

## Adsorption and desorption kinetics of gallium atoms on 6H-SiC(0001) surfaces

L. X. Zheng, M. H. Xie, and S. Y. Tong

*Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong*

(Received 13 September 1999)

Gallium (Ga) surface adsorption and desorption kinetics on 6H-SiC(0001) are investigated using reflection high-energy electron diffraction. It is found that for Ga adsorption, a wetting layer bonds strongly to the SiC(0001) surface. Additional Ga atoms form droplets on top of the wetting layer. The Ga droplets behave like a metallic liquid. The activation energies for desorption are determined to be 3.5 eV for Ga in the wetting layer and 2.5 eV for Ga in the droplets. It is further found that the desorption of Ga atoms from the wetting layer follows a zero-order kinetics, i.e., the desorption rate is independent of the number of adsorbed atoms.

### I. INTRODUCTION

Although significant progress has been made in the development of III-V nitride-based devices, such as short-wavelength light-emission diodes<sup>1</sup> and laser diodes,<sup>2</sup> the fundamental mechanisms controlling nitride epitaxial growth are still unknown. This knowledge is nevertheless needed to further improve the quality of the epitaxial films. Recent growth experiments by molecular beam epitaxy have shown that GaN films grown under the excess-N condition have a poor structural quality and rough surfaces, while films grown under the excess-Ga condition generally display better structural quality and smoother surface morphologies.<sup>3-7</sup> This trend is also confirmed by theoretical calculations.<sup>8</sup> Additionally, Smith and co-workers<sup>6,7</sup> reported that there could be Ga adatoms in excess of 1 ML on the surface of GaN, and that both Ga-polar and N-polar films were stably terminated by Ga atoms. All these results indicate that Ga adatoms play a very special role in the epitaxial growth of GaN films.

Studies of adsorption, surface diffusion, and desorption processes of Ga atoms have been carried out previously on sapphire,<sup>9</sup> Si,<sup>10</sup> GaN,<sup>11,12</sup> and LiGaO<sub>2</sub> (Ref. 13) surfaces. However, the results are not consistent. A range of desorption thermal activation energies have been reported, ranging from 2.05 to 3.25 eV.<sup>9,12</sup> In this paper, we study the Ga adsorption and desorption kinetics on a 6H-SiC(0001) surface by monitoring the variation of reflection high-energy electron diffraction (RHEED) beam intensities during adsorption and desorption. The intensity oscillations of the specular beam are measured during both the adsorption and desorption processes. Furthermore, the intensity of the fractional-order spots originating from the substrate's ( $\sqrt{3} \times \sqrt{3}$ )R30° reconstruction is monitored during the desorption process. The results are consistent with a Stranski-Krastanov (SK) mode for Ga adsorption. In this model, initial Ga adatoms form a wetting layer which bonds strongly to SiC(0001) substrate. Additional Ga atoms form droplets on top of this wetting layer. The Ga droplets behave like a metallic liquid. The activation energies for desorption are determined to be 3.5 eV for Ga in the wetting layer and 2.5 eV for Ga in the droplets. These results explain the earlier discrepancies. These results also suggest the possibility that by properly choosing flux and temperature conditions, the dif-

ferent desorption energies can lead to a formation of a steady state one-layer Ga on the surface.

### II. EXPERIMENTS

The experiments are carried out in an UHV chamber equipped with a conventional Ga effusion cell. The *in situ* RHEED operates at 10 K eV, and is directed along the [1100] azimuth of the 6H-SiC(0001) surface. The sample (Cree Research Inc.) surface is treated in UHV by heating it to about 1100 °C in a Si flux. This procedure results in atomically flat terraces (>1000 Å wide) and a ( $\sqrt{3} \times \sqrt{3}$ )R30° surface reconstruction, as indicated by *in situ* low-energy electron-diffraction and RHEED patterns. SiC is chosen because it is a substrate commonly used for GaN epitaxy, due to its relatively close lattice match with GaN and high thermal stability.

To follow the Ga adsorption process, we keep the substrate at a fixed temperature and monitor the RHEED specular beam intensity as a function of Ga adsorption time. For Ga desorption studies, we monitor intensities of the specular beam as well as the ( $\frac{1}{3}, \frac{1}{3}$ ) beam of the ( $\sqrt{3} \times \sqrt{3}$ )R30°-reconstructed surface.

### III. RESULTS AND DISCUSSIONS

#### A. Ga adsorption

Figure 1 shows the variation of the RHEED specular beam intensity during the Ga deposition process. Specifically, the SiC(0001) surface temperature is kept constant at 873 K, and the Ga source temperature is varied for different curves. The Ga source shutter is opened at time  $t=30$  sec. From the figure, it is seen that up to two oscillations can be discerned; however, the second oscillation is very weak and its period also appears to be longer than the first. It is generally accepted that the RHEED intensity oscillates as a film's morphology goes from rough (minimum RHEED intensity) to smooth (maximum intensity).<sup>14</sup> Therefore, the data suggest Ga adsorption on SiC(0001) to follow the SK mode. The first-layer deposition is two-dimensional (2D), while the second layer undergoes a transition from 2D to 3D. The longer period of the second oscillation can be attributed to partial adatom trapping in 3D Ga droplets, leaving a lesser

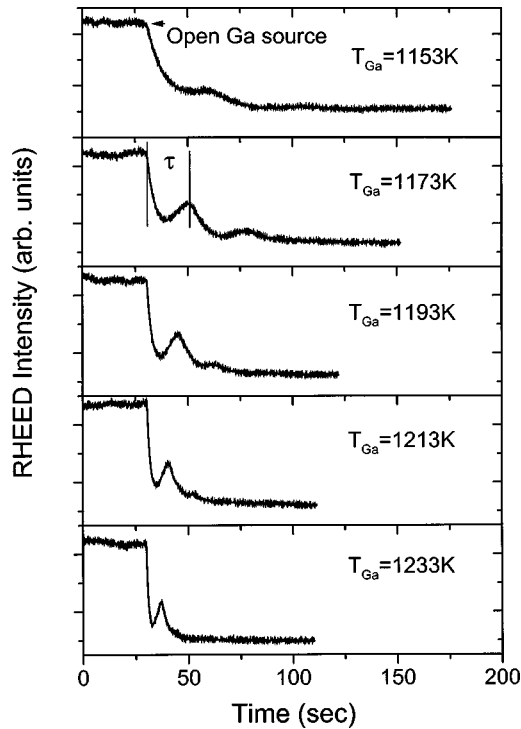


FIG. 1. Oscillations of the RHEED intensities for the specular beam during Ga deposition. The substrate temperature is 873 K in all the experiments.

amount that contributes to 2D growth. Further deposition leads to the formation of Ga droplets and the disappearance of the RHEED oscillations. In Fig. 2, we plot the period of the first oscillation,  $\tau$ , against the Ga source temperature  $T_{\text{Ga}}$ . From this plot, an activation energy of  $E=2.4$  eV is determined using the formula  $\tau = \tau_0 \exp(E/kT)$ . This energy  $E=2.4$  eV corresponds well with the heat of Ga evaporation from liquid Ga, which is reported to be 2.5 eV.<sup>15</sup> Therefore, this result supports the assumption that the first layer is 2D, with a constant sticking coefficient for Ga adatom adsorption.

### B. Ga desorption

We also monitor the intensity changes of the RHEED specular beam during Ga desorption process. The results are

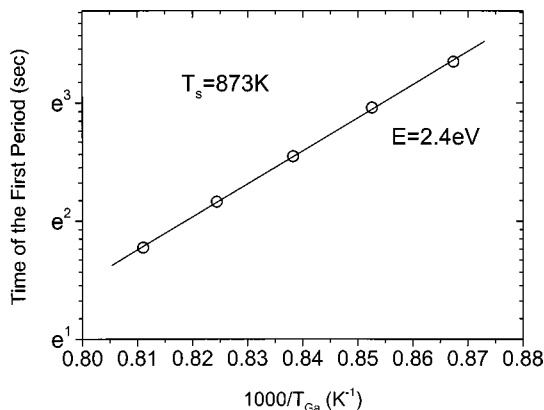


FIG. 2. Plot of periods of the first oscillations vs Ga source temperature  $T_{\text{Ga}}$ .

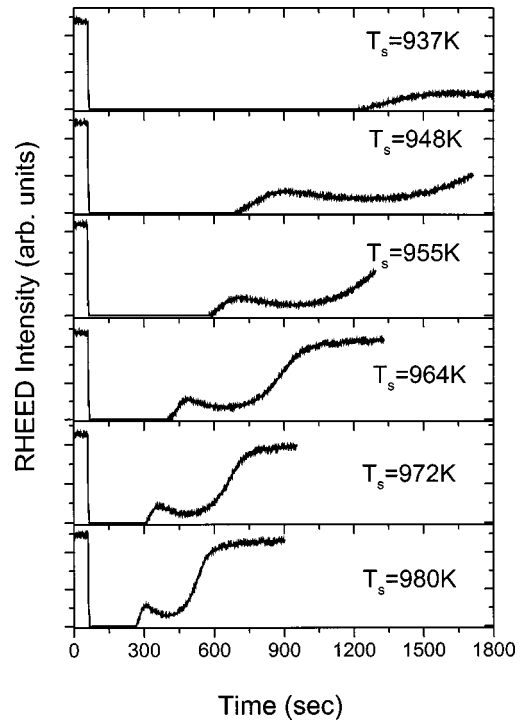


FIG. 3. RHEED intensity of the specular beam vs time for different substrate temperature,  $T_s$ , during deposition and desorption. The Ga source, with temperature of 1253 K, is opened at  $t=60$  sec and closed at  $t=80$  sec.

shown in Fig. 3 for different sample temperatures. The intensity again undergoes an oscillation before reaching a maximum. In the figure, the Ga shutter is opened at time  $t=60$  sec and closed at  $t=80$  sec. For all the curves, the Ga source temperature is held fixed at 1253 K. Figure 3 further shows that the RHEED oscillation emerges only after a time delay that depends on the sample's temperature. During this time delay, the specular beam does not show any intensity apart from the background. This behavior is only understood if we again assume that only one layer of Ga wets the surface, while additional Ga atoms are in the form of "islands" or droplets on top. Therefore, the observed oscillations simply correspond to the desorption of the wetting layer, while the time delay corresponds to desorption of Ga droplets. Hereafter, we shall refer to the desorption of Ga atoms from the wetting layer as "2D desorption," and that from the droplets as "3D desorption," for simplicity.

It is possible to obtain the activation energies for the 2D and 3D desorption processes from the measured temperature dependences. Using the temperature dependence of the time delays, we obtain a 3D desorption activation energy of 2.6 eV, whereas using the temperature dependence of the oscillation period itself, we obtain a 2D energy of 3.7 eV. The former agrees well with the heat of Ga evaporation from liquid (2.5 eV) determined earlier, supporting the model that the initial desorption is from 3D Ga droplets on top of the wetting layer. The higher energy obtained from the RHEED oscillation itself, on the other hand, corresponds to 2D desorption of Ga directly from the SiC(0001) substrate. The higher desorption energy indicates that Ga atoms form a stronger bond to SiC surface. Recently, Li *et al.* showed a scanning tunneling microscopy image of a 6H-SiC(0001)

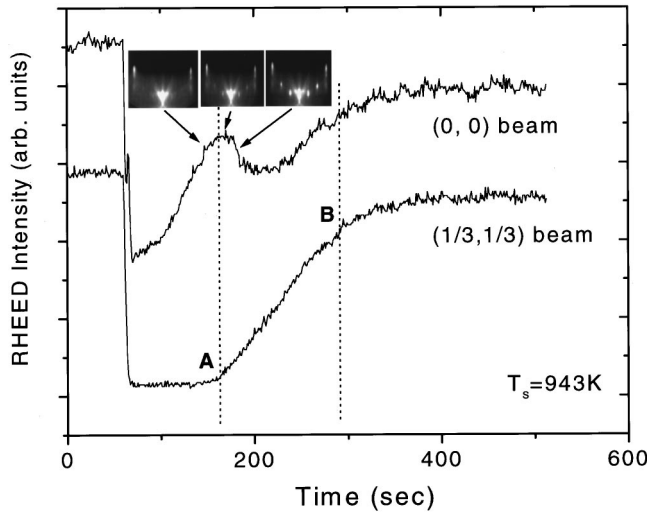


FIG. 4. Plots of intensities of the specular (0,0) beam and the  $(\frac{1}{3}, \frac{1}{3})$  beam vs time during Ga adsorption and desorption. The temperature of the Ga source is 1253 K. The source shutter is opened at  $t = 60$  sec and closed at  $t = 80$  sec. The RHEED patterns correspond to surfaces at different desorption stages. The electron beam is parallel to the  $[\bar{1}100]$  azimuth.

surface with a monolayer of Ga adsorption.<sup>16</sup> The image shows parallel rows of atoms arranged in three different domains.

The above experiment, though giving rise to energy values of Ga desorption, nevertheless does not provide any kinetic details of the process. The latter is revealed from monitoring the intensity of the fractional-order beam  $(\frac{1}{3}, \frac{1}{3})$  originating from the SiC(0001)- $(\sqrt{3} \times \sqrt{3})R30^\circ$  surface reconstruction. The later stage oscillations of the specular beam intensity during desorption coincides in time with the re-emergence of fractional-order diffraction spots, as illustrated in Fig. 4. The fractional-order spots disappear completely upon Ga adsorption, and the Ga-covered surface shows a  $1 \times 1$  periodicity. The re-emergence of the fractional-order spots, therefore, indicates desorption of Ga from the wetting layer. As the Ga atoms are desorbed, the exposed SiC surface atoms reconstruct to form patches with the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodicity. From Fig. 4, it is first seen that the reappearance of the fractional-order spots coincides with the oscillation peak of the specular beam intensity. Since surface reconstruction of the SiC sample occurs only at sizable exposed areas, this observation suggests that Ga desorption from the wetting layer must preferentially occur in patches such that it leaves a small number of large ‘‘holes’’ rather than a large number of small ‘‘holes’’ on the surface. A similar occurrence of Ga desorbing in stripes was in fact suggested on the Si surface.<sup>10</sup>

In the large hole model, it is reasonable to assume that the integrated intensity  $I$  of the fractional-order beam  $(\frac{1}{3}, \frac{1}{3})$  measured in this experiment is proportional to the surface areas  $S$  of SiC substrate that is exposed, i.e.,

$$I \propto S. \quad (1)$$

Then

$$dI/dt \propto dS/dt = R(S, t), \quad (2)$$

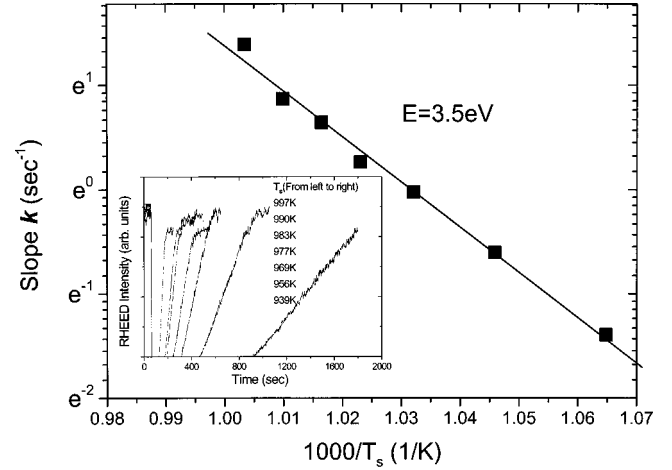


FIG. 5. Plot of the slope  $k$  of the  $(\frac{1}{3}, \frac{1}{3})$  beam intensity as a function of sample temperature  $T_s$ . The inset shows the linear recovery of the RHEED  $(\frac{1}{3}, \frac{1}{3})$  beam intensity during deposition.

where  $dI/dt$  is the slope  $k$  determined from Fig. 4, and  $R(S, t)$  is the rate of desorption, which is a function of area  $S$  and time  $t$ , in general.

The linear dependence of the intensity  $I$  versus  $t$  over a significant portion of times shown in Figs. 4 and 5 (inset) suggests, instead, a constant value for  $R$ . We have monitored other fractional-order spots in the RHEED pattern and repeated the experiment over a range of substrate temperatures between 873 and 1023 K. All results of  $I$  vs  $t$  show the same linear dependence. These results suggest a zero-order desorption kinetics, i.e., the desorption rate is independent of the number of adsorbed atoms. Such a desorption kinetics generally implies a mediated desorption process, e.g., by surface defects, or from edges of the existing holes.<sup>17</sup> This is consistent with the picture derived earlier that desorption occurs preferentially in patches. It proceeds by desorbing from the edges of the holes, and consequently enlarges the holes.

Figure 5 plots the slope  $k$  obtained by linear fit to the intensity curves, shown in the inset, as a function of the sample temperature  $T_s$ . An Arrhenius fit gives an energy of 3.5 eV, agreeing well with the 2D desorption energy of 3.7 eV determined earlier using the RHEED intensity oscillation data. Both measurements manifest the same 2D desorption process from the wetting layer. Our values also compare well with the upper limit for Ga desorption from a GaN surface, as reported by Hacke *et al.*<sup>12</sup>

#### IV. CONCLUSIONS

We have investigated Ga adsorption and desorption kinetics on 6H-SiC(0001) surface using reflection high-energy electron diffraction. We find that a wetting layer of Ga is formed on a SiC surface. During Ga adsorption (desorption), two-dimensional formation (evaporation) of the Ga wetting layer leads to RHEED intensity oscillations. The wetting layer shows a higher activation energy than Ga desorption from droplets. It might be possible to find growth conditions (e.g., by controlling Ga flux and the sample temperature)

under which only the wetting layer exists on the surface. Such conditions could be important to the initiation of, for example, GaN growth on a SiC(0001) substrate. Finally, it is found that Ga desorption from the wetting layer follows a zero-order kinetics, for which the exact microscopic description should be the subject of future studies.

#### ACKNOWLEDGMENTS

This work was supported in part by HK RGC Grant Nos. HKU 7118/98P, 7142/99P, and 260/95P; U.S. DOE Grant No. DE-FG02-84ER 45076; and NSF Grant No. DMR-9214054.

- 
- <sup>1</sup>S. Nakamura, T. Mukai, and M. Senish, *Appl. Phys. Lett.* **64**, 1687 (1994).
  - <sup>2</sup>I. Akasaki, H. Amono, S. Sota, H. Sakai, T. Tanaka, and M. Koike, *Jpn. J. Appl. Phys.* **34**, L1517 (1995).
  - <sup>3</sup>Zhonghai Yu, S. L. Buckzkowaki, N. C. Giles, T. H. Myers, and M. R. Richard-Babb, *Appl. Phys. Lett.* **69**, 2731 (1996).
  - <sup>4</sup>H. Riechert, R. Averbeck, A. Graber, M. Schienle, U. Straub, and H. Tews, In *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, MRS Symposia Proceedings No. 449 (Materials Research Society, Pittsburgh, 1997), p. 149.
  - <sup>5</sup>S. Wassermeier, A. Yamada, H. Yang, O. Brandt, J. Behrend, and K. H. Ploog, *Surf. Sci.* **385**, 178 (1997).
  - <sup>6</sup>A. R. Smith, R. M. Feenstra, D. W. Greve, J. Neugebauer, and J. E. Northrup, *Phys. Rev. Lett.* **79**, 3934 (1997).
  - <sup>7</sup>A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer, and J. E. Northrup, *J. Vac. Sci. Technol. B* **16**, 2242 (1998).
  - <sup>8</sup>Tosja Zywiets, Jorg Neugebauer, and Matthias Schettler, *Appl. Phys. Lett.* **73**, 487 (1998).
  - <sup>9</sup>R. P. Burns, K. A. Gabriel, and D. E. Pierce, *J. Am. Ceram. Soc.* **76**, 273 (1993).
  - <sup>10</sup>K. Fujita, Y. Kusumi, and M. Ichikawa, *Appl. Phys. Lett.* **68**, 631 (1996).
  - <sup>11</sup>S. Guha, N. A. Bojarczuk, and D. W. Kisker, *Appl. Phys. Lett.* **69**, 2879 (1996).
  - <sup>12</sup>P. Hacke, G. Feuillet, H. Okumura, and S. Yoshida, *Appl. Phys. Lett.* **69**, 2507 (1996).
  - <sup>13</sup>Ruth Klauser, P. S. Asoka Kumar, and T. J. Chuang, *Surf. Sci.* **411**, 329 (1998).
  - <sup>14</sup>J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, *Appl. Phys. A: Solids Surf.* **31**, 1 (1983).
  - <sup>15</sup>R. E. Honig and D. A. Kramer, *RCA Rev.* **30**, 285 (1969).
  - <sup>16</sup>L. Li, C. Tindall, Y. Hasegawa, and T. Sakurai, *Appl. Phys. Lett.* **71**, 2776 (1997).
  - <sup>17</sup>Ron Kaspi and P. Loehr, *Appl. Phys. Lett.* **71**, 3537 (1997).