Solar Energy Materials and Solar Cells xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Synthesis of InGaN nanowires via metal-assisted photochemical electroless etching for solar cell application

Adel Najar[a,*], Mustapha Jouiad[b]

[a] Department of Physics, College of Science, United Arab Emirates University, Al Ain 15551, United Arab Emirates
[b] Mechanical and Materials Engineering Department, Masdar Institute of Science and Technology, A part of Khalifa University of Science and Technology, PO 54224, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Keywords:
Etching
InGaN
Nanowires
Optical properties

ABSTRACT

This article reports on the studies of InGaN Nanowires (InGaN NWs) prepared via metal- assisted photochemical electroless etching method with Pt as catalyser. It has been found that etching time greatly influences the growth of InGaN NWs. The density and the length of nanowires are increased for longer etching time and excellent substrate coverage was observed. The synthesis mechanism of InGaN NWs using metal assisted photochemical electroless etching method and the energy band diagram were presented. Photoluminescence (PL) measurements of InGaN NWs shows a red-shift PL peaks compared to the as grown associated to the relaxation of compressive stress. Furthermore, Raman measurements shows a large shift of 20 cm^{-2} of the A_1(LO) modes, which is strongly related to the In composition. The Raman results confirm the reduction of the In composition in the epilayer due to the etching process and formation of nanowires. Therefore, the observed large shift to the lower frequency in Raman spectra confirms the stress relaxation. This new and low-cost etching method to synthesize strain relaxed InGaN NWs will be suitable for III-nitride solar cell applications.

1. Introduction

In recent years, semiconductor nanowires with nanometer width have attracted much attention because of their potential applications in energy research and nanodevices [1–4]. Ternary alloy systems, particularly InGaN, have attracted interest because of their ability to tune direct band gap from infrared to ultraviolet (0.7–3.4 eV) through control of their In/Ga ratio [5]. This property makes it a promising material for various energy applications [6].

An extensive field of research into InGaN laser diodes was conducted in the nineties [7], and this research has reached fruition in the blue-violet laser diodes currently utilized in modern compact disc technology [8]. More recently, as InGaN has become better characterized, there has been an upsurge in interest in InGaN nanowire structures. This is due to an increase in studies in the general field of nanowires [9], which have demonstrated that nanowires possess several capacities which make them uniquely suited as structures for InGaN. A one dimensional structure minimizes the large lattice constant mismatch between InN and GaN, and the large amount of surface area present in nanowires is ideally suited to InGaN's both traditional and emerging applications. The synthesis of InGaN nanowires was initially focused on the wide range of bandgaps available with InGaN, made possible by varying the stoichiometric ratio within the alloy. Any InGaN nanowire is not an equal mixture of the three constituent elements, but rather InN and GaN alloyed, giving possible formulas of the format $In_xGa_{1-x}N$, each having a slightly different bandgap, and thus bridging a very wide emissions spectrum. Developments in the synthesis of these nanowires have naturally focused on these band gaps, as creating conditions that allow for the full spectrum of InGaN stoichiometries is critical to any major utilization of the material's band gap properties. This presented a major challenge in InGaN, as there is a significant difference in the lattice constants of InN and GaN [10].

It is well known that the growth of semiconductor nanowires can effectively relax the strain accumulated in the material when the growth occurs on a lattice-mismatched substrate. Although the surface-to-volume ratio is very large in a nanowire geometry, proper surface passivation such as the growth of a slightly higher band gap structure can greatly suppress the non-radiative recombination loss that can occur on the nanowire surface. Moreover, the surface recombination velocity in GaN based materials has been shown to be extremely slow making the nanowire geometry a promising structure to overcome the lattice mismatch issue in growing optically thick InGaN films. Vertically-aligned InGaN nanowires have been shown using molecular-beam epitaxy (MBE), halide chemical vapor deposition (CVD), and

* Corresponding author.
E-mail address: adel.najar@uaeu.ac.ae (A. Najar).

http://dx.doi.org/10.1016/j.solmat.2017.06.008
Received 5 April 2017; Received in revised form 26 May 2017; Accepted 6 June 2017

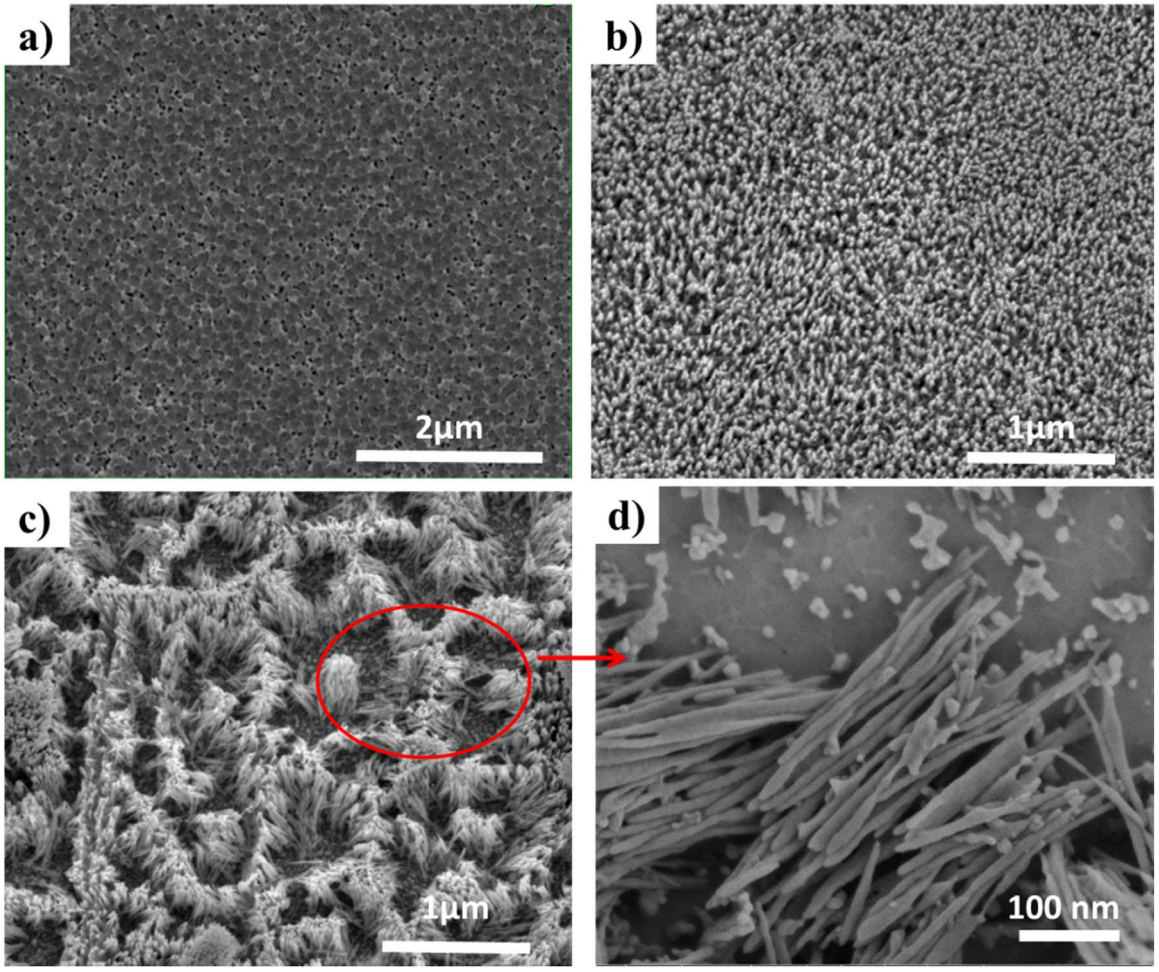

Fig. 1. SEM images for InGaN NWs samples for different etching times (a) 10 min, (b) 20 min, (c) 30 min, and (d) HRSEM for the sample etched for 30 min.

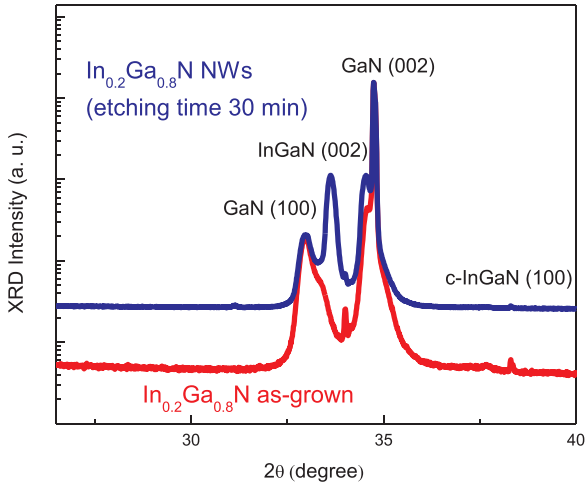

Fig. 2. X-ray diffraction pattern of InGaN as grown and InGaN NWs.

Hydride Vapor Phase Epitaxy (HVPE) [11–13]. The development of the metal assisted electroless etching to synthesize silicon nanowires was well established during the last few years [14,15]. However, no reports explored the synthesis of InGaN NWs using metal-assisted electroless etching and the etching mechanism is not established.

In this work, we report for the first time the fabrication of InGaN NWs, using metal assisted photochemical electroless method. The morphological structures of InGaN NWs prepared under different etching times were investigated. The etching mechanism of InGaN NWs was developed. The optical properties have been investigated using PL and Raman measurements.

2. Experimental procedure

400 nm undoped $In_xGa_{1-x}N$ epitaxy with x = 0.2 grown on 4 μm thick unintentionally doped GaN, on c-plane sapphire (α-Al_2O_3) substrate. The estimated dislocation density of the top InGaN layer is 1×10^8 cm^{-2} and measured carrier concentration of the sacrificial GaN layer is 5×10^{17} cm^{-3}. InGaN samples were cleaned by sonication in acetone and then followed by 2-propanol for 5 min in each solution. It is followed by immersing the sample in HNO_3 at 65 °C for 15 min. The samples were then rinsed in DI water and methanol. Two narrow stripes of 10 nm thick Pt, separated by a few millimeters, was deposited on the InGaN samples using a sputtering system. The samples were etched in the H_2O_2:HF:CH_3OH (2:1:2) solution under UV illumination equal to 700 W for different etching time (10, 20, and 30 min). After chemical etching, the samples were removed from the solution and rinsed with DI water. FEI's Magellan 400 FEG scanning electron microscopy (SEM) operating at 5 keV beam energy was used to analyse the crystal structure. The X-ray measurements was performed on Bruker system (D8 Avance). The PL measurements were performed at room and low temperatures using Jobin Yvon LabRAM HR 800 UV system. A He Cd laser emitting at 325 nm and a diode-pumped solid-state (DPSS) laser emitting at 532 nm were used as excitation sources for PL and Raman measurements, respectively. The incident laser power for both measurements was set to 10 mW.