Fabrication & Characterization of Nanoscale Electrochemical InN Sensors

Clara Ji-Hyun Cho, General Engineering, Franklin W. Olin College of Engineering
NNIN REU Site: Cornell NanoScale Science & Technology Facility, Cornell University

NNIN REU Principal Investigator: William J. Schaff, Electrical & Computer Engineering, Cornell University
NNIN REU Mentor: Ho-Young Cha, Electrical & Computer Engineering, Cornell University
Contact: clara.cho@students.olin.edu, schaff@iiiv.tn.cornell.edu

Abstract:

Indium Nitride (InN) has some advantages over other semiconductor materials in sensor applications because of high surface electron concentrations. In this project, we have patterned nanometer-size holes on InN to increase the surface area and electrochemical sensitivity. A patterning process involving an anodized aluminum oxide (AAO) etch mask and an ECR etch recipe was developed. Holes 100 nm in diameter and 100 nm in depth were achieved with this process. Preliminary experimental results indicate selective sensitivity with different gas exposures.

Introduction:

Recent advancements in the growth of singly crystalline InN has allowed more accurate identification of fundamental properties of InN, such as the narrow band gap (0.6-0.7eV) and the surface electron charge accumulation. These properties suggest the potential applications of InN and InGaN in fields such as photo-voltaic systems and optical fiber communications [1]. The charge accumulation on the surface of InN also makes it sensitive to environment, which brings up the possibility of using InN as an electrochemical sensor.

Although there has been a study done on wet chemical sensitivity of planar surface InN, no gas sensitivity study has been done on InN [2]. The goal of this research project is to fabricate electrochemical InN sensors with nanometer hole patterns in the channel area for gas sensing applications. An array of conventional and non-conventional lithographic methods was incorporated to fabricate InN sensor devices.

Procedures:

All samples in this study were grown by a conventional molecular beam epitaxy technique. Sensors were fabricated using a variety of methods. All hole patterns were first etched onto an SiO_2 layer and later transferred to InN and InGaN samples via the ECR etching process.

Electron-Beam Lithography: Hole patterns varying in size from 50 nm to 1.5 μm were written onto a 200 nm PMMA photoresist layer of the sample using Leica VB6-HR with a beam dose of 100 $\mu C/cm^2$. After developing the patterns, a CHF_3/Ar RIE process was used to etch the SiO_2 layer.

UV-Nanoimprint Lithography: A quartz master with nanometer-sized pillars was first fabricated via electron-beam lithography using negative photoresist and varying beam doses. Quartz etching was done using a CHF_3/Ar RIE process. Using molecular vapor deposition, a monolayer of fluorooctyltrichlorosilane (FOTS) was then deposited on the surface to serve as a release layer.

Approximately 600 nm of UV-curable resist PAK-01 was spun onto the sample prior to the imprinting process. The master was then pressed against the sample, and the entire apparatus was exposed with a UV light source for 30 seconds using CNF's EVG620-NIL contact aligner. The CHF_3/Ar RIE process was used to transfer the patterns onto SiO_2 layer.

AAO Etch Mask Process: 200 nm of Al was deposited onto the sample with an insulating layer of SiO_2 between the InN and Al layers. The Al layer was then anodized in an electrolyte solution of 0.3 M oxalic acid with a constant voltage of 40 V and copper as the cathode. The sample was subsequently immersed in a solution of 5% H_2PO_4 for 30 minutes. CH_4/O_2 and CHF_3/Ar RIE processes were used for the pattern transfer.

The patterns generated by optical lithography, electron-beam lithography, and the AAO etch mask were then transferred from the SiO_2 layer onto InN thin films using an ECR etch process. 12.5 sccm CH_4, 3 sccm Cl_2, and 4 sccm Ar gases were used with an etching rate of ~ 80 nm/min. A mesa etch was performed to create channel areas, followed by 30 nm Ti and 400 nm Au metallization layers for ohmic contacts.

Results and Conclusions:

The minimum hole feature we were able to fabricate using electron-beam lithography was 100 nm in diameter with 200 nm spacing. Although the holes were

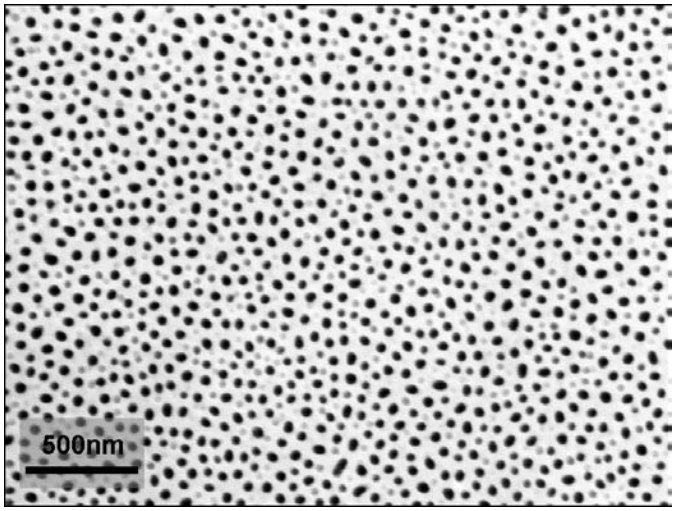


Figure 1: SEM micrograph of porous alumina layer.

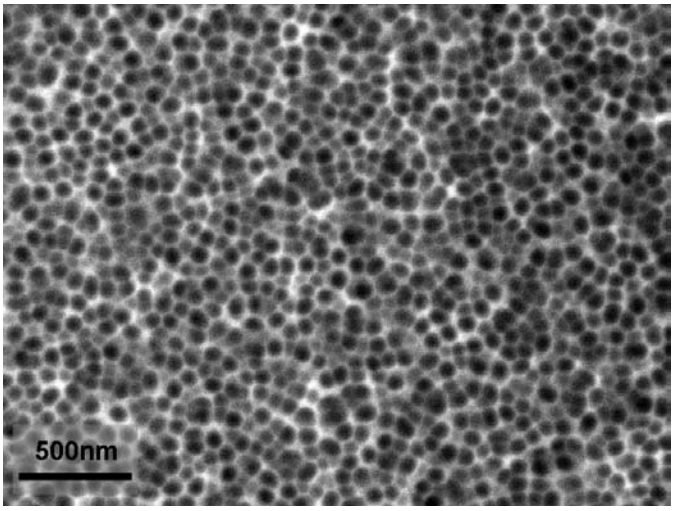
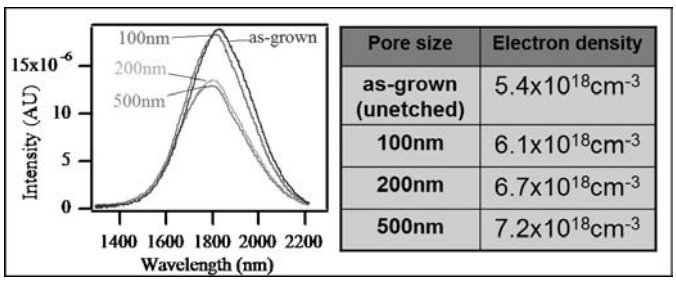


Figure 2: SEM of InN surface after the pattern transfer.

small, there was only a marginal increase in the surface area due to the large spacing. Using UV-nanoimprint lithography, densely packed holes 350 nm in diameter were fabricated. The hole size was actually limited by the smallest pillar size we were able to fabricate on the quartz master, which was around 300 nm in diameter and 200 nm in height.

Figures 1 and 2 respectively show the as-fabricated porous alumina layer and the surface of InN after the pattern transfer. Holes on AAO etch mask range from 30-50 nm in diameter, and the final holes on InN are 80-100 nm in diameter and 100 nm in depth. The increase of the final hole size is due to the H_2PO_4 soak and CH_4/O_2 RIE step in the process. These steps are needed, however, in order to guarantee that we etch through the thin layer of alumina underneath the porous alumina structure. Overall, using the AAO etch mask process, we were able to increase the surface area of InN by 76%.

Figure 3 shows photoluminescence spectra of InN sensors fabricated via electron-beam lithography. The results indicate the dependence on the size of fabricated holes. The increase in electron density with increasing hole size is because larger holes allow greater exposure to plasma during the etching process. Exposure to plasma might have induced some surface defects which in turn increased the electron density.



Pore size	Electron density
as-grown (unetched)	$5.4x10^{18}cm^{-3}$
100nm	$6.1x10^{18}cm^{-3}$
200nm	$6.7x10^{18}cm^{-3}$
500nm	$7.2x10^{18}cm^{-3}$

Figure 3: Photoluminescence spectra of InN sensors fabricated via electron-beam lithography.

The change in resistance as a function of time for InGaN:Mg upon various gas exposures is shown in Figure 4. Some selective responses with CO_2 and H_2 are shown, which are exciting results because gas detection selectivity in electrochemical sensors is a tough problem to solve. More data needs to be collected to verify the repeatability of these results.

Acknowledgements:

The author would like to thank Dr. William Schaff, Dr. Ho-Young Cha, Xing Qun Jiang, Rey Javier, Troy Richards, CNF, NBTC, NNIN, and NSF for all their support.

References:

[1] H. Lu, W. J. Schaff, L. Eastman, "Surface charge accumulation of InN films grown by molecular-beam epitaxy", American Institute of Physics, Vol. 82, No. 11, pp 1736-1738, March 2003.

[2] H. Lu, W. J. Schaff, L. Eastman, "Surface chemical modification of InN for sensor applications", American Institute of Physics, Vol. 96, No. 6, pp 3577-3579, September 2004.

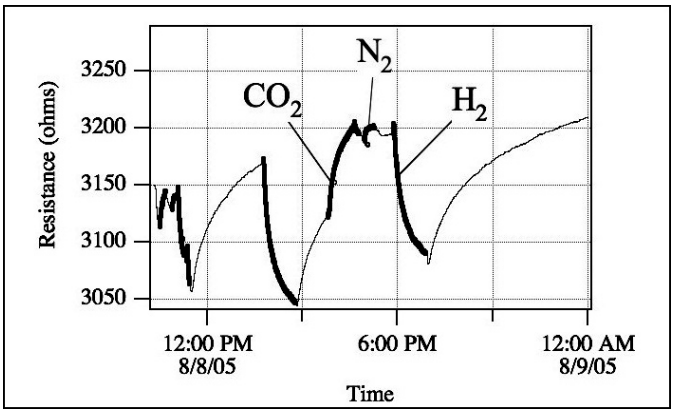


Figure 4: Preliminary gas exposure data on InGaN:Mg sensor.