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(72) Inventor EDWARD LINCOLN WOLF

(54) RADIATION RESPONSIVE DEVICE

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, 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 is directed to a radiation responsive device capable of modulating current flow therethrough as a function of incident radiation. This invention is also directed to a process for producing such a radiation responsive device.

A variety of photoconductive and semiconductive photoresponsive devices are known to the art. These devices are structurally dissimilar from the radiation responsive devices of the present invention, and exhibit fabrication, structural and performance disadvantages not encountered in the practice of the present invention.

According to the present invention there is provided a radiation responsive device comprising a radiation penetrable electrically conducting metal layer, a radiation penetrable first semiconductive layer of a first conductivity type conductively associated with the electrically conducting layer, a second semiconductive layer of the same conductivity type as the first semiconductor layer, an electrode conductively associated with the second semiconductive layer, and a barrier layer of a sensitizing dye located between the first and second semiconductive layers and cooperating therewith to limit current flow between the electrically conducting layer and the electrode as a function of incident radiation penetrating the electrically conducting layer and the first semiconductive layer.

The present invention also provides a method of making the radiation-responsive device comprising providing a substrate of a semiconductive material of a first conductivity type capable of transporting majority charge carriers in the presence of an applied electrical field. On the substrate is deposited a barrier generating material comprising a sensitizing dye capable of initially accepting the majority charge carriers and capable of releasing the majority charge carriers in response to absorbed incident radiation. The barrier material is overcoated with a radiation penetrable semiconductive overlayer also of a first conductivity type and also capable of transporting the majority charge carriers in the presence of an applied electrical field, and the overlayer is coated with a radiation penetrable conductive layer.

The invention may be better understood by reference to the following detailed description considered in conjunction with the drawings, in which

Figure 1 is a schematic diagram of a radiation responsive device according to this invention;

Figure 2 is a schematic circuit diagram for measuring the output of the radiation responsive device of the invention in response to radiation stimulus;

Figure 3 is a plot of current versus voltage for three levels of illumination;

Figures 4 and 5 are plots of differential conductance versus voltage for two levels of illumination;

Figure 6 is a plot of current versus voltage for three levels of illumination;

Figures 7, 8 and 9 are plots of current versus voltage for three levels of illumination, and

Figure 10 is a log scale plot of current density versus illumination.

A radiation responsive device 1 according to the present invention is schematically illustrated in Figure 1. For ease of comprehension and viewing the dimensions of the elements of the device have been exaggerated in width and are not drawn to scale. An electrode 3 lies in ohmic conductive contact with

one major face 5 of a semiconductive element or substrate 7. A barrier generating material 9 overlies the remaining major face 11 of the semiconductive substrate 7. A radiation penetrable semiconductive element or overlayer 13 overlies the barrier material 9. The semiconductive elements 7 and 13 are chosen to be of like conductivity type and are preferably comprised of similar semiconductive materials. A radiation penetrable electrically conducting layer 15 overlies the semiconductive overlayer 13 in conductive contact therewith. The electrically conducting layer 15 forms a conductive interface 17 with the semiconductive overlayer 13 that is preferably a rectifying junction. The electrically conducting layer 15 is a metal layer. An electrode 19 lies in conductive contact with the metal layer 15.

To place the radiation responsive device 1 in operation, it is placed in an electrical circuit as is schematically indicated by leads 21 and 23 attached to the electrodes 3 and 19, respectively. The device is preferably placed in a circuit supplying a d-c bias; however, an a-c or variable d-c bias can also be provided. Where the interface 17 between the metal layer 15 and semiconductive overlayer 13 forms a rectifying junction it is necessary to forward bias the junction. Where an a-c bias is provided it is only necessary that the junction be forwardly biased over some portion of a cycle. Where the metal layer 15 and semiconductive overlayer 13 do not form a rectifying junction the polarity of applied potential is not material to the practice of the invention, since the device responds to both directions of bias as if forward biased.

It is preferred to forward bias the device with an applied potential which is less than the conduction band gap potential—i.e. the potential difference between the conduction and valence bands—of the semiconductive elements present in the device. It is generally preferred to utilize forward biasing potentials of from 0.5 to 2.0 volts, although somewhat greater latitudes for biasing can be available, depending upon the particular semiconductive materials employed.

So long as the quantity of radiation reaching the barrier generating material 9 of the forwardly biased radiation responsive device is limited, very low levels of current are permitted by the device. Without intending to be bound by any particular theory of operation, it is believed that the behavior of the radiation responsive device can be explained as follows: The semiconductive substrate 7 and the semiconductive overlayer 13, being of like conductivity type, are provided with sufficient impurities to allow current conduction through the transport of like majority charge carriers in the presence of the electrical field provided by the forward bias applied to the electrodes of the device. The barrier generating material is, however, chosen initially to accept and, in the absence of incident radiation, effectively trap majority charge carriers from the adjacent portions of the semiconductive elements.

It is believed that the barrier generating material, because of its initial affinity for majority charge carriers, depletes both semiconductive elements to some extent of these charge carriers adjacent its interface therewith. The barrier generating material then exhibits a net charge corresponding in polarity and magnitude to that of the trapped majority charge carriers. The barrier generating material creates a space charge at the interface of the semiconductive elements and extending into the depletion layer of each of the semiconductive elements. The space charge effectively provides a barrier potential extending into the depletion region of the semiconductive elements that repels majority charge carriers which under the influence of the externally applied potential would otherwise be transported through the semiconductive elements between the electrode 3 and the metal layer 15.

The barrier generating material by reason of being decoupled from the electrode 3 and the metal layer 15 by the majority charge carrier depleted portions of the semiconductive elements behaves as though it lies at a potential which need not be intermediate between that of the metal layer and the electrode 13. If either of the semiconductive elements (and therefore their depletion regions) are omitted, the potential of the barrier generating material will be clamped to the potential of the adjacent electrode, and the device will no longer function to limit current as a function of incident radiation.

When the device is exposed to radiation as schematically illustrated by arrows 25 in Fig. 1, the radiation penetrates the metal layer 15 and the semiconductive overlayer 13 to impinge upon the barrier material and to penetrate the semiconductive substrate to a depth corresponding to the reciprocal of the absorption coefficient of the semiconductive material forming the semiconductive substrate. A very small amount of radiation incident upon the barrier material produces a large increase in current through the device between the electrodes 3 and 19 and in the leads 21 and 23 of the external circuit.

Again, without intending to be bound by any particular theory of operation, it is believed that the incident radiation absorbed adjacent the barrier generating material depletes trapped majority charge carriers. The trapped majority charge carriers are believed to be neutralized by minority charge carriers generated within the semiconductive elements by the absorbed incident radiation. The minority charge carriers are, of course, of opposite polarity to the space charge and therefore attracted to the barrier generating material. The physical effect can be viewed

as a diminution of the space charge and a resultant reduction of the barrier potential. Thus, with the barrier potential reduced, majority charge carriers flow between the electrode 3 and the metal layer 15.

The semiconductive elements incorporated within the radiation responsive device of this invention can be of either N or P conductivity type and can be either monocrystalline or polycrystalline. The semiconductive elements can be of any conventional type known to the art. It is preferred to utilize semiconductive compounds of elements chosen from Groups II and VI of the Periodic Table of elements, such as cadmium sulphide, cadmium selenide or zinc oxide. It also contemplated to use semiconductive compounds of elements from Groups III and V of the Periodic Table of elements, such as gallium arsenide and similar semiconductive compounds. It is preferred to employ the same semiconductive compound to form both of the semiconductive elements.

Since the semiconductive element 7 is not required to be either monocrystalline or radiation penetrable, its dimensions can be varied widely in the practice of this invention. The semiconductive element 7 is preferably of a thickness greater than the width of the depletion layer formed in use of the radiation responsive device for best performance, although this is not required. The depletion layer is typically a few hundred nanometres in thickness, and frequently ranges from 10 to 1,000 nm in thickness, depending on the impurity concentration of the semiconductive element and the barrier material chosen. The semiconductive element or overlayer 13 is preferably polycrystalline and therefore can be widely varied in its areal dimensions. The semiconductive overlayer is chosen of a thickness to allow radiation to be transmitted to the barrier layer. The thickness of the semiconductive overlayer is preferably less than the reciprocal of the absorption coefficient for the semiconductive material from which it is formed. For II—VI semiconductive materials, such as cadmium sulphide, the semiconductive overlayer is preferably in the range of from 2.5 to 7.0 nm in thickness, but can be up to 50 nm in thickness without excessively attenuating the transmitted radiation.

The barrier generating materials useful in the practice of this invention are sensitising dyes capable of accepting majority charge carriers from the semiconductive elements and releasing majority charge carriers as a function of absorbed incident radiation. These barrier generating materials exhibit a measurable surface photovoltage on the semiconductive substrate, preferably of at least 0.1 volt and, most preferably, of at least 0.5 volt.

As employed herein the term "surface photovoltage" refers to the change in the contact potential difference that occurs when a layer of a barrier generating material present on a semiconductive substrate surface is initially dark and then subjected to actinic radiation.

The contact potential difference is the difference between the potential at the surface of the semiconductive substrate in contact with the barrier generating material and the bulk of the semiconductive substrate. Barrier generating materials useful with N conductivity type semi-conductive substrates are relatively electron accepting and therefore trap electrons to render the contacted surface of the semiconductive substrate more negative than the bulk of the semiconductive substrate. On the other hand, barrier generating materials useful with P conductivity type semiconductive substrates are relatively electron donating, thus effectively trapping holes (positive charge carriers) to render the potential at the contacted surface of the semiconductive substrate more positive than in the bulk thereof. On subsequent radiation exposure barrier generating materials for N conductivity type semiconductive substrates become less negative and produce less negative contact potentials while barrier generating materials for P conductivity type semiconductive substrates become less positive and produce less positive contact potentials.

The procedure for measuring contact potential differences is well known to those skilled in the art. A suitable procedure for determining contact potential differences utilized in determining the surface photovoltages of the barrier materials of this invention is described in an article titled "Contact Potential Measurements on Clean CdS Surfaces", by C. L. Balestra and H. C. Gatos in *Surface Science*, Volume 28, pages 563 to 568 (1971).

To illustrate a surface photovoltage determination technique which is preferred, a semiconductive element corresponding to the semiconductive substrate to be utilized in forming a radiation responsive device is mounted in a vacuum chamber above a sublimation source for the barrier generating material and in proximity to a vibrating reference electrode, preferably of gold or platinum. The barrier generating material is deposited on a surface of the semiconductive substrate in a substantially monomolecular layer, giving substantially complete coverage of a surface of the semiconductive element while keeping the reference electrode free of barrier generating material. The contact potential difference between the reference electrode and the barrier generating material is then determined according to the procedure of the above article both while the barrier generating material is dark and after exposure of the barrier generating material to actinic radiation. The change in the contact potential difference provides a direct measure of the surface photovoltage.

The barrier generating materials exhibiting surface photovoltages which are particularly suited to the practice of this invention are chosen from among known sensitizing dyes for

negative working silver halide photographic emulsions, such as pyrylium and thiapyrylium dyes, cyanine and merocyanine dyes; monomethine cyanine dyes; nitro-substituted cyanine dyes; pyrylium cyanine dyes; pyrrole dyes; pyrimidine-dione dyes; imidazopyridine or imidazothiazole dyes; pyrolo-(2,3-b) quinoxaline dyes; nitro-substituted carbazole derived dyes; dyes containing desensitizing nuclei; so-called desensitizing dyes which sensitise reversal silver halide systems; dyes which desensitize negative silver halide systems; triarylmethane dyes, such as Rhodamine B and Crystal Violet; diarylmethane dyes; azine dyes, such as phenosafranine; anthraquinone dyes; formazan dyes; azo dyes; acridine dyes; xanthene dyes; phthalein dyes as well as dye mixtures. It is particularly preferred to choose dyes exhibiting surface photovoltages from among known sensitizing compounds for photoconductive compounds. For example, photosensitizers for II—VI compound photoconductors can be selected which produce excellent surface photovoltages on II—VI compound semiconductive substrates employed in the practice of this invention.

Exemplary of dyes within the categories above noted are those disclosed in the following issued patents U.S. Patents 3,597,196, 3,141,770, 3,250,615, 3,565,616, 3,542,548 and 3,565,615; British Patent 964,873; U.S. Patents 3,579,346, 3,560,207, 3,560,208, 3,549,362 and 3,579,331; Belgium Patents 695,364, 695,366 and 705,117; U.S. Patents 2,610,120, 2,670,286, 2,670,287, 2,732,301, 3,110,591, 3,128,179, and 3,121,008.

In its preferred form the barrier generating material forms a barrier layer within the radiation responsive device that is a single molecule in thickness. Layer thicknesses of up to about 5 molecules are contemplated. The barrier generating material need not be present over the entire major face 11 of the semiconductive substrate in order to allow the device to exhibit radiation responsive current gain. Current gain can be obtained when as little as 1 percent of this major face is provided with barrier generating material. It is generally preferred for the barrier material to cover at least 25 percent of the major face of the semiconductive substrate, and in the preferred form of the invention the barrier generating material substantially uniformly covers the entire major face of the semiconductive substrate.

The electrically conducting layer 15 can form either an ohmic or a rectifying conductive contact with the semiconductive overlayer 13. It is preferred that the electrically conducting layer 15 be chosen to form a rectifying conductive contact with the semiconductive overlayer 13, since this permits a potential barrier of greater magnitude to be formed by the barrier layer. Consequently larger forward bias potentials can be applied to the device without driving the device into conduction in the absence of incident radiation. Any metal or combination of metals can be used to form the electrically conducting layer known to be useful in forming ohmic and/or rectifying contacts to semiconductive elements. Preferred metals for forming rectifying contacts with the semiconductive overlayer are comparatively noble metals, such as gold, silver, copper platinum and palladium. The metal layer, if desired, can be a composite of several layers of like or dissimilar metals and, as employed herein, the term "metal layer" is intended to be inclusive of such composite layers. The metal layer is chosen to be of a thickness so that it remains penetrable to incident radiation. In its preferred form the metal layer is a substantially transparent layer of from 10 to 60 nm in thickness, and, most preferably, from 20 to 30 nm.

The electrodes 3 and 19 schematically shown in Figure 1 can be formed according to conventional practices of a single metallic element or as a composite of metal layers and elements, as is well understood in the art. In most instances the electrode 3 includes one or more metallic contact layers at the major face 5 of the semiconductive element 7. As is conventional practice for radiation receiving devices, the electrode 19 can be areally extended to produce a pattern or array covering portions of the outer surface of the metal layer 15. In some modes of use it is desirable to form a conductive contact with the metal layer 15 using a fluid electrolyte. In this instance the electrode 19 is formed by the electrolyte, or, alternatively viewed, the electrode 19 can be viewed as spaced from the metal layer 15 by a fluid electrolyte. In this instance the electrolyte and electrode 19 together form an electrode lying in conductive contact with the metal layer.

In Figure 1 no housing or packaging for the radiation responsive device is shown. It is appreciated that the radiation responsive device can be housed or encapsulated using techniques well known to those skilled in the art. For example, the radiation responsive device of the present invention can employ the housing of any conventional photodiode or phototransistor. In a simple form the device can be encapsulated in an insulative polymer. Where the polymer is transparent it can cover the metal layer 15, although this is not essential.

A glass layer or sheet can be provided overlying the metal layer 15 and the electrode 19, if desired. In protected environments, such as an inert atmosphere, no housing for the radiation responsive device is needed.

The devices of the present invention can be used to detect any source of actinic radiation. By proper choice of semiconductive materials the device can be specifically

adapted for response to the ultra-violet, visible and/or infra-red portions of the spectrum. Or, alternatively viewed, for a given radiation responsive device formed according to this invention a radiation source is chosen which delivers radiation within that portion or those portions of the spectrum which are readily absorbed by the semiconductive material. For example, relatively large band gap semiconductive materials, such as zinc oxide, readily absorb ultraviolet radiation while relatively small band gap materials, such as germanium, are particularly responsive to the infra-red spectrum. Cadmium sulphide devices respond well to the lower wavelengths of the visible spectrum.

Without intending to be bound by any particular theory of operation, it is believed that it is the incident radiation absorbed by the semiconductive material within the depletion region and within a distance from the barrier generating material corresponding to the reciprocal of the absorption coefficient for the semiconductive material that principally determines the response of the devices formed according to this invention. It is in theory possible to have most of the incident radiation absorbed within the depletion region of the semiconductive overlayer so that little radiation penetrates the barrier generating material to reach the semiconductive substrate. It is preferred to have the incident radiation absorbed principally by the semiconductive substrate, since the semiconductive substrates of the devices formed according to the process herein disclosed are believed to permit somewhat higher minority charge carrier mobilities. In practice it is believed that both the semiconductive elements absorb significant portions of the incident radiation within their respective depletion regions and therefore contribute to reducing the potential barrier to current conduction.

While any method known to those skilled in the art can be used to prepare radiation responsive devices according to the present invention, it is preferred to form the radiation responsive devices of the present invention according to an inventive procedure hereinafter set forth. The semiconductive substrate 7, which can be either polycrystalline or monocrystalline and which can, optionally, have attached thereto the electrode 3, is placed in a vacuum chamber. A barrier material source, a semiconductive material source and, optionally, a metal layer source are also located within the vacuum chamber. By preferred practice the barrier material is chosen to sublime or otherwise vapourise in the vacuum chamber on heating to form a thin molecular barrier layer of from 1 to 5 molecules in thickness over some or all of one major surface of the semiconductive substrate. Immediately thereafter, while the barrier layer coated substrate is still in the vacuum chamber, a thin, radiation penetrable overlayer of the semiconductive material is deposited on the barrier. The semiconductive material is preferably deposited by being heated so that it can be vapour deposited. However, other deposition techniques, such as sputtering and the like can also be employed. The metal source is then activated to form the metal layer by vacuum deposition or sputtering. Subsequent attachment of the electrode 19 to the metal layer, attachment of the electrode 3 and/or packaging can all be accomplished by techniques generally known to those skilled in the art.

While the radiation responsive device has been specifically described as capable of receiving radiation through only one of its semiconductive elements, it is appreciated that the radiation responsiveness of the device can be further increased by forming the device so that both semiconductive elements are radiation penetrable. One way in which this can be accomplished is to form the electrode 3 as a radiation penetrable coating on a transparent insulative substrate, such as a glass plate. The semiconductive element 7 can then be deposited on the electrode 3 and formed in the same manner as the semiconductive overlayer 13. The remainder of the device and the steps for its fabrication need not be altered.

Example 1

A cadmium sulphide-Rhodamine B-cadmium sulphide-gold radiation responsive device is fabricated according to the following procedure: An N conductivity type cadmium sulphide element corresponding to the semiconductive substrate 7 in Figure 1 is chosen which is monocrystalline and has a resistivity of approximately 0.4 ohm-centimetres an electron mobility of approximately 300 cm^2/volt-second and a carrier concentration at 300°K of 5×10^{16} cm^{-3}. The semiconductive substrate is provided with two parallel, square major faces and exhibits dimensions of 0.635 cm on an edge and is 0.159 cm in thickness. The major faces lie in the 0001 or A face of the cadmium sulphide crystal.

The semiconductive substrate is etched for thirty seconds in a solution consisting of equal parts by volume of concentrated hydrochloric acid, glacial acetic acid and distilled water, then rinsed in distilled water and acetone.

The semiconductive substrate is blotted on soft paper, dried and immediately mounted in a liquid nitrogen trapped diffusion pump evaporator with an etched major face approximately 5.8 cm above an electrically heated evaporation boat (R.D. Mathis type S19C) containing a few milligrams of purified Rhodamine B and approximately 38.1 cm above an electrically heated" baffled box " evaporation source containing large crystals of UHP grade

cadmium sulphide. The heating elements of both evaporation sources are formed of tantalum and are outgassed by heating after being filled with a charge of the material to be evaporated. The evaporation system is closed and evacuated to between 4 and 5×10^{-7} torr. over a period of several hours. Sublimation of a barrier layer of approximately 0.45 nm of Rhodamine B (between one and two molecules in thickness) on the etched major face of the substrate is initiated by electrically heating the evaporation boat containing this material. The temperature of the Rhodamine B source is monitored with a chromel-alumel thermocouple. The first evidence of a deposit appears at an indicated temperature of 130 to 150°C. The thickness of the barrier layer is determined by a frequency change of about 8 hertz on a 5 megahertz quartz crystal thickness monitor located about 7.6 cm from the dye source. No rise in pressure is measured during sublimation of the dye.

Next, an estimated 2.5 nm of cadmium sulphide is evaporated onto the barrier layer to form the semiconductive overlayer. This evaporation is carried out slowly at approximately 0.05 nm per second and typically results in a pressure rise in the evaporation system of from about 4×10^{-7} to about 7×10^{-7} torr.

After allowing the evaporation sources to cool, dry nitrogen gas is introduced into the evaporation system, and it is then opened. The sample is lightly clamped to a stainless steel screen with an array of 0.05 cm diameter holes so that the cadmium sulphide overlayer is in contact with the screen. The screen and sample are again placed in the evaporation system about 32 cm above an evaporation boat which has been previously outgassed and which contains gold. The screen allows deposition of a pattern of spaced 0.05 cm gold dots to be formed on the semiconductive overlayer surface. A heat shield is located about 1.9 cm above the gold boat to reduce the radiant energy falling on the semiconductive overlayer surface. The system is then evacuated to approximately 10^{-6} torr. and 30 nm of gold is deposited to form spaced dots on the semiconductive overlayer corresponding to the holes in the stainless steel screen.

Referring to Figure 2, the device is mounted in the circuit schematically shown for the purpose of measuring and plotting its current and voltage (I—V) characteristics as a function of incident radiation. The circuit of Figure 2 also permits measurement of the differential of current with voltage, differential conductance (dI/dV) through the application of an AC bias.

Contact to one of the evaporated gold electrodes on the sample is made with a gold ball probe which corresponds in Figures 1 and 2 to the electrode 19. The probe is electrically connected to point 34 and to the lead X1 in Figure 2. Ohmic contact to the major surface 5 of the semiconductive substrate is achieved by providing an indium-gallium liquid eutectic layer at its interface with an element serving as the electrode 3. Point 36 is in common with the lead Y1. Additional leads X2 and Y2 are provided between leads X1 and Y1. Leads X1 and X2 are connected to either side of the radiation responsive device to measure its I—V characteristics. Between leads Y1 and Y2 is disposed a resistor 40 to permit current measurement using the potential drop across it. Between the points 34 and 36 is located a resistor-capacitor parallel network generally designated 42 and comprising a resistor 44 and a capacitor 46. In series with the network 42 is another resistor 48. Between the resistor 48 and the network 42 is a lead Y3. The X1—X2 and Y1—Y2 terminals are connected to the X and Y axis inputs of a conventional X—Y recorder. An AC voltage source 30 and a variable DC potential source 32 apply voltage to points 34 and 36 within a range of about ±1.5 volts.

In differential conductance (dI/dV) measurements, the AC voltage at Y1—Y2, which is in synchronous phase with the AC voltage source 30, is detected with a lock-in detector. The output of the detector is plotted on the Y axis of the X—Y recorder. In an exemplary reading, the frequency of the source 30 is 2.3 kilohertz, although the AC voltage applied to the device 1 can be varied. The capacitive admittance of the device can be measured by setting the lock-in detector to respond to the out-of-phase voltage across Y1—Y2. Measurements of small changes in conductance or capacitance induced by light are made in an AC bridge configuration by using the lock-in detector on the AC voltage between Y2 and Y3. The lock-in detector can be used as a null detector and by changing the phase control of the lock-in detector, both the in-phase and out-of-phase null conditions can be precisely determined, allowing an accurate bridge measurement of the conductance and capacitance of the device 1.

The spectral response of the device 1 is confirmed by focusing light from the exit slit of a monochromator, such as the Eastman Kodak Company Monochromator Model 2, Serial No. 1, with all slits at 1 mm using a conventional tungsten light source. The device is noted to be radiation responsive over the entire spectral range of from about 480 to 650 nm investigated.

Figure 3 shows the I—V characteristics of the device 1 as fabricated above and forward biased so that the gold contact is positive with respect to the electrode 3. Curve A illustrates the current and voltage relationship in the dark; Curve B illustrates this relationship at room illumination and Curve C illustrates this relationship under intense illumination obtained from a B & L microscope illuminator.

The incident light intensities are estimated as 3.2×10^{14} photons/cm^{2}sec and 5×10^{17} photons/cm^2 sec in Curves B and C, respectively. The gain of the device in electrons per photon is estimated by comparing Curves A and B at 1.7 volts. The increase in current upon illumination is 0.9×10^{-1} amps or 5.6×10^{14} electrons/sec. Since the junction area is 2×10^{-3} cm^2, the number of photons incident per second on the junction in room light is 6.4×10^{11} photons/sec. The gain is thus the quotient of the increase in current divided by the incident photons per second or 8.7×10^3. From other measurements it is believed that the metal layer 15 of the device allows only about 10 percent of the incident photons to reach the semiconductive overlayer. With a transparent metal layer, gain approaches 10^4 electrons per photon.

Example 2

Two devices are made concurrently similarly as the radiation responsive device in Figure 1, except that the substrate of only one of these devices, D, is placed in a position to receive the Rhodamine B dye coating. The semiconductive substrate of the non-dye device, ND, is placed just below the S19C dye boat and a few centimetres laterally displaced so that it receives no dye. It is approximately 32 centimetres above the cadmium sulphide "baffled box" source as compared with the substrate of the D device, which is approximately 38 cm above the cadmium sulphide source. The ND device has a cadmium sulphide overlayer which has a thickness of 3.6 nm as compared to 2.5 nm for the D device.

Figures 4 and 5 contrast the differential conductance (dI/dV) curves at forward bias (gold electrode positive) and the radiation responsiveness of the ND and D devices, respectively. In Figure 4 the lower curve is in the dark and the upper curve in room illumination of roughly 3.2×10^{14} photons/cm^2 sec. These curves are noted to be quite close together, indicating a photocurrent that is small as compared to the dark current. Note that the differential conductance at 0.4 volts is near 1.4×10^{-3} mho.

In Figure 5 a generally lower conductance level is evident—e.g. about 1.5×10^{-6} mho in the dark at 0.4 volts, and, at the same time, the radiation responsiveness of the device D is much larger than that of the device ND. The upper curve 57 is obtained with room illumination while the lower curve 59 is obtained in the dark. The sawtooth pattern of the upper curve arises from the fact that as the voltage is being linearly increased with time at a rate of 0.25 volts/minute room light is periodically removed by covering the device with a dark cloth. Considering the behaviour at V=1.5 volts, note that the conductance in room light is increased by a factor of about 7, that the conductance increase is relatively rapid, being completed in about 5 sec., and the decay, while having a rapid start has a much slower final component persisting for several minutes.

The relationship between the current and the applied potential for the device D is shown in Figure 6 for dark, room light, and illumination, as curves 61, 63 and 65, respectively. It is noted that the dark curren tat 1.0 volt forward bias is less than 1 percent of the current under strong illumination.

Example 3

A device is fabricated according to the method described with reference to Example 1, except that the dye is 4 - (4 - dimethylaminobenzylidene) - 2 - phenyl - 2 - oxazolin - 5 - one. Sublimation occurs upon the heating of the dye to about 150°C. The I—V characteristics are shown in Figure 7 with various illuminations.

Example 4

A device is prepared using the procedure described in Example 1, except that the dye is 3 - ethyl - 5 - [(3 - ethyl - 2 - benzothiazolinylidene)ethylidene]rhodamine. Sublimation occurs upon heating to about 200°C. The I—V characteristics are shown in Figure 8.

Example 5

A device is made using the method of Example 1, except that the dye is Rhodamine 6G. Sublimation occurs near 170°C. The I—V characteristics are shown in Figure 9.

Example 6

A radiation responsive device is made similarly as the device of Example 1, using Rhodamine B, except that the overlayer is approximately 6.0 nm in thickness. The I—V characteristics of this device in the dark and under illumination generally resemble those shown in Figure 6, but show a greater increase in current in going from dark to room illumination. The increase in current density at 1.0 volt forward bias with illumination intensity L of 497 nm photons, making correction for the absorption of the gold electrode, is shown in Figure 10. The gain G in incremental electrons per photon increases from about 10^3 at 10^{14} photons/cm^2 sec to more than 10^4 at 10^{11} photons/cm^2 sec.

WHAT WE CLAIM IS:—

1. A radiation responsive device comprising a radiation penetrable electrically conducting metal layer, a radiation penetrable first semiconductive layer of a first conductivity type conductively associated with the electrically conducting layer, a second semiconductive

The incident light intensities are estimated as 3.2×10^{14} photons/cm^{2}sec and 5×10^{17} photons/cm^2 sec in Curves B and C, respectively. The gain of the device in electrons per photon is estimated by comparing Curves A and B at 1.7 volts. The increase in current upon illumination is 0.9×10^{-4} amps or 5.6×10^{14} electrons/sec. Since the junction area is 2×10^{-3} cm^2, the number of photons incident per second on the junction in room light is 6.4×10^{11} photons/sec. The gain is thus the quotient of the increase in current divided by the incident photons per second or 8.7×10^{2}. From other measurements it is believed that the metal layer 15 of the device allows only about 10 percent of the incident photons to reach the semiconductive overlayer. With a transparent metal layer, gain approaches 10^{1} electrons per photon.

Example 2

Two devices are made concurrently similarly as the radiation responsive device in Figure 1, except that the substrate of only one of these devices, D, is placed in a position to receive the Rhodamine B dye coating. The semiconductive substrate of the non-dye device, ND, is placed just below the S19C dye boat and a few centimetres laterally displaced so that it receives no dye. It is approximately 32 centimetres above the cadmium sulphide "baffled box" source as compared with the substrate of the D device, which is approximately 38 cm above the cadmium sulphide source. The ND device has a cadmium sulphide overlayer which has a thickness of 3.6 nm as compared to 2.5 nm for the D device.

Figures 4 and 5 contrast the differential conductance (dI/dV) curves at forward bias (gold electrode positive) and the radiation responsiveness of the ND and D devices, respectively. In Figure 4 the lower curve is in the dark and the upper curve in room illumination of roughly 3.2×10^{14} photons/cm^2 sec. These curves are noted to be quite close together, indicating a photocurrent that is small as compared to the dark current. Note that the differential conductance at 0.4 volts is near 1.4×10^{-3} mho.

In Figure 5 a generally lower conductance level is evident—e.g. about 1.5×10^{-6} mho in the dark at 0.4 volts, and, at the same time, the radiation responsiveness of the device D is much larger than that of the device ND. The upper curve 57 is obtained with room illumination while the lower curve 59 is obtained in the dark. The sawtooth pattern of the upper curve arises from the fact that as the voltage is being linearly increased with time at a rate of 0.25 volts/minute room light is periodically removed by covering the device with a dark cloth. Considering the behaviour at V=1.5 volts, note that the conductance in room light is increased by a factor of about 7, that the conductance increase is relatively rapid, being completed in about 5 sec., and the decay, while having a rapid start has a much slower final component persisting for several minutes.

The relationship between the current and the applied potential for the device D is shown in Figure 6 for dark, room light, and illumination, as curves 61, 63 and 65, respectively. It is noted that the dark curren tat 1.0 volt forward bias is less than 1 percent of the current under strong illumination.

Example 3

A device is fabricated according to the method described with reference to Example 1, except that the dye is 4 - (4 - dimethylaminobenzylidene) - 2 - phenyl - 2 - oxazolin - 5 - one. Sublimation occurs upon the heating of the dye to about 150°C. The I—V characteristics are shown in Figure 7 with various illuminations.

Example 4

A device is prepared using the procedure described in Example 1, except that the dye is 3 - ethyl - 5 - [(3 - ethyl - 2 - benzothiazolinylidene)ethylidene]rhodamine. Sublimation occurs upon heating to about 200°C. The I—V characteristics are shown in Figure 8.

Example 5

A device is made using the method of Example 1, except that the dye is Rhodamine 6G. Sublimation occurs near 170°C. The I—V characteristics are shown in Figure 9.

Example 6

A radiation responsive device is made similarly as the device of Example 1, using Rhodamine B, except that the overlayer is approximately 6.0 nm in thickness. The I—V characteristics of this device in the dark and under illumination generally resemble those shown in Figure 6, but show a greater increase in current in going from dark to room illumination. The increase in current density at 1.0 volt forward bias with illumination intensity L of 497 nm photons, making correction for the absorption of the gold electrode, is shown in Figure 10. The gain G in incremental electrons per photon increases from about 10^{3} at 10^{14} photons/cm^2 sec to more than 10^{4} at 10^{11} photons/cm^2 sec.

WHAT WE CLAIM IS:—

1. A radiation responsive device comprising a radiation penetrable electrically conducting metal layer, a radiation penetrable first semiconductive layer of a first conductivity type conductively associated with the electrically conducting layer, a second semiconductive

* C L M S *

layer of the same conductivity type as the first semiconductor layer, an electrode conductively associated with the second semiconductive layer, and a barrier layer of a sensitizing dye located between the first and second semiconductive layers and cooperating therewith to limit the current flow between the electrically conducting layer and the electrode as a function of incident radiation penetrating the electrically conducting layer and the first semiconductive layer.

2. A device as claimed in Claim 1 in which the sensitizing dye barrier layer exhibits a surface photovoltage, as herein defined, of at least 0.1 volt with respect to at least one of the semiconductive layers.

3. A device as claimed in Claim 1 in which the radiation penetrable electrically conducting layer is from 10 to 60 nm in thickness.

4. A device as claimed in Claim 3 in which the radiation penetrable electrically conducting layer is from 20 to 30 nm in thickness.

5. A device as claimed in any of the preceding claims in which the radiation penetrable electrically conducting layer forms a rectifying junction with the first semiconductive layer.

6. A device as claimed in any of the preceding claims in which the radiation penetrable electrically conducting layer is gold, copper, platinum, palladium, silver or a mixture thereof.

7. A device as claimed in any of the preceding claims in which the first and second semiconductive layers are both N-type conductors.

8. A device as claimed in any of the preceding claims in which the first and second semiconductive layers are a compound of groups II and VI.

9. A device as claimed in Claim 8 in which the first and second semiconductive layers are cadmium sulphide, cadmium selenide or zinc oxide.

10. A device as claimed in any of the preceding claims in which the first semiconductive layer has a thickness up to 50 nm.

11. A device as claimed in Claim 10 in which the first semiconductive layer has a thickness of from 2.5 to 7 nm.

12. A device as claimed in any of the preceding claims in which the second semiconductive layer comprises a depletion layer from 10 to 1000 nm in thickness on the face in contact with the barrier layer.

13. A device as claimed in any of the preceding claims in which the barrier layer exhibits a surface photovoltage of at least 0.5 volt with respect to at least one of the semiconductive layers.

14. A device as claimed in any of the preceding claims in which the sensitizing dye is a pyrylium or thiapyrylium.

15. A device as claimed in any of the Claims 1 to 13 in which the sensitizing dye is a cyanine or merocyanine.

16. A device as claimed in any of the Claims 1 to 13 in which the sensitizing dye is a triarylmethane dye.

17. A device as claimed in any of the Claims 1 to 13 in which the sensitizing dye is a Rhodamine type.

18. A device as claimed in any of the preceding claims in which the barrier layer has a thickness of from one to five molecules.

19. Radiation responsive devices as claimed in Claim 1 and as herein described.

20. Radiation responsive devices as claimed in Claim 1 and as particularly described in Examples 1 to 6 herein.

21. A method of making a radiation responsive device as claimed in Claim 1 comprising providing the second semiconductive layer as a substrate of a semiconductive material of a first conductivity type capable of transporting majority charge carriers in the presence of an applied electrical field, depositing on the substrate the barrier layer of a sensitizing dye capable of initially accepting the majority charge carriers and capable of releasing accepted majority charge carriers in response to incident radiation, overcoating the barrier layer with a radiation penetrable semiconductive overlayer of the same conductivity type as the substrate and also capable of transporting the majority charge carriers in the presence of an applied electrical field to form the first semiconductive layer, and depositing a radiation penetrable electrically conducting layer over the first semiconductive layer.

22. The method as claimed in Claim 21 wherein the barrier layer is formed by vacuum vapour deposition.

23. The method as claimed in Claim 22 wherein the barrier layer is sublimed in vacuum on the substrate.

24. The method as claimed in any of the Claims 21 to 23 wherein the first semiconductive layer is deposited on the barrier layer by vacuum deposition of the semiconductive material.

25. The method as claimed in any of the Claims 21 to 24 wherein the electrically conductive layer is formed by vapour deposition of a metal.

26. Methods of making radiation responsive devices as claimed in Claim 1 and as herein described.

L. A. TRANGMAR, B.Sc., C.P.A.,
Agent for the Applicants.

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