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Abnormal impurity photoconductivity in silicon with multiple charged manganese atoms

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ABSTRACT

The phenomenon of residual photoconductivity manifested itself in various semiconductor materials exposed to incident light or background light. The phenomenon is basically explained by the barrier mechanism. Nevertheless, the residual photoconductivity (RPC) in materials exposed to impurity infra-red light was barely investigated recently. Such investigations will help develop optical memory devices in IR-diapason and establish local nano-scale variband structures in the Si lattice jointly with multiple charged nanoclusters of Mn.

Keywords: Photoconductivity, silicon.

1. INTRODUCTION

The phenomenon of residual photoconductivity manifested itself in various semiconductor materials [1-3] and is basically implicated by the barrier mechanism [4]. Investigation of the residual photoconductivity and particularly, the impurity residual photoconductivity represents a certain interest in the development of various optical memory devices for infra-red diapason of spectra. The present research paper presents novel experimental effects reveled in silicon doped with manganese. The starting material used was *p*-type single-crystal silicon with a resistivity ρ~ 5 Ω·cm.

The doping of manganese was carried out via low-temperature diffusion [5] that allowed to obtain compensated *p*-type samples with resistivity value ρ~(2÷7)·10^{3}Ω·cm at T=300 K. Anticipating that manganese atoms in silicon produce two donor levels at E_1=E_C-0,27 and E_2=E_C-0,5 eV, in obtained samples where the Fermi level F=E_V+0,35 eV, then one can assume that practically all embedded manganese atoms are basically in the charge state Mn^{++}. In photoelectric measurements we used a double filter from polished silicon wafers mounted downstream the Globar of an IKS-21 spectrometer and in front of the window of a cryostat in order to prevent background light.

The results of investigation of the Hall effect demonstrate that in the experimental samples a certain concentration of holes (p=1,5·10^{12}÷8·10^{12}см$^{-3}$) still remain at T=300 K. As temperature decreases, the resistivity of samples significantly increases and, at T=77 K reaches the value ρ~10^9÷10^{10}Ω·cm, i.e. the concentration of holes decreases 10^6÷10^7 fold. While conducting investigation of photoconductivity as a function of spectra, we revealed various interesting phenomena. The onset of photoconductivity happened to take place in the range of hν=0,14÷0,15 eV. Photoconductivity (PC) increased continuously at samples exposed to light with stable hν, as if photons' detection seems to be taking place. The above persists at samples exposed to photon energy in the range hν=0,14÷0,42 eV. It's important to note that as photon energy increases, PC starts to decrease intensively, whereas PC saturation time decreases and PC value in the range of saturation increases respectively (Figure 1). These results are impossible to explain by the existing energy bands of manganese in the silicon lattice since the samples firstly were of *p*-type and energy bands of manganese atoms at E_1=E_C-0,27 and E_2=E_C-0,5 eV

were almost 100 % empty in those samples, and secondly the onset of PC in the samples starts to manifest itself at $h\nu$=0,15 eV and related to the move of electrons from valence band to energy bands laying near the valence band.

The Figure 2 demonstrates relaxation of impurity PC, i.e. relaxation of extrinsic residual PC after the light falling on the sample was switched off. As one can see from the above figure the PC, after the light was set to off, still remained constant, i.e. one can witness residual PC characterized by abnormally long duration of relaxation. On the basis of the results of the investigation of residual PC relaxation at comparatively long duration (10÷12 hours) we have been able to estimate approximate relaxation time at T=100 K, the value of which happened to be $\tau=10^{10}\div10^{11}$ seconds.

Investigation of relaxation of residual PC at various temperatures (Figure 3) have shown that up to temperatures of 200 K, one does not witness significant speedup of the relaxation process, whereas at T>200 K the relaxation curve consists of two starkly differing stages. At first stage residual PC significantly decreases, and at the second stage nature of relaxation is rather slow. The duration of the first stage and the order of magnitude of decrease of the residual PC increases as temperature increase (curves 3, 4). Such behavior of relaxation of residual photoconductivity persists up to temperature range 270÷280 K. Thus, one can state that the relaxation of extrinsic PC ($h\nu$=0,15÷0,4 eV) is characterized by abnormally long duration up to T=200 K, whereas at higher temperatures behaves conventionally, manifested at many semiconductor materials and does not change up to T=270÷280 K.

Before trying to explain the results, one has to pay attention to the following facts: firstly, why the concentration of non-compensated holes ($p\sim8\cdot10^{12}$см$^{-3}$) in the investigated samples tend to decrease 6 – 7 fold as temperature decreases down to T=100 K, i.e. where do they go after all? Secondly, why photo-response in the samples (of p-type) launches at $h\nu$=0,15 eV, even though, as is well known, manganese atoms do not establish energy bands with energy of ionization of $E=E_V$+0,15 eV, and third, why in the investigated samples such an abnormal extrinsic PC with colossal time of relaxation reveals itself? It is simply impossible to explain all these events by mere atomic state of manganese in silicon. As it has been shown in research works [6], in times of doping of silicon by method of low-temperature diffusion, it appears that manganese atoms tend to form nanoclusters consisting of four atoms around negatively charged boron. In compensated samples where the concentration of boron atoms happens to be slightly higher than of manganese atoms ($N_B \geq \frac{1}{2} N_{Mn}$), practically all manganese atoms participating in the process of formation of nanoclusters are located in the state Mn^{++}. This means that nanoclusters of manganese atoms in this case have the following structure $\left[(Mn)_4^{+8} B^{-1}\right]^{+7}$ and behave as multiple charged centers creating around itself strong potential barrier for holes.

If temperature decreases, non-compensated holes will be localized in potential pits formed between two multiple charged centers that prevent them from taking part in the charge carrier. As the result one can witness decrease in the concentration of non-compensated holes, i.e. significant surge in resistivity factor of the material. At the same time, a multiple charged center attracts with significant force valence electrons of silicon atoms located around this center. This force incidentally diminishes steadily as a function of distance of electrons away from this center. Therefore, one can assume that the launch of photo-response at $h\nu$=0,15 eV is caused by the capture of closest valence electrons of silicon atoms by the centers, whereas holes generated due to powerful repulsion from the center, will be localized in potential wells, where they tend to gather and thus, their share in PC increases. Since there is virtually no recombination between holes captured in potential wells and electrons captured by multiple charged centers, gathering process of holes on light, i.e. response to photons happens to translate into durable relaxation buildup of PC. When light is off as it was mentioned above due to the absence of recombination of carriers, PC generated by extrinsic light practically does not significantly change, i.e. one can witness abnormally long extrinsic residual conduction. The process of recombination starts only at higher temperatures whereby there is a statistical probability of recombination of localized holes or electrons caught up by multiple charged centers are freed, which evidenced during the experiment.

Evidence of photo-response in the samples in the range $h\nu$=0,15÷0,45 eV, increase of current build up rate, increase of PC in the saturation diapason, all this lead us to conclude that as the distance from the multiple charged center becomes longer, not only interaction of valence electrons with multiple charged centers diminishes which in turn leads to the increase of the energy of capture of such electrons (i.e. higher energy photons will be), but also there is a surge in the number of valence electrons around the

multiple charged centers, that leads to the increase of capture of electrons (i.e. the concentration of holes in wells increases that translates into the increase of PC). As evidenced by the experiments related to the relaxation of residual conductivity, in this case we are experiencing the character of residual conductivity similar to the one generated on IR light of $h\nu$=0,15eV.

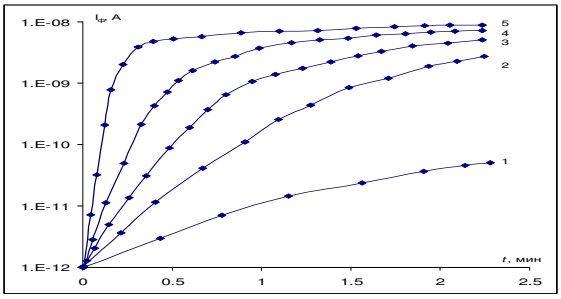

Figure – 1: Increase of PC at various extrinsic light $h\nu$.

1 – 0,15eV, *2* – 0,2 eV, *3* – 0,25 eV, *4* – 0,3 eV, *5* – 0,4 eV.

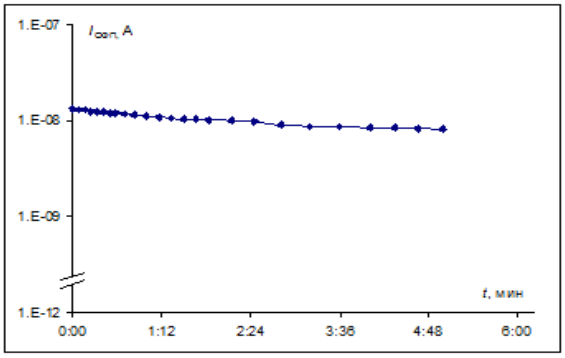

Figure – 2: Residual extrinsic PC ($h\nu$=0,2) in samples with multiple charged centers at T=100 K.

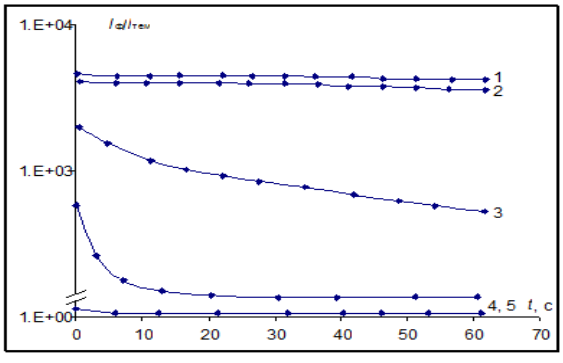

Figure - 3: Relaxation of residual PC at various temperatures *T*.

1 – 133 K; *2* – 150 K; *3* – 205 K; *4* – 260 K; *5* – 290 K.

Thus, one can eventually state that local nano-scale variband structure i.e. silicon nanocluster is created around multiple charged centers consisting of nanoclusters of manganese atoms $[(Mn)_4^{+8}B^{-1}]^{+7}$, wherein the width of the forbidden band changes from 0,15 to 1,16 eV at T=100 K. That is why in such samples the evidenced photo-response launches at $h\nu$=0,15eV and with the increase of energy of photons the PC increases jumpwise.

The obtained results provide a certain ground for assuming that nanoclusters of manganese atoms establish multiple charged centers and secondly, local nano-scale variband structures must have been formed between these nanoclusters and silicon, which in turn are characterized by unique properties, i.e. their forbidden band value varies in the wide range E_g=0,15÷1,16 eV. Such variband structure is a novel class of silicon-based materials. These materials provide an opportunity for manufacturing IR photo-detectors operating in the wavelength range of λ = l.55–8 micron and at operating temperature T=220 K.

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