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Structural and electronic properties of group III Rich $In_{0.53}Ga_{0.47}As(001)$

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ABSTRACT

The structural and electronic properties of group III rich $In_{0.53}Ga_{0.47}As(001)$ have been studied using scanning tunneling microscopy/spectroscopy (STM/STS). At room temperature (300 K), STM images show that the $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ reconstruction is comprised of undimerized In/Ga atoms in the top layer. Quantitative comparison of the $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ and $InAs(001)$–(4×2) shows the reconstructions are almost identical, but $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ has at least a 4× higher surface defect density even on the best samples. At low temperature (77 K), STM images show that the most probable $In_{0.53}Ga_{0.47}As(001)$ reconstruction is comprised of one In/Ga dimer and two undimerized In/Ga atoms in the top layer in a double (4×2) unit cell. Density functional theory (DFT) simulations at elevated temperature are consistent with the experimentally observed 300 K structure being a thermal superposition of three structures. DFT molecular dynamics (MD) show the row dimer formation and breaking is facilitated by the very large motions of tricoodinated row edge As atoms and z motion of In/Ga row atoms induced changes in As–In/Ga–As bond angles at elevated temperature. STS results show there is a surface dipole or the pinning states near the valence band (VB) for 300 K $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ surface consistent with DFT calculations. DFT calculations of the band-decomposed charge density indicate that the strained unbuckled trough dimers being responsible for the surface pinning.

1. Introduction

III–V compound semiconductors are becoming increasingly important for a wide range of potential applications such as optoelectronic devices and high-speed, low-power logic applications, owing to their high electron mobilities, direct bandgaps, and high breakdown voltages. Nearly all these devices employ oxide-semiconductor, metal-semiconductor, or semiconductor–semiconductor interfaces. Therefore, it is necessary to understand the chemistry and physics of III–V compound semiconductors' atomic-scale surface reconstructions since they play a critical role in interface formation.

$In_{0.53}Ga_{0.47}As$ is a convenient III–V compound semiconductor for a metal–oxide–semiconductor field-effect transistor (MOSFET) channel material due to its high electronic mobility (~14,000 $cm^2\ V^{-1}\ s^{-1}$), high breakdown field, and its ability to be grown lattice matched on the semi-insulator substrate, InP. The key to fabricating a practical III–V MOSFET is forming an unpinned oxide–semiconductor interface with low fixed charge and low trap density. The interface quality between the oxide and III–V compound semiconductor has been found to correlate with the type of semiconductor surface reconstruction [1]. Although the As-rich $InGaAs(001)$–(2×4) and (4×3) reconstructions have been the focus of many scanning tunneling microscopy (STM) investigations and a few theoretical studies [2–4], there is still no consensus on the surface structure of the group III rich $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$. The group III rich reconstructions may be especially important for gate oxides deposition. It is likely that the As-rich (2×4) reconstruction undergoes oxygen induced displacement reactions during gate oxide deposition because the dimerized arsenic atoms are likely to be displaced by ambient oxygen during oxide deposition [5–8]. Conversely, the group III rich (4×2) reconstructions are less reactive to oxygen and, therefore, probably more suitable for oxide deposition [9].

In this report, the first study of the surface reconstructions of the group III rich $In_{0.53}Ga_{0.47}As(001)$ at both 300 K room temperature (RT) and 77 K low temperature (LT), using STM is presented. STM images of the $In_{0.53}Ga_{0.47}As(001)$ show that the surface structures are different at 300 K and 77 K. At 300 K, the $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ surface appears to have only undimerized group III In/Ga topmost row atoms. At 77 K, the $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ surface has both undimerized and dimerized group III In/Ga topmost row atoms. The RT and LT reconstructions observed by STM for $In_{0.53}Ga_{0.47}As(001)$–$(4\times2)$ are nearly identical to those observed by STM for $InAs(001)$–(4×2). Standard DFT shows a bandgap for InGaAs(001) in contrast to InAs(001); therefore, the modeling of InGaAs(001) allows reasonably accurate calculations of the electronic structure for comparison to

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experimental results. For both $In_{0.53}Ga_{0.47}As(001)$–(4×2) and InAs (001)–(4×2) density functional theory (DFT) simulations predict that undimerized and dimerized structures have an energy difference of less than 10 meV per surface atom consistent with the 300 K structure not being a completely different structure than the 77 K structure but instead being a thermal superposition of three nearly degenerate structures; this was confirmed using DFT molecular dynamics (MD) simulations at elevated temperature. Both scanning tunneling spectroscopy (STS) and DFT calculations show that the $In_{0.53}Ga_{0.47}As(001)$–(4×2) 300 K structure is pinned.

2. Experimental and theoretical methods

MBE was employed to grow a 0.2 μm layer of 1×10^{18} cm^{-3} doped $In_{0.53}Ga_{0.47}As$, lattice matched on 500 μm thick InP(001) substrates (Wafer Technology) with 1×10^{18} cm^{-3} doping. Experiments were performed on both n-type and p-type wafers. The re-grown wafers were capped in situ with a 50 nm protective As_2 cap. The wafers were transferred to a vacuum container for transporting to the STM chamber. The STM chamber is equipped with low energy electron diffraction (LEED) for determination of the surface periodicity. Omicron VT-STM and LT-STM spectrometers were employed for determination of atomic structure at 300 K and 77 K. All the experiments were performed in ultra-high vacuum (UHV) systems with a background pressure less than 8×10^{-11} Torr. The As_2 capped samples were radiatively heated to obtain the desired $In_{0.53}Ga_{0.47}As(001)$ surface reconstruction. A three step decapping and annealing procedure was performed. First, the samples were initially held at 180 °C for at least 2 h of degassing. This removed the weakly bonded impurities from the surface such as water. Second, the sample temperature was raised to 330 °C for typically between 2 and 4 h to remove the As-cap. Finally, the sample was gradually heated to the peak temperature (around 450 °C for InAs (001)–(4×2) and 460 °C for $In_{0.53}Ga_{0.47}As(001)$–(4×2)) and held for 15 min followed by a quick quenching. Following the As-decapping and annealing procedure, the surface reconstruction was verified by LEED. Afterwards, the sample was transferred into the STM chamber. STM images were taken at both 300 K room temperature and 77 K low temperature. Typical imaging conditions for both room temperature and low temperature are constant-current mode with a typical 50–100 pA setpoint tunneling current and −2 V sample bias voltage relative to the tungsten tip.

All DFT simulations were performed with the Vienna Ab-initio Simulation Package (VASP) [10,11] using projector augmented-wave (PAW) pseudopotentials (PP) [12,13] and PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [14,15]. The choice of PBE functional and PAW PP's was validated by parametrization runs demonstrating good reproducibility of experimental lattice constants, bulk moduli, and formation energies for bulk crystalline GaAs, and InAs. A Brillouin zone integration was performed at 4×4×1 Monkhorst–Pack k-point mesh with 9 irreducible k-points and a plane wave energy cut-off of 250 eV. A double (4×2) reconstructed unit cell (~16.95×16.95 $Å^2$, 140 atoms) was used, consisting of 7 atomic layers with a (001) surface orientation. The bottom layer As atoms were passivated by H atoms with fractional 3/4 |e| charge to mimic a continuous InGaAs bulk according to Ref. [16]. The slabs were relaxed using Conjugate-Gradient (CG) relaxation algorithms with 0.05 eV/Å force tolerance level. During relaxation, the three bottom layers were fixed in their bulk positions. A vacuum layer of ~12 Å was added over the slabs to eliminate spurious interaction through periodic boundary conditions (PBC). To compensate for spurious electric field induced by PBC for this type of system, a dipole correction was applied [10,11,17]. The preliminary $In_{0.5}Ga_{0.5}As$ bulk unit cell was formed from GaAs unit cell by substituting half of Ga atoms by In atoms following checkerboard pattern and DFT optimizing the lattice constant of the alloy to equilibrium value. All slab total energies are reported per double (4×2) unit cell.

3. Results and discussions

3.1. Experimental results

3.1.1. Room temperature 300 K $In_{0.53}Ga_{0.47}As$ Surface

Shown in Fig. 1a is a typical large scale filled state RT-STM image of $In_{0.53}Ga_{0.47}As(001)$ surface after As-decapping and annealing at 460 °C. The surface exhibits large, well-ordered, flat terraces. The main feature for the group III rich $In_{0.53}Ga_{0.47}As(001)$ surface is rows running in the [110] direction. The distance between the rows is 17 Å. Between the rows are trough regions. STM images reveal that this (4×2) surface is similar to the surface reconstructions of several other low bandgap III–V materials like InSb(001)–(4×2) and InAs(001)–(4×2) surfaces, which have been observed by several groups [18–23]. However it is distinct from the Ga-rich GaAs(001)–(4×2) reconstruction [24–29]. Detailed reports of the surface reconstructions on GaAs(001) can been found in reports by Northrup et al. and Chadi et al. [24,30–33].

A quantitative comparison of the surface defect density on InAs (001)–(4×2) and $In_{0.53}Ga_{0.47}As(001)$–(4×2) was performed. Filled state STM images of group III rich InAs(001)–(4×2) and $In_{0.53}Ga_{0.47}As$ (001)–(4×2) surface are shown in Fig. 1a and b for comparison. The absence of chemical impurities on the surface was confirmed by X-ray photoelectron spectroscopy (XPS): no C and O peaks were found on the clean surface. For both clean (4×2) surfaces, there are at least four kinds of defects on the both surfaces. Fig. 1a shows the following defects types (D_n): D_1 as dark cuts on the row, D_2 as protrusion dots between the rows, D_3 domain boundaries as depression lines in the [−110] direction and D_4 domain boundaries as protrusion lines in the [110] direction. It is difficult to compare D_2, D_3 and D_4 defects between InAs and $In_{0.53}Ga_{0.47}As$ clean surfaces because quantities of these three defects are small or almost zero on the InAs(001)–(4×2) clean surface, so statistical errors are likely to occur. Therefore, only D_1 defects are analyzed. For the D_1 defects in Fig. 1a, there are 108 defects on the rows in 75 nm×75 nm $In_{0.53}Ga_{0.47}As(001)$–(4×2) surface. For the same size InAs(001)–(4×2) surface, there are only 23 D_1 defects on the rows. Therefore, there are at least 4 times more D_1 defects on the $In_{0.53}Ga_{0.47}As(001)$–(4×2) clean surface than on the InAs(001)–(4×2) clean surface since Fig. 1a represents one of the best $In_{0.53}Ga_{0.47}As(001)$–(4×2) surface that has been prepared while the InAs(001)–(4×2) in Fig. 1b is a typical surface.

Based on STM results, a RT $In_{0.53}Ga_{0.47}As(001)$–(4×2) structure model is proposed in Fig. 1e that shows undimerized In/Ga atoms in the top layer. The small scale filled state RT-STM images of the $In_{0.53}Ga_{0.47}As(001)$–(4×2) surface in Fig. 1c and d show more detailed information about the trough regions. For the RT $In_{0.53}Ga_{0.47}As(001)$, bright balls are imaged in the trough regions. The distance between the bright balls in the trough regions is 8.5 Å which is close to 2× the span of the $In_{0.53}Ga_{0.47}As(001)$ bulk unit cell (4.15 Å). However, the bright balls are not observed on InSb(001)–(4×2) and InAs(001)–(4×2) trough regions[18–23]. Conversely, the bright balls in the trough are observed for InAs growth on GaAs(001) surface by Xu et al. [34] and for indium-adsorbed onto the GaP(001) surface by Shimomura et al. [35], but the bright balls in the present study of group III rich $In_{0.53}Ga_{0.47}As$/InP(001) are smaller. In the present study of $In_{0.53}Ga_{0.47}As$/InP(001)–(4×2), the bright balls sometimes completely fill in the trough regions as shown in Fig. 1c, and sometimes only partially fill in the trough regions as shown in Fig. 1d. It is possible that these bright balls result from excess charges rather than atomic clusters, similar to what has been observed on the clean GaAs(001)–(4×2) surface [36,37]. However, further experiments are needed to better understand these results. Due to the lack of a regular, ordered existence of the bright balls on the surface and the fact that the bright balls appear to result from electrostatic rather than geometric origins, they will therefore not be considered for structural assignment on the $In_{0.53}Ga_{0.47}As(001)$–(4×2) surface.