Pis'ma v ZhETF, vol. 99, iss. 8, pp. 537 – 541 © 2014 April 25

The switching of GaAs(001) termination by action of molecular iodine

K. N. Eltsov, A. A. Vedeneev[1)]

Prokhorov General Physics Institute of the RAS, 119991 Moscow, Russia

Submitted 13 March 2014

This paper presents experimental results of an ultrahigh vacuum study of 4×2/c(8×2)⟶2×4/c(2×8) structural transition on GaAs(001) caused by the thermal removal of the saturated iodine monolayer formed at GaAs(001)-4×2/c(8×2). It has been found out that the original c(8×2) low energy electron diffraction pattern transforms into 4×1 at 0.6 ML of iodine coverage and then keeps up to its saturation at 1.0 ML. We have determined that GaI is the only chemical product of the iodine action, its double peak was observed in the thermal desorption spectra at $T = 150 \div 370\,^\circ$C. The explanation of surface processes underlying 4×2/c(8×2)⟶2×4/c(2×8) phase transition is presented below.

DOI: 10.7868/S0370274X14080098

In many ultrahigh vacuum applications, it is crucial to control the atomic structure of polar faces (001) of $A_{III}B_V$ semiconductors, notably GaAs(001). This can be done not only by thin film growth processes, such as molecular-beam or atomic-layer epitaxy, but also by using active agents selectively engaging either the atoms of the third or fifth group on the surface. In [1–4] it was found out that 4×2/c(8×2)⟶2×4/c(2×8) structural transition on (001) planes of GaAs, InAs, and InSb (from the third group rich to the fifth group rich reconstruction) takes place as a result of removal of saturated iodine monolayer by heating. The experimental temperature was not higher than 300 °C [1]. It was also determined [1–3] that at the room temperature molecular iodine usually did not etch $A_{III}B_V$(001)-4×2/c(8×2) surfaces (InSb was an exception [1]) and interacts only with the upper atomic layer of the substrate, perhaps due to lower chemical activity and bigger size of iodine atoms in comparison with other halogens [1, 2, 3]. Unfortunately, no real attempts to determine reaction products and direct atomic structure of the resulting 2×4/c(2×8) surface were done in [1–4], so the details and drivers of the process have yet to be clarified. We believe that a deeper understanding of how molecular iodine removes metal atoms may open the door to full control over the $A_{III}B_V$(001) atomic structure. In this letter, we describe some general features of the 4×2/c(8×2)⟶2×4/c(2×8) structural transition on GaAs(001) due to the action of molecular iodine.

The experiments were performed in multi-chamber ultrahigh vacuum setup equipped by cylindrical mirror analyzer (Riber OPC-100) for Auger electron spectroscopy (AES) studies, quadrupole mass-spectrometer (Riber QMM-17) for thermal desorption spectroscopy (TDS), three-grid electron spectra analyzer (VG RVL/17) for low energy electron diffraction (LEED) observation, scanning tunneling microscope (STM) (SigmaScan GPI-300), and gas inlet system with computer-controlled piezoceramic fine leak valve. The base pressure was not higher than $1{\cdot}10^{-10}$ Torr. The samples of 5×5 mm^2 size were cut out from an n-type GaAs(001) epi-ready wafer (Si, $1{\cdot}10^{18}$ cm^{-3}, plane orientation accuracy better than 0.1^0). In vacuum, the sample was degased at $T = 350\,^\circ$C during 5 h after that oxides and carbon contamination were removed by Ar^+ ion beam treatment ($E = 400$ eV, glancing angle 70°) along [110] direction. The crystallinity was restored by annealing at $T \approx 550\,^\circ$C during 15 min. This procedure led to the high-quality c(8×2) LEED pattern. In STM images wide (1000–2000 Å) atomic terraces with well ordered atomic structure were observed as well. In order of monitoring the iodine coverage and to record thermal desorption spectra molecular iodine was adsorbed in the chamber equipped with Auger- and mass-spectrometer. Iodine coverage was determined as an area inside iodine (I $M_5N_{4,5}N_{4,5}$, 512 eV) peak relatively to the area inside iodine peak in the spectrum of the saturated monolayer. Gas inlet, elemental and structural analysis of the surface were done at the room temperature. In thermal desorption measurements, the sample temperature was taken using a chromel-alumel thermocouple located on a sample holder. The absolute accuracy was not worse than 30 °C. Heating rate in TDS was approximately 1 °C per second.

Fig. 1 demonstrates an STM image of empty electronic states on GaAs(001)-4×2/c(8×2), with a clearly

[1)]e-mail: alex_ved@kapella.gpi.ru

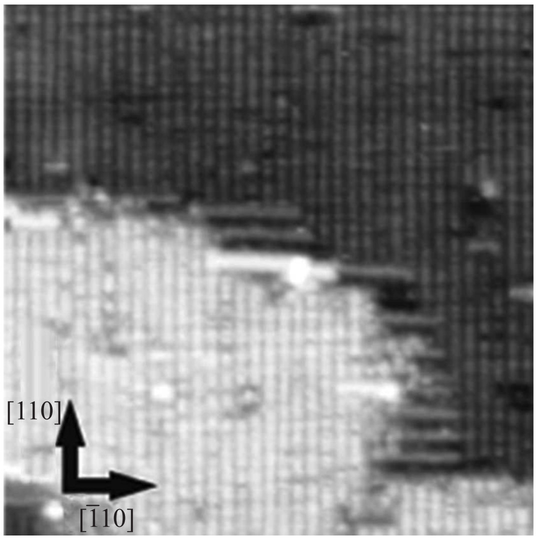

Fig. 1. STM image of empty electronic states of GaAs(001)-4×2/c(8×2): 800×800 Å^2; sample bias U_s = = +2.8 V, tunnel current $I_t = 0.1$ nA

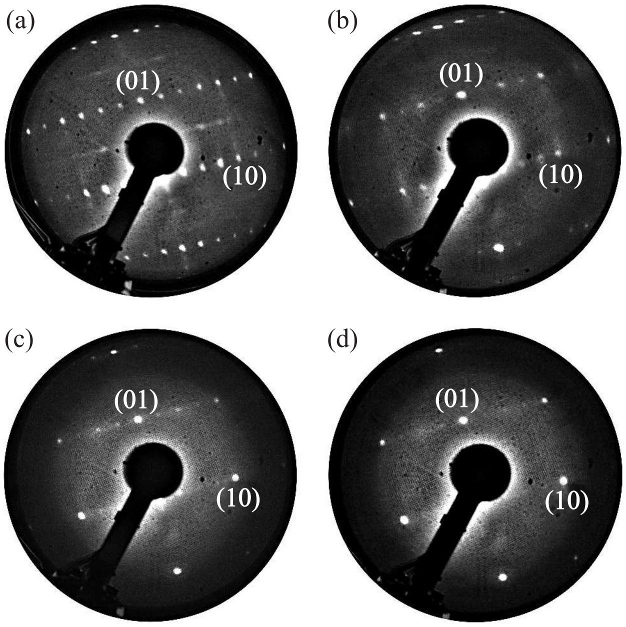

Fig. 2. Changes in the LEED pattern from GaAs(001)-4×2/c(8×2) during iodine adsorption ($E_p = 60$ eV), the background of the LEED pattern is removed. (a) – $\theta = 0$, (b) – $\theta = 0.6$, (c) – $\theta = 0.8$, (d) – $\theta = 1.0$

resolved biatomic step between two terraces having a linear striped structure of 16 Å periodicity along [−110] ($4a$ is the reconstruction period, $a = 4.0$ Å is the interatomic distance). The terraces contain a few structural atomic defects. A fraction of the surface along the step edge is n×6.

Fig. 2 demonstrates the changes of GaAs(001)-4×2/c(8×2) LEED pattern during the molecular iodine adsorption. The pattern of a clean surface is c(8×2) (Fig. 2a). At $\theta \approx 0.6$, weak 8×2 spots disappear, while 4×1 spots persist (Fig. 2b). At $\theta \approx 0.8$, 1×1 spots, which correspond to an unreconstructed substrate, become dominant, but 4×1 periodicity can evidently be observed (Fig. 2c). Longer iodine exposure results in further gradual weakening of 4×1 spots in the LEED pattern, which becomes almost perfect 1×1 with the very weak 4×1 spots at $\theta = 1.0$ (Fig. 2d). So after the saturation of iodine monolayer ×4 periodicity along [−110] persists but we cannot tell exactly whether ×2 periodicity along [110] direction disappear and Ga–Ga dimers are broken. Initial ×2 spots are weak and can be possibly screened by the LEED pattern background, intensity of which increases during iodine exposure. We could not get atomically resolved STM-images of the saturated iodine layer to establish its atomic structure but LEED analysis allows us to make a conclusion that iodine monolayer is not well ordered and it is incommensurate to the substrate structure.

We have prepared GaAs(001)-2×4/c(2×8) by the method described in [1]. Iodine saturated GaAs(001)-4×1-I sample was heated to 300 °C and then kept at this temperature during 15 min. As a result, Auger iodine peaks had disappeared and the LEED pattern transformed into c(2×8) (Fig. 3a). The STM image in Fig. 3b

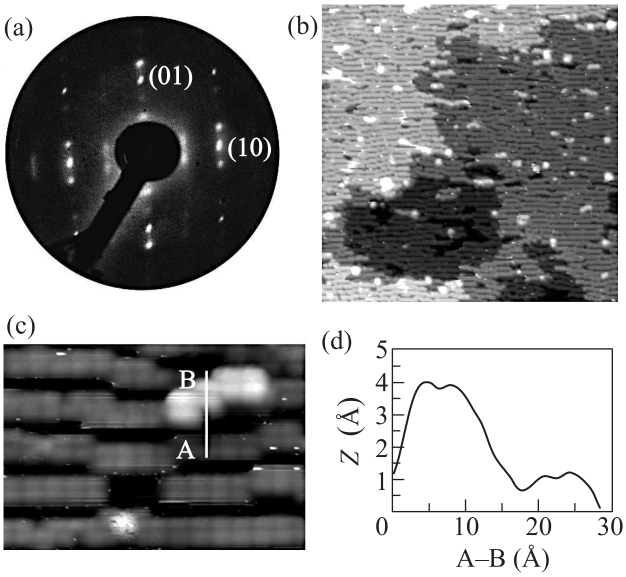

Fig. 3. (a) – LEED pattern of GaAs(001)-2×4/c(2×8) ($E_p = 70$ eV). (b) – STM image of filled electronic states of GaAs(001)-2×4/c(2×8): 800×800 Å^2, $U_s = -2.5$ V, $I_t = 0.1$ nA. (c) – A fragment of the STM image in (b): 120×70 Å^2, $U_s = -2.5$ V, $I_t = 0.1$ nA. (d) – A cross-section of the island in (c)

also demonstrates that atomic rows rotated by 90 degrees. Besides, much more atomic defects became visible in comparison with the STM image of the original GaAs(001)-4×2/c(8×2) (see Fig. 1). Fig. 3c demonstrates a better resolved fragment of the STM image with a characteristic surface defect. This image permits us to make two conclusions. First, the surface atomic structure consists of dimer rows separated by double vacancy rows. Second, the atomic-size defects are islands of the same structure as the substrate (As–As dimer rows) and lying above such dimer rows. Fig. 3d demonstrates a cross-section of the island. Since we suggest that the arsenic atoms on the terrace and in the upper layer of the island are in the same electronic state (dimers), the island height can be correctly measured with a simple STM image processing. The measured island height is about 3 Å, which rather well corresponds to the half of the crystal lattice constant of 5.65 Å [5]. Such an island has to consist of an As–Ga bilayer with the [001] interlayer distance of a quarter of the said constant. Another feature of the resulting GaAs(001)-2×4/c(2×8), which can be seen in Fig. 3c, is in the presence of multiple kinks of dimer rows. Such kinks are also the characteristic features of the 2×4/c(2×8) structures obtained by molecular beam epitaxy [6].

We have studied thermal desorption spectra to learn more about the adsorption sites and possible chemical compounds formed at GaAs(001)-4×2/c(8×2) during iodine adsorption. The spectra were recorded for the following ions: Ga^+(69, 71 a.u.), As^+(75 a.u.), I^+(127 a.u.), As_2^+(150 a.u.), GaI^+(196, 198 a.u.), AsI^+(202 a.u.), GaI_2^{++}(161.5 a.u.), and I_2^+(254 a.u.). Importantly, we have not found any arsenic iodides, while gallium iodides were observed in the spectra at any iodine coverage. The results for iodine saturated coverage are presented in Fig. 4. We think that iodine interacts mainly with the gallium atoms on GaAs(001)-4×2/c(8×2), since in [1, 3] it has been found out, that only peaks of the third group elements change their shape in the surface photo-electron spectra after iodine adsorption on $A_{III}B_V$(001)-4×2/c(8×2). We also believe that Ga–As bonds relax and can be broken down at low temperatures, leading to the removal of Ga and I atoms in a Ga–I compound. We have identified the desorbing iodide compound as GaI, since no ions heavier than GaI^+ were found in mass spectra during thermal desorption. The desorption process of saturated iodine monolayer, presented in Fig. 4, demonstrates a double peak at 150–370 °C for ions Ga^+ and GaI^+, two peaks of approximately equal amplitude at 230–550 °C for As_2^+, and zero order desorption curves (sublimation regime) at $T > 550$ °C for gallium and arsenic. The total similarity between Ga^+ and GaI^+ peaks makes us believe that there is no independent desorption of gallium atoms or clusters at 150–370 °C. Arsenic peaks at 230–550 °C could be due to As_2 and/or As_4, since these clusters are known to be stable [7]. Unfortunately, we were not able to distinguish between As_2 (150 a.u.) and As_4 (300 a.u.) clusters because the maximum mass range in the experiment was 270 a.u.

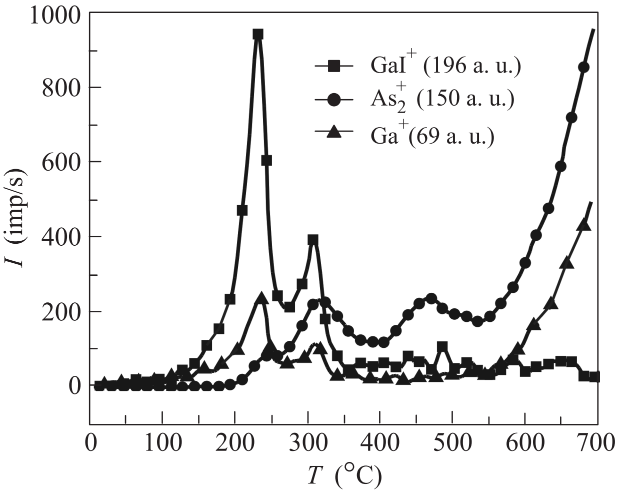

Fig. 4. Thermal desorption spectrum from iodine saturated GaAs(001)-(4×1)-I ($\theta = 1.0$). Heating rate is 1 ^{0}C/s

The changes in the surface structure of iodine saturated GaAs(001)-4×1-I ($\theta = 1.0$) caused by consecutive thermal desorption of the reaction products were studied by LEED. The sample was heated up to 370 or 400 or 550 °C (critical points in the thermal desorption spectrum in Fig. 4) at 1 °C per second, then left to cool down naturally to the room temperature, and then the LEED measurements were performed. After heating to 370 °C, as the iodine monolayer was completely removed, the LEED showed diffused c(2×8) pattern with domination of 1×1 spots. After heating to 400 °C, the LEED pattern presented a sharp c(2×8) structure which was similar to the one in Fig. 3a. The original Ga-stabilized 4×2/c(8×2) structure was restored at 550 °C and higher temperatures as the second arsenic peak in TDS had completely passed.

Discussions of the results obtained on GaAs(001)-4×2/c(8×2) under iodine action are based on ζ-model [8] (see Fig. 5a) which is confirmed in several experimental studies [9, 10]. In the model, gallium atoms in the upper atomic layer exist in the dimerized (D) and sp^2 single states (P). Necessary to note, that Ga atom density on a surface is twice bigger in P than in D state. As indicated in Fig. 5a, arsenic atoms are also of two types, As1 and As2, which have equal quantity. The

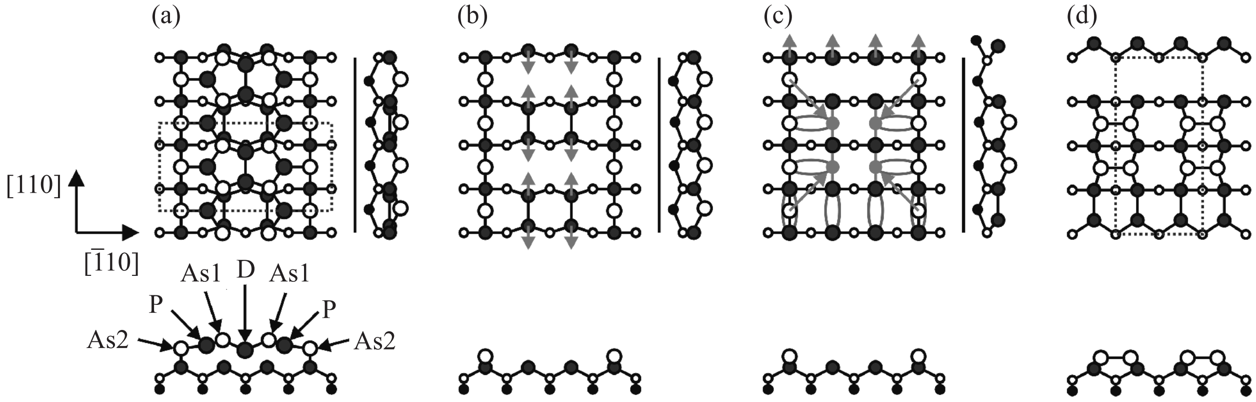

Fig. 5. Scheme of structural transformation of GaAs(001)-4×2 due to iodine action including thermal removing of reaction products and surface diffusion. The scheme is based on ζ-model [8], Ga atoms are black, As atoms are white. (a) – ζ-model of 4×2 initial clean surface. Unit cell is shown by dotted line. (b) – Surface after removal of all Ga atoms and As1 atoms from upper layer. Gray arrows show the directions of shifts of Ga atoms in Ga–Ga dimers of second layer. (c) – As atoms diffusion and As–As and Ga–Ga dimers formation. The possible positions for As atoms are shown as gray circles, dimers formation is shown by gray lines. (d) – 2×4 structure formed after As atoms moving and dimers creation. Unit cell is shown by dotted line

As1 atoms are bound only with Ga atoms from upper layer (D and P states) and have not any bonds with Ga atoms from lower layer. Each As2 atom has two bonds with Ga atoms from lower layer, one bond with Ga atom from first layer in P state and one dangling bond. So ζ-model permits to give the following explanation to our TDS data. The first (more intensive) GaI peak in TDS is caused by removal of Ga atoms from sp^2 state and the second one by removal of Ga atoms from dimers. We were not able to get atomically resolved STM images of a saturated iodine monolayer but we predict that at $\theta = 1.0$ iodine fills all (or almost all) dangling bonds of Ga. It means that the thermal desorption of iodine monolayer causes the removal of all gallium atoms of the initial GaAs(001)-4×2/c(8×2) upper layer in the form of GaI molecules. So we suggest the following picture of 4×2⟶2×4 transformation on GaAs(001) during and after thermal removal of reaction products (Fig. 5). If all Ga atoms are removed by heating, then all arsenic atoms of As1 type lose the bonds with Ga and could be described as adatoms with high mobility. We predict that As1 atoms could form clusters such as As2 or As4 with low activation energy of desorption. The first As_2^+ peak at 250–400 °C in TDS (Fig. 4) is explained as desorption of such surface As_n clusters. After removal of all Ga atoms and a half of As atoms (As1) from the upper substrate layer, surface structure could look as presented in Fig. 5b. There is perfect Ga–As bilayer with only As2 atoms above it. In frame of ζ-model, some of Ga atoms of second layer are in Ga–Ga dimers. As shown by gray arrows in Fig. 5b, these Ga–Ga dimers could be destroyed after upper Ga layer removal. Then, As2 atoms could move to the positions (gray arrows in Fig. 5c) in accordance with the scheme of 2×4 structure, and dimerize there (Fig. 5c and d). Gallium atoms also form dimers in vacancy rows (Fig. 5d). The process described in Fig. 5 is predicted to occur at 300–400 °C. At 300 °C, it takes 10–15 min, at 400 °C the process takes few seconds or shorter. At such temperatures, we predict surface mobility of As2 atoms to be very high. Taking into account that length of the moving is very short (1–2 interatomic distances) the scheme in Fig. 5 looks realistic.

We use two-dimers model of Farrel and Palmstroem [11], also known as α-model [12], to describe the resulting GaAs(001)-2×4/c(2×8) structure in Fig. 5d whereas only two-dimers model of Chadi [13] (known as β2-model [12]) has been directly experimentally confirmed [12] by means of STM-studies at MBE grown surfaces. Evidently, α-2×4 atomic structure seems to be unstable in MBE growth conditions and till now only its small fragments were experimentally observed [14]. The difference between α- and β2-models is in content of the second (gallium) atomic layer. If the surface corresponds to α-model this layer is complete while a quarter of gallium atoms are absent in the case of β2-model. Iodine atoms interact only with the upper atomic layer of the initial GaAs(001)-4×2/c(8×2) structure. In consequence of GaAs(001)-(4×1)-I ($\theta = 1.0$) only gallium atoms of the upper layer are removed by annealing from the surface in a form of GaI (Fig. 4). We suppose that the lower gallium layer should persist complete because we did not observe gallium atoms desorption (differing from GaI desorption, Fig. 4) at the temperatures of $4\times2\longrightarrow2\times4$ structural transition. Thus α-model seems to be favorable for the resulting $2\times4/c(2\times8)$ surface observed in our experiment. We explain the stability of the resulting α-$2\times4/c(2\times8)$ structure by lower temperatures ($T = (300{-}400)\,°C$) of $4\times2/c(8\times2)\longrightarrow2\times4/c(2\times8)$ transition in comparison with the temperature of MBE growth, which usually are distinctly higher [12, 14].

So we have confirmed that, as observed in [1], thermal removal of a saturated iodine monolayer from Ga-rich GaAs(001)-$4\times2/c(8\times2)$ leads to formation of As-rich GaAs(001)-$2\times4/c(2\times8)$. We also have found out the following features of such structural transformation.

Starting at 0.6 ML of iodine coverage, original $c(8\times2)$ LEED pattern transforms into 4×1 which is kept up to total filling of iodine monolayer which is incommensurate to substrate structure.

Iodine reacts selectively with gallium atoms, and the resulting GaI is completely removed by heating at $T = 300\,°C$ during 15 min. Additionally, arsenic clusters desorption (As_2 or/and As_4) is observed.

The scheme of structural $4\times2/c(8\times2)\longrightarrow2\times4/c(2\times8)$ transition based on the initial ζ-model [8] is suggested. The scheme describes the removal of all Ga atoms and a half of As atoms from the upper surface layer with a short lateral transfer of the rest of As atoms when heating to the temperatures 300–400 °C.

We also predict, that controllable change of As/Ga stoichiometry on GaAs(001)-$4\times2/c(8\times2)$ by adsorption (and further desorption) of an adjusted iodine coverage, as well as high mobility of surface atoms at rather low temperature (about 300 °C), opens up an opportunity to form different surface reconstructions.

Authors are grateful to B.V. Andryushechkin for helpful discussions. The work was supported by the Russian Foundation of Basic Research (Grant # 08-02-01396), Program "Basic Research in Nanotechnologies and Nanomaterials" of the Russian Academy of Sciences. A.A. Vedeneev is also thankful to the Russian Science Support Foundation and to the President of the Russian Federation for the young scientists support program (Grant # MK-4449.2008.2).

1. P.R. Varekamp, V.C. Hakkansson, J. Kanski, D.K. Shuh, M. Bjorkqvist, M. Gothelid, W.C. Simpson, U.O. Karlsson, and J.A. Yarmoff, Phys. Rev. B **54**, 2101 (1996).
2. P.R. Varecamp, M.C. Hakkansson, J. Kanski, M. Bjorkqvist, M. Gothelid, B.J. Kowalski, Z.Q. He, D.K. Shuh, J.A. Yarmoff, and U.O. Karlsson, Phys. Rev. B **54**, 2114 (1996).
3. W.K. Wang, W.C. Simpson, and J.A. Yarmoff, Phys. Rev. Lett. **81**, 1465 (1998).
4. W.K. Wang, W.C. Simpson, and J.A. Yarmoff, Phys. Rev. B **61**, 2164 (2000).
5. F.P. Kesamanly and D.N. Nasledov, *Gallium Arsenide: Production, Properties and Application*, Nauka, M. (1973) (in Russian).
6. M.D. Pashley and K W. Haberern, Phys. Rev. Lett. **67**, 2697 (1991).
7. C. Su, X. Ming, and D. Zi-Guo, Surf. Sci. **282**, 357 (1993).
8. S.-H. Lee, W. Moritz, and M. Scheffler, Phys. Rev. Lett. **85**, 3890 (2000).
9. A.A. Vedeneev and K.N. Eltsov, JETP Lett. **82**, 44 (2005).
10. Xu.Y.Y. Sun, Y.G. Li, Y.P. Feng, A.T.S. Wee, and A.C.H. Huan, Phys. Rev. B **70**, 081313 (2004).
11. H.H. Farell and C.J. Palmstroem, J. Vac. Sci. Technol. B **8**, 903 (1990).
12. V.P. LaBella, M.R. Krause, Z. Ding, and P.M. Thibado, Surf. Sci. Rep. **60**, 1 (2005).
13. D.J. Chadi, J. Vac. Sci. Technol. A **5**, 834 (1987).
14. A. Ohtake, Phys. Rev. B **74**, 165322 (2006).