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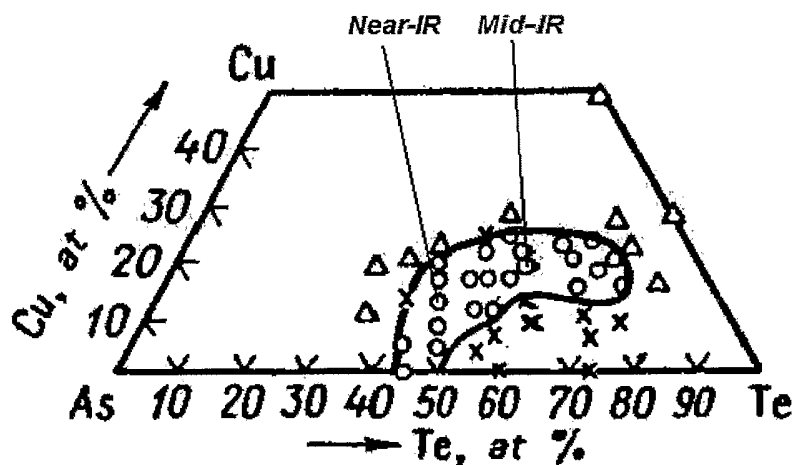
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(54) Title: INFRARED DETECTION MATERIAL AND METHOD OF PRODUCTION



(57) Abstract: A thin film quaternary compound semiconductor comprising arsenic (As), selenium (Se), tellurium (Te) and copper (Cu) atoms with adjustable molar concentrations during processing, whose atomic arrangement is predominantly amorphous, glassy or polycrystalline, and dominated by covalent chemical bonds between the said atoms. The amorphous nature of the atomic arrangement give predominance to short range atomic order, eliminating the constraints of lattice constant mismatch and polarity mismatch with the substrate, which opens the way to wide chemical compositional adjustments and to lower-cost deposition processes such

as thermal evaporation or sputtering.

INFRARED DETECTION MATERIAL AND METHOD OF PRODUCTION

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PRIORITY INFORMATION

This application claims priority from U.S. provisional applications serial nos. 60/620,612 filed on October 20, 2004, and 60/629,622 filed on November 19, 2004, both of which are incorporated by reference herein in their entireties.

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BACKGROUND OF THE INVENTION

The invention relates to a quaternary compound semiconductor comprising arsenic (As), selenium (Se), tellurium (Te) and copper (Cu) atoms, whose covalent atomic arrangement is predominantly amorphous or polycrystalline, and whose electronic properties can be tuned by an adjustment of the molar concentration of tellurium and copper atoms in the said compound, and whose electronic bandgap can be tuned to detect infrared radiation energy. The invention also relates to the method of fabricating thin films of this quaternary compound semiconductor at low cost.

There has been a major effort on the study of infrared semiconductor materials, such as In-Ga-As-P, Pd-Te and Hg-Cd-Te crystalline compounds, and on the monolithic integration of those materials on a variety of integrated circuit substrates for the fabrication of infrared detectors and infrared digital cameras. Unfortunately, the large lattice constant mismatches between the substrates and the epitaxial layers cause many defects to be created in crystalline semiconductor compound thin film, with detrimental effects on the material integrity, on the infrared detection performance and on the ability to fabricate infrared detectors or large infrared focal plane arrays at low cost. Some of the major problems facing heteroepitaxial growth of crystalline infrared compounds are the lattice constant mismatch, polarity mismatch and thermal expansion mismatch with the substrate, such that infrared device fabrication typically requires the use of expensive and exotic substrates, which involve severe constraints over the growth size and thickness of the heteroepitaxial layers, and which involve expensive fabrication processes such as molecular beam epitaxy. The development of crystalline infrared compounds for infrared detectors and cameras has been hampered time and again by the costs and constraints involving the heteroepitaxial growth of crystalline infrared compounds.

Continuous progress in science and technology imposes new and increased requirements on semiconducting materials. Germanium, silicon and the III-V semiconducting compounds no longer satisfy all these varied and specific requirements, which involve advanced infrared detection, material stability, CMOS compatibility and

~~low fabrication costs.~~ The search is for new more effective semiconducting materials with properties that can be varied in a wide range. Chalcogenide compounds, having either an amorphous, glassy or polycrystalline atomic arrangement, are produced with analogs of oxygen, namely sulfur, selenium and tellurium, and are promising in many respects. Depending on the composition, the conductivity of amorphous chalcogenide compounds varies in the range $\sigma=10^{-2}$ to $\sigma=10^{-18} \Omega^{-1}\text{cm}^{-1}$, and the bandgap energy is in the range $E_g=0.1\text{eV}$ to $E_g=3\text{eV}$. The conductivity increases exponentially with temperature and they have pronounced photoconductivity.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a new type of infrared detection material and a method of producing thin films of the same material on standard substrates at low processing costs. The invention relates to a quaternary compound semiconductor comprising arsenic (As), selenium (Se), tellurium (Te) and copper (Cu) atoms with adjustable molar concentrations during processing, whose atomic arrangement is predominantly amorphous or polycrystalline, and dominated by covalent chemical bonds between the said atoms. The amorphous nature of the atomic arrangement gives predominance to short range atomic order, eliminating the constraints of lattice constant mismatch and polarity mismatch with the substrate, which opens the way to wide chemical compositional adjustments and to lower-cost deposition processes such as thermal evaporation or sputtering. The flexibility of the chemical formula can be used to adjust the electronic properties of the semiconductor compound.

In one embodiment, the molar concentration of tellurium and copper atoms in the said quaternary compound is adjusted to modify the density of localized and extended electronic states in the material, and to modify the energy difference between the valence and conduction bands. This compositional adjustment provides a way to modify significantly the properties of the semiconductor compound, such as increasing its electrical conduction by up to 11 orders of magnitude and decreasing its electronic bandgap by 1 order of magnitude, and to tune the material for the detection of infrared light waves having energies between 1.8eV and 0.15eV. In another embodiment, a thin film of semiconductor compound with $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ chemical formulation is obtained by a thermal co-evaporation of As_2Se_3 glass and CuTe mineral.

The quaternary semiconductor compound comprising arsenic (As), selenium (Se), tellurium (Te) and copper (Cu) atoms can be produced in thin film form by a mixed physical vapor deposition process involving a vapor combination of at least two different vaporized sub-compounds of different enthalpies of evaporation. The co-evaporation

process provides a way to adjust easily the molar composition of the semiconductor compound, and to deposit thin films uniformly over a large area, with a wide range of thin film thicknesses, and onto various surfaces. The design is amenable to the production of infrared detectors of tunable infrared detectivity and of various light collecting areas.

5 The above and other features of the invention including various novel details of combinations of parts, and other advantages, will now be more particularly described with reference to the accompanying figures and pointed out in the claims. It will be understood that the particular method embodying the invention are shown by way of illustration and not as a limitation of the invention. The principles and features of this invention may be
10 employed in various and numerous embodiments without departing from the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a table showing exemplary compositions of the semiconductor compound,
15 showing large variations of electrical conductivity and bandgap energy upon addition of tellurium and copper;

FIG. 2 is a phase diagram of the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ system of the invention, with $x \sim 0\%$, showing the compositional region where glassy atomic arrangement is obtained;

FIG. 3 is a diagram of the bandgap energy for varying molar concentration of
20 copper in the compound of composition $(\text{As}_{50}\text{Se}_1\text{Te}_{49})_{100-x}\text{Cu}_x$ and $(\text{As}_{25}\text{Se}_1\text{Te}_{74})_{100-x}\text{Cu}_x$, where x corresponds to the molar concentration of copper in percent;

FIG. 4 is a diagram of the optical absorption spectra $\alpha(\lambda)$ as function of copper molar concentration in the compound of composition $(\text{As}_{40}\text{Se}_{30}\text{Te}_{30})_{100-x}\text{Cu}_x$, where x is the molar concentration of copper in percent; and

25 FIG. 5 is a diagram of the optical absorption spectra of thin films of $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$, with $y \sim 0\%$, produced by the method of thermal co-evaporation of As_2Se_3 and CuSe sub-compounds.

DETAILED DESCRIPTION OF THE INVENTION

The invention involves a quaternary compound semiconductor comprising arsenic
30 (As), selenium (Se), tellurium (Te) and copper (Cu) atoms, whose atomic arrangement is predominantly amorphous or polycrystalline, and whose electronic properties can be tuned during processing by an adjustment of the molar concentration of tellurium and copper atoms in the said compound, and whose electronic bandgap can be tuned to detect infrared radiation energy from the near-infrared regime to the long-infrared regime.

35 Continuous progress in science and technology imposes new and increased requirements on semiconducting materials. Germanium, silicon and the III-V

~~semiconducting compounds~~ no longer satisfy all these varied and specific requirements, which involve performance, material stability and fabrication costs. The search is for new more effective semiconducting materials with properties that can be varied in a wide range. Chalcogenide compounds, having either an amorphous, glassy or polycrystalline atomic arrangement, are produced with analogs of oxygen, namely sulfur, selenium and tellurium, and are promising in many respects. Depending on the composition, the conductivity of amorphous chalcogenide compounds varies in the range $\sigma=10^{-2}$ to $\sigma=10^{-18} \Omega^{-1}\text{cm}^{-1}$, and the bandgap energy is in the range $E_g=0.1\text{eV}$ to $E_g=3\text{eV}$. The conductivity increases exponentially with temperature, and they have strongly pronounced thermoelectric powers, photo-emfs, and photoconductivity. There are a wide variety of different compositions having varying semiconductor properties within the family of chalcogenide compounds.

Investigation of the electrical conductivity and other physicochemical properties of amorphous chalcogenide compounds shows that in three-component systems, just as in binary ones, a regular change takes place in the parameters of the electrical conductivity, microhardness, thermal stability, crystallizing ability, and other properties when each of the chemical components is replaced by its analogs in the periodic system. The increased delocalization of the chemical bonds in the sequences P–As–Sb–Bi and S–Se–Te causes the conductivity to increase and the corresponding bandgap energy to decrease. The greatest increase of conductivity is observed on going from phosphorous-containing to arsenic-containing amorphous compounds. The replacement of arsenic by antimony or bismuth is not accompanied by so appreciable a change in the electrical conductivity; however, it is accompanied by an appreciable reduction of the glass network stability and increased ability for crystallization. In the sixth group of the periodic table, the most appreciable increase of the conductivity is observed on going from selenides to tellurides amorphous chalcogenide compounds. This replacement is accompanied by an appreciable reduction of the glass network stability and increased ability for crystallization.

The electrical conductivity of binary chalcogenide compounds, such as As-S and As-Se is relatively low. Because of their low electrical conductivity and large bandgap energy, these amorphous compounds can be more readily regarded as dielectrics than semiconductors. A substantial increase of the conductivity of binary compounds is obtained by introducing into them a third component in the metal group – thallium, copper, silver, etc. The electrical conductivity is then increased by 6-10 orders of magnitude. A concomitant decrease of the bandgap energy is also observed when these metals are introduced into arsenic chalcogenides. With increasing content of metals in the arsenic chalcogenides a transition is observed from compounds having dielectric properties to

~~semiconductor properties.~~ The largest contribution to the increase of the conductivity and to the decrease of the bandgap energy of arsenic chalcogenides is made by thallium and copper.

The character of the change of the mechanical, thermal and other properties of the compound when metals are introduced in them depends on the composition and structure of the glassy network structural units produced in the material. Thus, when the large thallium atom is introduced into the glassy network, the mechanical and thermal stability of the arsenic chalcogenide compound decreases substantially. When the smaller copper atom is introduced, on the contrary, it is observed that the structure of the chalcogenide becomes stronger.

The semiconducting character of the conductivity, just as the high chemical stability of the glassy network, is determined by the predominance of covalent bonds in the compound. An increase of the fraction of the ionic component in the chemical bonds lowers both the conductivity and the chemical stability of the glassy network. When the delocalization of the covalent chemical bonds is strengthened, the conductivity of the compound is increased together with their chemical stability. Elemental copper can be introduced in appreciable amounts in arsenic chalcogenides and alter substantially the structural-chemical makeup of the glassy network, causing an abrupt change of the electrical conductivity and bandgap energy, and also an appreciable increase of chemical stability. This can counteract the reduction of chemical-interaction energy, and therefore the concomitant glassy network instability, of selenides being replaced by tellurides in the arsenic chalcogenides.

The introduction of tellurium and copper in the arsenic chalcogenide is beneficent from a standpoint of increasing the electrical conductivity and decreasing the bandgap energy of the compound; the introduction of copper and selenium in the arsenic chalcogenide is beneficent in maintaining a glassy network structural stability. The replacement of arsenic by antimony or bismuth is not accompanied by an appreciable change in the electrical conductivity, but is accompanied by an appreciable reduction of the glass network stability and increased ability for crystallization. Therefore, a compound of chemical formula As-Se-Te-Cu can be designed such as to achieve a combination of good semiconducting properties and stable amorphous atomic structure. It will be appreciated by those skilled in the art of infrared optical detection that the combination of good semiconducting properties and stable structure is a necessary feature of infrared detecting materials.

The near-infrared regime is a range of infrared radiation energies wherein the wavelength of light is between about 700nm ($h\nu=1.8\text{eV}$) to about 2000nm ($h\nu=0.6\text{eV}$).

~~The mid-infrared regime is~~ a range of infrared radiation energies wherein the wavelength of light is between about 2000nm ($h\nu=0.6\text{eV}$) to about 5000nm ($h\nu=0.25\text{eV}$). The long-infrared regime is a range of infrared radiation energies wherein the wavelength of light is between about 5000nm ($h\nu=0.25\text{eV}$) to about 100000nm ($h\nu=0.01\text{eV}$).

5 It will also be appreciated by those skilled in the art of infrared optical detection that it is desirable to obtain a semiconducting infrared detecting compound that 1) can be produced in thin film form over large areas at reasonable cost; 2) that can be processed monolithically using standard VLSI lithographic techniques; 3) that show substantial electrical conductivity for charge readout upon illumination, and; 4) that is characterized
10 by a bandgap energy, or activation energy, between 0.15 eV and 1.8 eV. The invention consists of a quaternary compound semiconductor thin film comprising arsenic (As), selenium (Se), tellurium (Te) and copper (Cu) atoms that meet these criteria.

In regard to the first abovementioned point, the As-Se-Te-Cu compound semiconductor can be produced in thin film form at reasonable cost by virtue of its
15 amorphous, or glassy, or polycrystalline atomic arrangement. The disordered structure of the thin film material eliminates the constraints of lattice constant matching and polarity matching with the substrate, which opens the way to flexible chemical compositional adjustments and to lower-cost, large-area, large-thickness deposition processes such as thermal evaporation, thermal co-evaporation, sputtering or co-sputtering, as opposed to
20 more expensive heteroepitaxial crystal growth techniques. The compound is dominated by covalent chemical bonds between the said atoms, and thin films can be deposited on a variety of different substrates, such as silicon, oxide, chalcogenide or polymer substrates, by thermal evaporation or sputtering due to the robust stoichiometry of bonding in the material.

25 The compound is characterized by an atomic arrangement of the arsenic, selenium, tellurium and copper atoms that is predominantly amorphous, glassy or polycrystalline. The atomic arrangement of an amorphous material is often described as a "random close packing", while the atomic arrangement of a glassy material is often described as a "continuous random network". In both cases the local environment, i.e., the location of
30 atomic nearest neighbors, of an atom is well-defined, but there is no repeating unit cell or crystalline order throughout the material.

The amorphous or glassy state is a state of a solid that has become disordered, the main feature being the absence of long range order. A substance in the amorphous or glassy state has short range order within the limits of one or several unit cells, in the range
35 1nm to 10nm. Beyond the unit cell the order is not maintained, each unit cell differs from the preceding one in its position and orientation. The atomic arrangement of a

polycrystalline material is described by local units of ordered crystalline domains or grains, in the range 10nm to 100nm, of various shapes and orientations, separated by disordered boundaries between the said units. In all cases, i.e., amorphous, glassy and polycrystalline states, the compound is characterized by an atomic long range order broken
5 by random network units, or by grain boundaries between ordered units.

In regard to the second abovementioned point, the As-Se-Te-Cu thin film compound semiconductor can be processed monolithically using standard VLSI lithographic techniques, such a contact stepper lithography, photoresist patterning, wet chemical etching using hydroxide solutions, or dry chemical etching using fluorine gases.
10 The post-deposition processing is not limited to these particular processing techniques.

In regard to the third and fourth abovementioned points, it is a characteristic of the invention that the electronic properties of the As-Se-Te-Cu thin film compound semiconductor can be tuned during the deposition process by an adjustment of the molar concentration of tellurium and copper atoms in the said compound. The electronic
15 properties include principally the electrical conductivity and the bandgap energy. The electrical conductivity of a material refers to the propensity of charges within the material, e.g. electrons, to be delocalized and bounded to no specific atoms or trapping defects such that the charges are free to flow upon application of a driving electrical potential.

The bandgap energy refers to the energy difference between the valence band and
20 the conduction band of the material, which corresponds to the energy barrier that must be overcome for a valence state to be activated to a conduction state. By a judicious adjustment of the molar concentration of tellurium and copper atoms in the said compound during processing, the electrical conductivity can be increased by several orders of magnitude, and the bandgap energy tuned to detect infrared radiation energy from the
25 near-infrared regime to the mid-infrared regime to the long-infrared regime. The disorder represented by deviations in the bond lengths and bond angles and bond defects upon adjustment of the molar concentration of tellurium and copper atoms in the compound during processing broadens the electron distribution states, induces electron interaction that splits the valence states into bonding and anti-bonding levels (resulting in a
30 modification of the bandgap energy), and causes electron localization as well as strong scattering of electrons upon application of an electric potential.

The three principal features of the structure of amorphous or glassy or polycrystalline semiconductors are the short range order of the network, the long range disorder and the significant presence of coordination defects. The preservation of short
35 range order results in a similar overall electronic structure of an amorphous material compared to the equivalent ordered crystal. The abrupt band edge of a crystal are replaced

by a broadened tail of states extending into the bandgap, called bandtail, which originates from the deviations of the bond length and angle arising from the long range structural disorder. The bandtails are important because electronic transport occurs at the band edge. Electronic states deep within the bandgap arise from departures from ideal network, such as coordination defects. These defects determine many electronic properties by controlling trapping and recombination of electronic charges. The electronic structure of an amorphous semiconductor comprises the bands (extended states), the bandtails (localized states) and the defect states (localized states) in the bandgap.

There is correspondence between the structure and the electrical conduction mechanism such that 1) the structural short range order determines the extended state conduction and the bandgap energy (i.e., usual conduction mechanism in intrinsic semiconductors), 2) the structural deviations of the bond length and angle determines the bandtail conduction (i.e., hopping conduction mechanism from localized to extended states) and 3) the departures from ideal network, such as coordination defects, determine the hopping conduction mechanism at the Fermi energy (i.e. tunneling of states deep within the bandgap). It is a characteristic of the invention that the electronic properties of the As-Se-Te-Cu thin film compound semiconductor can be tuned during the deposition process by an adjustment of the molar concentration of tellurium and copper atoms in the said compound by virtue of modifications of the short range order, deviations of the bond length and angle, and changes in the density of coordination defects, which result in changes in the bandgap energy, in the extended state conduction, in the bandtail conduction and in the hopping conduction at the Fermi level.

An exemplary embodiment of the invention is a thin film of molar composition given by the chemical formula $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$, where $w+x+y+z = 100\%$. FIG. 1 is a table that lists exemplary compositions of the said semiconductor compound, showing large variations of electrical conductivity and bandgap energy upon increase of concentration of tellurium (from $y=0\%$ to $y=50\%$) and copper (from $z=0\%$ to $z=25\%$). The listed electrical conduction represents a sum of the above-mentioned conduction mechanisms.

The extreme case of a compound with no tellurium and no copper, of composition $\text{As}_{40}\text{Se}_{60}\text{Te}_0\text{Cu}_0$, show essentially dielectric properties with negligible electrical conductivity, $\sigma=10^{-12.8}\Omega^{-1}\text{cm}^{-1}$, and a $E_g=1.8$ eV bandgap energy commensurate with the detection of near-infrared light. The progressive addition of tellurium and/or copper in the compound increases significantly the electrical conductivity and decreases the bandgap energy.

An exemplary embodiment of the invention is a thin film of molar composition given by the chemical formula $\text{As}_{25}\text{Se}_1\text{Te}_{49}\text{Cu}_{25}$ showing semiconductor properties with

markedly improved electrical conductivity, $\sigma=10^{-2.2}\Omega^{-1}\text{cm}^{-1}$, and a $E_g=0.2$ eV bandgap energy commensurate with the detection of mid-infrared to long-infrared light.

FIG. 2 is a phase diagram of the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ system, with $x\sim 0\%$, showing the compositional region where glassy atomic arrangement is obtained (outlined rounded dots).

The arrows point to the chemical compositions suitable for near-infrared detection and mid-infrared detection. When the selenium molar concentration is low, a glassy structure is generally obtained at about 60% of tellurium concentration and less than 30% copper concentration. It can be seen that, with increased copper concentration, the glassy regime is widened and the structure becomes amenable to a glassy atomic arrangement.

However, an increase of copper concentration above 30% increases the density of percolation channels in the material, corresponding to aggregates of Cu_2Te bonds in the glassy network, which promote crystallization and reduce material integrity. Such crystallization effects can be prevented by replacing tellurium with selenium in order to strengthen the covalent bonding and to improve glass stability, at the expense of a reduction of electrical conductivity. The arrows on the phase diagram point to the chemical compositions suitable for near-infrared light detection and mid-infrared light detection.

Additional exemplary embodiments of the invention include a quaternary compound in the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ chemical system, with a range of w , x , y , and z molar compositions encompassed by a glassy regime similar to the one shown in FIG. 2, and produced in thin film solid-state form. The amorphous, glassy or polycrystalline regime in the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ material system is generally achieved when the molar concentration of arsenic atoms is less than $w=75\%$, and when the molar concentration of selenium atoms is less than $x=75\%$, and when the molar concentration of tellurium atoms is less than $y=80\%$, and when the molar concentration of copper atoms is less than $z=40\%$, with the limit of $w+x+y+z=100\%$.

Due to limitations in the purity of materials synthesis, contamination of the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ thin film may occur such as to form a contaminated $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z\text{A}_b$ compound, where A is an impurity atom, or a group of impurity atoms, of elemental nature different than arsenic, selenium, tellurium or copper, and wherein $w+x+y+z+b=100\%$. The impurity atom, or group of impurity atoms, can be any atoms in the periodic table that establish covalent chemical bonding with the $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ compound, such as Group III atoms of the periodic table (B, Al, Ga, In, Tl), or Group IV atoms of the periodic table (C, Si, Ge, Sn, Pb), or Group V atoms of the periodic table (N, P, Sb, Bi), or Group VI atoms of the periodic table (O, Po), or metal atoms in Group II of the periodic table (such as Ag, Au, Zn, Cd, Hg, etc.). In order to maintain good

~~semiconductor properties.~~ It is usually desirable that the contamination molar concentration be less than $b=10\%$.

It is a characteristic of the invention that the bandgap energy of the quaternary compound semiconductor can be tuned during thin film deposition process by an adjustment of the molar concentration of tellurium and copper atoms in the said compound. FIG. 3 shows that, in the exemplary systems of $(As_{50}Se_1Te_{49})_{100-x}Cu_x$ (squares) and $(As_{25}Se_1Te_{74})_{100-x}Cu_x$ (circles), the bandgap of the thin film can be adjusted, or tuned, by a significant amount with a change of copper molar concentration. The bandgap energy can be adjusted from 0.9 eV ($(As_{50}Se_1Te_{49})_{100}Cu_0$) to 0.2 eV ($(As_{25}Se_1Te_{74})_{75}Cu_{25}$) by changing the copper molar concentration from $\sim 0\%$ to $\sim 25\%$ respectively, which is commensurate with infrared radiation energies of wavelength from about 1300nm (near-infrared) to about 6000nm (long-infrared), respectively.

Within the $w \times y \times z$ parameter space encompassed by the glassy regime, the bandgap energy can be tuned to shorter infrared wavelengths (higher E_g) by increasing the selenium-to-tellurium concentration ratio, or to longer infrared wavelengths (lower E_g) by decreasing the arsenic-to-tellurium concentration ratio. The range of bandgap energies allowable within the glassy regime of the $As_wSe_xTe_yCu_z$ system has an uppermost limit of about 1.8eV (tellurium poor and copper poor compositions) to a lowermost limit of about 0.15eV (tellurium rich and copper rich compositions), corresponding to infrared wavelengths from about 700nm (near-infrared regime) to about 8000nm (long-infrared regime).

The investigation of infrared absorption in amorphous semiconductor compound provides fundamental information regarding the atomic structure, chemical bonding and bonding defects in the material. In the region of the spectrum where the infrared radiation energy $h\nu$ is comparable to the bandgap energy E_g of the material, $h\nu \sim E_g$, there is a rapid increase in optical absorption as a function of infrared frequency because the electrons in the material are excited across the bandgap energy barrier.

Upon illumination by an infrared photon of light of energy $h\nu \sim E_g$ there is generation of an electron-hole pair in the material, resulting in an increase of the density of occupied conduction states (or extended states) in the material, and thus resulting in a photo-generated increase of electrical conductivity, known as photoconductivity. The spectral region where this occurs is called the optical absorption edge and the corresponding radiation energy gives a measure of the bandgap energy of the material. The optical absorption coefficient, $\alpha(\nu)$, shows approximately an exponential dependence on radiation energy, $h\nu$, and obeys the well known Urbach rule $\alpha(\nu) = \alpha_0 \exp(h\nu/E_g)$,

Where α_0 is a constant, ν is the frequency of the incident optical radiation, and E_g is the bandtails width of the localized states in the amorphous semiconductor, which corresponds closely to the bandgap energy.

The spectral measurement of the optical absorption $\alpha(\nu)$ of the material, near the absorption edge, can reveal with a good precision the bandgap energy E_g of the material. The spectral measurement of the optical absorption $\alpha(\nu)$ of the material can also reveal the optical frequency range at which infrared radiation is absorbed for the application of these semiconductor materials as infrared light detectors. The spectral measurement of the optical absorption $\alpha(\nu)$ can also be performed equivalently as function of wavelength $\alpha(\lambda)$ via the well known frequency-wavelength conversion $\lambda=c/\nu$, where c is the speed of light.

FIG. 4 is a diagram showing the optical absorption spectra $\alpha(\lambda)$ as function of copper molar concentration in the exemplary embodiment of composition $(\text{As}_{40}\text{Se}_{30}\text{Te}_{30})_{100-x}\text{Cu}_x$, where x is the molar concentration of copper. It can be seen that, within a fairly small range of copper enrichment in the semiconductor from $x=0\%$ to $x=15\%$, the optical absorption bandtail of the material can be tuned from near-infrared wavelengths ($\lambda \sim 1300\text{nm}$) to mid-infrared wavelengths ($\lambda \sim 2000\text{nm}$). This range of absorption bandtail wavelengths is commensurate with a range of bandgap energies from about 0.95eV to about 0.60eV. The $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ matrix is known to be a stable glassy material, and the enrichment of this matrix with copper such as to form a $(\text{As}_{40}\text{Se}_{30}\text{Te}_{30})_{100-x}\text{Cu}_x$ compound is not followed by thin film crystallization.

In accordance with the invention, the bandgap energy of the As-Se-Te-Cu thin film compound semiconductor can be tuned during the deposition process by an adjustment of the molar concentration of tellurium and copper atoms in the said compound. The adjustment of the molar concentration of tellurium and copper atoms modifies the bandgap energy and the optical absorption spectrum $\alpha(\nu)$ of the compound, which shifts the optical frequency of the optical absorption edge.

Consequently, the spectral response of photo-generated increase of electrical conductivity, or equivalently the spectral response of photoconductivity, is shifted in optical frequency upon adjustment of the molar concentration of tellurium and copper atoms in the said compound. The spectral response of photoconductivity is shifted to longer infrared wavelengths upon enrichment of tellurium and/or copper in the As-Se-Te-Cu compound.

To ensure that the As-Se-Te-Cu thin film is uniform across the chosen substrate, the thin film deposition process relies on a mass-transport-limited deposition technique so that all locations of the substrate surface are supplied with an equal flux of reactant species. Typically, the thin film deposition process relies on physical vapor deposition (PVD),

which comprises the well known techniques of thermal evaporation, electron-beam evaporation and ion sputtering.

Thermal evaporation is generated by heating in vacuum a solid source above its melting temperature using electrically-heated crucibles, and the condensation of the vapors to a solid thin film on the substrate surface. Electron-beam evaporation is generated by heating in vacuum a solid source above its melting temperature using a high-energy electron beam incident on the solid source, and the condensation of the vapors to a solid thin film on the substrate surface. The ion sputtering process involves the ejection of surface atoms from an electrode surface by momentum transfer from the bombarding ions to the electrode surface atoms. The generated vapor of electrode material is then condensed on the substrate. The thin film deposition process can also rely on a physical vapor deposition involving vapor-phase chemical reactions, such as vapor adsorption and desorption at the thin film, encountered typically in chemical vapor deposition, which is defined as the formation of a non-volatile solid film on a substrate by the reaction of vapor-phase chemicals (reactants) that contain the required precursor constituents of arsenic, selenium, tellurium and copper.

A problem arises by the fact that a quaternary compound in the $As_wSe_xTe_yCu_z$ chemical system does not necessarily evaporate or sputter stoichiometrically during the deposition process, or in other words does not evaporate or sputter in maintaining the original molar composition $w\ x\ y\ z$ during the deposition process. This problem comes from the different covalent bond energies between the As, Se, Te and Cu atoms in the compound, and from the different bond coordination numbers between the As, Se, Te and Cu atoms in the compound. In a glassy network of $As_wSe_xTe_yCu_z$, the arsenic is usually 3-fold bond coordinated, the selenium and tellurium are usually 2-fold bond coordinated, and copper is usually 1-fold bond coordinated, all the said covalent bonds having various different energies, which results in different bond detachment energies within the network unit of the glass structure.

When bringing the compound to the melting temperature for thermal evaporation, or when bombarding the compound with ions for sputtering, the lower-bond-energy and lower-coordination-number atoms may break away first, and be released as vapor first, and the $As_wSe_xTe_yCu_z$ compound may generate a non-stoichiometric vapor as the glassy network units are broken, and condensed into a non-stoichiometric thin film of different glassy network units onto the substrate. It has been observed in such glasses that tellurium elements tend to vaporize first, and arsenic and copper elements tend to vaporize last. The resulting $As_wSe_xTe_yCu_z$ thin film is usually tellurium-rich, and arsenic-poor, and copper-poor, as compared to the initial $As_wSe_xTe_yCu_z$ bulk source.

In accordance with the invention, and to avoid the abovementioned problem, the deposition process of the quaternary $As_wSe_xTe_yCu_z$ semiconductor compound relies on a mixed physical vapor deposition technique. The mixed physical vapor deposition technique consists of co-evaporating, or co-sputtering, a combination of at least two different solid sources having different enthalpies of evaporation. Sub-compounds of low bond energies are evaporated or sputtered independently at low temperature or low ions energy, while other sub-compounds of higher bond energies are evaporated or sputtered independently at higher temperature or higher ions energy.

Equivalently, sub-compounds of low enthalpies of evaporation are evaporated or sputtered independently at low temperature or low ions energy, while other sub-compounds of higher enthalpies of evaporation are evaporated or sputtered independently at higher temperature or higher ions energy. The enthalpy of evaporation is the thermodynamic energy required for a material at a characteristic pressure and temperature to attain first-order phase transition from solid/liquid to vapor. The enthalpy of evaporation depends on the bond energy and bond configuration.

Two materials of different bond energies will attain first-order phase transition from solid/liquid to vapor at a different characteristic temperature, or at a different vaporization temperature. In accordance with the present invention, and to avoid the abovementioned problem of non-stoichiometric vaporization of the $As_wSe_xTe_yCu_z$ semiconductor compound, the deposition process relies on a mixed physical vapor deposition technique comprising at least two different solid sources that vaporize stoichiometrically. The sub-compounds must have chemical compositions comprising one, two or three of either arsenic, selenium, tellurium or copper atoms, and must vaporize stoichiometrically; these sub-compounds are generally found to have different enthalpies of evaporation. Each sub-compound vaporizations is controlled to a desired vaporization rate, up to a deposition rate of 100 Angstrom per second, and at least two vapors resulting from the said vaporizations of said at least two sub-compounds will combine, and recreate an overall vapor composed of arsenic, selenium, tellurium and copper atoms with molar concentration matching the desired $As_wSe_xTe_yCu_z$ compound.

This overall vapor composed of arsenic, selenium, tellurium and copper atoms with molar concentration matching the desired $As_wSe_xTe_yCu_z$ compound will condense on a substrate to form a solid-state thin film of $As_wSe_xTe_yCu_z$ compound. Such co-deposition process is done usually in a vacuum chamber at a residual pressure of less than 1 millitorr, or preferably less than 10^{-5} torr. It is known that $As_wSe_xTe_yCu_z$ thin films adhere well to a variety of substrates, such as metallic, semiconductor, ceramic, dielectric or polymer substrates. Due to limitations in the purity of the sub-compounds, and the cleanliness of

the vacuum chamber, the overall vapor combination may contain impurity atoms of elemental nature different than arsenic, selenium, tellurium, or copper.

In order to generate inside the vacuum chamber an overall vapor composed of arsenic, selenium, tellurium and copper atoms with molar concentration matching the desired $As_wSe_xTe_yCu_z$ compound, the co-deposition process preferably involves thermal evaporation and/or electron-beam evaporation and/or ion sputtering of at least two sub-compounds of the following chemical composition categories: arsenic-selenide, arsenic-telluride, arsenic-selenide-telluride, copper-selenide, copper-telluride, pure selenium, pure tellurium, and pure copper.

Several chemical compositions encompassed by these categories are known to vaporize stoichiometrically and with different enthalpies of evaporation; exemplary chemical compositions are $As_{40}Se_{60}$, $As_{40}Te_{60}$, $As_{40}Se_{60-x}Te_x$, $CuSe$, $CuTe$, Cu_2Se , Cu_2Te , pure Se, pure Te, pure Cu, etc. The method of producing thin films of $As_wSe_xTe_yCu_z$ by co-deposition is not limited to these particular sub-compound chemical compositions. The main requirement is that the sub-compounds must have chemical compositions comprising one, two or three of either arsenic, selenium, tellurium or copper atoms, and must vaporize stoichiometrically. The at least two sub-compounds can be all vaporized by thermal evaporation, or all vaporized by electron-beam evaporation, or all vaporized by ion sputtering, or a combination of thermal evaporation and/or electron-beam evaporation and/or ion sputtering can be used. Since all the sub-compounds are vaporized independently, attaining the desired molar composition $w x y z$ of $As_wSe_xTe_yCu_z$ is possible by taking into account the molar composition of the sub-compounds, the respective surface adhesion efficiency of the sub-compounds to the substrate, the geometric arrangement of the respective vapor source inside the vacuum chamber with respect to the substrate, and by controlling and adjusting their respective vaporization rates.

A preferred method of adjusting the molar concentration of tellurium and copper in the $As_wSe_xTe_yCu_z$ thin film semiconductor compound comprises the control of the respective vaporization rates of the sub-compounds and the adjustment of the geometric arrangement of the sub-compound vapor source inside the vacuum chamber with respect to the substrate. A preferred method of producing an $As_wSe_xTe_yCu_z$ thin film semiconductor compound involves the thermal evaporation of at least two commercially-available sub-compounds of the following chemical composition categories: arsenic-selenide, arsenic-telluride, arsenic-selenide-telluride, copper-selenide, copper-telluride, pure selenium, pure tellurium, and pure copper.

FIG. 5 is a diagram of the optical absorption spectra of exemplary $1\mu m$ thin films of $As_wSe_xTe_yCu_z$, with $y \sim 0\%$, produced by the method of co-deposition of As_2Se_3 and

~~CuSe sub-compounds on a silicon~~ substrate. The As_2Se_3 and CuSe sub-compounds have been vaporized by thermal evaporation at relative vaporization rates of 100-to-0, 92-to-8 and 70-to-30, in order to obtain final thin film compositions of $(\text{As}_2\text{Se}_3)_{100}(\text{CuSe})_0$, $(\text{As}_2\text{Se}_3)_{92}(\text{CuSe})_8$, and $(\text{As}_2\text{Se}_3)_{70}(\text{CuSe})_{30}$. In accordance with the invention, it can be

5 seen that the optical band edge is shifted to longer infrared wavelengths by increasing the copper molar concentration, as explained previously. Other exemplary co-depositions can be performed with stable glass sub-compounds As_2Se_3 and $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$, and binary alloys CuSe and CuTe, in order to obtain final glassy thin film compositions of $(\text{As}_2\text{Se}_3)_{100-x}(\text{CuSe})_x$, $(\text{As}_2\text{Se}_3)_{100-x}(\text{CuTe})_x$, $(\text{As}_{40}\text{Se}_{30}\text{Te}_{30})_{100-x}(\text{CuSe})_x$ or $(\text{As}_{40}\text{Se}_{30}\text{Te}_{30})_{100-x}(\text{CuTe})_x$.

10 The co-deposition process can be followed by a thermal treatment of the thin film, such as a thermal annealing at the glass transition temperature of the compound, in order to modify the free volume in the glassy thin film, or consolidate the material, or activate polycrystallization of the thin film, or activate migration of copper in the material. Such thermal treatment can be used to improve electric mobility of the thin film compound.

15 It is recognized that those skilled in the art may make various modifications and additions to the embodiments described above without departing from the spirit and scope or the present contribution to the art, namely the method of production of amorphous $\text{As}_w\text{Se}_x\text{Te}_y\text{Cu}_z$ thin film infrared semiconductor compounds. Accordingly, it is to be understood that the protection sought to be afforded hereby should be deemed to extend to

20 the subject matter claims and all equivalents thereof fairly within the scope of the invention.

What is claimed is:

- 1 1. A quaternary semiconductor thin film compound comprising arsenic, selenium,
2 tellurium and copper atoms; covalent chemical bondings between said atoms; an
3 amorphous, glassy or polycrystalline atomic arrangement of the said atoms; and localized
4 and extended electronic states associated with said compound, wherein the molar
5 concentration of tellurium and copper atoms in said thin film compound is adjusted during
6 the deposition process in order to modify electrical conductivity and bandgap energy of
7 said semiconductor, and wherein said bandgap energy is equivalent to infrared optical
8 radiation energy.
- 1 2. The semiconductor thin film compound of claim 1, wherein said thin film
2 compound is produced by a mixed physical vapor deposition process involving a vapor
3 combination of at least two different vaporized sub-compounds; wherein the said sub-
4 compounds have different enthalpies of evaporation; and wherein said sub-compounds are
5 chemically composed of one, two or three of either arsenic, selenium, tellurium or copper
6 atoms.
- 1 3. The semiconductor thin film compound of claim 1, wherein molar composition of
2 the said compound is $As_wSe_xTe_yCu_z$, where $w+x+y+z = 100\%$.
- 1 4. The semiconductor thin film compound of claim 1, wherein molar composition of
2 said compound is $As_wSe_xTe_yCu_zA_b$, where A is an impurity atom, or a group of impurity
3 atoms, of elemental nature different than arsenic, selenium, tellurium or copper, and where
4 $w+x+y+z+b = 100\%$.
- 1 5. The semiconductor thin film compound of claim 1, wherein molar concentration of
2 arsenic atoms in said compound is less than $w=75\%$.
- 1 6. The semiconductor thin film compound of claim 1, wherein molar concentration of
2 selenium atoms in said compound is less than $x=75\%$.
- 1 7. The semiconductor thin film compound of claim 1, wherein molar concentration of
2 tellurium atoms in said compound is less than $y=80\%$.
- 1 8. The semiconductor thin film compound of claim 1, wherein molar concentration of
2 copper atoms in said compound is less than $z=40\%$.
- 1 9. The semiconductor thin film compound of claim 4, wherein said impurity atoms
2 establish covalent chemical bonding with the $As_wSe_xTe_yCu_z$ compound.

1 10. The semiconductor thin film compound of claim 4, wherein said impurity atoms
2 belong to Group II, or Group III, or Group IV, or Group V, or Group VI of the periodic
3 table.

1 11. The semiconductor thin film compound of claim 1, wherein said bandgap energy
2 is between 0.15 and 1.8 electron-volts.

1 12. The semiconductor thin film compound of claim 1, wherein infrared light is
2 absorbed by mechanism of generation of electron-hole pairs.

1 13. The semiconductor thin film compound of claim 1, wherein an electron-hole pair
2 can be generated under illumination by infrared light having a wavelength in the range
3 between 700nm and 8000nm.

1 14. The semiconductor thin film compound of claim 1, wherein said bandgap energy
2 is decreased by increasing the molar concentration of tellurium and copper in said
3 compound.

1 15. The semiconductor thin film compound of claim 3, wherein the bandgap energy of
2 said $As_wSe_xTe_yCu_z$ semiconductor is 1.8 electron-volts at a composition of $w=40\%$,
3 $x=60\%$, $y=0\%$ and $z=0\%$.

1 16. The semiconductor thin film compound of claim 3, wherein the bandgap energy of
2 said $As_wSe_xTe_yCu_z$ semiconductor is 0.1 electron-volt at a composition of $w=20\%$, $x=0\%$,
3 $y=50\%$ and $z=30\%$.

1 17. The semiconductor thin film compound of claim 1, wherein said electrical
2 conductivity is increased by increasing the molar concentration of tellurium and copper in
3 said compound.

1 18. The semiconductor thin film compound of claim 1, wherein the optical band edge,
2 and the photoconduction spectral response, are shifted to longer infrared wavelengths by
3 increasing the molar concentration of tellurium and copper in the said compound.

1 19. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process is done in a vacuum chamber at a residual atmospheric pressure
3 below 1 millitorr.

1 20. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process is performed by thermal evaporation.

1 21. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process is performed by electron-beam evaporation.

1 22. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process is performed by ion sputtering.

1 23. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process involves vapor-phase chemical reactions, such as chemical vapor
3 deposition.

1 24. The semiconductor thin film compound of claim 2, wherein said mixed physical
2 vapor deposition process is performed by a combination of the said thermal evaporation
3 and the said electron-beam evaporation and the said ion sputtering processes.

1 25. The semiconductor thin film compound of claim 2, wherein said vapor
2 combination comprises the thermal evaporation of two or more independently vaporized
3 sub-compounds composed of either arsenic-selenide, or arsenic-telluride, or arsenic-
4 selenide-telluride, or copper-selenide, or copper-telluride, or pure selenium, or pure
5 tellurium, or pure copper.

1 26. The semiconductor thin film compound of claim 2, wherein said vapor
2 combination comprises the electron-beam evaporation of two or more independently
3 vaporized sub-compounds composed of either arsenic-selenide, or arsenic-telluride, or
4 arsenic-selenide-telluride, or copper-selenide, or copper-telluride, or pure selenium, or
5 pure tellurium, or pure copper.

1 27. The semiconductor thin film compound of claim 2, wherein said vapor
2 combination comprises the ion sputtering of two or more independently vaporized sub-
3 compounds composed of either arsenic-selenide, or arsenic-telluride, or arsenic-selenide-
4 telluride, or copper-selenide, or copper-telluride, or pure selenium, or pure tellurium, or
5 pure copper.

1 28. The semiconductor thin film compound of claim 2, wherein said vapor
2 combination comprises impurity atoms of an elemental nature different than arsenic,
3 selenium, tellurium, or copper.

1 29. The semiconductor thin film compound of claim 2, wherein said vapor
2 combination is deposited on metallic, semiconductor, ceramic, dielectric or polymer
3 substrates.

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Compound	Refractive index	Bandgap	Electrical conductivity at 20°C
As ₂ Se ₃	2.8	1.8 eV	$10^{-12.8} \Omega^{-1}\text{cm}^{-1}$
As ₄₀ Se ₃₅ Te ₂₅	3.0	1.25 eV	$10^{-7.4} \Omega^{-1}\text{cm}^{-1}$
As ₅₀ Se ₁ Te ₄₉ Cu ₀	~3.5	0.90 eV	$10^{-4.2} \Omega^{-1}\text{cm}^{-1}$
As ₅₀ Se ₁ Te ₄₉ Cu ₅	~3.5	0.79 eV	$10^{-3.9} \Omega^{-1}\text{cm}^{-1}$
As ₅₀ Se ₁ Te ₄₉ Cu ₁₀	~3.5	0.61 eV	$10^{-2.8} \Omega^{-1}\text{cm}^{-1}$
As ₅₀ Se ₁ Te ₄₉ Cu ₁₅	~3.5	0.51 eV	$10^{-2.6} \Omega^{-1}\text{cm}^{-1}$
As ₅₀ Se ₁ Te ₄₉ Cu ₂₀	~3.5	0.39 eV	$10^{-1.5} \Omega^{-1}\text{cm}^{-1}$
As ₂₅ Se ₁ Te ₄₉ Cu ₁₉	~3.5	0.30 eV	$10^{-2.9} \Omega^{-1}\text{cm}^{-1}$
As ₂₅ Se ₁ Te ₄₉ Cu ₂₁	~3.5	0.24 eV	$10^{-2.6} \Omega^{-1}\text{cm}^{-1}$
As ₂₅ Se ₁ Te ₄₉ Cu ₂₅	~3.5	0.20 eV	$10^{-2.2} \Omega^{-1}\text{cm}^{-1}$

FIG. 1

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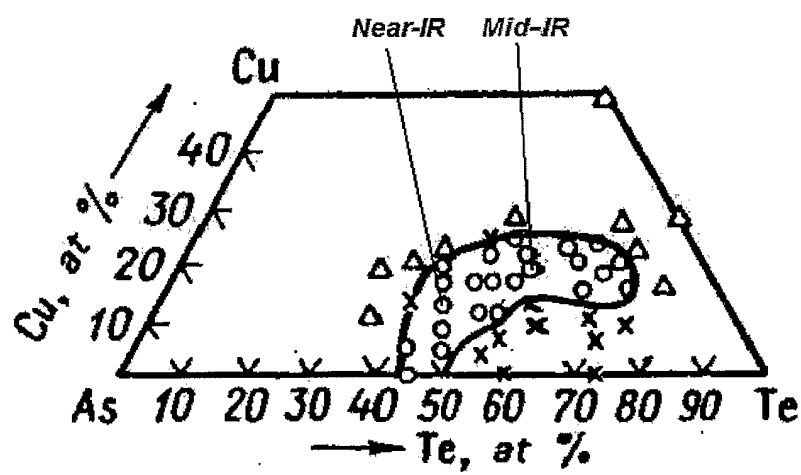
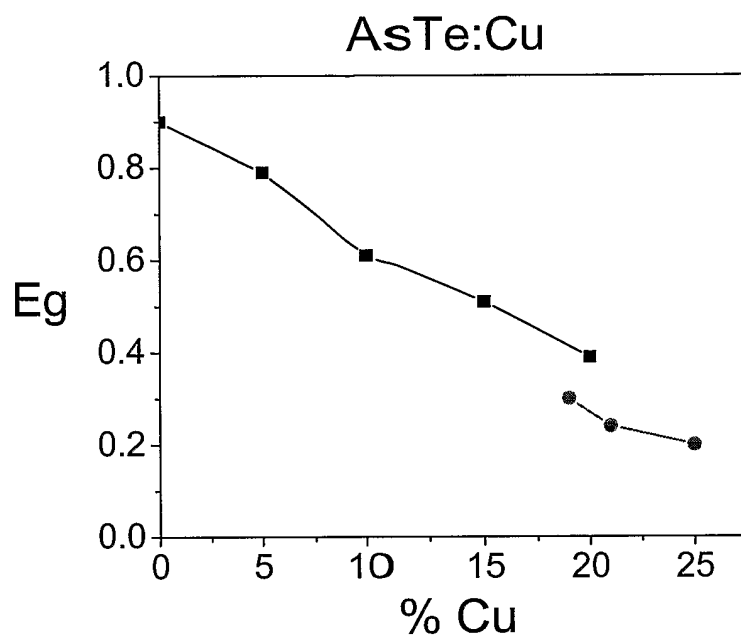
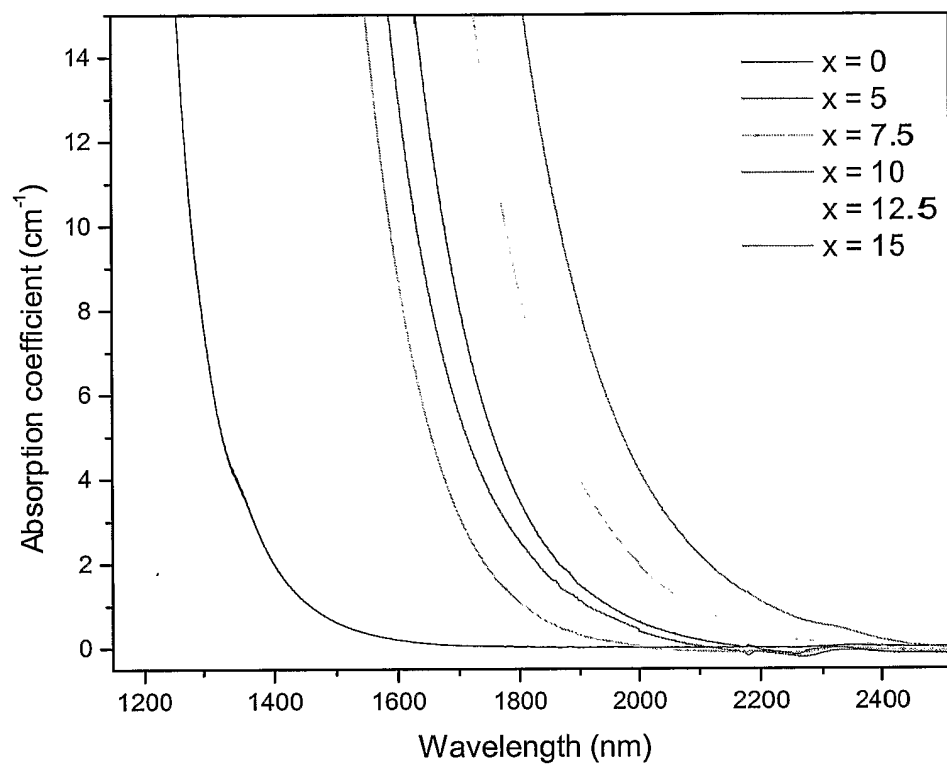


FIG. 2

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**FIG. 3**

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**FIG. 4**

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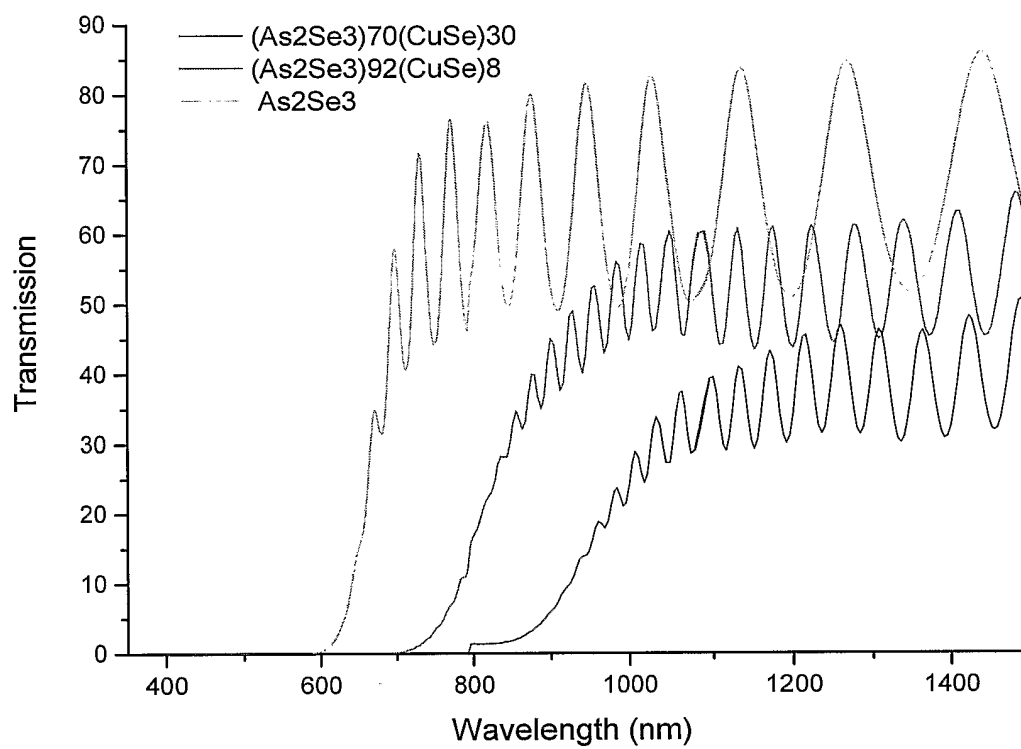


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2005/037632

A. CLASSIFICATION OF SUBJECT MATTER
H01L31/032

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A E OWEN: "Chalcogenide Glasses as Ion-selective Materials for Solid-State electrochemical sensors" JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 35-36, 1 February 1980 (1980-02-01), pages 999-1004, XP002366929 page 1002, line 14 - page 1003, line 10 ----- -/--	1,3,5-8, 11-18,29

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

9 February 2006

Date of mailing of the international search report

24/02/2006

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2005/037632

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCHONING M J ET AL: "Thin film sensors on the basis of chalcogenide glass materials prepared by pulsed laser deposition technique" SENSORS AND ACTUATORS B, ELSEVIER SEQUOIA S.A., LAUSANNE, CH, vol. 68, no. 1-3, 25 August 2000 (2000-08-25), pages 254-259, XP004216623 ISSN: 0925-4005 Part "2. Experimental" figures 1-3	1,3,5-8, 11-18,29
A	M I FRASER ET AL.: "The Electronic Properties of Glasses in the $Cu_x(As_{0.4}Se_{0.6})_{100-x}$ System with x Between 5 and 30" JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 59,60, 1983, pages 1031-1034, XP002366930 part "4. OPTICAL ABSORPTION"	1,11-14
A	MAHADEVAN S ET AL: "Copper as an additive in the $As_{0.4}Se_{0.3}Te_{0.3}$ glass: Mean atomic volume and T_g" JOURNAL OF NON-CRYSTALLINE SOLIDS, NORTH-HOLLAND PHYSICS PUBLISHING. AMSTERDAM, NL, vol. 221, no. 2-3, December 1997 (1997-12), pages 281-289, XP004112905 ISSN: 0022-3093 table 1	1,3,5-8, 11,14, 17,29