5.1 Introduction

Persistent photoconductivity (PPC) is the Photoinduced conductivity which persists for a long time after removal of the photoexcitation. Recently, considerable efforts have been given towards the understanding of PPC, which has been observed in several semiconductors. It was first observed in n-type AlGaAs due to DX center[1,2] and subsequently in other semiconductors[3-6]. Recently, PPC has been observed in magnetite materials[7,8]. Zukalyski and coworkers[13] have proposed an interesting model for the microscopic origin of PPC in Si-doped Al$_x$Ga$_{1-x}$As. The PPC decay has been explained by an effective mass model of the impurity wave function with a wave packet centered near but not at the $\Gamma$ point in the Brillouin zone. The shift of the impurity wave function in the k-space has been explained in terms of long-range compositional ordering in Al$_x$Ga$_{1-x}$As. In most semiconductors, PPC was observed to be pronounced at low temperature due to the recombination preventing barrier, except in Zn$_x$Cd$_{1-x}$Se[6], which shows pronounced PPC effect at higher temperature and has been explained[6] as a phase transition from a hopping conduction to percolation transport.

PPC is always observed either in undoped or lightly doped semiconductor. It was never attempted to observe PPC in heavily doped semiconductors. To know the microscopic origin and the role of impurity wave function on PPC, we have chosen heavily doped SiC for our experiments for several reasons. SiC has excellent physical, electronic and chemical properties that make it most suitable material for fabrication of high temperature, high frequency
and high power electronic devices[10]. But development of electronic devices based on SiC has been hampered due to lack of high quality materials. However, a considerable progress has been achieved in the growth of high quality SiC epitaxial layers in last few years, which triggered the research activities on SiC material and devices. The presence of various types of defects and lattice imperfections can remarkably influence the material properties. Despite the vigorous research activities on SiC material and device, many fundamental properties related to defects, for example PPC[11], slow photoconductive response[12] and early saturation of photoconductivity[13] are not well understood.

We have observed an anomalous temperature dependence of PPC in heavily doped n-6H SiC epitaxial layer. It has been observed that as the photoexcitation is terminated the photoexcited carriers decay following a simple exponential law with time constant $\tau$. When the electron concentration in SiC is quite large($>10^{19}$ cm$^{-3}$), such that the Fermi level lies inside the conduction band, $\tau$ increases anomalously with temperature. However, when the electron concentration($\sim 10^{18}$ cm$^{-3}$) is not so high, such that Fermi level lies inside the forbidden gap, $\tau$ becomes temperature independent and does not show anomalous behavior. The increase of lifetime of the photoexcited carriers with temperature correlates with a corresponding decrease of recombination probability of photoexcited carriers with different region of impurity wave function in k-space. Physical properties of defects in semiconductor are studied by first principle theoretical calculations and experimentally verified by several spectroscopic techniques. Till today it is not possible to measure localized wave function of impurity in solid. We have shown for the first time it is indeed possible to measure the localized wave function of impurity in SiC from this anomalous temperature dependent recombination rate of photoexcited electrons.

5.2 Experimental Details

The samples used in this study are n-type 6H-SiC epitaxial layer grown by chemical vapor deposition(CVD) on 6H-SiC substrate. We have done the secondary ion mass spec-
trosopic (SIMS) analysis (The finger-print spectrum of one sample is shown in Appendix C) of the epitaxial layer and found nitrogen as the source of n-type conduction. Four Ohmic contacts in the Van der Pauw geometry were made by evaporating Ni and then annealing at 900°C for 30 minutes for Hall experiments. We have done Hall measurements on the sample from 10K to 300K to measure the temperature dependence of electron concentration. Room temperature electron concentration was $8.8 \times 10^{17}$ cm$^{-3}$ in sample A, $1.1 \times 10^{18}$ cm$^{-3}$ in sample B and $3.1 \times 10^{19}$ cm$^{-3}$ in sample C. The sample was cooled to low temperature in dark in a closed cycle helium refrigerator and was then exposed to white light from a Tungsten-Halogen lamp or He-Ne laser photocurrent growth and subsequently light was blocked by a mechanical shutter to measure the decay of photoexcited carriers. More details of the sample and photoconductivity measurements are given in Appendix C and H, respectively.

In order to perform the PPC decay measurement at different temperatures, following sequence was used

(i) the sample was cooled in dark at desired temperature and equilibrated for one hour and then sample was illuminated for photocurrent growth and finally illumination was terminated for measuring temporal decay of photocurrent.

(ii) the sample temperature was raised to 320K and equilibrated for an hour.

(iii) the sample temperature was again brought down to another desired temperature and step (i) was followed.

Photocurrent decay was measured in such a way that the whole cycle ensures identical initial conditions at each temperature.

5.3 Results and Discussions

Fig.1 shows the decay of normalized photocurrent at various temperatures for sample A and B. The room temperature electron concentration in sample A was $8.8 \times 10^{17}$ cm$^{-3}$ and in sample B it was $1.1 \times 10^{18}$ cm$^{-3}$. Photocurrent decay is almost temperature independent in both cases. Fig.2 shows the semi-log plot of the normalized photocurrent decay for the two samples. It is clear from Fig.2 that photocurrent $I(t)$ decays following exponential law.
Figure 1: Photocurrent decay at different temperatures after termination of photoexcitation (a) in sample A with room temperature electron concentration of $8.8 \times 10^{17} \text{cm}^{-3}$ and (b) in sample B with room temperature electron concentration of $1.1 \times 10^{18} \text{cm}^{-3}$. Solid line shows the exponential fit to photocurrent decay.
Figure 2: Semi-log plot of normalized Photocurrent decay after termination of photoexcitation (a) in sample A and (b) in sample B. Solid line shows the exponential fit to photocurrent decay.

\[ I(t) = I(0) \exp \left( -\frac{t}{\tau} \right) \]  

where \( I(0) \) is the buildup current at \( t=0 \) and \( \tau \) is the relaxation time of the photoexcited electrons and given by \( \tau = 1/\sigma_e v_{th} n \), where \( \sigma_e \) is the capture cross-section of the impurity, \( v_{th} \) is the thermal velocity of electrons and \( n \) is the electron concentration. Relaxation time has been found to be \( \sim 800 \text{ms} \) which estimates a small capture cross section \( \sim 10^{-21} \text{cm}^2 \) for the trap giving rise to this slow photoconductivity. Similar slow photoconductive response has been observed\[12,14\] in n-type 3C-SiC and 6H-SiC. The relaxation rate of photocarriers in sample B is faster than that in sample A due to higher electron concentration in sample B. Fig.3 shows the normalized photocurrent decay for sample C with room temperature electron concentration of \( 3.1 \times 10^{19} \text{cm}^{-3} \), which is more than Mott critical concentration in SiC\[15\]. The semi-log plot of the decay is shown in Fig.4. It is clear in Fig.3 and Fig.4 that the photocurrent decays faster as temperature increases in sample C and follows simple
Figure 3: Photocurrent decay at different temperatures after termination of photoexcitation in sample C. The room temperature electron concentration in sample C was $3.1 \times 10^{19}$ cm$^{-3}$. Solid line shows the exponential fit to photocurrent decay.

The temperature dependence of Fermi level (determined from temperature dependent Hall electron concentration) in sample A, B and C is shown in Fig.5. Fermi levels in sample A and B lie inside the forbidden gap from 10K to 200K. In sample C, Fermi level lies inside the conduction band at low temperature. In this case, Fermi level decreases as temperature increases and finally enters forbidden gap around 130K. The temperature dependence of $\tau$ in sample C is shown in Fig.6. In this case $\tau$ increases anomalously from 600ms to 2600ms as temperature increases and becomes temperature independent after 120K. This increase of $\tau$ with temperature cannot be explained by capture barrier model[1,2,16,17], which predicts completely opposite behavior. There is only one report[6], where this anomalous behavior of $\tau$ with temperature has been observed in Zn$_x$Cd$_{1-x}$Se. It has been claimed[6] that the stretched-exponential relaxation of photocurrent and increase of $\tau$ with temperature can be
Figure 4: Semi-log plot of normalized Photocurrent decay after termination of photoexcitation in sample C. Solid line shows the exponential fit to photocurrent decay.

observed in highly resistive (\(\rho \approx 10^9\) ohm cm) alloy semiconductor with strong composition fluctuation, which induces phase transition from hopping to percolation transport and results anomalous dependence of \(\tau\) with temperature. Our SiC samples are extremely high quality single crystalline epitaxial layer and heavily doped semiconducting (\(\rho \approx 0.01\) ohm cm) material, hence, neither hopping nor percolation transport is possible in our samples.

We now discuss the anomalous temperature dependence of \(\tau\) in case of heavily doped sample C. We can attribute decay of photoexcited excess electrons into the ground state of impurity, which is macroscopically modeled with capture cross-section. The rate of decay of conduction electrons can be expressed as

\[
\frac{dn}{dt} = -N_T^+ \int T(k)f(E_K, E_F) \frac{d\kappa}{4\pi^3}
\]  

(2)
Figure 5: Temperature dependence of Fermi level in sample A (empty triangles), B (empty squares) and C (empty circles) with different room temperature electron concentration of $8.8 \times 10^{17} \text{cm}^{-3}$, $1.1 \times 10^{18} \text{cm}^{-3}$ and $3.1 \times 10^{19} \text{cm}^{-3}$ respectively.

Where $N_T^+$ is the number of unoccupied impurity levels. $T(k)$ is the transition rate and $f(E_k, E_F)$ is the Fermi-Dirac distribution function. $E_F$ is the quasi Fermi level for electrons. To calculate $T(k)$ we need to know the ground state k-space wave function $A(k)$ of the impurity in k-space. $T(k)$ is proportional to $|A(k)|^2$. If the light intensity is low during photoexcitation of electrons from impurity level to the conduction band and the number of photoexcited electrons is small compared to the conduction band electron concentration, we can assume that $E_F$ is time independent and the right hand side of Eqn.2 will also be time independent during the decay process. Now, the solution of the Eqn.2 will be exponential which is confirmed by the simple exponential fit to the photocurrent decay curves in case of sample A, B and C. We have controlled the light intensities in such a way that the decay characteristics does not depend on the light intensity and photocurrent decay always follows exponential law. In case of degenerate semiconductor, when Fermi level lies inside

---

95
Figure 6: The characteristic decay time constant $\tau$ of photocurrent as a function of temperature is shown for sample C. Solid line shows the theoretical fit.

the conduction band, photoexcited electrons near Fermi level can participate in the capture process. It should be noticed that we have observed the increase of $\tau$ with temperature in sample C as long as Fermi level lies inside the conduction band. It is clear from Fig.5 and 6 that as $E_F$ shifts towards the conduction band minima, $\tau$ increases with temperature till 120K and as the temperature increases further, Fermi level enters the forbidden gap and $\tau$ becomes temperature independent as in the case of sample A and B. Essentially k-space density of impurity wave function is reduced in the range of k-values corresponding to the region of Brillouin zone occupied by photoexcited electrons and causes the PPC effect. At low temperature, the electrons near Fermi level can recombine with the impurity and rate of recombination can be given by(from Eqn.2)
The proposed model of the wave function envelop of impurity and its position relative to conduction band minimum. The direct recombination paths at different temperatures are also shown.

\[ \frac{1}{\tau} = \int T(k) f(E_k, E_F) \frac{d^3k}{4\pi^3} \]  \hspace{1cm} (3)

At very low temperature Fermi function \( f(E_k, E_F) \) can be replaced by \( \theta \)-function and \( T(k) \) (which is proportional to \( |A(k)|^2 \)) can be evaluated directly from the experimental \( \tau \). At relatively higher temperature \( T(k) \) can be determined from Eqn.3 either by using Sommerfield expansion[18] or by numerically solving Eqn.3. We have found that Gaussian-like localized wave function can fit the temperature dependence of \( \tau \), which is shown in Fig.6. It is clear from Fig.6 that \( \tau \) in sample C increases with temperature and this behavior can be explained if we assume that the impurity wave function is shifted in \( k \)-space from the minima of the conduction band in the Brillouin zone. Hence, the increase of \( \tau \) reflects the different region of impurity wave function in \( k \)-space.

This is schematically represented in Fig.7. Now, we can determine the impurity wave
Figure 8: $|\phi(k)|^2$ the probability density of impurity in SiC. Empty squares show the value of $|\phi(k)|^2$ directly determined from experimental τ by replacing the Fermi function with θ-function in Eqn.3 at low temperature ($T\leq30K$).

This behavior suggests that there is an underlying periodicity in the distribution of impurity inside host lattice with wavelength $\lambda$. In this case $\lambda$ is equal to $\frac{2\pi}{k_0} \sim 55\text{Å}$, which is of the order of mean distance between the impurities($\sim 40\text{Å}$) in sample C with $3\times10^{19}\text{cm}^{-3}$ electron concentration. Experimental support for underlying periodicity in the system comes from two facts, (i) the mean distance between impurities is of the order of $\frac{1}{k_0}$ and (ii) the mean distance between impurities is of the order of Bohr radius $a_B^*$ in SiC[15] and hence a substantial interaction can be expected between impurities. Periodic fluctuations in the electron density of the crystal matrix caused by Si and C in SiC are expected to lead to shift in the impurity state wave packet away from minima of the conduction band. There are
theoretical and experimental reports regarding the long range periodic fluctuation in charge densities around Si and C in SiC[19-21], which might favor ordered distribution of impurity in SiC instead of complete random distribution. Indeed, there are several investigations[22-26], which claim to observe the long-period ordering of impurities inside the host lattice. There are both theoretical[27] and experimental[28] evidences for long range periodic fluctuations in the Al-Ga sub-lattice in Al_{x}Ga_{1-x}As. It has been shown[9] that the periodic fluctuation in the electron density due to Al vs. Ga concentration fluctuation can lead to periodicity in the impurity distribution, which gives rise to shift in the impurity wave function away from the minima of the conduction band in the Brillouin zone. Now, it is possible to visualize that high concentration of donor impurities in SiC may develop an ordered lattice inside SiC, which leads to shift of the impurity wave function away from the minima of the conduction band in Brillouin zone. We have chosen the level of doping such that the Fermi level lies inside the conduction band till certain temperature and further increase in temperature results pushing the Fermi level in the forbidden gap. This way the recombination probability between photoexcited electrons around Fermi level and the different region of the impurity wave function in k-space can be controlled by simply varying temperature.

5.4 Conclusions

In conclusion, we have observed anomalous temperature dependence of relaxation time of photoinduced carriers in n-type 6H-SiC. The reverse PPC effect can be explained by an effective-mass like model of impurity with wave-packet centered away from minima of the conduction band possibly due to long-range correlation in the distribution of impurity. The temperature dependent recombination probability depends on the position of the Fermi level inside conduction band and lifetime reflects the different region of the impurity wave function in k-space. The impurity wave function in k-space has been determined from temperature dependent recombination rate of photoexcited electrons.
References


