

Synthesis of Self-Assembled Metal-Oxide Nanostructures in a Diblock Copolymer Matrix and Integration onto Semiconductor Surfaces

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ABSTRACT

The synthesis of self-assembled ZnO nanostructures at room temperature using a microphase separated diblock copolymer as a template is reported. Poly(norbornene) / poly(norbornene-dicarboxylic acid) diblock copolymers were synthesized using Ring Opening Metathesis Polymerization (ROMP). The polymers were dissolved and the solutions were doped with ZnCl₂. Films were formed from this solution, and subsequently reacted with NH₄OH. This converted the ZnCl₂ into ZnO contained within the microphase-separated nanodomains of the block copolymer. Fourier Transform Infrared Spectroscopy verified the association of the metal to the second block of the polymer, and X-ray Photoelectron Spectroscopy verified the conversion of the salt to ZnO nanoclusters. The development of such ZnO - block copolymer nanocomposites is targeting the functionalization of nanostructures into device technologies.

INTRODUCTION

The next generation of nanoscale electronic devices and circuits require the development of novel engineered materials that can be successfully integrated into existing Si technology. The synthesis and selective application of such engineered materials is of critical importance to the development of functional nano-devices. Nanocomposites, such as metal oxide nanoclusters within a polymer matrix, are expected to be an important class of materials in the area of nano-device fabrication.

Microphase separated diblock copolymers have been recognized for their potential role in self-assembly of nanostructures. Microphase separation is a phenomenon that has been studied extensively through methods such as microscopy, rheology and small angle x-ray diffraction. The diblock copolymer morphology can serve as templates for the formation of nanostructures. Depending on the volume ratio of blocks a diblock polymer is synthesized with, the resulting morphology can be spherical, cylindrical, or lamellar.

The templating of nanostructures within diblock copolymer nanodomains has been successful with several metals and semiconductors [1,2,3]. Metal atoms can either be introduced to one block as a salt when the polymer is dissolved, or to one monomer prior to the polymer synthesis. ZnO is a wide band gap ($E_g = 3.3\text{eV}$) semiconductor with important piezoelectric and optical properties in the UV range. In this study, ZnO

nanoclusters were synthesized at room temperature by templating within the microstructure of a synthesized block copolymer. This strategy is similar to a "universal" approach to synthesizing metal nanoclusters within diblock copolymers as proposed by Clay et al [4]. We have modified and optimized this approach for the specific templating of ZnO nanoclusters.

New and enhanced properties are expected when controlled nanocrystalline forms of the ZnO system are developed. The development of ZnO in its nanocrystalline and / or nanocomposite form and its successful integration into current and future CMOS and other device technologies is one of the goals of our research.

EXPERIMENTAL

The diblock copolymer poly(norbornene)-poly(norbornene-dicarboxylic acid) was synthesized using Ring Opening Metathesis Polymerization (ROMP) with the Ruthenium based Grubb's catalyst. ROMP allows the presence of functional groups on the monomer, which other polymerization techniques may not tolerate. ROMP also produces a relatively narrow molecular weight distribution, which is necessary for templating uniformly sized nanostructures.

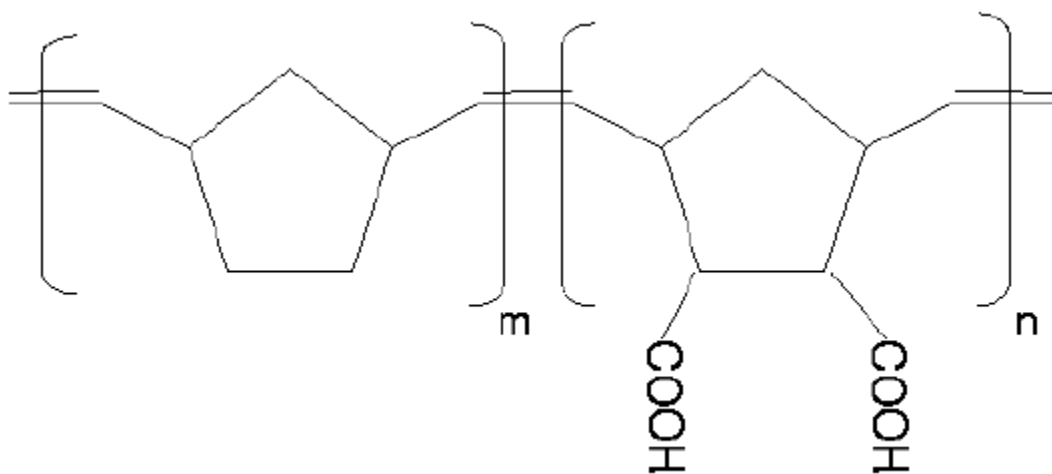


Figure 1. Structure of the poly(norbornene)-poly(norbornene-dicarboxylic acid) diblock copolymer.

Figure 1 shows the structure of the diblock copolymer used in the piezoelectric nanocluster synthesis. The monomers and initiators were combined to give a m/n ratio of 400/50. A polymer with this ratio of blocks will have a spherical morphology, based upon the volume fraction of the blocks used. Therefore, it is expected that the templated nanoclusters are spherical.

ZnCl₂ was added to a 0.05% (w/v) of polymer in THF. From this solution, a polymer film could be static cast from solution into a Teflon cup, or it could be spin cast onto a substrate. The films were then treated with NH₄OH for 24 hours to convert the salt

to ZnO, then washed with water to remove soluble impurities and decompose any unstable $\text{Zn}(\text{OH})_2$. The nanocluster synthesis scheme is presented in Figure 2.

Static cast films were produced by slowly evaporating the solvent over 36 hours, and then placed under vacuum to remove residual solvent. Films were analyzed with x-ray photoelectron spectroscopy (XPS) to verify the conversion of the salt to the oxide. A Perkin Elmer 5800 XPS-Auger Spectrometer was used to collect the spectra. XPS survey scans up to 1200 eV, and high-resolution scans of the specific peaks of interest (Zn, Cl) were obtained and the binding energy shifts of Zn were monitored. Fourier Transform Infrared Spectroscopy (FTIR) verified the association of the metal to the carboxylic groups on the second block of the polymer. The spectra were taken in the range of 4000 cm^{-1} to 400 cm^{-1} on a Nicolet Fourier Transform Spectrophotometer.

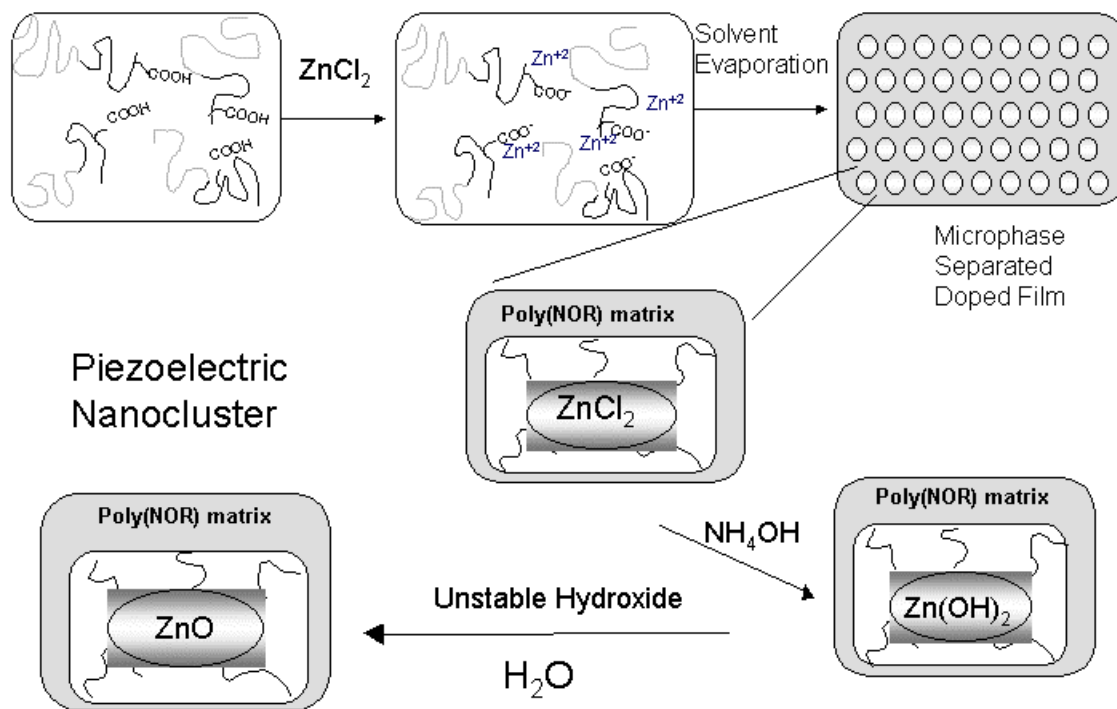


Figure 2. Room Temperature wet chemical synthesis scheme for ZnO nanostructures.

RESULTS

The synthesized diblock copolymers had a Poly Dispersity Index (PDI) of 1.15, as determined by Gel Permeation Chromatography (GPC). Solutions of this polymer took 24 hours to dissolve, after which a stoichiometric amount of ZnCl_2 was added. The amount of ZnCl_2 was determined by calculating the concentration of carboxylic groups present in the solution, and taking into account that Zn^{2+} will react with 2 carboxylic

groups. The ZnCl₂ doped solutions were stirred for 24 hours to allow association of the cations to the polymer chains.

Static cast films were approximately 0.05 mm in thickness and black in color. ZnCl₂ doped films changed to an orange-brown color following the treatment with NH₄OH, after stirring for 24 hours. Films were also spin cast on Si and SiO₂ substrates at speeds between 1000 and 3000 rpm for various time periods. These films were reacted by placing a drop of NH₄OH on the surface of the film.

A schematic representation for the self-assembly of ZnO nanostructures using the templating strategy described earlier is shown in Figure 2. The advantages to this templating process is that nanostructures are self-assembled at room temperature and through wet chemical methods, thus making it appropriate to integrate with current Si processing technology, without additional thermal cycling steps.

FTIR verified that the metal was associated to the second block of the copolymer, and not dispersed randomly as filler in the matrix. The carboxylic peak at 1710 cm⁻¹ was studied for the formation of metal carboxylates after doping with the metal salt. The FTIR peak present at 1630 cm⁻¹ can be assigned to the asymmetrical stretching of the carboxylic anion. Normally this peak will exist at 1578 cm⁻¹, but it is displaced to a higher value due to the Zn atom associated with it. Therefore, the metal exists within the microphase separated domains of the second block.

The XPS survey scans of ZnCl₂ doped films showed that Zn and Cl was present in the sample. When the ZnCl₂ was replaced by the ZnO in the films using NH₄OH, the spectra displayed that Zn was present but Cl was absent, demonstrating that processing with NH₄OH successfully replaced Cl. High resolution scans of the Zn 2p³ peak was performed on ZnCl₂ and ZnO doped films. A downfield shift in the energy of the peak from 1023.1 eV to 1021.4 eV was observed, following the reaction with NH₄OH. This demonstrates the binding and association of the carboxylates to the Zn atom. (Table I). The experimental values obtained here, agree well with literature values and observations for bulk ZnCl₂ and ZnO [5,6].

Table I. Zn 2p³ binding energies determined through High Resolution XPS

Compound	Experimental B.E. (eV)	Literature B.E. (eV)
ZnCl ₂	1023.1	1023.3
ZnO	1021.4	1021.7

CONCLUSIONS

Self-assembled ZnO nanoclusters were successfully synthesized at room temperature by using the microphase separation property of di-block copolymers. FTIR verified that the metal existed within the microphase separated domains. XPS was

employed to verify the conversion of the metal salt precursors to ZnO by wet chemical methods. The reported room temperature templating method for self-assembly is an example of how block copolymers are being explored for use in an increasing number of high technology applications. We are currently conducting experiments to incorporate such nanocomposite materials into the mature Si CMOS technology.

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