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PHOTOELECTRIC EFFECTS IN HIGH-RESISTIVITY EuSe

K. Yamada(†), J. Heleskivi and H. Stubt

Technical Research Centre of Finland, Semiconductor Laboratory and Helsinki University of Technology, Electron Physics Laboratory, Otakaari 5 A, SF-02150 ESPOO 15, Finland.

Résumé.- On a étudié les propriétés des monocristaux d'EuSe rouge transparent de haute résistivité au moyen de la photoconductivité et de la tension de photodiffusion avec des photons d'énergie plus basse ou égale à celle-ci de la bande interdite E_g. Les points principales des spectres obtenus par la photoconductivité ou photovoltaïque se trouvent à l'énergie de 1,85 eV équivalente à E_g dans EuSe. On a trouvé deux niveaux de défaut aux énergies 1,3 eV et 1,67 eV respectivement.

Abstract.- The properties of red-transparent high-resistivity EuSe single crystals have been studied by means of the photoconductivity and photodiffusive voltage with photon energies less or equal to the forbidden energy gap E_g. In both the photoconduction and photovoltage spectra the main peak is situated at a photon energy of 1.85 eV corresponding to E_g in EuSe. Two defect levels were found at photon energies 1.3 and 1.67 eV.

1. Introduction.- As-grown EuSe single crystals are n-type magnetic semiconductors with a room temperature dark conductivity σ of 1 Ω^{-1}cm^{-1} and a carrier concentration n of the order of 10^{18} cm^{-3} [1]. The carrier source seems to be a shallow donor level caused by a small deviation from stoichiometry to the Eu rich side [2]. The crystals exhibit a large dip in the conductivity near the magnetic ordering temperature and an anomalously strong negative magnetoresistance. The reason for these phenomena at least at small external fields has recently been shown to be the localization of the free electrons at the donor levels [3,4]. Annealing of the crystals decreases the conductivity by orders of magnitude and makes them red transparent. A plausible explanation for the conductivity decrease is a decrease in the carrier concentration caused by highly improved stoichiometry. In the annealed crystals no large negative magnetoresistance can be found and also detections of other galvanomagnetic properties become difficult because of the high resistivity [4]. On the other hand photoconductivity has been used to study the properties of the crystals [5,6]. In these studies the main peak of the photoconductivity has been found in the vicinity of the energy gap E_g, whereas no detailed structure was found at photon energies hν < E_g. In some cases the results were interpreted as p-type conduction in a broad valence band overlapping the 4f level.

The purpose of this work is to study the defect levels situated in the forbidden gap by photoconductivity measurements. Additionally, the photodiffusive voltage is measured in order to verify the diffusion of both types of carriers.

2. Experimental procedure.- The EuSe single crystals were grown in sealed crucibles from a Eu rich solution [2]. The (100) cleavage planes of the crystals showed dislocation etch pits with a density in the range 10^{6}-10^{8} cm^{-2}. Besides an almost uniform pit distribution, there were also linear [100] and [110] oriented arrays resulting from slip bands.

The studied as-grown sample (assigned by SI in the following) showed n-type conduction of the order of 10^{8}-10^{10} Ω^{-1}cm^{-1} at room temperature and a free electron concentration of about 10^{18} cm^{-3}. No photoelectric phenomena could be observed in this crystal because of the high equilibrium carrier concentration.

(+†) On leave from Saitama University, JAPAN.
In order to decrease the carrier concentration and increase the transparency of crystals with intrinsic radiation (\( \lambda = 6700 \AA \)) show conduction dominated by electrons, an annealing procedure was carried out in an argon atmosphere at a temperature of 1600 °C for times between 50 to 100h. This process makes the crystals transparent to red light. Cubic voids with dimensions of some \( \mu m \) were seen, the total amount being a few per cent by volume. After annealing the room temperature dark conductivity of the crystals ranged from \( 10^{-7} \Omega^{-1} \text{cm}^{-1} \) (S2) to \( 10^{-9} \Omega^{-1} \text{cm}^{-1} \) (S3, S4 and S5).

There have been several well known difficulties in making contacts on high-resistivity EuSe crystals. The methods, which have been used in earlier studies include In soldering by an ultrasonic iron and alloying LaAg to the material. The former method results in rectifying contacts on high-resistivity samples whereas the second method includes doping of the crystal by the alloy material. In the following study we have started the procedure to make contacts by soldering In onto the surfaces by an ultrasonic iron. An electric discharge technique was then used to break down the barriers between the In and the semiconductor. The discharge field was concentrated to the barrier regions by lowering the resistance of the semiconductor bulk by strong illumination. As a result of the procedure low-noise barrierless contacts were obtained, which made it possible to detect bulk photodiffusive voltages.

3. Experimental results and discussion.

Figure 1 shows the generated photodiffusive voltages \( V_p(x) = V_1 - V_2 \) of the samples. The results of S2 and S5 show almost ideal characteristics for a uniform bulk photodiffusive voltage. S3 and S4 on the other hand show a randomly distributed voltage, indicating the presence of inhomogeneties. The microscope inspection actually revealed several defect arrays across the sample S3 but only one near the electrode of the sample S4. The following studies are made on the uniform crystals S2 and S5. The polarities of the voltages for these...
supposed in the introduction, S2 should have a carrier concentration of $10^{12}$ cm$^{-3}$ and S3 to S5 a concentration of $10^{15}$ cm$^{-3}$. If the crystals further are supposed to have normal conduction and valence bands they should be ideal for photoelectric studies of impurity levels and diffusion of carriers.

In the more conductive sample S2 a peak additional to the fundamental peak at 1.85 is seen at 1.2 eV in the photocurrent and 1.3 eV in the photodiffusive voltage. The peak is believed to correspond to an impurity level at 0.55 eV below the conduction band in accordance with the thermal activation energy of S2. The polarity of the photovoltage corresponds to conduction by electrons in the whole spectral range and most likely also in the dark condition. In the more resistive sample S5 only the fundamental peak can be seen in the photoconduction. On the other hand, the photovoltage shows a sign reversal with a peak value at the energy 1.67 eV corresponding to a level 0.18 eV above the valence band and to conduction dominated by holes.

Further investigations will be made in order to clarify the nature of the defect levels and to detect possible movements of the levels comparing with the fundamental peak at low temperatures and external magnetic fields. Also the role of the internal barriers in connection with thermally activated photoconduction and the transient photoconductivity will be clarified.

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