacuum chamber, and the at least one mount
14 and the at least first and second magnetron sputtering devices being
15 arranged such that, when each substrate is moved through the
16 germanium sputtering zone on the at least one movable mount,
17 germanium is deposited on the said substrate, and when each substrate is
18 moved through the carbon sputtering zone on the at least one movable
19 mount, carbon is deposited on the said substrate.
- 20 2. The apparatus according to claim 1 comprising at least one deposition
21 sensor configured to measure a parameter indicative of the amount of
22 germanium and/or carbon which is deposited onto a sensing surface of
23 the said deposition sensor.
- 24 3. The apparatus according to claim 2 comprising a controller configured to
25 receive measurements of the said parameter from the at least one
26 deposition sensor and to cause a change in the movement of the at least
27 one movable mount and/or a change in the intensity of sputtering at the
28 first magnetron sputtering device and/or the second magnetron sputtering
29 device responsive to the received measurements.
- 30 4. The apparatus according to claim 2 or claim3, comprising a first deposition
31 sensor and a second deposition sensor, the first deposition sensor being
32 configured to measure a first parameter indicative of the amount of
33 germanium which is deposited onto a sensing surface of the said first
34 deposition sensor from the first magnetron sputtering device, the second
35 deposition sensor being configured to measure a second parameter
36 indicative of the amount of carbon which is deposited onto a sensing

- 1 surface of the said second deposition sensor from the second magnetron
2 sputtering device.
- 3 5. The apparatus according to any one of claims 2 to 4, wherein the at least
4 one deposition sensor or one or both of the first and second deposition
5 sensors comprise a quartz crystal microbalance.
- 6 6. The apparatus according to any one preceding claim, wherein both the
7 first and second magnetron sputtering devices are pulsed DC magnetron
8 sputtering devices.
- 9 7. The apparatus according to any one preceding claim, wherein the at least
10 one mount is rotatable and wherein the apparatus comprises means for
11 rotating the at least one mount such that the one or more substrates
12 supported by the said at least one mount are moved through the
13 germanium and carbon sputtering zones
- 14 8. The apparatus according to claim 7, wherein the at least one mount is a
15 drum rotatable about a longitudinal axis thereof.
- 16 9. The apparatus according to claim 8 dependent on any one of claims 2 to
17 5, wherein the at least one deposition sensor or one or both of the first and
18 second deposition sensors are mounted within the drum.
- 19 10. The apparatus according to any one preceding claim, wherein the
20 germanium sputtering zone and the carbon sputtering zone do not
21 overlap.
- 22 11. The apparatus according to any one preceding claim comprising at least
23 one plasma processing device configured to direct plasma towards the at
24 least one mount, thereby defining a plasma treatment zone within the
25 vacuum chamber.
- 26 12. The apparatus according to claim 11, wherein the plasma processing
27 device is configured to direct hydrogen ions towards the mount, thereby
28 defining a plasma hydrogenation zone within the vacuum chamber.
- 29 13. The apparatus according to any one preceding claim, wherein the one or
30 more substrates are one or substrates formed from chalcogenide glass.
- 31 14. A method for depositing germanium and carbon onto one or more
32 substrates, the method comprising: at least one first magnetron sputtering
33 device sputtering germanium from a first sputtering target comprising
34 germanium to thereby define a germanium sputtering zone within a
35 vacuum chamber; at least one mount moving the one or more substrates
36 through the germanium sputtering zone so that germanium is deposited
37 on each said substrate; at least one second magnetron sputtering device

- 1 sputtering carbon from a second sputtering target comprising carbon to
2 thereby define a carbon sputtering zone within the vacuum chamber; and
3 the at least one mount moving the one or more substrates through the
4 carbon sputtering zone so that carbon is deposited on each said
5 substrate.
- 6 15. The method according to claim 14 comprising a deposition sensor
7 measuring a parameter indicative of the amount of germanium and/or
8 carbon which is deposited onto a sensing surface of the said deposition
9 sensor.
- 10 16. The method according to claim 15 comprising a controller receiving
11 measurements of the said parameter from the deposition sensor and
12 causing a change in the movement of the at least one movable mount
13 and/or a change in the intensity of sputtering at the first magnetron
14 sputtering device and/or the second magnetron sputtering device
15 responsive to the received measurements.
- 16 17. The method according to claim 15 or claim 16 comprising a first deposition
17 sensor measuring a first parameter indicative of the amount of germanium
18 which is deposited onto a sensing surface of the said first deposition
19 sensor from the first magnetron sputtering device and a second deposition
20 sensor measuring a second parameter indicative of the amount of carbon
21 which is deposited onto a sensing surface of the said second deposition
22 sensor from the second magnetron sputtering device.
- 23 18. The method according to any one of claims 15 to 17, wherein the at least
24 one deposition sensor or one or both of the first and second deposition
25 sensors comprise a quartz crystal microbalance.
- 26 19. The method according to any one of claims 14 to 18, wherein both the first
27 and second magnetron sputtering devices are pulsed DC magnetron
28 sputtering devices.
- 29 20. The method according to any one of claims 14 to 19, wherein the at least
30 one mount is rotatable and the method comprises rotating the at least one
31 mount such that the one or more substrates supported by the said at least
32 one mount are moved through the germanium and carbon sputtering
33 zones
- 34 21. The method according to claim 20, wherein the at least one mount is a
35 drum rotatable about a longitudinal axis thereof.

- 1 22. The method according to claim 21 dependent on any one of claims 14 to
2 18, wherein the at least one deposition sensor or one or both of the first
3 and second deposition sensors are mounted within the drum.
- 4 23. The method according to any one of claims 14 to 22, wherein the
5 germanium sputtering zone and the carbon sputtering zone do not
6 overlap.
- 7 24. The method according to any one of claims 14 to 23 comprising at least
8 one plasma processing device directing plasma towards the at least one
9 mount, thereby defining a plasma treatment zone within the vacuum
10 chamber.
- 11 25. The method according to claim 24 comprising the plasma processing
12 device directing hydrogen ions towards the mount, thereby defining a
13 plasma hydrogenation zone within the vacuum chamber.
- 14 26. The method according to any one of claims 14 to 25, wherein the one or
15 more substrates are one or substrates formed from chalcogenide glass.
- 16 27. An optical device comprising a substrate and a thin film, comprising
17 germanium and carbon, deposited thereon by the method according to
18 any one of claims of 14 to 26.
- 19 28. The optical device according to claim 27, wherein the substrate comprises
20 an infra-red transmissive optical region.
- 21



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Examiner: Dr Karen Payne

Claims searched: 1 - 28

Date of search: 29 September 2017

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1, 6 - 8, 10, 14, 19 - 21, 23	US 2014/0329070 A1 (HIGH TECH COATINGS GMBH) See pages 1 & 3 - 5 and figure 2.
X	27, 28	Applied Surface Science, Vol. 252, No. 23, September 2006, Hu et al., "Ge _{1-x} C _x double-layer antireflection and protection coatings", pp. 8135 - 8138. See pages 8135 & 8136.
A	-	Journal of Non-Crystalline Solids, Vol. 357, No. 24, August 2011, Jiang et al., "Chemical bonding and optical properties of germanium carbon alloy films prepared by magnetron co-sputtering as a function of substrate temperature", pp. 3952 - 3956. See pages 3952 & 3953.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

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Worldwide search of patent documents classified in the following areas of the IPC

C23C

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI, XPESP, XPSRNG, Patent Fulltext

International Classification:

Subclass	Subgroup	Valid From
C23C	0014/35	01/01/2006
C23C	0014/06	01/01/2006
C23C	0014/50	01/01/2006