Evidence for Bistable Defects in 6H-SiC

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Electrical properties of nitrogen (N) doped 6H-SiC have been investigated throughout the temperature range from 10 K to 550 K. Scattering mechanisms in different temperature regions have been investigated. Persistent photoconductivity (PPC) has also been observed. Because of the existence of PPC, we have been able to vary continuously the electron concentration, n, within a *single* sample at fixed temperatures, through the variation of the excitation photon dose. The electron mobility as a function of the electron concentration, $\mu(n)$, has been measured at fixed temperatures. The temperature dependence of the photogenerated electron concentration in the PPC state, Δn, has also been investigated. Experimental results indicate that the defect centers responsible for the PPC effect are bistable in nature, which is analogous to the DX centers in AlGaAs.

Recently, wide bandgap silicon carbide (SiC) semiconductors have been studied intensively.[1,2] This renewed interest arises because they hold great promise for device applications, including electronic devices operating at high-temperature, high-frequency, and high-power combined with high resistance to radiation damage. In the past several years, considerable effort has been directed towards understanding the electrical properties of SiC. For 6H-SiC, it is believed that the nitrogen donor resides at three different lattice sites (one hexagonal, two cubic sites) and that the N donor at different lattice sites have different ground state energies.[3-6] Despite the many investigations conducted, many fundamental properties remain to be understood. The low temperature (T < 50 K) transport properties have never been investigated in the past, probably because SiC has been of interest as a high temperature semiconducting material. Additionally, very little information is available concerning the mobility at low temperatures.

In this paper, we report the results of Hall-effect measurements performed on a N-doped 6H-SiC sample throughout the temperature range from 10 K to 550 K. As reported previously,[7] persistent photoconductivity (PPC) effect has been observed at low temperatures. The electron mobilities, μ, in the dark and in the PPC state has been measured throughout the temperature range of 10 K < T < 550 K. The temperature dependence of the photogenerated free electron concentration has also been measured. Our results indicate that defect centers responsible for the PPC effect are bistable in nature, which is analogous to the properties of DX centers in AlGaAs. N impurities associated with structure defects may be the cause of the bistable defects.

The sample used for this study was a N-doped 6H-SiC bulk single crystal obtained from Cree Research, Inc. Contacts for Hall measurements were made by depositing four Pd spots under vacuum on the corners of a square shaped sample with a subsequent thermal annealing at 950 °C for 5 minutes in Ar. Ohmic behavior for all four contacts was observed. The sample was then attached to a copper sample holder and placed inside a closed cycle He refrigerator with variable temperature from 10 K to 600 K, with care taken to ensure good thermal contact and electrical isolation. A temperature controller enabled us to stabilize the temperature to within 0.2 K. The sample resistivity at room temperature is about 0.1 Ωcm. Resistivity increases by 9 orders of magnitude when the temperature changes from 300 K to 10 K in this sample. The electron concentration and mobility were measured by the standard Van der Pauw method. The magnetic field for the measurements was 0.46 T. The Van der Pauw data are corrected for the finite size contact and the resistivity ratio $R_1:R_2$, where R_1 and R_2 are resistances measured in two different configurations. During the measurements, the difference in R_1 and R_2 never exceeds 10%. The carrier concentration was calculated from $n = (eR_H)^{-1}$, assuming the Hall factor to be 1. The electron concentration at different temperatures in the PPC state was varied by controlling the excitation photon dose, which was the product of the excitation intensity and the illumination time. Similar results have been obtained by using either a Ne lamp, He-Ne laser, or a Hg lamp as an excitation source.

Figure 1 shows the free electron concentration n as a function of reciprocal temperature obtained in the dark in the temperature range from 10 K to 550 K. From the appearance of the Hall data, we can clearly see two separate slopes. Assuming compensation is negligible, the donor ionization energy estimated from the slope of the $\ln(n)$ vs. $1/T$ plot of Fig. 1 (slope $= E_d/2k$) in the temperature region T > 80 K is 110 meV, which is very close to the average between the donor ground state energies associated with the cubic and hexagonal lattice sites as measured by optical measurements.[3-6] Previously, attempts have also been made to determine the donor ionization energies by fitting the Hall data to the equilibrium equation of charge neutrality for a two-donor-level system:[8]

$$n + N_k = \frac{N_1}{1 + (ng_d/N_C)\exp(E_1/kT)} + \frac{N_2}{1 + (ng_d/N_C)\exp(E_2/kT)},$$

where n is the equilibrium free electron concentration, $g_d = 2$ the spin degeneracy factor, and N_C is the density of states in the conduction band and can be written as $N_C = 2M_C(2\pi m_{de}kT/h^2)^{3/2}$ with m_{de} being the density-of-states effective mass of the electron. By taking m_{de} to be 0.3m_0, and M_C, the number of equivalent conduction band minima, to be 6,[6] we have also determined the donor concentration of the hexagonal and the cubic sites N_1 and N_2, ionization energies E_1 and E_2, and the concentration of the compensating acceptor, $N_k = k(N_1 + N_2)$, by the least squares fitting of the above equation to experimental data obtained at T > 60 K. We obtain $E_1 = 86$ meV for the hexagonal site and $E_2 = 131$ meV for the average between
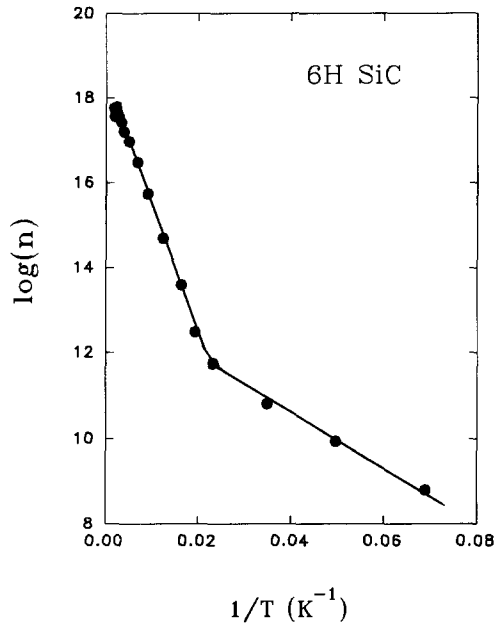
Fig. 1 Dark free electron concentration n_d *versus* reciprocal temperature as obtained from Hall-effect measurements for a N-doped 6H-SiC sample. The solid line shows the linear behavior in the low temperature (T < 60 K) and high temperature (T > 80 K) regions.
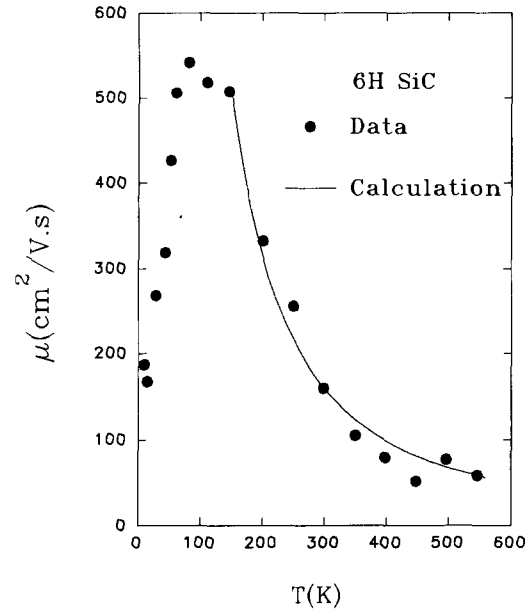

Fig. 2 Electron mobility μ as a function of temperature in darkness for a nitrogen doped 6H-SiC sample. The solid dots are the experimental data and the solid curve above 150 K is the calculation result using $\mu = A'T^{-1.67}$ with $A' = 2.2 \times 10^6$.

the two cubic lattice sites, $N_1 = 2.0 \times 10^{17}$, $N_2 = 8.0 \times 10^{17}$ cm^{-3}, and the concentration of the compensating acceptors N_k is about 8×10^{14} cm^{-3}. In 6H-SiC, there are two cubic lattice sites per every hexagonal lattice site due to the nature abundance. However, this does not mean that $N_2 = 2N_1$ as assumed previously.[6] It can be shown from the free energy calculation that the condition of $N_2 = 2N_1$ cannot be satisfied unless the impurity acquisition energies are the same for the two inequivalent lattice sites. The binding energy of the shallow level as determined from the slope ($= E_d/2k$) of the low temperature Hall data (T ≤ 50 K) in Fig. 3 is 27 meV. The existence of a shallow level is 6H-SiC has been suggested previously,[9] however, its origin was not understood.

Electron mobility μ as a function of temperature in the region of 10 K < T < 550 K has also been measured in darkness as shown in Fig. 2. Since the known binding energies of the ground states of the N donor are relatively deep (averaged to be 110 meV), one would expect that it is the neutral impurity scattering dominating at low temperatures, leading to a mobility behavior independent of temperature.[10] However, in the low temperature region, μ increases with increasing temperature following approximately the relation $\mu \sim T^{3/2}$, which suggests that ionized impurity scattering dominates at low temperatures and hence the existence of a shallow level.[10] Previously, a sudden drop in mobility by more than one order of magnitude as temperature decreases from 100 K to 80 K has also been reported for some 6H-SiC samples, which is much steeper than what we have observed here, e.g., see Fig. 2 of Ref. 6 and there may be an indication of onset temperature for impurity conduction.

At temperatures T > 150 K, the electron-phonon scattering predominantly determines the electron mobility. By considering the electron-acoustic phonon scattering,[10] the mobility μ as a function of temperature for the region of 150 K < T < 550 K can be written as $\mu = AT^{-3/2}$, where the constant A depends on the elastic modules, the

longitudinal and transverse effective masses, and the deformation potential constant. Intervalley scattering is not considered at these temperatures because this scattering mechanism dominates at high temperatures, T > 550 K.[11] If one includes both the electron-acoustic and electron-optical phonon scattering,[10] then the mobility can be written as $\mu = A'T^{-1.67}$. The constant A' differs from the constant A by including both acoustic and optical phonon scattering. At the present, the physical parameters describing A and A' in SiC are not all available. We have used both these equations to compare with our experimental results and found that $\mu = A'T^{-1.67}$ describes the experimental results better. Therefore, electron-optical phonon scattering is also important at higher temperatures and can not be neglected.

The PPC effect has been observed previously in N-doped 6H-SiC samples at low temperatures T < 100 K with lifetimes on the order of 3000 s.[7] The slow relaxation of photoexcited electrons indicates the existence of a potential barrier that prevents the recapture of electrons by the defect ground state. The PPC effect has been most intensively studied in Si- (or Te-) doped $Al_xGa_{1-x}As$.[12] However, the low temperature PPC decay time constants observed in AlGaAs could be as long as 10^{13} s.[13] In AlGaAs, it is believed that bistable deep donor centers (called the DX centers) are responsible for the PPC effect. PPC occurs in AlGaAs because there is a potential barrier which prevents the capture of the photoexcited electrons by the DX center ground state at low temperatures. With the known value of the capture barrier on the order of 200 meV in $Al_xGa_{1-x}As$, we would expect that the capture barrier in SiC must be much smaller because the PPC lifetimes are much shorter. Experiments below 10 K are necessary in order to determine the capture barrier in SiC.

Since the sample under investigation exhibits the PPC effect at low temperatures, the free electron concentration at a fixed temperature can be varied continuously to a certain extent by varying the excitation
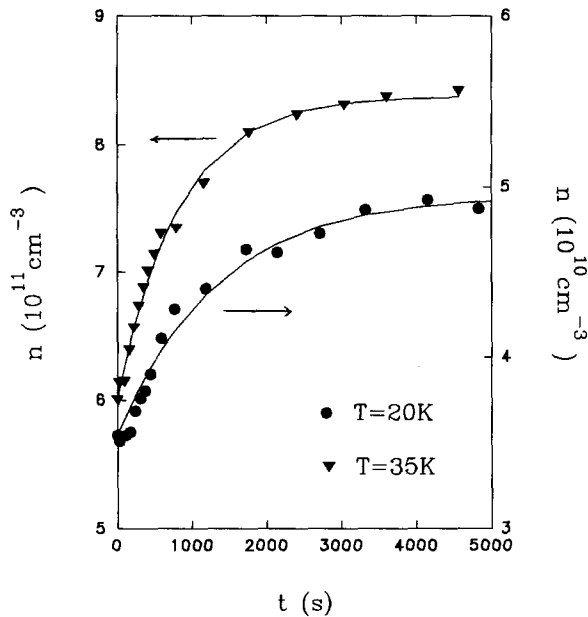
Fig. 3 The variation of the free electron concentration n with illumination time t in the PPC state at two representative temperatures, T=20 K (● ● ●) and 35 K (▼ ▼ ▼). The solid lines are the least squares fitting using Eq. (1).

photon dose. Fig. 3 shows the variation of the free electron concentration n with illumination time under light excitation at two representative temperatures (T=20 and 35 K). Fig. 3 shows that n increases linearly with time at early times, but saturates in about 3000 seconds. We want to point out the fact that in any sample which exhibits only the conventional photoconductivity (PC), n should saturate almost instantaneously upon light exposure with a typical buildup transient time on the millisecond scale or less. The slow buildup of n with time shown in Fig. 3 is another indication that photogenerated electrons are in the PPC state. The buildup transients can be described well by the following equation,

$$n(t) = n_d + \Delta n(1 - e^{-\alpha t}), \qquad (1)$$

which is similar to the PPC buildup transient behavior observed in Si-doped AlGaAs.[14] Here, Δn is defined as the maximum amount of increase in the free electron concentration due to photoexcitation and n_d is the dark free electron concentration before light excitation. The fitted values for T=20 and 35 K are $\Delta n = 1.41 \times 10^{10}/cm^3$ and $2.38 \times 10^{11}/cm^3$, $\alpha = 7.45 \times 10^{-4}$ s^{-1} and 1.21×10^{-3} s^{-1}, respectively. From Fig. 3, we see that Δn, the amount of increase in n due to photoexcitation is in fact increased with an increase of temperature. We have measured Δn at various temperatures and the results are shown as solid dots in Fig. 4. Experimental results shown in Figs. 3 and 4 are peculiar. In general, one expects that the absolute increase in n due to photoexcitation should decrease with increasing of temperature due to the presence of fewer neutral impurities as well as increased capture rates at higher temperatures. Additionally, the buildup electron concentration in the PPC state is very low ($\sim 10^{12}$ cm^{-3}), which seems to suggest that a defect center with low concentration may be responsible for PPC.

The results shown in Figs. 3 and 4 can be explained if the defects which causes the PPC effect are bistable. Bistability is a common phenomenon associated with deep level defects. In Si- (or Te-) doped AlGaAs, Hall data also show two levels, a deep state and a shallow one.[15] However, recent observation of a photoinduced far infrared absorption indicates that shallow state and deep
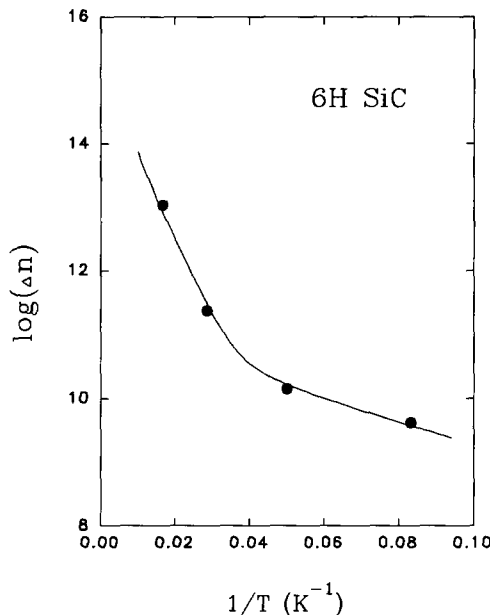

Fig. 4 The maximum amount of increase in free electron concentration due to photoexcitation in the PPC state, Δn, as a function of reciprocal temperature. The solid line is a guide to the eyes.
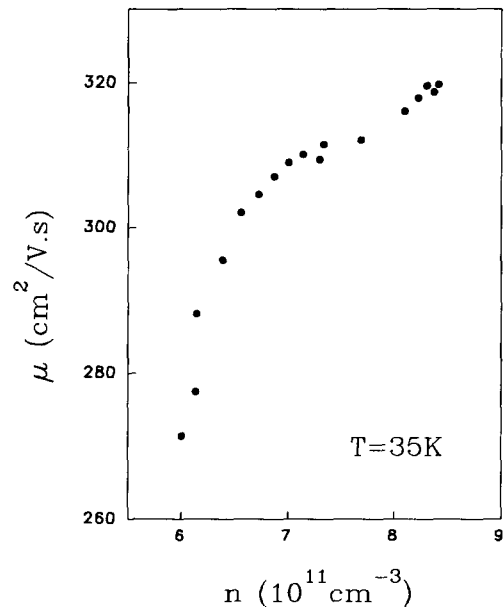

Fig. 5 Electron mobility as a function of electron concentration in the PPC state at temperature T=35 K.

state are just two different appearances of the same chemical species.[16,17] For bistable defect centers, after photoionization of their ground state, electrons would be transferred to the metastable state of the same defect. At low temperatures, this state is in thermal equilibrium with the conduction band and its level determines the free electron concentration in the dark and in the PPC state: it should exhibit electron freeze-out with an activation energy corresponding to the observed energy level of the shallow state shown in Hall data of Fig. 1; the concentration of the photogenerated free electrons excited from the ground state should increase with increasing temperature due to fewer electrons being trapped by the metastable state at higher temperatures, which is what we observed in Figs. 3 and 4. The metastable state is also responsible for the observed ionized impurity scattering at low temperatures as shown in the mobility data of Fig. 2. The PPC effect is a consequence of an electron capture barrier, which arises from the different lattice configurations around each of the two defect states.

Previously, the carrier mobility as a function of carrier concentration at a fixed temperature was obtained by making measurements on many samples with different doping levels.[18] Here, because of the PPC effect, the measurement of μ versus n in a single sample is possible. The advantages of measuring μ as a function of n in a *single* sample using PPC include (1) the obvious simplicity of the measurement, (2) the variations in experimental conditions such as the sample growth conditions and the differences in sample contacts are minimal, and (3) the total impurity concentration in a single sample is fixed, which is closer to the case of real devices. We have measured the electron mobility as a function of electron

concentration at different temperatures in the PPC state. A representative result is shown in Fig. 5 for temperature T=35 K. The general feature is that μ increases with an increase of n in the PPC state. However, it increases rapidly when n is just above the dark concentration and more slowly at higher concentrations. A similar behavior has been observed for different temperatures from 10 K to 60 K. The behavior of μ increasing with an increase of n in the PPC state has been observed in Si-doped AlGaAs materials previously.[19] It has been pointed out that such a behavior could be accounted for by electron-ionized impurity scattering by including the effect of screening by electrons.[20]

In conclusion, electrical properties of a N doped 6H-SiC sample have been investigated using Hall-effect, conductivity, and photoconductivity measurements in darkness and in the PPC state. Experimental results indicate that the defect centers, which are responsible for the PPC effect, are bistable. Many features observed in the PPC state in 6H-SiC are similar to those observed in Si- (or Te-) doped AlGaAs. In 6H-SiC, there are structure defects such as pin-holes, inclusions, and stacking faults. Nitrogen impurities associated with these structure defects at certain locations may be a candidate for the bistable defects, which would explain why the electron buildup level in the PPC state as well as the bistable defect concentration is quite low.

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