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Anomalous hybridization in the In-rich InAs(0 0 1) reconstruction

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ABSTRACT

The surface bonding arrangement in nearly all the confirmed reconstructions of InAs(0 0 1) and GaAs(0 0 1) have only two types of hybridization present. Either the bonds are similar to those in the bulk and the surface atoms are sp^3 hybridized or the surface atoms are in a tricoordinated bonding arrangement and are sp^2 hybridized. However, dicoordinated In atoms with sp hybridization are observed on the InAs(0 0 1), In-rich, room temperature and low temperature surfaces. Scanning tunneling microscopy (STM) images of the room temperature (300 K) InAs(0 0 1) surface reveal that the In-rich surface reconstruction consists of single-atom rows with areas of high electron density that are separated by ~4.3 Å. The separation in electron density is consistent with rows of undimerized, sp hybridized, In atoms, denoted as the β3′(4 × 2) reconstruction. As the sample is cooled to 77 K, the reconstruction spontaneously changes. STM images of the low temperature surface reveal that the areas of high electron density are no longer separated by ~4.3 Å but instead by ~17 Å. In addition, the LEED pattern changes from a (4 × 2) pattern to a (4 × 4) pattern at 77 K. The 77 K reconstruction is consistent with two (4 × 2) subunit cells; one that contains In dimers on the row and another subunit cell that contains undimerized, sp hybridized, In atoms on the row. This combination of dimerized and undimerized subunit cells results in a new unit cell with (4 × 4) periodicity, denoted as the β3(4 × 4) reconstruction. Density functional theory (DFT) and STM simulations were used to confirm the experimental findings.

1. Introduction

Due to its high electron mobility (30,000 $cm^2 V^{-1} s^{-1}$), InAs is a potential channel material for III–V metal-oxide-semiconductor field effect transistors (MOSFETs) [1]. Formation of a defect-free oxide–InAs interface is a key challenge in InAs MOSFET development. During the growth of the gate oxide layer using techniques such as molecular beam epitaxy (MBE) or atomic layer deposition (ALD), the InAs surface may be exposed to oxygen [2,3]. Since oxygen has been shown to cause defects and Fermi level pinning on other III–V surfaces [4–6] it would be preferable to find an InAs surface that is relatively unreactive to oxygen. The InAs(0 0 1)-(4 × 2) surface has been shown to have very low reactivity to molecular oxygen [7] making it a viable potential starting template for subsequent ALD or MBE growth in MOSFET fabrication. However, the In-rich InAs(0 0 1) surface reconstruction is not well understood, and having an atomic understanding of the clean surface is critical. A clear understanding of the surface structure allows for the analysis of defects, expands the knowledge base of semiconductor surfaces, and aids in the development of new and specific chemistry.

Since InAs and GaAs have similar chemical properties, it might be assumed that the (4 × 2) reconstruction of the two semiconductors would be the same. However, scanning tunneling microscopy (STM) images of the two surfaces differ dramatically. Despite the differences in STM images between InAs(0 0 1)-(4 × 2) and GaAs(0 0 1)-(4 × 2) reconstructions [4,6,8–11], some computational studies still propose that the InAs structure is the ζ(4 × 2) [11,12] reconstruction that has been well documented for GaAs. Both of the theoretical studies that conclude the InAs(4 × 2) structure was the ζ(4 × 2) reconstruction did not employ STM for comparison to the structural model, and one study did not compare the β3 model to other structures they proposed. Other studies have

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proposed different (4 × 2) structures that include the α(4 × 2) [8,9], β2(4 × 2) [12], and β3(4 × 2) [4,10,13]. These structures along with four other possible (4 × 2) reconstructions [α2(4 × 2), α3(4 × 2), β(4 × 2), and S(4 × 2)] are shown in Fig. 1. Although numerous studies have attempted to determine the InAs(0 0 1)-(4 × 2) reconstruction, the majority focused either on experimental determination [4,8,13] or computational determination [11,12,14] of the surface but did not employ both techniques. In addition, many of the computational studies only considered a small subset of the possible (4 × 2) reconstructions and none of the experimental procedures involved cryogenic experiments.

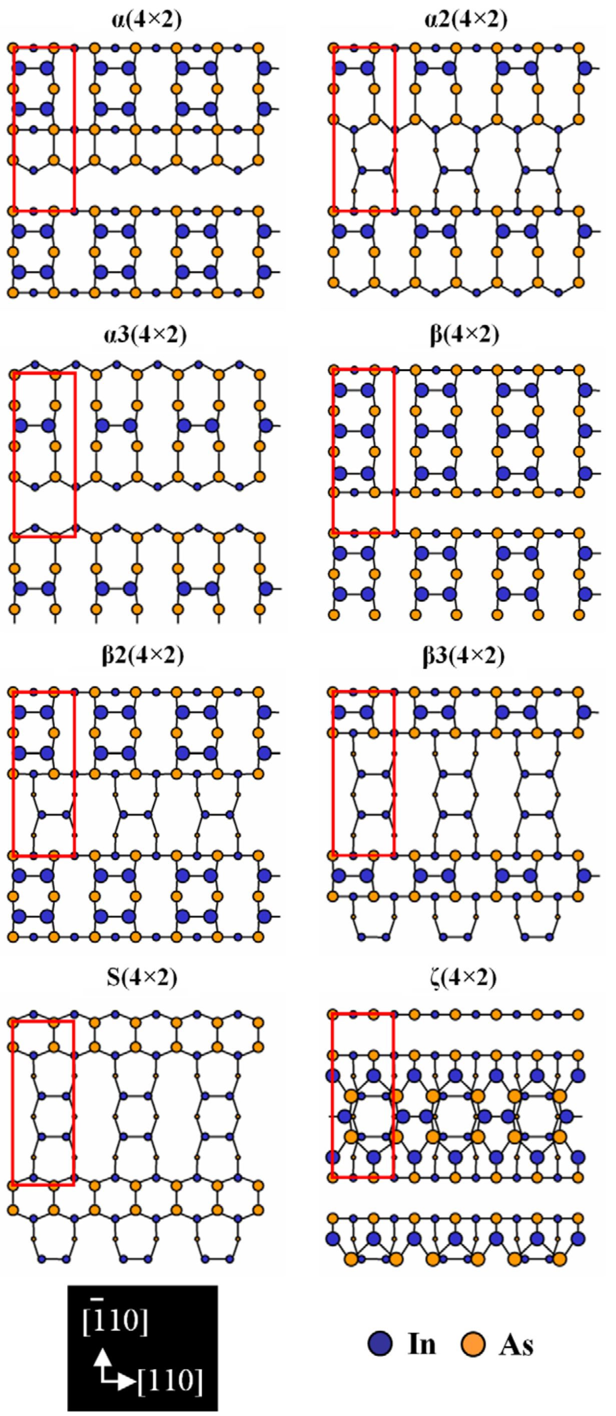

Fig. 1. Ball-and-stick diagrams of the possible structures for the InAs(0 0 1)-(4 × 2) reconstruction. The red boxes denote the unit cells of each reconstruction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Experimental and computational studies were employed to determine the room temperature (300 K) and low temperature (77 K) reconstructions of the In-rich InAs(0 0 1) surface. Detailed room and low temperature STM images of the clean surface revealed that neither reconstruction was an identical match to the possible (4 × 2) structures shown in Fig. 1. The 300 K STM images identified that the most probable InAs(0 0 1)-(4 × 2) reconstruction was similar to the β3(4 × 2) structure. However, instead of having row In atoms that were dimerized, the row In atoms were undimerized, thereby making it the β3′(4 × 2) structure. The β3′(4 × 2) structure consists of rows of sp hybridized, dicoordinated In atoms which run in the [1 1 0] direction. As the sample was cooled from room temperature to 77 K, low energy electron diffraction (LEED) revealed that the sample underwent a spontaneous and reversible change in surface periodicity from a (4 × 2) reconstruction to a (4 × 4) reconstruction. STM images confirmed that the real space periodicity of areas of high electron density changed from ~4.3 Å to ~17 Å. LEED and STM findings suggested that the 77 K surface reconstruction results from the combination of two (4 × 2) unit cells; one subunit cell being a β3(4 × 2) unit cell and the other subunit cell being a β3′(4 × 2) unit cell. This results in a new unit cell with (4 × 4) periodicity denoted as the β3(4 × 4) reconstruction. Density functional theory (DFT) calculations were performed to confirm the experimental findings.

2. Experimental and computational techniques

Experiments were performed in two different UHV chambers that were both equipped with a LEED and an STM. One chamber housed a Park Scientific VP STM while the other chamber housed an Omicron LT STM. Images taken with the Omicron STM are labeled within the text of the paper. In addition, the Omicron machine was capable of taking STM images at both 300 K and 77 K. As_2-capped InAs(0 0 1) samples were grown offsite via MBE on epi-ready wafers and then were transferred into one of the UHV chambers. The samples were then thermally decapped to produce the In-rich InAs(0 0 1) surface by different procedures in the two STM chambers. In the Park Scientific VP STM chamber, the wafers were decapped by performing ramping cycles to ~450 °C as previously described.[15] In the Omicron LT STM chamber, the wafers were decapped by radiantly heating the sample via a PBN sample stage heater as described previously.[7] In both chambers, after the decapping procedure was complete, LEED was used to verify the surface periodicity, after which the samples were transferred into the STM for analysis. Both LEED and STM data from each chamber show that both preparation methods produce the identical β3′(4 × 2) reconstruction of the InAs(0 0 1) surface at room temperature. Atomically resolved STM images were recorded at both 300 K and 77 K with the Omicron machine.

Other STM studies of decapped InAs(0 0 1) have been performed and revealed similar room temperature (4 × 2) STM images. In addition, no other (4 × 2) reconstructions have been seen by this group or published by other groups for thermally decapped samples. The authors concede that other (4 × 2) reconstructions may be possible on non As-capped MBE grown samples; however, there are no published STM studies on in situ grown (4 × 2) reconstructions. Therefore, the focus of this paper will be on the reconstructions that correlate to current and previous STM studies on decapped samples.

DFT calculations were used to confirm and interpret the experimental results. Plane wave (periodic boundary) calculations were performed using the Vienna *ab-initio* simulation package (VASP) code on double slabs (two (4 × 2) unit cells) [16–19]. The current