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# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Amorphous Glass Compositions

We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organized according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to amorphous compositions of matter. More particularly it relates to infrared transparent glasses.

The invention appertains to germanium-selenium amorphous glass compositions modified by the inclusion of antimony or tellurium so that the ternary composition lies within line A of the ternary diagram of Figure 1 of the accompanying drawings when the added element is antimony and within the line C of the ternary diagram of Figure 3 of the accompanying drawings when the added element is tellurium. An amorphous glass composition can be formed in accordance with the invention which has good transmission properties in the 1–20 micron wavelength region of the electromagnetic spectrum. Such a composition can be produced which has a high softening point in the same wavelength range.

An amorphous glass composition according to the invention can be used to form a transmitting member in an infrared detection system, the transmitting member being in optical contact with a detector sensitive to infrared energy.

By way of example the invention will be described in greater detail with reference to the accompanying drawings wherein:

Figure 1 depicts a ternary diagram of the atomic percentages of germanium, antimony, and selenium for various amorphous compositions of matter of the invention;

Figure 2 is a graphical representation of per cent transmission at room temperature at various wave lengths of the electromagnetic

spectrum for various glass compositions according to this invention;

Figure 3 depicts a ternary diagram of the atomic percentages of germanium, selenium, and tellurium for various amorphous compositions of matter of the invention;

Figure 4 is a graphical representation of per cent transmission at room temperature at various wave lengths of the electromagnetic spectrum for various glass compositions according to this invention; and

Figure 5 illustrates one particular form of the glass compositions of this invention, usable as an infrared transmitting element, such as a dome or lens, within an infrared detection system.

Referring to Figure 1, various compositions of germanium, antimony, and selenium were compounded and evaluated to determine whether they were amorphous or crystalline. The general procedure for making the various compositions is described hereinafter.

Various atomic percentages of germanium, antimony, and selenium were chosen for each sample to be made. The appropriate amounts of the constituents were weighed and then placed in a previously cleaned quartz ampoule. An example of a suitable cleaning step for the ampoule is brushing in a suitable detergent for 30 minutes in solution, rinsing thoroughly in deionized water, and then drying. The total weight of each of the samples was between five and 15 grams. The constituents were placed in the cleaned tube, evacuated to about  $10^{-4}$  torr, and sealed. The sealed tube was then placed in a furnace and gradually heated to a temperature of about 800°C to 900°C and held at that temperature for about 16 hours to provide sufficient time for the constituents to react completely with each other. The furnace was a rocking furnace which may be of any suitable design to provide agitation of the constituents so as to achieve complete reaction thereof. The samples were then removed from the furnace and held in

a vertical position in air for air quenching and allowed to cool to room temperature. Care was taken throughout the process to prevent heating the constituents in air to avoid causing any oxide formation. In particular, in some cases the inside surface of the ampoule was carbon coated for the purpose of chemically reducing any extraneous oxides present.

The sample compositions which failed to form amorphous glass by the air quench-cooling technique and became crystalline after quenching are presented in Table I below.

whereas the compositions which formed amorphous glass are presented in Table II below, with the softening point results obtained for the glass. The softening point is defined as the temperature at which a pointed quartz rod under a 70 gram load penetrates a smooth surface to a depth of 0.05 mm where the rod is in perpendicular alignment with respect to the sample and the point defines a 90° included angle. The reaction conditions for the samples in Tables I and II below were the same:

TABLE I

| Sample No. | Composition<br>Atomic Per Cent |    |    |
|------------|--------------------------------|----|----|
|            | Ge                             | Sb | Se |
| 1011       | 30                             | 25 | 45 |
| 1113       | 35                             | 15 | 50 |
| 1115       | 5                              | 35 | 60 |
| 1116       | 15                             | 35 | 50 |
| 1117       | 25                             | 35 | 40 |
| 1118       | 10                             | 40 | 50 |
| 1119       | 20                             | 40 | 40 |
| 1120       | 5                              | 45 | 50 |
| 1121       | 15                             | 45 | 40 |
| 1122       | 45                             | 5  | 50 |
| 1123       | 45                             | 20 | 35 |
| 1124       | 30                             | 30 | 40 |
| 1125       | 35                             | 35 | 30 |
| 1128       | 20                             | 55 | 25 |
| 1129       | 25                             | 30 | 45 |
| 1130       | 40                             | 20 | 40 |
| 1131       | 15                             | 55 | 30 |
| 1132       | 5                              | 55 | 40 |
| 1139       | 40                             | 20 | 40 |
| 1140       | 25                             | 25 | 40 |
| 1141       | 10                             | 30 | 60 |
| 1171       | 35                             | 10 | 55 |

TABLE II  
Composition  
Atomic Per Cent

| Sample No. | Ge | Sb | Se | Softening Point in °C. |
|------------|----|----|----|------------------------|
| 1003       | 10 | 15 | 75 | 190                    |
| 1004       | 20 | 15 | 65 | 280                    |
| 1005       | 10 | 25 | 65 | 198                    |
| 1108       | 15 | 5  | 80 | *175                   |
| 1109       | 25 | 5  | 70 | *350                   |
| 1110       | 20 | 10 | 70 | 272                    |
| 1111       | 30 | 10 | 60 | 326                    |
| 1112       | 25 | 15 | 60 | 312                    |
| 1114       | 20 | 25 | 55 | 275                    |
| 1133       | 35 | 5  | 60 | 355                    |
| 1134       | 10 | 5  | 85 | 162                    |
| 1142       | 5  | 20 | 75 | *125                   |
| 1143       | 25 | 10 | 65 | 347                    |
| 1170       | 30 | 15 | 35 | *320                   |
| 1172       | 25 | 20 | 55 | 288                    |
| 462        | 20 | 7  | 73 | 270                    |

\* Approximate Value.

- 5 In Figure 1, the peripheral line A generally circumscribes the amorphous compositions of germanium, antimony, and selenium according to the invention. The samples which failed to form amorphous glass by the air quench-cooling technique (listed in Table I) are plotted on Figure 1 by block triangle and identified by sample numbers. The sample compositions forming amorphous glass (listed in Table II) are also plotted in Figure 1 within the area generally circumscribed by line A and designated by black dots, each dot being identified by a sample number.
- 10 In Figure 2, the per cent transmission of the electromagnetic spectrum at room temperature in the one to 20 micron wave length region is plotted for various of the glass samples listed in Table II. Curve 1 represents a "typical" set of transmission characteristics common to the amorphous glass compositions designated in Figure 1 except for the composition

Ge<sub>25</sub>Sb<sub>10</sub>Se<sub>65</sub>. A moderately strong absorption band at approximately 13 $\mu$  was observed, as shown by Curve 1, possibly due to the presence of extraneous oxides in these represented compositions. This absorption band was decreased, however, when the ampoule in which the samples were prepared had its inside surface initially coated with a material, such as carbon for example, in order to reduce these extraneous oxides. Other materials may be added to the melt, as for example aluminum, which will tend to reduce the extraneous oxides. The resulting curve, after elimination of the absorption band, is represented by the dotted line. Curve 2 represents the transmission characteristics of the composition Ge<sub>25</sub>Sb<sub>10</sub>Se<sub>65</sub>, these characteristics having been observed to depart from the "typical" set of Curve 1.

Referring now to Figure 3, various compositions of germanium, selenium, and tellurium were compounded and evaluated to determine

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- whether they were amorphous or crystalline. The general procedure for making the various compositions is the same as that for making the germanium, selenium and antimony compositions described previously with reference to Fig. 1, except that various atomic percentages of germanium, selenium, and tellurium were chosen for each sample to be made.
- 5 The sample compositions which failed to form amorphous glass by the air quench-cooling technique and were crystalline after quenching are presented in Table III below, whereas the compositions which formed amorphous glass are presented in Table IV below, with the softening point (as previously defined) results obtained for the glass. The reaction conditions for the samples in Tables III and IV below were the same: 15

TABLE III

| Sample No. | Composition<br>Atomic Per Cent |    |    |
|------------|--------------------------------|----|----|
|            | Ge                             | Se | Te |
| 1007       | 30                             | 55 | 15 |
| 1008       | 15                             | 55 | 30 |
| 1024       | 25                             | 50 | 25 |
| 1025       | 50                             | 25 | 25 |
| 1026       | 40                             | 30 | 30 |
| 1056       | 10                             | 65 | 25 |
| 1058       | 13                             | 62 | 25 |
| 1059       | 15                             | 15 | 70 |
| 1060       | 35                             | 15 | 50 |
| 1061       | 10                             | 30 | 60 |
| 1062       | 30                             | 10 | 60 |
| 1063       | 15                             | 35 | 50 |
| 1083       | 10                             | 40 | 50 |
| 1084       | 20                             | 35 | 45 |
| 1085       | 25                             | 45 | 30 |
| 1087       | 40                             | 20 | 40 |
| 1088       | 45                             | 35 | 20 |
| 1098       | 5                              | 60 | 35 |
| 1099       | 5                              | 35 | 60 |
| 1144       | 40                             | 40 | 20 |
| 1148       | 20                             | 25 | 55 |
| 1154       | 25                             | 30 | 45 |

TABLE IV  
Composition  
Atomic Per Cent

| Sample No. | Ge | Se | Te | Softening Point in °C. |
|------------|----|----|----|------------------------|
| 1006       | 30 | 40 | 30 | 305                    |
| 1009       | 15 | 70 | 15 | 155                    |
| 1023       | 25 | 25 | 50 | 220                    |
| 1027       | 30 | 30 | 40 | 275                    |
| 1028       | 35 | 45 | 20 | 350                    |
| 1029       | 20 | 45 | 35 | 307                    |
| 1055       | 25 | 65 | 10 | *275                   |
| 1057       | 20 | 60 | 20 | 220                    |
| 1064       | 20 | 20 | 60 | 164                    |
| 1073       | 10 | 50 | 40 | 137                    |
| 1082       | 5  | 48 | 47 | *150                   |
| 1086       | 35 | 30 | 35 | 296                    |
| 1089       | 15 | 45 | 40 | 132                    |
| 1090       | 30 | 45 | 25 | 312                    |
| 1091       | 20 | 50 | 30 | 190                    |
| 1092       | 10 | 55 | 35 | *175                   |
| 1093       | 20 | 55 | 25 | 199                    |
| 1094       | 35 | 50 | 15 | 374                    |
| 1095       | 30 | 65 | 5  | 326                    |
| 1096       | 5  | 75 | 20 | *125                   |
| 1097       | 10 | 70 | 20 | 142                    |
| 1127       | 35 | 40 | 25 | 331                    |
| 1145       | 35 | 35 | 30 | 318                    |
| 1146       | 30 | 35 | 35 | 286                    |
| 1147       | 30 | 25 | 45 | 293                    |
| 1149       | 5  | 55 | 40 | *150                   |
| 1155       | 25 | 20 | 55 | 251                    |

\* Approximate Value.

In Figure 3, the peripheral line C generally circumscribes the amorphous compositions of germanium, selenium, and tellurium according to the invention. The samples which failed to form amorphous glass by the air quench-cooling technique (listed in Table III) are plotted on Figure 3 by block triangles and identified by sample numbers. The sample compositions forming amorphous glass (listed in Table IV) are also plotted in Figure 3 within the area generally circumscribed by line C and designated by black dots, each dot being identified by a sample number.

In Figure 4, the per cent transmission of radiation of the electromagnetic spectrum at room temperature in the one to 20 micron wave length region is plotted for various of the glass samples listed in Table IV. Curve 3 represents a "typical" set of transmission characteristics common to the amorphous glass compositions designated in Figure 3. A moderately strong absorption band at  $13\mu$  was observed, as shown by Curve 3, due in large part to the presence of extraneous oxides in these represented compositions. This absorption band was substantially eliminated, however, when the ampoule in which the samples were prepared had its inside surface initially carbon coated in order to reduce these oxides. The resulting curve, after elimination of the absorption band, is represented by Curve 4.

Figure 5 depicts a form of the glass compositions of this invention usable within a particular infrared detecting system. The detecting system is normally composed of a detector 1 having a responsive element sensitive to infrared energy striking its surface, and an infrared transmitting element 2 such as a dome or lens in optical contact with the detector. The optical properties of the amorphous glass compositions of this invention make them particularly suited, among other applications, for use as the transmitting element 2. In addition to being substantially transparent to infrared rays over a broad range of the infrared spectrum, as depicted in Figure 2, all of the compositions have relatively high indexes of refraction, ranging from approximately 2.3 to 3.0 at  $3-5\mu$  wave length. Consequently, when infrared rays strike the dome 2 at the incident angle  $\Phi$ , as pictured in Figure 5, the high index of refraction of the dome material causes the rays to be bent toward the detector unit 1 at the angle of refraction  $\beta$ , thus increasing the efficiency of detection.

The amorphous glass compositions of this invention offer substantial advantages for the fabrication of the transmitting elements for a variety of other reasons. First, there is a wide range of physical properties from which the designer may choose. For example, the softening points range from approximately  $132^\circ\text{C}$  to  $398^\circ\text{C}$ , and the Knoop hardness of the compositions have been measured from 90 to as high as 174. Second, these compositions

offer substantial advantages over crystalline material in that they may be heated to a molten state and easily worked into desired shapes and sizes. Third, the reasonably high softening points and available hardnesses offer greater ease in grinding, polishing, and handling operations, as well as stability to thermal shocks.

In particular, the amorphous compositions generally defined by the Line B in Figure 1 (specifically  $\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{70}$ ,  $\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{65}$ ,  $\text{Ge}_{20}\text{Sb}_{25}\text{Se}_{55}$ ,  $\text{Ge}_{20}\text{Sb}_{35}\text{Se}_{45}$ ,  $\text{Ge}_{25}\text{Sb}_{20}\text{Se}_{55}$ ,  $\text{Ge}_{25}\text{Sb}_{15}\text{Se}_{60}$ , and  $\text{Ge}_{30}\text{Sb}_{10}\text{Se}_{60}$ ) were found to be exceptionally stable up to about  $550-650^\circ\text{C}$  in an inert atmosphere, such as nitrogen, approximately  $50-100^\circ\text{C}$  above that temperature required in order to pour the molten material into molds for fabricating optical hardware. In addition, these amorphous compositions were cooled slowly (as slow as  $1^\circ\text{C}$  per minute) and remained substantially, if not completely, amorphous.

It should be understood that although most of the samples discussed above were essentially germanium, selenium, and either antimony or tellurium, minor percentages of, for example, silicon, sulfur, phosphorus, arsenic, bismuth, and tellurium or antimony (if not included as a major constituent), may be used in the glass of the invention to provide variations in the softening point and wave length transmission of the glass compositions.

Although only the air-quench cooling method has been described for making the amorphous compositions of matter, other methods could be used. It is also to be appreciated that other variations and changes in the manner of producing compositions according to the invention, as described above, are possible.

#### WHAT WE CLAIM IS:—

1. A ternary glass composition consisting essentially of germanium, selenium, and as a third element either antimony or tellurium, the composition lying within line A of the ternary diagram of Figure 1 of the accompanying drawings when the third element is antimony and within line C of the ternary diagram of Figure 3 of the accompanying drawings when the third element is tellurium.

2. A composition as claimed in claim 1, including a minor proportion of a fourth element which is silicon, phosphorus, sulphur, arsenic, bismuth or the non-selected third element.

3. A ternary glass composition consisting essentially of germanium, selenium, and antimony and lying within line A of the ternary diagram of Figure 1 of the accompanying drawings.

4. A ternary glass composition consisting essentially of germanium, selenium, and antimony and lying within line B of the ternary diagram of Figure 1 of the accompanying drawings, the said ternary glass composition

In Figure 3, the peripheral line C generally circumscribes the amorphous compositions of germanium, selenium, and tellurium according to the invention. The samples which failed to form amorphous glass by the air quench-cooling technique (listed in Table III) are plotted on Figure 3 by block triangles and identified by sample numbers. The sample compositions forming amorphous glass (listed in Table IV) are also plotted in Figure 3 within the area generally circumscribed by line C and designated by black dots, each dot being identified by a sample number.

In Figure 4, the per cent transmission of radiation of the electromagnetic spectrum at room temperature in the one to 20 micron wave length region is plotted for various of the glass samples listed in Table IV. Curve 3 represents a "typical" set of transmission characteristics common to the amorphous glass compositions designated in Figure 3. A moderately strong absorption band at  $13\mu$  was observed, as shown by Curve 3, due in large part to the presence of extraneous oxides in these represented compositions. This absorption band was substantially eliminated, however, when the ampoule in which the samples were prepared had its inside surface initially carbon coated in order to reduce these oxides. The resulting curve, after elimination of the absorption band, is represented by Curve 4.

Figure 5 depicts a form of the glass compositions of this invention usable within a particular infrared detecting system. The detecting system is normally composed of a detector 1 having a responsive element sensitive to infrared energy striking its surface, and an infrared transmitting element 2 such as a dome or lens in optical contact with the detector. The optical properties of the amorphous glass compositions of this invention make them particularly suited, among other applications, for use as the transmitting element 2. In addition to being substantially transparent to infrared rays over a broad range of the infrared spectrum, as depicted in Figure 2, all of the compositions have relatively high indexes of refraction, ranging from approximately 2.3 to 3.0 at  $3-5\mu$  wave length. Consequently, when infrared rays strike the dome 2 at the incident angle  $\Phi$ , as pictured in Figure 5, the high index of refraction of the dome material causes the rays to be bent toward the detector unit 1 at the angle of refraction  $\beta$ , thus increasing the efficiency of detection.

The amorphous glass compositions of this invention offer substantial advantages for the fabrication of the transmitting elements for a variety of other reasons. First, there is a wide range of physical properties from which the designer may choose. For example, the softening points range from approximately  $132^\circ\text{C}$  to  $398^\circ\text{C}$ , and the Knoop hardness of the compositions have been measured from 90 to as high as 174. Second, these compositions

offer substantial advantages over crystalline material in that they may be heated to a molten state and easily worked into desired shapes and sizes. Third, the reasonably high softening points and available hardnesses offer greater ease in grinding, polishing, and handling operations, as well as stability to thermal shocks.

In particular, the amorphous compositions generally defined by the Line B in Figure 1 (specifically  $\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{70}$ ,  $\text{Ge}_{20}\text{Sb}_{15}\text{Se}_{65}$ ,  $\text{Ge}_{20}\text{Sb}_{25}\text{Se}_{55}$ ,  $\text{Ge}_{20}\text{Sb}_{35}\text{Se}_{45}$ ,  $\text{Ge}_{25}\text{Sb}_{20}\text{Se}_{55}$ ,  $\text{Ge}_{25}\text{Sb}_{15}\text{Se}_{60}$ , and  $\text{Ge}_{30}\text{Sb}_{10}\text{Se}_{60}$ ) were found to be exceptionally stable up to about  $550-650^\circ\text{C}$  in an inert atmosphere, such as nitrogen, approximately  $50-100^\circ\text{C}$  above that temperature required in order to pour the molten material into molds for fabricating optical hardware. In addition, these amorphous compositions were cooled slowly (as slow as  $1^\circ\text{C}$  per minute) and remained substantially, if not completely, amorphous.

It should be understood that although most of the samples discussed above were essentially germanium, selenium, and either antimony or tellurium, minor percentages of, for example, silicon, sulfur, phosphorus, arsenic, bismuth, and tellurium or antimony (if not included as a major constituent), may be used in the glass of the invention to provide variations in the softening point and wave length transmission of the glass compositions.

Although only the air-quench cooling method has been described for making the amorphous compositions of matter, other methods could be used. It is also to be appreciated that other variations and changes in the manner of producing compositions according to the invention, as described above, are possible.

#### WHAT WE CLAIM IS:—

1. A ternary glass composition consisting essentially of germanium, selenium, and as a third element either antimony or tellurium, the composition lying within line A of the ternary diagram of Figure 1 of the accompanying drawings when the third element is antimony and within line C of the ternary diagram of Figure 3 of the accompanying drawings when the third element is tellurium.

2. A composition as claimed in claim 1, including a minor proportion of a fourth element which is silicon, phosphorus, sulphur, arsenic, bismuth or the non-selected third element.

3. A ternary glass composition consisting essentially of germanium, selenium, and antimony and lying within line A of the ternary diagram of Figure 1 of the accompanying drawings.

4. A ternary glass composition consisting essentially of germanium, selenium, and antimony and lying within line B of the ternary diagram of Figure 1 of the accompanying drawings, the said ternary glass composition



being stable up to approximately 550—650°C in an inert atmosphere.

5 5. A ternary glass composition consisting essentially of germanium, selenium, and tellurium and lying within line C of the ternary diagram of Figure 3 of the accompanying drawings.

10 6. A composition as claimed in claim 3 or claim 4, including a minor proportion of a fourth element which is silicon, phosphorus, sulphur, arsenic bismuth, or tellurium.

15 7. A composition as claimed in claim 5, including a minor proportion of a fourth element which is silicon, phosphorus, sulphur, arsenic, bismuth, or antimony.

8. An infrared detection system comprising a detector sensitive to infrared energy and a transmitting member in optical contact with the detector, the transmitting member comprising a ternary glass composition as claimed 20 in any one of the preceding claims.

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