Effect of Surface Polarity on Gallium Adsorption on 6H-SiC(0001) Surfaces : An STM Study(STM-other surfaces)

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Effect of Surface Polarity on Gallium Adsorption on 6H-SiC(0001) Surfaces: An STM Study*

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We have performed the first STM study of gallium adsorption on both the Si and C terminated 6H-SiC(0001) surfaces. The development of surface structures was followed as a function Ga coverage. On both the Si-terminated $\sqrt{3}$ x $\sqrt{3}$ and C-terminated $2\sqrt{3}$ x $2\sqrt{3}$ surfaces, coverages of less than 1/2 ML resulted in a disordered phase. Increasing the coverage to greater than 1/2, but less than 1 ML produced ordered phases. On the Si-terminated side this consisted of parallel rows of Ga atoms arranged in three different domains, oriented at angles of 120 degrees with respect to each other. Thus the surface symmetry was reduced from three-fold to two-fold. On the C-terminated side, it consisted of interlocking rings of 12 atoms, which appear alternately bright and dark in the STM image. Thus the original threefold symmetry of the SiC surface was preserved. On both surfaces, full monolayer coverage led to the formation of the (1x1)Ga structure.

KEYWORDS: SiC, Ga, adsorption, surface structure, STM

1. Introduction

Because of their favorable electronic and chemical properties[1], the group III nitrides (Al, Ga, and In) are excellent materials for a variety of high power micro and opto-electronic devices, including field effect transistors[2] and blue laser diodes.[3] However, a number of obstacles must still be overcome in order to optimize the epitaxial growth processes. These include a lack of a lattice-matched substrate, high growth temperatures, and detrimental pre-deposition reactions between commonly used metal-organic chemical vapor deposition precursors. Because of its relatively low cost and high crystalline quality, sapphire is currently the most popular substrate for the growth of single crystal group III nitride thin films.[4] However, because 6H-SiC(0001) has a much smaller mismatch in both lattice parameter and thermal expansion coefficient,[5] the difficulty in producing single crystal epitaxial layers is corresponding reduced.[6] Nonetheless, when used as a substrate material for GaN growth, 6H-SiC(0001) displays a strong polarity dependence. On the (0001) silicon terminated surface, 2D GaN growth results in a smooth film. In contrast, 3D growth occurs on the carbon terminated surface, producing hexagonal pyramids of GaN on the SiC surface.[7] It has been suggested that this marked difference in film morphology arises from differences in the lattice mismatch due to interfacial charge.[8] In order to further elucidate the initial stages of growth of GaN on 6H-SiC(0001), we have performed the first STM study of the adsorption of Ga on this surface. In a seperate paper we will describe our study of N_2H_4 adsorption on 6H-SiC(0001).[9] N_2H_4 is an active nitrogen precursor which can be used to lower the growth temperature, and also to avoid unfavorable predeposition chemistry during the growth process.[10]

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2. Experimental

The experiments were carried out in a UHV chamber containing an STM equipped with a low energy electron diffraction (LEED) and a field-ion microscope (FIM) which is used to monitor and fabricate the tip. The base pressure was in the 10^{-11} torr range. The samples were n-type ($n=2x10^{18}cm^{-3}$) 6H-SiC(0001) single crystals supplied by Cree research. Elemental Ga (99.999%) was evaporated onto the surface.

3. Results and Discussion

Fig. 1. Filled state image of the clean C-terminated 6H-SiC(0001) $2\sqrt{3}x2\sqrt{3}$ surface. Bias = -1.5 volts. Image size = 160Å x 160Å.

We will start with the C-terminated surface. Fig. 1 shows a filled state image of the clean, $2\sqrt{3}x2\sqrt{3}$ reconstructed surface. In figure 2, a gallium coverage of less than 0.5 ML is shown. At these low coverages, an overlayer with local 2x2 order formed. As the coverage is

increased to approximately 1 ML, the Ga rearranges into a very ordered structure. It consists of interlocking rings of Ga atoms. The individual rings exhibit 12 distinct spots in the STM image. Thus the original three fold symmetry of the substrate is maintained. In addition there is an inner ring of 6 atoms, with a vacancy at the center. Overall, the Ga forms a $4\sqrt{3}$ x $4\sqrt{3}$ structure. This image is shown in figure 3. Based on the model which we discuss in detail below, the Ga coverage is one monolayer. Some striking features are observed in this image. First, there is a large amount of contrast between the inner and outer rings, with the atoms in the inner ring appearing lower. Second, the atoms of the inner ring appear alternately higher and lower.

Fig. 2. Empty state image of the disordered phase obtained at one half monolayer coverage of Ga on C-terminated SiC(0001). Sample was annealed at 570C for 5 minutes. Sample bias= +2.5 volts. Image size = 260Å x 260 Å.

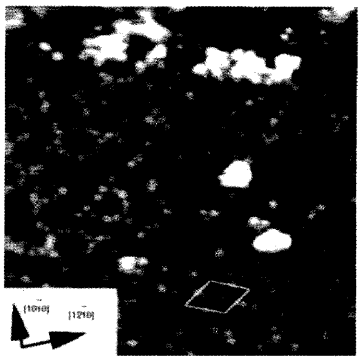

Fig. 3. Filled state image of one monolayer of Ga on the $2\sqrt{3}$x$2\sqrt{3}$ C-terminated 6H-SiC(0001). Sample bias = -1.6 volts. Image = 86Å x 86Å.

This observed contrast can be explained based on the structural model which we propose below. After increasing the coverage further to more than one monolayer, a metallic gallium layer is formed. Because of the delocalized nature of the charge density in this structure, the corrugation of the surface is correspondingly reduced. For this reason, our images do not show any details of the surface structure. However, most likely it is the Ga(1x1) phase.

Figure 4 shows our proposed model for the SiC(0001)-{$4\sqrt{3}$ x $4\sqrt{3}$}Ga surface phase. The first key feature of the model is the substitution of the first layer C atoms by Ga. The substitutional Ga resides at both the fcc and hcp sites. The substitution of Ga for the C atoms in the first layer is similar to the case of adsorption on Si and Ge surfaces. On those surfaces, the Ga atoms substitute for Si (Ge) respectively, forming a domain wall structure. The driving force for those structures is the relaxation of strain induced by the large lattice mismatch between Ga and Si (Ge). The inner ring is formed by Ga atoms which are adsorbed on top of the substitutional Ga. This ring consists of six Ga atoms. Each adsorption formed by 3 substitutional Ga atoms, all three of which lay in fcc or hcp sites respectively. The Ga atoms within the ring alternate between adsorption on hcp substitutional Ga and fcc substitutional Ga. Thus, the inner ring is composed of three Ga atoms on hcp substitutional Ga atoms and three on fcc substitutional Ga. In contrast, the 12 atoms which make up the outer ring all sit in sites composed of three hcp substitutional Ga atoms.

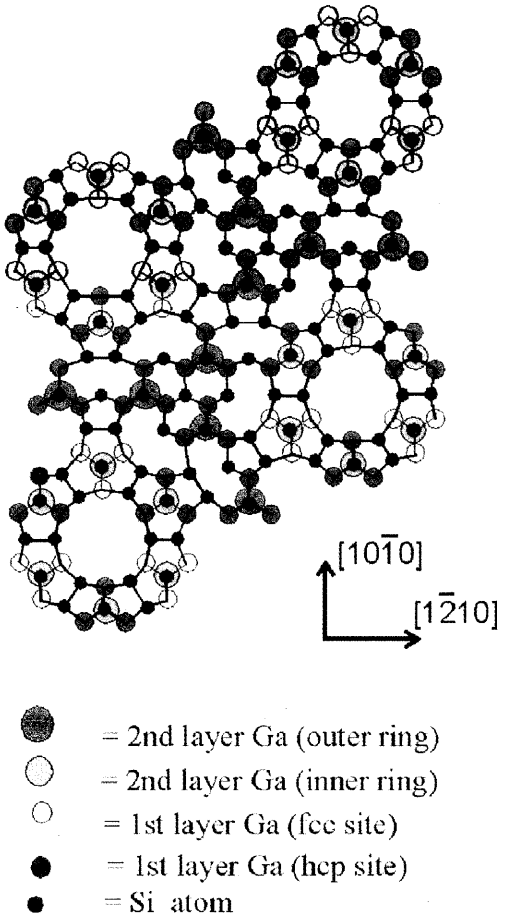

Fig. 4. Filled state image of the $\sqrt{3}$x$\sqrt{3}$ Si-terminated 6H-SiC(0001) surface. Bias = -1.2 volts. Image size = 86Å x 86Å.

The second key feature is that although, in the model, all of the top layer Ga atoms are geometrically at the same height, a large amount of contrast is observed between the Ga atoms comprising the outer ring, and those which form the inner ring. (See Fig. 3.) That is, the outer ring atoms appear higher. This can be explained by the difference in the bonding site of the Ga atoms, which give rise to a different local electronic density of states at the different Ga atoms in the structure. This type of effect is also seen in the classic Si(111)-7x7 structure.[11] Finally, a small apparent height difference is seen in the case of the inner ring Ga as well. Alternate atoms of the inner ring appear to be higher. This can also be explained in terms of the electronic structure of the proposed model. Three of the

inner ring Ga atoms sit in hcp sites while the other three sit in fcc sites. Thus the electronic structure of these two types of Ga atoms should be different.

Turning now to the Si-terminated surface, Figure 5 shows an empty state image of the clean $\sqrt{3}x\sqrt{3}$ phase. The structure of this surface is discussed detail in a seperate paper.[12] Based on the growth conditions and STM image we have proposed a surface vacancy model. In this model, one third of a monolayer of the surface silicon layer is removed in order to form the $\sqrt{3}x\sqrt{3}$ structure.

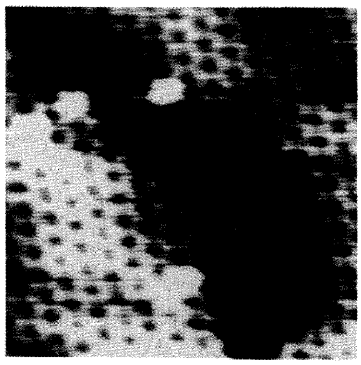

Fig. 5. Filled state image of the $\sqrt{3}x\sqrt{3}$ Si-terminated 6H-SiC(0001) surface. Bias = -1.2 volts. Image size = 86Å x 86Å.

Figure 6 shows an empty state image of the $\sqrt{3}x\sqrt{3}$ surface with less than one-half monolayer of adsorbed Ga. In this image, the Ga again forms a local 2x2 phase on the surface seen in the left-hand side of the image. The right hand side exhibits the $\sqrt{3}x\sqrt{3}$ structure of the clean surface.

Fig. 6. Empty state image of submono-layer coverage of Ga on the 6H-Si(0001) $\sqrt{3}x\sqrt{3}$ surface after annealing @ 480C for five minutes.

However, the Ga aggregates into relatively large domains, rather than forming small clusters. This type of aggregation is indicative of a large cofficient of diffusion on this surface. This is reasonable given the very low corrugation (0.2Å) of the $\sqrt{3}x\sqrt{3}$ surface. Increasing the coverage to about one monolayer results in ordering of the Ga domains. The adsorbed gallium forms a row structure consisting of domains oriented 120 degrees with respect to each other. The image shown in figure 7 illustrates the three possible domains of the row structure. The direction of the rows is oriented 30 degree away from the [1 $\bar{2}$ 10] direction of the clean surface. Some meandering of rows is also visible, with the changes in direction of the rows is always 120 degrees. The spacing between the rows was measured as 9.6Å. In addition to the primary order, i.e. formation of rows on the surface, some fine structure can be seen in the image. The rows are not perfectly straight, but rather "zig-zag" slightly back and forth regularly, so that the average direction is still a straight line.

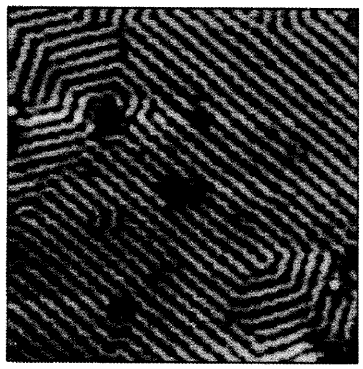

Fig. 7. Empty state image of the Ga row structure obtained on the Si-terminated 6H-SiC(0001) $\sqrt{3}x\sqrt{3}$ surface. Row spacing is 9.6Å. Structure was obtained after annealing @ 500C for five minutes. Bias = +1.0 volts. Image size = 260Å x260Å.

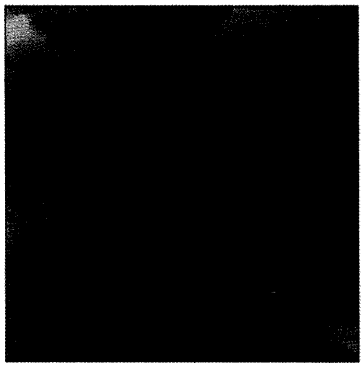

Fig. 8. Filled state image of the Si-terminated 6H-SiC(0001) $\sqrt{3}x\sqrt{3}$ surface showing the three phases of adsorbed Ga. bias = -2.5 volts. Image size = 450Å x 450Å.

Figure 8 shows, all three of the different suface phases of gallium which we observed on the 6H-SiC(0001) $\sqrt{3}x\sqrt{3}$ surface. In right hand side of the image, a third phase was observed. As was observed for the C-terminated surface, this "metallic" phase didn't show any structure in the STM image. However, it is most likely 1x1 Ga.

4. Conclusion

Absorption of Ga on both the C-terminated and Si-terminated 6H-SiC(0001) surfaces was studied using STM. While at submonolayer and multilayer coverages, very similar surfaces were formed, dramatically different surface structures were observed at approximately one monolayer coverage. At low coverages, a locally ordered 2x2 stucture was observed on both surfaces. At multilayer coverages a 1x1 metallic gallium layer was seen. However, at one monolayer, an ordered row structure was observed on the Si-terminated face, while Ga on the C-terminated face formed a

ring structure reminiscent of the Si(111)-7x7 surface. A detailed model of the ring structure was proposed. The model explains the contrast between the different Ga atoms observed in the STM image.

The different structures observed at one monolayer coverage provides new insight into the behavior of these two surfaces as substrates for GaN growth.

Acknowledgments

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