Photoluminescence of Sequential Infiltration Synthesized ZnO nanostructures

Leonidas E. Ocola, David Gosztola
Argonne National Laboratory, Argonne, IL 60439
ocola@anl.gov

Kyle Chen
Illinois Mathematics and Science Academy, Aurora, IL 60506

With the increased portfolio of materials that can be deposited using atomic layer deposition (ALD) there has been an increased interest in materials with unusual optical properties, such as zinc oxide and aluminum doped zinc oxide for plasmonic applications [1,2]. In this paper we present a method of creating large arrays of zinc oxide (ZnO) nanostructures that can be used for both plasmonic and photonic applications by combining lithography and a modified ALD process named Sequential Infiltration Synthesis (SiS) [3].

The SiS method utilizes similar concepts of ALD process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a polymer matrix (e.g polymethyl methacrylate or PMMA) and allow the reaction to occur inside the polymer matrix. To achieve this it is necessary to allow time for the gases to diffuse (longer exposure times and higher pressures). Although SiS has been used mainly for applications with block copolymers [3], it can be also used in conjunction with lithography [4].

Combining ZnO and PMMA for photoluminescence (PL) studies is not new [5], but it has not been studied in conjunction with the SiS process. In Figure 1 we demonstrate that SiS process of ZnO allows the formation of ZnO throughout at least 200 nm of PMMA. The EDS data was taken at two different incident electron energies so that different x-ray lines could be queried and rule out any substrate artifact on the profile data. In Figure 2 we show PL data of three substrates: bare silicon, 1 micron PMMA spin coated on a silicon substrate, and ZnO SiS treated 1 micron PMMA spin coated on a silicon substrate. All samples were baked at 180 ^{o}C for 3 min. Excitation source was 300 nm light, integration time 5 s per data point. It is apparent a strong interaction between the ZnO and PMMA film.

We also show we can create unusual ZnO nanostructures by combining ZnO SiS process with lithographically patterned PMMA as illustrated in Figure 3. The first SEM image shows an array of patterned structures after development and after ZnO SiS processing. The organics are then removed by baking the samples at 700 ^{o}C in an oxygen atmosphere for 25 minutes. It is apparent that during the bake the resist flowed and pores (or nanotubes) of 200 nm in diameter lined with ZnO are formed. The energy dispersive spectroscopy (EDS) data clearly show excess presence of ZnO in the pores. PL data of these structures will be presented.

References:

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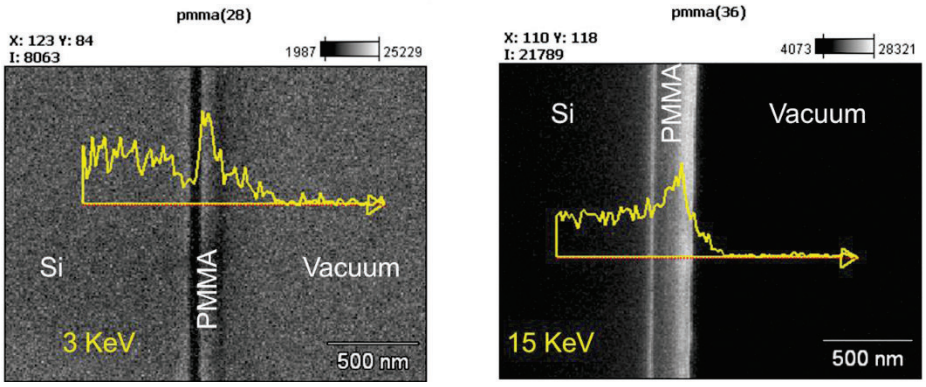

Figure 1. SEM cross section micrographs of Si/PMMA, treated with ZnO SiS process, test samples with superimposed EDS data. (Left) EDS data using 3 KeV electrons, signal is Zn L line, (Right) EDS data using 15 KeV electrons, signal is Zn K line.

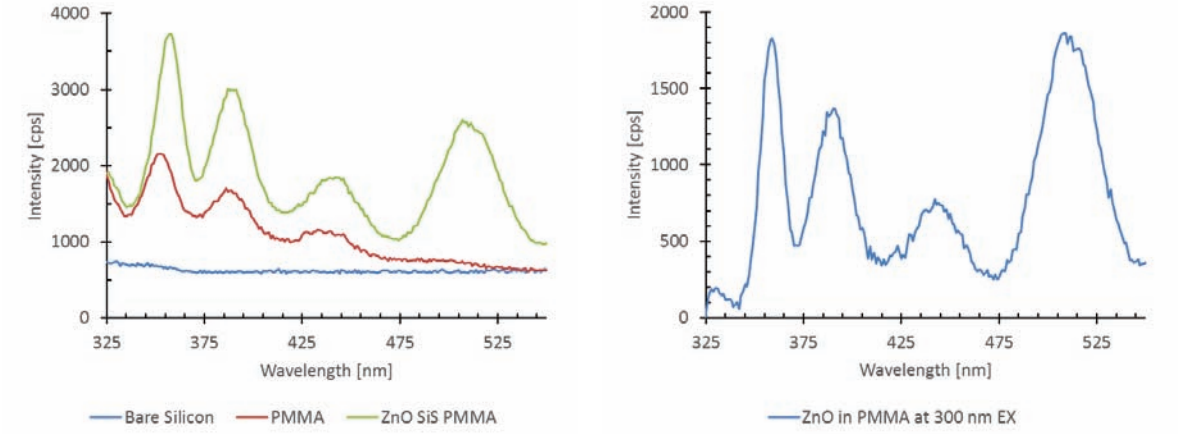

Figure 2. Photoluminescence emission data from blank ZnO SiS treated PMMA, 300 nm excitation. (Left) Three PL emission spectra for bare silicon, 1 micron PMMA spin coated on a silicon substrate, and ZnO SiS treated 1 micron PMMA spin coated on a silicon substrate. (Right) ZnO SiS spectra from the left after subtracting the PMMA spectra. Main PL SiS ZnO in PMMA peak is located at 360 nm. Bulk ZnO PL peak is known to be at 379 nm.

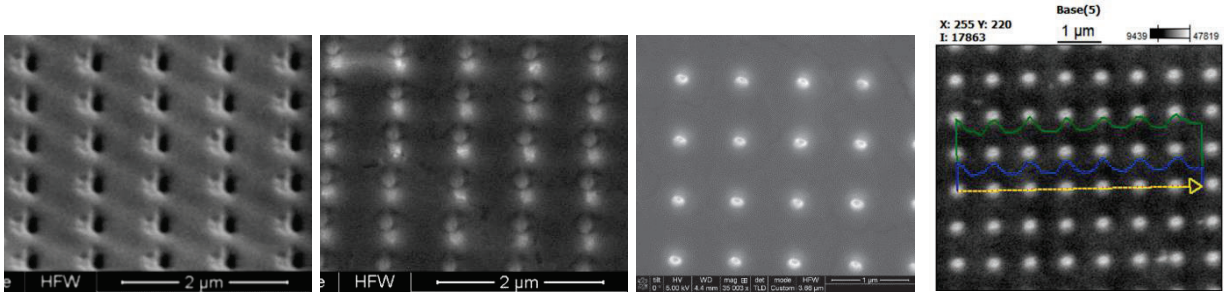

Figure 3: SEM micrographs of an array of holes patterned in PMMA with ZnO SiS process treatment. (Far left) PMMA exposed, developed and after SiS process with ZnO. (Center Left) Same sample after organic burnout at 700 ºC for 25 min in an oxygen atmosphere. Both images taken at a 52 degree tilt. (Center right) SEM top-down micrographs showing 200 nm outer diameter and 30 nm inner diameter nanotubes. (Far right) EDS data line scan (yellow line) over an array of the nanotubes. Blue line is the L-line data for Zinc and the Green line the K-line data for Oxygen.

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