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SiC MOS Interface States: Similarity and Dissimilarity from Silicon

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We here discuss SiC MOS interface states based mainly on microscopic information given by electron spin resonance (ESR) spectroscopy. Despite structural similarities between Si-SiO_2 and SiC-SiO_2, SiC MOS interfaces exhibit some dissimilarities from Si MOS ones. One example is the presence of carbon-related defects at there. Reactions to hydrogen and nitrogen atoms are also quite different between the two interfaces. We present recent our findings on the behaviors of these atoms at SiC MOS interfaces.

SiC MOS interfaces

In the last two decades, silicon carbide (SiC) is intensively studied as a promising wide-band-gap semiconductor for power electronics. This material is unique compared to other wide-band-gap semiconductors [1], because it has a high compatibility to the silicon technology. For instance, ion implantation techniques are available for both *n*- and *p*-doping, making it possible to design a variety of device structures with both small and large sizes. Moreover, we can use thermally grown silicon dioxide (SiO_2) for dielectric/insulating layers in SiC devices. These features realize normally-off metal-oxide-semiconductor field effect transistors (MOSFETs) of SiC as similarly to Si MOSFETs. Currently, SiC devices including SiC MOSFETs are going to be commercialized into many electric apparatus. Since SiC-SiO_2 interfaces have structural similarities to Si-SiO_2 ones (abrupt interfaces [2] consisted of Si-O bonds [3]), the Si MOS system will set a good model for SiC MOS systems.

On the other hand, it is also known that there are some dissimilarities between Si and SiC MOS systems. Such dissimilarities seem to link with unresolved issues in SiC MOS technology. The primary issue is that microscopic origins of SiC MOS interface states are not yet established. In silicon, main interface states originate from the P_b centers (Si dangling bonds (DBs) at the interface) [4]. Since the P_b centers can interact with hydrogen (H) atoms, H passivation is quite useful for the Si MOS technology. On the contrary, this technique was often ineffective for SiC MOS interfaces. This is a big difference between Si and SiC, and is related to a different nature of SiC MOS interface states. So far, these states have been studied by many groups [5-13] including Afanas'ev-Stesmans [5] and Lenahan [10] who are also great specialists of Si MOS interfaces. Briefly looking at the whole results, carbon-related defects are believed to play an important role in this interface. The microscopic information about such defects was mainly revealed by electron-spin-resonance (ESR) spectroscopy, as similarly to the case of Si-SiO_2 interface states. In this paper, we discuss SiC MOS interface states based on

ESR data. Here our discussions are limited to 4H-SiC MOS interfaces of *c*-facet wafers, because the state-of-the-art SiC devices were fabricated on such wafers. The 4H-SiC crystal (band gap = 3.26 eV) exhibits excellent physical properties and the highest wafer quality.

Si face vs. C face. In 4H-SiC, it is notable to distinguish two different surfaces and interfaces, called SiC(0001) (Si face) and SiC(000$\bar{1}$) (C face). These surfaces have quite different chemical properties. For instance, an oxidation rate is much lower for Si face (a few % of the case of Si(001)) than for C face (ibid ~80%) at 1200 °C. A method for improving their MOS interfaces is also quite different between Si and C faces [13]. For C face, hydrogen incorporation into the interface is often effective to reduce the interface-state density (D_{it}) and increase the channel mobility. On the contrary, for Si face, nitrogen or phosphorous incorporation into the interface gains the highest improvement. Currently, Si face is mostly studied and used for device fabrication. Since most of SiC MOSFETs are operated using *n*-channel, interface states near the conduction band edge (E_C) are of the highest importance. The D_{it} value was successfully reduced to ~10^{11} cm^{-2}/eV at E_C – 0.2 eV after some improving processes. Owing to this reduction, the field-effect mobility (μ_{FE}) was increased from 1 ~ 5 cm/V·s to 20 ~ 100 cm/V·s. However, these improved values are still much lower than μ_{FE} in a low doped bulk region of 4H-SiC (~1000 cm/V·s), which is one of the most serious problem in SiC MOS technology.

ESR analysis on SiC MOS interfaces

Current status and issues

ESR spectroscopy is a powerful tool for identifying microscopic origins of singly-occupied energy levels. In particular, ESR has a fruitful history in Si MOS technology [4]. On the contrary, for SiC MOS interfaces, ESR may not be so successful in spite of their higher D_{it}. Possible reasons for this are considered as follows. One essential reason is supposed that SiC-SiO_2 interface states may not be singly-occupied defect levels (either empty or doubly-occupied levels) unlike the case of Si. This situation is more likely for shallower interface states near the band edge. To observe such shallow states, it may be necessary to perform low-temperature ESR studies under charge pumping (photo excitation or current injection). However, previous ESR studies on SiC MOS samples were mostly carried out at room temperature (R.T.).

Another technical reason is related to the quality of SiC substrates. In general, SiC substrates include residual defects (mainly vacancy-related defects) and impurities (e.g., unintentionally doped nitrogen). A typical density is > 10^{14} cm^{-3} or > 10^{12} cm^{-2} for a 0.01-cm-thick specimen. Their ESR signals are overlapping over interface signals, especially at low temperatures. To avoid such a disturbance, a few methods have been attempted. One is to enhance interface signals using porous-SiC samples [9]. The other is to apply electrically detected ESR technique (EDMR: Electrically Detected Magnetic resonance) [10] which can focus on an interface region by means of electrical currents. We tried the latter approach.

Table I summarizes ESR signals in SiC MOS structures. In the early stages, carbon-cluster signals (amorphous carbon DB signals) were reported for oxidized SiC wafers [5,6]. The Afanas'ev-Stesmans's group proposed that carbon clusters with various sizes are the origin of a continuous distribution of D_{it} near the band edge [5]. This model may be valid for the valence band side of 3C-SiC MOS interfaces, because the carbon-cluster signals were strong in *p*-type 3C-SiC. In 4H-SiC and 6H-SiC, however, such signals were

usually absent. In addition, residual carbon clusters in the interface region has not been observed by other spectroscopic analyses [2,3]. Judging from these facts, the carbon clusters are probably negligible in D_{it} near E_{C} at the-state-of-the-art 4H-SiC MOS interfaces. The 2nd signal in Table I (assigned to a sort of Si DBs [7]) may be also negligible nowadays, because of its absence in the present MOS samples.

Later, the $P_{b\mathrm{C}}$ center (interfacial carbon DB) was found in porous SiC-SiO_2 samples [8]. This name means "the P_b center on a carbon atom", and it was really similar to the original P_b center, except a difference between Si and C. In fact, the $P_{b\mathrm{C}}$ center was passivated by a H atom in the temperature range of 400~800 °C [9]. However, this center has not been observed in single-crystal samples. Its areal density as well as its location (either Si face or C face) is also unclear. Therefore, it is also unclear whether this defect relates to the major part of D_{it}.

More recently, the Lenahan's group have found a strong Si-vacancy signal [10] (the V_{Si}^{-} signal of negatively charged Si vacancy at *k* (quasi-cubic) site [14]) by taking advantage of EDMR technique. This signal was observed in 4H/6H-SiC MOSFETs (Si face) with dry oxidation. The location of the Si vacancies seems to be separated from the interface, because they preserved the same high symmetry (T_{d}) and high spin state (electron spin = 3/2) as they are in bulk. In 4H-SiC, a Si vacancy in low symmetric positions should appear as a different ESR signal such as the T_{V2a} signal (negatively charged Si vacancy at *h* (hexagonal) site, $C_{3\mathrm{v}}$ symmetry [14]). With lowering the symmetry, a fine splitting should become detectable in ESR.

In nitrided SiC MOSFETs, the Si-vacancy signal vanished [10], suggesting that the Si-vacancy levels (close to the midgap [14]) were eliminated by the nitridation. The Lenahan's group also reported another interesting signal (the 5th signal in Table I) which was observed in the other type of 4H-SiC MOSFET [10]. This signal was assigned to a sort of *c*-axial interface DBs. For these centers, further experiments are desired to clarify their roles in SiC MOS interfaces.

TABLE I. ESR signals of SiC MOS interfaces. *g* means gyromagnetic value (g value) of each signal.

	Center	Method (Temp.)	Sample & Remarks	ESR signatures	Ref.
1	C cluster (carbon DB in amorphous-C)	ESR (R.T.)	oxidized 3C-SiC (*p*-type), some re-oxidized 4H/6H-SiC	g = 2.003 (isotropic)	[5] [6]
2	DB center (Si DB?)	ESR (R.T.)	oxidized 4H/6H-SiC (*p*-type)	g = 2.0028~2.0062	[7]
3	$P_{b\mathrm{C}}$ (carbon DB at interface)	ESR (R.T.)	oxidized porous-SiC, reacting with H at 400~800°C	g = 2.0023~2.0032	[8] [9]
4	V_{Si}^{-} (Si vacancy near interface)	EDMR (R.T.)	4H/6H-SiC MOSFET (Si face), in sub. current	g = 2.0027 (isotropic)	[10]
5	new DB center (*c*-axial DB at interface)	EDMR (R.T.)	4H-SiC MOSFET (Si face, ONO gate), in sub. current	g = 2.0026~2.0010	[10]
6	$P_{\mathrm{H0}}/P_{\mathrm{H1}}$ (carbon DBs interacting with H)	EDMR (20K)	4H-SiC MOSFET (Si face, H_2 annealed), in channel current	g = 2.004~2.003 & ^{1}H hfs (isotropic)	[11]
7	Nh (channel N donor)	EDMR (4K)	4H-SiC MOSFET (Si face, NO annealed), in channel current	g = 2.0047~2.0008	[12]

Our low-temperature ESR and EDMR studies

We have also investigated SiC MOS interfaces using ESR and EDMR. Our measurements were carried out mainly at low temperatures for exploring shallow

interface states. In fact, we have found different signals and results from the previous studies, as is seen in the following two subsections.

Hydrogen and SiC MOS interfaces. So far the relationship between H and interfaces has been revealed in two cases. The first one is the P_{bC} center [9] as noted in the above. Probably, the P_{bC} center associates with relatively deep interface states, because its signal was observable at R.T. The second case is our EDMR study on 4H-SiC MOSFETs (Si face) with a typical hydrogen treatment (H_2 annealing at 600°C) [11]. The observed signals were named "the P_{H0}/P_{H1} centers" (see the inset of Fig. 1) which were observable at around 20 K in the channel current of the MOSFETs. Therefore, they surely correlated with the conduction-band-side interface states. These centers were formed after γ-ray irradiation (energy ~ 1.4MeV, dose = 6 Mrad) to the MOSFETs, suggesting that they were initially passivated by H atoms. In addition, the P_{H1} signal revealed an isotropic hyperfine splitting (hfs) due to ^{1}H nuclear spin (5.4 mT). This signature indicates the presence of a H atom in a nearest-neighbor site of the P_{H1} center. A small anisotropy of their g values suggests that they are carbon-related defects.

Accordingly, we proposed a model of the P_{H0}/P_{H1} centers as shown in Fig. 1. At the interface, there are DB-like sites due to carbon-related defects. They reacted with H atom(s) during H_2 annealing. After γ-ray irradiation, H passivation is broken, and the defect site shows ESR signals. The dissociated H atoms may diffuse far away from the defect sites, which create the P_{H0} centers at there. On the other hand, when the dissociation is partial or the dissociated H atom is captured again in a neighboring site of a defect, the P_{H1} center is generated. In 4H-SiC MOSFETs with dry oxidation, an EDMR signal similar to P_{H0} was observed at around 20 K [12].

The P_{H0}/P_{H1} centers may be consistent with carbon-dimer defects predicted by the theoretical calculation on SiC-SiO_2 interfaces [13]. Such defects hold DB-like orbitals on their threefold coordinated C atoms, which can interact with H atoms. They were proposed as the origin of the major interface states [13]. However, we suggest that the P_{H0}/P_{H1} centers are minor defects at the interface. The reason for this is based on their small signal intensities in both H-incorporated and dry-oxidation MOSFETs (Si face). Our idea is consistent with the small response of Si face MOS interfaces against H treatments. On the contrary, C face MOS interfaces show a higher reactivity to H treatments, so that we have to also examine C face.

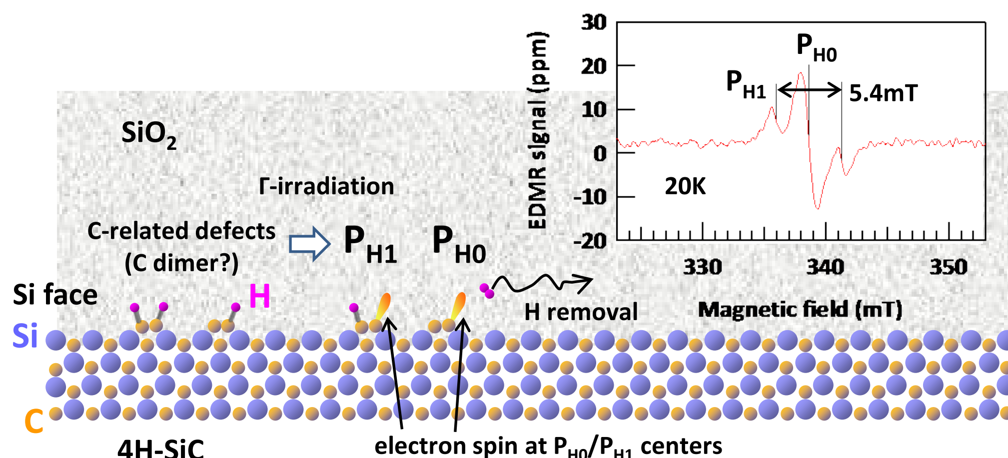

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Figure 1. Model of hydrogen and the P_{H0}/P_{H1} centers in 4H-SiC MOS interface (Si face). The graph shows a typical EDMR spectrum of P_{H0}/P_{H1} at 20 K in the channel current of 4H-SiC MOSFET [11].

Nitrogen and SiC MOS interfaces. In nitrided 4H-SiC MOSFETs (NO/N_2O annealing at 1250°C for 6-nm dry SiO_2), we have not detected the P_{H0}/P_{H1} signals, indicating that nitrogen (N) incorporation eliminates shallow interface states due to carbon-related defects [12]. Even after γ-ray irradiation, no defects were detectable at 20 K. N atoms at the interface may form stable bonding. Alternatively, at lower temperatures such as 4 K, a strong EDMR signal was observed, which we name "Nh". The signal is shown in the inset of Fig. 2. From its ESR signature, the Nh center has been identified as channel N shallow donors (at *h* site) [12]. The Nh signal resembled close to the N shallow donor signal, $N_C(h)$, in N-doped bulk region. However, there were found quantitative differences between Nh and $N_C(h)$, which may reflect on different environments of a shallow donor in channel and bulk regions.

In addition to the channel N donors, we have also found "fixed N atoms" at the interface [15]. After the nitridation of the interface, chemically unremovable N atoms were formed at there, and their density increased over 10^{14} cm^{-2} or up to 0.4 monolayer coverage. They were evidenced by x-ray photoemission spectroscopy (XPS), as shown in the inset of Fig. 2. This XPS spectrum was taken after removal of a top SiO_2 layer by hydrofluoric (HF) treatments (both diluted and concentrated conditions were subjected). The density of the fixed N atoms was linearly increased with nitridation temperature (Fig. 2). The capacitance-voltage analyses revealed that the fixed N atoms eliminate shallow interface states by a fraction of 1 interface state to ~1000 fixed N atoms. The origin of these N atoms may be analogue to a silicon oxynitride epitaxial layer observed for nitrided 6H-SiC surfaces [16].

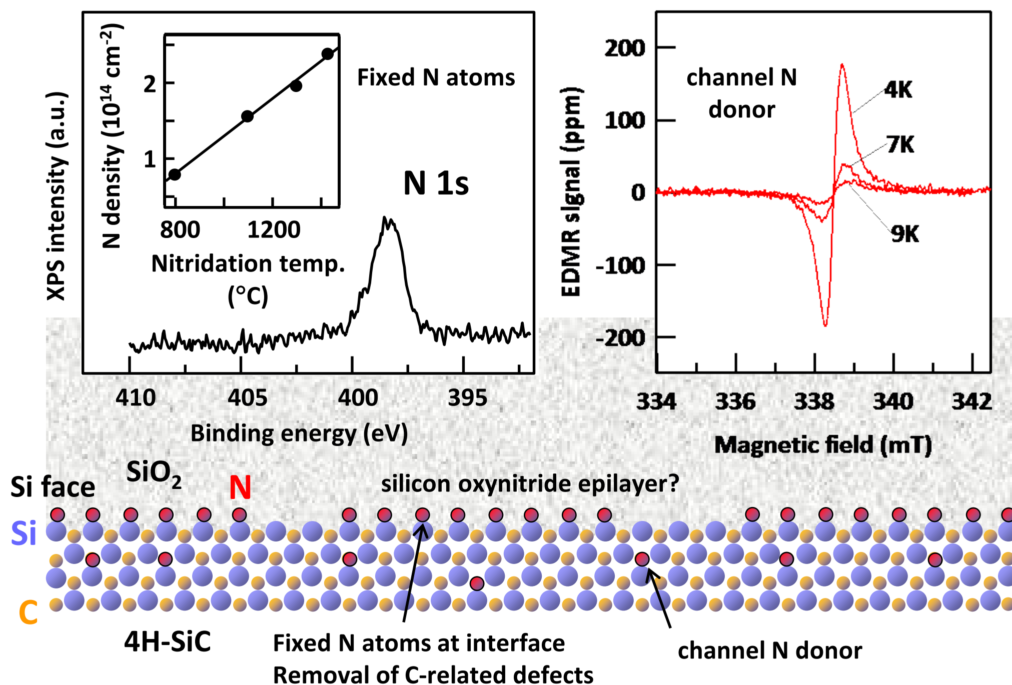

Figure 2. Model of fixed N atoms and channel N donors in 4H-SiC MOS interface (Si face) after nitridation. The left graphs show a typical XPS spectrum of fixed N atoms and

their areal density as a function of nitridation temperature [15]. The right graph shows a typical EDMR spectrum of channel N donors [12].

Those two behaviors of N (the formation of the fixed N atoms and N doping to the channel region) are characteristic of Si face SiC MOS interfaces. Using ESR, the amount of the N doping was estimated to be ~10^{12} cm^{-2} (we will report separately in the forthcoming paper), which is comparable to a carrier density in the inversion layer of the channel. Thus, the N doping should have a large impact on electrical properties of the MOSFET channel. We have to optimize the nitridation processes in terms of the reduction in D_{it} as well as the N doping effect.

Summary

4H-SiC MOS interface states were discussed based on ESR and EDMR results of previous pioneering works and by our group. Several ESR/EDMR signals have been reported in this interface system as summarized in Table I. They were connected mainly to carbon-related defects. We pointed out that there are notable dissimilarities between Si and SiC MOS interfaces. One is a small reactivity of H atoms at SiC MOS interfaces. We observed minor reactive sites (the P_{H0}/P_{H1} centers) on 4H-SiC MOS interfaces (Si face). The other notable dissimilarities were seen in nitrided 4H-SiC MOS interfaces (Si face), where we have found the formation of the fixed N atoms and the N doping to the channel region. These behaviors are the key to utilize the nitridation processes. For SiC MOS interfaces, it is still necessary to accumulate more complete data not only on Si face but also on C face, *a*-facets ((11$\bar{2}$0) planes), and off-angled interfaces (note that standard 4H-SiC wafers are prepared with a 8°-off angle), and so on.

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