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(56) Documents Cited
GB 2273605 A **US 5545443 A** **US 5288684 A**
US 5215588 A **US 5014646 A** **US 4910044 A**
US 4859492 A **US 4753818 A** **US 4728528 A**
US 4702936 A **US 4371587 A**
WPI Accession no 91-374621/199151 & JP 030253573 A

(58) Field of Search
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INT CL^6 **C03C 17/23 17/245 , C23C 16/48**
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(54) Abstract Title
CVD manufacturing a multilayer optical mirror using ultra-violet light

(57) A multilayer optical mirror is made by depositing optically reflective substantially amorphous thin films of at least two materials such as titania or silica on a substrate 5 by metallo-organic chemical vapour deposition. A gas stream containing a precursor material and an oxidant material is passed over the substrate which is heated to a temperature in the range of from 150° to 250°C whilst ultra-violet light is shone onto the gas stream in the vicinity of the substrate 5 to photodissociate the oxidant and accelerate breakdown of the precursor material. In this way the temperature of the deposition can be kept below the crystalline growth temperature for the deposited material which is therefore amorphous. The mirror may be a ring laser gyroscope mirror.

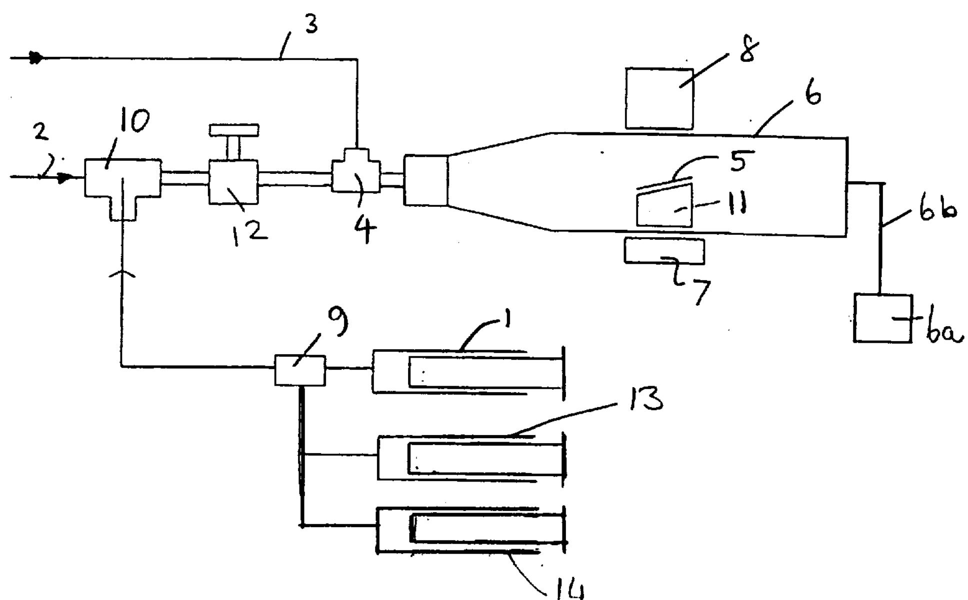

FIG 1.

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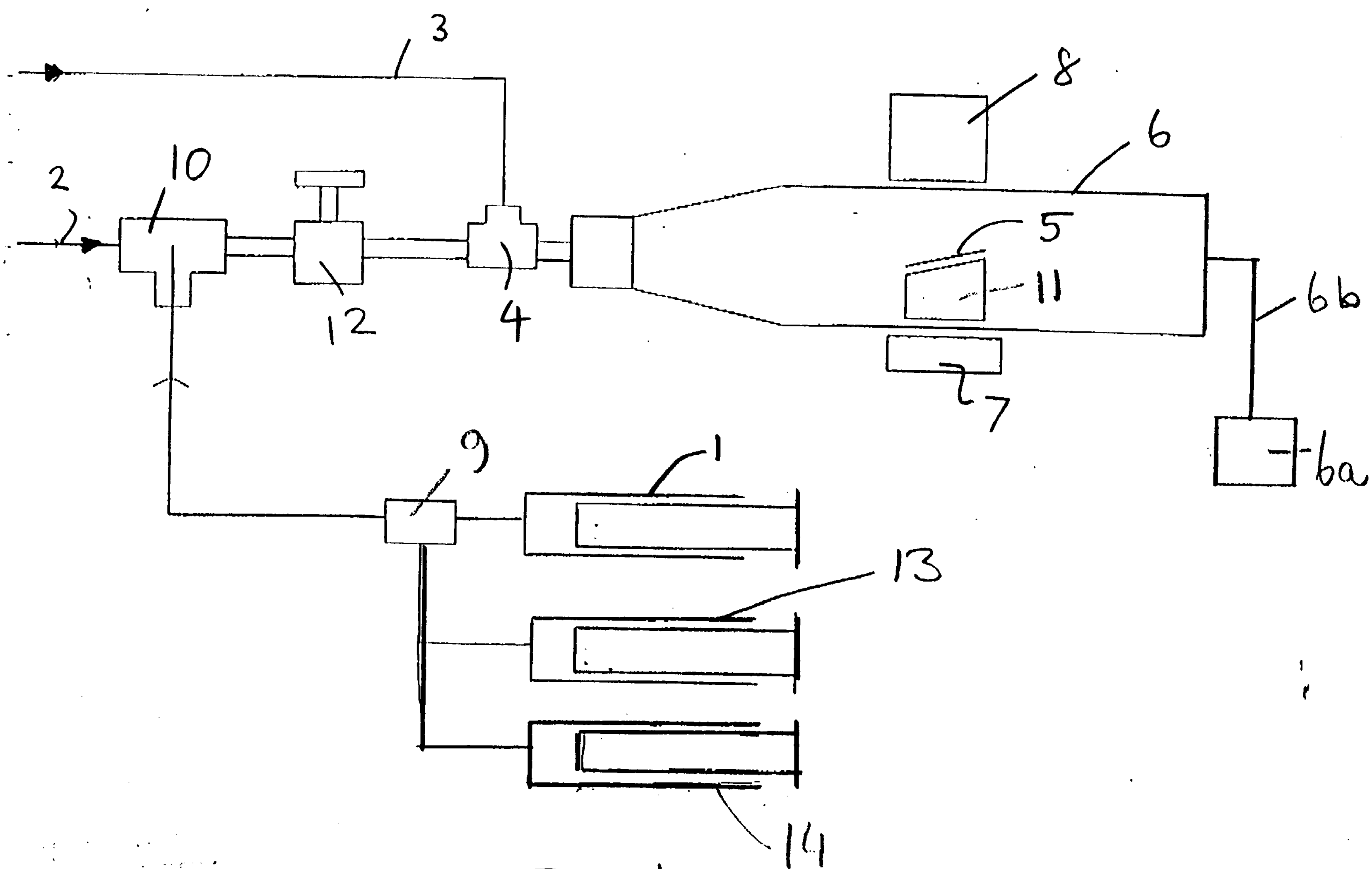

FIG 1.

METHOD AND APPARATUS FOR MANUFACTURING A MULTILAYER OPTICAL MIRROR

This invention relates to a method and apparatus for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, particularly, but not exclusively suitable for manufacturing laser mirrors.

Thin films, that is to say films having a thickness of less than 100 microns, which are optically reflective, can be produced on a substrate in many different ways such as by thermal evaporation, electron beam induced thermal evaporation, radio frequency and direct current sputtering, ion beam assisted electron beam thermal evaporation, and ion beam sputtering.

Thermal evaporation of the film material is a relatively low cost approach but suffers from problems of nucleation, and potential crystalline growth. The problem is that the size of the particulates grows with increasing nucleation giving rise to scatter in the film. The nucleation depends on the temperature of the substrate on which the films are deposited, and happens more easily at higher temperatures. This is typically kept at 300°C to ensure good adhesion of the film. At these temperatures, there is enough energy to allow the depositing material to move about on the surface and nucleate on preferred locations giving micro-crystallites. For most optical applications the ideal film is amorphous with no crystalline structure to give the highest quality. This however is not thermodynamically preferred so that a non-equilibrium process is required. There is also the possibility of spitting, giving rise to particulates being deposited on the film, with consequent degradation of the film quality.

Electron beam thermal evaporation is a similar technique, but is seen as a cleaner process than heating up the material in a boat. Very high temperatures are required for heating in a crucible especially for oxide materials (silica, titania), which leads to contamination from the crucible materials for thermal evaporation, while with careful control of an electron beam system purity can be maintained. Again for adhesion reasons the substrate is normally kept at a high temperature (200-300°C) which encourages nucleation.

RF and DC sputtering avoid the need for high temperatures on the substrates, but being plasma processes these tend to have plasma local to the substrate with the possibility of contamination. Both are not thermal processes, so there are more energetic species within the plasma which tends to reduce the nucleation and crystalline growth. While the substrates are not normally directly heated, the plasma heats up the substrate which may tend towards nucleation.

Ion beam assisted growth introduces a non-thermal element with a higher energy into the system, and this helps to suppress nucleation to give a higher quality film.

With ion beam sputtering there are high energy particles (1-10 eV) incident on the substrate, and the substrate is held at room temperature. The process dumps the sputtered atoms directly onto the substrate and there is no possibility of nucleation. This gives rise to very high quality mirrors with very low scatter and very low losses due to the dense films. This process is commonly used for ring laser gyro mirrors which require this very high quality for producing optical films. One disadvantage of ion beam sputtering is the presence within the films of low levels of contaminants at the parts per thousand level. These arise due to the need for carbon grids and aluminium parts within the system which tend to also get sputtered. Also the stainless steel used for the chamber walls and fittings may be sputtered to give harmful impurities of iron, etc, within the film, which tend significantly to increase the loss. The presence of these minor contaminants limits the quality of the films produced by virtue of increasing the loss.

Additionally MOCVD (metallo-organic chemical vapour deposition) is known to produce very high quality films, in multilayers for semiconductor lasers. These are normally grown by MOCVD using materials such as gallium, arsenic and aluminium. The process is normally epitaxial growth with lattice matching, so it is in effect a crystalline growth. The process also usually requires a high operating temperature.

There is thus a need for an improved method and apparatus for manufacturing a multilayer optical mirror by depositing optically reflective thin films of at least two materials on a substrate, which films are substantially amorphous. The films are required to be amorphous to reduce scattering.

According to one aspect of the present invention there is provided a method for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, in which a gaseous, organic, film precursor material is injected into a stream of carrier gas, an oxidant gas is introduced into the injected carrier gas stream, the resulting oxidant, precursor, carrier gas stream is passed over a substrate on which thin films are to be deposited from the gas stream, which substrate is heated to a temperature less than the crystalline growth temperature of the desired film material, and a beam of ultra-violet light is impinged on the gas stream in the vicinity of the substrate to photodissociate the oxidant and accelerate break down of the precursor material so that substantially amorphous film material is deposited on the substrate at a temperature less than the crystalline growth temperature of the film material.

Preferably the injected carrier gas and introduced oxidant gas are mixed and passed over the substrate at a pressure of substantially 5 mbar to minimise condensation of particulates directly from the gaseous precursor material.

Conveniently the beam of ultra-violet light is produced by mercury discharge.

Advantageously the temperature to which the substrate is heated, and at which the thin film material is deposited thereon, is in the range of from 150 to 250°C.

Preferably the precursor material is injected in gaseous form into the carrier gas stream at substantially 100°C. Conveniently the carrier gas is argon.

Advantageously the oxidant is nitrous oxide.

Preferably the precursor material is titanium tetra-isopropoxide and the resulting thin film deposited is titania.

Conveniently the precursor material is tetra-ethylorthosilicate and the resulting thin film deposited is silica.

Advantageously alternate layers of titania and silica are deposited at substantially the same deposition temperature to produce a multilayer thin film deposit.

According to a further aspect of the present invention there is provided apparatus for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, including a reaction vessel for housing a substrate on which thin films are to be deposited, means for heating the substrate to a temperature less than the crystallisation temperature of the film material to be deposited, means for passing a carrier gas stream into the reaction vessel over the substrate, means for injecting a gaseous precursor material into the carrier gas stream before passage over the substrate, means for introducing an oxidant gas into the injected gas stream before passage over the substrate and means for generating and impinging a beam of ultra-violet light on the gas stream in the vicinity of the substrate.

Advantageously the means for generating and impinging a beam of ultra-violet light on the gas stream in the vicinity of the substrate includes a mercury discharge lamp.

According to yet another aspect of the present invention there is provided a multilayer optical laser mirror provided with alternate layers of high and low refractive index optically reflective substantially amorphous thin films of material by the method of the present invention and/or by the apparatus of the present invention.

According to another aspect of the present invention there is provided a ring laser gyroscope mirror having layers of optically reflective, substantially amorphous, thin films of at least two materials deposited on a substrate by metallo-organic chemical vapour deposition by the method and/or apparatus of the present invention.

For a better understanding of the present invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawing, in which:-

Figure 1 is a diagrammatic view of apparatus for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition according to the present invention suitable for use with the method of the present invention.

Optically reflective thin films need to be amorphous to reduce scattering, with a high packing density to ensure a good refractive index and to give the best film integrity. The films need to be highly pure, with parts per million of impurities compared to the parts per thousand that is typical for sputtering processes. Certain contaminants, such as iron, nickel and chrome are known to increase the optical losses of films as their oxides are not transparent within the normally used wavebands. Reducing the overall contamination level will reduce these particular contaminants in an effective manner. In order to make highly reflective films, such as for multilayer optical laser mirrors, a dielectric stack of films needs to be built up on a substrate based on alternating layers (usually quarter wave at the wavelength of interest) of a high and low refractive index material. Typical materials used in the visible waveband include titania, hafnia, tantala and alumina which offer a high refractive index. Titania is known to offer an index of 2.3-2.5 while tantala offers 2.1-2.2 amd alumina 1.7.

For a low refractive index silica, with an index of 1.46, is preferred. Fluorides are also usable, but the oxides are generally preferred due to their better abrasion resistance and lack of water absorption.

Figure 1 of the accompanying drawings shows in diagrammatic form apparatus according to the present invention for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition utilising the method of the present invention. In this method a gaseous, organic, film precursor material is injected by injector means 1 into a stream 2 of carrier gas. Conveniently this is done by injecting the precursor material in liquid form at substantially 100°C so that it flash evaporates into the carrier gas stream 2. An oxidant gas is introduced from a source via line 3 and a mixer unit 4 into the injected carrier gas stream and the resulting oxidant, precursor, carrier gas stream is passed over a substrate 5 housed in a reaction vessel 6 conveniently made of quartz.

An exhaust pump 6a is connected by a gas conduit 6b to the end of the vessel 6 downstream of the substrate 5 to reduce the pressure over the substrate 5 and thereby control the vapour deposition mechanism. The substrate 5, on which thin films are to be deposited from the gas stream 2, is heated to a temperature less than the crystalline growth temperature of the desired film material by any convenient heater means which preferably includes an infra-red radiant heater 7. A beam of ultra-violet light produced in any convenient manner such as by an ultra-violet source which preferably is a mercury discharge lamp 8, is impinged on the gas stream in the vicinity of the substrate 5 to photodissociate the oxidant and accelerate breakdown of the precursor material in the gas stream so that substantially amorphous film material is deposited on the substrate 5 at a temperature less than the crystalline growth temperature of the film material.

The injected carrier gas and introduced oxidant gas are mixed in the mixer unit 4 and passed over the substrate at a pressure of substantially 5 mbar to minimise condensation of particulates directly from the gaseous precursor material.

The most convenient materials to deposit as thin films on the substrate 5 are titania and silica. Of these titania has a high refractive index and silica has a relatively low refractive index. Preferably these two film materials should be deposited in a stack on the substrate as alternate film material layers. The apparatus and method of the present invention are suitable for depositing such film layers within a single deposition run and a complete stack which may consist of 30 to 40 layers is achievable in one deposition run at substantially the same deposition temperature.

The temperature to which the substrate 5 is heated and at which the thin film is deposited thereon should be in the range of from 150° to 250°C. In order to achieve amorphous titania films a deposition temperature in the preferred range of from 150° to 250°C is suitable. Increasing the temperature to within a range of 300° to 350°C produced undesirable crystalline growth as determined by electron diffraction techniques. Deposition of silica films at temperatures above 620°C produces undesirable crystalline structures.

The precursor material is injected via the injection means 1 in gaseous form into the carrier gas stream at substantially 100°C. Conveniently this is done by injecting the precursor material in liquid form at substantially 100°C so that it flash evaporates into the carrier gas stream 2. Such a precursor for titania is organic and is TTIP (titanium tetra-isopropoxide) which is normally available in the form of a liquid at room temperature. The liquid is vaporised and injected into the carrier gas stream at 100°C. Preferably the carrier gas utilised is argon. Heptane may be used as a flush or purge gas between runs with one precursor and runs with another precursor material for a change in film material being deposited. The precursor material in liquid form may be introduced into the injection means 1 which conveniently is in the form of a motorised syringe which feeds the liquid precursor material via a switch 9 to a flash evaporator 10 in which it is vaporised and introduced into the carrier gas stream 2.

Preferably the carrier gas utilised is argon at substantially 100°C which is introduced via the line 2. Preferably the oxidant gas is nitrous oxide which is mixed with the carrier gas.

In order to achieve a relatively low deposition temperature of the film such as 200°C with a reasonable rate of deposition without particulate formation, the deposition must be photoassisted. This is done by impinging a beam of ultra-violet light from the discharge lamp 8 onto the gas stream in the vicinity of the substrate 5 which in turn is removably mountable on a susceptor 11 in the reaction vessel 6. The susceptor 11 comprises a carbon block which is radiantly heated by the heater 7 to approximately 200°C. It is therefore the hottest feature within the carrier gas flow so that any thin film deposition will happen on the susceptor 11 and on the substrate 5 carried thereby, rather than on the inner walls of the reaction vessel 6. Preferably the mercury discharge lamp 8 is a 100 watt mercury lamp focused through a quartz lens (not shown) in the quartz wall of the reaction vessel 6. The purpose of the ultra-violet light provided by the lamp 8 is to photodissociate the nitrous oxide or any other oxidant utilised to give a reactive oxygen species. At temperatures in excess of 250°C such as 350°C the nitrous oxide will break down in the absence of ultra-violet light but in this case the substrate temperature is too high and crystalline growth will result.

As the ultra-violet light is focused onto the substrate 5 on the susceptor 11 and as the substrate and susceptor are the only items at high temperature the effect of the temperature is to accelerate the breakdown of the precursor material in the presence of the oxidant. This happens at a microlevel so that the growth process involves small particles. It has been shown, using atomic force microscopy, that the method and apparatus of the invention produces thin film deposition with grains smaller than 20 nm in size and with a surface roughness typically of 0.4 nm as measured by optical profilemeter typically used for measuring surface roughness of optical thin films. The ultra-violet light does not increase the temperature in the reaction but accelerates the breakdown of the oxidant material and allows thin film deposition to proceed at a much lower temperature than would otherwise be possible. Without ultra-violet light a temperature of at least 350°C would typically be required for formation of titania films on the substrate 5 but these films would be crystalline in nature and therefore not of high enough quality.

For deposition of silica films the precursor material is TEOS (tetra-ethylorthosilicate). For deposition below 250°C the use of ultra-violet photo-assistance is necessary. In this way silica can be deposited at a temperature in the range of from 150 to 250°C which is below the crystalline growth temperature for silica.

The apparatus shown in Figure 1 also includes a restrictor valve 12 for controlling the pressure differential between the flash evaporator 10 and the reaction vessel 6.

Additional injection means 13 and 14 can be provided where the injection means 13 contains liquid heptane as a source of a purging gas and where the injection means 14 can contain a precursor material such as the TEOS in liquid form.

The method and apparatus of the present invention allow thin optically reflective films to be deposited having a high purity level which may be of the order of one part per million thus giving rise to lower reflectivity losses. The apparatus is relatively cheap to operate and avoids the necessity for changing a target material such as by using multi targets, which is necessary with sputtering techniques. Instead it is a simple matter to switch to a different precursor material by switching to a different injection means 1 or 14. Of course any number of injection means can be provided depending upon the number of precursor or carrier materials which it is desired to utilise in the process and apparatus of the present invention. Thus the method and/or apparatus of the present invention can be employed to manufacture a ring laser gyroscope mirror having layers of optically reflective substantially amorphous, thin films of at least two materials deposited on a substrate by metallo-organic chemical vapour deposition.

CLAIMS

1. A method for manufacturing a multilayer optical mirror by depositing optically reflective, substantially amorphous, thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, in which a gaseous, organic, film precursor material is injected into a stream of carrier gas, an oxidant gas is introduced into the injected carrier gas stream, the resulting oxidant, precursor, carrier gas stream is passed over a substrate on which the thin films are to be deposited from the gas stream, which substrate is heated to a temperature less than the crystalline growth temperature of the desired film material, and a beam of ultra-violet light is impinged on the gas stream in the vicinity of the substrate to photodissociate the oxidant and accelerate break down of the precursor material so that substantially amorphous film material is deposited on the substrate at a temperature less than the crystalline growth temperature of the film material.

2. A method according to claim 1, in which the injected carrier gas and introduced oxidant gas are mixed and passed over the substrate at a pressure of substantially

5 mbar to minimise condensation of particulates directly from the gaseous precursor material.

3. A method according to claim 1 or claim 2, in which the beam of ultra-violet light is produced by mercury discharge.

4. A method according to any one of claims 1 to 3, in which the temperature to which the substrate is heated, and at which the thin film material is deposited thereon, is in the range of from 150 to 250°C.

5. A method according to any one of claims 1 to 4, in which the precursor material is injected in gaseous form into the carrier gas stream at substantially 100°C.

6. A method according to any one of claims 1 to 5, in which the carrier gas is argon.

7. A method according to any one of claims 1 to 6, in which the oxidant is nitrous oxide.

8. A method according to any one of claims 1 to 7, in which the precursor material is titanium tetra-isopropoxide and the resulting thin film deposited is titania.

9. A method according to any one of claims 1 to 7, in which the precursor material is tetra-ethylorthosilicate and the resulting thin film deposited is silica.

10. A method according to claim 8 and claim 9, in which alternate layers of titania and silica are deposited at substantially the same deposition temperature to produce a multi layer thin film deposit.

11. A method for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, substantially as hereinbefore described.

12. Apparatus for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least two materials on a substrate by metallo-organic chemical vapour deposition, including a reaction vessel for housing a substrate, on which the thin films are to be deposited, means for heating the substrate to a temperature less than the crystallisation temperature of the film material to be deposited, means for passing a carrier gas stream into the reaction vessel over the substrate, means for

injecting a gaseous precursor material into the carrier gas stream before passage over the substrate, means for introducing an oxidant gas into the injected gas stream before passage over the substrate, and means for generating and impinging a beam of ultra-violet light on the gas stream in the vicinity of the substrate.

13. Apparatus according to claim 12, including a susceptor made of carbon on which the substrate is removably mountable in the reaction vessel.

14. Apparatus according to claim 13, wherein the means for heating the substrate includes an infrared radiant heater operable to heat the substrate indirectly via the susceptor.

15. Apparatus according to any one of claims 12 to 14, wherein the means for generating and impinging a beam of ultra violet on the gas stream in the vicinity of the substrate includes a mercury discharge lamp.

16. Apparatus for manufacturing a multilayer optical mirror by depositing optically reflective substantially amorphous thin films of at least one material on a substrate by metallo-organic chemical vapour deposition,

substantially as hereinbefore described and as illustrated in Figure 1 of the accompanying drawings.

17. A multilayer optical laser mirror provided with alternate layers of high and low refractive index optically reflective substantially amorphous thin films of material by the method of any one of claims 1 to 11.

18. A multilayer optical laser mirror provided with alternate layers of high and low refractive index optically reflective substantially amorphous thin films of material by the apparatus of any one of claims 12 to 16.

19. A ring laser gyroscope mirror having layers of optically reflective, substantially amorphous, thin films of at least two materials deposited on a substrate by metallo-organic vapour deposition by the method of any one of claims 1 to 11 and/or by the apparatus of any one of claims 12 to 16.

Application No: GB 9714342.4
Claims searched: 1-19

Examiner: Peter Beddoe
Date of search: 11 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7F (FHB, FHE)

Int Cl (Ed.6): C23C 16/48, CO3C (17/23, 17/245)

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2273605 A	(FUJITSU) see esp p10 lines 19-25, p13 lines 12-16, the embodiments & fig 5	1,12 at least
X	US 5545443	(YOSHIDA) see esp col4 lines 38-60, col5 lines 24-45 & fig 1	1,12 at least
X	US 5288684	(SEMICONDUCTOR) see whole doc & esp figs	12 at least
X	US 5215588	(AMTECH) see whole doc & esp figs	12 at least
X	US 5014646	(MATSUSHITA) see esp col2 lines 51-65, col3 line 53 - col4 line 17, claim 9 & fig 1	1,12 at least
X	US 4910044	(SEMICONDUCTOR) see esp col3 line 64 - col4 line 54 & fig 7	1,12 at least
X	US 4859492	(HUGHES) see esp col5 line 47 - col6 line 34 & col6 lines 50-60	1,12 at least
X	US 4753818	(HUGHES) see esp col2 lines 13-23 & col3 lines 46-62	1,12 at least
X	US 4728528	(CANON) see esp ex 1, col6 lines 8-61 & fig 3	1,12 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family
A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

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Application No: GB 9714342.4
Claims searched: 1-19
Examiner: Peter Beddoe
Date of search: 11 September 1997

Category	Identity of document and relevant passage	Relevant to claims
X	US 4702936 (APPLIED) see esp col2 line 55 - col3 line 17 & fig 1	1,12 at least
X	US 4371587 (HUGHES) see esp col5 lines 9-49, col7 lines 34-42 & figs 1,2	1,12 at least
X	WPI Accession no 91-374621/199151 & JP 3253573 A (HOKUSAN) see abstract	1,12 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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E Patent document published on or after, but with priority date earlier than, the filing date of this application.