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Growth study of thin indium nitride layers on InP (1 0 0) by Auger electron spectroscopy and photoluminescence

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ABSTRACT

This article investigates the growth of InN layers on (1 0 0) InP in ultra-high vacuum using a glow discharge source (GDS). Auger electron spectroscopy (AES) was used to understand the different steps of the nitridation process with the analysis of In-MNN, N-KLL and P-LMM transitions. A modeling of Auger signals using a stacked layers model allows us to confirm that four monolayers of indium nitride are created on (1 0 0) InP.

InN layers grown on (1 0 0) InP were studied optically by photoluminescence (PL) spectroscopy versus the excitation power and the sample temperature (10–300 K). Results show broad spectral band energy close to the lowest reported InN bandgap.

The temperature dependence of the PL peak energy showed a S-shaped behavior (decrease–increase–decrease). The results suggest that the InN-related emission is significantly affected by the change in carrier dynamics with increasing temperature: the effect can be due to the large exciton localization effects.

1. Introduction

The highly attractive properties of III-nitride (InN, GaN and AlN) semiconductors have prompted many studies. Many reviews and papers have been published on the properties of III-nitride semiconductors and on different devices [1,2]. Most of these were focused on GaN and its alloys [3]. However, during the last few years, the interest in indium nitride (InN) has been remarkable and the number of papers concerning InN has significantly increased. Recent results obtained by Pan et al. have shown the nitridation of InP(1 0 0) surfaces by N_2^+ ion beam bombardment [4].They confirmed the formation of a thin InN layer on the nitrided InP surface.

A detailed knowledge of the optical properties of InN thin films is important for many device applications. However, the properties of InN thin films are not well known, since growing high-quality InN thin films is still a challenge, due to their stoechiometric instability and low dissociation temperature and the lack of suitable lattice-matched substrates [5–7]. With regards to optical properties of InN, an exciting conflict has recently arisen about the optical bandgap energy value. This conflict was raised recently when many groups showed by optical measurements different bandgaps for InN: between 0.65 and 0.9 eV [8–10], which is smaller than 1.1 eV [5] and 1.2 eV [11] and much smaller than 1.89 eV [12].

In this paper, thin InN films are realized by the nitridation of InP substrates using a glow discharge source (GDS). This nitridation process and the surface evolution are followed by Auger electron spectroscopy (AES). The Auger signals were modeled using a stacked layers model to interpret the experimental results. We also report in this paper photoluminescence (PL) studies of the optical properties of InN as a function of temperature and of laser excitation power.

2. Experimental

An ultra-high vacuum (UHV) system (10^{-7} Pa) has been used for this study. Experiments have been performed using a nitrogen source, an indium evaporation cell and a retarding field analyser (OPR 309 Riber) for AES analysis. The Auger signals were recorded in direct mode.

S-doped InP (1 0 0) samples have been used; they were cleaned ex-situ in ultrasonic bath before introduction in the ultra-high vacuum chamber (10^{-7} Pa) [13,14]. After introduction into the

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UHV system, a low amount of carbon and oxygen contamination was detected. These impurities were removed with low energy Ar^+ ions (ion energy 300 eV; sample current 2 μA/cm^2, 15 min) [15–20].

2.1. Indium-based precursor state

The ionic bombardment is a key step for the first nitridation process since it creates, at the surface, metallic indium in well-controlled quantities (mean coverage: 25%, mean height: 4 atomic monolayers) by preferential phosphorus sputtering [36]. The amount of metallic indium created is equivalent to one atomic monolayer of In. Therefore, the maximum number of indium nitride layers on InP (1 0 0) which can be formed by the consumption of the metallic indium is two monolayers. We developed a technique for a second nitridation by including another step in the process. This step consists in the deposition of a controlled amount of indium on the two first monolayers of InN; indium was evaporated in the UHV system using an evaporation cell (the evaporation rate was around 0.25 mL/min) and a quantity of In equivalent to one monolayer was condensed on InN/InP. So, four monolayers of InN are obtained by two indium-based precursor steps: ionic bombardment and the deposition of a controlled amount of indium.

2.2. Nitridation process

The nitridation process was performed with a high voltage plasma discharge cell to create two or four monolayers of InN on InP (1 0 0) substrates through the consumption of indium by nitrogen atoms. Heating processing is important during the nitridation of InP. Since the InP decomposition temperature is about 350 °C, the sample was heated to 250 °C, according to previous work investigating the influence of the temperature on the nitridation process [21–23].

In each nitridation, the sample was kept under a nitrogen flow for 37 min. The pressure inside the chamber was equal to 10^{-1} Pa. The different steps have been monitored by AES.

Optical properties of the samples were studied by photoluminescence. The room-temperature PL was excited with the 5145 Å line of an argon ion laser, dispersed with a double monochromator and detected with an InGaAs cathode photomultiplier detector. PL measurements were carried out between 10 and 300 K while keeping the samples in a closed-cycle helium circulation cryostat.

3. Results and discussion

3.1. Processing and Auger analysis

The nitridation of InP (1 0 0) substrates was investigated using AES. The measurements were carried out before and after each nitridation process. We have recorded the Auger signals of In-MNN (E=403 and 411 eV), N-KLL (E=383 eV) and P-LMM (E=117 eV).

Fig. 1 presents the evolution of In-MNN, N-KLL and P-LMM Auger transitions with the different steps of the nitridation process. The transition N-KLL (E=383 eV) appears after the first nitridation, confirming the presence of nitrogen on the surface: the appearance of this peak is accompanied simultaneously by an attenuation of the indium and phosphorus signals (Fig. 1). We notice a change in the phosphorus peak shape, which is related to the presence of P–N bonds.

To interpret the AES experimental results, a model based on stacked layers has been used. As we are interested in the indium AES signal, we have to know the different contributions of the indium atoms.

3.1.1. Step 1

Briefly, let us point out the different contributions for a substrate of InP (1 0 0) bombarded by ions. The ionic bombardment creates at the surface metallic indium in well-controlled quantities (mean coverage: 25%, mean height: 4 atomic monolayers) [36] by preferential phosphorus sputtering.

Moreover, from Fig. 2, we can calculate for each environment the intensity of the indium Auger signal:

Contribution A: indium atoms present inside the substrate.

Contribution B: indium atoms present in the crystallites.

i_{In} is the intensity of one atomic monolayer of indium

$$I_A = 0.25\alpha^4 \frac{\alpha}{1-\alpha^2} i_{In} + 0.75 \frac{\alpha}{1-\alpha^2} i_{In}$$

$$I_B = 0.25(1+\alpha+\alpha^2+\alpha^3) i_{In}$$

With α=exp($-d/b\lambda_i$) the attenuation coefficient of the indium Auger current through a P or In atomic monolayer where d is the thickness layer, b=0.84 is the apparatus factor and λ_i is the inelastic mean free path of the Auger electrons calculated with the TPP-2M formula [24]. Then the numerical value of α is equal to 0.71.

After the Ar^+ cleaning, the total intensity of the indium AES signal is: I_1=I_A+I_B

3.1.2. Step 2

After the first nitridation, all In crystallites were consumed, one can consider that the surface is totally covered by nitride layers and that there were two layers of InN. From Fig. 2, different contributions can be found for nitridated InP: the In–N contribution and the In–P contribution from the substrate.

The Auger intensity coming from the indium atoms of the nitride overlayers is given by the following expression:

$$I_D = 0.5 i_{In} + 0.5\alpha\, i_{In}$$

The theoretical intensity coming from the indium atoms in the volume of the substrate (In–P) is written:

$$I_E = \frac{\alpha^3}{1-\alpha^2} i_{In}$$

Thus, the theoretical intensity of the indium Auger signal after the first nitridation I_2 is equal to I_E+I_D=I_2={0.5(α+1)+(α^3/1−α^2)}i_{In}

The theoretical value of the ratio I_2/I_1 gives 0.8, close to the experimental ratio which is equal to 0.75.

3.1.3. Step 3

After the In deposit, from Fig. 2 the theoretical intensity of the indium Auger signal can be calculated from the following formula: I_3=αI_2+$i_{In.}$

By comparing the experimental ratio I_3/I_2 (=1.2) with the theoretical ratio (=1.3), one deduces that one indium monolayer has been deposited on the 2InN/InP.

3.1.4. Step 4

This is the second nitridation, again we have considered that the coverage of the surface by the nitride layers was equal to unity and then there were four monolayers of InN on the InP substrate.

The intensity of the indium coming from the In–N contribution is written by

$$I_F = 0.5(1+\alpha+\alpha^2+\alpha^3) i_{In}$$