University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Stephen Ducharme Publications

Research Papers in Physics and Astronomy

2011

Cluster synthesis of monodisperse rutile-TiO₂ nanoparticles and dielectric TiO₂-vinylidene fluoride oligomer nanocomposites

Balamurugan Balasubramanian

University of Nebraska-Lincoln, balamurugan@unl.edu

Kristin L. Kraemer

University of Nebraska-Lincoln

Shah R. Valloppilly

University of Nebraska-Lincoln, svalloppilly2@unl.edu

Stephen Ducharme

University of Nebraska, sducharme1@unl.edu

David J. Sellmyer

University of Nebraska-Lincoln, dsellmyer@unl.edu

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsducharme>

Part of the [Physics Commons](#)

Balasubramanian, Balamurugan; Kraemer, Kristin L.; Valloppilly, Shah R.; Ducharme, Stephen; and Sellmyer, David J., "Cluster synthesis of monodisperse rutile-TiO₂ nanoparticles and dielectric TiO₂-vinylidene fluoride oligomer nanocomposites" (2011). *Stephen Ducharme Publications*. 71. <https://digitalcommons.unl.edu/physicsducharme/71>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Stephen Ducharme Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Cluster synthesis of monodisperse rutile-TiO₂ nanoparticles and dielectric TiO₂–vinylidene fluoride oligomer nanocomposites

Balamurugan Balasubramanian, Kristin L Kraemer,
Shah R Valloppilly, Stephen Ducharme and David J Sellmyer

Nebraska Center for Materials and Nanoscience and Department of Physics and Astronomy,
University of Nebraska, Lincoln, NE 68588, USA

E-mail: bbalasubramanian2@unl.edu and dsellmyer@unl.edu

Received 31 May 2011, in final form 18 August 2011

Published 13 September 2011

Online at stacks.iop.org/Nano/22/405605

Abstract

The embedding of oxide nanoparticles in polymer matrices produces a greatly enhanced dielectric response by combining the high dielectric strength and low loss of suitable host polymers with the high electric polarizability of nanoparticles. The fabrication of oxide–polymer nanocomposites with well-controlled distributions of nanoparticles is, however, challenging due to the thermodynamic and kinetic barriers between the polymer matrix and nanoparticle fillers. In the present study, monodisperse TiO₂ nanoparticles having an average particle size of 14.4 nm and predominant rutile phase were produced using a cluster-deposition technique without high-temperature thermal annealing and subsequently coated with uniform vinylidene fluoride oligomer (VDFO) molecules using a thermal evaporation source, prior to deposition as TiO₂–VDFO nanocomposite films on suitable substrates. The molecular coatings on TiO₂ nanoparticles serve two purposes, namely to prevent the TiO₂ nanoparticles from contacting each other and to couple the nanoparticle polarization to the matrix. Parallel-plate capacitors made of TiO₂–VDFO nanocomposite film as the dielectric exhibit minimum dielectric dispersion and low dielectric loss. Dielectric measurements also show an enhanced effective dielectric constant in TiO₂–VDFO nanocomposites as compared to that of pure VDFO. This study demonstrates for the first time a unique electroactive particle coating in the form of a ferroelectric VDFO that has high-temperature stability as compared to conventionally used polymers for fabricating dielectric oxide–polymer nanocomposites.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hybrid nanocomposites made of polymer matrix and inorganic nanoparticles show great promise for optical, electronic, and magnetic device applications by offering functional properties arising collectively from both the host polymer and the nanoparticle fillers [1–6]. Recently, ferroelectric polymers, especially poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene P(VDF–TrFE), have emerged as potential candidates for dielectric layers in

high-energy-density capacitors due to their large dielectric strength (E_b), high electric displacement density (D), and low dielectric loss [7–9]. The relatively low dielectric constant k (<10) and early saturation of the polarization P at electric fields well below E_b in ferroelectric polymers limit the energy density of these capacitors, but it can be greatly improved by embedding oxide nanoparticles (TiO₂, SrTiO₃, BaTiO₃, BaSrTiO₃, etc) to increase the effective dielectric constant [4, 10–14]. The enhancement of dielectric properties is a complex function of the uniform distribution

Figure 1. (a) Schematic diagram of the experimental set up used for the deposition of TiO_2 -VDFO nanocomposites and (b) the molecular structure of the dipolar oligomer highlighting the VDF monomer (red-dotted ellipse) as well as the terminating CF_3 molecule (blue-dotted ellipse) and iodine atom (black-dotted ellipse).

of nanoparticles and their interfacial interactions with the polymer matrix.

The requirement of high growth temperature for oxides ($\geq 300^\circ\text{C}$) as compared with the low melting and decomposition temperatures of polymers ($\leq 200^\circ\text{C}$) [15–18], however, necessitates a multi-step process for the fabrication of these dielectric layers. This technique involves a simple mixing of commercially available oxide nanoparticles of relatively large size (~ 30 – 70 nm) into the polymers followed by a spin or dip coating, but it does not control the nanoparticle distribution well, leading to agglomeration and severe limits on concentration [4, 10–14]. These studies point toward the importance of finding suitable host polymers having high-temperature stability, which is highly desirable from the point of view of the fabrication process of oxide-polymer nanocomposites and improving the operating temperature of these nanocomposites-based devices. In this regard, vinylidene fluoride oligomer (VDFO) is an attractive ferroelectric material that is stable against decomposition to well over 300°C , as compared to PVDF and its copolymers [19–21].

Our recent work on plasma-condensation-type cluster-deposition has shown that TiO_2 nanoparticles having a mixture of anatase and rutile phases can be deposited at room temperature [22]. The unique advantage of the cluster-deposition method is that the growth, phase formation, and crystallization of nanoparticles occur in the gas phase, and thus it is feasible to functionalize or coat them with inorganic or organic layers [22, 23]. Note that the dielectric constant of TiO_2 increases from 40 to 100 on varying the phase from anatase to rutile [22, 24]. The growth of rutile- TiO_2 is, however, challenging due to the requirement for a high growth temperature as compared to anatase TiO_2 [15–17, 25–27]. The present study shows the following important observations:

monodisperse TiO_2 nanoparticles having predominant rutile phase were produced without high-temperature heat treatment using the cluster-deposition method, and subsequently coated with ferroelectric VDFO using *in situ* thermal evaporation prior to deposition on suitable substrates (the latter being schematically illustrated in figure 1(a)). The main advantage of this method as compared to the conventionally used wet-chemical techniques is that the VDFO coatings prevent the nanoparticles from contacting each other and also act as a matrix. Note that this study demonstrates for the first time that VDFO is a promising material for use in nanocomposite dielectrics for high-energy-density capacitors.

2. Materials and methods

The procedure for fabricating thin films composed of bare TiO_2 and TiO_2 -VDFO nanocomposites, as depicted in figure 1(a), is as follows. First, Ti nanoparticles were produced in a gas-aggregation chamber by an inert-gas condensation process described elsewhere [28–30] and simultaneously oxidized to form TiO_2 nanoparticles by well-controlled mixing of oxygen into the gas-aggregation chamber [22, 31]. In particular, the DC magnetron sputtering power (P_{dc}) was varied from 120 to 200 W to predominantly obtain the rutile TiO_2 phase in the present study, while keeping the flow rates of argon [FR (Ar)], helium [FR (He)], and oxygen [FR (O_2)] at about 275, 100, and 50 sccm (standard cubic centimeters per minute), respectively. TiO_2 nanoparticles were then extracted from the gas-aggregation chamber as a well-focused cluster beam into a deposition chamber and collected on a substrate (substrate 2) kept at room temperature, as shown in figure 1(a). Prior to deposition, TiO_2 nanoparticles were coated with VDFO molecules by *in situ* condensation of VDFO vapors produced

Figure 2. The structure and size of the uncoated TiO_2 nanoparticles are probed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). (a) XRD of TiO_2 nanoparticles deposited at different DC magnetron sputtering powers (P_{dc}), where the standard positions of diffraction peaks corresponding to rutile (R) and anatase (A) phases of TiO_2 are given as blue-solid and red-dotted vertical lines, respectively [33, 34]. (b) TEM image of the TiO_2 nanoparticles deposited at $P_{dc} = 200$ W, where the corresponding particle size histogram is given as the inset. σ and d are the standard deviation and average particle size, respectively.

using thermal evaporation of bulk VDFO powder (obtained from Kunshan Hisense) in an evaporation chamber following the gas-aggregation chamber as shown in figure 1(a).

The structure of VDFO, having the formula $\text{CF}_3\text{-(VDF)}_n\text{-I}$, consists of a finite length linear chain of VDF molecules, $n\text{-(CF}_2\text{-CH}_2\text{)}$, that is terminated on one end by a CF_3 molecule and on the other end by an iodine (I) atom as shown in figure 1(b). The evaporation temperature of VDFO (T_e) was varied from 200 to 400 °C to change the thickness of the VDFO coating on TiO_2 nanoparticles, and therefore the relative volume fractions of TiO_2 and VDFO in the resulting nanocomposites. Pure VDFO films were also deposited at different T_e in the absence of the TiO_2 cluster beam on the Si substrate (substrate 1) as shown in figure 1(a).

The sample substrates were chosen according to the intended measurement. Single crystalline Si (001) wafers were used for x-ray diffraction (XRD), which was carried out with a Rigaku D/Max-B diffractometer using $\text{Cu K}\alpha$ (1.5418 Å) wavelength x-rays. Carbon-coated copper grids were used for transmission electron microscopy (TEM), which was carried out using a JEOL model 2010 operated at an acceleration voltage of 200 kV and an operating pressure of approximately 10^{-9} Torr with a resolution of approximately 1.9 Å. The Si substrate was also used for field-emission scanning electron microscopy (FESEM) using a Hitachi S4700 with magnification up to 500 000 $\times$ and resolution up to 1.2 nm. Parallel-plate capacitors with VDFO and $\text{TiO}_2\text{-VDFO}$ nanocomposite layers as the dielectric were fabricated on glass substrates with orthogonal striped top and bottom aluminum electrodes of thickness 100 nm and width 3 mm. The capacitance measurements were carried out on these capacitors using an impedance analyzer (HP 4192A) at 0.1 V amplitude.

3. Results and discussion

The average particle size, size-distribution, and phase of the TiO_2 nanoparticles were controlled during the gas-aggregation

process by varying the gas flow rates and P_{dc} , prior to coating them with VDFO layers. Our previous study indicates that the fractions of anatase and rutile phases having tetragonal lattice can be varied by changing the oxygen flow rates [22]. At $P_{dc} = 165$ W, a mixture of anatase and rutile phases was observed for $\text{FR}(\text{O}_2) = 40\text{--}50$ sccm and an increase in $\text{FR}(\text{O}_2)$ to 80 sccm led to predominant anatase phase [22]. In the present study, we have improved the fraction of rutile phase in TiO_2 nanoparticles to be predominant by keeping $\text{FR}(\text{O}_2)$ at 50 sccm and varying P_{dc} from 120 to 200 W as shown in figure 2(a).

TiO_2 nanoparticles deposited at $P_{dc} = 120$ W show a predominant anatase- TiO_2 phase along with weak diffraction peaks corresponding to the rutile- TiO_2 phase (curve (i) in figure 2(a)). On increasing the power to $P_{dc} = 150$ W, the intensity of diffraction peaks corresponding to the anatase phase decreases and that of the rutile phase increases as clearly seen in curve (ii) of figure 2(a). For $P_{dc} = 200$ W, TiO_2 nanoparticles have a predominant rutile phase, and near the diffraction peak corresponding to the (110) reflection of the rutile phase is seen the weaker (101) reflection from the anatase phase (curve iii figure 2(a)). Note that these uncoated TiO_2 nanoparticle samples were deposited on single crystalline Si(001) wafers (substrate 2 in figure 1(a)) in the absence of VDFO coating and a diffraction peak corresponding to (002) reflection is selectively present in the XRD patterns of these samples. In the case of the powder diffraction experiment set up in Bragg–Brentano geometry, (002) reflection of Si is forbidden. This (002) peak could be observed from the single crystalline Si substrates, when mounted at certain azimuthal rotation angles (128 different angles in a full 360° scan). In brief, a slight variation in azimuthal angle strongly decides the absence or presence of the (002) reflection of the single crystalline Si substrate and its peak width [32]. Note that diffraction from polycrystalline samples deposited on an Si substrate, for example TiO_2 nanoparticles in the present study, is independent of this azimuthal orientation.

As already mentioned, the rutile TiO_2 phase requires a high growth temperature as compared to anatase TiO_2 [25–27]. For example, wet-chemical techniques yield only amorphous TiO_2 nanoparticles and subsequent annealing at 200°C results in anatase- TiO_2 nanoparticles [25, 26]. A high annealing temperature of above 550°C is, however, required for the transformation of anatase to the rutile phase [27]. In the present study, predominant rutile phase was directly obtained in TiO_2 nanoparticles by varying P_{dc} without subsequent thermal annealing. The oxidation of aggregating Ti nanoparticles is promoted by the oxygen feeding into the gas-aggregation chamber and thermal energy gained from the sputtered Ti atoms and inert-gas ions. Thus, with a high P_{dc} of 200 W and a favorable FR (O_2) of 50 sccm, Ti nanoparticles get sufficient energy for oxidation to form the rutile TiO_2 phase. In addition, the TEM image (figure 2(b)) and the corresponding particle size histogram (inset of figure 2(b)) of rutile TiO_2 nanoparticles deposited at $P_{\text{dc}} = 200$ W yield an average particle size of $d = 14.4$ nm with a narrow size-distribution characterized by an rms standard deviation of $\sigma/d = 0.15$. Generally, the σ/d value of the cluster-deposited nanoparticles depends on the gas-aggregation temperature, gas flow rates, sputtering power, and material systems. Our previous studies reveal that cluster-deposited Ti and TiO_2 nanoparticles produced at $P_{\text{dc}} = 165$ W show $\sigma/d \leq 0.1$ [22]. The higher σ/d of about 0.15 observed in the present study is probably due to the high P_{dc} of 200 W. In brief, XRD and TEM results reveal that TiO_2 nanoparticles deposited at $P_{\text{dc}} = 200$ W are predominantly rutile phase with a narrow size distribution.

We have also deposited pure VDFO films (in the absence of TiO_2 cluster beam) on Si substrates (substrate 1 in figure 1(a)) kept at ambient temperatures above the evaporation source in the evaporation chamber, as shown in figure 1(a), and studied their structural and dielectric properties. This investigation allowed us to calibrate the layer thickness and optimize the crystal structure of the VDFO coatings that would be deposited on TiO_2 nanoparticles. It was observed that VDFO evaporated with a high deposition rate (R_e), without decomposition of the oligomer, at evaporation temperatures (T_e) ranging from 100 to 400°C . For example, at working pressures of 10^{-4} Torr, VDFO evaporates at $T_e = 60^\circ\text{C}$ with $R_e = 0.02$ nm s $^{-1}$. R_e increases to 12 nm s $^{-1}$ at $T_e = 120^\circ\text{C}$ and reaches 60 nm s $^{-1}$ at $T_e = 200^\circ\text{C}$ as shown in figure 3(a). Further elevation of T_e above 200°C results in a rapid increase of R_e beyond 99.9 nm s $^{-1}$ and this is the maximum limit that can be measured using a quartz crystal thickness monitor. A high evaporation rate in the range of several tens of nanometers as observed in the present study is desirable to coat TiO_2 nanoparticles with a reasonable VDFO thickness while nanoparticles pass through the evaporation chamber. For example, a paraffin shell thickness of 2–3.5 nm was obtained in the case of TiO_2 –paraffin nanoparticles at similar range of R_e of paraffin and was shown to result in effective modification of their dielectric properties [22].

The crystal structure of the bulk VDFO powder and VDFO thin films made by vacuum evaporation was determined by x-ray diffraction (XRD), as shown in figure 3(b). Note that the Si(002) peak is also selectively present in TiO_2 –VDFO

Figure 3. (a) Evaporation rate (R_e) as a function of the evaporation temperature (T_e) of VDFO. (b) X-ray diffraction patterns for: (i) bulk VDFO powder and as-deposited VDFO thin films on Si substrate at different evaporation temperatures (T_e); (ii) 170°C ; (iii) 200°C ; (iv) 250°C ; (v) 300°C ; and (vi) 400°C . The red-solid and blue-dotted vertical lines represent the standard peak positions corresponding to (110) reflections of the orthorhombic structure (ferroelectric polar phase, form I) and (110) of the monoclinic or pseudo-orthorhombic structure (non-polar phase, form II), respectively [19–21, 35, 36]. (c) FESEM image of the VDFO film deposited at $T_e = 300^\circ\text{C}$.

nanocomposites and this is again caused by slight variations in the azimuthal angles upon mounting the samples for x-ray diffraction, as explained earlier [32]. Generally, VDFO

crystallize into orthorhombic structure (ferroelectric polar phase known as form I) or monoclinic/pseudo-orthorhombic structure (non-polar phase known as Form II) [19–21, 35–39]. The maximum-intensity XRD peak of both the polar and non-polar phases corresponds to (110) reflections that appear in the lower angle region ($2\theta = 15^\circ$ – 32°) and their standard peak positions are very close to each other, as marked by the red-solid and blue-dotted vertical lines in figure 3(b), respectively [35, 36]. As shown in figure 3(b), XRD patterns of the VDFO powder (curve i) and VDFO thin films (curves ii–vi) show an intense diffraction peak in the lower angle region, which is in good agreement with the standard peak position of (110) reflection corresponding to the polar phase (form I) [19–21, 35, 36]. Note that the broadness and asymmetric nature of this peak, however, possibly indicate a very weak presence of (110) peak of the non-polar phase. In addition, a distinct diffraction peak corresponding to (020) reflection of the non-polar phase (form II) was also observed in the low angle region as shown in figure 3. In the case of VDFO thin films, the relative intensity of (110) of the polar phase and (020) of the non-polar phase varies on changing T_e (curves ii–vi in figure 3(b)), revealing the changes in the fractions of polar and non-polar phases. For example, the XRD pattern of the VDFO film prepared at intermediate temperatures ($T_e = 170$ and 200°C) shows only a broad peak at the lower angle region, which clearly seems to be a combination of the (110) peak of the polar phase and the relatively intense (020) peak of the non-polar phase (curves ii and iii), whereas the (110) peak becomes sharp and intense as compared to the (020) peak at intermediate temperatures ($T_e = 250$ and 300°C), as shown in curves iv and v of figure 3(b), respectively. The film deposited at high $T_e = 400^\circ\text{C}$, however, shows again the predominant intense (020) reflection of the non-polar phase (curve vi).

In addition to the diffraction peaks observed in the lower angle region, a few diffraction peaks corresponding to the polar phase were also observed in the higher angle region ($2\theta = 34^\circ$ – 45°) as indexed in figure 3(b). These higher angle diffraction peaks of VDFO were observed to be broad and to show a shift toward the lower angle side as compared to the standard peak position of the corresponding reflections of pure PVDF. The peak broadness and shift is expected in the PVDF based copolymers and oligomers on increasing the TrFE or fluorine content due to lattice expansion, and a collective effect of the decrease in crystallite size and increase in the Debye–Waller factor, respectively [39]. Generally, *in situ* heating of substrates during deposition or post-deposition annealing at optimum temperature in the range of 50 – 80°C is required to obtain a predominant polar phase (form I) in the vacuum-evaporated VDFO films [19–21]. In the present study, for the deposition of VDFO films, the Si substrates were kept at ambient temperatures [above the evaporation source (substrate 1 in figure 1(a))], which strongly depend on T_e . XRD patterns reveal that T_e of 250 and 300°C result in a favorable and optimum ambient temperature to obtain the predominant polar phase. At a high T_e of 400°C , the VDFO films show a disordered nature as revealed by the broad diffraction peaks (curve vi in figure 3(b)), probably due to higher ambient growth temperatures than the required optimum temperature to

crystallize the polar phase. Thus, in the present study, an inert-gas atmosphere and ambient temperatures probably promote the predominance of the polar phase in the as-deposited films at $T_e = 250$ – 300°C . The surface morphology of the pure VDFO film, as shown in the FESEM image of VDFO films deposited at 300°C , deposited on Si substrate reveals grain sizes in the range of 100 nm (figure 3(c)).

As already mentioned, ferroelectric polymers have a high D and a large E_b . These polymers, however, attain early saturation in electric fields well below E_b and have a large remanent polarization (D_r), which are disadvantages from the point of view of attaining high energy densities. It is worth noting that the relaxor polymer made of ferroelectric P(VDF–TrFE) copolymers with 7.5 mol% of reversible chlorofluoroethylene (CFE) has been observed to avoid early saturation and minimize D_r to approximately zero [7]. While the predominant polar phase in VDFO films is expected to produce a large D , the minor presence of the non-polar phase in VDFO films is advantageous in avoiding early saturation and minimizing D_r .

Based on the structural properties of vacuum-evaporated VDFO films, we coated the TiO_2 nanoparticles with VDFO at $T_e = 200$ and 300°C to fabricate dielectric TiO_2 –VDFO nanocomposite layers; the corresponding XRD patterns are shown in figure 4(a). As previously explained, the XRD pattern of uncoated TiO_2 nanoparticles reveals the presence of the predominant rutile phase along with a weak anatase phase (curve i in figure 4(a)). For TiO_2 –VDFO nanocomposites deposited at $T_e = 200^\circ\text{C}$, the XRD pattern shows only a weak and broad diffraction peak corresponding to VDFO as compared to that of TiO_2 nanoparticles, revealing only a relatively small fraction of VDFO (curve ii in figure 4(a)). In addition, the R (110) peak becomes sharp and the A (101) peak disappears in the TiO_2 –VDFO nanocomposite samples, indicating the stabilization of rutile phase upon VDFO coating. In the case of TiO_2 –VDFO nanocomposites prepared with $T_e = 300^\circ\text{C}$ (curve iii in figure 4(a)), the diffraction peaks corresponding to (110) of the polar phase and (020) of the non-polar phase of VDFO become intense as compared to that of TiO_2 nanoparticles, and higher angle broad diffraction peaks of the polar phase of VDFO completely dominate over the diffraction peaks corresponding to (101) and (111) of TiO_2 . XRD results show an increase in the VDFO fraction with respect to TiO_2 phase and also reveal an increase in the fraction of polar VDFO phase with respect to non-polar VDFO phase on increasing T_e from 200 to 300°C .

The relative concentrations of TiO_2 and VDFO were estimated by fitting the experimental XRD data for TiO_2 –VDFO nanocomposites at a lower angle region, as shown in figure 4(b), using Rietveld analysis [40]. Note that this estimation only includes the crystalline phases of form I and form II and a significant fraction of non-crystalline phase seems to exist as shown by the broadness of the diffraction peaks corresponding to VDFO (figure 4(b)). In addition, the noisy diffraction data also introduce uncertainty in the estimation of the relative weight percentages TiO_2 and the VDFO nanoparticles. This analysis shows that TiO_2 –VDFO nanocomposites prepared at $T_e = 200^\circ\text{C}$ have 95 ± 2.3 wt%

Figure 4. (a) XRD patterns for: (i) uncoated TiO_2 nanoparticles and TiO_2 -VDFO nanocomposites prepared at different VDFO evaporation temperatures (T_e); (ii) 200°C and (iii) 300°C . The red-solid vertical line represents the standard peak positions corresponding to the (110) reflection of the polar phase (form I). (b) Experimental XRD patterns (red-solid lines) of TiO_2 -VDFO nanocomposites prepared at different T_e were fitted using Rietveld analysis (black-dotted curves) [40].

Figure 5. FESEM images of (a) pure TiO_2 nanoparticles, where nanoparticle aggregates are marked by dotted ellipse and (b) TiO_2 -VDFO nanocomposites prepared at $T_e = 300^\circ\text{C}$.

of R- TiO_2 phase along with a small VDFO fraction of 5 ± 2.8 wt%. The fraction of TiO_2 and VDFO increases to 60 ± 4.3 wt% and 40 ± 7.3 wt%, respectively, in the TiO_2 -VDFO nanocomposites prepared at $T_e = 300^\circ\text{C}$.

The nanostructure of uncoated TiO_2 and TiO_2 -VDFO nanocomposites was investigated by FESEM, as shown in figure 5. A FESEM image of the uncoated TiO_2 nanoparticles, as shown in figure 5(a), reveals that nanoparticles physically touch each other. On the other hand, FESEM images of TiO_2 -VDFO nanocomposites prepared at $T_e = 300^\circ\text{C}$ show that TiO_2 nanoparticles are prevented from contacting each other due to the presence of VDFO coatings (figure 5(b)). This is important to maintain the uniform distribution of nanoparticles and control the interfacial interactions, which are highly desirable to realize the improved dielectric properties in these nanocomposites. It is worth noting that the surface morphology of TiO_2 -VDFO nanocomposites (figure 5(b)) is entirely different from that of pure polymer film, but similar to that of uncoated TiO_2 nanoparticles (figure 5(a)). The coating of VDFO is clearly evident from an increase in the particle size of TiO_2 -VDFO nanoparticles in figure 5(b) as compared to the individual TiO_2 nanoparticles in figure 5(a).

In addition, TiO_2 -VDFO nanoparticles show comparatively wider dispersion (figure 5(a)) as compared to that of uncoated TiO_2 nanoparticles (figure 5(a)) and this result reveal that individual nanoparticles are coated with varying thicknesses while they were passing through the evaporation chamber. It is also worth noting that the size of the individual coated TiO_2 nanoparticles in figure 5(b) is much smaller than that of TiO_2 nanoparticle aggregates as marked by a dotted ellipse in figure 5(a), and this result supports the isolation of individual TiO_2 nanoparticles upon VDFO coating.

As already mentioned, at $T_e = 300^\circ\text{C}$, VDFO crystallizes into a predominantly polar phase and TiO_2 -VDFO nanocomposites also show a reasonable VDFO presence of 40 wt%. Thus, two types of parallel-plate capacitors were fabricated for dielectric studies using a pure VDFO layer and VDFO-coated TiO_2 nanoparticles as dielectric layers, as shown in figures 6(a) and (b), respectively. T_e for the deposition of both samples was maintained at 300°C . Note that the TiO_2 -VDFO dielectric layer is also expected to have a small fraction of voids due to the nature of the nanoparticle deposition technique [19, 26]. The frequency-dependent dielectric response and loss of the parallel-plate capacitors

Figure 6. Dielectric properties of TiO_2 -VDFO nanocomposites: schematic views of the parallel-plate capacitors using (a) pure VDFO film and (b) TiO_2 -VDFO nanocomposites as dielectric layers. And (c) the corresponding frequency-dependent dielectric constant and dielectric loss spectra are also given.

made of pure VDFO and TiO_2 -VDFO nanocomposites are shown in figure 6(c). The effective dielectric constant of the TiO_2 -VDFO nanocomposites (curve ii in figure 6(c)) increases as compared to the pure VDFO (curve i in figure 6(c)), due to the incorporation of high k - TiO_2 nanoparticles. These capacitors also exhibit a low dielectric loss of less than 0.1 (curves iii and iv in figure 6(c)) in the frequency range of 0.1–100 kHz, which is an important property for use in high-efficiency capacitors.

4. Conclusions

We have deposited VDFO films using thermal evaporation and TiO_2 -VDFO nanocomposites by combining a plasma-condensation-type cluster-deposition to produce monodisperse TiO_2 nanoparticles and an *in situ* thermal evaporation source to coat the TiO_2 nanoparticles with VDFO. XRD studies reveal that the fraction of polar conformation in the VDFO layer can be tailored by varying the evaporation temperature of VDFO. Structural and dielectric properties of TiO_2 -VDFO nanocomposites prepared at $T_e = 200$ and 300°C were investigated using XRD, FESEM, and capacitance measurements. The wt% of VDFO in these nanocomposites increases from 5 to 40% upon increasing T_e from 200 and 300°C . TiO_2 -VDFO nanocomposites have an enhanced dielectric constant as compared to that of pure VDFO film, minimal dielectric dispersion, and low dielectric loss in the frequency range of 0.1–100 kHz.

Acknowledgments

We are grateful for the financial support of the US Office of Naval Research (BB, KLK, SD (grant no. N00014-06-1-0604)), Advanced Research Projects Agency-Energy (SRV (grant no. DE-AR 0000046)), the National Science Foundation-Materials Research Science and Engineering Center (DJS (grant no. DMR-0820521)), and the Nebraska Center for Materials and Nanoscience. We would also like to acknowledge Zhiqiang Sun for his technical assistance and Ralph Skomski for helpful discussions.

References

- [1] Seo J, Kim W J, Kim S J, Lee K S, Cartwright A N and Prasad P N 2009 *Appl. Phys. Lett.* **94** 133302
- [2] Kim K, Woo J, Jeong S and Han C 2011 *Adv. Mater.* **23** 911
- [3] Wilson J L, Poddar P, Frey N A, Srikanth H, Mohamed K, Harmon J P, Kotha S and Wachsmuth J 2004 *J. Appl. Phys.* **95** 1439
- [4] Kim P, Doss N M, Tillotson J P, Hotchkiss P J, Pan M J, Marder S R, Li J, Calame J P and Perry J W 2009 *ACS Nano* **3** 2581
- [5] Mezzenga R and Ruokolainen J 2009 *Nature Mater.* **8** 926
- [6] Sarasqueta G, Choudhury K R, Kim D Y and So F 2008 *Appl. Phys. Lett.* **93** 123305
- [7] Chu B, Zhou X, Ren K, Neese B, Lin M, Wang Q, Baurer F and Zhang Q M 2006 *Science* **313** 334
- [8] Jung S W, Baeg K J, Yoon S M, You I K, Lee J K, Kim Y S and Noh Y Y 2010 *J. Appl. Phys.* **108** 102810
- [9] Park Y J, Chang J, Kang S J and Park C 2009 *Appl. Phys. Lett.* **95** 102902
- [10] Li J, Seok S, Chu B, Dogan F, Zhang Q and Wang Q 2009 *Adv. Mater.* **21** 217
- [11] Arbatti M, Shan X and Cheng Z Y 2007 *Adv. Mater.* **19** 1369
- [12] Li J, Claude J, Norena-Franco L E, Seok S and Wang Q 2008 *Chem. Mater.* **20** 6304
- [13] Kim P, Jones S C, Hotchkiss P J, Hotchkiss J N, Haddock J N and Kippelen B 2007 *Adv. Mater.* **19** 1001
- [14] Li J Y, Zhang L and Ducharme S 2007 *Appl. Phys. Lett.* **90** 132901
- [15] Mialon G, Gohin M, Gacoin M T and Boilot J P 2008 *ACS Nano* **2** 2505
- [16] Zumeta I, Díaz D and Santiago P 2010 *J. Phys. Chem. C* **114** 11381
- [17] Yang H, Zhang K, Shi R, Li X, Dong X and Yu Y 2006 *J. Alloys Compounds* **413** 302
- [18] Bruice P Y 2001 *Organic Chemistry* (Englewood Cliffs, NJ: Prentice-Hall)
- [19] Noda K, Ishida K, Horiuchi T and Matsushige K 1999 *J. Appl. Phys.* **86** 3688
- [20] Kuwajima S, Horie S, Horiuchi T, Yamada H, Matsushige K and Ishida K 2009 *Macromolecules* **42** 3353
- [21] Nakhmanson S M, Korlacki R, Johnston J T, Ducharme S, Ge Z and Takacs J M 2010 *Phys. Rev. B* **81** 174120
- [22] Balasubramanian B, Kraemer K L, Reding N A, Skomski R, Ducharme S and Sellmyer D J 2010 *ACS Nano* **4** 1893
- [23] Bai J and Wang J P 2005 *Appl. Phys. Lett.* **87** 152502
- [24] Dionne G F, Fitzgerald J F and Aucoin R C 1976 *J. Appl. Phys.* **47** 1708
- [25] Ranga Rao A and Dutta V 2007 *Sol. Energy Mater. Sol. Cells* **91** 1075
- [26] Tang J, Redl F, Zhu Y, Siegrist T, Brus L E and Steigerwald M L 2005 *Nano Lett.* **5** 543
- [27] Zhang H and Banfield B L 2000 *J. Phys. Chem. B* **15** 3481

- [28] Haberland H, Karrais M, Mall M and Thurner Y 2000 *J. Vac. Sci. Technol. A* **10** 3266
- [29] Balasubramanian B, Skomski R, Li X, Valloppilly S R, Shield J E, Hadjipanayis G C and Sellmyer D J 2011 *Nano Lett.* **11** 1747
- [30] Balamurugan B, Skomski R and Sellmyer D J 2010 *Magnetic Clusters and Nanoparticles in Nanoparticles: Synthesis, Characterization and Applications* ed R S Chughule and R V Ramanujan (California: American Scientific Publishers) pp 127–62
- [31] Ducati C, Barborini E, Bongirone G, Vinati S, Milani P and Midgley P A 2005 *Appl. Phys. Lett.* **87** 201906
- [32] Hwang B-H 2001 *J. Phys. D: Appl. Phys.* **34** 2469
- [33] ICDD 2010 *International Center for Diffraction Data* Card No. 00-004-0477
- [34] ICDD 2010 *International Center for Diffraction Data* Card No. 04-004-0551
- [35] ICDD 2010 *International Center for Diffraction Data* Card No. 00-042-1649
- [36] ICDD 2010 *International Center for Diffraction Data* Card No. 00-042-1650
- [37] Hasegawa R, Takahashi Y, Chatani Y and Tadokoro H 1972 *Polym. J.* **3** 600
- [38] Horibe H and Taniyama M 2006 *J. Electrochem. Soc.* **153** G124
- [39] Bellet-Amalric E and Legrand J F 1998 *Eur. Phys. J. D* **3** 225
- [40] Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65