Armenian Journal of Physics, 2013, vol. 6, issue 2, pp. 72-81

TRANSIENT AND STATIONARY PHOTOCONDUCTIVITY OF SEMICONDUCTOR NANOWIRES

S. G. PETROSYAN[1,2]*, S. NERSESYAN[1], A. YESAYAN[2]

[1]*Russian-Armenian (Slavonic) University, O.Emin str. 123, 0051, Yerevan, Armenia*

[2]*Institute of Radiophysics and Electronics, Alikhanyan Brs. 1, 0203, Ashtarak, Armenia*

**e-mail: spetrosyan@rau.am*

Received 12 November, 2012

Abstract–We developed an analytical model for the photoconductivity (PC) of semiconductor nanowires (NWs). The model takes into account the enhanced role of surface recombination in the lifetime of nonequilibrium carriers in NW due to large surface-to-volume ratio. The main peculiarities of the NW PC are governed by radius and time dependent recombination barrier, which varies in time with interplay between the NW quasi-neutral core radius and the space charge layer thickness near the surface. Assuming acceptor-like-traps located on the surface of NW we find the relationship between the thickness of space-charge region and nonequilibrium surface charge density in NW and thus calculate the size-dependent PC. Time variation of surface band bending in the course of carrier capture by surface states leads to a non-exponential character of transient PC. The instantaneous relaxation time grows with time after turning of the illumination and it can become so large that persistent PC can be observed even at room temperatures. The results are in good agreement with available experimental data.

Keywords: semiconductor, nanowires, photoconductivity, surface states

1. Introduction

Recently a great number of experimental works has been reported to fabrication, synthesis and characterization of semiconductor nanowires (NW) [1,2]. Among other nanostructures, semiconductor NWs with a diameter of several hundred nm and aspect ratios as high as 10^2, even without quantum size effects, offer exciting possibilities as building blocks for different photovoltaic devices, in particular, for photosensitive elements in highly integrated optoelectronic devices [2] and for third generation of solar cells [3]. NW based photo detectors can yield higher light sensitivity than their bulk or thin film counterparts due to the large surface-to volume ratio and small dimensions comparable to the carrier diffusion length [4,5].

The size-dependent PC of NWs has been experimentally studied in [6-11]. Depending on the power of illumination, the resistivity of NW can reversibly be changed by 4 to 6 orders of magnitude. It has been also shown that the surface recombination rate, as well as the absolute value of the photocurrent density are very sensitive to the wire diameter. When the radius of NW becomes comparable with the Debye screening length the total volume of NW is filled by the space charge region. This causes the radical changes in equilibrium and nonequilibrium properties of NWs. If the nonequilibrium carriers are generated in such systems, their drift-diffusion distribution and lifetime become dependent on the NW radius and surface band bending. Such dependence is mainly governed by the relationship between the diffusion length of electrons (holes), the radius and the screening length of NW.

The observation of NW shows that the surface recombination of nonequilibrium

electron-hole pairs through the surface states is the prevailing mechanism in PC [12-16]. When the NW absorbs the light, due to the existing near-surface band bending minority carriers are swept to the surface where they recombine with the trapped majority carriers. The part of separated majority carriers continue to contribute to the NW photocurrent until they are transferred (as a rule thermionically) from core to the surface states over the barrier. As a result free carrier's separation by the surface space charge layer of NW leads to the significantly enhanced photo carrier lifetime and long-period relaxations after turning on (off) the illumination. The variation of the surface collective recombination barrier height in the course of carrier capture by surface states leads to a non- exponential character of PC kinetics.

However despite the great number of experimental works there is still lack of detailed theoretical studies on PC in semiconductor NWs.

In this paper we study the transient and steady-state PC of NWs by putting forward the importance of surface recombination in the photocurrent formation. Analytic equations are derived to calculate the lux-ampere characteristics and the photocurrent kinetics under the excitation of light pulses.

Later we will consider the NW radius R to be greater than de Broglie wave length, so that we neglect all quantum size effects. We will consider, that $L_D \sim R \ll L_p$, where L_D is the Debye screening length, L_p is the minority carrier diffusion length.

2. The Size Dependent Surface Band Bending and Critical Radius of NW

We consider NW of *n*-type conductivity with uncompensated concentration of shallow donors N_D and acceptor-like recombination traps on the surface with the concentration N_s, capturing electrons from the volume. For the simplicity we assume that only one type of acceptor-like states with ionization energy E_s exists on the surface and participate in the PC transients. The negative charge of surface states give rise to a positively charged depleted region, which is formed near the surface of the NW and has the width W. This causes surface band bending with the equilibrium potential barrier U_{s0} and results in an undepleted conducting neutral core of radius $(R-W)$ within the NW. Therefore to recombine with the holes trapped on surface states electrons have to surpass this potential barrier. We assume only thermionic transfer of free electrons from core of NW to the surface over the radius dependent barrier. The tunneling of electrons through the near-surface barrier can be neglected for NWs with a radius and depletion length of several hundred nm. The schematic band bending diagrams for NWs [7] with different radiuses are illustrated in Fig.1.

As it is seen from the Fig.1b there is a certain radius of NW, so called critical radius (R_c), when the total NW is totally depleted from free charge carriers. For thinner NWs, the total charge

per unit length of NW decreases, which causes the reduction of the surface potential barrier at equilibrium (Fig.1.c), and so the surface recombination barrier becomes radius dependent for NWs with $R < R_c$.

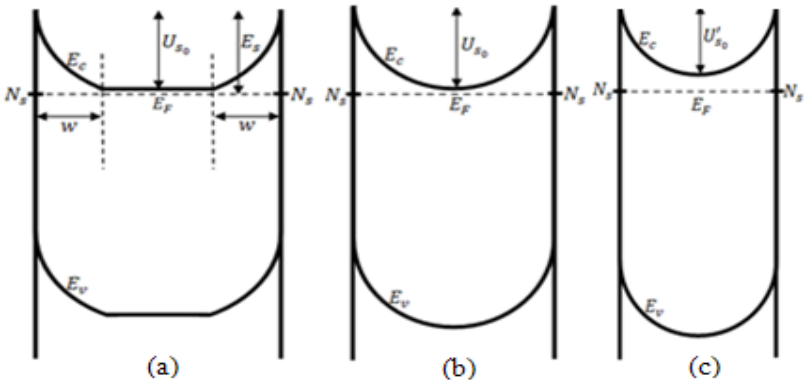

Fig.1. The band bending in NWs with different radius.

Unlike depletion effects in bulk materials the depletion region thickness in a semiconductor NW is a size (radius) dependent [17]. For NW a more subtle effect is the increase in depletion depth as NW radius is reduced. This occurs even when all other parameters (N_D, U_s) are held constant and is due to relative scaling of surface area and NW volume. The surface charge $Q_s \approx RL$, goes as the first power of radius, while the volume charge $Q_v \approx R^2 L$, scales as the square of NW radius. Therefore at large radii, less depletion depth is required to neutralize a given areal density of the surface charge. Conversely, smaller NWs require greater depletion length to maintain neutrality.

To define the radius dependent depletion width and a critical radius of NW the Poisson equation in cylindrical coordinates must be solved [12], which for infinitely long NW reduces to the one dimensional equation. The extent to which the depletion layer penetrates the NW will vary with NW radius, dopant concentration, surface barrier height and relevant dielectric properties of NW material.

The solution of Poisson equation with appropriate boundary conditions [17,18] gives the surface potential barrier height U_s as a function of electron concentration in surface states (surface charge) and the expression for the critical radius R_c. Using the charge balance equation we define the dimensionless surface electron concentration in Schottky approximation:

$$x = 2n_s / N_D R = 1 - \left(1 - W/R\right)^2, \tag{1}$$

The surface barrier height and critical radius can be presented as

$$U_s = U_0 \left[x + \left(1 - x\right) \ln\left(1 - x\right) \right], \tag{2}$$

$$R_c = 2\sqrt{\varepsilon\varepsilon_0 U_s / e^2 N_D}, \tag{3}$$

where $U_0 = e^2 N_D R^2 / 4\varepsilon\varepsilon_0$, e is the elementary electric charge, ε_0 is the electric constant, ε is the dielectric permittivity, N_D is the donor concentration. For instance the critical radius for GaN nanowire with $N_D = 6\times10^{17}$ cm^{-3}, $\varepsilon = 10$, $U_s = 0.55$ eV is $R_c = 45$ nm.

3. The Model of Photoconductivity

Let us consider NW with $R \geq R_c$ (Fig.1a), so that in equilibrium conditions depletion layer with thickness W_0 occupy only part of NW and there is a quasi-neutral conducting core in the center of NW. Therefore the conductance of NW in the dark can be written as

$$\Sigma_0 = eN_D\mu_n \pi\left(R - W_0\right)^2 / L. \tag{4}$$

where μ_n is the mobility of electrons and L is the length of NW.

A pulse of light with photon energy $\hbar\omega$ near/above the band-gap of NW will create electron-hole pairs. Such process takes place both in quasi-neutral core and in depletion region of NW. For sufficiently thin NW when absorption length is larger than NW radius ($\alpha^{-1} \gg R$, where α is the absorption coefficient) electron-hole pairs generation rate G can be taken constant and equal to $P\alpha/\hbar\omega$, where P is the illumination intensity. In general there are two channels for the electron-hole recombination: bulk recombination through middle band-gap recombination centers and surface recombination through the acceptor-like surface states. These two mechanisms are characterized by different lifetimes. In III-V based NWs the typical bulk lifetime for minority carriers is of order of ns [9]. The surface recombination usually is governed by thermionic transfer of majority carriers from the bulk to the surface states over the barrier and for the sufficiently large surface band bending the corresponding characteristic time can be very large (seconds and even hours) [7,9,11]. Therefore all transients of non-equilibrium phenomena, including PC, in NW must contain, in general, fast and slow components. In a considered case, when the light is on, a part of photo-generated holes will be captured by bulk recombination centers and undergo bulk recombination. Another part will be swept towards the surface by the strong near-surface electric field and quickly captured by surface states causing a decrease of surface negative charge. On the other hand a part of electrons generated in depletion layer will be swept towards the core, increasing concentration of electrons in the core and partially neutralizing the space charge. As a result of such processes during the short time (comparable to minority carrier bulk lifetime) a diffusion-drift distribution of non-equilibrium carries will be established everywhere in NW. After that the processes of thermionic transfer of free electrons from core to surface and recombination with holes captured by surface states will govern the establishment of charge stationary distribution. The same processes are occurred when the illumination is ceased. After the fast bulk recombination of holes

with a part of non-equilibrium electrons in core, the final restoration of equilibrium will be governed by slow transfer of remaining non-equilibrium electrons from core to the surface and recombination with non-equilibrium holes trapped at the surface. Therefore one can conclude that the main part of PC decay is governed by the majority carrier capture time rather than the minority carrier lifetime in NW.

The surface states can be partially or completely filled with photo-generated holes and when the light is on the dynamics of PC is determined by rate equation written for the surface density of electrons (n_s):

$$dn_s/dt = svn(R)\left(N_S - n_s(t)\right) - \left(dn_s/dt\right)_{capt.holes} - vsN_C n_s(t) e^{-E_S/kT}, \quad (5)$$

where the first and second terms describe electron and hole capture rates and the third term electron back thermal activation from surface states. Here v is the thermal velocity, s is the electron capture cross section by surface traps, N_C is the effective density of states in the conduction band, $n(R)$ is the volume density of electrons at the surface, k is the Boltzmann constant, T is the absolute temperature. Here we took into account that the rate of electron-hole surface recombination is proportional to the density of holes at the surface states $(N_s - n_s)$ and to the concentration of free nonequilibrium electrons at the energy U_s calculated from the bottom of the conduction band in core of NW. Note that mentioned above processes have different characteristic times. The processes of hole generation in NW and their capture by surface states are very quick, so during the slow process of electron capture the hole distribution and their flux to the surface states can be considered as quasi-stationary process.

To calculate the second term in (5) we need to take into account both non-equilibrium holes generated in the space-charge region and also their flux from the quasi- neutral core to the space charge layer, thus we have

$$2\pi RL\left(dn_s/dt\right)_{capt.holes} = \left(\pi R^2 - \pi\left(R-W\right)^2\right)LG + 2\pi(R-W)L\left(-D_p\, d\Delta p/dr\right)_{r=R-W}. \quad (6)$$

Next we have to find the established distribution of non-equilibrium carriers in a core of NW solving the continuity equation for non-equilibrium carriers in cylindrical coordinates, assuming that all photogenerated hole reaching the edge of the depletion region immediately roll down and the boundary condition $\Delta p(R-W) = 0$ is valid. The radial distribution of hole concentration is given by modified Bessel function of zero order as:

$$\Delta p(r) = \Delta n(r) = G\tau_p\left(1 - I_0\left(r/L_p\right)/I_0\left((R-W)/L_p\right)\right). \quad (7)$$

Here Δn and Δp are non-equilibrium densities of electrons and holes respectively and in quasi-neutral core $\Delta p \approx \Delta n$, D_p and τ_p are diffusion coefficient and lifetime of minority carriers.

Substituting (7) into (6) we have a final expression for the second term of (5)

$$\left(\frac{dn_s}{dt}\right)_{capt.holes} = \frac{GR}{2}\left\{1-\frac{(R-W)^2}{R^2}+\frac{2(R-W)L_p}{R^2}\frac{I_1\left((R-W)/L_p\right)}{I_0\left((R-W)/L_p\right)}\right\}, \tag{8}$$

where $I_1(x)$ is the Bessel function of first order.

Note that in equilibrium ($G=0$, $dn_s/dt=0$) as it follows from (5) the density of captured electrons on surface states is:

$$n_{s0} = \frac{N_S}{1+\left(N_C/n(R)\right)e^{-E_S/kT}}. \tag{9}$$

By substituting (8) into (3) we have the final equation for $n_s(t)$:

$$\frac{dn_s}{dt} = vsn(R)\left(N_S - n_s(t)\right) - vsN_C n_s(t)e^{-E_S/kT} - \frac{GR}{2}\left\{x+\frac{2L_p}{R}\sqrt{1-x}\frac{I_1\left((R/L_P)\sqrt{1-x}\right)}{I_0\left((R/L_P)\sqrt{1-x}\right)}\right\}, \tag{10}$$

where as a result of quasi-equilibrium distribution of carriers in space charge region we can approximately take

$$n(R) = \left(N_D+\Delta n\right)\exp\left(-U_S/kT\right). \tag{11}$$

Here in case of small illumination intensities and large doping level of NW a good approximation is $\Delta n \ll N_D$.

Thus by solving (10) we can define the surface density of electrons at any instant of time $n_s(t)$ and so having the width of conducting channel (1) we can easily find the photoconductance $\Sigma(t)$ of NW and therefore the photocurrent $I_P = V\Sigma$, where V is the applied voltage.

Note the conductivity of NW in the dark is defined with (4) where W_0 can be computed from (1) and (9). Usually the density of surface states of NW is very large $N_s = 10^{11} \div 10^{12}$ cm^{-2} [19] and they are filled only partially so the Fermi level is very close to the surface levels and it can be considered pinned with them. Therefore for the U_{s0} we can have an approximate expression

$$U_{s0} \approx E_s - kT\ln\left(N_c/N_d\right). \tag{12}$$

When the illumination is switched on the conductivity of NW grown up at first very sharply (characteristic time is τ_p) then continues to rise slowly due to decrease of surface band bending and depletion region width $W(t)$ in time. The photoconductivity can be calculated with the help of (1), (2), (7) and (10):

$$\Sigma = eN_D\mu_n\frac{\pi(R-W)^2}{L}+e\left(\mu_n+\mu_p\right)\frac{1}{L}\int_0^{R-W}2\pi r\Delta p(r)\,dr. \tag{13}$$

To compute the stationary photoconductivity Σ_{st} we solve at first (10) with zero in left hand side to define n_{st} under steady state illumination then we substitute it into (1) to define W_{st} and with the help of (7) and (13) find Σ_{st}.

When the light is switched off the photoconductivity at first falls down very fast due to volume recombination of minority carriers then starts to decrease more slowly due to electron surface recombination with the holes trapped at the surface until the band bending reaches its value in the dark. During this process the electron recombination rate slows in time because the increasing band bending results in a greater barrier to thermionic emission. To follow the kinetics of photoconductivity we must numerically integrate Eq.(10), calculate $n_s(t)$ and compute $\Sigma(t)$ by taking into account that when the light ceases only the first two terms remain in (10).

4. Results and Discussions

When the NW radius is larger than the critical radius as it was mentioned above there is a conducting channel also in the dark (quasi-neutral core surrounded by space charge shell). The larger is the NW radius the larger is the conducting channel at the same doping concentration and density of surface charge.

Fig.2 illustrates the dependence of dark conductivity as a function of NW radius calculated with equation (4), where the width of depletion region is expressed through equations (1) and (9). The following typical parameters for GaN NWs [9,14] were used for calculations: $N_s = 6.5\times10^{11}$ cm^{-2}, $E_s = 0.85$ eV, $N_c = 2\times10^{18}$ cm^{-3}, $\mu_n = 700$ cm^2/(V s).

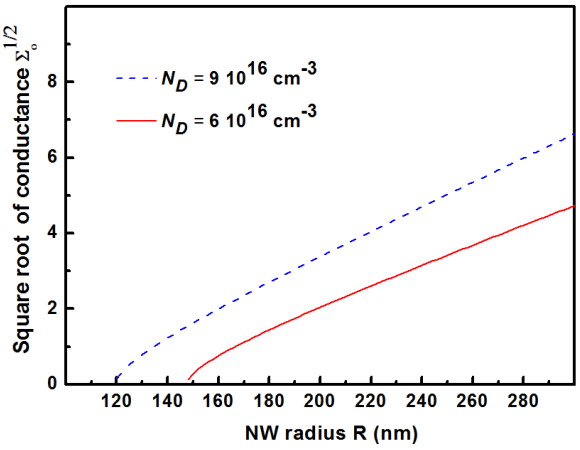

Fig.2. The dependence of conductance in the dark on NW radius.

It is seen that the conductance of NW vanishes when it's radius becomes close to the R_c. The current–voltage characteristics calculated with the derived analytical expressions are illustrated in Fig.3(a). These analytical results can be compared with the experimental data [9] (Fig.3(b)). These data measured for thicker NW, ($R = 160$ nm), which show non-zero current in the dark.

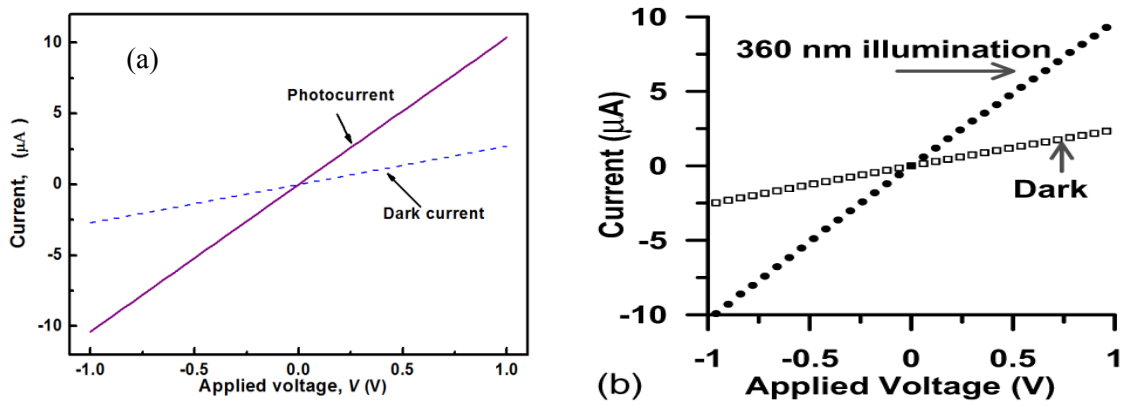

Fig.3. Current–voltage characteristics in the dark and under the illumination with illumination intensity about 3.6 mW/cm^2, (a) analytical calculations, (b) measurements [9]. We take the following parameters for calculations $R = 160$ nm, $N_D = 9\times10^{16}$ cm^{-3}, $s = 5\times10^{-17}$ cm^2, $L = 3.4$ μm, $\mu_p = 250$ cm^2/(V s).

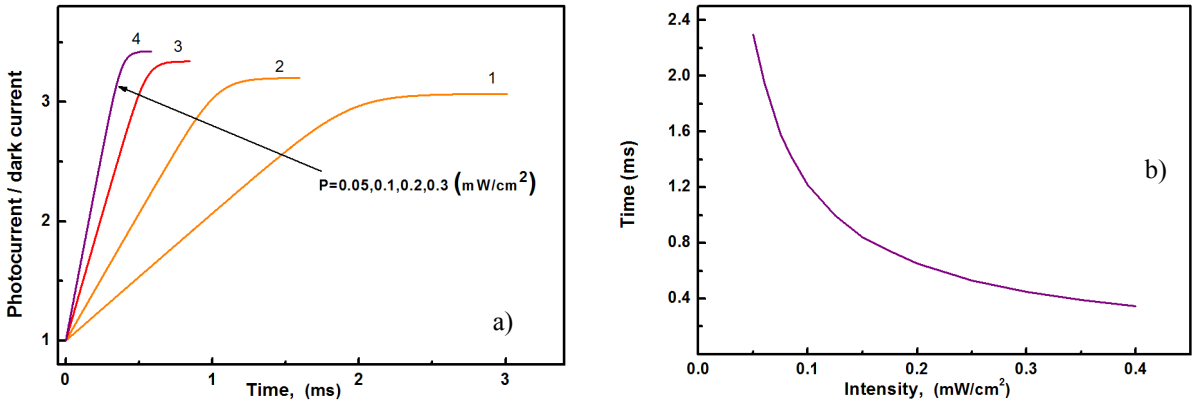

Fig.4. Photocurrent over time graph illustrated in the scale of milliseconds (a) and rise time as a function of illumination intensity (b). Dark band bending is $U_{s0} = 0.66$ eV, while under illumination the stationary band bending U_s decreases with increasing the illumination power. For the presented curves the values of U_s and P, respectively, are 1. 0.55 eV, 0.05 mW/cm^{-2}; 2. 0.28 eV, 0.1 mW/cm^{-2}; 3. 0.26 eV, 0.2 mW/cm^{-2}; 4. 0.25 eV, 0.3 mW/cm^{-2}.

Fig.4 illustrates that the act of turning the light on leads to the immediate rise of the conductivity and after hundreds of nanoseconds the photocurrent reaches its stationary value. The rise time depends on excitation power. The higher is the illumination intensity the smaller is the height of surface potential barrier and also the PC rise time is decreasing (Fig.4b).

Fig.5 illustrates the PC decay after turning the light off. Immediately after cessation of illumination due to bulk recombination of non-equilibrium holes the photocurrent will decrease very fast to a some extend (during nanosecond time scale) and further the current will continue to return to its original value very slowly (minutes or hours time scale). It has to be mentioned that the slow decay component is not exponential but much slower (very often logarithmic). After turning the light off and by the end of bulk recombination process, a remaining part of non equilibrium electrons from the NW core must be thermicaly transferred to the surface states over the near-surface time dependent barrier. The more electrons move to the surface and are captured by the surface traps the more the potential barrier is increasing and thus, it becomes more difficult for the

rest of photoelectrons to reach the surface. For sufficiently large band bending the persistent PC can be observed [9]. We have got a good comparison with experimental data for GaN NW [9] taking in our calculations given above typical values for GaN. In addition it has to be noted that the comparison with experimental results for dark conductance and PC transient times do not allow independent determination of band bending and electron capture cross section (s), although we believe that the cross section of $10^{-19} \div 10^{-21}$ cm^{-2} used in [9] to explain the experimental data is unreasonably small for traps in semiconductors [14,19].

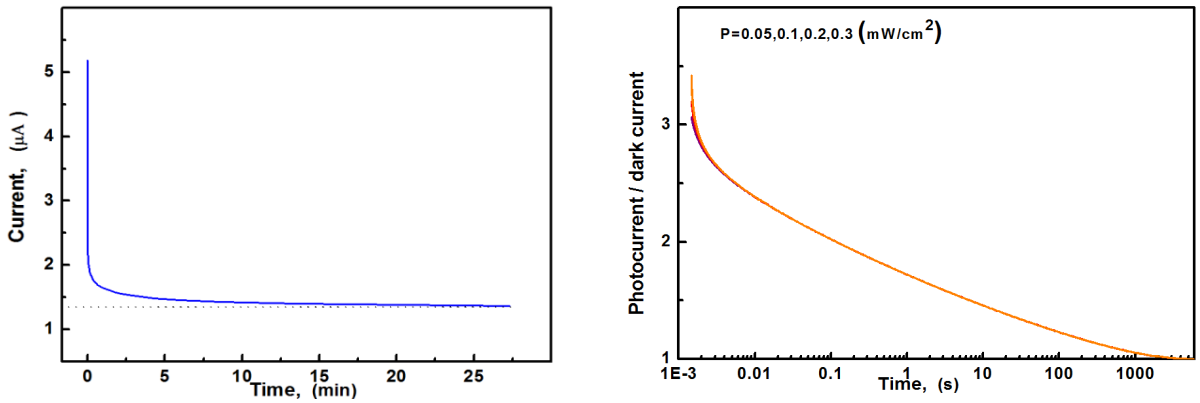

Fig.5. The PC decay after turning the light off in minutes scale (a), the plotted PC decay for different illumination intensities show practically the independence of decay time on excitation level (b).

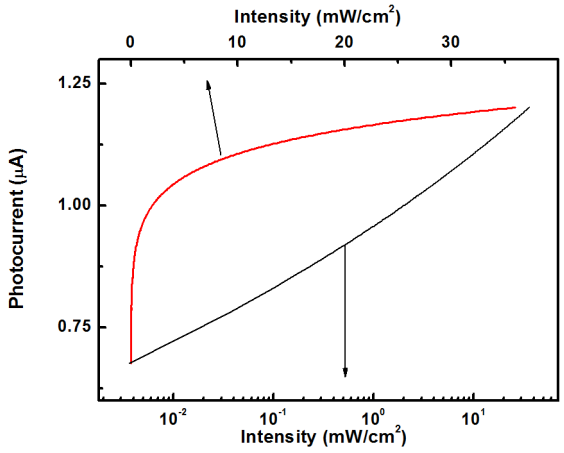

Fig.6. Lux-ampere characteristics in linear and semilog scale.

The dependence of stationary photocurrent on intensity of illumination is depicted in Fig.6. The photocurrent increases linearly with excitation intensity and starts to saturate for larger intensities. Transition from linear regime to saturation corresponds to a full screening of surface recombination barrier, leading to the sharp decrease in lifetime of electron-hole pairs. Calculations confirm that the lux-ampere characteristics of PC can be expressed by a simple power law $I_{pc} \approx P^{\nu}$, where $\nu < 1$. Experiments on GaN [9] and ZnO [5] NWs gave for the exponent $\nu = 0.5$ and $\nu = 0.8$, correspondingly.

5. Conclusions

The phenomenological model based on existence of radius and time dependent surface band bending (recombination barrier for non-equilibrium carriers) is able to explain both the dark conductivity and dynamics of PC transients in semiconductor NWs by using only two fitting parameters (s and E_s). The photoelectric characteristics of NW are a result of a complicated interplay between radius, doping level, density of surface traps and ionization energy. According to the developed model the acceptor-like surface states are emptied of electrons under illumination and filled back after the light cessation due to the thermionic transfer of free electrons from the core to the surface states over the near surface potential barrier. We study the stationary photoconductivity and restoration of the band bending at the surface of doped NW under the above-bandgap illumination. The kinetics of the photoconductivity is characterized by long-period relaxation processes. The instantaneous relaxation time grows with time after turning off the illumination and it can become so large that persistent PC can be observed even at room temperatures. The results are in good agreement with available experimental data. The photoconducting NWs could serve as highly sensitive light detectors, chemical and biological sensors and switching devices for nanoscale optoelectronic applications.

REFERENCES

1. **S.J.Pearton, B.S.Kang, B.P.Gila, et al.**, J. Nanosci. Nanotechnol., **8**, 99 (2008).
2. **C.Soci, A.Zhang, X-Y.Bao H.Kim, et al.**, J. Nanosci. Nanotechnol., **10**, 1 (2010).
3. **V.Sivakov, G.Andra, A.Gawlik, A.Berger, et al.**, Nano Lett., **9(4)**, 1549 (2009).
4. **R-S.Chen, H.Y.Chen, C.Y.Lu, et al**., Appl. phys. Lett., **91**, 223106 (2007).
5. **H.Kind, H.Yan, B.Messe, et al.**, Adv. Mater., **14(2),** 158 (2002).
6. **S.Mathur, S.Barth, H.Shen, et al.**, Small, **1(7)**, 713 (2005).
7. **R.Calarco, M.Marso, T.Richter, A.I.Aykanat, et al**, Nano Lett., **5**, 981 (2005).
8. **R.Calarco, M.Marso**, Appl. Phys. A, **87**, 499 (2007).
9. **N.A.Stanford et al.,** J. Appl. Phys. **107**, 034318 (2010).
10. **A.Armstrong, G.T.Wang, A.A.Talin**, J. Electr. Mat., **38**, 484 (2009).
11. **Q.Li, T.Gao, Y.G.Wang, T.H.Wanga**, Appl. Phys. Lett., **86**, 123117 (2005).
12. **Sh.Zhang, E.Hemesath, D.E.Perea et al.**, Nano Lett., **9**(9), 3268 (2009).
13. **S.Han W.Jin, D.Zhang et al**., Chem. Phys. Lett., **389,** 176 (2004).
14. **M.A.Reshchikov, S.Sabuktagin et al**., J. Appl. Phys. **96**(5), 2556 (2004).
15. **B.Polyakov, B.Daly, J.Prikulis**, Adv. Mat. **18**, 1812 (2006).
16. **J.P.Long and V.M.Bermudez**, Phys. Rev. B, **66**, 121308 (2002).
17. **J.H.Luscombe C.L.Frenzen**, Solid State Electron., **46**, 885 (2002).
18. **B.S.Simpkins, M.A.Mastro, C.Eddy et al.**, J. Appl. Phys., **103**, 104313, (2008).
19. **I.Shalish, Y.Shapira, L.Burstein, J.Salzman**, J. Appl. Phys., **89(1),** 390 (2001).