Structural studies of sulfur-passivated GaAs (100) surfaces with LEED and AFM

Y. Ke, S. Milano, X.W. Wang, N. Tao, Y. Darici *
Department of Physics, Florida International University, Miami, FL 33199, USA

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Abstract

We present the results of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and atomic force microscopy (AFM) analysis of sulfur-passivating layers on the GaAs (100) surface. The GaAs surfaces were passivated with both inorganic \([\text{NH}_4]^2\text{S}_x\) and organic \([\text{octadecylthiol (ODT)}\) S-based compounds. We prepared the inorganic sulfur-passivated GaAs(100) surfaces with a wet chemical treatment using \([\text{NH}_4]^2\text{S}\) solution. This was followed by thermal annealing of the treated sample in an ultra-high vacuum (UHV). After ex-situ and in-situ treatments, the surface resulted in a \((2 \times 1)\) LEED pattern. The LEED data (I–E curves) were recorded and compared with dynamical LEED calculations for different structural models for the sulfur-passivated GaAs (100) surface. The results showed that the sulfur-passivated \((2 \times 1)\) surface structure is an arsenic–sulfur dimer on a Ga-terminated substrate. The ex-situ AFM results also revealed a \((2 \times 1)\) structure for the inorganic passivation and a very smooth surface for the organic ODT in the ethanol-treated sample. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Atomic force microscopy; Gallium arsenide; Low-energy electron diffraction; Roughness; Sulfur; Surface structure

1. Introduction

A major hindrance to the broader use of GaAs in electronic and optoelectronic devices is due to its surface properties, especially the large densities of GaAs surface electronic states \((10^{13} \text{ states cm}^{-2})\) that pin the Fermi level at midgap, and result in a large surface recombination velocity [1].

Sulfur adsorption on to the GaAs surface has been shown to be very effective in reducing the band gap state density of the (100) surface. There are a large number of reports on the improved electronic properties of passivated GaAs (100) surfaces in terms of enhanced photoluminescence, reduced band bending and improved I–V characteristics [1–6]. The lack of detailed structural studies on the sulfur-passivated surfaces has prevented understanding of the physical basics of the changes, and the reasons for success or failure. As a result, the surface structure of the passivated GaAs (100) remains controversial. Previous studies show that the superstructure of sulfur passivated GaAs (100) surface after thermal annealing is \((2 \times 1)\), and before annealing, it is \((2 \times 2)\) [7–9]. Several structural models have been proposed to describe this \((2 \times 1)\) phase. Wang and Weinberg suggest S-Ga dimers on top of the second Ga layer of the GaAs(100) [7]. Sandroff et al.’s model consists of S-S dimers inserted between surface As atoms [10]. Berkovits and Page suggest that the surface is terminated with

* Corresponding author. Fax: +1 305 548 3053; e-mail: dariciy@servax.fiu.edu

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S–S and As–As dimers above the Ga layer [11]. Some studies have found that the passivated surfaces were As-deficient, and there were suggestions that the formation of a Ga–S bond was the key for passivation [4,12,13]. Recently, Ow and Wang reported a first-principles pseudopotential study on the surface and electronic structures of several passivated GaAs(100) \((2 \times 1)\) structures [14]. They have found that S bound strongly with Ga, but that the Ga-terminated \((100)\) surface covered with a Ga–S dimer layer was still metallic. However, the As–S dimer layer on the Ga-terminated \((100)\) surface is non-metallic. Due to the lack of a complementary experimental technique, the results are inconclusive.

Here, we present the results of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and atomic force microscopy (AFM) analysis of sulfur passivating layers on the GaAs \((100)\) surface.

2. Experimental

The samples used in these experiments were \((100)\) GaAs n-type wafers doped with \(1 \times 10^{18}–3 \times 10^{19} \text{ cm}^{-3}\) Si. The samples were passivated in inorganic and organic solutions in order to study the surface atomic structure, roughness and uniformity. For the \((\text{NH}_4)_2\text{S}_x\) passivation (inorganic), the samples were first degreased in an ultrasonic bath in trichlorofluoroethane, acetone, methanol and deionized water (resistivity >18 MΩ cm\(^{-1}\)). Following the degreasing procedure, the sample was placed in an argon-gas-filled glove-box for etching and passivation. In the glove box, the sample was placed into a reservoir with a drain cock at the bottom. A solution of 1:4 HCl:H\(_2\)O (DI) was poured over the sample and kept there for 30 s for etching. This solution was then diluted by gradually adding DI H\(_2\)O to the reservoir while the drain cock was open, effectively leaving the sample in clean DI H\(_2\)O. Then, the passivation \((\text{NH}_4)_2\text{S}_x\) solution was added to the DI H\(_2\)O while the drain cock was kept open, until the solution was effectively pure \((\text{NH}_4)_2\text{S}_x\) \((x=6\%)\). The sample was left in this solution for 30 min. Then, it was washed by DI H\(_2\)O. At no time during the etching/passivation process was the sample exposed to the argon gas in the glove box. After the DI H\(_2\)O was drained away, the wet sample was blown dry with argon gas. The same degreasing procedure was used for ODT passivation. The sample was first etched with NH\(_2\)OH:H\(_2\)O\(_2\):H\(_2\)O \((1:1:19)\) for 20 s, rinsed with DI water for 1 min, etched again with HCl:H\(_2\)O \((1:4)\) for 30 s, and rinsed again with DI water. Two different methods were used to passivate the GaAs surface with ODT. One was molten ODT, and the other was dissolving ODT in ethanol solution. The molten ODT method is a common method of forming self-assembled monolayers of ODT on GaAs(100) [15]. Inside the glove box, the ODT powder (98% purity) was heated to melt. Here, we present the results of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and atomic force microscopy (AFM) analysis of sulfur passivating layers on the GaAs sample.
and water to desorb. Then, it was annealed to about 580 °C [6]. The LEED data (intensity versus energy curves) were recorded with a very sensitive, low-light, computer-controlled video-camera (Dage, MTI). A snapshot of the diffraction pattern was recorded at each electron energy and stored in an IBM computer. The intensities of diffraction spots (10), (01) and (11) were measured as a function of energies from these recorded pictures via a computer program. The background subtraction from the recorded I–E curves was carried out carefully using two different approaches. The first approach was to subtract the background recorded during the intensity-versus-energy measurements of the beams from the video screen. The second approach was a high-degree polynomial fit. Both methods gave approximately the same results.

AFM (Nanoscope III system, Digital Instruments) was used to study the surface uniformity and to determine the surface structure of the samples. The AFM tips were made of Si₃N₄ attached to triangular cantilevers with a force constant of ~0.38 N m⁻¹. The operating force was minimized to typically a few nanonewtons in each measurement to minimize tip perturbation of the sample surfaces.

3. Theory

A complete analysis of surface structure by LEED requires a careful collection of experimental I–E curves for a large number of LEED spots and a systematic comparison with theoretical calculations. The LEED intensities can be calculated by quasidynamical LEED (QL), full dynamical LEED (FD), and a tensor LEED (TLEED) method ([19] and references therein). We have, in the past, successfully employed FD LEED calculations to determine the structure of various surfaces [20]. To enhance the reliability and efficiency, we use the combination of FD and first-principle total energy calculations to determine the structure of passivated GaAs (100) surfaces [14].

The FD theory has been very successful in producing accurate and consistent results for a wide variety of surfaces. We use the computer code developed by Van Hove and S.Y. Tang for dynamical LEED calculations [21]. In this approach, the scattering potential is modeled by an array of spherically symmetric non-overlapping potentials embedded in a constant background potential. The two-dimensional translational symmetry within each atomic layer is assumed. The electronic wavefunction is represented by spherical partial waves in the crystal and by superposition of plane waves outside of the crystal. Scattering by a single atom is characterized by its phase shifts, scattering by an atomic layer is calculated using Green’s self-consistent function method and matrix inversion method, and then the diffraction by a stack of atomic layers is calculated by the renormalized-forward-scattering perturbation method. Extensive discussion of the dynamic LEED calculation methods was given in Ref. [20]. The atomic scattering phase shifts for Ga, As and S are calculated using local-density-approximation atomic calculations [22].

Our first-principle total energy study has examined several possible passivated surface models. For each model, the equilibrium structure is determined by the minimum in total energy as well as minimized to typically a few nanonewtons in each measurement to minimize tip perturbation of the sample surfaces.

4. Results and discussion

We investigated the chemical composition, structure and roughness of (100) GaAs surfaces after the in-situ Auger spectrum of the (NH₄)₂Sx-treated sample showed a large sulfur peak, moderate amounts of carbon and small amounts of oxygen peaks, as well as gallium (1070 eV) and arsenic (1228 eV) peaks (Fig. 1a). To prepare the sample for LEED experiments, it was first annealed to 300 °C to allow the weakly
bonded hydrocarbons and water to desorb [7]. Then, it was annealed to about 580 °C [6]. After annealing at 300 °C, the carbon and oxygen peaks were reduced. The 580 °C annealing (~2 min) process reduced oxygen and carbon further (Fig. 1b). Even though some loss of arsenic was detected, there was no sulfur desorption. The As (1228 eV)-to-Ga (1070 eV) ratio stayed approximately the same after 300 °C annealing and 580 °C annealing. The LEED pattern showed a (2 × 1) structure. The ex-situ AFM (Nanoscope III) experiments also showed a (2 × 1) structure for the (NH₄)₂Sₓ-treated samples that were annealed in UHV and a (2 × 2) structure for the samples that were not annealed.
The AES results of the molten-ODT-treated sample showed that the passivation film was uniform with a large carbon concentration and that the surface was arsenic-rich. After annealing of the sample at 300°C, the carbon peak was reduced, but it was still the largest peak.

AFM results showed that the ODT-in-ethanol-solution-treated sample had the smoothest surface, and its roughness was much less than that of the molten-ODT-treated sample and (NH₄)₂Sₓ-treated sample (Fig. 3a-c). The roughness of the molten-ODT-treated samples was attributed to the fact that molten ODT condensed into a solid after cooling. The roughness of the (NH₄)₂Sₓ-treated samples was partly due to its etching effects and partly due to the electron damage from Auger and LEED experiments.

At high resolution, AFM images (Fig. 2a and b) of (NH₄)₂Sₓ-treated samples showed that the distance between the two nearest atoms along both the (110) and the (110) azimuths were 8 Å. Compared with the lattice constant of the GaAs(100) surface, a₀ = 4 Å, this surface had 2a₀ periodicities along the two azimuths, which meant that it was a (2 × 2) surface. After annealing, dimers were formed, and the distance between the two dimers was 8 Å. AFM images of molten-ODT- and ODT-in-ethanol-treated samples had a similarly ordered atomic structure with a lattice constant at about 5 Å. This structure is identified as the monolayer ODT chain group structure other than a GaAs(100) reconstruction (Fig. 4). This is because the crossing angle of atom rows should be 90° for GaAs(100), whereas this image revealed an angle of 60°, and the lattice constant of ODT on Au(111) substrate was also found to be 5.2 ± 0.6 Å [17].

The (2 × 1) LEED frames at 1 eV intervals for the inorganically treated sample were saved on the computer. The experimental intensity-versus-energy (I-E) curves for the beams (10), (01), (−10), (0−1), (11), (−1−1), (1−1) and (−1−1) were recorded. The symmetry-related beams were averaged to correct for any small misalignment. Extensive first-principles pseudopotential calculations were carried out on this system and identified the possible structures of the passivated surface [14]. The possible structures studied were a S-Ga

![AFM images of (NH₄)₂Sₓ-treated GaAs (100) surface](image-url)
dimer on a Ga- or As-terminated surface, a S–As dimer on a Ga- or As-terminated surface, and S on a Ga- or As-terminated surface. Among these, the S–Ga dimer on the As-terminated surface and the S–As dimer on the Ga-terminated surface are most promising. Both are insulating, and both have the observed (2 × 1) structure. Dynamical LEED calculations were performed on all these structures, and the theoretical (I–E) curves were compared with the experimental (I–E) curves. The comparison of the experimental (I–E) curves with different theoretical models showed that it was a S–As dimer model on a Ga-terminated surface with an R-factor of 0.25 (Fig. 5). The S–As dimer model corresponds to a half monolayer S and half monolayer As covering the Ga-terminated surface (Fig. 6). An R-factor of 0.25 is not very satisfactory, but other models tried all resulted in substantially larger R-factors. The S–Ga dimer on the As-terminated surface gives an R-factor of 0.3, whereas S–Ga on the Ga terminated surface and S–As on the As-terminated surface give R-factors of 0.35. Substrate relaxation had not been attempted to improve the R-factor.
structure for annealed (NH$_4$)$_2$S$_x$-treated samples and a (2 × 2) structure for the samples that were not annealed.

(3) The ODT-in-ethanol-solution-treated sample had the smoothest surface compared with the molten-ODT-treated sample and (NH$_4$)$_2$S$_x$-treated sample.

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