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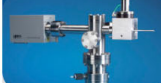
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Lattice relaxed impurity and persistent photoconductivity in nitrogen doped 6H-SiC

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The impurity properties in *n*-type N doped single crystal 6H-SiC semiconductors have been studied by conductivity measurements. A slow decay of the dark current and persistent photoconductivity (PPC) have been observed at low temperatures. Different energy barriers have been obtained at different conditions. Measured donor binding energy, the electron capture barrier, and the emission barrier are 34.6 ± 1.0 , 14.9 ± 0.3 , and 45.6 ± 1.2 meV, respectively. Our results suggest that PPC in SiC has a similar origin as that in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. However the amount of lattice relaxation in SiC is much smaller compared with that in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Experimental results reported in this letter will help to understand the properties of lattice relaxed impurities. It also explains why different energy levels have been obtained previously by different methods.

Recently, silicon carbide (SiC) semiconductors have been intensively studied because of their promising applications which include blue light emitting diode (LED) and high temperature, high frequency, and high power device applications. Nitrogen is an important impurity in *n*-type SiC. Previous infrared absorption experiments showed that the nitrogen impurity in SiC has an energy level of 50–90 meV.^{1,2} However, Hall measurements on the same impurity yielded an energy level of 15–20 meV.³ Other values of donor level of 34–37 meV have also been reported.⁴ Thus the N impurity properties in SiC are still not clear.

Persistent photoconductivity (PPC), photoinduced conductivity that persists after the termination of the photoexcitation, has been observed in II-VI⁵⁻⁷ and III-V⁸⁻¹⁰ semiconductors as well as in amorphous materials.¹¹ However, PPC has never been observed previously in group IV semiconductors. Several mechanisms have been proposed to explain the origin of PPC. PPC in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x \geq 0.22$) is caused by the *DX* centers which undergo a large lattice relaxation (LLR).⁸ According to this model, at low temperatures, PPC decay is prevented by a large electron capture barrier. The large Stokes shift between the optical and the thermal ionization energies can be explained by LLR. It has been suggested recently that the *DX* centers have negative *U* characters,¹² which is supported by many experiments, but it is still under current debate.

In this letter, we report the observations of PPC and of the evidence of lattice relaxation in N-doped SiC. The measured N donor binding energy in SiC is 35 meV, which agrees with the previous value of 34–37 meV.⁴ The behavior of PPC observed in SiC is similar to that in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, but the decay time constant and hence the electron capture barrier are much smaller than those in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$. The decay time constant of PPC in SiC is of the order of a few thousand seconds at low temperatures. This small decay time constant is the result of a small capture barrier of 14.9 meV associated with the N impurity in SiC. This is a sharp contrast with the value of about 160 meV in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$.¹³ The results indicate that the amount of lattice relaxation of N impurity in SiC is much smaller than that of *DX* centers in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. The re-

sults reported here not only can help to understand the properties of lattice relaxation of impurities, but also provide an explanation for different energy values obtained by different experimental methods.

The sample used for this study was a nitrogen doped 6H-SiC single crystal obtained from Cree Research, Inc. Nitrogen impurity concentration was about $2 \times 10^{17} \text{ cm}^{-3}$. Contacts were made by depositing two Pd spots on the sample surface and later annealed at 900 °C for 5 min in Ar atmosphere.¹⁴ Gold leads were attached to the Pd spots using indium and the distance between two Pd spots was about 3 mm. The sample was attached to a copper sample holder, which is inside a closed cycle He refrigerator. A temperature controller enabled us to stabilize temperature within 0.1 K. A 1.5 V bias was supplied by a battery. The sample cooling rate was 6 K per min and slow warmup rate was 0.2 K per min. The low temperature PPC data were taken by using a Ne lamp as the photoexcitation light source. For PPC data, because of the decay of the dark current, we waited for more than 5 h before turning on the excitation light source in order to reach the true dark current level.

The first thing we observed is the decrease of the dark current after the sample is being cooled down to a fixed temperature. The decay of the dark current is very slow and it takes many hours before reaching equilibrium. Figure 1 shows the dark current as a function of decay time at three different temperatures. The dark current is found to decay exponentially with time at a fixed temperature. The solid lines in Fig. 1 are the least square fit using

$$I_d(t) = I_\infty + I_0 \exp(-t/\tau), \quad (1)$$

where $I_d(t)$ is the dark current at different time, I_∞ is the dark current at $t \rightarrow \infty$, and τ is the decay time constant. From the fit we can get I_∞ , the equilibrium dark current at different temperatures. The slow decay behavior of the dark current shown in Fig. 1 together with the observation of PPC discussed later suggests that the N donor in SiC is not a common effective mass type impurity, but it is most likely an impurity with lattice relaxation, just as the *DX* centers in AlGaAs.

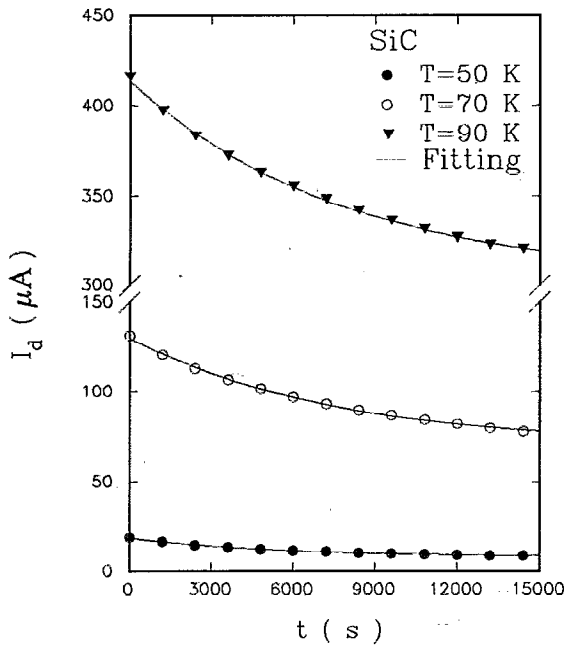


FIG. 1. Plot of dark current as a function of time at three different temperatures. The solid lines are the least square fit using $I_d(t) = I_\infty + I_0 \exp(-t/\tau)$.

The solid triangles in Fig. 2 are the plot of $\ln I_\infty$ vs $1/T$, where I_∞ at different temperatures are obtained by fitting experimental data with Eq. (1). Since the variation of the mobility with temperature is negligible in this temperature range (50 to 150 K),¹⁵ what we plotted in Fig. 2

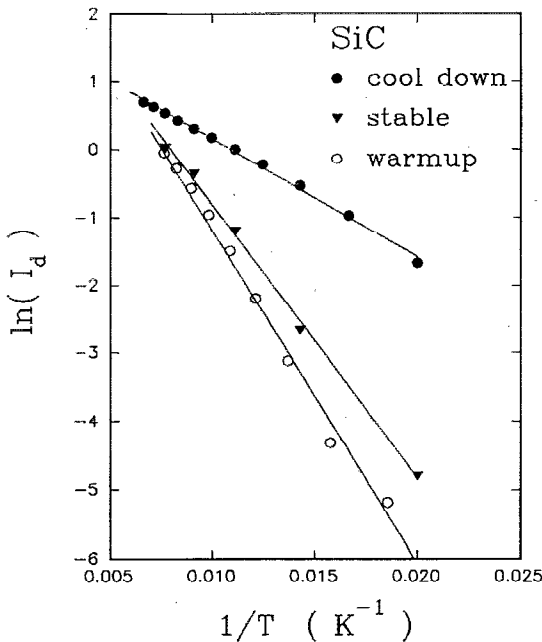


FIG. 2. Solid triangles are the semilogarithmic plot of equilibrium dark current I_∞ vs $1/T$. Solid (open) circles show semilogarithmic plot of dark current vs $1/T$ for cooling down (slow warmed up) process. The linear behavior shows exponential decrease of dark current with temperature at three different experimental conditions. Three different slopes give donor binding energy, 34.6 ± 1.0 meV, and the electron capture and emission barriers, 14.9 ± 0.3 and 45.6 ± 1.2 meV, respectively.

is the relative equilibrium electron concentration in the conduction band at different temperatures, which depends only on the donor binding energy even for a lattice relaxed impurity. As a result, we expect that I_∞ depends exponentially on temperature. The linear behavior of this plot shows that $I_\infty \propto \exp(-\Delta E/kT)$, where ΔE is the donor binding energy or the energy difference between the conduction band minimum and the nitrogen impurity level. ΔE obtained from Fig. 2 is 34.6 ± 1.0 meV. From the observations of the dark current decay and PPC, we expect that the N impurity in SiC is different from the effective-mass type impurity. We thus measured the dark current as a function of temperature by cooling the sample at a rate of about 6 K per min. The cooling rate is selected so that the sample has enough time to come to the surrounding temperature. Solid circles in Fig. 2 show the experimental results. The Arrhenius plot for this condition in Fig. 2 indicated an electron capture barrier of 14.9 ± 0.3 meV. We also measured the dark current as a function of temperature during the warm up process. The open circles in Fig. 2 have been obtained as the sample is being warmed up slowly from 59 to 150 K at a rate of 0.2 K per min. Again a linear behavior is obtained with an activation energy level of 45.6 ± 1.2 meV. This energy level is corresponding to the electron thermal emission barrier.

Figure 2 shows that one can obtain different energies under different experimental conditions, which can be explained by the lattice relaxation model. Electrons in the conduction band will be captured by ionized impurities as the temperature is being decreased. The results of triangles and solid (or open) circles in Fig. 2 correspond to the equilibrium and nonequilibrium processes, respectively, thus different energy levels have been obtained. Therefore, the measured 14.9 meV during the cooling process is the electron capture barrier that prevents an immediate capture of electrons by ionized impurities. During the warm-up process, the electron concentration in the conduction band is determined by the emission barrier. The measured thermal emission barrier energy 45.6 ± 1.2 meV is expected to be approximately equal to the donor binding energy 34.6 ± 1.0 meV plus the electron capture barrier energy 14.9 ± 0.3 meV, which is consistent with the experimental results within the experimental error. The behavior here is similar to that of the DX centers with lattice relaxation.⁸ Our experimental results indicate that different energies reported previously for N donors in SiC correspond to these different energy barriers. The energy level of 50–90 meV obtained from infrared absorption experiments may be corresponding to the optical emission barrier, which is larger than the electron thermal emission barrier. This indicates that most likely there exists a Stokes shift for nitrogen impurities in SiC.

Figure 3 shows the PPC decay characteristics of N doped SiC at $T=10$ K. The solid curve is fitted by the stretched-exponential function

$$I_{\text{PPC}}(t) = I_0 \exp[-(t/\tau)^\beta], \quad (2)$$

where I_0 ($=89$ nA) is the current at time $t=0$, the moment the excitation light has been terminated, τ is the decay time

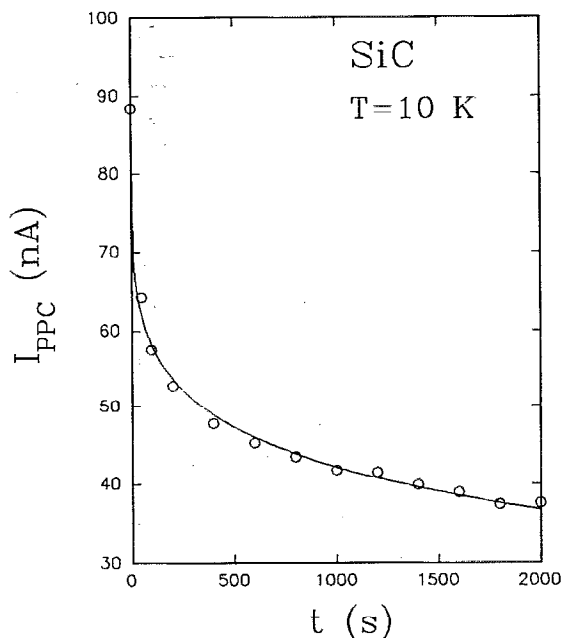


FIG. 3. The decay of PPC in SiC at temperature $T=10$ K. The solid line is the fit by the stretched-exponential function, $I_{PPC}(t) = I_0 \exp[-(t/\tau)^\beta]$. The dark current has been subtracted from I_{PPC} .

constant, and β is the decay exponent. The dark current has been subtracted in Fig. 3. The fitted values are $\beta=0.22$ and $\tau=3387$ s. The results obtained here is no surprise since PPC decay behaviors in II-VI^{6,7} and III-V¹³ semiconductors also follow the stretched-exponential function. The decay curve clearly shows that the photoconductivity persists even after 2000 s of the termination of excitation light source. The PPC in N doped SiC is observable at temperature below 150 K. The decay time constant τ here is much smaller than those in $Al_{0.3}Ga_{0.7}As$ at low temperatures,¹³ which is expected from a smaller capture barrier of 15 meV. In $Al_xGa_{1-x}As$, the capture barrier is 160 meV and the decay time constant at low temperature is of the order of 10^{13} s.¹³ Our results suggest that PPC in SiC has a similar origin as that in $Al_xGa_{1-x}As$. However, the origin of the lattice relaxation in SiC may be different compared with that in $Al_xGa_{1-x}As$. The lattice relaxation of N impurity in SiC is not due to the alloy effect or the application of pressure as that in $Al_xGa_{1-x}As$. Here, nitrogen substitute mostly carbon atoms in SiC.¹⁶ Because of the complicated structure of 6H-SiC, substitutional nitrogen may occupy three inequivalent sites for C in 6H-SiC.^{16,17} For example, N can occupy either a cubic or a hexagonal environment with respect to the adjacent layers. These non-equivalent positions may cause lattice relaxation after the impurity substitution. This interpretation is consistent with the results of the self-consistent pseudopotential calculations, which reveals the structure relaxation in SiC polytypes.¹⁸ As indicated by Qteish *et al.*¹⁸ that symmetry allows for the existence of inequivalent Si—C bonds which, in turn, allows for bond-to-bond charge transfer and hence structure relaxation. The small decay time constant of PPC

and small electron capture barrier in SiC suggest that the lattice relaxation involved here is small. The results obtained from this material together with the previous results from III-V semiconductors suggest that lattice relaxation may be a very common phenomenon in certain types of semiconductors.

In summary, properties of N impurities in SiC have been studied by measuring the conductivity and photoconductivity at different temperatures. We found that the dark current decays exponentially with time at low temperatures. Low temperature PPC has also been observed for the first time in group IV semiconductors and the decay time constant of PPC is of the order of 10^3 s. N donor binding energy of 34.6 meV has been obtained from the measurement of the equilibrium dark current as a function of temperature in *n*-type SiC semiconductors and it agrees with the published data. Measured electron capture and emission barriers are 14.9 and 45.6 meV, respectively. The decay behavior of PPC in SiC is similar to those in II-VI and III-V semiconductors and follows the stretched-exponential function. Lattice relaxation of N impurity has been used to explain the experimental results. However, the amount of the observed lattice relaxation of the N impurity is much smaller than that of DX centers in III-V semiconductors.

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