Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2007) 4445–4449
applied surface science
www.elsevier.com/locate/apsusc

Combined EELS, LEED and SR-XPS study of ultra-thin crystalline layers of indium nitride on InP(1 0 0)—Effect of annealing at 450 °C

C. Robert-Goumet [a,*], M. Petit [a,d], L. Bideux [a], B. Gruzza [a], G. Monier [a], V. Matolín [b], T. Skála [b], N. Tsud [b], K.C. Prince [c]

[a] LASMEA, UMR 6602 CNRS, Blaise Pascal University, Campus Scientifique des Cézeaux, 63177 Aubière Cedex, France
[b] Charles University, Faculty of Mathematics and Physics, Department of Electronics and Vacuum Physics, V Holesovičkách 2, 180 00 Prague 8, Czech Republic
[c] Sincrotrone Trieste S.C.p.A., Strada Statale 14-km 163,5 in AREA Science Park, 34012 Basovizza, Trieste, Italy
[d] LEMA UMR 6157 CNRS-CEA, François Rabelais University, Avenue Monge, 37200 Tours, France

Received 8 June 2006; received in revised form 22 September 2006; accepted 27 September 2006
Available online 20 November 2006

Abstract

In this study, InP(1 0 0) surfaces were bombarded by argon ions in ultra high vacuum. Indium metallic droplets were created in well controlled quantities and played the role of precursors for the nitridation process. A glow discharge cell was used to produce a continuous plasma with a majority of N atomic species. X-ray photoelectron spectroscopy (XPS) studies indicated that the nitrogen combined with indium surface atoms to create InN thin films (two monolayers) on an In rich-InP(1 0 0) surface. This process occurred at low temperature: 250 °C. Synchrotron radiation photoemission (SR-XPS) studies of the valence band spectra, LEED and EELS measurements show an evolution of surface species and the effect of a 450 °C annealing of the InN/InP structures. The results reveal that annealing allows the crystallization of the thin InN layers, while the LEED pattern shows a (4 × 1) reconstruction. As a consequence, InN related structures in EELS and valence bands spectra are different before and after the annealing. According to SR-XPS measurements, the Fermi level is found to be pinned at 1.6 eV above the valence band maximum (VBM).

PACS : 79.60.Dp; 81.65.Lp; 81.05.Ea; 79.20.Uv; 79.60.−I; 61.14.Hg

Keywords: Nitridation; III–V semiconductors; Thin films; EELS; Synchrotron radiation; SR-XPS; LEED

1. Introduction

Indium nitride (InN) is a material with potential application in photonic devices such as LEDs, lasers and especially in high efficiency solar cells [1–2]. Nevertheless, InN is the least studied of the group III-nitrides, partly because there is a lack of lattice-matched substrates.

Different methods have been studied in numerous works [3–4] to determine the growth conditions for obtaining the best physical properties of InN films. One of the solutions is to use an InN buffer layer between the substrate and the epitaxial InN films. A low temperature InN buffer layer can improve the quality of the InN films [5–7]. Accordingly, we investigate in this work the possibility to create InN thin films by nitridating InP(1 0 0) surfaces.

InP(1 0 0) surfaces were chosen because of the presence of metallic indium after an ionic treatment. Indeed indium droplets can be created on the surface by argon ion bombardment in well controlled quantities and these indium clusters are suitable precursors for the formation of InN monolayers. However, the dissociation temperature of InP(1 0 0) substrates is around 370 °C, that does not allow a great range for the temperature process. We have already published works regarding the first steps of the InP(1 0 0) surfaces nitridation [8–9] through the reaction of atomic nitrogen atoms with indium droplets at 250 °C. These studies showed the creation of two InN monolayers on the surface of InP(1 0 0). This article pursues the study of the annealing of nitride layers. We report the effect of annealing on the electronic energy loss and on the valence bands at different energies using synchrotron radiation XPS and LEED

* Corresponding author. Tel.: +33 4 73 40 51 61; fax: +33 4 73 40 73 40.
E-mail address: robert@lasmea.univ-bpclermont.fr (C. Robert-Goumet).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2006.09.067

pattern provide information on the crystallinity of the nitride layers.

2. Experimental procedures

2.1. Sample preparation

S-doped InP(1 0 0) samples with carrier concentration of $4.7 \times 10^{16}\,cm^{-3}$ were chemically cleaned ex situ with successive ultrasonic baths (H_2SO_4, 3% bromine–methanol deionised water) before introduction into an ultra high vacuum chamber (10^{-6} to 10^{-7} Pa). The InP(1 0 0) surfaces have been cleaned by in situ Ar^+ ion bombardment ($E = 300$ eV, sample current density 2 μA cm^{-2}, $t = 30$ min) before the nitridation. This ionic cleaning allows to remove the contamination layers mainly due to carbon species [10], and to create metallic indium droplets in well controlled quantity by preferential phosphorus sputtering [11,12] (mean coverage, 25%; mean height, 4 atomic layers). These indium droplets will play an important key role during the nitridation process.

2.2. Nitridation process

The nitridation process has been performed with a high voltage plasma discharge source (GDS). In this kind of nitrogen cell, continuous plasma is produced by a high voltage (about 2 kV) and a majority of N atomic species are created (ionic current 0.6 μA cm^{-2}). Through the consumption of metallic indium droplets (created by the Ar^+ ionic bombardment), the nitrogen flow allows to create two monolayers of InN on InP(1 0 0) substrates.

Low temperature processing is essential during the nitridation process, indeed the InP decomposition temperature is about 370 °C. According to previous work investigating the influence of the temperature on the nitridation process [13], the sample temperature has been chosen around 250 °C. And then, the final structure has been heated to 450 °C for 20 min.

2.3. LEED and EELS measurements

The LEED pattern was obtained with an electron beam energy of 50 eV. A pattern of mica was used as a reference to prove the crystallinity of the InN thin films.

An electron beam with an energy of 1000 eV was used for the EELS spectra. They were recorded with a hemispherical analyser available in our laboratory at constant pass energy of 30 eV. The zero of the spectra is given by the position of the elastic peak of the electrons.

2.4. SR-XPS synchrotron radiation photoemission measurements

Synchrotron radiation photoemission measurements were carried out at the Material Science Beamline 6.1 at the ELETTRA synchrotron in Trieste. It is a bending magnet beamline with a tuning range from 40 to 800 eV. All spectra were recorded with a Phoibos 150 hemispherical electron analyser using photon energies of 48, 191 and 663 eV. The total resolution (photons + analyser) is about 0.15 eV at 48 eV and 0.7 eV at 663 eV. The binding energy (BE) scale and total resolution were calibrated using the Fermi edge of a gold reference plate.

To study the valence band density of states versus different surface treatments, measurements were performed at different photon beam energies (43, 50 and 77 eV). The spectra were acquired at normal emission to the sample surface and at room temperature.

3. Results and discussions

In a previous article [8], SR-XPS studies of nitridated InP(1 0 0) surfaces have been reported and the essential information is summarized here in Table 1. The In4d and P2p core levels can be decomposed into contributions corresponding to different chemical In and P environments of bulk and surface according to the state of the surface (ionic cleaned, nitridated, annealed). The spectra were fitted using a Shirley background and decomposed into Gaussian and Lorentzian line shapes. Table 1 summarizes the binding energy of the different contributions. After ionic bombardment In–In bonds are detected, the beginning InP(1 0 0) surfaces are rich –In. These features disappear during the nitridation step because of the consumption of indium droplets by the nitrogen flow, and In–N contribution appears. The N1s core level has been recorded too at a binding energy of 396.7 eV.

Comparison between a theoretical model based on stacked layers and experimental data showed that almost two monolayers of indium nitride have been formed on the surface. After the heating of the final structure up to 450 °C, there is a very low diffusion of phosphorus atoms in the nitride film and no metallic indium enrichment at the surface sample. Synchrotron radiation photoelectron spectra did not show any deterioration of the nitride films until 450 °C although the

Table 1
Binding energies of the different contributions in P2p and In4d peaks after nitridation process

Contributions obtained in P2p	Binding energy (eV)	Contributions obtained in In4d	Binding energy (eV)
P–In bulk	129.05 ± 0.05	In–P bulk	17.20 ± 0.05
P–In surface	128.40 ± 0.05	In–In top	17.60 ± 0.05
P–N	133.00 ± 0.05	In–In cluster	16.70 ± 0.05
		In–N top	17.70 ± 0.05
		In–N	18.30 ± 0.05