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PHOTOELECTRICITY OF β-AgI UNDER SUB-BANDGAP ILLUMINATION

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An experimental study of the spectral, intensity and temperature dependences of the photoconductivity and contact photovoltage of β-AgI single crystals under sub-bandgap illumination is carried out. Both dc and ac photoconductivity experiments are performed and dark-to-light relaxation characteristics of the contact photovoltage are investigated. It is found that the processes under consideration are of a unified character in the spectral region below 2.20 eV, in which the photoconductivity spectrum follows Urbach's rule, temperature behaviour is opposite to that of dark conductivity and dependence on exciting light intensity is linear. A simple model is proposed to explain qualitatively the results obtained, based on the assumption for photoexcited ionic-type conductivity.

1. Introduction

There has been in the last decade a great number of papers devoted to the study of the optical [1–6], and transport [7–10] properties of β-AgI. Among those properties a most explored one is photoconductivity. However there has been a large disproportion in the progress in our knowledge of β-AgI photoconductivity spectra in the intrinsic and extrinsic (sub-bandgap) absorption ranges respectively. While the former ones have been rather thoroughly studied, the sub-bandgap spectral region is far less known. This is due in large extent to difficulties in carrying out the experiment: small single crystal dimensions, presence of small output signals, spurious electrode effects, etc. The present paper is concerned with such an experimental study of the spectral, intensity and temperature behaviour of the photoconductivity and contact photovoltage of β-AgI single crystals under sub-bandgap illumination. Some relaxation processes as well as the dependence of both dark and photocurrent on the drift-voltage frequency have also been investigated. The following main results have been obtained:

(i) Extrinsic photocurrent and contact photovoltage follow Urbach's rule in a large interval.

(ii) They both depend upon light intensity in a sublinear way in the vicinity of the absorption edge while being linear at lower energies.

(iii) The temperature behaviour of photoconductivity is just opposite to that of dark conductivity.

A simple model is proposed to explain qualitatively these results by the assumption for a photoexcited ionic-type conductivity of β-AgI samples.

2. Experimental

Numerous hexagonal β-AgI single crystals grown from AgI solution in iodine acid [11,12] were investigated. The average samples dimensions were of order of 3 × 2 × 1 mm^3, with dark resistivity of about 10^7 Ω m. Either silver or carbon pastes were used for preparing the sample electrodes. Direct as well as alternating current measurements were performed, the results obtained being to a large extent identical in the two cases. A prism monochromator and a high-power filament lamp were used as exciting sources.

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All the experiments were carried out in ambient atmosphere.

2.1. Spectral dependences

A typical experimental photocurrent spectrum of a (Ag/AgI/Ag) cell detected under application of an 0.1 V dc electric voltage is shown in fig. 1. The two curves in the figure present the results obtained by scanning the light wavelength in opposite directions (curve a corresponds to increasing the wavelength). All the photocurrent values were read long enough after the onset of the illumination (i.e. under steady state conditions). The difference between the two curves observed in the vicinity of the absorption edge (430 nm) appears to relate to very slow relaxation recharge processes involving defect or impurity levels. Such processes are known to be very sensitive to conditions prior to illumination. As is seen, no differences of this kind are observed at light wavelengths greater than 540 nm.

The spectrum a from fig. 1, normalized to a constant light intensity of about 5×10^{20} m^{-2} s^{-1} is given in fig. 2. The normalization procedure was applied only to the spectral region $\lambda > 540$ nm where the photocurrent intensity dependences were found linear (see further). The more complicated sublinear intensity dependences, observed for $\lambda < 540$ nm, were not used to normalize the spectrum. Using the method of least squares the following exponential

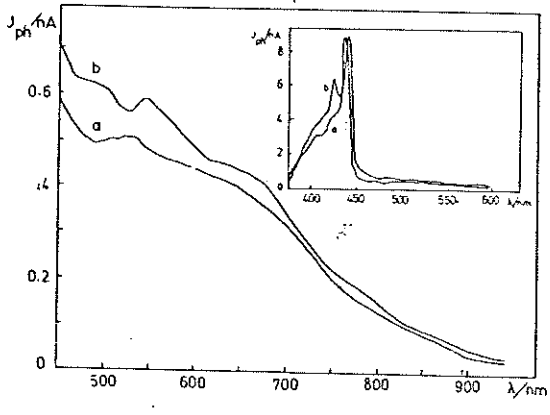

Fig. 1. Photocurrent J_{ph} versus exciting-light wavelength λ. (a) Spectrum obtained by increasing the wavelength; (b) Spectrum obtained by decreasing the wavelength. Insert: spectra of the photocurrent in the intrinsic spectral region.

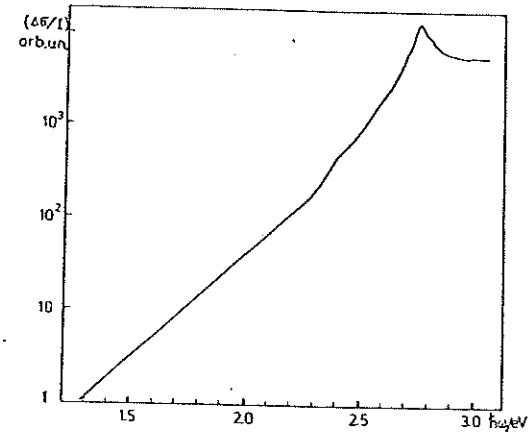

Fig. 2. Normalized photoconductivity $\Delta\sigma/I$ versus photon energy $\hbar\omega$.

approximation of the experimental data was obtained:

$$\Delta\sigma \propto \exp(\beta\epsilon) , \quad (1)$$

where $\epsilon = \hbar\omega$ is the excitation light energy, and β is a constant. The value of β for the sample under consideration is $4.92 \pm 0.5\%$ eV^{-1}. Other investigated crystals have given values lying between 4.3 and 5.4 eV^{-1}, with an average value of $5.0 \pm 8\%$ eV^{-1}.

Another aspect of the experimental results here obtained is that the illumination of the β-AgI cells was found possible to produce a dc voltage, having values up to 0.2–0.3 V. We suppose that this voltage is due to a difference in the electrodes' parameters, which gives rise to different contact-potential barriers at the two crystal ends under illumination. The spectral dependences of this contact "photovoltage", measured in an (Ag/AgI/Ag)-cell are shown in fig. 3 (curves are marked in the same way as in fig. 1). An inversion of the photovoltage sign at about 432 nm wavelength was typical for all investigated cells.

Measurements have also been carried out on (Ag/AgI/C)-cells and results principally different from previous ones were obtained. In fact, no sign inversion was observed in this case and the magnitude of the contact photovoltage was much greater. Additionally, the photovoltage spectrum was found quite similar to that of the photocurrent (fig. 1). In all the experiments the carbon electrode of such a "photobattery" was positively charged. Besides, if the positive pole of the dc drift-source was connected to the carbon electrode the current was about two orders of

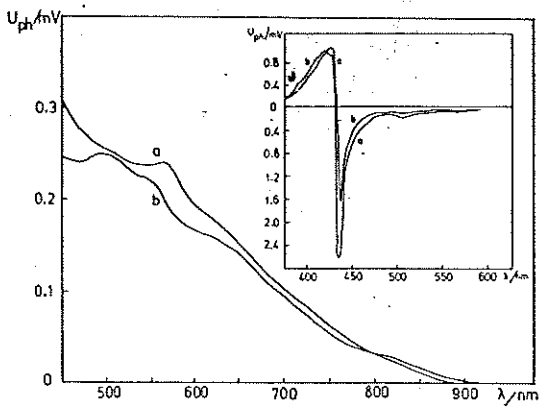

Fig. 3. Contact photovoltage U_{ph} versus exciting-light wavelength λ. (a) Spectrum obtained by increasing the wavelength; (b) Spectrum obtained by decreasing the wavelength. Insert: spectra of the contact photovoltage in the vicinity of the absorption edge.

magnitude lower than the opposite one, both in darkness and under illumination.

2.2. Intensity dependences

The photocurrent intensity dependences obtained at various wavelengths are given in fig. 4. As is evident the relationship between the photoconductivity and the exciting light intensity can be approximated by

$$\Delta\sigma \propto I^{s}\,, \tag{2}$$

where s depends on the light- wavelength. The intensity dependences are linear ($s = 1$) in the spectral region $\lambda > 540$ nm and sub-linear ($s < 1$) for $\lambda < 540$ nm, at 430 nm s is equal to 0.70 in consistence with the results, obtained by Cochrane [3].

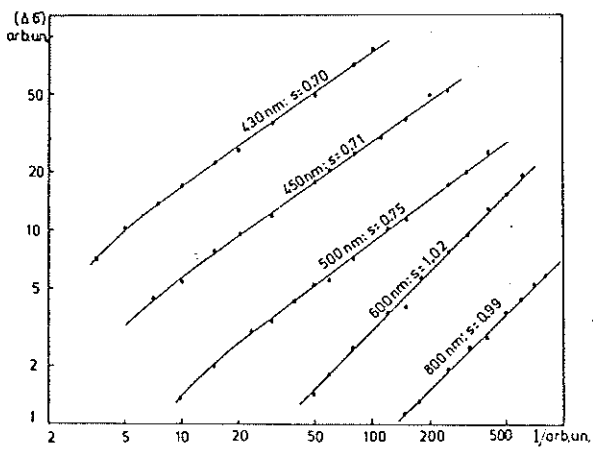

Fig. 4. Photoconductivity $\Delta\sigma$ versus exciting-light intensity I at various wavelengths.

2.3. Temperature dependences

Temperature measurements of dark- and photoconductivity have been carried out in the temperature range from 20° to 110°C. The dark-conductivity activation energies obtained for different crystals lie between 0.5 and 0.9 eV, in accordance with previous studies [7,8,13] (a typical curve of dark-conductivity versus the inverse temperature for a (Ag/AgI/Ag)-cell is inserted in fig. 5). Photoconductivity dependences on the inverse temperature are given in fig. 5 at various wavelengths. In this case the following exponential approximation is possible

$$\Delta\sigma \propto \exp(\mu/kT)\,, \tag{3}$$

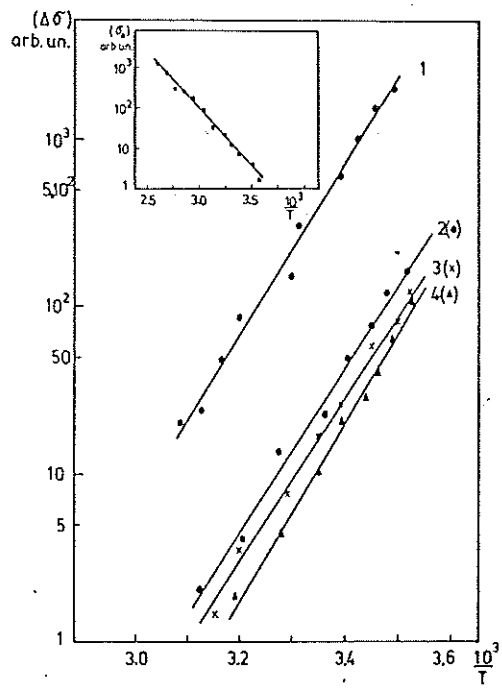

Fig. 5. Photoconductivity $\Delta\sigma$ versus the inverse temperature $10^3/T$ at various light wavelengths. (1) $\lambda = 430$ nm, $\mu = 1.02$ eV; (2) $\lambda = 450$ nm, $\mu = 0.98$ eV; (3) $\lambda = 600$ nm, $\mu = 0.97$ eV; (4) $\lambda = 700$ nm, $\mu = 1.07$ eV. The dependences are measured with a (Ag/AgI/Ag)-cell. The accuracy in determining μ is about 10%. Insert: dark conductivity σ_0 versus the inverse temperature, corresponding activation energy is 0.57 eV.

where k is Boltzmann's constant, T is the absolute temperature, and μ acquires values in the interval 0.9–1.5 eV for different crystals. In addition μ was found to change weakly with the light wavelength. The eq. (3), however, could not be checked out precisely because the photoconductivity practically vanished at about 45°C. For the same reason the determination of the temperature dependence of the constant β in eq. (1) was rather difficult to carry out.

2.4. Frequency dependences

ac photoconductivity experiments were also carried out at various frequencies of the electric field. The photocurrent was found to be independent of the drift-voltage frequency up to about 3 kHz both in the cases of silver and silver-carbon electrodes. Above this frequency it decreased due to the circuit impedance losses.

2.5. Relaxation processes

The dark-to-light transient characteristics of the contact photovoltage are shown in fig. 6 at various light wavelengths. An approximation involving linear recombination processes was applied to their treatment, the results obtained showing the presence of two principally different types of relaxation processes. The first one characterized with a relaxation-time constant of about 100 s, was observed in the whole spectral region under consideration. The second one ($\tau \lesssim 10$ s), manifested itself only in the region $\hbar\omega >$ 2.20 eV and was related to peculiarities in the transient characteristics at energies 2.35, 2.56 and 2.83 eV. It is noticeable that the latter energy is equal to the energy gap of β-AgI.

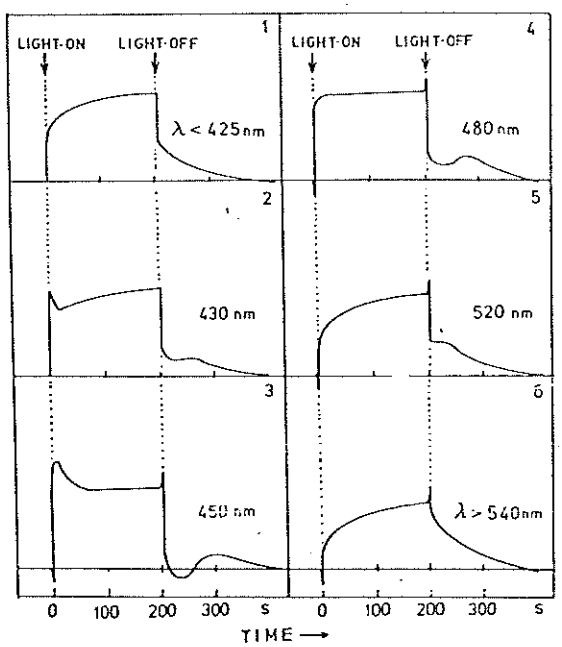

Fig. 6. Relaxation dark-to-light transient characteristics of the contact photovoltage at various light wavelengths.

3. Discussion

The observed processes are of unified, unchangeable character only in the spectral region $\hbar\omega \lesssim 2.20$ eV, where the intensity dependences of both photocurrent and contact photovoltage are linear and their normalized spectra follow Urbach's rule (1) with temperature dependence given by eq. (3). In this spectral region the sign of the contact photovoltage is opposite to that corresponding to band-to-band electron excitation ($\hbar\omega > 2.83$ eV) and coincides with the sign of the dark voltage. This fact suggests that light-excited carriers are positively charged, a result confirmed also by the above mentioned dc photocurrent measurements of cells with two silver and silver–carbon electrodes. Transient dark-to-light characteristics of the contact photovoltage are exponential and do not exhibit any special features.

On the grounds of these results it is natural to assume that β-AgI photoconductivity in the $\hbar\omega < 2.20$ eV spectral region predominantly has ionic origin. Possible basis of such light-stimulated ion conductivity might be the photoionization of Ag and I atoms, located in the lattice sites or in the interstitials. The concentration of thus excited ion pairs is described by Boltzmann's factor (Kostadinov [14])

$$N \propto \exp[-U(R)/kT] \,, \tag{4}$$

where R is the distance between ions and $U(R)$ is the pair-interaction energy, equal to absorbed light energy

$$\hbar\omega = -U(R) = E_{\mathrm{fin}} - E_{\mathrm{in}} \,. \tag{5}$$

For such a mechanism of excitation both optical absorption and photoconductivity follow Urbach's rule,

the additional Ag^+ "photoions" moving through the interstitials in a similar way to equilibrium ones.

The increase of light energy above 2.20 eV is accompanied by an electron component that adds to the discussed above and is due to light-stimulated electron transitions into the conduction band. This electron component strongly increases in the vicinity of the absorption edge ($\hbar\omega \sim 2.83$ eV), thus making the ionic component undetectable. For this reason the contact photovoltage sign in fig. 3 is inversed and changes of the transient characteristics arise.

To support the mixed character of the excitation processes in the spectral region $\hbar\omega > 2.20$ eV come the sub-linear intensity dependences of the photocurrent and the contact photovoltage, with s tending to 0.5 for light energies higher than bandgap energy.

It should be noticed that the considerations presented here are of preliminary character, and further experimental and theoretical studies are expected to show the extent to which such a hypothesis for light-excited ionic conductivity in β-AgI is reasonable.

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