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Electrically Detected Magnetic Resonance (EDMR) Studies of SiC-SiO_2 Interfaces

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Abstract. We discuss the results of electrically detected magnetic resonance (EDMR) spectroscopy on SiC-SiO_2 interfaces interacting with hydrogen and nitrogen. Three types of Si-face 4H-SiC metal-oxide-semiconductor field effect transistors (MOSFETs) were examined by EDMR in the temperature range of 4–300 K. These samples revealed several different characteristics from those of the earlier electron spin resonance (ESR) and EDMR studies on SiC-SiO_2 interfaces. The most significant finding was the high-density doping of nitrogen shallow donors into the channel region after the post nitridation anneal. The incorporated nitrogen donors were observed as an "Nh" EDMR signal at 4–20 K. The roles of these nitrogen donors are discussed in connection with the electrical properties of SiC MOSFETs.

ESR and EDMR Studies on SiC-SiO_2 Interface Systems

ESR spectroscopy on metal-oxide-semiconductor (MOS) systems was first demonstrated in 1971 [1]. It successfully detected three types of ESR centers, P_a, P_b, and P_c in Si-SiO_2 interfaces [1], and currently, we are familiar with the P_b centers [Si dangling bonds (DBs)] which are dominant and intrinsic defects in this interface system. Many other ESR centers in this MOS system have since been reported [2]. In contrast, ESR might not be so successful for studying SiC-SiO_2 interfaces, despite them being similar to the Si-SiO_2 interface and having a much higher interface-state density. There is a clear difference between Si and SiC; ESR measurements on Si always require a special pre-treatment of the sample surface, owing to undesirable ESR signals from the surface/interface region. In contrast, such a pre-treatment is not necessary for SiC samples, even if their surfaces are oxidized.

Why doesn't ESR work the same way for SiC-SiO_2 as it does for Si-SiO_2 interfaces? There is as yet no answer, but it may be related to several differences between the two MOS systems.

The first notable difference is the wider band gap of SiC (e.g., 3.24 eV for 4H-SiC) [3]. In principle, this wider band gap makes it possible to involve novel types of interface states in SiC MOS systems that are different from the P_b-like centers in Si. The other notable difference is the presence of carbon atoms in the SiC-SiO_2 interface. Thus, carbon-related defects have been proposed as the origin of the SiC MOS interface states [3-6]. For example, ESR studies revealed an amorphous carbon signal of g (g value) ≈ 2.003 in some oxidized 3C/4H/6H-SiC wafers [3,4] (in particular, this signal was strong in *p*-type 3C MOS samples). In addition, theoretical studies predicted a high density of carbon dimers (a pair of threefold coordinated carbons) in the interface [5,6]. Although such carbon dimers have not been experimentally detected so far, similar defects (the HEI5/6 centers) have been identified by conducting ESR on bulk samples [7]. Therefore, ESR may have the potential for detecting the key defects arising from carbon atoms.

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There are several important reports on carbon-related interface defects detected by ESR and electrically detected ESR [we shall call this "electrically detected magnetic resonance (EDMR)"]. One famous study reported a carbon DB center (labeled "P_{bC}", their g values are $g_{\|} = 2.0023$ and $g_{\perp} = 2.0032$) in oxidized *porous*-SiC [8,9]. This is a really P_b-like center at the SiC-SiO_2 interface, and it exhibited a chemical reaction with hydrogen [9], similarly to the P_b center [2]. Unfortunately, the same ESR signal has not been detected from single-crystal wafer samples, so the areal density of P_{bC} at the interface is not yet known. Accordingly, we cannot conclude if the P_{bC} center accounts for the major part of the high-density interface states.

Another type of carbon-related interface center was found in 4H/6H-SiC MOSFETs by taking advantage of the EDMR technique [10-12]. This center had $g = 2.0027$ and the same signatures as the well-studied silicon vacancy in bulk (the V_{Si}^- center [13]). Accordingly, the $g = 2.0027$ center has been identified as a silicon-vacancy center *in the interface* [12]. Basically, a silicon vacancy has four carbon DBs which generate several energy levels in the mid gap of SiC [13]. The important features of this center are that (1) it was present in some 4H/6H-SiC MOSFETs because it has been detected by EDMR on these devices, (2) its signal intensity was extremely high, suggesting a high concentration of this defect, and (3) it could be annihilated when the MOS interface was nitrided [12]. From these results, this center was proposed as a dominant interface defect [12]. Moreover, after the nitridation of the interface, another type of P_b-like defect was observed by EDMR [11,12]. This was taken to be a sort of DB perpendicular to the interface, with new g values of $g_{\|} = 2.0026$ and $g_{\perp} = 2.0010$.

The above ESR/EDMR studies indicate that it is possible to correlate the origin of the SiC-SiO_2 interface states with carbon-related interface defects. Furthermore, their reactions with hydrogen and nitrogen at the interface were also observed. We should, however, point out that these findings are only the beginning, and it will be necessary to continue ESR and EDMR studies on a wider variety of SiC-SiO_2 interfaces. The reason is that we have obtained different EDMR results using different samples.

Low-temperature EDMR Study

We employed the same EDMR technique [10-12] as used in SiC MOSFETs. However, contrary to the earlier ESR/EDMR studies [4,8-12] that were done at room temperature, our EDMR measurements were mainly done at low temperatures (down to 4 K). It is generally known that many ESR centers, related to shallow energy levels or associated with thermal activation processes, become detectable when the temperature goes down (e.g., carbon dimers in the bulk were clearly detected under such conditions [7]). As expected, our study revealed such low-temperature signals.

For the EDMR measurements, we prepared three different MOSFET samples. They are *n*-channel lateral 4*H*-SiC MOSFETs (gate length = 100 µm, gate width = 150 µm) fabricated on *n* or *p* epitaxial layers of Cree 8°-off 4*H*-SiC(0001) Si-face wafers (for the *n* epitaxial layer, $[N] \approx 5\times10^{15}$ /cm^3 and Al implantation was performed with $[Al] \approx 1\times10^{20}$ /cm^3). Source/drain regions were formed by high-dose phosphorus implantation ($[P] \approx 1\times10^{20}$ /cm^3) and were connected to Ni contacts. Gate oxides were grown by dry oxidation (dry SiO_2 thickness = 50 or 60 nm) and were subjected to post-nitridation annealing (NO-N_2O ambient at 1250°C) or post-hydrogen annealing (H_2 ambient at 650°C). We used poly-Si gate electrodes. Finally, three 4*H*-SiC MOSFET samples, labeled "Nitrogen," "Hydrogen," and "Dry" (dry oxidation only), were prepared. Their field-effect channel mobilities (μ_{FE}) varied from 2.5 cm^2/V·s (the Dry sample) to 19.2 cm^2/V·s (the Nitrogen sample). Some of the MOSFETs were subjected to γ-ray irradiation (average energy = 1.2 MeV, dose = 2.3 Mrad) at room temperature.

The EDMR spectra were measured using lateral channel currents (I_{ds}) between the source and drain of each MOSFET in the dark. Only ESR centers interacting with the channel current could be detected in this regime. In principle, the inversion layer of the channel region allows paramagnetic states only in the vicinity of the conduction band edge (E_C). Thus, ESR centers in such a shallow region will be detectable. The currents I_{ds} were 1–100 nA under drain-source biases (V_{ds}) of 1–5 V

and gate-substrate biases (V_{gs}) of 1–30 V at 4–300 K. We were not able to measure V_{gs} over 30 V because of large gate leakage currents. At 4 K, only the Nitrogen samples could activate the channel current, and only for these samples could we measure the 4 K EDMR spectra. The reason for this exception will be explained later. To excite the ESR transition, we used a Bruker Bio-Spin TE_{011} microwave cavity and 9.4-GHz microwaves at a power of 32–200 mW. Small changes in I_{ds} (expressed in ppm) due to ESR were monitored by a lock-in amplifier synchronized with a magnetic-field modulation at 1.56 kHz. The readers may consult our papers (Refs. [14] and [15]) for more details on the experimental parameters.

In the following sections, we separately present our EDMR results for the Hydrogen sample and the Nitrogen/Dry samples, from which we will discuss the behaviors of shallow interface defects, hydrogen, and nitrogen in the SiC-SiO_2 interfaces.

Hydrogen-related Interface Defects

EDMR results for the Hydrogen sample were already presented in Ref. [14]. Here, we shall review the important points of those results. (1) In the as-prepared MOSFETs, no EDMR signals were observed at 20–300 K. We emphasize that no interface signals of P_{bC} [8,9], silicon vacancy [10,12], or new DB center [11,12] were observed in our samples. (2) After the γ-ray irradiation, two EDMR signals were detected at 20 K, labeled "P_{H0}" and "P_{H1}" (Fig. 1). The role of γ-ray irradiation is most likely to remove the effect of hydrogen passivation in the Si MOS system [2]. (3) The P_{H1} signal exhibited an isotropic doublet hyperfine splitting (hfs) of 5.4 mT, which is most probably due to a hydrogen nucleus (^{1}H, nuclear spin I = 1/2, natural abundance = 99.99%) nearby this defect. In summary, the observed defects should be related to hydrogen.

The P_{H0}/P_{H1} signals disappeared in the temperature range between 20 and 50 K, most probably due to the lifetime broadening. This feature was not seen in the previous interface signals [3,4,8-12]. The g values of P_{H0}/P_{H1} (g = 2.003–2.004, slightly anisotropic) were close to those of the silicon-vacancy signal (g = 2.0027) [10,12,13] or amorphous carbon signal (g = 2.0030) [3,4]. The signal width was found to be fairly anisotropic (peak-to-peak width = 1.3 mT and 0.8 mT for the [0001] and [11-20] directions, respectively), and this indicated an anisotropic structure for the P_{H0}/P_{H1} centers.

Our provisional assignment for the P_{H0}/P_{H1} centers is that they are a family of carbon DBs with/without a nearest hydrogen atom [14]. We imagined that in as-prepared samples, they were passivated by hydrogen atoms and became visible after breaking C-H bonds by γ-ray irradiation. A single ^{1}H hfs (5.4 mT) of the P_{H1} center suggests that a passivated hydrogen is immediately captured at the neighboring site of a carbon DB. In contrast, in the case of the P_{H0} center, a hydrogen atom may diffuse far away from a defect site. These centers may be consistent with the predicted carbon-dimer defects [5,6]. The carbon dimers hold DB-like orbitals on threefold coordinated carbons, which can interact with hydrogen atoms [5].

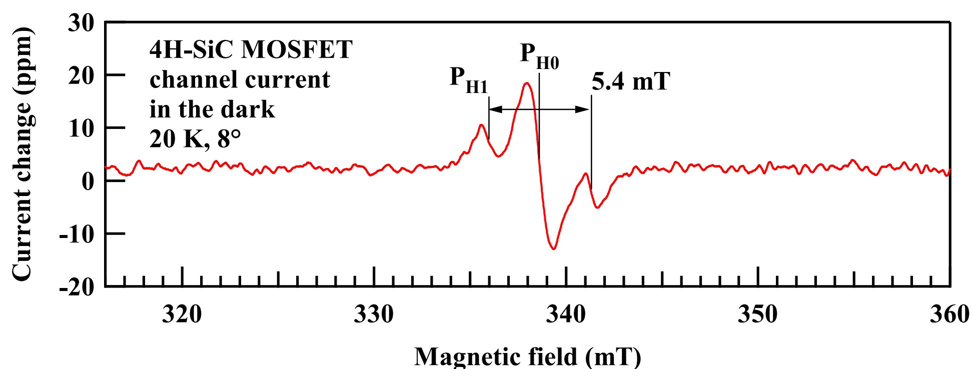

Fig. 1. P_{H0}/P_{H1} EDMR signals in the Hydrogen sample [14]. These signals were observable at 20 K and after γ-ray irradiation.

However, we *do not* consider that the P_{H0}/P_{H1} centers are dominant defects at the interface. Their EDMR signal intensities were smaller than 30 ppm in I_{ds}; they were too small, e.g., compared with the case of the interface silicon-vacancy center (10^2–10^3 ppm) [12]. Furthermore, it should be mentioned that some of the Hydrogen samples did not exhibit these signals even after γ-ray irradiation. Thus, it is difficult to correlate the P_{H0}/P_{H1} centers with the major part of the SiC-SiO_2 interface states. This conclusion seems consistent with the general agreement about SiC-SiO_2 interfaces such that the hydrogen annealing is often ineffective for improving their quality [3,5], and it is strikingly in contrast to the case of Si-SiO_2 interfaces [2].

Nitrogen Shallow Donors in the Channel

We compared the Nitrogen and Dry samples fabricated with almost the same process. EDMR results for these samples will appear in a separate paper in detail [15], and we pick up again notable points of those results. (1) In both the Nitrogen and Dry samples, the room-temperature signals of the P_{bC} center, the interface silicon vacancy, and the new DB center [8-12] were below the detection limit. Therefore, in some types of MOSFETs like ours, these interface defects may not be dominant. (2) On the other hand, at 20 K, EDMR signals became detectable in the Dry sample [Figs. 2(a) and (c)]. One signal was similar to the P_{H0} signal [Fig. 2(c)]. There might also be a very broad resonance in higher magnetic fields [Fig. 2(a)]. If this broad resonance was a powder-pattern signal, its g values were roughly estimated in the range between 1.0 and 1.4. Since this range was out of the normal range of ESR centers in SiC, we can draw no conclusion about this signal at present. However, its signal intensity would be 100 times larger than that of the P_{H0}-like signal because of its large signal width. Thus, this signal might be a candidate for the origin of the interface states. (3) The above EDMR signals were absent in the Nitrogen sample [Figs. 2(b) and (c)]. This behavior is similar to those reported for the room-temperature EDMR signals [10,12]. In summary, nitrogen atoms are effective for removing some interface defects detectable at room temperature and at 20 K as well. (4) Even after γ-ray irradiation, the Nitrogen samples did not show any EDMR signals at 20 K. This behavior was in contrast to the case of hydrogen. Therefore, nitrogen atoms should form stable binding states in the interface region. (5) At 4 K, a very strong sharp signal was observed in the Nitrogen samples (Fig. 3). This signal was unchanged after the γ-ray irradiation. We labeled it "Nh".

The Nh signal was strongly anisotropic. The angular dependence of this signal showed a *c*-axial (C_{3v}) symmetry with $g_{\parallel} = 2.0047$ and $g_{\perp} = 2.0008$, which is similar to the case of nitrogen shallow donors at the carbon *h* site of 4*H*-SiC ($N_C(h)$) [16]. Table 1 summarizes the ESR signatures of the Nh center and two shallow donors, $N_C(h)$ and $N_C(k)$. Nh and $N_C(h)$ showed similar hyperfine splitting of the ^{14}N nucleus ($I = 1$, natural abundance = 100%) and observable temperatures. Therefore, we concluded that the Nh signal originates from the *h*-site nitrogen shallow donors *in the channel region*. The Nh signal exhibited strong lifetime broadening (Fig. 3) and eventually disappeared above 20 K.

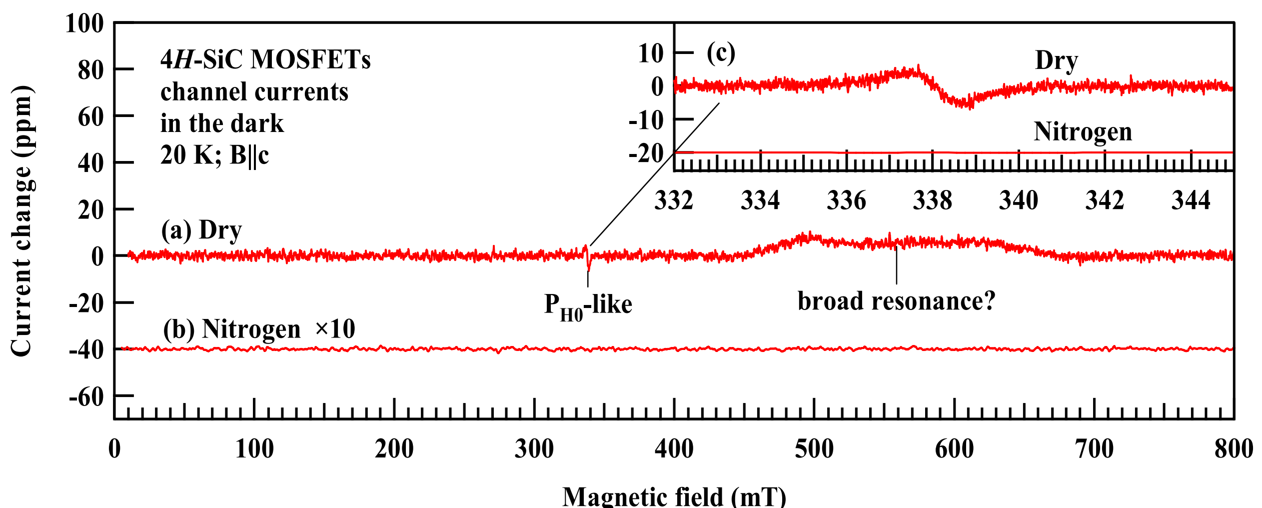

Fig. 2. EDMR signals of shallow interface defects in the Dry sample [15]. These signals became observable at 20 K.

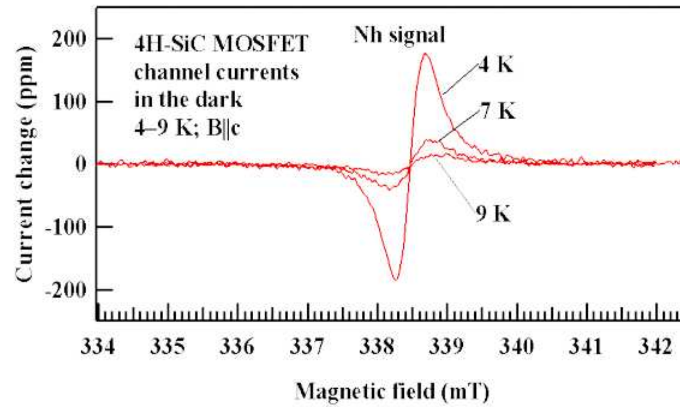

Fig. 3. Nh EDMR signal in the Nitrogen sample, observable below 20 K [15].

Table 1. ESR parameters of nitrogen shallow donors in 4*H*-SiC MOSFET and bulk 4*H*-SiC.

Nitrogen center	Symmetry	$g_{\parallel}$ $g_{\perp}$	^{14}N hfs (mT)	Observable Temp. (K)	Ionization energy to E_C (meV)	Activation energy of lifetime broadening	Ref.
Nh (MOSFET channel)	C_{3v}	2.0047 2.0008	<< 0.4	≤ 20 K	N/A	3.3 meV	[15]
$N_C(h)$ (bulk)	C_{3v}	2.0055 2.0010	0.2	≤ 20 K	52 meV	7.6 meV	[16]
$N_C(k)$ (bulk)	C_{3v}	2.0043 2.0013	3.6	≤ 80 K	92 meV	45.5 meV	[16]

The present results indicate that after post-nitridation annealing, nitrogen atoms can diffuse even into the channel region and act as shallow donors there. In fact, the Nitrogen sample showed an enhanced channel current at 4 K owing to this "nitrogen doping" effect, while the other MOSFET samples could not activate the channel current at the same temperature. Moreover, the very intense Nh signal (= 10^2–10^3 ppm) suggested a substantial level of nitrogen doping.

In fact, we could have measured the "doped" nitrogen atoms by means of x-ray photoemission spectroscopy (XPS) [17]. For the XPS measurements, we prepared "Nitrogen" and "Dry" wafer samples similarly to the corresponding Nitrogen and Dry MOSFET samples. Then, after completely etching the oxide layer with a diluted hydrofluoric acid, we measured the XPS spectra of the two wafer samples. In the Nitrogen and Dry wafer samples, the oxygen peaks due to the oxide layer were completely eliminated after the etching. However, in the Nitrogen wafer sample, nitrogen peaks were still clearly detectable, in addition to silicon and carbon peaks of the substrate. On the basis of this observation, we estimated the nitrogen concentration in the substrate to be on the order of 10^{14} cm^{-2}. Some of the nitrogen atoms may change into shallow donors as a result of the high-temperature annealing during the nitridation. The total nitrogen concentration measured by XPS increased linearly as the nitridation temperature increased in the range between 800 and 1400 °C. Simultaneously, the interface-state density was found to decrease from 2×10^{12} cm^{-2}eV^{-1} to 5×10^{11} cm^{-2}eV^{-1} at $E_C - 0.2$ eV.

Effect of Nitrogen Donors on SiC MOSFET

We consider that nitrogen atoms play two significant roles in the Si-face SiC MOS system. One is to remove some interface defects, as evidenced in both the room-temperature EDMR studies [10-12] and our low-temperature EDMR studies. Another is that they behave as a shallow donor in the channel region. Below, we briefly discuss how the nitrogen shallow donors influence the electrical properties of SiC MOSFETs.

First, nitrogen shallow donors increase the carrier concentration (Q_{ch}) of the channel region. This increase may amount to up to 10^{14} cm^{-2} at maximum. Simultaneously, they cause a drop in the threshold voltage (V_{th}) of the SiC MOSFET via compensation of the acceptor concentration (N_A) in the channel (c.f., $V_{th} \propto N_A^{1/2}$). In fact, a drop in V_{th} has been observed in many nitride SiC MOSFETs [18], and in ours as well [15].

Second, nitrogen shallow donors increase the "Coulomb mobility" [19] of electrons in the channel. Since high-density free carriers suppress the Coulomb scattering mechanism [19], the channel mobility (μ_{FE}) may be improved by the free carriers emitted from the "doped" nitrogen donors. In addition, the increase in Q_{ch} causes a higher I_{ds} current, which appears as a higher μ_{FE} value. Of course, the reduction in the interface states caused by binding nitrogen atoms also contributes to increasing μ_{FE}.

In contrast, the high-density nitrogen donors increase the surface potential fluctuation, causing "surface roughness" scattering [19]. This mechanism degrades μ_{FE}. Consequently, the nitrogen donors may have opposing effects on the channel conductivity, and hence, their presence may result in an intermediate level of performance. This model offers one reason why the nitridation process could not fully alleviate the channel mobility degradation of SiC MOSFETs.

Summary

We studied the SiC-SiO_2 interface regions of three types ("Hydrogen", "Nitrogen", and "Dry") of 4*H*-SiC MOSFETs by means of low-temperature EDMR measurements. The earlier ESR/EDMR studies were done at room temperature, and our study revealed novel behaviors of this interface system at low temperatures. We observed that hydrogen and nitrogen atoms at the interface could passivate or annihilate some of the shallow interface defects. In the case of nitrogen, another significant role was found: nitrogen doping of the channel region. We supposed that the high-density nitrogen donors in the channel region greatly influence the channel conductivity of SiC MOSFETs. We conducted that the post-nitridation technique for SiC MOSFETs must be optimized to make better use of the different behaviors of nitrogen atoms.

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