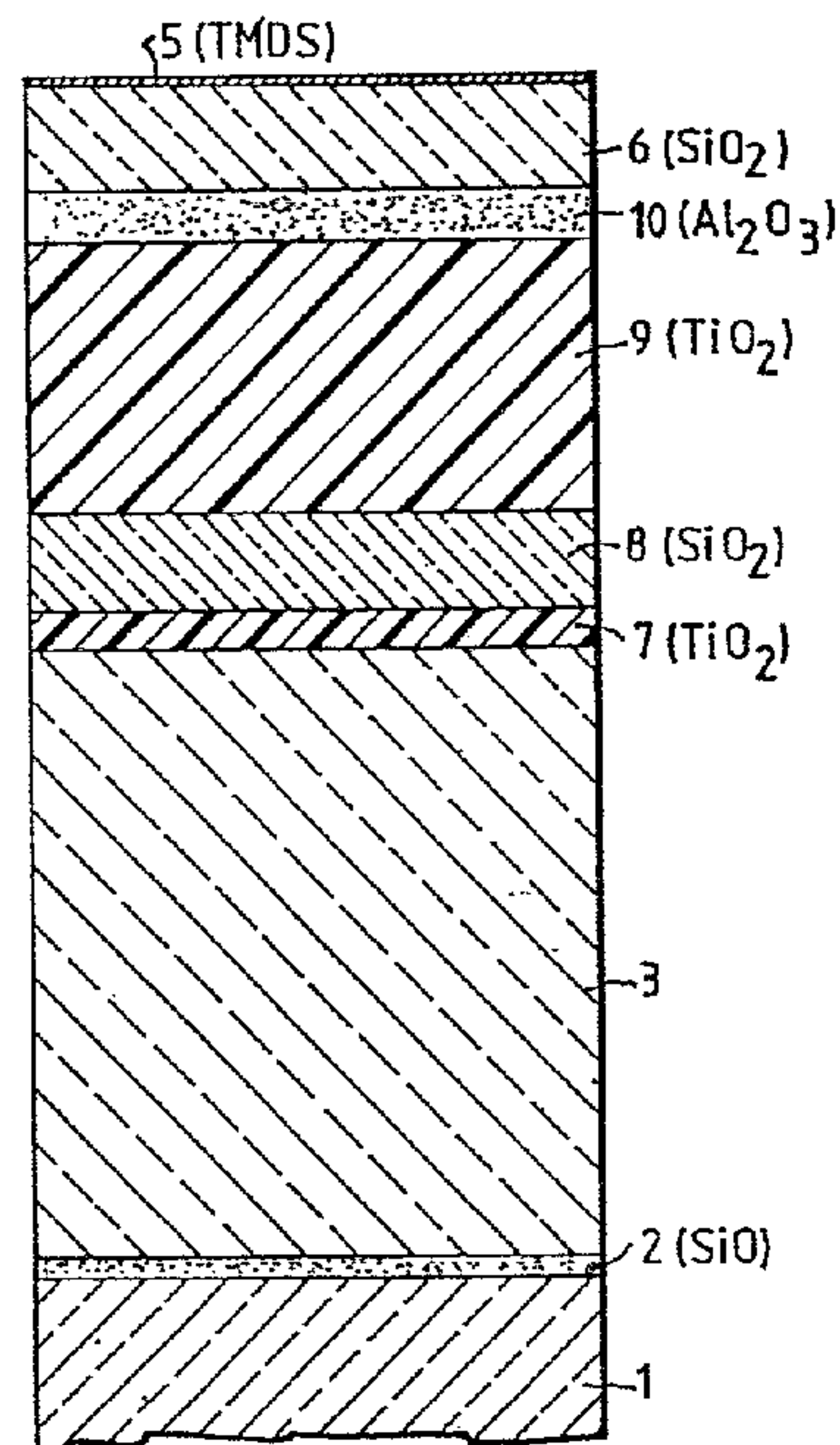




(22) 1995/08/28  
(43) 1996/02/27  
(45) 2001/05/01

(72) Zültzke, Walter, DE  
(72) Arhilger, Detlef, DE  
(73) BALZERS UND LEYBOLD DEUTSCHLAND HOLDING AG, DE  
(51) Int.Cl.<sup>6</sup> G02B 1/10  
(30) 1994/08/26 (P 44 30 363.7) DE  
(54) LENTILLE OPTIQUE EN PLASTIQUE  
(54) OPTICAL LENS OF TRANSPARENT PLASTIC



(57) Coated optical lens with a substrate of transparent plastic (1) with a first layer (2) of SiO directly on the substrate and a second layer (3) of borosilicate glass with an index of refraction of 1.47 ( $\lambda = 550$  nm) to ensure shift-free spectral behavior. The borosilicate glass layer can be up to 3  $\mu$  thick, preferably 2,550 nm; layers 3-7 are formed of TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> to provide an antiglare effect.

LYB 371-JEL/FBF

Abstract of the Disclosure

Coated optical lens with a substrate of transparent plastic (1) with a first layer (2) of SiO directly on the substrate and a second layer (3) of borosilicate glass with an index of refraction of 1.47 ( $\lambda = 550$  nm) to ensure shift-free spectral behavior. The borosilicate glass layer can be up to 3  $\mu$  thick, preferably 2,550 nm; layers 3-7 are formed of TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> to provide an antiglare effect.

LYB 371-JEL/FBF

## OPTICAL LENS OF TRANSPARENT PLASTIC

Background of the Invention

The invention pertains to an optical lens of transparent plastic with a first layer of SiO serving as an adhesive layer directly on the substrate.

The problem of how to provide lenses with a protective layer which is transparent but also reduces glare is often encountered. This is true both for camera lenses and also for eyeglass lenses. For example, eyeglass lenses can be subjected to extreme conditions when handled improperly. As a result, not only plastic lenses but even those made of silicate glass can thus be scratched. A sharp-edged object, pulled under pressure across the surface of the lens, is usually responsible for this type of damage. The sharp-edged object can be a grain of sand present in the cleaning cloth or spectacle case, for example, or even a piece of coarse fabric.

Plastic glasses, which are being used more and more frequently in place of silicate glasses, because they combine the properties of lighter weight and higher shatter resistance with the possibility of custom tinting, nevertheless suffer from the serious disadvantage of having a much softer surface than that of silicate glasses, which thus makes them highly vulnerable to mechanical damage.

The thermosetting plastics, which consist of macromolecules chemically bonded to one another to form a tight mesh, are in widespread use. At room temperatures, they are usually very

LYB 371-JEL/FBF

brittle. They are also resistant to heat, infusible, insoluble, and swellable to only a slight extent. A thermoset which is preferred for eyeglass lenses is CR 39, a diallyl diethylene glycol carbonate. Until recently, this plastic had the field of eyeglass lenses almost exclusively to itself, but now there are other plastics such as polymethyl methacrylate (PMMA), polystyrene (PS), and polycarbonate (PC) which have become important.

Because eyeglass lenses made of plastic, especially of CR 39, are not scratch-resistant, they are usually coated with a hard resin. A resin-coating process such as this is complicated, however, and requires not only a uniform thickness but also an index of refraction  $n$  which must be matched to that of the substrate material to avoid interference phenomena. To eliminate this resin-coating process, the initial effort was made to deposit a wear-resistant quartz layer on the substrate in a vacuum vapor-deposition system. An anti-glare system was deposited as part of the same process. To obtain layers with the required high packing density without having to heat the substrates (maximum allowable substrate temperature =  $85^{\circ}\text{C}$ ), the vapor deposition process was carried out with a plasma ion assisted deposition (plasma IAD) process.

The materials used here resulted in a layer system showing increased wear resistance and an antiglare effect. The previously known layer system (DE 41 28 547), however, is not

LYB 371-JEL/FBF

stable in its spectral behavior, and its antiglare effect is inadequate.

#### Summary of the Invention

The present invention is therefore based on the task of creating a layer system which has the properties of the known system but which is also insensitive to stress and therefore highly stable and shift-free in its spectral behavior.

This task is accomplished in that the second layer consists of borosilicate glass with an index of refraction of 1.47 and a thickness of up to 3  $\mu$ , preferably 2,550 nm, and in that layers 3-7 are formed of  $TiO_2$ ,  $SiO_2$ ,  $Al_2O_3$  for the purpose of providing the antiglare effect.

#### Brief Description of the Drawing

Figure 1 shows a two-layer structure on a plastic lens substrate;

Figure 2 shows an eight-layer structure on a plastic lens substrate; and

Figure 3 shows a schematic diagram of a plasma-IAD process for producing thin layers.

#### Detailed Description of the Preferred Embodiments

Figure 1 shows a lens substrate 1 consisting of a plastic such as CR 39, on top of which a very thin  $SiO$  layer 2, with a thickness ranging from one atomic layer to 20 nm, is provided. Layer 2 serves essentially to improve the adhesion of a protective layer 3 with a thickness of at least 500 nm, consist-

ing of borosilicate glass.

It has been found that, when a layer of borosilicate glass is applied directly to a plastic, it adheres only moderately well. In the so-called boiling test, coated substrates are immersed for defined periods of time in a boiling salt solution, which contains, for example, 5% NaCl, and then quenched in cold water. This cycle is then repeated a certain number of times. A protective layer applied directly to the plastic comes loose quickly, i.e., in 5-10 minutes, during these boiling tests. When, however, an SiO layer 2 is applied between protective layer 3 and the plastic substrate, which is coated from the vapor phase under simultaneous bombardment with plasma and ions or with an electronic beam gun, the adhesion of protective layer 3 is considerably improved. Even after 40 minutes of the boiling test, no layer separations at all could be found in layers 2 and 3.

A thick borosilicate glass layer 3 results in a considerable improvement in the abrasion properties in comparison with those of plastic substrate 1. CR 39, for example, has a hardness of about 180-200 N/mm<sup>2</sup>. Solid borosilicate glass, however, has a hardness which is 100 times greater. The hardness of protective layer 3 can be varied over a very wide range through the adjustment of the plasma and coating parameters.

Figure 2 shows an embodiment in which a combination of four additional layers 7-10 is provided on top of borosilicate glass

LYB 371-JEL/FBF

layer 3; this combination serves exclusively to reduce reflections. They consist, from bottom to top, of  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$ . A cover layer 6 consists of  $\text{SiO}_2$  and a hydrophobic layer 5 of TMDS (tetramethyldisiloxane).

The layers are vapor-deposited in a standard vacuum system 20 by means of an electron beam evaporator 21. A plasma source 22 is installed in the middle, on floor 23 of system 20, facing an electrically insulating substrate holder 24. A cylindrical, electron-emitting LaBc cathode 25 is surrounded in plasma source 22 by a cylindrical anode 26 with a diameter of about 50 mm. A glow-discharge plasma is produced; a noble gas, primarily argon, is introduced through a line 28.

A cylindrical magnetic coil 29 surrounds anode 26 and has the effect of considerably increasing the mobility of the electrons, which generate the plasma, in the axial direction and of significantly reducing their mobility in the radial direction. The electrons move in spirals around the magnetic field lines, as a result of which the plasma ultimately arrives at substrate holder 24. On roof 30 of coating chamber 20 and above substrate holder 24 there is a ring-shaped magnetic coil (31) with an inside diameter which is greater than the diameter of the substrate holder. The magnetic field of this ring-shaped coil 31 and the magnetic field of cylindrical coil 29 are superimposed on each other to form a guide field for the electrons on their way from cathode 25 and for all of the plasma between plasma source

LYB 371-JEL/FBF

22 and substrate holder 24. The cathode is heated indirectly by a heater 27, which is fed in turn by an energy supply 32. A dome-shaped plasma boundary layer is generated in front of dome-shaped substrate holder 24. Because the potential of substrate holder 24 is negative relative to the plasma, the ions are accelerated out of the plasma boundary layer and bombard the growing film, the density of which is therefore increased. An essential advantage of this production method over conventional IAD processes with an ion source is that the ions which start from a plasma boundary layer parallel to the entire inside surface of the substrate holder are accelerated over only a short distance. In the case of an ion source in which the acceleration proceeds from the bottom of the chamber, the situation is different. In the case of the device according to Figure 3, the ions from the plasma boundary layer are not affected by collisions and energy losses. In addition, the plasma is spread out over the entire area between plasma source 22 and substrate holder 24, so that the ion source basically covers the same surface area as substrate holder 24. With a conventional ion source with grid extraction, however, the surface of the extraction grid must be approximately the same as the impact surface on the substrate.

A reactive gas such as  $O_2$  or  $N_2$  is introduced through a line 34 into chamber 20. Because of the plasma present in chamber 20, this gas is ionized and activated. Material 35 evaporated by

LYB 371-JEL/FBF

electron beam gun 21 must also pass through the plasma in front substrate holder 24, with the result that it is ionized and activated.

Plasma source 22 is electrically insulated from chamber 20. In addition to the supplied discharge voltage, therefore, there is also a potential difference between source 22 and chamber 20. Source 22 assumes a variable positive potential with respect to chamber 20, whereas substrate holder 24 has almost the same potential as chamber 20. The ion energy is determined by the potential difference between anode tube 26, which is fed from a DC power source 36 at a positive potential, and substrate holder 24. The variable potential of source 22 depends on the discharge voltage, the partial pressures of the gases, and the intensity of the magnetic field. As a result of the positive, "floating" potential of source 22, an electric field is generated which reflects the electrons between source 22 and substrate holder 24. If they do not strike anode tube 26, they are reflected at the cathode potential and can emerge from the source again. Oscillating electron paths are therefore obtained, which are highly effective at ionizing and exciting gas atoms and molecules. Because of the repulsion effect which the electric fields generate near the anode, the plasma in front of substrate holder 24 is dominated by ions. This can be concluded from the potential of substrate holder 24, which is somewhere between 3 and 5 volts, relative to chamber wall 20. The discharge

LYB 371-JEL/FBF

parameters comprise a discharge voltage of up to 80 V, a discharge current of 70 A, and a plasma power of 5 kW. The pressures are in the range of  $1 \times 10^4$  to  $8 \times 10^4$  mbar with a ratio of  $O_2$  to argon of up to 4:1. The method for operating the plasma source described above makes it possible to separate the plasma generation process from the evaporation process.

Any starting material which can be evaporated, e.g., oxides and fluorides, can be evaporated in evaporator 21, because there is no coupling between the plasma source and the evaporator source.

For the vapor deposition of a scratch-resistant borosilicate layer, either granulate or plate material can be used, which is evaporated in electron beam evaporator 21 by means of electron beam generator 40. A relatively low evaporator power is required to evaporate borosilicate glass. To minimize the evaporator power required even for highly refractive material, it is preferable to use a multiple-bowl crucible with the smallest possible bowls; only one such bowl 41 is illustrated in the drawing. After chamber 20 has been pumped out to a pressure of less than  $2 \times 10^{-5}$  mbar, the layer system is deposited from the vapor phase.

The  $SiO$  adhesive layer is deposited from the vapor phase at a rate of about 0.1 nm/s. Plasma source 22 is turned on at the same time the evaporator aperture is opened. Source 22 is operated in this case with pure argon at a partial pressure of

about  $1.5 \times 10^{-4}$  mbar. The discharge current is about 30 A at a discharge voltage of about 30 V. After the layer has reached the desired thickness, plasma source 22 is turned off at the same time the evaporator aperture is closed.

Then the thick protective layer of borosilicate glass is deposited from the vapor phase. Here, too, plasma source 22 is operated with argon.

The hardness of the protective layer depends on the plasma discharge power, that is, on the current and voltage; on the gas pressure; and on the coating rate. These parameters are used to set the hardness gradient of the layer. Low hardness values are achieved at a low plasma power ( $< 1$  kW), at relatively high pressure (about  $6 \times 10^{-4}$  mbar), and at a fast coating rate (about  $5 \times 10$  nm/s). The greatest hardness values were achieved in experiments with a plasma power of about 5 kW at a pressure of  $1.5 \times 10^{-4}$  a mbar and at rate of 0.1 nm/s. After the layer has reached the desired thickness, plasma source 22 is turned off at the same time the evaporator aperture is closed.

Then the first high-refraction layer of  $\text{TiO}_2$  is deposited from the vapor phase. In principle, it is also possible to use other highly refractive materials such as zirconium oxide, etc. For the highly refractive layers, plasma source 22 is also operated with argon at a pressure of about  $1.5 \times 10^{-4}$  mbar. In addition, oxygen is introduced into chamber 20 at a partial pressure of about  $2 \times 10^{-4}$  mbar through line 34. An oxygen inlet

LYB 371-JEL/FBF

(not shown) leading directly into the plasma source, similar to inlet 28, is also possible. During the deposition of the  $\text{TiO}_2$ , the plasma source is operated at a discharge voltage of about 5 kW. The coating rate is about 0.2 nm/s. The next layer, consisting of  $\text{SiO}_2$ , is deposited from the vapor phase essentially in the same manner as the protective layer, namely, at a pressure of  $2 \times 10^{-4}$  mbar, at a plasma power of about 4 kW, and at a coating rate of about 0.5 nm/s.

The deposition of the following highly-refractive layer which follows is carried out with the same parameters as those used for the first highly refractive layer. The last layer, consisting of  $\text{SiO}_2$ , is then deposited like the preceding  $\text{SiO}_2$  layer.

It is obvious that, to produce atoms, molecules, or clusters of materials such as  $\text{SiO}$  or  $\text{SiO}_2$ , it is also possible to use a thermal evaporator or a sputter cathode instead of an electron beam evaporator. The only essential point is that the plasma must be produced in a device separate from the electronic beam gun, etc. Because the plasma is produced in plasma source 22 and the small particles to be deposited are produced by an evaporator source 21, coatings with a very high degree of uniformity can be obtained. In addition, the coating parameters can be adjusted in almost complete independence of each other, which is extremely important for the production of layers with strength gradients.

LYB 371-JEL/FBF

Substrate holder 24, the lower edge of which is designated by the number 33, can be rotated by way of a shaft 42. It can carry numerous lenses to be coated or the like on its lower surface. In addition, substrate holder 24 can be provided with protection (not shown) against deposition which, when insulating materials are being applied, prevents part of the surface of the substrate holder from being coated with these insulating materials. If such a coating were to be formed, it would be impossible for electrical charges to flow away via the substrate holder. Further details of the device according to Figure 3 can be derived from EP 463 230 and are therefore not described here in any further detail.

When the process described here is used, the layers are shift-free, and the antiglare effect matches the low values achieved by conventional processes.

The freedom from shift is achieved in that the quartz ( $\text{SiO}_2$ ) of the wear resistant layer is replaced by a borosilicate glass with an index of refraction of  $n = 1.47$  ( $\lambda = 550 \text{ nm}$ ). The boron present in the glass prevents the intrusion of water and oxygen into the layer, so that the layer retains its homogeneity on exposure to the atmosphere. It has also been found that the stress in borosilicate glass layers is less pronounced than that in pure  $\text{SiO}_2$  layers, which leads to an increase in the temperature resistance.

LYB 371-JEL/FBF

Interrupting the deposition of the thick borosilicate glass layer for a short plasma bombardment leads to a premature disruption of the growth of the layer, so that scattering emanating from so-called "seeds" is avoided. The low level of scattering thus achieved increases the transparency of the layer.

Another means used in this process to reduce the scattering in the borosilicate glass layer is the simultaneous introduction of small amounts of water during the evaporation process. The factors responsible for this effect are not known at the present time.

Because of the low optical losses, it is possible to increase the thickness of the wear-resistant glass layer to as much as 3  $\mu\text{m}$ , as a result of which the wear resistance of the overall system is considerably increased.

The antiglare effect is achieved by means of a 5-layer system consisting of the materials  $\text{Ti}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ . The material indices of refraction required for a good antiglare effect are produced by means of PIAD.

The  $\text{SiO}_2$  present in the antiglare system can be replaced by borosilicate glass, as a result of which this layer system also becomes shift-free with respect to its spectral behavior. An improvement in the thermal and chemical resistance can also be expected.

All the layers except for the adhesion primer are applied by means of PIAD with the advanced plasma source (APS). The

2157070

LYB 371-JEL/FBF

substrates are exposed prior to coating to a plasma bombardment, which significantly increases the adhesion.

LYB 371-JEL/FBF

## CLAIM(S)

1. Coated optical lens comprising a transparent plastic substrate, a first layer of SiO directly on said substrate, and a second layer of borosilicate glass directly on said first layer, said second layer having a thickness up to  $3\mu$  and an index of refraction of 1.47 at  $\lambda = 550$  nm.
2. Coated optical lens as in claim 1 wherein said first layer has a thickness ranging from one atomic layer to 50 nm, and said second layer has a thickness of at least 500 nm.
3. Coated optical lens as in claim 1 further comprising a multilayer antiglare system on said second layer, said multilayer system comprising materials selected from  $TiO_2$ ,  $SiO_2$ , and  $Al_2O_3$ .
4. Coated optical lens as in claim 3 wherein said multilayer antiglare system comprises a third layer of  $TiO_2$  directly on said second layer.
5. Coated optical lens as in claim 1 wherein said second layer has a thickness of 2550 nm.

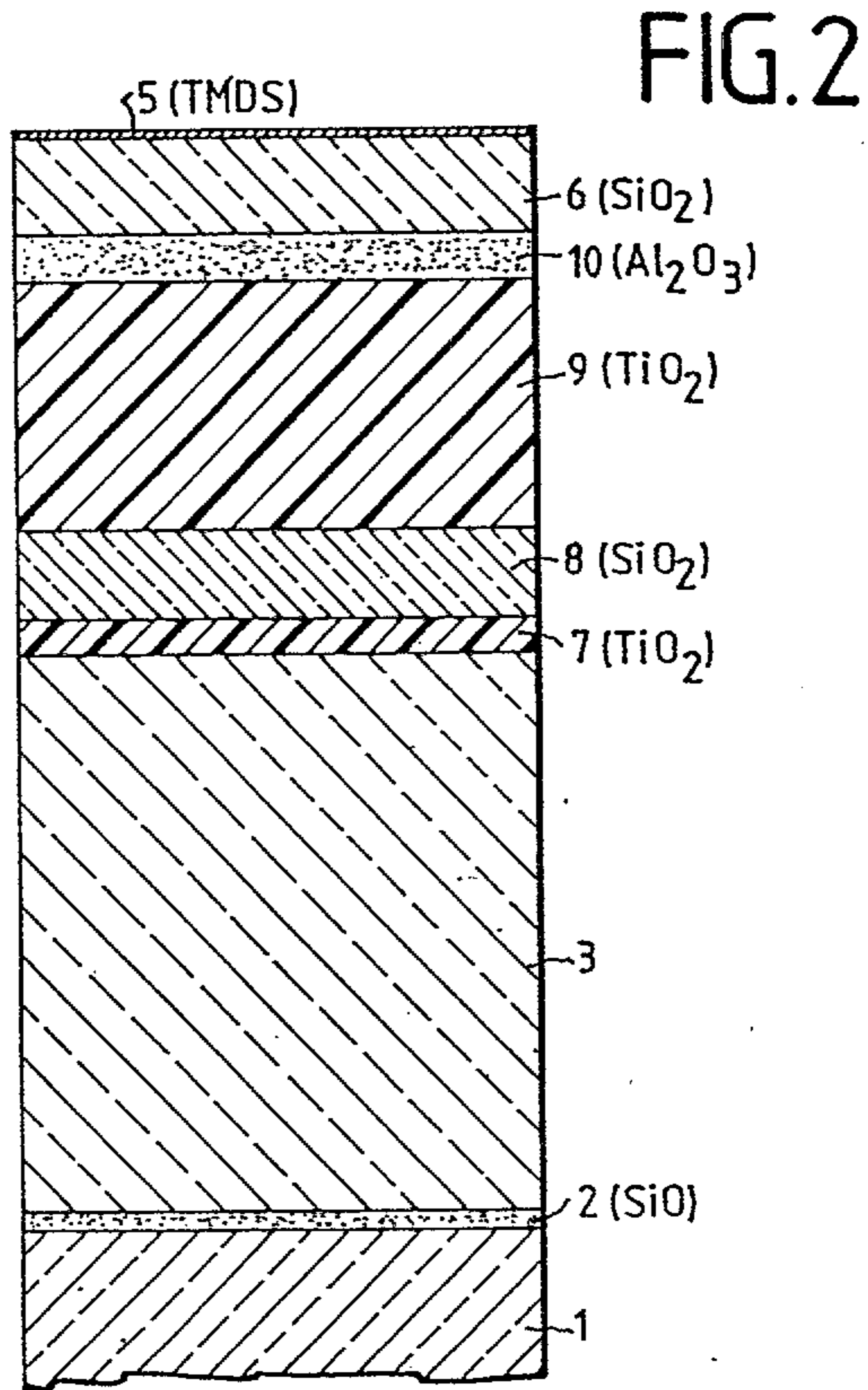
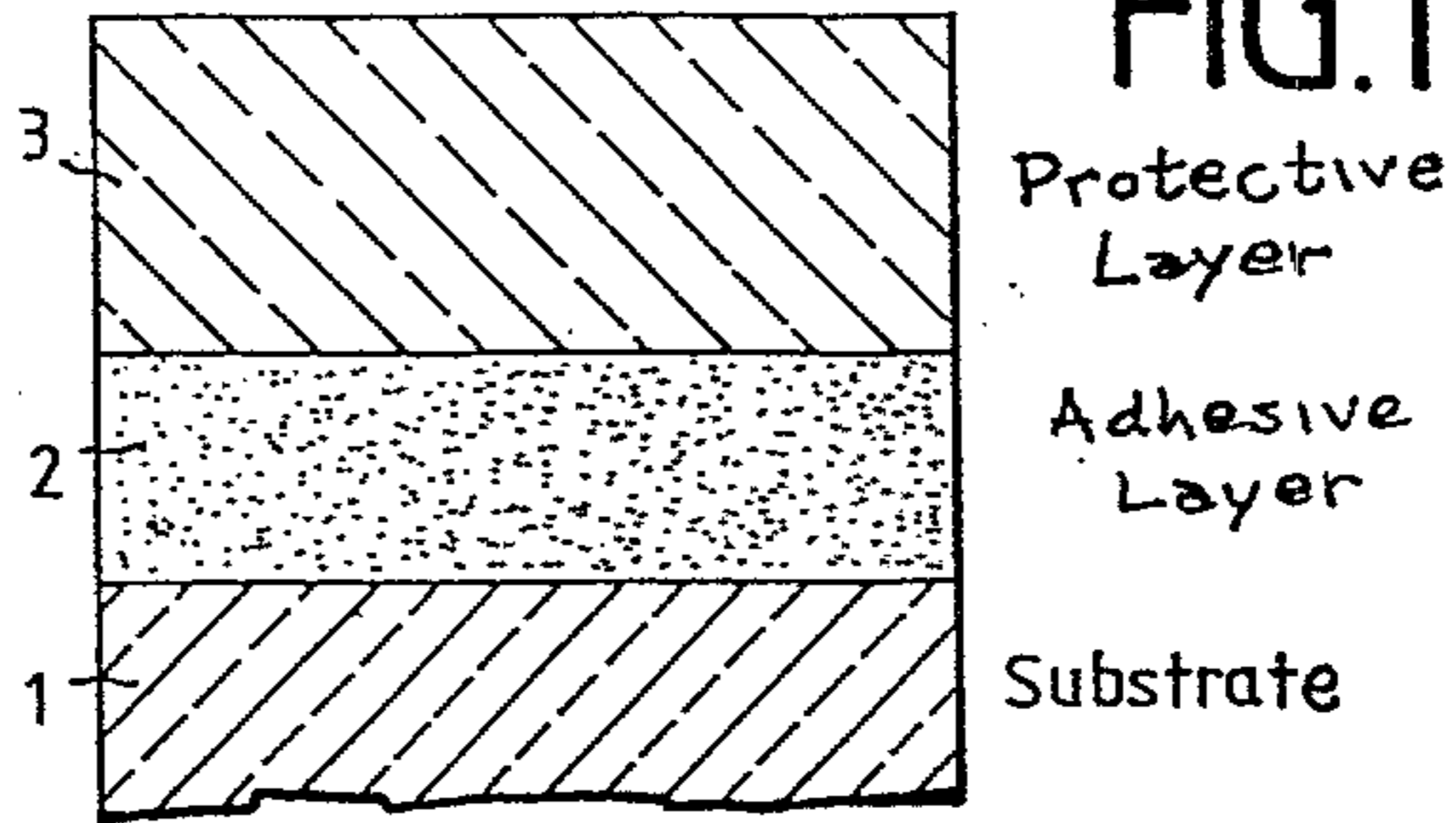


FIG.3

