



## Properties of self-assembled ZnO nanostructures

H.A. Ali <sup>a</sup>, A.A. Iliadis <sup>a,\*</sup>, R.F. Mulligan <sup>b</sup>, A.V.W. Cresce <sup>b</sup>, P. Kofinas <sup>b</sup>,  
U. Lee <sup>c</sup>

<sup>a</sup> Department of Electrical and Computer Engineering, University of Maryland, College Park, MD 20742, USA

<sup>b</sup> Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD 20742, USA

<sup>c</sup> Army Research Laboratory, Adelphi, MD 20783, USA

Received 17 December 2001; accepted 5 February 2002

---

### Abstract

The formation of self-assembled ZnO nanoclusters using diblock copolymers, is reported. The diblock copolymers, consisting of a majority polymer (norbornene) and a minority polymer (norbornene-dicarboxylic acid), were synthesized with a block repeat unit ratio of 400/50, to obtain spherical microphase separation and hence a spherical morphology for the metal oxide nanoclusters. The self-assembly of the inorganic nanoparticles was achieved at room temperature in the liquid phase, using ZnCl<sub>2</sub> precursor dopant and wet chemical processing compatible with semiconductor manufacturing to convert to ZnO. FTIR and XPS spectroscopy, confirmed the association of the ZnCl<sub>2</sub> precursor with the minority block and the formation of ZnO, while TEM showed the spherical morphology of ZnO nanoparticles as targeted, and a relatively narrow size distribution ranging between 7 and 15 nm.

© 2002 Published by Elsevier Science Ltd.

---

### 1. Introduction

The development of self-assembled nanostructured materials has attracted significant attention recently, as it presents a promising approach for the functionalization of nanostructures into devices and systems. One approach to self-assembly is through the microphase separation observed in diblock copolymers [1]. Diblock copolymers, consisting of a “majority” and a “minority” block, are macromolecules composed of sequences of blocks of chemically distinct repeat units. The chemical link between different blocks prevents phase separation on the macroscopic length scale, but allows microphase separation of the two blocks leading to self-assembled spherical, cylindrical, bi-continuous, and lamellar morphologies of the minority polymer block. These self-assembled domains are essentially monodisperse and have nanometer dimensions, with morphology and domain sizes generally controlled by adjusting the

length of each block and the total molecular mass. The synthesis of metal or semiconductor nanoparticles within microphase separated diblock copolymers has been reported previously [2,3]. In that work the introduction of doping (metal or semiconductor) into the copolymer matrix was accomplished by diffusing the doping agent in the solid phase. In the present work the incorporation of the dopant precursor and the conversion into self-assembled ZnO nanostructures within the diblock copolymer matrix, is achieved at room temperature in liquid phase, using wet chemical processing techniques [4]. Furthermore, in order to develop large area nanocrystalline systems that are compatible with current device processing techniques, spin-on application of the ZnO-nanocomposite diblock polymer on Si and SiO<sub>2</sub>/Si wafer surfaces is examined, and photolithographic processing and metallization schemes are being developed. The interest in ZnO is due to the piezoelectric and optoelectronic properties of this wide band ( $E_g = 3.3$  eV) metal-oxide semiconductor. ZnO crystallizes in the wurtzite structure and exhibits strong piezoelectric properties [5] when the *c*-axis is oriented perpendicular to a substrate. Due to its high room

---

\* Corresponding author.

E-mail address: [agis@eng.umd.edu](mailto:agis@eng.umd.edu) (A.A. Iliadis).

temperature exciton binding energy (60 meV), it shows promise for UV lasing action and optical detection [6]. The growing interest in electronic transport devices [7,8], its well known gas-sensing capabilities, and transparency to visible light, make it one of the technologically important material systems for devices ranging from solar cells, to UV light emitting/detecting devices, to pressure/gas sensor applications. When controlled nanocrystalline structures of this system are developed, reduced dimensionality and confinement to nanoscale dimensions can be studied in order to develop a better understanding of the capabilities of such material.

## 2. Experimental procedure

Diblock copolymers consisting of norbornene (NOR), the majority block, and norbornene-dicarboxylic acid (NORCOOH), the minority block, were synthesized in tetrahydrofuran (THF) via ring opening metathesis polymerization (ROMP) [9] using a Ruthenium based catalyst developed by Grubbs. This technique for copolymer synthesis is advantageous because it results in a narrow molecular weight distribution and allows the presence of specific functional groups on the monomers. Copolymers with block ratios of  $[\text{NOR}]_m\text{-}[\text{NORCOOH}]_n$  (Fig. 1) where  $m/n = 400/50$  repeat units, were produced. Based on the chosen volume fractions of the two blocks of the copolymer, a spherical morphology was targeted for the self-assembled nanoclusters. Gel permeation chromatography (GPC) was used to monitor the molecular weight distribution and determine the poly-dispersity-index (PDI) of the synthesized diblock copolymers. Copolymer PDIs between 1.15 and 1.4 were obtained, and then doped with  $\text{ZnCl}_2$  in solution (THF) at room temperature. The  $\text{ZnCl}_2$  precursor is expected to associate with the dicarboxylic acid ( $-\text{COOH}$ ) groups (Fig. 1).

A Nicolet Fourier transform infrared spectrophotometer (FTIR) was used to verify association of the metal cations to the carboxylic groups of the minority block of the copolymer, and X-ray photoelectron spectroscopy (XPS) was performed to identify the conversion

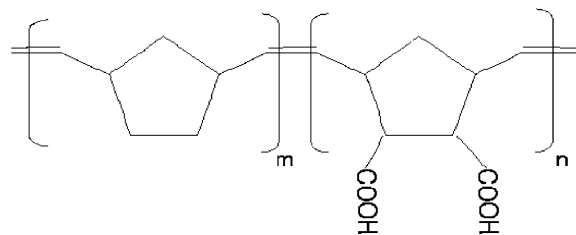


Fig. 1. Chemical structure of the poly(norbornene)-poly(norbornene-dicarboxylic acid) diblock copolymer.

of  $\text{ZnCl}_2$  into ZnO. Transmission electron microscopy (TEM) was employed to examine the morphology and physical parameters of the resultant ZnO nanostructures.

## 3. Results and discussion

After the synthesis of the copolymer was completed and the  $\text{ZnCl}_2$  precursor doping was done in solution at room temperature, the doped copolymer was examined by FTIR and XPS, in order to verify the association of the precursor to the carboxylic group of the minority block, and confirm the conversion to ZnO upon treatment with the weak base. FTIR analysis was performed on a series of samples, to examine the stretch of the bond in the carboxylic group, which would indicate neutralization with the metal cation of the  $\text{ZnCl}_2$ . It has been previously reported [10] that, in FTIR spectroscopy, the carbonyl stretch of the carboxylic group is observed at  $1710\text{ cm}^{-1}$ . If these carboxylic groups are ionized into carboxylic anions (in solution), the peak at  $1710\text{ cm}^{-1}$  is replaced by two new peaks at  $1578\text{ cm}^{-1}$  and  $1414\text{ cm}^{-1}$  [11]. These two new peaks are due to the asymmetrical and symmetrical stretching, respectively, of the carboxylate anion. When the metal is attached, the metal carboxylates display also two peaks due to the asymmetrical and symmetrical stretch, but depending on the metal, the peaks will shift to different values in the range of  $1300\text{--}1750\text{ cm}^{-1}$  [10,11]. Fig. 2 shows the FTIR spectrum of the copolymer film in solution without any doping. The peak observed at  $1710\text{ cm}^{-1}$  is due to the carboxylic group ( $-\text{COOH}$ ) of the minority copolymer, as expected. Fig. 3 shows the FTIR spectrum of the copolymer film in solution after doping with the  $\text{ZnCl}_2$  precursor. The peak for the carboxylic group ( $-\text{COOH}$ ) of the minority polymer at  $1710\text{ cm}^{-1}$  is evident as before, while a new peak at  $1630\text{ cm}^{-1}$  appears, which is due to the metal (Zn) carboxylate. As can be seen, not all carboxylic groups have been neutralized by the metal cation, indicating that saturation rather than stoichiometric doping is necessary for complete neutralization. Fig. 4 shows the FTIR spectrum after treatment with  $\text{NH}_4\text{OH}$ . The peak due to the association of the Zn cation to the carboxylic group has now changed to  $1575\text{ cm}^{-1}$  indicating a shift in bond energy due to the Zn–O association. Thus, the observed peak at  $1575\text{ cm}^{-1}$  is ascribed to the formation of ZnO attached to the minority block of the copolymer. In order to verify the conversion to ZnO by an independent technique, XPS spectra were obtained from the doped copolymers before and after treatment with  $\text{NH}_4\text{OH}$ . Fig. 5 shows the XPS spectra of the copolymer as obtained from the untreated ( $\text{ZnCl}_2$ ) and the treated (ZnO) samples. The Zn  $2p^3$  peak is present in the upper spectrum along with the  $\text{Cl}_2$  peak, indicating the presence of  $\text{ZnCl}_2$  in the untreated sample. After treatment with  $\text{NH}_4\text{OH}$ , no  $\text{Cl}_2$

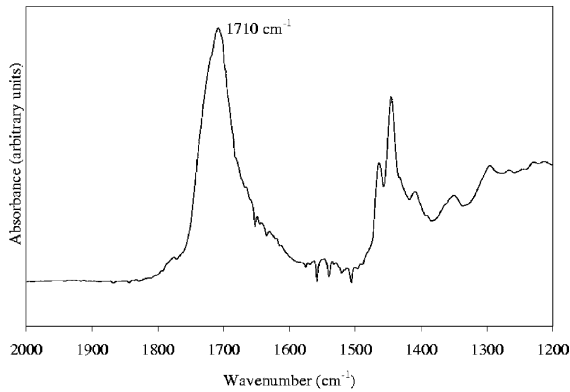


Fig. 2. FTIR spectrum of the undoped copolymer. The peak at  $1710\text{ cm}^{-1}$  is due to the carboxylic group.

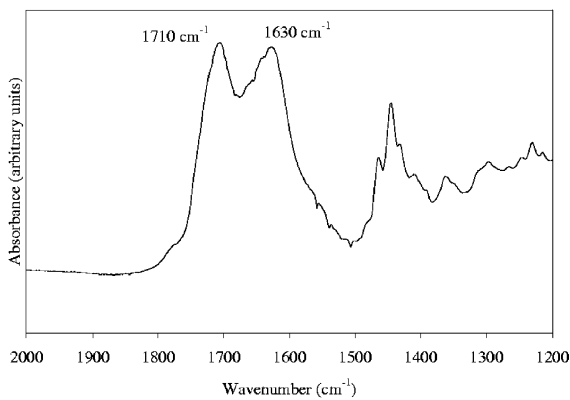


Fig. 3. FTIR spectrum of the doped copolymer. The peak at  $1630\text{ cm}^{-1}$  is due to the Zn carboxylate. Partial neutralization of the carboxylic also is evident due to the presence of the  $1710\text{ cm}^{-1}$  peak also.

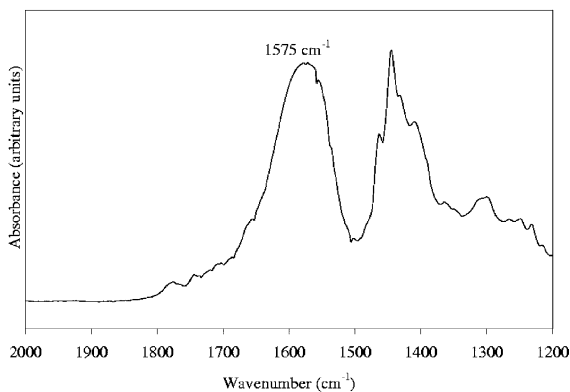


Fig. 4. FTIR spectrum of the doped copolymer after treatment to convert to ZnO. The peak due to the association of the Zn cation to the carboxylic group has now changed to  $1575\text{ cm}^{-1}$  indicating a shift due to the Zn–O association.

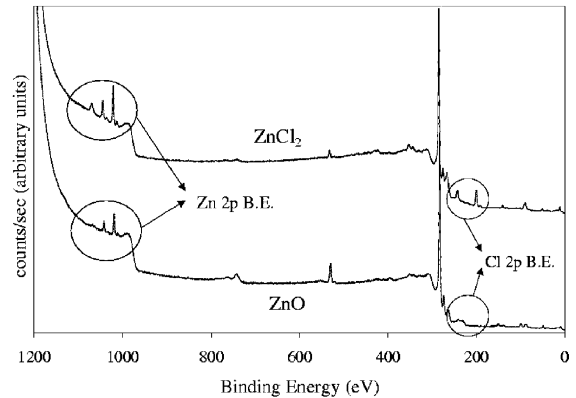


Fig. 5. XPS spectra of the copolymer. Upper spectrum is the doped copolymer with  $\text{ZnCl}_2$ , where the  $2p^3$  Zn and  $\text{Cl}_2$  peaks are observed. Lower spectrum is the copolymer after treatment with  $\text{NH}_4\text{OH}$  to convert to ZnO. The  $\text{Cl}_2$  peak is not observed, indicating the successful conversion from  $\text{ZnCl}_2$  to ZnO.

peak is observed (lower spectrum), and the Zn  $2p^3$  peak has shifted its energy as seen in the high-resolution spectra in Fig. 6. It is observed that the energy of the Zn  $2p^3$  peak after treatment shifts from  $1022.1\text{ eV}$  to the lower value of  $1020.2\text{ eV}$ , which, in agreement with existing literature (see Table 1), is characteristic of ZnO. It is evident from the XPS spectra that the  $\text{ZnCl}_2$  precursor has been converted into ZnO nanostructures associated with the minority block copolymer which provides the self-assembly capability of this system.

The TEM image of the resultant ZnO nanoparticles within the polymer matrix, is shown in Fig. 7. Spherical morphology is evident in the nanostructures as targeted by the copolymer choice. The size dispersion of the nanoparticles, is observed to be relatively narrow, with sizes ranging between 7 and 15 nm. The size dispersion

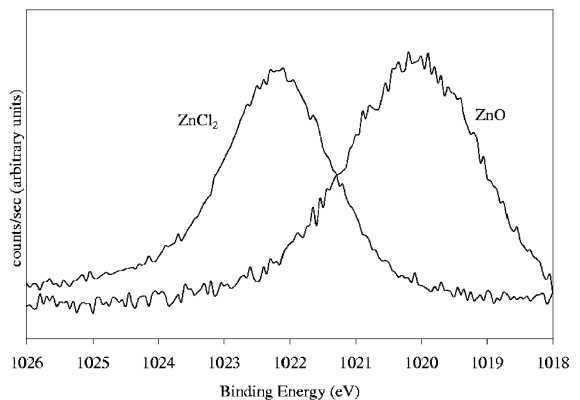


Fig. 6. High resolution XPS spectra of the Zn  $2p^3$  peak binding energy for the copolymers containing  $\text{ZnCl}_2$  and ZnO. The shift of the Zn peak to lower energy is evident, showing the ZnO formation.

Table 1  
Experimental data of the Zn 2p<sup>3</sup> energy peak obtained here by XPS high-resolution analysis and existing literature data

	Literature (eV)	Experimental (eV)
ZnCl <sub>2</sub>	1023.3	1022.1
ZnO	1021.7	1020.2

The difference of 1.9 eV between the ZnCl<sub>2</sub> and ZnO in the experimental data is in good agreement with the 1.6 eV difference in the literature indicating the conversion of ZnCl<sub>2</sub> to ZnO within the copolymer matrix.

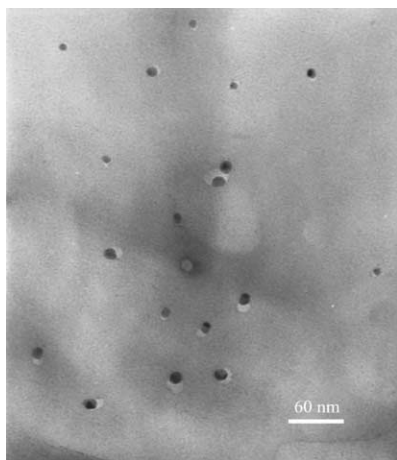


Fig. 7. TEM image of ZnO nanoparticles in the copolymer matrix. Spherical morphology and a relatively narrow size distribution (7–15 nm) are observed.

of the nanoparticles depends on the polydispersity index (PDI) of the copolymer, and for near monodisperse nanoparticles, a PDI close to unity is required.

#### 4. Conclusions

A diblock copolymer system containing ZnO nanoparticles, has been developed and applied on Si and

SiO<sub>2</sub>/Si wafer surfaces. The synthesis and doping of the copolymer is reported, and the formation of ZnO nanostructures associated with the self-assembled minority block of the copolymer, is confirmed with XPS, FTIR and TEM analysis. Spin-cast and static-cast techniques have been studied and wet chemistry compatible with CMOS technology has been developed at room temperature.

#### Acknowledgements

The support of this research by a National Science Foundation Grant # ECS-9980794, is gratefully acknowledged.

#### References

- [1] Bates FS, Fredrickson GH. *Ann Rev Phys Chem* 1990; 41:525.
- [2] Ciebien JF, Clay RT, Sohn BH, Cohen RE. *New J Chem* 1998;22:685.
- [3] Sohn BH, Cohen RE. *Chem Mater* 1997;9:264.
- [4] Mulligan RF, Iliadis AA, Lee U, Kofinas P. In: Fafard S, Huffaker D, Leon R, Noetzel R, editors. *Semiconductor quantum dots*, vol. 42. Materials Research Society; 2000.
- [5] Verghese PM, Clarke DR. *J Appl Phys* 2000;87:4430.
- [6] Tareja RK, Mitra A. *Appl Phys B Lasers and Opt* 2000;71: 181.
- [7] Chang CC, Fang SK. *Int J Electron* 2000;87:1013.
- [8] Krishnamoorthy S, Iliadis AA, Inumpudi A, Choopun S, Vispute RD, Venkatesan T. *Int Semic Dev Res. Symp (ISDRS)*, Washington DC, Proceedings, 2001. p. 450–3.
- [9] Thomas EL, Lescanec RL. *Phil Trans Royal Soc London A* 1994;348:149.
- [10] Silverstein RM. *Spectrometric identification of organic compounds*. 6th ed. NY: Wiley; 1998.
- [11] Nakamoto K. *Infrared and Raman spectra of inorganic and coordination compounds*. 5th ed. NY: Wiley; 1997.