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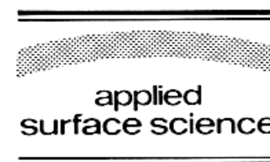

Surface structures of GaAs passivated by chalcogen atoms

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Abstract

When a GaAs(001) surface with Se adsorbates was flash-heated under a low chemical potential condition, a 2 × 3 RHEED pattern, previously reported as an intermediate structure, remained even after the sample was cooled. The atomic structure observed by STM is in good agreement with the dimer model proposed to explain the chalcogen-passivated GaAs(001) surfaces. Se dimers were found to be buckled, but the 2 × -periodicity was maintained in the [$\bar{1}$10] direction, unlike the previously observed 4 × -structure forming the dimer row pairs. Some other structures, the axes of which are in directions different from [110], were also observed on the Se/GaAs(001) surface. The S-passivation effect was studied by measuring current–voltage properties for the S/GaAs(001) surface.

1. Introduction

Passivation of semiconductor surfaces/interfaces is a crucial issue in the development of semiconductor technology. Recently, surface treatments with chalcogen atoms (S, Se, Te) have been reported to effectively improve compound semiconductor surface/interface properties [1–7]. According to photoemission studies and theoretical calculations, Ga–metal bonds at the interfaces are replaced by Ga–chalcogen or metal–chalcogen bonds through the introduction of the chalcogen atoms; thereby, the density of the surface band-gap states formed by metal–GaAs structures is markedly reduced [8–11]. In addition, the structures created by chalcogen atoms at the interfaces are thermally more stable than the original structures in many cases. In order to clarify and develop the passivation mechanism of these surfaces, characterization of the structures of the terminated layers on an atomic scale is urgently needed. The study of chalcogen/GaAs surfaces is also of interest for understanding of

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the epitaxial growth mechanism of II–VI semiconductors on GaAs surfaces [12–15].

In this paper we report the surface structures of Se/S–GaAs surfaces studied by scanning tunneling microscopy.

2. GaAs surfaces with chalcogen adsorbates

Surface structures of GaAs with chalcogen adsorbates are summarized in Table 1 [16–21]. In each frame, the phases are arranged in order of decreasing chemical potential. The 2×3 structure of Se/GaAs(001) was previously reported as an intermediate structure [21], however, a stable 2×3 structure was obtained under lower chemical potential conditions in this work, as is described later. According to photoemission and theoretical studies on those surfaces, surface chalcogen atoms are more stably bonded to Ga atoms than to As atoms, and all the surfaces of passivated GaAs(001) form 2×1 structures by forming chalcogen dimers at lower temperatures [5,22]. Since the chalcogen atom has 6 electrons, each chalcogen dimer has one excess electron which will occupy the Ga–chalcogen or chalcogen–chalcogen antibonding state. Thereby, repulsive interaction between the adjacent dimers caused by the excess electrons is thought to form the symmetric 2×1 structure, contrary to the clustered dimer structures appearing on the As/GaAs(001) surface [23]. Upon heat treatment at high temperatures, charge transfer is expected to play an important role in stabilizing the passivated surfaces, as in the reconstruction of the As/GaAs(001) surfaces [23]. According to the electron counting model [9], 2×2 ad-dimer structures [24], for example such as those in an Al/Si surface, are candidates for yielding the stable passivated surfaces. Chalcogen 2×1 dimers with further adsorbates of 1/4 ML chalcogens, the structure of which depends on the additional adsorption site, is also a candidate. If chalcogen atoms on the on-top sites are dimerized through charge transfer, the 2×6 structure can be included: 4 chalcogen dimers on the bridge site sandwiched by two chalcogen dimers on the on-top site. However, instead of these simple structures more complex models including multilayered surfaces have been supported experimentally, even for the basic 2×1 structure concerning the Se/GaAs(001) surface [25]. It is necessary to clarify this point to understand the passivation mechanism.

Table 1
Surface structures of GaAs with chalcogen adsorbates [16–21]

	GaAs(111)A	GaAs(001)	GaAs(111)B
S	1×1	2×1	1×1
		2×2	
Se		2×1	
		(4×1)	
		2×3	
		4×3	
		4×1	
Te		2×1	
		6×1	
		* ×3	

3. Se / GaAs(001) surface studied by STM

Selenium of 100–300 nm thickness was evaporated at room temperature onto GaAs(001) surfaces, oriented to within 0.5° of the [001] direction, Si-doped at 1×10^{18} cm^{-3}, and prepared by thermal cleaning.

With the sample temperature being increased continuously, the 2×3 RHEED pattern shown in Fig. 1 appeared at ~520°C. This structure was reported as an intermediate phase appearing at high temperatures (> 550°C); the 2×3 structure transformed back into the 2×1 structure when the substrates were cooled down again [21]. However, for samples flash-heated with the back pressure kept lower than ~1×10^{-10} Torr throughout the heat treatment, the 2×3 RHEED pattern was obtained at ~400–500°C and was found to be stable even after the samples were cooled.

For the Se/GaAs(001) surfaces with a 2×3 RHEED pattern, elliptical protrusions ordered with 0.6 nm periodicity in the [110] direction were observed by scanning tunneling microscopy (STM), as shown in Fig. 2 ($V_s = -2.0$ V, $I_s = 20$ pA). The distance between the rows aligned in the [110] direction was about 0.8 nm. The differ-

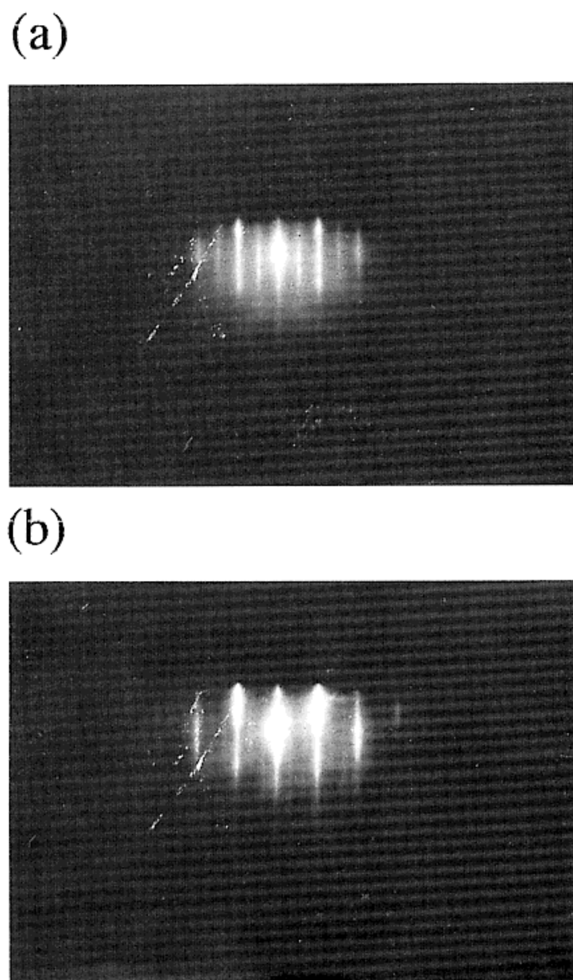

Fig. 1. RHEED 2×3 patterns obtained for Se/GaAs(001); (a) [110], (b) [$\bar{1}$10].

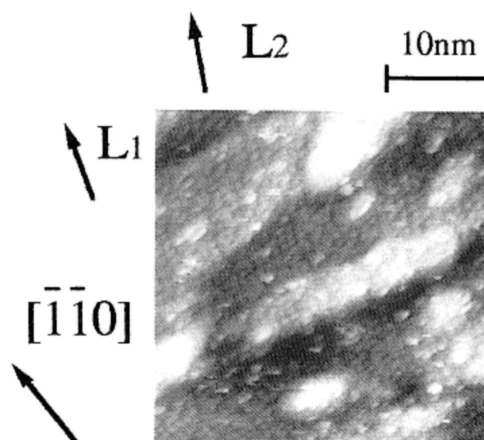

Fig. 2. STM image of Se/GaAs(001) surface ($V_s = -2.0$ V, $I_s = 20$ pA). L_1, L_2: main axes of the rows different from [110].

ence in height between the two neighboring terraces was ~ 0.28 nm and the axes of the rows on both terraces were shifted by about 0.2 nm. These results are in good agreement with the double-layer structure of Se dimer rows adsorbed on the second Ga layer.

A possible explanation of the structure is to attribute the elliptical images to the Se dimers adsorbed on the bridge and the on-top-like sites of the second Ga layer. Such a structure may be stabilized through charge transfer of the excess electrons into the Ga dangling bond states which appear by desorption of chalcogen dimers (Fig. 3a). Structures forming Ga dimers in the second layer may result in the 0.6 nm periodicity, as shown in Fig. 3b, where two Se dimers are pulled toward the Ga dimers between them. When Ga atoms between the Ga dimers are removed and As atoms in the third layer are replaced by Se atoms (Fig. 3c), the structure becomes closer to the Ga_2Se_3 structure [25]; the second Ga layer has 1/4 ML Ga vacancies, and As atoms in the third and fifth As layers are partially replaced by Se atoms. In our experiment, Se atoms were adsorbed at room temperature on the Ga-rich GaAs surface and flash-heat treatment of the sample was performed, whereas samples were prepared at higher temperatures in Se atmosphere in previous experiments [22,25]. Therefore, the reconstructed region is expected to grow inward during longer and higher heat treatments. Actually, the ratio between two photoemission

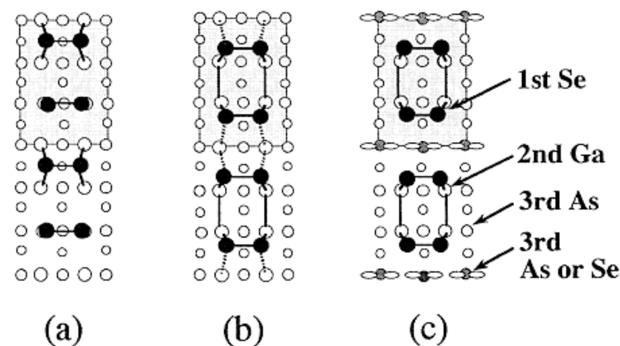

Fig. 3. Structural models for the Se/GaAs(001) 2×3 surface.

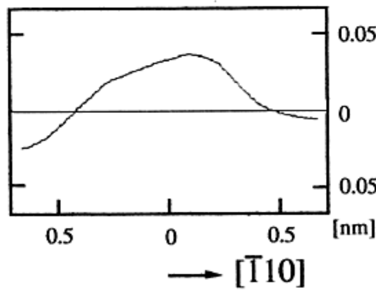

Fig. 4. Cross section of Se dimer in the [$\bar{1}$10] direction.

peaks appearing in the Se/GaAs(001) surface [22,25], which are attributed to the two kinds of Ga–Se bonding states, respectively with and without Ga vacancy in the nearest neighbor site, changes during the heat treatments. This structural change is considered to be related to the inital formation process of Ga_xSe_y/GaAs interfaces [25].

Fig. 4 shows a cross section of Se dimers in the 2×3 region. As is shown in the figure, the Se dimers are buckled [26], suggesting the existence of some charge transfer in the surface layers. The buckling structure is similar among the dimers and results in the $2\times$-structure in the [$\bar{1}$10] direction, contrary to the pairing of dimer rows observed for the Se/GaAs(001)-4×1 surface upon slightly higher heat treatment (~ 530°C) [20].

In addition to the 2×3 structure mentioned above, other structures having axes different from the [110] direction were observed, as shown in Fig. 2. In the figure, the main axes of the rows are indicated by the arrows L_1 and L_2. Those structures may be related to the $* \times 3$ structures observed for the Te/GaAs(001) surface [12,16].

Mechanisms to explain the formation of the $4\times$-structure and the structures with axes different from the [110] direction, as described above, are under consideration.

4. S/GaAs surface

Recently, Dagata and Tseng performed STM/STS on $P_2S_5/(NH_4)_2S$-passivated GaAs in air [27] and obtained I–V characteristics close to the I–V properties of the free surface with ultra-thin oxide. On the contrary, $(NH_4)_2S_x$-treated GaAs surfaces have been known to retain Ga–S bonds forming the 2×1 structure on the surface even after exposure to air, and band bending has been observed [1–11]. In order to clarify this point, we performed STM/STS on the $(NH_4)_2S_x$-treated GaAs(001) surface in air.

Sulfur-passivated surfaces were prepared by dipping the GaAs wafers with Si-doping levels of $\sim 10^{18}$ cm^{-3} for n-type, and a Zn-doping level of $\sim 10^{20}$ cm^{-3} for p-type, into a $(NH_4)_2S_x$ solution kept at ~ 60°C for 36 min. When these samples were heated at ~ 400°C in the vacuum, the 2×1 RHEED pattern was observed for (001) surfaces. Surfaces were rather rough and atomic structures could not be seen. For the samples prepared using MBE-grown GaAs, STM images were completely flat, which may be caused by the small corrugation for this surface, as was observed for the Se/GaAs(001) surface [28]. No particular difference was observed between n-type and p-type STM images.

Fig. 5 shows I–V curves obtained for a S/GaAs(001)-2×1 surface in air. The top of the valence band E_v and bottom of the conduction band E_c are indicated by arrows for (a) n-type and (b) p-type, respectively. Using the value of the GaAs band gap of ~ 1.4 eV, Fermi levels of both samples are estimated as ~ 0.9 eV below E_c for the n-type and ~ 0.9 eV above E_v for the

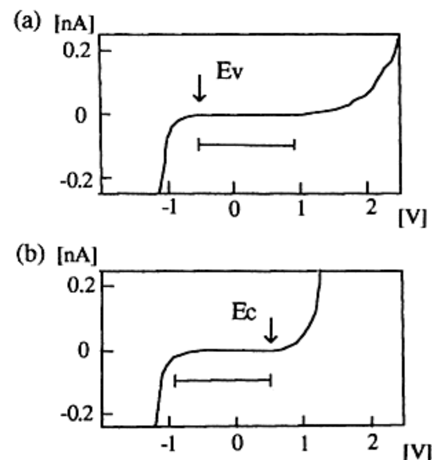

Fig. 5. I–V curves obtained for S/GaAs(001) surfaces of (a) n-type, (b) p-type. E_c and E_v indicate the conduction band and valence band edges.

p-type, which shows band bending properties. Thereby, the effect of S-treatment for these surfaces is contrary to the flat band obtained for the $P_2S_5/(NH_4)_2S$-passivated surfaces. The amount of band bending obtained here is greater than the values obtained by photoemission studies (~ 0.55–0.8 eV for n-type and ~ 0.8 eV for p-type) [10,11], which may be due to the effect of the light used in the photoemission process on band bending, as was mentioned by Yablonovitch et al. [29].

For the S/GaAs(111)B surface, the structure observed by STM was similar to the 2×2 structure observed for the GaAs(111)B surface by Biegelsen et al. [30] instead of the 1×1 structure reported previously [17]. However, the surfaces observed here were rather rough and the images were slightly distorted; therefore, further studies are necessary to determine the structure.

5. Conclusions

Se-passivated GaAs surfaces under low chemical potential conditions were studied by scanning tunneling microscopy. The 2×3 structure was observed on an atomic scale, and is in good agreement with the dimer model proposed to explain the chalcogen-passivated GaAs(001) surfaces. Se dimers are buckled, indicating the existence of charge transfer in the surface layers. Other structures, the axes of which are in directions different from [110], were also observed on the Se/GaAs(001) surface. S-passivation effect was shown by studying current–voltage measurements.

Acknowledgements

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