Passivation of Surface Recombination at the Si-Face of 4H-SiC by Acidic Solutions

Yoshihito Ichikawa,1 Masaya Ichimura,1 Tsunenobu Kimoto,2 and Masashi Kato 1,2

1Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Nagoya 466-8555, Japan
2Department of Electronic Science and Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

We carried out carrier lifetime measurements for 4H-SiC single crystals in aqueous solutions with various pH by the microwave photoconductivity decay method. For both n- and p-type 4H-SiC, carrier lifetimes measured by Si-face excitation were longer in acidic aqueous solutions compared with carrier lifetimes measured in other solutions. On the other hand, for C-face excitation, carrier lifetimes did not depend on immersion solutions. These results indicate that carrier recombination centers at the surface of the Si-face was passivated by hydrogen ions. We also estimated surface recombination velocities $S_S$ by a numerical analysis. $S$ of the Si-face was reduced from 700 cm/s (in Na$_2$SO$_4$ 1 M) to 200 cm/s (in H$_2$SO$_4$ 1 M) for the n-type 4H-SiC.

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Experimental

Samples used in this work were freestanding n- and p-type 4H-SiC epilayers which were originally grown with $\sim 150 \mu m$ thick on the (0001) Si-face with 4° woff angle toward <11 20> of bulk single crystal 4H-SiC substrates and then the substrates were completely polished. The n-type samples have a nitrogen donor concentration of $1 \times 10^{15} \text{cm}^{-3}$, while the p-type samples have an aluminum accepter concentration of $6 \times 10^{15} \text{cm}^{-3}$. Such relatively low-concentration doping in the samples is to induce long bulk carrier lifetimes and it facilitates estimation of surface recombination. Chemical mechanical polishing was performed for both the Si- and (0001) C-faces and roughness and damaged layer were removed as much as possible. Resulting thickness of the samples were 100 and 40 $\mu m$ for the n-type and 100 and 60 $\mu m$ for the p-type, and, in this paper, we show results for the 100 $\mu m$ thick samples unless otherwise noted. All measurements in this study were performed for the Si- and C-faces of the samples. Carrier lifetimes for all the samples were measured by the microwave photoconductivity decay (µ-PCD) method at room temperature. In fact, although there have been several methods for the carrier lifetime measurement, due to easiness of signal detection from the sample in the aqueous solutions, we adopted µ-PCD in this study. In the µ-PCD method, we employed 266 or 355 nm pulsed yttrium aluminum garnet (YAG) lasers with a pulse width of 1 ns as an excitation source. The penetration depths for 4H-SiC are 1.2 $\mu m$ and 48 $\mu m$ for 266 nm and 355 nm, respectively, and only 1.2 $\mu m$ penetration for 266 nm excitation makes surface recombination dominant in measured carrier lifetimes. Microwave of 10 GHz was irradiated to the samples and its reflection was used as a probe. We measured the carrier lifetime with injected photon densities of $8 \times 10^{13} \text{cm}^{-2}$ to keep the low injection condition for reliable measurements with a sufficient signal-to-noise ratio. In the measurements, the samples were immersed into a quartz cell filled with an aqueous solution or held in air ambient as a reference condition. For the aqueous solutions, we employed H$_2$SO$_4$, HCl, Na$_2$SO$_4$ and NaOH with concentration of 1 mM to 1 M corresponding to pH range of the solution from 0 to 14. In addition, HF of 1 wt% was also employed. Whenever we changed the aqueous solutions, we cleaned the samples by ultrasonic cleaning within acetone and pure water. In the estimation of carrier lifetimes, we defined the 1/e lifetime $\tau_{1/e}$ as the µ-PCD decay time from a peak to 1/e. We numerically solved a differential equation of the excess carrier density to reproduce experimental $\tau_{1/e}$ and estimated $S$ (the detail of the numerical analysis which has improvement in accuracy from the analysis in Refs. 7 and 9 was described in the Supporting Information).

Results and Discussion

Figure 1 shows µ-PCD decay curves for the n-type sample with excitation on the Si-face by 266 nm in the air and aqueous solutions. The aqueous solutions were H$_2$SO$_4$, HCl, Na$_2$SO$_4$ and NaOH with concentration of 1 M or HF with concentration of 1 wt%. When the sample was immersed into the acidic aqueous solutions (i.e. H$_2$SO$_4$, HCl or HF), the decay curves were more gradual than in the other conditions, and HF has less influence than H$_2$SO$_4$ and HCl. This indicates that the n-type sample in acidic solutions show longer carrier lifetimes than in the neutral or alkaline solutions and lower pH will have more effects on the carrier lifetimes. Figure 2 shows µ-PCD decay curves of the n-type sample with excitation on the C-face by 266 nm in the air or in the aqueous solutions. When the C-face was excited, µ-PCD decay curves are almost independent on immersing solutions.

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Silicon carbide (SiC) has attracted attention for high-power, high-frequency and high-temperature electronic devices due to its superior electrical and physical properties. In particular, bipolar devices based on 4H-SiC single crystals are operable in higher voltage ranges than conventional Si devices and thus development of bipolar devices is highly expected. Furthermore, SiC is applicable as photocathode for solar-to-hydrogen energy conversion. For 4H-SiC, although formation of high quality oxide layers is applicable to passivate SiC surfaces are required and, to establish passivation methods for surface recombination velocities $S_S$ have been estimated for the Si- and C-faces of 4H-SiC. However, passivation methods for surface recombination on SiC have been rarely reported. In the case of Si, formation of surface oxide layers or immersion into HF suppress surface recombination and they have been utilized in practical applications. For 4H-SiC, although formation of high quality oxide layers is applicable to suppress surface recombination, processes to form such layers are relatively complicated. In addition, SiC with insulating oxide layers cannot operate as photocathodes. Therefore, other methods to passivate SiC surfaces are required and, to establish passivation methods, we need to understand physics and chemistry for surface recombination phenomenon. In this report, we focus on passivation of surfaces of 4H-SiC single crystals by aqueous solutions. We measured carrier lifetime for 4H-SiC in various aqueous solution and discussed effects of the solutions on the surface condition.

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Figure 1. \(\mu\)-PCD decay curves for the Si-face of the 100 \(\mu\)m n-type sample excited by 266 nm in the air or in the aqueous solutions. (The lines are calculated curves with \(\tau_B = 3\) \(\mu\)s, \(S_C = 2500\) cm/s, and \(S_{Si} = 200\) or 700 cm/s).

Figure 2. \(\mu\)-PCD decay curves for the C-face of the 100 \(\mu\)m n-type sample excited by 266 nm in the air or in the aqueous solutions. (The lines is calculated curve with \(\tau_B = 3\) \(\mu\)s, \(S_C = 2500\) cm/s, and \(S_{Si} = 700\) cm/s).

Although H\(_2\)SO\(_4\) is more effective compared with HCl as shown in Fig. 1, the observed decay curves indicated that carrier lifetime mainly depends on pH. Thus, we plot pH dependence of \(\tau_{1/e}\) obtained from the \(\mu\)-PCD decay curves for the n-type sample as shown in Fig. 3. H\(_2\)SO\(_4\), HCl, Na\(_2\)SO\(_4\) and NaOH were used to control pH, and pH are calculated by molar concentrations. In the measurements for the Si-face with 266 nm excitation, \(\tau_{1/e}\) depends on pH. \(\tau_{1/e}\) was longer in more acidic solutions, and at similar pH it is longer in H\(_2\)SO\(_4\) than in HCl. On the other hand, with 355 nm excitation, \(\tau_{1/e}\) shows less dependence on pH compared with 266 nm excitation. For excitation of the C-face, \(\tau_{1/e}\) does not show significant dependence on pH for excited by 266 and 355 nm.

Figure 4 shows pH dependence of \(\tau_{1/e}\) for the p-type samples obtained from the \(\mu\)-PCD decay curves. As observed for the n-type samples, \(\tau_{1/e}\) is longer at lower pH when the Si-face was excited by 266 nm. Considering penetration depth, \(\mu\)-PCD decay curves obtained by excitation with 266 nm are more sensitive to surface recombination than those obtained by 355 nm excitation. Therefore, the pH dependence of \(\tau_{1/e}\) for the Si-face excitation by 266 nm indicates that the acidic solutions suppress surface recombination at the 4H-SiC Si-face.

To observe the stability of suppression of surface recombination, we measured the samples in air after immersion into 1 M H\(_2\)SO\(_4\) for 5 minutes. Figure 5 shows \(\tau_{1/e}\) for the n- and p-type samples before (the bare samples) and after immersion, and the measurements were for the Si-face excitation by 266 nm. Even if the samples were measured in the air after immersion, \(\tau_{1/e}\) were longer than the bare samples (difference in \(\tau_{1/e}\) enhancement by immersion between the n- and p-types samples is due to difference in bulk carrier lifetimes as described later). As time elapsed, \(\tau_{1/e}\) became shorter with a time constant of 200 min for the n-type and 500 min for the p-type. In fact, we also tried Fourier transform infrared spectroscopy measurements to observe chemical bonds between the acidic solutions and the Si-face surfaces. However, no significant difference was observed between immersion in acidic and other solutions due to very weak signals from chemical bonds at the surface.

We considered two possible origins for the suppression of surface recombination by the acidic solutions: (i) increase of the band bending at the surface, and (ii) passivation of surface states by substances in the

Figure 3. pH dependence of \(\tau_{1/e}\) for the 100 \(\mu\)m n-type sample obtained from \(\mu\)-PCD decay curves. At similar acidic pH with the same excitation wavelength and crystal face, larger \(\tau_{1/e}\) are obtained in H\(_2\)SO\(_4\) and smaller ones are in HCl.

Figure 4. pH dependence of \(\tau_{1/e}\) for the 100 \(\mu\)m p-type sample obtained from \(\mu\)-PCD decay curves. At similar acidic pH with the same excitation wavelength and crystal face, larger \(\tau_{1/e}\) are obtained in H\(_2\)SO\(_4\) and smaller ones are in HCl.

Figure 5. Time dependence of \(\tau_{1/e}\) for the 100 \(\mu\)m n- and p-type samples excited by 266 nm for the Si-face after immersed into 1 M H\(_2\)SO\(_4\) for 5 min, and bare indicates \(\tau_{1/e}\) before immersion.
acids. Origin (i) can be considered as follows. In general, an interface of a semiconductor with an aqueous solution introduces the band bending at the semiconductor surface. The band bending and resulting the electric field will introduce drift velocities to electrons and holes, and either ones are attracted to the surface and the other ones are pushed to the bulk. Since surface recombination requires presence of both electrons and holes at the surface, the band bending induces surface recombination.6,10,19 In addition, the band bending generally depend on pH of the aqueous solution theoretically with a ratio 59 mV/pH,22,23 and for n-type semiconductors, contact with acidic aqueous solutions reduces the band bending. If pH dependence of the band bending dominates the surface recombination for the n-type 4H-SiC, carrier lifetimes should be longer in alkaline solutions. However, our experimental results show long carrier lifetimes in acidic solutions for the n-type sample, and pH dependence also shows the same tendency regardless of the conductivity type of 4H-SiC. Thus origin (i) is unlikely as a suppression mechanism of surface recombination. Turning to origin (ii), passivation of interfaces between an oxide film and SiC by nitrogen or other elements has widely been reported,14,15,22 and theoretical calculation for passivation of the surface states on the Si-face of 4H-SiC by hydrogen has also been reported.21 Furthermore, there has also been reported that photoluminescence from deep levels is suppressed for SiC microcrystals in acidic solutions.24 Considering all the acidic solutions observed in this work suppressed the surface recombination at the Si-face of 4H-SiC, hydrogen passivation of the surface states on the Si-face is most probable. Hydrogen passivation has also been reported for Si, and the effects are not stable in air similarly to our experimental results.11,12 Slight difference in passivation effects between HCl and H2SO4 has also been observed for Si, although the origin of the difference has never been understood.13

We estimated the surface recombination velocity S to quantify the effects of the passivation. In this analysis, we solved a differential equation of excess carrier density as described in the Supporting Information. From the experimental τB for the samples with two different thicknesses obtained by both 266 and 355 nm excitation, we estimated the bulk lifetime τB and S to reproduce τB, by calculation for all the conditions. For the n-type samples, we estimated τB of 3 μs and S for the C-face of 2500 cm/s. When we set S for the Si-face of 700 cm/s, the calculation well reproduced the experimental decay curve measured in air and neutral pH (1 M Na2SO4). On the other hand, a calculation with S of 200 cm/s reproduced the experimental decay curve in the acidic condition (1 M H2SO4). Calculated decay curves for the Si-face excited by 266 nm were also shown in Figs. 1 and 2 by the solid lines. The calculations with these parameters also reproduced the experimental decay curves obtained by 355 nm excitation. This analysis indicates that, in acidic aqueous solutions, S for n-type 4H-SiC is significantly reduced from ~700 to ~200 cm/s. The same analysis was carried out for the p-type samples. In air or 1 M Na2SO4, estimated S is 1000 cm/s, S at 6000 cm/s and τB is 1.5 μs. On the other hand, calculation with S of 300 cm/s reproduced the experimental decay curves in the acidic conditions. Since obtained S in H2SO4 is smaller than those in air and neutral and alkaline solutions, we consider that recombination centers at the Si-face of 4H-SiC is effectively passivated by hydrogen.

Conclusions

We measured carrier lifetimes for 4H-SiC in various aqueous solutions. For both n- and p-type, 4H-SiC with Si-face excitation by 266 nm showed longer carrier lifetimes in the acidic solutions than in the other solutions. This result indicates that the acidic solutions suppress surface recombination on the Si-face. Hydrogen in the acidic solutions would passivate surface states which act as carrier recombination centers. Estimated surface recombination velocities in 1 M H2SO4 were 200 and 300 cm/s for the n- and p-type, respectively. Unfortunately, since passivation effects gradually decrease with time in air at room temperature, passivation by acidic solutions cannot be used for fabrication processes for electronic devices. However, when we can stabilize bonding of hydrogen to atoms at the Si-face of 4H-SiC, hydrogen passivation will induce small S resulting in low on-resistance bipolar SiC devices. In addition, crystalline quality inspection by carrier lifetime measurements requires low S as in common inspections in the Si industry, because only τB reflects crystalline quality. Therefore, surface passivation by acidic solutions will be available for crystalline quality inspection of SiC. Furthermore, photocatalytic reaction of SiC will be enhanced in acidic solutions, and thus SiC photocatalysts will effectively work in acidic conditions.

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ORCID

Masashi Kato  https://orcid.org/0000-0002-2921-709X

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