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Estimation of Influence on Carbon Vacancy Regarding 4H-SiC Substrate Grown by HTCVD Method

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Abstract. In order to increase productivity and reduce the cost of wafers, we have developed a high temperature chemical vapor deposition (HTCVD) method that can realize the high-speed growth of 4H-SiC crystals. Tokuda *et al.* reported an interesting study in which the carrier lifetime of a substrate grown by HTCVD (HTCVD substrate) was considerably shorter than that of the substrate grown by physical vapor transport (PVT); moreover, bipolar degradation was highly suppressed when the HTCVD substrate was applied to PiN diodes [1]. Herein, we demonstrate that the short carrier lifetime of the HTCVD substrate is mainly attributable to the carbon vacancy (V_C) and that V_C particularly diffuses from the HTCVD substrate to the epitaxial layer.

Introduction

Recently, the mass production of SiC materials as power devices has spread worldwide. One of the largest markets is the automotive industry, which needs to meet the rapid demand for electrification. SiC-metal oxide semiconductor field-effect transistors (SiC-MOSFETs) are widely applied from the viewpoint of the operating voltage in the automotive industry, and every company is involved in their development and mass producing. SiC-MOSFETs with built-in diodes are generally utilized for reducing the production cost. These are expected to outperform Si owing to their excellent material properties, although the high cost remains a major concern. There are several reports on the cost breakdown of SiC-MOSFETs [2-4], with the substrate and yield losses accounting for roughly half and one-fourth of the total cost, respectively. Since yield loss is also related to crystal quality, high-quality low-cost substrates are desired.

In order to meet these demands, we have developed a high-temperature chemical vapor deposition (HTCVD) method for preparing 4H-SiC crystals. The fundamental concept of HTCVD for 4H-SiC crystal growth and the fabrication of a 150-mm high-quality 4H-SiC wafer have been reported before [5-6]. Interestingly, an HTCVD substrate that can prevent bipolar degradation has also been reported [1]. In the previous study, the carrier lifetime of the HTCVD substrate was < 2.5 ns and this extremely short carrier lifetime could contribute to the single Shockley stacking faults (1SSFs) suppression. However, the origin of this short carrier lifetime is not precisely known.

In this study, we investigate how HTCVD substrates are beneficial to bipolar degradation. We demonstrate that the short carrier lifetime of the HTCVD substrates originates from the carbon vacancy (V_C), which is well known as the origin of the $Z_{1/2}$ center—a common lifetime killer [7]. Additionally, we demonstrate that V_C particularly diffuses from the HTCVD substrate to the epitaxial layer.

Experimental

The number of atomic vacancies in crystals generally increases with increasing exposed temperature. We deduced that the short carrier lifetime of the HTCVD substrate originated from the large number of V_C because the surface temperature of crystals during their growth is approximately 2500 ºC in HTCVD, and the temperature in HTCVD is higher than that in physical vapor transport (PVT). If this assumption is correct, the carrier lifetime can be expected to increase upon the introduction of carbon ions (C-ions) to fill the vacancies. Ion implantation was achieved at a substrate temperature of 500 ºC with a C-ion density of 1.4×10^{16} cm^{-2}, and acceleration voltage of 350 keV. Following the ion implantation, annealing was performed at 1600 ºC with a carbon cap, following which the cap was removed by O_2 annealing. We estimated the carrier lifetime from the microwave photoconductance decay (μ-PCD) measurements using a yttrium lithium fluoride third harmonic generation laser ($\lambda = 349$ nm) as the excitation source at a microwave probe frequency of 26 GHz. We confirmed the density of V_C by electron paramagnetic resonance (EPR) spectroscopy using an undoped crystal. EPR spectroscopy was conducted at a microwave frequency of 9.45 GHz by applying a magnetic field along the c-axis. The field was swept from 3270 to 3470 G in the temperature range of 30-80 K.

Considering the diffusion coefficient in 4H-SiC [8-9], it is evident that the thermal diffusion of V_C is easier than that of impurities. Particularly, V_C can easily diffuse from the substrate to the epitaxial layer for substrates containing a large number of V_C. However, the EPR technique has no spatial resolution. Thus, we confirmed the diffusion of V_C in the epitaxial layer as a distribution of the $Z_{1/2}$ density measured by deep level transient spectroscopy (DLTS). The ratio between the $Z_{1/2}$ density and V_C density was considered 1:1 in this study. We prepared commercialized substrates grown by PVT (PVT substrate) and an HTCVD substrate. We grew 9.5-μm thick epitaxial layer with donor density of 1.0×10^{15} cm^{-3} on the Si-surface of these substrates. The epitaxial growth temperature and C/Si ratio were 1625 ºC and 1.0, respectively. Following the epitaxial growth, we diced to prepare 5 mm × 5 mm chips and fabricated Schottky Barrier Diodes (SBDs) to perform the DLTS measurement. We evaluated not only the as-epi samples but also the samples which exhibited activation annealing equivalent to the maximum thermal load in a device process (1750 ºC, 30 min).

Details of each sample in this study are provided in Table 1. Here, PVT (A) and (B) refer to commercialized substrates supplied by different venders.

Table 1

Measurement	Substrate	Epitaxial layer	Process
μ-PCD	HTCVD	w/o	None
μ-PCD	HTCVD	w/o	C-ion implantation and annealing
EPR	HTCVD (undoped)	w/o	None
DLTS	HTCVD	w/	None
DLTS	PVT (A)	w/	None
DLTS	PVT (B)	w/	None
DLTS	HTCVD	w/	Annealing
DLTS	PVT (A)	w/	Annealing
DLTS	PVT (B)	w/	Annealing

Results and Discussion

Influence of V_C on the HTCVD substrate. The results of the μ-PCD measurement of the HTCVD substrate are shown in Figure 1. The time resolution of the measurement system was 2.5 ns. Because sufficient signal intensity and S/N ratio were not obtained, carrier lifetime of the as-polished sample (before implantation and annealing) was concluded to be < 2.5 ns. However, the signal clearly recovered after ion implantation and annealing, and its 1/e carrier lifetime was estimated to be 113 ns. The change can be attributed to the filling of vacancies by external carbon injection, as expected. Therefore, we concluded that the shortened carrier lifetime of the HTCVD substrate is primarily attributable to V_C. Moreover, we confirmed the density of V_C in the HTCVD substrate by EPR spectroscopy using an undoped crystal, assuming a density of 3.1×10^{15} cm^{-3}.

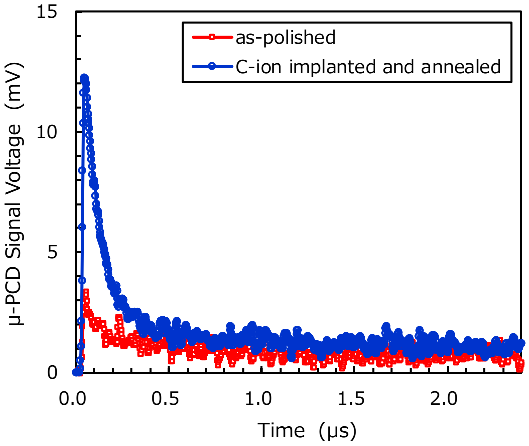

Fig. 1. μ-PCD for the HTCVD substrate before and after C-ion implantation and annealing

Diffusion of V_C from substrate to epitaxial layer. We confirmed the influence of V_C diffusion from the substrate to epitaxial layer by performing DLTS using the fabricated SBD. For the distribution of $Z_{1/2}$ density, the observable depth from the surface was limited to 6 μm in this study owing to the upper limit in applying bias in this system, although the epitaxial layer was 9.5 μm thick. Figure 2 shows the results of the DLTS measurement for the as-epi samples. The distribution trend of all the samples remained largely consistent up to a distance of 5 μm from the surface, and the $Z_{1/2}$ concentration was higher toward the surface. It is considered that the carbon atoms easily leave the crystals because the surface is exposed during the epitaxial growth. A difference is observed only in the regions deeper than 5 μm. We confirmed that the $Z_{1/2}$ density increased only in the HTCVD sample in the deeper region. This indicates that V_C diffuses to the epitaxial layer from the HTCVD substrate even at a relatively low temperature of 1625 ºC. A nearly identical trend is observed for the samples annealed at 1750 ºC with a carbon cap (Figure 3). An increase in the density of $Z_{1/2}$ for the HTCVD sample due to the thermal diffusion of V_C from the substrate could be clearly observed. We presume that the differential concentration of V_C between the epitaxial layer and substrate acts as the driving force for diffusion because the HTCVD substrate has more V_C than the PVT substrate. The drop in concentration at the surface may be due to the carbon cap during annealing. The carbon cap prevents the carbon atoms from leaving the system and instead, supplies carbon atoms to fill the vacancies.

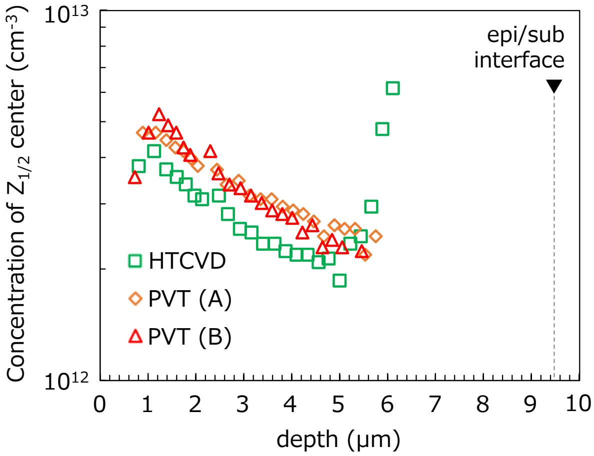

Fig. 2. Distribution of $Z_{1/2}$ density for the as-epi samples

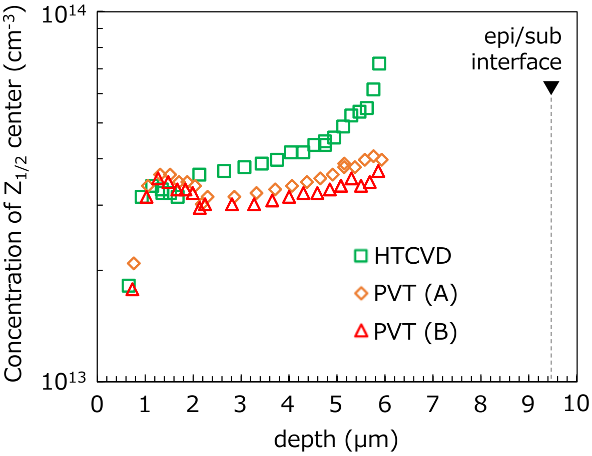

Fig. 3. Distribution of $Z_{1/2}$ density for the annealed samples

The result in Figure 3 was simulated through calculations using formulas reported previously [9]:

$$\frac{\partial[V_C]}{\partial t} = G_{V_C} + \frac{\partial}{\partial x}\left(D_{V_C}\frac{\partial[V_C]}{\partial x}\right) - 4\pi R\left(D_{C_i} + D_{V_C}\right)[C_i][V_C], \tag{1}$$

$$\frac{\partial[C_i]}{\partial t} = G_{C_i} + \frac{\partial}{\partial x}\left(D_{C_i}\frac{\partial[C_i]}{\partial x}\right) - 4\pi R\left(D_{C_i} + D_{V_C}\right)[C_i][V_C], \tag{2}$$

Here, $[X]$, V_C, C_i, and R denote the density of X, carbon vacancy, interstitial carbon, and the capture radius for the recombination annihilation of V_C and C_i, respectively. G and D denote the thermal generation rate and diffusion coefficient corresponding to V_C or C_i, respectively. We referred to previous study to obtain the coefficient and boundary conditions and solved these equations using FlexPDE—a universal solver for partial differential equations [9-10]. Based on the simple model shown in Figure 4 which is followed the real samples, we first determined the initial V_C density in the epitaxial layer and then calculated the thermal diffusion of V_C at 1750 ºC for 30 min. The initial V_C density of the entire epitaxial layer was taken to be 3.25×10^{12} cm^{-3} as an average $Z_{1/2}$ density for depth of 1-5 µm using experimental results (Figure 2). We changed the initial V_C density of the substrate from 5×10^{13} to 1×10^{16} cm^{-3}, solved the equations, and confirmed the correspondence between the experimental and simulation results. The simulation results are shown in Figure 5. The results were in good agreement with the case for a V_C density of 3×10^{15} cm^{-3} for the HCTVD substrate and 1×10^{14} cm^{-3} for the PVT substrate. Furthermore, for the HTCVD substrate, the V_C density estimated by simulation was close to that obtained by EPR measurement.

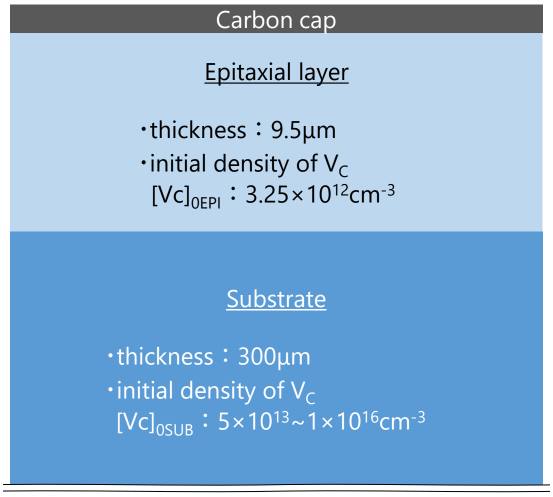

Fig. 4. Simulation model

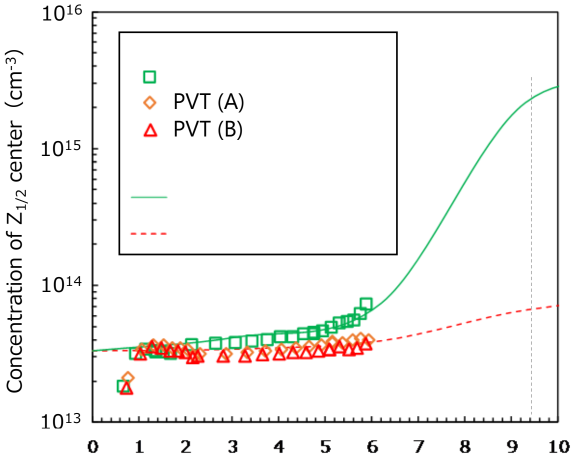

Fig. 5. Calculation results for V_C diffusion in annealed samples

Conclusion

We implanted C-ions, annealed, and performed µ-PCD measurements to evaluate the influence of V_C on the lifetime of an HTCVD substrate. The lifetime of the as-polished sample (before implantation and annealing) was evaluated to be < 2.5 ns owing to the insufficient signal intensity and poor S/N ratio in the µ-PCD experiment. In contrast, for the sample after ion implantation and annealing, the signal intensity recovered notably, and the 1/e lifetime was evaluated to be 113ns. Thus, we concluded that the short lifetime of the HTCVD substrate was primarily attributable to V_C. EPR measurements using an undoped sample revealed that the density of V_C in the HTCVD substrate was 3.1×10^{15} cm^{-3}.

V_C has been reported to diffuse more easily than impurities such as Al, B, and N in 4H-SiC [8-9]. Since there is a possibility that V_C diffuses from the substrate to the epitaxial layer during thermal processes, we carried out DLTS measurements to evaluate the distribution of V_C in terms of $Z_{1/2}$ in the epitaxial layer on each substrate. The ratio between the density of $Z_{1/2}$ and density of V_C was considered 1:1 in this study. As a result, we observed that V_C clearly diffused to the epitaxial layer from the HTCVD substrate for both as-epi and annealed samples, compared to the case of commercialized PVT substrates. As for a sample equivalent to activation annealing, the simulated curve with an initial density of V_C as 3×10^{15} cm^{-3} in the substrate was in good agreement with the experimental data for the HTCVD substrate. Furthermore, this initial value used for the simulation was close to the V_C density estimated from the EPR measurements.

The HTCVD substrate and its epitaxial layer have more V_C than PVT substrates. Therefore, an HTCVD substrate is beneficial to bipolar degradation because the large number of V_C acts as a lifetime killer and effectively suppresses the hole density around the epi/substrate interface and the 1SSFs expansion.

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