

The invention relates to infra red transparent windows useful on high speed aircraft and missiles.

Such vehicles may fly through rain clouds that can destroy conventional infra red transparent windows. The effect of impacting rain drops is to produce high local stresses in the surface. This can gradually erode the surface making it scattering to the infra red and thus reducing transmission. Also the local stresses can cause cracking which can build up to total collapse of the window. These windows have previously been made of germanium, or zinc selenide, or zinc sulphide. Unfortunately germanium becomes opaque with increasing temperature making it unsuitable for high speed vehicles which heat up due to air friction. Zinc sulphide is preferred because of its better transmission at high temperatures. Unfortunately it is quite soft and brittle. These problems are most severe for 8-14  $\mu\text{m}$  wavelength detector systems. At the 3-5  $\mu\text{m}$  wavelength systems there is a wider choice of materials, e.g. sapphire may be used.

One attempt to overcome these problems used a very thin hard carbon coating. Such coatings are diamond-like in their hardness and infra red transparent. Techniques for forming such coatings are described for example in G.B. Patent Nos. 2,069,008, 2,082,562. These coatings have proven to be excellent in static imaging systems and as windows on tracked vehicles, tanks etc. However, when used on ZnSe they helped cracks propagate in the ZnSe when subjected to high speed impact by rain drops. Attempts were made to produce thicker hard carbon coatings but these failed because internal stresses in the coatings could cause breaking on the underlying substrate. Also the coatings were too absorbing to the infra red radiation.

One infra red transparent material that can be prepared in stress free thick coatings is  $\text{Ge}_x\text{C}_{1-x}$ . This material has a hardness that varies with the value of  $x$ ; high values of  $x$  give a soft material whilst low values of  $x$  give a material of extreme hardness similar to that of diamond-like carbon coatings. Processes for making this are described in G.B. Patent Nos. 2,129,833 A, and 2 132 636 A. These have been found suitable for use in static applications as coating on windows and lenses.

Problems of high speed rain drop impact damage to infra red transparent windows are solved according to this invention by providing a layered structure of a substrate and a thick coating of the material  $\text{Ge}_x\text{C}_{1-x}$  which is itself protected by a thin layer of hard carbon.

According to this invention an infra red transparent window for high speed aircraft and missiles comprises a substrate of ZnSe or ZnS coated with a  $5\mu\text{m}$  or more thick layer of the material infra red transparent  $\text{Ge}_x\text{C}_{1-x}$  where  $0 < x < 1$ , itself coated with a thin layer of infra red transparent hard carbon or germanium nitride having a thickness of not more than  $1.5\mu\text{m}$ .

The thickness of the  $\text{Ge}_x\text{C}_{1-x}$  is dependant on the expected aircraft speed; higher speeds require thicker coatings than slower speeds. The thickness is also affected by the angle of the window relative to the air flow. A further constraint on thickness is anti-reflection properties. When calculating anti-reflection properties of layers it is necessary to consider both refractive index and layer thickness.

Typical coating layer thicknesses are  $7\mu\text{m}$  giving protection up to impact speeds of 235 metres/sec to  $23\mu\text{m}$  giving protection up to speeds of 433 m/s. Thicker coatings e.g.  $50\mu\text{m}$  or more may also be used. The final coating of hard carbon is typically 0.5 to  $1.5\mu\text{m}$  thick.

The invention will now be described by way of example only, with reference to the accompanying drawings of which:-

Figure 1 is a cross sectional view of a window,

Figure 2 is a sectional view of apparatus for growing coatings by reactive sputtering,

Figure 3 is a sectional view of apparatus for growing coating by cathodic deposition in a plasma discharge, and

Figures 4, 5, and 6 show infra red transmission curves.

As shown by Figure 1 an infra red transparent window 1 comprises a zinc selenide, or zinc sulphide substrate 2. Typically the thickness is about 4mm thick, and its diameter about 10cm. A coating 3 of  $\text{Ge}_x\text{C}_{1-x}$  covers the upper surface and is itself coated with a hard carbon layer 4. Typical thickness for the first coating 3 is 5-30  $\mu\text{m}$ , and for the second coating 4 about 0.5-1.5  $\mu\text{m}$ . The precise thicknesses are determined by the likely impact velocity of rain drops, the wavelength of operation i.e. 3-5 or 10-14  $\mu\text{m}$ , the composition value of x and hence refractive index, and the positioning of the window in the vehicle i.e. the inclination of the window to the air flow. For anti-reflection properties the optical thickness 28 of layers (i.e. thickness times refractive index) are each approximately Wavelength/4, although layer 3 may be increased in units of Wavelength/2.

For an uncoated zinc sulphide substrate rain impact damage will occur for impact speeds above about 135 m/s. Impact speeds of about 500 m/s require the coating 3 about 27  $\mu\text{m}$  thick. The increase in thickness seems to be about linear with increasing speeds.

The layer 3 absorbs impact pressure and reduces the stress in the front surface of the substrate. Also due to its toughness the layer resists propagation of stress cracks. Erosion of layer 3 is reduced by the very hard layer 4. Tests have shown that the layer 4 is undamaged after repeated wipes by a wiper blade when immersed in a sand and water mixture.

The value of  $x$  can vary from 1 to 0. At the interface with the ZnSe  $x$  may be nearer 1 to give a good bonding layer whilst for the last coat 4,  $x = 0$ . In between  $x$  is typically 0.5-0.7 and can remain constant or vary across the layer 3 depending on the value of refractive index required.

As an alternative to a hard carbon coating 4 the layer may be a thin layer of germanium nitride deposited in a similar manner using a nitrogen instead of a carbonaceous feedstock.

Coatings 3, 4 may be produced by the apparatus of Figures 2 and 3.

The apparatus of Figure 2 comprises a pressure tight chamber 6 formed by an annular wall 7 closed by earthed top and bottom plates 8, 9 respectively. The plates 8, 9 form anodes. A vacuum pump 10 is connected by a pipe 11 and valve 12 to evacuate the chamber 6 and maintain a desired vacuum during growth. Supplies of gases e.g. argon and a hydrocarbon gas such as butane are bled into the chamber 6 via valves 13, 14, 15, and pipes 16, 17, 18. A cathode structure 19 is mounted in the chamber 6 and electrically isolated from the bottom plate 9 by a sleeve 20. Electrical power is supplied to the cathode 19 by a power source 21. For an A.C. supply this is through a capacitor 22, a D.C. supply needs no capacitor.

A piece of germanium 23, is located on the upper surface of the cathode structure 19 to form the target. Above the target 23 a substrate 2 is held by a holder 24 electrically isolated from the top plate 8 by a sleeve 25. Inside the holder 24 is an electrical resistance heater 26 supplied with power from a heater control/power supply 27. The substrate 2 may be regular, flat or curved, or irregular. To ensure even coating of a substrate 2 it may be rotated with or by the holder 24.

Operation to grow  $\text{Ge}_x\text{C}_{1-x}$  is as follows. A target material 23 of Ge is mounted on the cathode 19 to form the cathode in a glow discharge. A ZnS substrate 2 is fixed to the holder 24. The chamber 6 is evacuated to about  $10^{-5}$  Torr. to remove contaminants. Argon and butane gas is bled into the chamber through the valves 13, 14, 15, and the pump 11 operated to maintain a pressure of about 0.7 to  $1 \times 10^{-2}$  Torr. on an air calibrated gauge. The substrate 2 is heated to about  $550^\circ\text{C}$  and maintained at this temperature during growth of the layer 3.

R.F. power of typically 1 Kvolt, 13 MHz and 200 watts power is supplied to the cathode 19, 23. This ionises the gas mixture. Positively charged carbon ions are attracted to and stick to the target 23 acting as a cathode. Without the presence of argon ions this would result in growth of a carbon layer on the target 23. The positively charged argon ions sputter both these newly deposited carbon molecules and germanium molecules from the target 23. Sputtered molecules of carbon and germanium land and adhere to the substrate 2 gradually building up a layer 3 of  $\text{Ge}_x\text{C}_{1-x}$ . The value of x is adjustable by adjusting the argon:butane ratio inputs. When the required thickness of layer 3 has grown the argon:butane ratio is adjusted to give a value of  $x = 0$  and hence deposit a hard carbon layer 4. The glow discharge is then stopped and the substrate 2 allowed to cool.

For a D.C. generated plasma the supply is typically at 2 kvolts.

An electrical bias may be applied to the substrate 2 during growth of the layers 3, 4.

The apparatus of Figure 3 comprises a vacuum tight container 31 formed by an annular wall 32 and earthed top and bottom plates 33, 34 respectively. A pump 35 is connected through an exhaust pipe 36, and valve 37 to the chamber 31. Gas supplies of argon, germane and a hydrocarbon gas such as butane are fed into the chamber via inlet pipes 38, 39, 40, 41 and valves 42, 43, 44, 45. A cathode structure 46 is supported inside the chamber 31 and electrically insulated from the bottom plate 34 by a sleeve 47. Inside the cathode structure is a heater 48 for heating the substrate 2 arranged on the cathode 46. Cathode temperature is controlled by a heater control 50 which also supplies power to the heater 48. A power supply 51 feeds electrical power to the cathode 46. This power may be D.C. or A.C. via a blocking capacitor 52. Alternatively an A.C. coil may surround the chamber 1 and induce a plasma within the chamber.

A ZnS, or ZnSe window is coated with a layer 3 of  $\text{Ge C}_{x1-x}$  followed by a layer 4 of hard carbon as follows. The substrate 2 is mounted on the cathode 46 with the surface to be coated uppermost. The chamber 31 is evacuated by the pump 35 to less than  $10^{-5}$  Torr. to remove contaminants. Argon gas is admitted through the valve 43 and the chamber pressure kept at about  $10^{-2}$  Torr on an air calibrated gauge.

A plasma is generated in argon by energising the cathode 46 from the power supply 51. This provides an argon ion bombardment of the substrate 2 to clean it prior to coating. About 2 minutes cleaning is usually adequate.

The cathode heater 48 is operated to raise the substrate 2 temperature to above about  $500^{\circ}\text{C}$  typically  $530^{\circ}\text{C}$  and maintain it at this value during growth of the coating layers 3, 4. This inhibits inclusion of hydrogen within the growing layers 3, 4.

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The argon is removed by the pump 35 and a mixture of germane ( $\text{GeH}_4$ ) and butane ( $\text{C}_4\text{H}_{10}$ ) admitted via the inlet pipe 38, 40, 41 and valves 42, 44, 45. Pressure is maintained at around  $0.7$  to  $1.10^{-2}$  Torr. A.C. power of typically 1 kvolt at 13 MHz and 200 watts power level is applied to create a plasma. Positively charged ions of C and of Ge strike and remain on the substrate gradually building up a layer 3 of  $\text{Ge}_x\text{C}_{1-x}$ . The value of  $x$  varies with the germane:butane ratio and can remain constant, or be varied during growth.

The layer 3 thickness is time and composition dependent and is selected for required impact resistance and optical properties (anti-reflection). Typical layer thickness is 7 to 30  $\mu\text{m}$ . When the layer 3 has grown to its desired thickness the germane supply is stopped. A layer 4 of infra red transparent carbon is then grown to a typical thickness of 0.5 to 1.5  $\mu\text{m}$ . The discharge is stopped when the required thickness of both layers 3, 4 are grown and the substrate 2 allowed to cool.

To assist in growing the layers 3, 4 the substrate 2 may be rotated during growth.

Varying the Ge:C ratio varies the refractive index. With the apparatus of Figure 3 the refractive index can be changed from about 2.2 for the diamond like carbon when  $x = 0$  to about 4.2 when  $x$  approaches unity. This compares with a refractive index of 4 for bulk germanium. With the reactive sputtering of Figure 2 the refractive index can be changed from 2.9 to about 4.2. Below this lower value of 2.9 the sputtering rate for germanium is insufficient to prevent the target becoming poisoned with diamond-like carbon preventing deposition of the carbide.

The layer 4 can be formed of germanium nitride instead of hard carbon. In this case the deposition can be carried out using the apparatus of Figure 2 but using only nitrogen in the plasma both to sputter the germanium target and to react to form the nitride. Germanium nitride has excellent mechanical properties and good infra red transmission below 10  $\mu\text{m}$ . Above this value the absorption is too high, thus preventing use in 10 - 14  $\mu\text{m}$  systems.

Figures 4, 5 show transmission curves for a GeC coating on a Ge substrate, and Figure 6 shows transmission curves for GeN on ZnS. Coating of GeC on ZnS would be similar to Figures 4, 5.



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Claims:-

1. An infra red transparent window for high speed aircraft and missiles comprising a substrate of ZnSe or ZnS coated with a  $5\mu\text{m}$  or more thick layer of the material infra red transparent  $\text{Ge}_x\text{C}_{1-x}$  where  $0 < x < 1$ , itself coated with a layer of infra red transparent hard carbon or germanium nitride having a thickness of not more than  $1.5\mu\text{m}$ .
2. The window of claim 1 wherein the optical thickness of the  $\text{Ge}_x\text{C}_{1-x}$ , and hard carbon layer are arranged to provide anti-reflection of infra red radiation wavelengths.
3. The window of claim 1 wherein the thickness of  $\text{Ge}_x\text{C}_{1-x}$  is between 5 and  $30\mu\text{m}$ .
4. The window of claim 1 wherein the thickness of the hard carbon is between 0.5 and  $1.5\mu\text{m}$ .
5. The window of claim 1 wherein the value of x varies within the range 0.5 to  $0.7\mu\text{m}$ .
6. The window of claim 1 wherein the value of x varies across the thickness of the  $\text{Ge}_x\text{C}_{1-x}$  layer.
7. The window of claim 1 constructed, arranged and adapted to operate substantially as hereinbefore described with reference to the accompanying drawings.