

METHODOLOGICAL NOTES

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Persistent photoconductivity in semiconducting III – V compounds

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Contents

Abstract. **Evidence for persistent photoconductivity, i.e. electrical conductivity changes existing for a very long time after the excitation of nonmetallic solids by photons, was furnished back in the 19th century and put to practice even before modern solid-state physics had developed. At present, two complementary models are basically used to explain this phenomenon. One involves the trapping of nonequilibrium charge carriers by point centres of localization (traps) which slows down the recombination of electrons and holes generated by light or charged particles. In the other, electrons and holes are also separated spatially and prevented by potential barriers from recombination. Both types of relaxation process are discussed and experimental data, with special emphasis on the charge separation idea, presented.**

1. Introduction

Since the quantum nature of photoionization was established by Gudden and Pohl in their classical experiments [1] it has been known that the quantum yield of photoconductivity, i.e. the ratio of the number of nonequilibrium charge carriers (NEC) passing through a semiconductor excited by photons to the number of the ionizing photons can many times exceed unity. The notion of secondary photoelectric currents and the 'intrinsic amplification' effect were used rather frequently in the early studies of photoconductivity. A quantitative analysis of photoconductivity in homogeneous semiconductors was carried out by R Bube [2] and S M Ryvkin [3]. A review of the numerous works published before 1976 was made by Sheĭnkman and Shik [4]. At present there exist two complementary models to account for the above-mentioned phenomena. The first to appear was the model based on the concept of NEC trapping by strongly localized states in the vicinity of point defects or deep impurities. The recently published works by Volkov and Khokhlov [5] disseminate new ideas concerning the important role of metastable states of the trapping centres in the occurrence of long-time relaxation or 'persistent photoconductivity' (PPC). The second model involves spatial inhomogeneities near a semiconductor surface or in the vicinity of clusters of defects due to crystallization or to bombardment by heavy ions and fast neutrons [6, 7].

Queisser and Theodorou [8, 9] published extensive data on PPC in GaAs layers containing macroscopic potential barriers.

2. Experimental data

It is a well-known fact that as distinct from the effect of heavy ions (implantation), irradiation by fast electrons or gamma-rays entails first of all the appearance of randomly distributed point defects, originally – Frenkel pairs. Their components — the interstitial atoms and vacancies — subsequently interact with one another and with chemical impurities. The indicated distinction between the properties of semiconductors subjected to ion implantation or irradiation by fast neutrons on the one hand and to irradiation by fast electrons or gamma-rays on the other hand may assist in clarification of the role of principal mechanisms responsible for PPC.

Important results were published by Brailovskii et al. [10]. The authors observed PPC in the compound GaP exposed to electrons of very high energies (7.5 and 50 MeV). They revealed PPC in the spectral region corresponding to photon energies much lower than the energies of interband optical transitions. According to the authors, PPC is due to point defects caused by electron irradiation; however, after high-temperature annealing the same crystals exhibited clusters of defects and the specimen became inhomogeneous.

Goldberg et al. [11] reported new data on the temperature dependence of the spectral distribution for the quantum yield of photoionization in GaP near the surface potential barrier. In the authors' opinion, the increase in the quantum yield with increasing sample temperature was caused by the following processes: for light absorption, along with the generation of pairs of nonequilibrium carriers there also

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occur excitons. To the best of our knowledge, the ratio between the number of pairs of NEC and excitons has not been theoretically evaluated, but the fact that excitons do occur is undoubted. Some of the excitons dissociate as a result of thermal excitation, thus promoting an increase of the quantum yield with temperature. The PPC effect in GaP was observed by a number of authors at liquid nitrogen temperature [12–15]. Recently, Zardas et al. [16] discovered the PPC effect at 300 K in GaP single crystals doped with sulfur. The light source used in the experiment had a wavelength of 640 nm.

A model of the PPC effect induced by clusters has been proposed by Theodorou and Symeonidis [17] who claim that the potential barrier on the boundary of a cluster of defects spatially separates the carriers due to light absorption, thus multiply decreasing their recombination rate. When PPC is produced in crystals containing planar potential barriers, the ratio of the number of nonequilibrium carriers to the logarithm of the radiation dose must be linear. In the case of PPC due to defect clusters, the dependence may be other than linear. Data on PPC kinetics (the rise and decay of the PPC signal) in GaP : S at 300 K were first presented in Ref. [16] where they were associated with the action of the clusters of defects. The photoelectric current increases with the radiation dose and then tends to saturation (Fig. 1). The decrease (attenuation) of the photoelectric current with time after turning off the excitation by light is shown in Fig. 2. The decrease of the photoelectric current, more precisely the current corresponding to PPC, is described by a logarithmic function, as follows from Ref. [17].

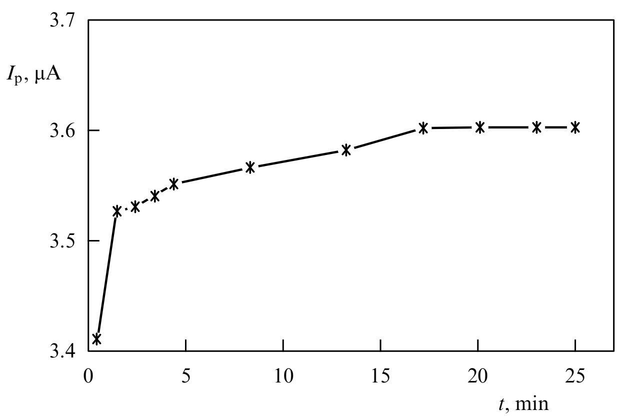

Figure 1. Heightening of the PPC effect with the duration of irradiation (the photon fluence); $T = 300$ K, $\lambda = 640$ nm.

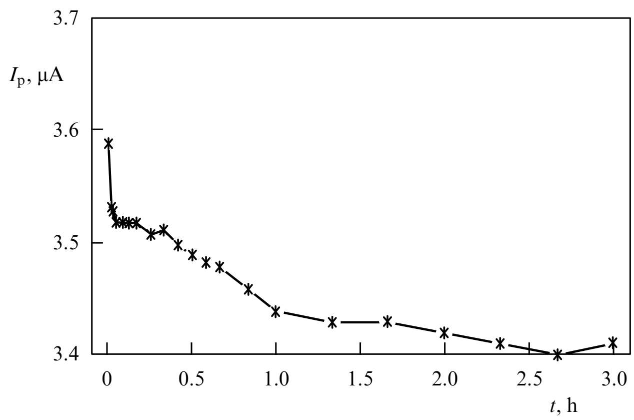

Figure 2. Attenuation of the photoelectric current with time; $\lambda = 640$ nm.

3. PPC-like relaxation phenomena initiated by fast electrons

It is well known that not only photons, but also other types of ionizing radiation (fast electrons and other charged particles) generate a large number of nonequilibrium charge carriers when they pass through semiconductors [7]. The recombination processes may proceed through different 'channels', and when the carriers are trapped by local centres or are spatially separated, the reversion of the excited semiconductor to the original equilibrium state may be exceedingly slow. In semiconductors characterized by effective luminescence, its intensity and attenuation kinetics can be used to obtain data on the relaxation of the unsteady state instead of or in parallel with PPC measurements. One should bear in mind that fast electrons, like other types of ionizing radiation, affect the concentration of the radiation defects and their migration in an exposed sample [18]. One of the advantages of the luminescence-based methods of studying the relaxation of excited semiconductors is the feasibility of applying sharply focused electron beams. This method was used by Saparin and his colleagues [19] in a study on gallium nitride and other semiconductors. The authors examined the kinetics of cathodoluminescence (CL) in heteroepitaxial GaN : Zn layers, as well as in CdS and ZnO single crystals using a Stereoscan MK-11 scanning electron microscope (SEM) with a high electron-beam density (up to 100 A cm^{-2}). At high excitation levels, local heating could result in the rupture of chemical bonds and in the formation of defects [20]. Figure 3 demonstrates the kinetics of room-temperature cathodoluminescence efficiency for three substances: GaN : Zn, ZnO, and CdS [19]. The run of the curve for CdS is apparently due to degradation of the material in the course of which the number of nonradiative recombination centres increases. The cathodoluminescence efficiency in ZnS crystals did not change. In the GaN : Zn samples, at the beginning of irradiation with electrons (nearly 100 s) the intensity of cathodoluminescence increased. The maximum intensity for different current densities corresponded to the integral flux (dose) $Q \simeq 2 \times 10^2$ C cm^{-2}. The increase in the cathodoluminescence intensity is assumed to be either due to the generation of new radiative recombination centres or to a weakening of the parallel channel of nonradiative recombination. The growth

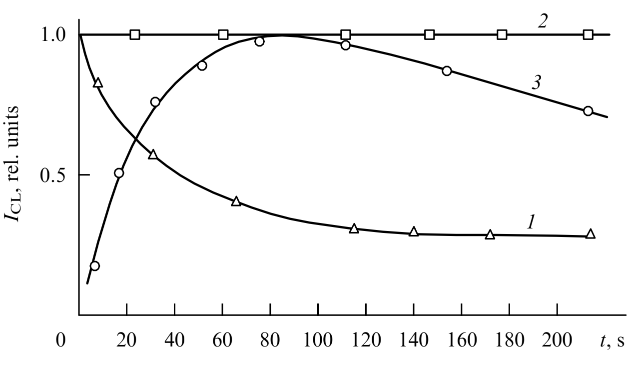

Figure 3. Kinetics of room-temperature cathodoluminescence yield for CdS (*1*), ZnO (*2*) and GaN : Zn (*3*) [19].

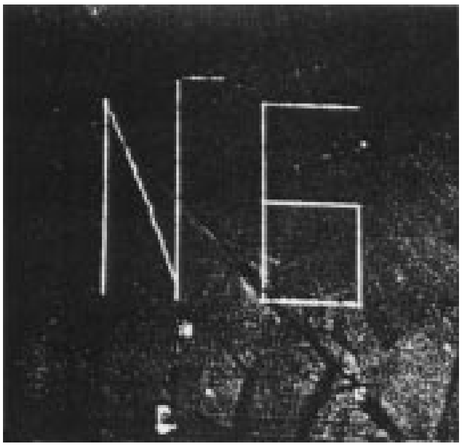

Figure 4. Memory effect in GaN : Zn. The diameter of the electron spot is $\simeq$ 700 A, the current $I \simeq 1$ mA, and the width of the light strip is $\simeq$ 1 µm [19].

of the cathodoluminescence intensity induced by irradiation does not vanish after cessation of the excitation, and thus the image appears in the irradiated regions. The contrast K for images of the type of those presented in Fig. 4 is equal to

$$K = \frac{I_{\text{irrad}} - I_{\text{nonirrad}}}{I_{\text{nonirrad}}}\,,$$

where I_{irrad} is the cathodoluminescence intensity in irradiated regions, and I_{nonirrad} is the same outside these regions. The K values for the investigated GaN samples reached 100. Room-temperature storage induced no decrease of the contrast over 30 months. The minimum width of the lines in the image did not exceed 0.6 mm. The image storage time decreased with temperature and was about 3.5 h at 100 °C (see Fig. 4).

4. Conclusions

The PPC phenomena in semiconducting III – V compounds are likely to find new technical applications. However, as in other fields of application of these compounds, serious difficulties have not yet been eliminated. It is pertinent to recall the long and successful path to improving semiconductor injection lasers. The experimental results available to the authors point to the necessity of creating quite definite geometrical structures that would be optimal for the construction of PPC resistors or two-dimensional memory systems.

As has been mentioned above, the two basic theoretical models permit a qualitative description of the experimental data. However, predictions and quantitative descriptions of concrete structures of photoresistors or planar memory systems based on the PPC effect with optimal parameters will require additional research work. The example of the modern technology of silicon systems is promising. Those acquainted with the situation know that since the 1960s this problem has been principal for many leading research centres.

As when review article [4] was published and until the present time real objects of successful experiments have always contained inhomogeneities such as surface potential barriers, clusters or grain boundaries (e.g., PbS surrounded by PbO interlayers).

As can be seen from the preceding sections, models of PPC-generating processes had existed long before the development of modern technology which allows the creation of reproducible systems with quantum wells and superlattices. The concepts of inhomogeneous systems with layers separating photosensitive crystallites were developed first and foremost in application to photoresistors based on PbS and related compounds by Petritz [21] as far back as in late 1950s. Now, theoretical models of superlattices have been created and great progress has been made in the technology of their production, primarily on the basis of III – V compounds. In their detailed review [22] Ploog and Dohler paid attention to the fact that in superlattices created by a periodic change of the doping level the NEC lifetime can reach an exceedingly high value owing to the spatial separation of electrons and holes. According to the analysis carried out by the authors, the increase in the lifetime of NEC depends exponentially on the geometric parameters of the superlattice and can attain values of the order of 10^{12}.

The lifetime of NEC pairs in structures of the superlattice type markedly depends on the period of the layer parameters variation. A change of this period in double measure must entail a difference of about 10^3 in the lifetimes of such NEC pairs.

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