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FAR-INFRARED PHOTODETECTOR

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1 Claim

ABSTRACT OF THE DISCLOSURE

A new class of semiconductor photodetectors are fabricated by doping ionic single crystals with rare-earth dopants. When these doped crystals are cooled and a potential is applied across the crystal, it functions as an image converter, converting incident infrared radiation into visible components.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to photodetection devices and more particularly to the use of rare-earth-doped ionic crystals as the active material for semiconductor photodetection devices. Ionic single crystals have been considered to be poor materials for use in photoelectric applications because of the large energies necessary to raise either valence or trapped electrons into conduction bands. These crystals have also been considered poor materials because of the short lifetime of the conduction electrons thus produced. In these crystals the free electrons that might have existed within the crystal are attracted and held by either impurity ions or other defects, such as vacancies in the crystal lattice. It is therefore necessary to supply more energy to the crystal to free these electrons for conduction than in the covalently bonded substrate configurations.

The present invention is a rare-earth-doped ionic single crystal which exhibits only shallow trapping effects. Because of the relatively high concentration of rare earth dopants, a relatively wide impurity band is formed. The increased width of this impurity band allows the electrons trapped by the rare earths to be effective charge carriers in this ionic crystal. These shallow traps can either directly absorb low energy photons in the near infrared or phonons of still lower energy. Either of the effects will cause an increase in the electrical conductivity of the sample. Thus, for example, rare-earth-doped ionic crystals of CdF_2 will detect radiation in the far infrared as well as light in the visible portion of the spectrum. The term "rare-earth dopant," for the purpose of this application, is not meant to exclude the use of closely related metals such as scandium and yttrium in group 3b of the periodic chart.

It is therefore an object of this invention to produce a new class of semiconductors, consisting of ionic crystals which have shallow electron traps that result from either rare-earth doping or doping with closely related metals.

It is a further object of this invention to rare-earth-dope ionic crystals so that they function as semiconductor photodetection devices.

It is a still further object of this invention to utilize rare-earth-doped ionic crystals as image converters.

Rare-earth-doped ionic crystals as semiconductor photodetection devices

In semiconductor-photodetection devices there are two processes by which valence electrons acquire enough energy to move into the conduction band; one a photo-

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electric process, the other a thermal process. Electrons having the requisite energy are freed from their respective atoms to flow through the semiconducting material. The amount of energy necessary to produce this electron flow in ionic crystals is relatively large as compared to covalently bonded crystals. In order to produce this flow, energy on the order of 5 to 10 ev. must be supplied to the crystal. Heavy doping with rare-earth elements, whose outer shells have different properties than the host atom for which they have been substituted, produces centers for which the needed energy is considerably less than for the pure crystal. The use of relatively high concentrations of rare-earth dopants allows broad energy absorption from either photoelectric or thermal sources. For the purpose of this application, relatively high concentrations of dopants refers to atomic concentrations exceeding .01%. Prior art photodetectors have relied primarily on photoelectric sources to provide the energy needed to produce electron flow. Since pure ionic crystals are relatively transparent over most of the visible and infrared spectrum, broad-band absorption by multiple doping not only supplies photoelectric energy but also supplies thermal energy to the ionic crystal.

In one configuration, single ionic crystals of rare-earth-doped CdF_2 exhibited such shallow trap properties that energies of 2×10^{-9} watts were able to cause current flow. CdF_2 doped with rare-earth ions becomes a semiconductor when it is baked in a cadmium vapor. As grown, the crystals have trivalent rare-earth ions substituted for Cd^{++} and charge compensation is obtained through interstitial F^- ions. It is believed that during the baking process, neutral fluorine ions diffuse to the surface to react with the cadmium vapor leaving a free electron behind. Electron spin resonance studies indicate that at low temperatures the electron is only weakly bound to the rare-earth ion. For 0.1% doped samples, Hall effect studies show that between room temperature and 100° K., the concentration of free electrons varies as

$$n = n_0 e^{-E/kT}$$

where the activation energy is about 0.16 ev. Below 100° K. the decay is much slower; the conductivity activation energy is about 0.003 ev. All these observations indicate that at low temperature conductivity is through an impurity band. Lightly doped samples in the semi-conducting state have an absorption band in the far infrared. For more highly doped samples, 0.1% gadolinium, this band extends into the visible. Typical optical densities run as high as 0.2 at 6000 Å. This absorption remains even at helium temperatures and is thus not due to free carriers. Photoconductivity due to absorption in this band has been observed at 4.2° K. for 0.1% lutetium, 0.3% yttrium, 0.1% gadolinium and 0.06% terbium from 0.4μ to 20 μ. For 0.1% lutetium and 0.1% gadolinium samples, the photoconductive response has been shown to be proportional to the absorbed power and independent of incident wavelength. Between 5 μ and 20 μ, the linearity with energy is good to within 3%. As one goes further towards the visible, the response increases slightly; however, the deviation from linearity is only 20% at 0.5μ. Although the spectral response of the system is similar to thermal detectors, the time constant of the system, as measured with a Q switched CO_2 laser operating at 10.6μ, is approximately 10^{-6} sec. for a 0.06% terbium sample. This is much faster than the usual 10^{-2} sec. decay times for existing thermal detectors.

The responsivity of 0.1% lutetium and 0.3% yttrium samples were both in the range of 40 volts/watt with only a 25-volt bias across the sample. For 0.01% ytterbium and gadolinium samples, the response was down by a 1000. This sharp decrease is consistent with the impurity banding model for the system. A preliminary rough measure-

ment found a minimum value for D^* to be 4×10^9 cm. (c.p.s.) W^{-1} for a 0.3% yttrium-doped sample with a 2π window to 300° K.

The observed far-infrared photoconductivity is due to impurity banding-type effects. Nevertheless, the high temperature, semiconductive behavior indicates the pure host crystal has a conducting band of its own. Consequently, the mobility of a given electron can be a complex function of both its own energy and the temperature of the crystal lattice. The infrared-induced free carrier could very well be excited to a state of very different mobility than the majority of thermal electrons. In the process of decaying into a hypothetical reservoir of thermalized free carriers with low mobility, it might very well excite some of the carriers to states of higher mobility and thus enhance the "quantum efficiency" of the device.

It will be appreciated that elements other than the rare earths lutetium, gadolinium and terbium and the non-rare earth yttrium may be used as dopants on other ionic monocrystalline substrates. For example, the rare earths neodymium, samarium, dysprosium, holmium, erbium, thulium and terbium and the non-rare earth scandium have all been shown to yield good semiconductors when added to CdF_2 . One should also expect HgF_2 to behave analogously to CdF_2 . Similar electronic properties (i.e. semiconduction) have also been observed in other compounds, $SrTiO_3$, NiO and TiO_2 . It will be appreciated that any ionic crystal will have similar properties with the formation of the appropriate low energy trap.

It will be further appreciated that any method of epitaxial deposition, such as zone melting or baking, may be used to fabricate these semiconductors.

Rare-earth-doped ionic crystals as image converters

Infrared radiation may be made visible to the human eye only if the infrared radiation is converted into light in the visible region of the spectrum. One method of conversion encompasses illuminating atoms with infrared radiation in such a manner that reradiation from the excited atoms falls in the visible region. While this method has been used with conventional semiconductors, it has not been applied to ionic crystals.

Application to rare-earth-doped ionic crystals involves both cooling the crystal and applying a large-bias voltage normal to its faces. When rare-earth-doped ionic crystals are cooled to a region between 1° K. and 77° K., conductivity of the doped crystal ceases due to the removal of energy from the crystal lattice. However, by applying a large bias voltage to the cooled crystal when infrared radiation is incident upon the crystal, the resultant free carriers move in the applied field and excite other rare-earth ions. When these excited ions fall back to their

ground states, they emit visible radiation. This phenomena is explained in terms of a depletion layer at one surface of the crystal since electric fields large enough to give the free carriers sufficient energy to excite the visible light cannot be attained in a crystal of even modest conductivity. Thus what is necessary is a "depletion layer" which is relatively free of high mobility charge carriers or true electrons. Thus an infrared-induced electron that gets into this layer will find a large field there and be rapidly accelerated to the necessary energy. Inhomogeneous CdF_2 crystals, where one region is semiconducting and another is insulating, may be used for image conversion from the infrared to visible portion of the spectrum. Emission results only when electrons move from the semiconducting region to the insulating region. This effect may be produced from a device made in the form of a flat plate, one surface of which being reduced and therefore photoconductive. The other surface of the plate is not reduced and is therefore insulating. If either an AC or DC voltage is applied normal to the face, the infrared-induced electroluminescence mechanism operates to produce visible radiation.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claim the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A radiant energy responsive element for use in the far infrared comprising:

an ionic single crystal selected from the group consisting of CdF_2 , HgF_2 , $SrTiO_3$, NiO and TiO_2 ; and a dopant added to said crystal,

said dopant being selected from the group consisting of lutetium, yttrium, gadolinium and terbium and the atomic percentage of the selected dopant being 0.1% lutetium, 0.3% yttrium, 0.1% gadolinium and 0.06% terbium.

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