



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

<p>(51) International Patent Classification<sup>6</sup> : C23C 14/00, 14/06, 14/54, G02B 5/28</p>	<p>A2</p>	<p>(11) International Publication Number: <b>WO 98/37254</b></p> <p>(43) International Publication Date: 27 August 1998 (27.08.98)</p>
<p>(21) International Application Number: PCT/GB98/00556</p> <p>(22) International Filing Date: 23 February 1998 (23.02.98)</p> <p>(30) Priority Data: 9703616.4 21 February 1997 (21.02.97) GB</p> <p>(71) Applicant (for all designated States except US): THE COURT OF THE UNIVERSITY OF PAISLEY [GB/GB]; University of Paisley, High Street, Paisley PA1 2BE (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): PLACIDO, Frank [GB/GB]; Fairwater, 10 Donaldfield Road, Bridge of Weir, Renfrewshire PA11 3JJ (GB).</p> <p>(74) Agent: MURGITROYD &amp; COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i></p>	
<p>(54) Title: THIN FILMS</p> <p>(57) Abstract</p> <p>The invention provides a thin film comprising successive layers of aluminium oxide, aluminium oxynitride and aluminium nitride, which varies sinusoidally throughout the depth of the film. The film can be used to coat and protect tools with sharp working edges, to provide a stress free thermal protective coating for natural or man-made diamonds, as a light filter and/or as a pigment. It is made by sputtering aluminium using a suitable noble gas in a variable atmosphere of oxygen and nitrogen at room temperature. The film is transparent and has a refractive index which varies between 1.6 to 2.2, again sinusoidally with depth.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<b>AL</b>	Albania	<b>ES</b>	Spain	<b>LS</b>	Lesotho	<b>SI</b>	Slovenia
<b>AM</b>	Armenia	<b>FI</b>	Finland	<b>LT</b>	Lithuania	<b>SK</b>	Slovakia
<b>AT</b>	Austria	<b>FR</b>	France	<b>LU</b>	Luxembourg	<b>SN</b>	Senegal
<b>AU</b>	Australia	<b>GA</b>	Gabon	<b>LV</b>	Latvia	<b>SZ</b>	Swaziland
<b>AZ</b>	Azerbaijan	<b>GB</b>	United Kingdom	<b>MC</b>	Monaco	<b>TD</b>	Chad
<b>BA</b>	Bosnia and Herzegovina	<b>GE</b>	Georgia	<b>MD</b>	Republic of Moldova	<b>TG</b>	Togo
<b>BB</b>	Barbados	<b>GH</b>	Ghana	<b>MG</b>	Madagascar	<b>TJ</b>	Tajikistan
<b>BE</b>	Belgium	<b>GN</b>	Guinea	<b>MK</b>	The former Yugoslav Republic of Macedonia	<b>TM</b>	Turkmenistan
<b>BF</b>	Burkina Faso	<b>GR</b>	Greece	<b>ML</b>	Mali	<b>TR</b>	Turkey
<b>BG</b>	Bulgaria	<b>HU</b>	Hungary	<b>MN</b>	Mongolia	<b>TT</b>	Trinidad and Tobago
<b>BJ</b>	Benin	<b>IE</b>	Ireland	<b>MR</b>	Mauritania	<b>UA</b>	Ukraine
<b>BR</b>	Brazil	<b>IL</b>	Israel	<b>MW</b>	Malawi	<b>UG</b>	Uganda
<b>BY</b>	Belarus	<b>IS</b>	Iceland	<b>MX</b>	Mexico	<b>US</b>	United States of America
<b>CA</b>	Canada	<b>IT</b>	Italy	<b>NE</b>	Niger	<b>UZ</b>	Uzbekistan
<b>CF</b>	Central African Republic	<b>JP</b>	Japan	<b>NL</b>	Netherlands	<b>VN</b>	Viet Nam
<b>CG</b>	Congo	<b>KE</b>	Kenya	<b>NO</b>	Norway	<b>YU</b>	Yugoslavia
<b>CH</b>	Switzerland	<b>KG</b>	Kyrgyzstan	<b>NZ</b>	New Zealand	<b>ZW</b>	Zimbabwe
<b>CI</b>	Côte d'Ivoire	<b>KP</b>	Democratic People's Republic of Korea	<b>PL</b>	Poland		
<b>CM</b>	Cameroon	<b>KR</b>	Republic of Korea	<b>PT</b>	Portugal		
<b>CN</b>	China	<b>KZ</b>	Kazakstan	<b>RO</b>	Romania		
<b>CU</b>	Cuba	<b>LC</b>	Saint Lucia	<b>RU</b>	Russian Federation		
<b>CZ</b>	Czech Republic	<b>LI</b>	Liechtenstein	<b>SD</b>	Sudan		
<b>DE</b>	Germany	<b>LK</b>	Sri Lanka	<b>SE</b>	Sweden		
<b>DK</b>	Denmark	<b>LR</b>	Liberia	<b>SG</b>	Singapore		
<b>EE</b>	Estonia						

1     **THIN FILMS**

2

3     This invention relates to thin films.

4

5     Thin film materials have attractive properties for  
6     applications in security printing of banknotes, credit  
7     cards, telephone cards, smart cards, etc. For example  
8     thin films can have highly individual and  
9     characteristic reflection properties which are easily  
10    recognised by eye, which makes automated recognition a  
11    possibility. For security purposes they are not easy  
12    to duplicate, requiring expertise and equipment which  
13    is outside that commonly available. Thin film pigments  
14    can be produced where the colour changes with the  
15    viewing angle, making it impossible to duplicate these  
16    pigments with normal colour copiers or printers.

17

18    For automated recognition it is possible, for example,  
19    to produce a film which highly reflects light in one  
20    given wavelength range while not reflecting light in a  
21    different wavelength range. The reflecting wavelength  
22    range is varied by controlling the growth and  
23    composition of the film, allowing different,  
24    distinguishable films to be produced.

25

1 Thin film coatings have been used to protect vulnerable  
2 surfaces and to extend the lifetime of sharpened tools  
3 such as drill bits and knives. A variety of durable  
4 materials have been used for this purpose previously,  
5 these materials include titanium nitride and tungsten  
6 carbide.

7

8 A limitation of some other materials with desirable  
9 properties such as aluminium oxide and aluminium  
10 nitride is the tendency to fail as coatings because of  
11 inherent stresses in the thin films which lead to  
12 cracking or buckling of the coatings.

13

14 Heterogeneous films wherein the refractive index varies  
15 with thickness have been a subject of great interest  
16 for a number of years.

17

18 The ideal material would be one whose refractive index  
19 could be varied continuously over a large range  
20 although the so-called "digital" technique in which a  
21 high-low pair is used to approximate a continuous index  
22 range has been used with success.

23

24 Previous attempts to produce continuously variable  
25 films have used radio frequency (RF) power variation to  
26 vary the stoichiometry and/or the density of the  
27 growing film, ion-assisted deposition (IAD) and plasma  
28 enhanced chemical vapour deposition (PECVD). Of these,  
29 PECVD would seem to produce the best quality films.

30

31 According to a first aspect of the present invention  
32 there is provided a thin film comprising successive  
33 layers of aluminium oxide, aluminium oxynitride and  
34 aluminium nitride.

35

36 Suitably the thin film is stress matched to a substance

1 to which it is applied.

2

3 Preferably the thin film is stress free.

4

5 More preferably the layers are such that the  
6 composition of the film varies generally sinusoidally  
7 with depth.

8

9 The thin film preferably has a refractive index which  
10 varies, preferably sinusoidally between 1.6 and 2.2.

11

12 Preferably the refractive index varies between 1.6 and  
13 2.0.

14

15 Suitably the thin film is transparent at thicknesses of  
16 up to 9 microns.

17

18 The invention further provides a method for producing a  
19 thin film on a substrate depositing aluminium in an  
20 atmosphere of oxygen and/or nitrogen, and varying the  
21 oxygen to nitrogen ratio to allow a film of aluminium  
22 oxide and/or aluminium nitride and/or aluminium  
23 oxynitride to be obtained as necessary. Preferably  
24 noble gas is also present in said atmosphere.

25

26 Preferably the deposition is performed at room  
27 temperature.

28

29 The deposition may be by sputtering which may be  
30 reactive d.c., reactive low frequency or reactive radio  
31 frequency sputtering.

32

33 Preferably the low frequency sputtering has a power  
34 supply operating in the kilohertz region.

35

36 Suitably the aluminium atoms may be removed from the

1 aluminium target by a noble gas plasma.

2

3 Optionally reactive sputtering of the aluminium atoms  
4 may be achieved solely in the presence of nitrogen  
5 and/or oxygen.

6

7 The flow rates of the noble gas may be in the range of  
8 0 - 100 sccm.

9

10 Suitably the noble gas may be argon.

11

12 Suitably the aluminium atoms may react with oxygen  
13 and/or nitrogen to form a film or coating on a suitable  
14 surface.

15

16 Preferably the variation of the oxygen/nitrogen ratio  
17 is effected by varying the relative flow rates of the  
18 oxygen and nitrogen while maintaining the field  
19 strength of the reactive radio frequency.

20

21 Suitably the flow rates of the oxygen and nitrogen may  
22 be typically in the range of 0 - 10 sccm (standard  
23 cubic centimetres per minute). In one example, the  
24 thin film produced by the method of the invention  
25 consists solely of aluminium nitride.

26

27 Preferably the oxygen and nitrogen flow rates are  
28 varied generally sinusoidally in anti-phase.

29

30 Preferably, also the deposition rate is in the range of  
31 100-800 nm per hour.

32

33 Most preferably, the deposition rate is in the range of  
34 100-400 nm per hour.

35

36 Further according to the invention there is provided a

1 pigment comprising a thin film as previously defined.

2

3 The thin film may be ground to a suitable particle size  
4 to achieve the desired spectral properties.

5

6 The thin film can be incorporated into a suitable  
7 carrier material to form a paint.

8

9 Preferably the carrier material is transparent such  
10 that the resulting paint retains the same  
11 characteristic features of the original films.

12

13 In a further aspect, the invention provides a stress  
14 matched thin film for coating a diamond surface.

15

16 The diamond surface can be of a natural or man-made  
17 diamond.

18

19 The stress matched thin film can be varied in  
20 composition to provide a surface with stress  
21 characteristics which match those stress  
22 characteristics of another material to which the  
23 diamond surface can be attached.

24

25 Suitably the thin film can be used to allow diamond  
26 surfaces to be attached to tools.

27

28 Preferably the diamond surface can be coated with a  
29 thin film which confers thermal protection to the  
30 diamond.

31

32 In another aspect, the invention provides a filter  
33 comprising a thin film as previously defined wherein  
34 the filter has high transmission except for a narrow  
35 region centred on wavelength  $\lambda_0$ .

36

1 Suitably the filter may be used as or in laser goggles,  
2 laser rejection filters, laser mirrors, head-up  
3 displays or any other suitable application.

4  
5 Still further, the invention provides the use of a thin  
6 film as previously defined to coat and protect  
7 vulnerable surfaces from chemical attack and/or to  
8 extend the lifetime of tools, for example, tools with  
9 sharp working edges.

10  
11 The surfaces may include metals, dielectrics,  
12 semiconductors and plastics.

13  
14 Optionally, once the surfaces have been coated with a  
15 thin film as previously described, the thin film can be  
16 used to allow an additional coating of diamond to be  
17 applied to the surface.

18  
19 The invention will now be further described, without  
20 limitation, by reference to the accompanying drawings,  
21 wherein:

22  
23 Fig 1 is a graph that illustrates how transmission  
24 varies as  $\lambda_0$  varies with the number of deposition  
25 cycles.

26  
27 Fig 2 is a graph that illustrates both the calculated  
28 and the measured transmission of the films.

29  
30 Figs 3 (a), (b) and (c) are spectra which illustrate  
31 depth profiling of a thin film using X-ray Photon  
32 Spectroscopy (XPS) of O 1s, N 1s and Al 2p binding  
33 energies.

34  
35 Figure 1 shows how the transmission varies as  $\lambda_0$  varies  
36 with the number of cycles deposited for the following



1 parameters, which are in a range appropriate to the  
2 aluminium oxynitride films.

3  
4 Table 1

5 $n_{\text{mean}}$	$n_{\text{range}}$	$\lambda_0$ (nm)	$t_0$ (nm)
6 1.78	0.36	392	110

7  
8 The calculations for Figure 1 have been performed for a  
9 coating on a finite thickness glass substrate immersed  
10 in air; the phase of the sine wave is  $\phi = 0$ . It can be  
11 seen that optical densities of 4 (which seems to be a  
12 benchmark figure) can be obtained for the above film  
13 parameters with 35 deposited cycles, corresponding to a  
14 film thickness of  $3.85\mu\text{m}$ .

15  
16 Figure 2 shows the experimental realisation (full line)  
17 of such a filter on glass. After measurement of the  
18 transmission the films are broken and the thickness  
19 measured on a Hitachi S4100 field emission scanning  
20 electron microscope (SEM).

21  
22 The dotted line in Fig. 2 is calculated spectrum, using  
23 the measured cycle thickness and the measured  $\lambda_0$  to  
24 calculate  $n_{\text{mean}}$  from Eqn.2 (see Example 3) and adjusting  
25  $n_{\text{range}}$  for a good fit to the spectral width. The  
26 calculation takes into account the glass absorption,  
27 but assumes the oxynitride films to be dispersion free.  
28 The fit to the side lobes is very sensitive to the  
29 assumed starting phase of the sine wave, but is also  
30 sensitive to the end layer at the film-air boundary  
31 (the end phase of the sine wave in a sense). The  
32 spectrum in Fig.2 has 35.4 cycles and  $\phi$  has been  
33 adjusted for a good fit to the sidelobes.

34  
35 Similar filters have been made with  $\lambda_0$  ranging from 300

1 - 1100 nm and with up to 70 deposited cycles. The  
2 centre wavelength is predictable and reproducible when  
3 the deposition parameters (target-substrate distance,  
4 RF power, gas flow rates, chamber pressure) are  
5 unchanged, being dependent only on the deposition time  
6 for one cycle. The visual quality of the deposition  
7 films is generally very good.

8

9 Figure 3 shows that these films are varying  
10 continuously in composition and hence in refractive  
11 index since alternating layers of aluminium oxide and  
12 aluminium nitride with thicknesses close to quarter  
13 waves can show similar optical performance. X-ray  
14 Photon Spectroscopy (XPS) shows that the oxygen 1s and  
15 nitrogen 1s peaks vary sinusoidally and in antiphase  
16 with depth from the surface. The aluminium 2p peak, in  
17 contrast, is of constant height but varies in energy  
18 with depth. This is consistent with the composition of  
19 the film varying continuously from aluminium oxide to  
20 aluminium nitride. The observed Al 2p shift varies by  
21 around 2.9 eV. The aluminium peak is a single peak  
22 which varies in position rather than two peaks with  
23 varying heights which supports the conclusion that  
24 aluminium oxynitrides are continuously variable  
25 compounds rather than a mixture of phases of aluminium  
26 oxide and aluminium nitride.

27

28 This invention relates to the growth of aluminium  
29 oxynitride films where the composition is varied  
30 continuously from  $\text{Al}_2\text{O}_3$  to AlN through intermediate  
31 compositions  $\text{AlO}_x\text{N}_y$ . This material has a number of  
32 highly desirable properties being hard, wear-resistant,  
33 adhering strongly to a variety of substrates,  
34 transparent to around 9 microns with low absorption,  
35 resistant to chemical attack and offers a potential  
36 refractive index range of 1.6 to over 2.2.

1 Additionally, this invention provides for high quality  
2 rugate filters, pigments and durable, chemical  
3 resistant coatings in which the refractive index varies  
4 sinusoidally with thickness.

5

6 Example 1

7 Aluminium Oxynitride Films

8

9 To produce aluminium oxynitride films, a sputtering  
10 chamber of suitable size containing a magnetron and a  
11 target of aluminium, typically a disk of diameter 200  
12 mm, is loaded with the substrate or substrates onto  
13 which the film is to be deposited. We have  
14 demonstrated that stress-free coatings of hard, wear-  
15 resistant, adherent coatings can be deposited on a wide  
16 variety of surfaces including metals, dielectrics,  
17 semiconductors and plastics by co-depositing aluminium  
18 oxide and aluminium nitride whereby inherent stresses  
19 are cancelled. This can be done as sequential layers  
20 of aluminium oxide and aluminium nitride or as layer of  
21 layers of aluminium oxynitride.

22

23 A removable shutter can be positioned between the  
24 substrates and the target and/or a means for moving the  
25 substrates into and out of the sputtering position is  
26 also commonly used.

27

28 The chamber is evacuated by suitable vacuum pumps,  
29 preferably to a residual vacuum of the order of  $10^{-7}$   
30 torr. The chamber is then filled with a noble gas,  
31 typically argon, to a pressure which is typically in  
32 the range of 1 - 10 millitorr.

33

34 A plasma discharge is created by means of a radio-  
35 frequency power supply, typically 1 kilowatt in power,  
36 for a 200 mm diameter aluminium target. After some

1 time, typically 30 minutes with the shutter obscuring  
2 the substrates or having moved the substrates out of  
3 the sputtering position, the surface of the target will  
4 be conditioned by the plasma and suitable amounts of  
5 the reactive gases, oxygen and nitrogen can be added to  
6 the noble gas to commence reactive sputtering.

7  
8 The desired amounts of noble gas, oxygen and nitrogen  
9 can be controlled by commonly available mass-flow  
10 controllers with mass flows of noble gas, of oxygen and  
11 of nitrogen in the range of 0 - 10 sccm (standard cubic  
12 centimetres per minute). The shutter can be opened or  
13 the substrates then moved into the sputtering position  
14 for the time necessary to produce the required  
15 thickness of deposit. A typical system as described  
16 can produce film deposition rates in the region of 150  
17 - 800 nm/hr (dependent of film composition and target  
18 to substrate distance). Higher deposition rates can be  
19 achieved using reactive d.c. sputtering or preferably  
20 "low-frequency" sputtering whereby a power supply  
21 operating at a frequency in the kilohertz region is  
22 used to reduce the charging effects encountered with  
23 d.c. power supplies.

24

## 25 Example 2

### 26 Pigments

27

28 Pigments can be produced from thin films by depositing  
29 onto and subsequently removing the film from, a  
30 suitable surface or substrate. The film can then be  
31 ground down to produce a pigment which is long lasting,  
32 chemically resistant and can be incorporated into a  
33 suitable host to form paints which retain the same  
34 characteristic features of the original films which can  
35 then be applied to surfaces in a variety of ways.

36

1 The colour of pigments manufactured from such films  
2 varies with the viewing angle and cannot be reproduced  
3 by a photocopier or colour printer.

4  
5 For this type of application the films may be easily  
6 removed and recovered if they are deposited onto  
7 substrates or surfaces which are flexible or which can  
8 be dissolved in a suitable solvent.

9

10 Example 3

11 Diamond Surfaces

12

13 It is not possible to form a diamond layer on some  
14 materials. For example, carbon diffuses into hot iron  
15 and steel to form iron carbide. In order to obviate  
16 this problem, a coating of a suitable material may be  
17 layed down onto the steel or iron, for instance, before  
18 laying down the diamond. Or alternatively, a thin film  
19 of material may be layed down onto a diamond surface  
20 first.

21

22 A thin film of aluminium oxynitride and/or oxide and/or  
23 nitride can be deposited by the technique described  
24 using the technique described herein. The stress  
25 properties of the film can be modified to match those  
26 of the diamond surface so that the film forms a  
27 coherent layer on the diamond surface. The composition  
28 of the film can then be altered so that the stress  
29 properties of the film match those of another material  
30 which is to be stuck to the diamond surface via the  
31 thin film of aluminium oxynitride and/or oxide and/or  
32 nitride.

33

34 This technique can be used for example in the  
35 manufacture of tools with diamond components where  
36 there are significant difficulties in depositing or

1 attaching diamond films onto certain materials. For  
 2 instance: in the manufacture of diamond tipped drill-  
 3 bits, grinding and polishing tools. The tool can be  
 4 treated initially with a thin film of aluminium  
 5 oxynitride and/or oxide and/or nitride. After this  
 6 stage is completed the treated tool can be coated with  
 7 an additional layer of diamond, grown by standard  
 8 techniques.

9

10 Further applications include providing a thermally  
 11 stable coating for diamond windows for use in optical,  
 12 IR or UV sensors.

13

14

15 Example 4

16 Rugate Filters

17

18 Rugate filters have a spectral response similar to that  
 19 of a rejection filter: having high transmission  
 20 everywhere except a narrow region centred on  
 21 wavelength,  $\lambda_0$ . The refractive index variation is  
 22 generally given by

23

24 Equn. (1) 
$$n(z) = n_{\text{mean}} + \frac{n_{\text{range}}}{2} \sin \left( \frac{4\pi n_{\text{mean}} z}{\lambda_0} + \phi \right)$$

25

26

27 where  $n_{\text{mean}}$  is the average refractive index,  $n_{\text{range}}$  is the  
 28 refractive index range and the geometrical thickness of  
 29 one sinusoidal cycle,  $t_0$ , is

30

31 Equn. (2) 
$$t_0 = \frac{\lambda_0}{2n_{\text{mean}}}$$

32

33

34 leads to a rejection filter centred on  $\lambda_0$  and with a  
 35 bandwidth of

36

37

1     Equn. (3)                    $\Delta \lambda = 2\lambda_0 \frac{|n_{\text{range}}|}{n_{\text{mean}}}$   
2

3

4     The phase factor  $\phi$  in Equn.(1) is the optical density  
5     at  $\lambda_0$  is important in determining the magnitudes and  
6     positions of the sidebands which are observed with this  
7     type of filter'

8

9     Equn. 2 shows that the centre wavelength is varied by  
10    changing the physical thickness of one cycle and Equn 3  
11    shows that the bandwidth can be varied by changing the  
12    refractive index range of the sinusoid. In addition the  
13    optical density at  $\lambda_0$  is dependent on the number of  
14    cycles deposited.

15

16    Such filters have application in laser goggles for  
17    protection of humans and laser rejection filters for  
18    instruments, as general purpose laser mirrors, and in  
19    head-up displays. They may also be used instead of the  
20    holographic filters in the new generations of compact  
21    Raman spectrometers.

22

23    The foregoing description of embodiments of the present  
24    invention is illustrative of specific embodiments only  
25    and is not intended to be limiting. It is to be  
26    understood that additional embodiments which may be  
27    perceived by those skilled in the art are considered to  
28    be within the scope of the present invention.

29    /u/mur/specs18/p18104-

30

## 1 REFERENCES

- 2
- 3 1 R Jacobson, "Optical properties of a class of  
4 inhomogeneous thin films", *Optica Acta* 10, 309-  
5 323; (1963).  
6
- 7 2 E Delano, "Fourier synthesis of multilayer  
8 filters", *J Opt. Soc. Am.* 57, 1529-1533, (1967).  
9
- 10 3 J A Dobrowolski and D Lowe. "Optical thin film  
11 synthesis program based on the use of Fourier  
12 transforms", *Appl. Opt.* 17, 3039-3050, (1978).  
13
- 14 4 W H Southwell, "Spectra response calculations of  
15 rugate filters using coupled-wave theory", *J Opt.*  
16 *Soc. Am.* A5, 1558-1564, (1988).  
17
- 18 5 B G Bovard, "Derivation of a matrix describing a  
19 rugate dielectric thin film", *Appl. Opt.* 27, 1998-  
20 2005, (1988).  
21
- 22 6 R R Wiley, "Rugate Broadband antireflection  
23 coating design", *SPIE* 1168-26, San Diego, (1989)  
24
- 25 7 P G Verly, J A Dobrowolski, W J Wild, and R L  
26 Burton, "Synthesis of high rejection filters with  
27 the Fourier transform method", *Appl. Opt.* 28,  
28 2864-2867, (1989).  
29
- 30 8 R R Wiley, "Basic nature and properties of  
31 inhomogeneous antireflection coatings" in  
32 *Inhomogeneous and Quasi-inhomogeneous Optical*  
33 *Coatings*, Jerzy A Dobrowolski, Pierre G Verly,  
34 Editors, *Proc SPIE* 2046, 69-77, (1993).  
35
- 36 9 A K Tikhonravov, "Mathematical aspects of the



- 1 synthesis of *Inhomogeneous and Quasi-inhomogeneous*  
2 *Optical Coatings*, Jerzy A Dobrowolski, Pierre G  
3 Verly, Editors, Proc SPIE 2046, 18-29, (1993).  
4
- 5 10 J A Dobrowolski and A V Tikonravov, "Series of  
6 optimal and near-optimal solutions to an  
7 antireflection problem", in *Inhomogeneous and*  
8 *Quasi-inhomogeneous Optical Coatings*, Jerzy A  
9 Dobrowolski, Pierre G Verly, Editors, Proc SPIE  
10 2046, 62-68, (1993).  
11
- 12 11 C K Hwangbo, L J Lingg, J P Lehan, H A MacLeod and  
13 F Suits, "Reactive ion assisted deposition of  
14 aluminium oxynitride thin films", Appl Opt. 28,  
15 2779-2784, (1989).  
16
- 17 12 M F Oullette, R V Lang, K L Yan, R W Bertram and R  
18 S Owles, "Experimental studies of inhomogeneous  
19 coatings of optical applications", J Vac Sci,  
20 Technol. A9, 1188-1192. (1991).  
21
- 22 13 A F Jankowski, L R Schrawyer and P L Perry,  
23 "Reactive sputtering of molybdenum-oxide gradient-  
24 index filters", J Vac. Sci. Technol. A9, 1184-  
25 1187, (1991).  
26
- 27 14 S Lim, J H Ryu, J F Wager and T K Plant, "Rugate  
28 filters grown by plasma-enhanced chemical vapour  
29 deposition", Thin Solid Films, 245, 141-145,  
30 (1993).  
31

- 1     15     J N Kidder, J S Kuo, A Ludviksson, T P Pearsall, J  
2           W Rogers, J M Grant, L R Allen and S T Hsu,  
3           "Deposition of AlN at lower temperatures by  
4           atmospheric metalorganic chemical vapour  
5           deposition using dimethylethylamine alane and  
6           ammonia", J Vac. Sci. Technol. A13, 711-715,  
7           (1995).  
8
- 9     16     Experimental techniques centre (ETC), Brunel  
10           University, Uxbridge, Middlesex UB8 3PH, England.  
11  
12  
13

1     **CLAIMS**

2

3     1. A thin film comprising successive layers of  
4     aluminium oxide, aluminium oxynitride and aluminium  
5     nitride.

6

7     2. A thin film as claimed in Claim 1, which is stress  
8     matched to a substance to which it is applied so as to  
9     be stress-free.

10

11    3. A thin film as claimed in Claims 1 and 2, the layers  
12    of which are such that the composition of the film  
13    varies sinusoidally with depth.

14

15    4. A thin film as claimed in Claims 1, 2 and 3, which  
16    has a refractive index that varies sinusoidally between  
17    1.6 and 2.2.

18

19    5. A thin film as claimed in any of the preceding  
20    claims, which is transparent at thicknesses of up to 9  
21    microns.

22

23    6. A method for depositing a thin film as claimed in  
24    claims 1 to 5, which comprises depositing aluminium in  
25    an atmosphere of oxygen and/or nitrogen, and varying  
26    the oxygen to nitrogen ratio to allow a film of  
27    aluminium oxide and/or nitride and/or aluminium  
28    oxynitride to be obtained as necessary.

29

30    7. A method as claimed in Claim 6 wherein the  
31    deposition of aluminium occurs at room temperature.

32

33    8. A method as claimed in Claims 6 and 7 wherein the  
34    deposition occurs by sputtering, the type of sputtering  
35    chosen from the group consisting of reactive d.c.,  
36    reactive low frequency and reactive radio frequency sputtering.

- 1 9. A method as claimed in Claims 6, 7 and 8 wherein the  
2 low frequency sputtering has a power supply operating  
3 in the kilohertz region.  
4
- 5 10. A method as claimed in Claims 6 to 9 wherein the  
6 aluminium atoms are removed from the target by a noble  
7 gas plasma, flowing at between 0-100 sccm.  
8
- 9 11. A method as claimed in Claims 6 to 10 wherein the  
10 aluminium atoms are removed from the target solely in  
11 the presence of nitrogen and/or oxygen.  
12
- 13 12. A method as claimed in Claims 6 to 11, wherein the  
14 noble gas is argon.  
15
- 16 13. A method as claimed in Claims 6 to 12 wherein the  
17 aluminium atoms react with oxygen and/or nitrogen to  
18 form a thin film on a suitable surface.  
19
- 20 14. A method as claimed in Claims 6 to 13 wherein the  
21 flow rates of the argon, oxygen and nitrogen may be  
22 varied sinusoidally in anti-phase in the range 0-10  
23 sccm.  
24
- 25 15. A method as claimed in Claims 6 to 14 wherein the  
26 rate of deposition is in the range 100-800 nm per hour.  
27
- 28 16. A method as claimed in Claims 6 to 15 wherein the  
29 rate of deposition is in the range 100-400 nm per hour.  
30
- 31 17. A thin film as claimed in Claims 1-5 which is used  
32 as a pigment.  
33
- 34 18. A thin film as claimed in Claims 1 to 5 and 17  
35 wherein the thin film is ground to a suitable particle  
36 size to achieve the desired spectral properties.

1 19. A thin film as claimed in Claims 1 to 5 and 17 and  
2 18 wherein the thin film is incorporated into a  
3 transparent carrier material to make a paint.  
4

5 20. A thin film as claimed in Claims 1 to 5 and 17 to  
6 19 wherein the thin film is used to provide a stress  
7 matched film to natural or man-made diamond.  
8

9 21. A thin film as claimed in Claims 1 to 5 and 17 to  
10 20 wherein the thin film is stress matched to provide a  
11 surface with stress characteristics which match those  
12 stress characteristics of another material to which the  
13 diamond surface can be attached.  
14

15 22. A thin film as claimed in Claims 1 to 5 and 17 to  
16 21 wherein the thin film is used to allow diamond  
17 surface to be attached to tools.  
18

19 23. A thin film as claimed in Claims 1 to 5 and 17 to  
20 22 wherein the thin film confers thermal protection to  
21 the diamond surface.  
22

23 24. A filter comprising a thin film as claimed in  
24 Claims 1 to 5 and 17 to 23 wherein the filter has a  
25 high transmission except for a narrow region centred on  
26 a wavelength .  
27

28 25. A filter as claimed in Claim 24 wherein the filter  
29 is used in laser goggles, laser rejection filters,  
30 laser mirrors, head up displays and any other suitable  
31 application.  
32

33 26. A thin film as claimed in Claims 1 to 5 and 17 to  
34 23 wherein the thin film is used to coat and protect  
35 vulnerable surfaces from chemical attack and to extend  
36 the lifetime of tools with sharp working edges.

1 27. A thin film as claimed in Claims 1 to 5, 17 to 23  
2 and 26 wherein the thin film is used to coat and  
3 protect vulnerable surfaces chosen from the group  
4 consisting of metals, dielectrics, semiconductors and  
5 plastics.

6  
7 28. A thin film as claimed in Claims 1 to 5, 17 to 23,  
8 26 and 27 wherein the thin film used to coat and  
9 protect vulnerable surfaces chosen from the group  
10 consisting of metals, dielectrics, semiconductors and  
11 plastics is used to allow an additional coating of a  
12 diamond to be applied to the surfaces.

13

14

1 / 3

Optical density vs Number of cycles deposited for a sine-wave rugate

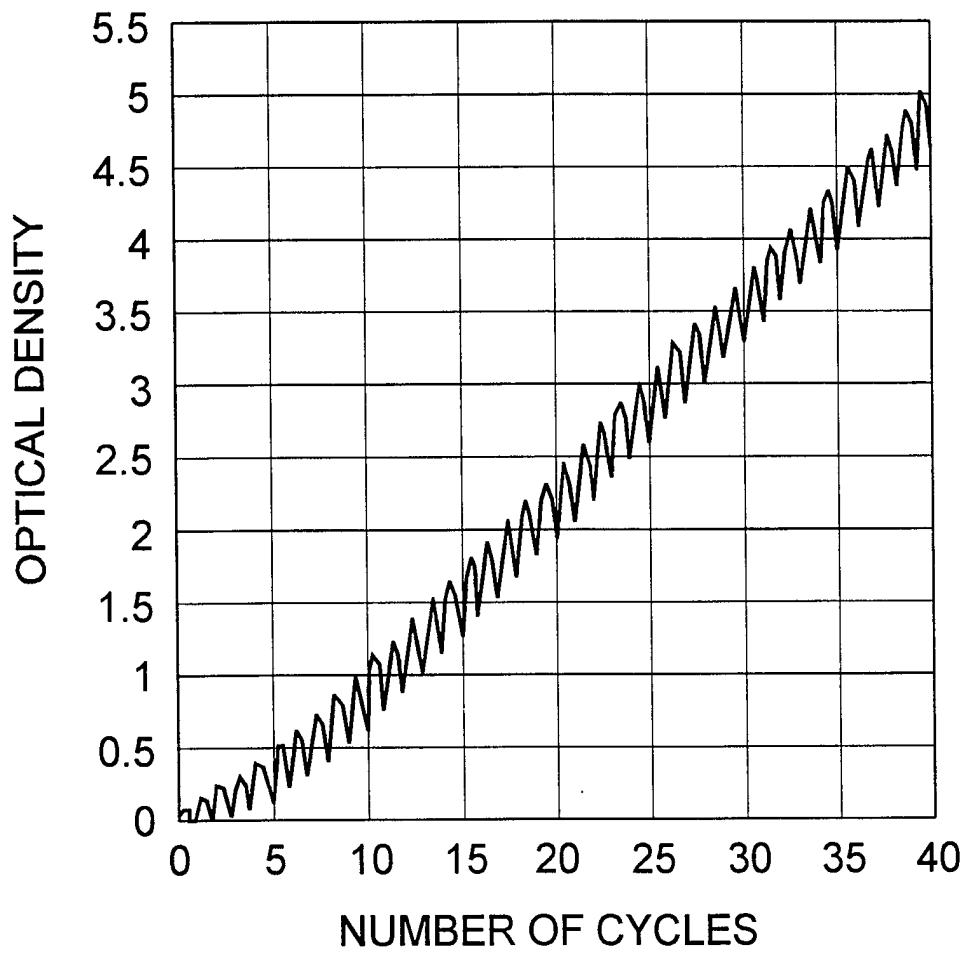
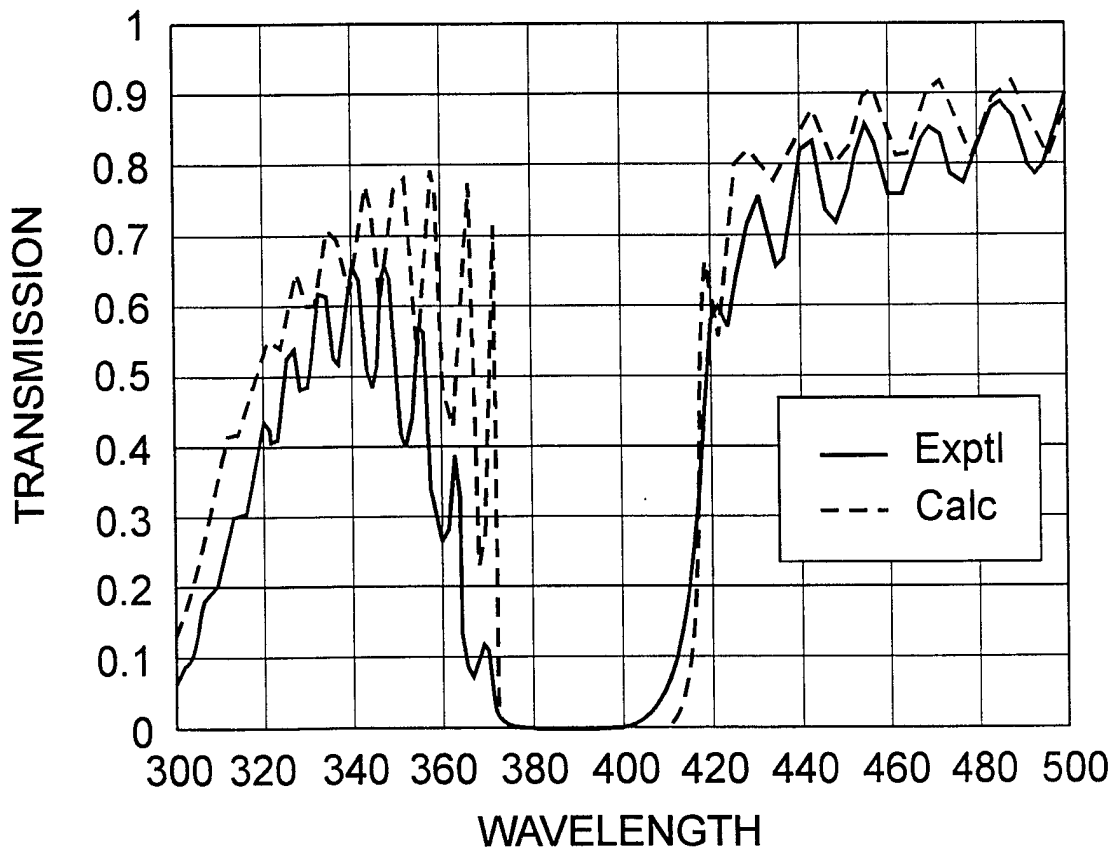
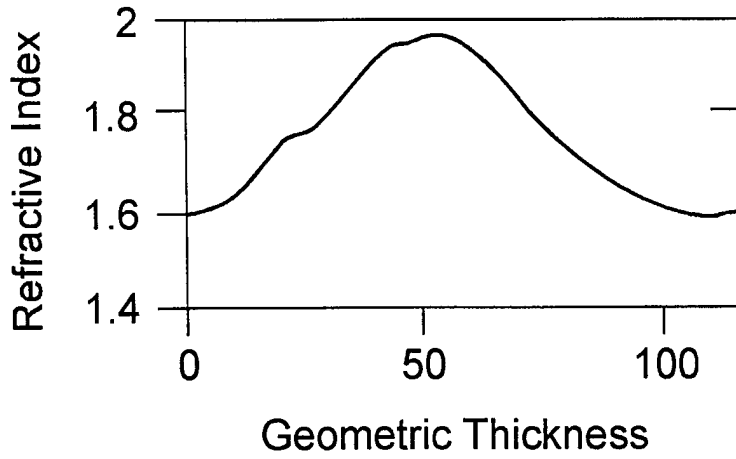


Fig. 1

2 / 3



Transmission of an experimental rugate on glass with calculated spectrum

Fig. 2



3 / 3

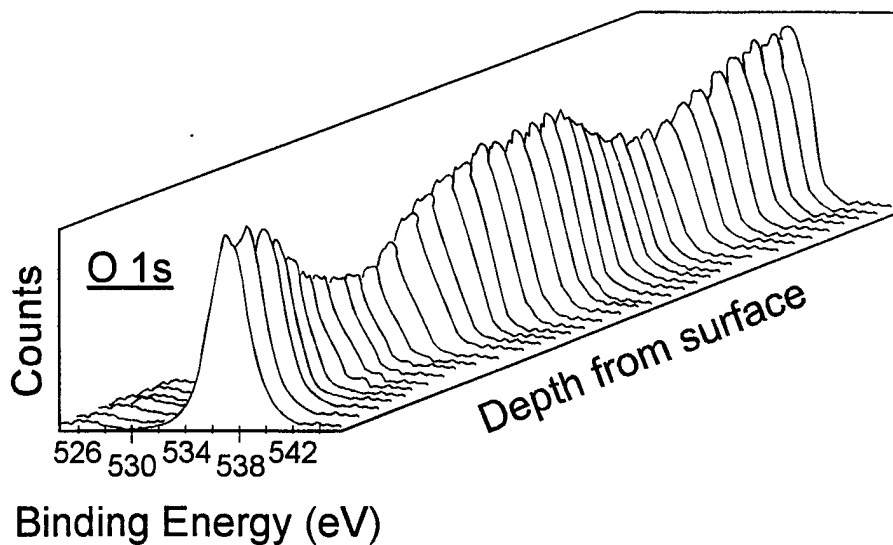


Fig. 3a

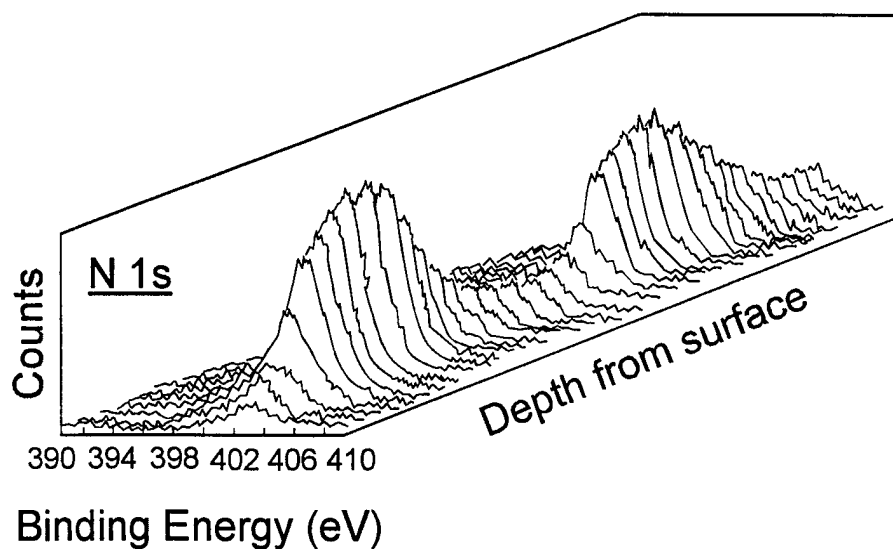


Fig. 3b

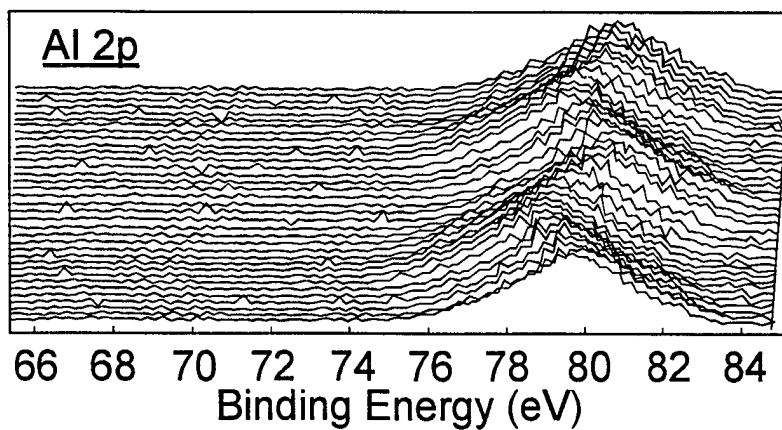


Fig. 3c

Depth profiling XPS:  
Oxygen, nitrogen and aluminium