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Kinetics of Ga and In desorption from (7 × 7) Si(1 1 1) and (3 × 3) 6H-SiC(0 0 0 1) surfaces

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Abstract

The desorption characteristics of Ga and In on (7 × 7) Si(1 1 1) and (3 × 3) 6H-SiC(0 0 0 1) surfaces have been determined using temperature programmed desorption. Two peaks were observed for desorption of a 1.5 ± 0.25 monolayer of Ga from the latter surface. The peak at $T_{\max} = 670$ °C exhibited zeroth order kinetics; the activation energy and pre-exponential were determined to be 2.6 ± 0.1 eV and $6 \times 10^{27 \pm 0.5}$ atom/cm^2 s, respectively. The peak at $T_{\max} = 535$ °C exhibited first order desorption kinetics with an activation energy and pre-exponential of 6.2 ± 0.3 eV and $7 \times 10^{21 \pm 2}$ s^{-1}, respectively. In contrast, only zeroth order kinetics and a lower activation energy of 2.0 ± 0.1 eV were determined for desorption of a 1.5 ± 0.25 monolayer of Ga from (7 × 7) Si(1 1 1). The values of these results in tandem with those of related studies of desorption from Si and SiC surfaces indicate that the low and high temperature Ga peaks from SiC are due to desorption from either a wetting layer or adatom sites and from Ga islands, respectively. The difference in desorption activation energies for Ga on Si(1 1 1) and on 6H-SiC(0 0 0 1) surfaces is attributed to differences in lattice matching of Ga to these surfaces. By contrast, only multilayer desorption was observed for 4 ± 1 monolayer of In on SiC(0 0 0 1). The zeroth order desorption activation energy and pre-exponential were 2.4 ± 0.1 eV and $6 \times 10^{27 \pm 0.5}$ atom/cm^2 s; they are consistent with the heat of sublimation (2.45–2.5 eV) for liquid In.

Keywords: Silicon carbide; Gallium; Indium; Temperature programmed desorption; Kinetics

1. Introduction

The deposition and formation of interfaces between III–V compounds and silicon surfaces has been the subject of numerous studies [1–8]. This research stems from the desire to integrate silicon microelectronics and III–V optoelectronics [3,9,10] as well as to take advantage of the higher electron mobilities in the latter materials [11]. The recent explosion of III-Nitride-based optoelectronics [12] and the considerable potential of these materials for high power microelectronics [13] has also prompted several studies concerned with the growth of these materials on both Si and SiC [14–20]. Interest in growth on the later substrate has been primarily a result of the desire to take advantage of the improved lattice matching of SiC to III-Nitride materials (≈1–3.5%) relative to other substrates commonly used, e.g. Al_2O_3 and Si(>10%).

Due to the inherent lack of both chemical and structural similarity between III–V and Group IV semiconductors, nucleation and growth of these materials on one another is a non-trivial task typically resulting in heteroepitaxial films with a variety of different lattice defects, e.g., dislocations,

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antiphase domains (APDs), inversion domain boundaries (IDBs) and unintentional doping [1–3,21,22]. To limit the formation of these defects, several studies have focused in detail on the initial stages of the nucleation and heteroepitaxial growth of III-V materials on Si and SiC substrates [23–32]. For the case of GaAs on Si, saturation of the Si surface with either Ga or As before initiating GaAs growth was observed to be an important factor in reducing the formation of APDs [1,23]. Similarly, for GaN on SiC, the formation of a Ga wetting layer prior to GaN growth initiation has also proven beneficial in achieving two-dimensional growth [30] versus the three-dimensional growth typically observed [14,16,20,29]. Additional studies have shown the importance of the growth sequence initiation (group III first vs. group V) in influencing both the interface chemistry and electronic structure (i.e. valence band alignment) for III-N/SiC interfaces [33–35]. These results indicate that understanding the kinetics of adsorption and desorption during the formation of Group III or Group V nucleation layers can be important for achieving both control of defect densities and interface properties for III–V materials heteroepitaxially grown on Group IV substrates.

Adsorption and desorption of Group III metals has also been used as a low temperature method for reducing and desorbing the native surface oxides of Si and SiC [36,37]. This technique has most recently been employed by several groups to remove surface oxides from 6H-SiC(0001) substrates prior to GaN growth via molecular beam epitaxy [30–32]. Group III metal desorption kinetics on Si and SiC surfaces is also of particular importance to growth processes such as those now widely used in the selective heteroepitaxial growth of Ga, GaAs and III-Nitride semiconductors [38–45]. In these techniques, one relies on the differences in the adsorption and desorption kinetics for different surfaces to selectively grow a material on one versus the other. Accordingly, accurate knowledge of kinetic parameters for these desorption processes can greatly improve the understanding and aid the modeling of these processes. For these many reasons, we have chosen to investigate the desorption kinetics of Ga and In from SiC surfaces. Several studies of the adsorption and desorption kinetics of Ga and In on/from the (100) and the (111) surfaces of Si have been performed [46–66]. However, published reports of analogous studies for either Ga or In on SiC surfaces are relatively few [30,67–70].

Scanning tunneling microscopy studies by Nogami et al [59] showed that <0.5 monolayer (ML) of Ga (1 ML = 6.8×10^{14} atom/cm^2) deposited on (2 × 1) Si(100) at room temperature remained at the outermost atomic layer and aligned with the Si–Si dimerization on the surface. The X-ray standing wave studies of Zegenhagen et al. [60] also indicated that a submonolayer of Ga deposited at room temperature on (7 × 7) Si(111) remained at the outermost atomic layer and occupied the T_4 site in a $\sqrt{3} \times \sqrt{3}$ periodicity to 1/3 ML (1 ML = 7.83×10^{14} atoms/cm^2). The AES studies by Bourguignon et al. [61] revealed that Ga grew epitaxially on Si(100) via a Stranski-Krastanov (SK) growth mechanism when deposited in vacuum at room temperature to a coverage exceeding one monolayer. The 2D–3D growth transition occurred at ∼5 ML. Annealing these films at 600 K resulted in the formation of Ga droplets; however, a 1 ML-2D Ga wetting layer remained on the Si. Similar STM, LEED, and AES studies have shown that In deposited on Si at room temperature remains at the outmost atomic Si layer. The metal aligns perpendicular to the Si dimers on the (100) surface and occupies the three-fold hollow sites on the (111) surfaces [62–66]. Indium has also been observed to grow epitaxially at room temperature via a SK growth mechanism with the 2D–3D transition occurring at 2–3 ML on both (100) and (111) surfaces [55,56,65,66].

The STM study by Li et al. [67] showed that 1 ML of Ga, evaporated onto ($\sqrt{3} \times \sqrt{3}$) 6H-SiC(0001) surfaces at room temperature that had been previously prepared via annealing in a silicon flux, occupies the outermost atomic layer and forms a row structure consisting of domains oriented 120° from one another. However, the atomic force microscopy (AFM) study by Jeganathan et al. [30] showed oval-shaped island formation for 1.2 ML Ga evaporated onto the same surface at room temperature. These features grew into triangular-shaped islands as the Ga coverage increased to 4 ML. By contrast, Jeganathan obtained Ga wetting layers with either a ($\sqrt{3} \times \sqrt{3}$) or a (3 × 3) surface reconstruction via adsorption of 1/3–1 ML of Ga at higher temperatures (740–800 °C). Density functional theory (DFT) calculations by Grossner et al. [69] indicate that the T_4 site on the ($\sqrt{3} \times \sqrt{3}$) surface (immediately above second layer carbon atom) is energetically the most favored site for adsorption of up to 1/3 ML Ga, Al, or In. Lastly, the soft X-ray photoelectron spectroscopy studies by Klauser et al. [68] showed that 1–4 ML of Ga, evaporated onto (1 × 1) 6H-SiC(0001) surfaces at room temperature and previously prepared by thermal desorption, are chemically stable to 600 °C; the formation of a gallium silicide or gallium carbide was not detected.

Studies of Ga and In desorption from Si have shown different kinetics for the 2D wetting layers vs. the 3D islands/droplets (see Tables 1 and 2 for details). Using isothermal AES measurements, Bourguignon et al. [46] concluded that a Ga wetting layer having a coverage of $\leqslant$0.5–1 ML on Si(100) exhibited first order kinetics (desorption activation energy (E_d) = 2.3 ± 0.2 eV, desorption jump frequency/pre-exponential (ν_d) = $8 \times 10^{12\pm1.2}$ s^{-1}). Ga droplets formed for Ga coverages exceeding 1 ML, and zeroth-order kinetics were determined ($E_d = 2.61 \pm 0.07$ eV, $\nu_d = 4 \pm 3 \times 10^{13\pm3}$ MLs^{-1}). Similar desorption behavior for Ga deposited on Si(100) at 550–600 K was observed using isothermal laser-induced fluorescence and TPD by Carleton et al. [47,48]. They observed similar first order Ga desorption kinetics with E_d = 2.9–3.0 eV and $\nu = 6 \times 10^{14}$ s^{-1} for Ga coverage < 1 ML. In contrast, Zinke-Allmang et al. [49] observed significantly different kinetics using isothermal Rutherford back scattering (RBS) for desorption of 20 ML Ga from (2 × 1) Si(100) and (7 × 7)

Table 1
Reported pre-exponential and activation energy for desorption of Ga from Si, SiC, and other relevant surfaces

Substrate	Order	Coverage (ML)	E_d (eV)	ν_d (ν_0 cm^{-2} s^{-1}) (ν_1 s^{-1})	Method	Reference
Si(100)	1st	<0.5	2.9 ± 0.2	$3 \times 10^{16\pm1}$	AES Isothermal	[46]
Si(100)	1st	0.5–1	2.3 ± 0.2	$8 \times 10^{12\pm1.2}$	AES Isothermal	[46]
Si(100)	0th	>1 (islands)	2.61 ± 0.07	$4 \times 10^{13\pm3}$	AES Isothermal	[46]
Si(100)	1st	<1	2.9 ± 0.1	6×10^{14} (4×10^{13}–1×10^{16})	LIF Isothermal	[47]
Si(100)	1st	<1	3.4 ± 0.2	2×10^{17} (3×10^{16}–3×10^{18})	TPD-Redhead analysis	[47]
Si(100)	NS	<1	3.0 ± 0.02	4×10^{14}	LIF TPD	[48]
Si(100)	1st	1 (1st layer)	2.2 ± 0.3	$1 \times 10^{11\pm3}$	RBS Isothermal	[49]
Si(100)	1st	>20 (islands)	3 ± 0.3	$1 \times 10^{15\pm3}$	RBS Isothermal	[49]
Si(111)	1st	1 (1st layer)	2 ± 0.3	$1 \times 10^{10\pm3}$	RBS Isothermal	[49]
Si(111)	1st	>20 (islands)	2.9 ± 0.3	$1 \times 10^{15\pm3}$	RBS Isothermal	[49]
Si(111)	1st	>7	2.88 ± 0.2	1×10^{13}	AES Isothermal	[50]
Si(111)	NS	1.5–2.0	1.22	NS	EDX Isothermal	[38]
Si(111)	0th	1.5 ± 0.25	2.0 ± 0.1	$7.5 \times 10^{26\pm0.5}$	TPD	This work
6H-SiC(0001)	0th	Droplets-NS	2.5	NS	RHEED-Isothermal	[70]
6H-SiC(0001)	0th	Wetting-NS	3.5	NS	RHEED-Isothermal	[70]
6H-SiC(0001)	1st	1.5 ± 0.25	6.2 ± 0.3	$7 \times 10^{21\pm2}$	TPD	This work
6H-SiC(0001)	0th	1.5 ± 0.25	2.6 ± 0.1	$6 \times 10^{27\pm0.5}$	TPD	This work
AlN(0001)	1st	1.0 ± 0.1	6.2 ± 0.3	NS	Isothermal QMS	[88]
AlN(0001)	1st	1.7 ± 0.3	3.8 ± 0.1	NS	Isothermal QMS	[88]
AlN(0001)	1st	Droplets	3.2 ± 0.1	NS	Isothermal QMS	[88]
GaN(0001)	1st	1	4.9	6.6×10^{24}	Isothermal QMS	[89]
GaN(0001)	1st	2.4	3.7	6.2×10^{18}	Isothermal QMS	[89]
GaN(0001)	1st	Droplets	3.2	1.9×10^{16}	Isothermal QMS	[89]
Al_2O_3	NS	<2	2.05	NS	TDP	[83]
SiO_2	NS	<2	2.03	NS	TDP	[83]
SiO_2	NS	1.5–2.0	1.33	NS	EDX Isothermal	[38]
Ga	0th	NA	2.8	6×10^{29}	NS	[84]

NS = not specified.

Table 2
Reported pre-exponential and activation energy for desorption of In from Si, SiC, and other relevant surfaces

Substrate	Order	Coverage (ML)	E_d (eV)	ν_d (ν_0 cm^{-2} s^{-1}) (ν_1 s^{-1})	Method	Reference
Si(100)	1st	<0.07	2.8 ± 0.2	$3 \times 10^{14\pm1}$	Isothermal-modulated beam desorption	[55]
Si(100)	0th	>1 (islands)	2.5	NS	AES Isothermal	[55]
Si(100)	1st	<0.5	2.5 ± 0.2	$10^{14\pm1}$	Isothermal LIF	[56]
Si(100)	2/3	>0.5	1.9 ± 0.1	$10^{10.5\pm0.5}$ ML$^{1/3}$ s^{-1}	Isothermal LIF	[56]
Si(100)	1/2	$\leqslant 1$	2.65	1.85×10^{13}	AES Isothermal	[57]
Si(111)	1st	<1	2.48	1.25×10^{12}	Isothermal-modulated beam desorption	[51]
Si(111)	1st	<1	2.54	1.25×10^{12}	TPD-flash desorption-redhead analysis	[52]
Si(111)	1st	<0.5	2.87	1.67×10^{16}	Isothermal RHEED	[53]
Si(111)	1st	<1	2.74	3.3×10^{14}	Isothermal RHEED	[53]
Si(111)	0th	$\leqslant 1/3$	1.9	16 ML s^{-1}	RHEED-Isothermal	[54]
Si(111)	0th	$\leqslant 0.56$	1.6	4.5×10^{7} ML s^{-1}	RHEED-Isothermal	[54]
Si(111)	0th	$\leqslant 0.96$	1.5	3×10^{7} ML s^{-1}	RHEED-Isothermal	[54]
Si(111)	0th	1–2	0.48	4.6×10^{8} ML s^{-1}	RHEED-Isothermal	[54]
Si(111)	1st	10^{-4}	1.93	1 × 1013	PAC	[58]
Si(111)	1st	0.05	2.6	1 × 1013	PAC	[58]
SiC(0001)	0th	4 ± 1	2.4 ± 0.1	$6 \times 10^{27\pm0.5}$	TPD	This work
In	0th	NA-Bulk	2.44	2×10^{28}	**NS**	[84]

NS = not specified.

Si(111) surfaces at 835–920 K. For island desorption from Si(111) and (100), they observed slightly higher values of E_d of 2.9 and 3.0 eV, respectively, ($\nu = 10^{15\pm3}$) than those reported by Bourguignon et al. [46]. However, for the "last layer," i.e. the wetting layer, they observed significantly lower values of E_d of 2.0 and 2.2 eV from the same surfaces ($\nu = 10^{10\pm3}$ and $10^{11\pm3}$, respectively). A still lower E_d of 1.22 eV has been reported by Shibata et al. [38] for Ga desorption from Si(111) based on isothermal energy-dispersive X-ray spectroscopy (EDX) measurements at 480–620°C.

Similar conflicting results have also been reported for In desorption from both the Si(100) and (111) surfaces. Isothermal modulated beam desorption and TPD have been used by Knall et al. [55] to examine In desorption from (2×1) Si(100) surfaces at 0–3 ML coverage. For <1 ML coverage, a 2D wetting phase and first order desorption kinetics with $E_d = 2.8 \pm 0.2$ eV and $v = 3 \times 10^{14\pm1}\ s^{-1}$ were observed. At $\geqslant$1.5 ML coverage and after annealing to 400 °C, In droplets formed on top of the 2D phase. The former exhibited zeroth order desorption kinetics with $E_d = 2.45 \pm 0.2$ eV and $v = 9 \times 10^{13\pm1\ -1}$. The results of Knall et al. for <1 ML In, however, are in stark contrast to the isothermal AES and RHEED studies by Kim et al. [56]. The latter investigators reported half order kinetics for the desorption of <1 ML In, deposited at room temperature, from (2×1) Si(1 0 0) at 480–550 °C. They also determined values of $E_d = 2.65$ eV and $v = 1.85 \times 10^{13}\ s^{-1}$ from the time variation of AES In coverage and RHEED spot intensities. The results of isothermal molecular beam desorption and TPD studies by Nguyen et al. [51,52] for desorption of <1 ML In from a (7×7) Si(1 1 1) surface indicated first order kinetics with $E_d = 2.48$–2.54 eV and an assumed value of $v = 1.25 \times 10^{13}\ s^{-1}$. A later isothermal RHEED study by Baba et al [53] for 1/3 ML In on (7×7) Si(1 1 1) provided a slightly higher E_d of 2.74–2.87 eV assuming first order kinetics. However, from the results of a subsequent isothermal RHEED study, Minami et al. [54] concluded that In desorption kinetics from the Si(1 1 1) surface at 360–460°C is zeroth order and exhibit a range of E_d of 1.9–0.48 eV as the surface coverage (order) increases from <1/3 ML $(\sqrt{3} \times \sqrt{3})$ to >1 ML (1×1).

The only reported study of the desorption kinetics of Ga (or any group III metal) from a SiC surface appears to be the isothermal RHEED research conducted by Zheng et al. [70]. These investigators determined values of $E_d = 3.5$ eV and 2.5 eV, respectively, for Ga desorption between 873 K and 980 K from 2D wetting layers and 3D droplets on $(\sqrt{3} \times \sqrt{3})$ 6H-SiC(0 0 0 1) surfaces prepared via annealing in a Si flux. However, these authors did not report additional specifics regarding the full desorption kinetics such as v, the desorption order and the Ga coverage at which the 2D and 3D Ga surface phases existed. In the present investigation, TPD was used to determine the full desorption kinetics for both Ga and In on 6H-SiC(0 0 0 1) surfaces. This technique was also used to observe the desorption kinetics of Ga from Si(1 1 1) surfaces for both comparison to the 6H-SiC(0 0 0 1) surfaces and to clarify the range of kinetics reported for Ga desorption from Si(1 1 1) surfaces.

2. Experimental

The substrates and the sample preparation procedures used in these experiments have been described in detail elsewhere [71–73]; however, a brief overview is presented herein. The boron doped (0.8–1.2 Ω cm), chemomechanically polished, on-axis Si(1 1 1) wafers (2.54 cm diameter) were obtained from Virginia Semiconductor, Inc. The polished, off-axis (4° toward $(11\bar{2}0)$), n-type ($N_d = 10^{18}\ cm^3$), 6H-SiC(0 0 0 1) substrates (2.54 cm diameter) were acquired from Cree, Inc. Both substrates were ultrasonically rinsed in acetone and methanol, exposed to the vapor from a 10:1 buffered HF solution for 10 min and immediately loaded into a ultra-high vacuum (UHV) transfer line [74] having a base pressure of 9×10^{-10} Torr. This line connected to the TPD/III-N gas source molecular beam epitaxy (GSMBE) system, the low-energy electron diffraction (LEED) unit, and the X-ray photoelectron spectroscopy (XPS) system used in this research. The capabilities of these UHV systems have been detailed elsewhere [75]. The (7×7) Si(1 1 1) surface was prepared by heating the sample to 900 °C in $<1 \times 10^{-9}$ Torr in the TPD/GSMBE system. The (3×3) 6H-SiC(0 0 0 1) surfaces were prepared in 10^{-5}–10^{-6} Torr SiH_4 for ≈15–20 min at 950–1050 °C. Either Ga or In was deposited on these substrates at room temperature (23 °C) via evaporation from the Knudsen solid source cells attached to the TPD/GSMBE system. The reported coverage for each metal was determined from the attenuation of the Si 2p and C 1s core level spectra from these substrates using XPS [76]. The details of these calculations are reported elsewhere [34]. As errors would be introduced into these calculations by the occurrence of three-dimensional growth [45,55,61], the Ga coverage was also estimated based on the length of the Ga exposure. Calibration of the Ga flux was achieved via measuring the growth rate of GaN films deposited in the GSMBE system [28]. Both estimates of Ga surface coverage agreed within ±0.25 ML.

The TPD experiments were conducted in the GSMBE using a Hiden Analytical 0–200 amu quadrapole mass spectrometer fitted inside a differentially pumped chamber having a 0.5 cm diameter opening. The sample holder/heater was positioned in front of this opening. The opening was located <2.5 cm from the sample surface. The TPD experiments were conducted using a heating rate of 60 °C/min while sampling m/e^- 2, 28, 69 (Ga) and 115 (In) with the quadrapole mass spectrometer. Calibration of the Ga and In desorption rates were achieved via integrating the area under the Ga and In TPD peaks and equating this area to the Ga and In coverage determined by XPS. To assure that all the desorbed Ga and In detected originated only from the substrate and not from other surfaces (e.g. sample heater), TPD measurements were also performed on clean Si samples (no Ga or In exposure) loaded into the GSMBE after Ga/In evaporation. In these ''blank'' experiments, neither Ga nor In desorption was observed.

Kinetic treatments of TPD spectra normally use the Polanyi-Wigner desorption rate equation [77–80]:

$$-d\theta/dt = \text{desorption rate (DR)} = v_d\ \theta^n \exp(-E_d/RT)$$

where

θ	surface coverage
v_d	desorption jump frequency/pre-exponential
n	rate order
E_d	desorption activation energy

In principal, v_d, n, and E_d can all be dependent on θ; however, most analyses assume these parameters to be independent of θ. Using the latter approach and taking the logarithm of both sides of the above equation accompanied by mathematical rearrangement, one obtains:

$$\ln(\mathrm{DR}) - n\ln\theta = \ln \nu_\mathrm{d} - E_\mathrm{d}/RT$$

If the correct rate order (n) is chosen, a plot of ($\ln(\mathrm{DR}) - n\ln\theta$) versus ($1/T$) yields a straight line and has a slope of $-E_\mathrm{d}/R$ and a y-intercept of $\ln\nu_\mathrm{d}$. The mathematical methods used for analyzing ($\ln(\mathrm{DR}) - n\ln\theta$) versus ($1/T$) were identical to those of Parker et al. [78].

3. Results

Fig. 1 shows the $m/e^- = 69$ TPD spectrum acquired during desorption of 1.5 ± 0.25 monolayer of Ga (ML = 7.83×10^{14} Ga/cm^2) previously evaporated onto a (7 × 7) Si(111) surface. The $1/T$ vs. $\ln(\mathrm{DR}) - n\ \ln(\theta)$ plot for the spectrum shown in Fig. 1 assuming $n = 0$, 1/2, 1, and 2 is presented in Fig. 2. As can be seen, a linear plot is only obtained for $n = 0$ which is indicative of zeroth order kinetics. The E_d and ν_d are 2.0 ± 0.1 eV and $7.5 \times 10^{26\pm0.5}$ atom/cm^2 s, respectively. An excellent fit to the spectra using these parameters is demonstrated in Fig. 1.

By contrast, two peaks were observed in the desorption spectrum obtained from 1.5 ± 0.25 ML Ga (ML = 2.3×10^{15} atom/cm^2 s) evaporated onto a (3 × 3) 6H-SiC(0001) surface, as shown in Fig. 3. The $1/T$ vs. $\ln(\mathrm{DR}) - n\ln(\theta)$ plot for the peak at $T_\mathrm{max} = 670$ °C clearly indicated zeroth order desorption kinetics with E_d and ν_d of 2.6 ± 0.1 eV

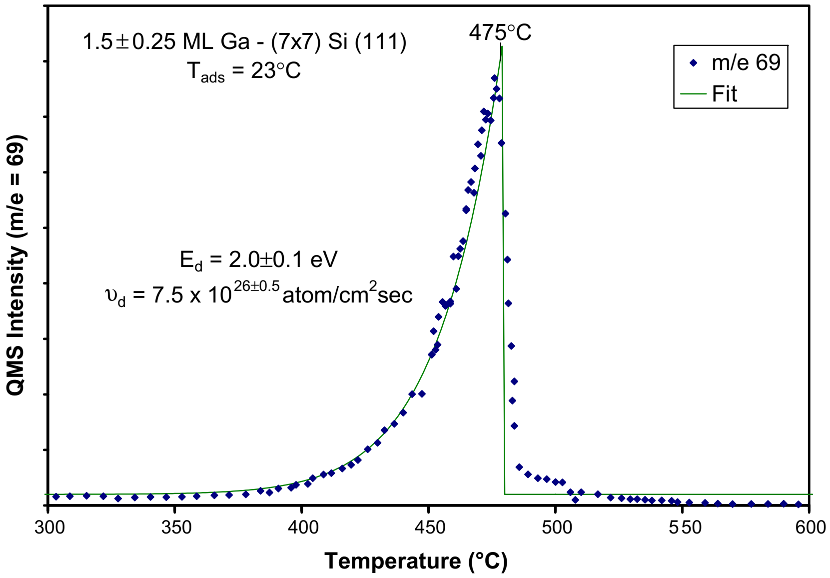

Fig. 1. TPD spectrum for $m/e^- = 69$ from 1.5 ± 0.25 ML Ga (7 × 7) on Si(111) surface.

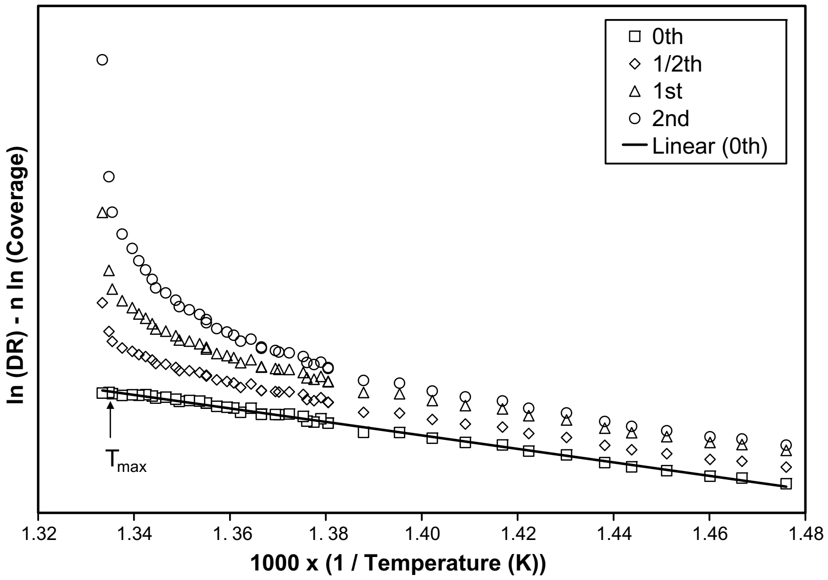

Fig. 2. Plot of $\ln(\mathrm{DR}) - n$ ln (coverage) for TPD spectrum in Fig. 1 with $n = 0$, 1/2, 1 and 2.

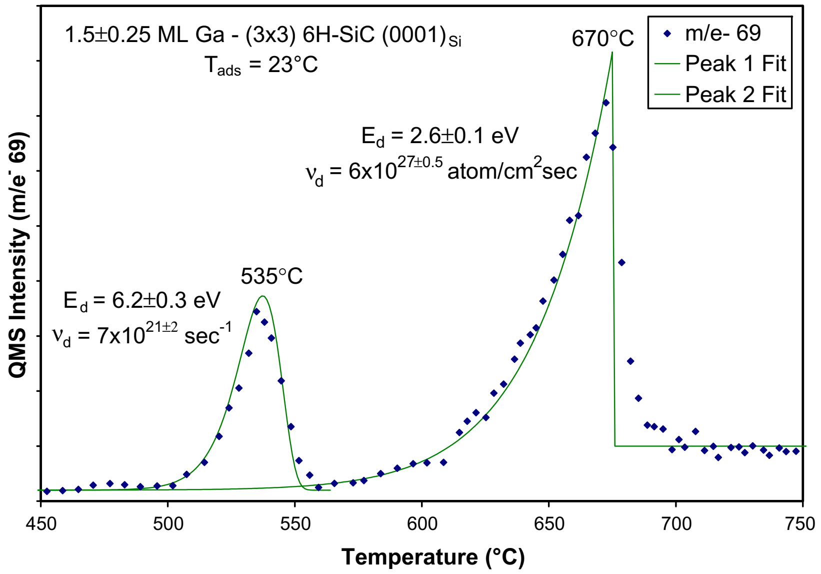

Fig. 3. TPD spectrum for $m/e^- = 69$ from 1.5 ± 0.25 ML Ga (3×3) on 6H-SiC(0001) surface.

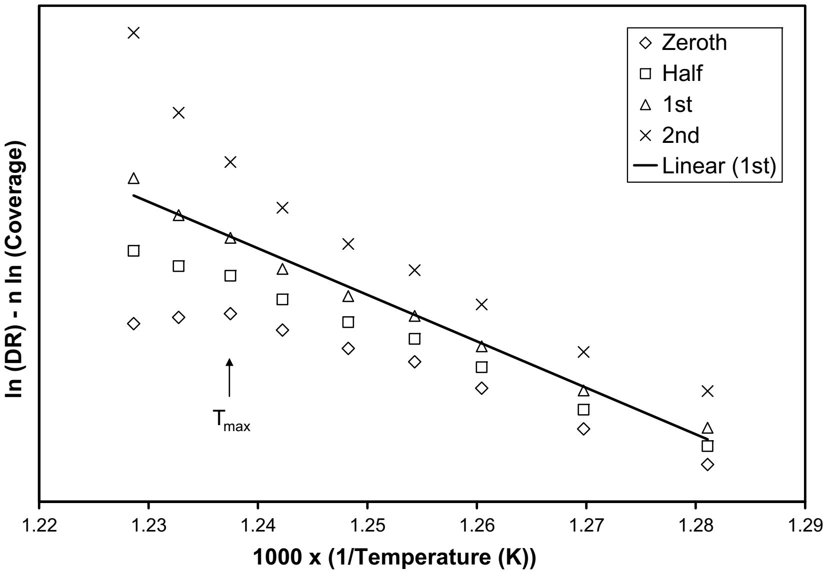

Fig. 4. Plot of $\ln(\mathrm{DR}) - n\ln$ (coverage) for low temperature peak in TPD spectrum in Fig. 3 with $n = 0$, 1/2, 1 and 2.

and $6 \times 10^{27\pm0.5}$ atom/cm^2 s, respectively. However, the analogous plot shown in Fig. 4 for the peak at $T_{\max} = 535$ °C indicates the possibilities of either half or first order desorption kinetics. Based on the best fit of the data, the latter kinetics is believed to describe first order desorption with E_d and ν_d equal to 6.2 ± 0.3 eV and $7 \times 10^{21\pm2}$ s^{-1}, respectively. However, half order kinetics cannot be completely ruled out. For the latter case, E_d and ν have been calculated to be 5.45 ± 0.2 eV and $4 \times 10^{40\pm1}$ atom/cm^2 s, respectively. Based on the total Ga surface coverage and the ratio of peak areas, we estimate the Ga coverage for the low and high temperature peaks to be 0.5 ± 0.1 and 1.0 ± 0.1 ML, respectively.

The m/e^- 115 TPD spectrum acquired from 4 ± 1 ML of In previously evaporated onto a (3×3) 6H-SiC(0001) surface at room temperature is shown in Fig. 5. Only one strong desorption peak was observed with the maximum desorption occurring at 645 °C. The peak shape and the $1/T$ vs. $\ln(\mathrm{DR}) - n\ln(\theta)$ plot (not shown) both indicate zeroth-order desorption. The calculated values for E_d and ν_d are 2.4 ± 0.1 eV and $6 \times 10^{27\pm0.5}$ atom/cm^2 s, respectively.

4. Discussion

For Ga on (7×7) Si(111), our value of $E_d = 2.0 \pm 0.1$ eV is in excellent agreement with the isothermal RBS study by Zinke-Allmang [49] in which a value of 2.0 ± 0.3 eV was reported for desorption of the last monolayer of Ga from the same surface. However, there is an apparent difference in reported rate order. Zinke-Allmang

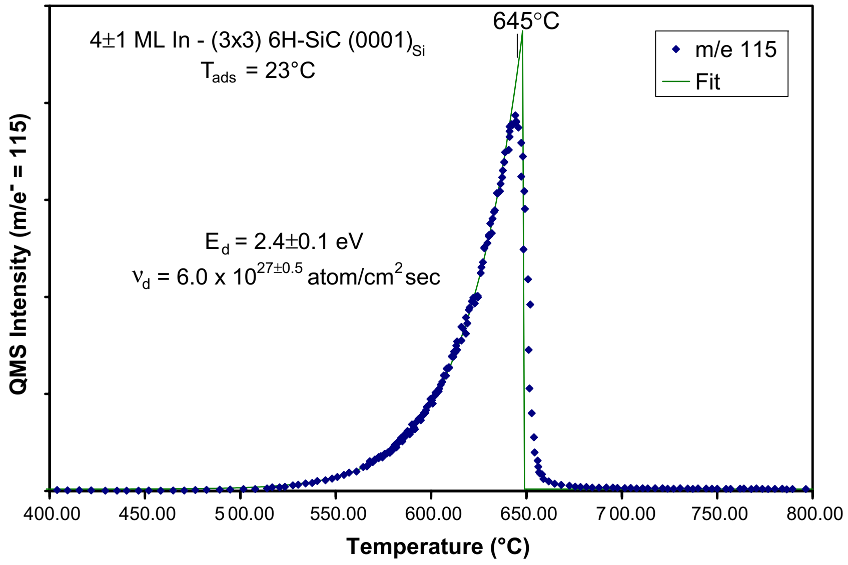

Fig. 5. TPD spectrum for $m/e^- = 115$ from 4 ± 1 ML In on (3×3) 6H-SiC(0001) surface.

reported first order kinetics; whereas, our results clearly indicate zeroth order kinetics. This difference can be resolved by taking into consideration that zeroth order desorption is typically observed from thick metal deposits or islands where the surface coverage is constant [79,80]. In these cases, desorption is actually first order but is experimentally observed to be zeroth order due to the surface coverage being effectively constant. This point explains the observed differences in rate order. In the Zinke-Allmang experiments, isothermal RBS was used to directly measure the Ga surface coverage vs. time and infer the desorption activation energy from an Arrhenius plot. In contrast, our TDS experiments directly measured the effective desorption rate. Thus, the difference in observed rate order is due to Zinke-Allmang monitoring Ga surface coverage changes which are first order for thick metals or islands. For similar surface layers, TDS measurements will instead indicate zeroth order kinetics due to monitoring the effective desorption rate.

The only other report of E_d for a similar Ga coverage on the Si(111) surface is that by Shibata [38] in which a significantly lower value of 1.22 eV was determined. These investigators also reported an E_d of 1.33 eV for desorption of a similar Ga coverage on SiO_2. This value is markedly lower relative to the E_d of 2.0 eV for Ga/SiO_2 desorption determined by Burns et al [83] using TPD. The desorption rate in the former study was determined at room temperature using EDX to measure the change in Ga surface coverage on a sample that had been annealed at 480–620 °C for a few minutes. The desorption activation energy (E_d) was deduced from an Arrhenius plot of the desorption rate; however, each rate does not represent a value for a specific temperature but rather the amount of material desorbed over a specific temperature profile. We believe this distinction between our TPD measurements and those performed by Shibata et al. [38] is the primary factor that accounts for the differences between the two values of E_d for this surface.

Zeroth order kinetics was observed for the Ga/(3×3) 6H-SiC(0001) desorption peak at $T_{max} = 670$ °C with a significantly higher value of E_d of 2.6 ± 0.1 eV relative to the zeroth order Ga desorption observed for Ga/(7×7) Si(111). However, this value of E_d is a close match to the E_d of 2.5 eV determined by Zheng et al. [70] via isothermal RHEED measurements of Ga droplet desorption from a $(\sqrt{3} \times \sqrt{3})$ 6H-SiC(0001) surface prepared in a manner similar to ours. For our Ga/(3×3) 6H-SiC(0001) surface, some Ga island/droplet formation is to be expected based on the AFM studies of Jeganathan et al. [30] that showed Ga island formation for 1.2 ML Ga coverage on 6H-SiC(0001) surfaces. Based on these similarities, we conclude that our observed high temperature Ga desorption peak and Zheng's Ga droplet desorption have the same origin.

It is tempting to also compare the E_d of 6.2 ± 0.3 eV for our low temperature peak ($T_{max} = 535$ °C) for Ga desorption from (3×3) 6H-SiC(0001) to the value reported by Zheng et al. [70] for desorption of a Ga wetting layer from $(\sqrt{3} \times \sqrt{3})$ 6H-SiC(0001). However, there is a significant discrepancy between our $E_d = 6.2$ eV and that reported by Zheng et al. 3.6 eV. The latter authors also reported zeroth order desorption kinetics for the wetting layer; whereas, we clearly observe first order kinetics for our low temperature peak. If we assume zeroth order kinetics, the calculated value of $E_d = 3.6$–4.8 eV for our low temperature peak suggests that (1) it is related to Zheng's wetting layer and (2) the difference in the values of E_d is simply due to a difference in interpretation of the desorption order kinetics. It is also worth noting that although our 6H-SiC surfaces were prepared in a similar fashion, the surface reconstructions are different. The (3×3) surface consists of a full Si bilayer on top of a Si–C bilayer; whereas the

($\sqrt{3} \times \sqrt{3}$) surface consists of a Si–C bilayer with a Si adatom occupying the T_4 site immediately above the C atom in the Si–C bilayer [73]. Thus some differences in E_d and reaction order for a Ga wetting layer on these two surfaces should be expected.

One apparent peculiarity of note in the analysis of the Ga/(3 × 3) 6H-SiC TPD spectrum is that the E_d for the low temperature peak is substantially larger than the E_d for the high temperature peak (6.2 vs. 2.6 eV). Intuitively, the peak with the larger E_d should occur at a higher temperature then the peak with the lower E_d. This, however, is true only if all other parameters controlling desorption are equal or similar for the two peaks. In the case for Ga/(3 × 3) 6H-SiC, the desorption order for the two peaks are different and most importantly the pre-exponential for the low temperature peak is substantially larger then that typically assumed for 1st order desorption (10^{21} vs. $10^{13}\ \mathrm{s}^{-1}$). The large pre-exponential for the low temperature peak allows the large E_d of 6.2 eV to be overcome and desorption to occur at a lower temperature than that from Ga droplets where $E_d = 2.6$ eV. The authors currently do not have a strong model to explain the physical mechanism leading to the increased pre-exponential for the low temperature Ga desorption peak. However, as we will show latter, pre-exponentials of the same order of magnitude have been reported for desorption from similar surfaces.

A related peculiarity for Ga desorption from (3 × 3) 6H-SiC concerns the relative temperatures at which island and wetting layer desorption occurs. For Si(100) surfaces, both Bourguignon et al. [46] and Knall et al. [55] reported both first order wetting layer and zeroth order island desorption for both Ga and In, respectively. In these two studies, island desorption was observed to occur first followed by desorption of the wetting layer at a higher temperature. This behavior is typically explained by island growth and agglomeration followed by desorption from the islands until depleted in size to that of a two dimensional wetting layer [49,81,82]. For Ga/(3 × 3) 6H-SiC, our TDS analysis indicates the opposite behavior, e.g. wetting layer desorption first followed by island desorption. This indicates there is a possible competition between island formation and direct desorption of isolated Ga atoms from the SiC surface.

It is worth further comparing the TPD results from (7 × 7) Si(111) and (3 × 3) 6H-SiC(0001) surfaces. They both consist of a full Si bilayer at the outermost surface, however, the surface lattice constants, number of dangling bonds, and potential adsorption sites are different.For Ga droplet/island desorption from 6H-SiC(0001) surfaces, an E_d of 2.5–2.6 eV has been determined. This value is close to that for bulk Ga sublimation (2.8 eV) [84]. However, for Ga droplet/island desorption from Si(111), an E_d of 2.0 eV was determined and is significantly lower then that for either Ga sublimation or desorption from 6H-SiC(0001). In either case, the activation energy for Ga desorption could be attributed to the breakage of Ga–Si bonds. Such an interpretation is supported by previous studies of Ga desorption from both SiO_2 and Al_2O_3 surfaces by Burns et al. [83] in which the measured E_d was closely correlated to the Ga–O bond energy. In our case, the close match of the reported Ga-Si bond energy of 2.1 eV [85] to the Ga/Si(111) E_d of 2.0 ± 0.1 eV also supports the application of a bond breaking model to our observed desorption activation energies, and indicates that only one Ga–Si bond is broken in the desorption process. Given the preference of Ga to occupy T_4 or substitutional sites on Si surfaces where three Ga–Si bonds can be formed, this may seem surprising. However, the calculations by Zegenhagen [60] and Kawazu et al. [86] show that adsorbed Ga induces a large compressive deformation in the Si surface and hence some of the Ga–Si bonds may be weakened by strain.

An alternative possibility is that the E_d for zeroth order Ga desorption from Si(111) and SiC(0001) is indicative of the Ga–Ga binding energy within the Ga islands, droplets or nanoclusters on the surface. In this case, a lower binding energy relative to bulk Ga, could also be expected due to the reduced size of the island/droplet. The publications of Ohtake [87] and Shibata [38] clearly show the formation of Ga nanoclusters (0.25 ML) and 20–200 nm round Ga droplets (2 ML) for Ga evaporated on Si(111) surfaces at 400 and 510 °C, respectively. Similarly, the AFM study of Jeganathan et al. [30] revealed nano-sized islands formed for Ga evaporated onto 6H-SiC(0001) surfaces. The Ga islands formed on the SiC surfaces were triangular in shape, which suggests more organized bonding and perhaps a higher dissociation/desorption energy. Thus, the difference in zeroth order E_d between Si(111) and SiC(0001) could also be due to the shape, size or atomic arrangement of the Ga islands/droplets formed on these surfaces.

An additional difference between our Ga TPD spectra acquired from the Si(111) and the 6H-SiC(0001) surfaces is our observation of an additional lower temperature peak with first order kinetics from the SiC surface. By analogy to the results of Zheng et al. [70], this peak could be attributed to desorption of a Ga wetting layer from the SiC surface. Using TPD, Carleton and Knall et al. [47,48,55] observed desorption of both 2D-wetting (1st order) and 3D-island/droplet (0th order) layers of Ga and In, respectively, from the Si(100) surface. However in both cases, desorption of the wetting layer occurred at a higher temperature than the 3D-droplet phase and only exhibited a 0.3–0.4 eV higher binding energy. Thus insight into the origin of our low temperature Ga/SiC(0001) desorption feature by analogy to the chemically similar Si(100) and (111) surfaces does not seem possible. Better insight, however, can be gained by comparison to the observed kinetics of Ga desorption from AlN(0001) and GaN(0001) surfaces. Though the chemical termination of these surfaces is different, they do exhibit similar surface lattice constants and adsorption site sizes. Additionally, desorption from both a Ga wetting layer and droplets have been experimentally observed from these surfaces [88,89]. First order Ga desorption kinetics have been observed for the wetting layers from both the AlN and GaN surfaces with E_d of 6.2 [88] and 4.9 eV

[89], respectively. A pre-exponential of $6 \times 10^{24}\ \mathrm{s}^{-1}$ was determined [89] for Ga desorption from Ga/GaN. These values of E_d and ν_d for Ga wetting layer desorption are in much better agreement with our results for the low temperature TPD peak from 6H-SiC(0001).

It is noteworthy to again consider the correlation between bond breakage and the activation energy for our first order Ga desorption peak from 6H-SiC(0001). The model in this case would predict the breakage of 3 Ga-Si bonds (i.e. $6.2 \pm 0.3/\ 2.1 = 3$). This is fully consistent with DFT calculations by Grossner et al. [69], which indicate that the energetically preferred site for Ga adsorption on the $(\surd\ 3 \times \surd 3)$ SiC(0001) surface is the T_4 site where the Ga atom passivates 3 Si dangling bonds. Likewise for desorption of Ga wetting layers from GaN and AlN(0001) surfaces, breakage of 3 Ga–Ga or Ga–Al bonds would also be predicted based on the reported desorption activation energies and Ga–Ga and Ga–Al bond energies of 1.45 [84] and 1.9 eV,[4] respectively. Such an observation is also consistent with DFT calculations that have shown the T_4 site to be the energetically preferred site for Ga adatoms on GaN(0001) surfaces [90]. However, the (3×3) 6H-SiC(0001) surface is passivated by a planar adlayer of eight silicon atoms topped with a tetrahedral Si adcluster [91]. This reconstruction produces only one Si dangling bond per (3×3) unit cell and does not have any open T_4 sites. For Ga to desorb from a T_4 like site, it would have to replace a Si atom at the top of the tetrahedral adcluster. This might be energetically favorable due to the elimination of the last dangling bond; however, the areal density of these sites is not consistent with the coverage we estimated for the source of our first order desorption peak. Other possible desorption sites for our first order peak could be areas of incomplete (3×3) formation, surface defects, and surface steps. The latter is a strong possibility given our use of off axis wafers and would be consistent with the partial agreement of our results with half order kinetics.

A perusal of the similarities and differences for Ga desorption from Si(111), SiC(0001), GaN(0001) and AlN(0001) surfaces reveals that the surface lattice constant and the chemical bonding play significant roles vis á vis the kinetics of this process. Si(111) and SiC(0001) surfaces present similar bond types for Ga, yet the activation energies and reaction orders for Ga desorption from these surfaces are significantly different. Each of the (0001) surfaces of SiC, GaN, and AlN produce different chemical bonds on Ga adsorption, yet exhibit similar desorption activation energies. The only commonality for the SiC, GaN and AlN(0001) surfaces is the lattice constant. It thus seems that the Ga wetting layer desorption energy is more strongly governed by the size of the adsorption sites.

By contrast with our Ga/6H-SiC TPD spectrum, only one zeroth order desorption peak was observed for 4 ± 1 ML In desorption from (3×3) 6H-SiC(0001). Desorption of an In wetting layer was not observed. The values of E_d and ν_d of 2.4 ± 0.1 eV and $6 \times 10^{27 \pm 0.5}$ atoms/cm^2 s, respectively, are in excellent agreement with those for liquid In sublimation (2.44 eV and 2×10^{28} atoms/cm^2 s) [84]. The most plausible explanation for the closer agreement is the higher surface coverage used in the In desorption experiments (4 ML) relative to the Ga desorption experiments (1.5 ± 0.25 ML). This result is also in agreement with the In/Si(100) desorption study of Knall et al. [55] in which zeroth order kinetics with $E_d = 2.5$ eV were observed for an In coverage >1–2 ML. The reason for the absence of the observation of an In wetting layer on the 6H-SiC(0001) surface is not known. The DFT calculations of Grossner et al. indicate that the T_4 site is energetically the preferred adsorption sight for both Ga and In on SiC(0001) surfaces. However, their calculations do not consider the equilibrium of a Ga or In multilayer on SiC surfaces, the energetics of Ga/In wetting layers vs. droplet formation, and the presence of a Si adlayer. Based on our results, it does not seem that such a wetting layer is energetically favorable on the (3×3) 6H-SiC(0001) surface.

Due to the importance of III–V growth on Group IV semiconductors, it is hoped that the present work will stimulate further investigations of the adsorption and desorption kinetics of Group III and V growth precursors on Group IV substrates. Studies of Group III and V adsorption/desorption kinetics on SiC surfaces in particular are largely uninvestigated and the results presented herein for Ga on SiC are clearly not exhaustive. The kinetics of Group III metal adsorption/desorption on SiC should be more closely investigated as a function of both Ga coverage and SiC surface reconstruction, orientation, and Si/C ratio. These studies should be further combined with AFM and STM studies to enable clear correlation of the observed desorption kinetics with the surface structure of the adsorbed group III overlayers (i.e. adsorption site, wetting layer, or islands/droplets).

5. Conclusions

Activation energies (E_d) and pre-exponential values (ν_d) for desorption of Ga and In from (7×7) Si(111) and (3×3) 6H-SiC(0001) surfaces were determined from data acquired via temperature programmed desorption. Zeroth-order desorption kinetics were observed for both metals from each surface. The values of E_d and ν_d determined for Ga desorption from Si(111) were 2.0 ± 0.1 eV and $7.5 \times 10^{26 \pm 0.5}$ atoms/cm^2 s, respectively. In contrast to Si(111), two peaks were observed for Ga desorption from (3×3) 6H-SiC(0001). The peak at 670 °C was attributed to Ga island desorption. E_d and ν_d were determined to be 2.6 ± 0.1 eV and $6 \times 10^{27 \pm 0.5}$ atoms/cm^2 s, respectively. The peak at 535 °C was attributed to either a Ga wetting layer or adatom desorption and was determined to have first order kinetics with E_d (ν_d) 6.2 ± 0.3 eV ($7 \times 10^{21 \pm 2}\ \mathrm{s}^{-1}$). The high activation energy for the wetting

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[4] Ga–Al bond energy based on the average of Al–Al and Al–Si bond energies from Ref. [79] and Ga–Si bond energy of 2.1 eV from Ref. [80].

layer/adatom desorption was correlated to the Ga-Si bond energy that indicated the breakage of three Ga–Si bonds. Based on this, it was concluded that Ga wetting layer desorption occurred primarily from sites where Ga adatoms can satisfy three Si dangling bonds. The values of E_d and ν_d for In desorption from (3×3) 6H-SiC(0001) surfaces were 2.4 ± 0.1 and $6 \times 10^{27 \pm 0.5}$ atom/cm^2 s, respectively, which are comparable to the pre-exponential (2.44 eV) and heat of sublimation (1.9×10^{28} atom/cm^2 s) for liquid In.

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