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Structure and composition of chemically prepared and vacuum annealed InSb(0 0 1) surfaces

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Abstract

The InSb(0 0 1) surfaces chemically treated in HCl–isopropanol solution and annealed in vacuum were studied by means of X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and electron energy-loss spectroscopy (EELS). The HCl–isopropanol treatment removes indium and antimony oxides and leaves on the surface about 3 ML of physisorbed overlayer, containing indium chlorides and small amounts of antimony, which can be thermally desorbed at 230 °C. The residual carbon contaminations were around 0.2–0.4 ML and consisted of the hydrocarbon molecules. These hydrocarbon contaminations were removed from the surface together with the indium chlorides and antimony overlayer. With increased annealing temperature, a sequence of reconstructions were identified by LEED: (1 × 1), (1 × 3), (4 × 3), and (4 × 1)/c(8 × 2), in the order of decreasing Sb/In ratio. The structural properties of chemically prepared InSb(0 0 1) surface were found to be similar to those obtained by decapping of Sb-capped epitaxial layers.

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1. Introduction

The preparation of chemically clean, well-ordered, atomically flat and stoichiometric III–V semiconductor surfaces is an important stage in the substrate preparation for epitaxial growth and subsequent manufacture of electronic devices. For InSb(0 0 1) surface a variety of cleaning procedures have been used including thermal oxide desorption in the absence and in the presence of Sb overpressure [1,2], wet and gaseous treatments [3], ion bombardment and annealing (IBA) [1,4], ion bombardment at elevated temperatures [5,6], atomic hydrogen treatment [1], and exposure to radio frequency (rf)-generated hydrogen radicals [7], and electron cyclotron resonance (ECR) plasma-generated hydrogen radicals [8]. Surface preparation by in situ desorption of oxides is problematic for InSb(0 0 1) surface since the desorption temperature lies close to the melting point of the bulk material (~530 °C) and well in excess of the non-congruent temperature (~350 °C) [9]. Annealing above the non-congruent evaporation temperature results in significant Sb desorption, while annealing above 400 °C radically changes the surface morphology and stoichiometry, with the formation of In droplets. Thermal desorption of native oxide from the InSb(0 0 1) surface in the presence of Sb overpressure prevents the loss of Sb from the surface [2]. However, in many cases [1] this again led to rough surfaces with no reconstruction present because of high temperature desorption of the oxide. The growth of passivation films which were composed of indium chlorides, rather than native oxides, has been proposed in Ref. [3]. The chloride was found to be easily removed at low temperatures, and carbon contamination was minimized. No evidence of surface structure ordering on the chemically treated and vacuum annealed surfaces was found. Another widely used method of cation rich InSb(0 0 1) surface preparation is the ion bombardment and annealing. High energy ion bombardment (3 keV, Ar^+) causes significant compositional changes in the surface of III–Sb compounds resulting in the enrichment at the outermost layer of one component with subsequent depletion of this component in the subsurface region [10]. Low energy argon ion bombardment at both room and elevated temperatures efficiently removed the oxide layer from the InSb(0 0 1) surface. Only several cycles of low energy ion bombardment and annealing has been shown to

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result in clean, ordered c(8 × 2) reconstructed InSb(0 0 1) surface [11,12]. However, in common with other III–V semiconductors, the ion treatment induces residual damages, both structural and electronic and allows to prepare only the cation rich surfaces. The atomic hydrogen treatment of InSb(0 0 1) surface was compared with the IBA treatment in Ref. [1]. The resulting surface was not as sharp as the one produced by IBA and the surface was notably rougher. Although successful cleaning of the InSb(0 0 1) surface, yielding the In-rich (4 × 2) reconstruction, at 275 °C using rf plasma-generated H radicals was reported [7], the presence of energetic ions in plasma can result in structural and electronic damage in the surface and sub-surface region. The use of Sb capping layers and subsequent decapping of InSb(0 0 1) surface in the temperature range of 200–350 °C is an effective method of producing clean surfaces with various reconstructions [13,14]. Those reconstructions studied during epitaxial growth or during Sb desorption are the Sb-terminated (1 × 1), c(4 × 4) and asymmetric (1 × 3) structures and In-terminated c(8 × 2) structure [15]. On the other hand, an alternative method of the preparation of well-ordered InSb(0 0 1) surface is required to eliminate the need for the in situ MBE and the substrate preparation in device manufacturing in the absence of Sb overpressure. In case of GaAs and InAs (0 0 1) surfaces it has been reported that a wet chemical treatment of As-based III–V semiconductors can be used as a method alternative to the As capped procedure [16,17]. In the latter work it was shown that the HCl–isopropanol (HCl–iPA) treatment removes gallium and arsenic oxides from the surface, leaving an overlayer of elemental arsenic. This overlayer is desorbed upon annealing in UHV, yielding a clean surface characterized by (2 × 4)/c(2 × 8) and (4 × 2)/c(8 × 2) reconstructions.

It is interesting and important to find out whether the HCl–iPA preparation technique is applicable to other III–V semiconductors and in particular to III–Sb materials. The fundamental importance of this problem is due to the creation of the unified passivation method for III–V semiconductors and understanding the interaction mechanism between HCl–iPA and III–V to elucidate common and specific features of the chemical passivation characteristic of various III–V crystal faces. The practical interest of the problem is due to the use of InSb(0 0 1) surfaces in various applications. In the present paper, we investigated the structure, composition and stoichiometry of InSb(0 0 1) surfaces after treatment in HCl–isopropanol solution and subsequent annealing in UHV. The cleaning procedure, using chemical treatment and annealing in the temperature range 200–380 °C, resulted in a clean, Sb-terminated asymmetric (1 × 3) and In-terminated (4 × 1)/c(8 × 2) structure.

2. Experimental

The InSb samples were cut from a 500-μm-thick wafer of bulk n-type material that had previously been mechanically and then electrochemically polished. The final chemical treatment was done in a glove box filled with nitrogen. This treatment resulted in the removal of surfaces oxides in the solution of HCl–isopropanol at room temperature for 30 s. After the treatment the samples were rinsed for 1 min in isopropanol, blown dry with flowing nitrogen and then fixed on molybdenum sample holder by means of tantalum clips. A hermetic transfer vessel filled with nitrogen was used to transfer the sample, without exposure to air, from the glove box into the loading chamber of the electron spectrometer ADES-500. The base pressure in the analytical chamber was 4×10^{-11} mbar and did not exceed 10^{-10} mbar during measurements.

The composition of the surface was determined by X-ray photoelectron spectroscopy (XPS) and by electron energy-loss spectroscopy (EELS). Non-monochromatized Al Kα (1486.6 eV) and Zr Mζ (151.4 eV) lines were used for XPS measurements. Electrons emitted normally to the sample surface plane were analyzed with a spectral resolution of about 1 eV. To decompose the overlapped XPS peaks, we used mixed Gaussian and Lorentzian line shape functions with the parameters of the peaks measured on a clean surface.

3. Results and discussion

3.1. Surface structure

The LEED patterns for the chemically treated and UHV annealed InSb(0 0 1) surface are shown in Fig. 1. These diffraction patterns were recorded at primary electron energies in the range of 40–50 eV. The (1 × 3), (4 × 3), and (4 × 1)/c(8 × 2) structures are seen in Fig. 1(a–c), respectively. After chemical treatment and before annealing, LEED showed a weak (1 × 1) pattern (not shown), which appeared on top of an intense background at the energy of primary electrons equal to 180 eV. After annealing in the temperature range of 100–200 °C, the background progressively decreased and the (1 × 1) LEED pattern was observed for the incident electron energies down to about 50 eV. Since at these energies LEED detects the structural order in the top 1–2 monolayers, it can be concluded that the annealing in the 100–200 °C temperature range sublimated the weakly bonded part of the adsorbed species. Near $T \approx 230$ °C, a weak asymmetric (1 × 3) structure was appeared, as shown in Fig. 1(a). The asymmetric (1 × 3) pattern can be described as the (1 × 2) structure with split half-order spots. This structure was observed within the 230–270 °C temperature range. The poor quality and asymmetry of the LEED pattern for this reconstruction indicates that this structure is not well-ordered. It is known that the asymmetric (1 × 3) structure is the evidence of considerable disorder at the atomic scale [15]. For these reasons no model was proposed for the asymmetric (1 × 3) structure. This structure could be formed either by annealing the Sb-capped surface to 230 °C in order to desorb the elementary Sb or by deposition of Sb onto In-rich InSb(0 0 1) surface at a substrate temperature of ∼230 °C [5,15]. The photoemission measurements of asymmetric (1 × 3) structure showed that this structure was most likely terminated by a mixture of In and Sb [5]. The symmetric (1 × 3) structure can also be generated on InSb(0 0 1) surface by using Sb flux and keeping the substrate temperatures lower than 250 °C [5]. The model proposed for symmetric (1 × 3)