

Blue-shift photoluminescence from porous InAlAs

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Received 21 June 2010, in final form 6 September 2010

Published 4 October 2010

Online at stacks.iop.org/SST/25/115006

Abstract

A porous InAlAs structure was first obtained by electrochemical etching. Nano-pore arrays were formed when the $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ membrane was anodized at constant voltages in an HF aqueous solution. These self-assembled structures showed evident blue-shift photoluminescence emissions. While a quantum size effect alone underestimates the blue-shift energy for a sample with a relatively large average pore wall thickness, a novel effect caused by the asymmetric etching is proposed to account for this phenomenon. The results inferred from the x-ray double crystal diffraction are in good agreement with the experimental data.

(Some figures in this article are in colour only in the electronic version)

Introduction

Porous silicon has aroused great interest since the striking discovery of strong visible photoluminescence [1] compared with bulk silicon. Much effort has been made to understand its formation mechanisms [2, 3] and potential applications such as photonic crystal [4, 5], optical shortpass filters [6] and biomedical scaffolds [7]. Inspired by progress in porous Si, researchers have also explored porous III–V binary semiconductors [8] and found some appealing applications such as waveguide structures [9] and biochemical sensors [10].

However, there is no such report on the ternary III–V compound InAlAs. Since $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ is an important material for optoelectronic integrated circuits as well as a lattice-matched barrier material for InP-based quantum devices, its nano-pore structure is expected to bring some novel properties and similar applications as mentioned above. In this paper, we will present porous InAlAs arrays for the first time and their unusual photoluminescence (PL) will be discussed in detail.

All these porous semiconductors are fabricated by electrochemical etching, which is a cost-efficient method to obtain nano-pore structures. Although many studies have been carried on porous semiconductors as summarized in a review paper [11], the pore formation mechanism is still in dispute. This dilemma may be due to the complexity of the pore formation process which is rather sensitive to a number of variables such as applied current/voltage, crystal orientation,

electrolyte composition, doping type and density. In spite of that, the existing models give hints to the electrochemical processes. Briefly speaking, the bonds of the semiconductors are attacked by the holes generated by illumination or avalanche breakdown at a high electric field, and dissolved with the help of the acid solution. Usually, ‘seed pits’ are formed randomly at the surface, induced by impurities or defects, which then grow along the crystallographic orientation at relatively small anodic current densities or along the current line at large current densities [12]. The diameter of pores keeps increasing until the thickness of wall reaches twofold of the space charge layer [13] which is depleted of carriers.

Experimental details

In our experiments, a (100)-oriented n-type InP wafer with the Si doping concentration of about $8 \times 10^{17} \text{ cm}^{-3}$ was used as a substrate. An $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ membrane with a nominal thickness of 412.5 nm was grown by solid-source MBE onto the substrate. Anodization was performed at room temperature using a standard cell with three electrodes, i.e. an InAlAs/InP electrode, a Pt counterelectrode and a reference saturated calomel electrode. The samples were cut into $5 \text{ mm} \times 5 \text{ mm}$ squares and then pressed against an O-ring in the electrochemical cell, leaving 20 mm^2 exposed to the electrolyte. Anodization was carried out in a 12.5% HF aqueous solution for a few seconds at 3 V and 4 V.

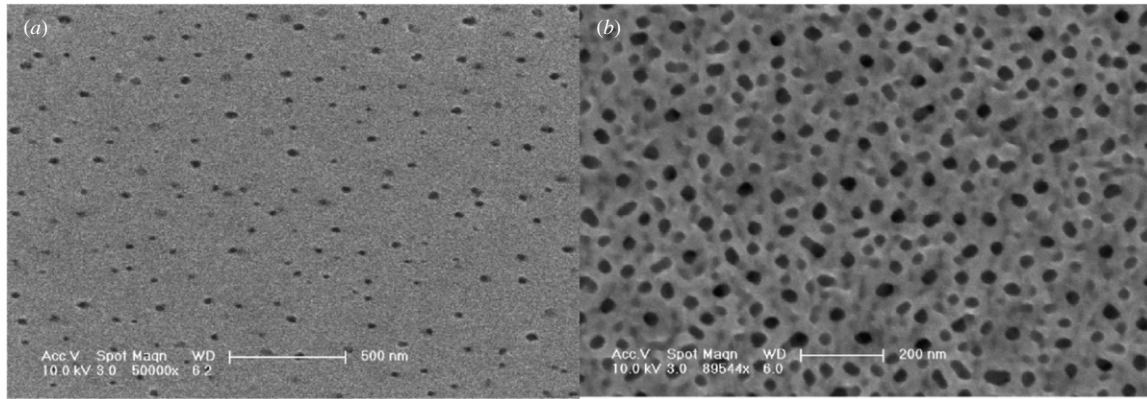
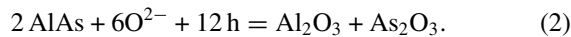
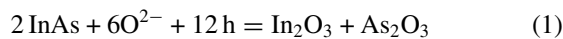


Figure 1. SEM images of the porous samples formed in 12.5% HF electrolyte at anodization voltages of (a) 3 V and (b) 4 V.

We use a Potentiostat/Galvanostat Model 263A (Princeton Applied Research) to control the applied voltage and the anodization time. The anodic process was stopped by turning off the current at the moment when the InP wafer just started to be anodized and the InAlAs film had been completely anodized. This moment was demonstrated by a sudden decrease of the anodic current in the I - t curve. After such an anodization, the samples were rinsed carefully in de-ionized water to remove the residual products. The morphology of the as-prepared porous InAlAs membranes was observed using a scanning electron microscope (SEM). PL spectra were performed with a He-Cd laser (325 nm) and a photomultiplier detector. Crystallization was measured by double crystal x-ray diffraction (XRD) rocking curve (Panalytical, X'PertPro MPD) with Cu $K\alpha$ radiation.

Results and discussion

Typical plan-view SEM images of the porous InAlAs are shown in figure 1. The difference of porosities can be explained by an avalanche breakdown model. The stronger electrical field leads to a stronger breakdown effect, resulting in more holes generated and consumed at the pore tips. The hole-involved electrochemical reaction of InAlAs could be divided into two relatively independent sub-processes of its binary component, namely AlAs and InAs, which could be written as follows, similar to the case in GaAs [14]:



These oxides then dissolved in the acid and the process went on.

Figure 2 shows the XRD spectra of the InP-based porous InAlAs as well as the as-grown sample for comparison. In each curve, the strongest peak is attributed to the reflection of the (4 0 0) plane of the InP substrate and the wider peak on the right comes from the InAlAs membrane. Assuming that only the thin InAlAs layer is elastically deformed but not the InP substrate, the measured angle differences between InP and InAlAs of 41.96'', 146.81'' and 86.79'' correspond to a relative lattice mismatch $\Delta a/a = -1.649 \times 10^{-4}$, -5.769×10^{-4} ,

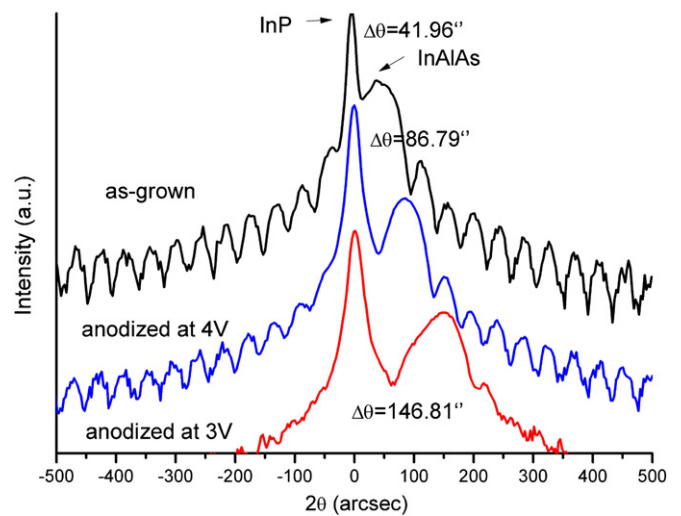


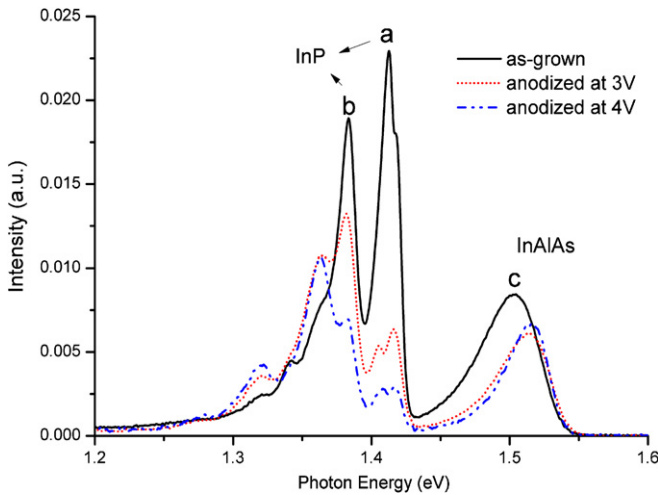
Figure 2. XRD spectra of porous InAlAs anodized at 3 V and 4 V. The As-grown sample is also shown for comparison.

-3.411×10^{-4} , respectively. The tensile strain of the InAlAs material is increased after electrochemical etching. This could be explained by the asymmetric etching in InAlAs, namely InAs is more vulnerable to corrosion than AlAs. Because the lattice constant of InAs is larger than that of AlAs, an increase of the AlAs component leads to a decrease of the lattice constant of InAlAs, resulting in an increase of tensile strain.

The PL spectra measured at 12 K are shown in figure 3. In the as-grown sample, the strongest peaks labeled a (1.413 eV) and b (1.384 eV) are attributed to the bound exciton (BE) transition and the donor-hole (D, h) transition in InP bulk, respectively [15]. The higher energy peak c (1.504 eV) is derived from the $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ material [16]. After electrochemical etching, the porous InAlAs structures show evident blue shifts of 13 and 16 meV, respectively. Besides, the overetching at the InAlAs/InP interface leads to a great attenuation in the InP peaks, especially for the BE transition which is very sensitive to the coulomb field caused by the free carrier. Some lower energy peaks also appear due to deep energy level defects.

Table 1. Two possible origins for blue-shift phenomenon.

Samples	Experimental data (meV)	Average wall thickness (nm)	Quantum size effect (meV)	Al composition	AlAs increasing effect (meV)
As-grown	—	—	—	0.477 26	—
3 V	13	100	0.86	0.483 35	13.517
4 V	16	30	9.6	0.479 86	5.779

**Figure 3.** PL spectra of the porous InAlAs structures. Blue-shift PL of 13 and 16 meV can be observed.

In order to quantitatively explain the more interesting blue-shift phenomenon in porous InAlAs, two possible effects are considered. One is quantum size effect which has been observed in other porous semiconductors. A quantum wire model [17, 18] was employed to calculate the quantized energy level in the pore wall, and the thickness of the pore wall q could be viewed as the width of the quantum wire. Then the energy shift can be expressed by

$$\Delta E = \hbar^2 / (4m^*q^2) \quad (3)$$

$$1/m^* = 1/m_e^* + 1/m_h^*. \quad (4)$$

The results are listed in table 1. However, this model alone greatly underestimates the blue-shift energy for the sample anodized at 3 V and with a relatively large average wall thickness.

Therefore, another effect caused by the asymmetric etching is included. As mentioned earlier, AlAs concentration is increased during the electrochemical anodization. Because AlAs has a much larger bandgap than InAs, an increase in Al composition would lead to growth in the bandgap energy. Wakefield *et al* [19] had determined the composition dependence

$$\Delta E_g = 2.22 \cdot \Delta x \text{ [eV]}, \quad (5)$$

where Δx is the deviation of the Al concentration from the origin value. It should be mentioned that equation (5) was obtained at the temperature of 4 K while our experiment was carried out at 12 K. But for preliminary study, this small discrepancy could be tolerable.

The Al composition can be inferred from the amount of mismatch [20]. The deduced values of Al composition as well

as the as-grown value are also listed in table 1. As we can see, such AlAs increasing effect is in reasonable agreement with the experimental data for the sample anodized at 3 V.

On the other hand, the sample anodized at 4 V has a thinner average wall thickness and is expected to be more dominated by the quantum size effect in this situation. The quantum size effect gives a value of about 9.6 meV, which is closer to the experimental value than AlAs increasing effect. A combination of these two effects ($9.6 + 5.78 = 15.38$ meV) would be an excellent explanation. However, since the geometry of porous InAlAs is more complex than assumed for our calculations, and given the experimental uncertainty in the determination of the pore diameters, the calculated energy changes have to be considered as preliminary estimates.

Conclusion

Preliminary porous InAlAs arrays were prepared by electrochemical etching in an HF aqueous solution, the morphology of which could be further improved by precise control of the anodization condition. We observe blue-shift PL spectra from porous InAlAs, which are well explained by both asymmetric etching effect and quantum size effect. This cost-efficient method will have potential applications for InAlAs related devices.

Acknowledgments

This work was supported by the National Research Projects of China (grant numbers are 60525406, 60736031, 60806018, 60906026, 2006CB604903, 2007AA03Z446 and 2009AA03Z403, respectively). The authors would like to thank X L Zhou for useful discussion and an anonymous reviewer of Journal of Applied Physics for helpful suggestions.

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