Erratum: Structure and performance of dielectric films based on self-assembled nanocrystals with a high dielectric constant

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Limin Huang\textsuperscript{1,2}, Shuangyi Liu\textsuperscript{1,3}, Barry J Van Tassell\textsuperscript{1,4}, Xiaohua Liu\textsuperscript{1,5}, Andrew Byro\textsuperscript{1,5}, Henan Zhang\textsuperscript{5}, Eli S Leland\textsuperscript{1}, Daniel L Akins\textsuperscript{5}, Daniel A Steingart\textsuperscript{1,4}, Jackie Li\textsuperscript{3} and Stephen O’Brien\textsuperscript{1,5}

\textsuperscript{1} The CUNY Energy Institute, City University of New York, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
\textsuperscript{2} Department of Chemistry, South University of Science and Technology of China, Shenzhen 518005, People’s Republic of China
\textsuperscript{3} Department of Mechanical Engineering, The Grove School of Engineering, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
\textsuperscript{4} Department of Chemical Engineering, The Grove School of Engineering, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
\textsuperscript{5} Department of Chemistry, The City College of New York, Marshak Building, 160 Convent Avenue, NY 10031, USA

E-mail: sobrien@ccny.cuny.edu

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Due to a typesetting error, an incorrect version of scheme 1 was published in this paper. Please see the corrected scheme 1.

\textbf{Scheme 1.} Schematic of a nanocrystal/polymer composite thin film for improved dielectric properties.
Structure and performance of dielectric films based on self-assembled nanocrystals with a high dielectric constant

Limin Huang1,2,6, Shuangyi Liu1,3,6, Barry J Van Tassell1,4, Xiaohua Liu1,5, Andrew Byro1,5, Henan Zhang5, Eli S Leland1, Daniel L Akins5, Daniel A Steingart1,4, Jackie Li3 and Stephen O’Brien1,5

1 The CUNY Energy Institute, City University of New York, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
2 Department of Chemistry, South University of Science and Technology of China, Shenzhen 518005, People’s Republic of China
3 Department of Mechanical Engineering, The Grove School of Engineering, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
4 Department of Chemical Engineering, The Grove School of Engineering, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA
5 Department of Chemistry, The City College of New York, Marshak Building, 160 Convent Avenue, NY 10031, USA
E-mail: sobrien@ccny.cuny.edu

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Abstract
Self-assembled films built from nanoparticles with a high dielectric constant are attractive as a foundation for new dielectric media with increased efficiency and range of operation, due to the ability to exploit nanofabrication techniques and emergent electrical properties originating from the nanoscale. However, because the building block is a discrete one-dimensional unit, it becomes a challenge to capture potential enhancements in dielectric performance in two or three dimensions, frequently due to surface effects or the presence of discontinuities. This is a recurring theme in nanoparticle film technology when applied to the realm of thin film semiconductor and device electronics. We present the use of chemically synthesized \((\text{Ba}, \text{Sr})\text{TiO}_3\) nanocrystals, and a novel deposition–polymerization technique, as a means to fabricate the dielectric layer. The effective dielectric constant of the film is tunable according to nanoparticle size, and effective film dielectric constants of up to 34 are enabled. Wide area and multilayer dielectrics of up to 8 cm\(^2\) and 190 nF are reported, for which the building block is an 8 nm nanocrystal. We describe models for assessing dielectric performance, and distinct methods for improving the dielectric constant of a nanocrystal thin film. The approach relies on evaporatively driven assembly of perovskite nanocrystals with uniform size distributions in a tunable 7–30 nm size range, coupled with the use of low molecular weight monomer/polymer precursor chemistry that can infiltrate the porous nanocrystal thin film network post assembly. The intercrystal void space (low \(k\) dielectric volume fraction) is minimized, while simultaneously promoting intercrystal connectivity and maximizing volume fraction of the high \(k\) dielectric component. Furfuryl alcohol, which has good affinity to the surface of \((\text{Ba}, \text{Sr})\text{TiO}_3\) nanocrystals and miscibility with a range of solvents, is demonstrated.
1. Introduction

Thin films with a high dielectric constant have widespread applications in embedded capacitors, multilayer capacitors, gate dielectrics for field effect transistors, memory and power storage devices [1–16]. In addition to the basic and essential criterion of being an insulating material, a high dielectric constant is desirable in order to enhance the field effect or energy density. With the ever growing trend towards integration, versatility and miniaturization in electronic devices, discrete surface mounted passive components (capacitors, resistors and inductors, and the range of types therein) are assessed for their ability to become embedded in integrated circuit (IC) design [2, 3]. Such embedded capacitors require dielectric thin films with stable and high dielectric constants over a wide frequency and temperature range, high dielectric strength, low dielectric loss, low leakage current and ideally a low processing temperature that is compatible with the fabrication techniques of an integrated device manufacturer (IDM) [8–10, 16]. One such application is the design of capacitors for switched DC–DC power conversion, for which specialized operation is desired at high frequency and with low equivalent series resistance (ESR) [17, 18].

Ceramic barium titanate (BaTiO\(_3\))-based materials, featuring high dielectric constants and low intrinsic dielectric loss over a wide frequency range, have been widely used as high \( k \) dielectric components for several decades [15]. The market for discrete ceramic capacitors grew to 8.3 \( Bn \) in 2011 [1]. The majority of this market is based on MLCCs (multilayered ceramic capacitors), with a smaller fraction of single-layer ceramics serving high voltage, high frequency applications. For manufacturing these components firing of the ceramic is a critical, and it is referred to as a HTCC (high temperature co-fired ceramic; fired at \( >1000^\circ C \)) or a LTCC (low temperature co-fired ceramic; fired at \( <1000^\circ C \)) or a LTCC (low temperature co-fired ceramic; fired at \( >1000^\circ C \)) or a LTCC (low temperature co-fired ceramic; fired at \( <1000^\circ C \), typically \( \sim 900^\circ C \)). Both co-firing steps are at too a high temperature for IC design, and so the capacitor component remains discrete—capacitors must be added to the circuit board later. With the advent of synthesis methods for approaching monodisperse, highly crystalline nanocrystals, a solution processing method based on the self-assembly of nanocrystal building blocks from a liquid dispersion phase (nanocrystal ‘inks’) becomes one of several possible procedures for fabricating thin films under conditions compatible with IC design [11, 19–29]. Materials selection indicates the use of a material with a high dielectric constant, such as BaTiO\(_3\) or (Ba, Sr)TiO\(_3\). The approach is an alternative to other forms of thin film fabrication procedures such as pulsed laser deposition, metalorganic chemical vapor deposition (MOCVD), sputtering or conventional sol–gel processing that still may exhibit their own limitations, such as high temperature processing steps necessary for product crystallization (>500°C) and/or ultrahigh vacuum (UHV) instrumentation [30–35].

Low temperature deposition from pure nanocrystal building blocks of thin films having a high dielectric constant generate a number of issues that need to be addressed. First, the evaporation driven self-packing of the pure barium titanate (BT) nanocrystals forms intercrystal void spaces if no further sintering process is applied for film densification. The model is akin to close packing of identical spheres with a maximum packing factor of 0.74, except that these nanocrystals may not be completely spherical and have a mean variance in distribution of diameters. The thin film normally presents a porous structure with 25–35 vol% empty space, which demonstrates the characteristics of air—a low dielectric constant (∼1) and a low breakdown voltage (∼3 V \( \mu m^{-1} \)). Moisture or other molecular adsorbates from the air can also be absorbed into the void space, causing a dramatic change in dielectric behavior due to space charge effects, especially in the lower frequency range (0.1–10 kHz). Secondly, the corresponding thin film has a relatively low mechanical strength because the assembled nanocrystals are adhered to each other through mainly short range intermolecular forces (dipolar, van der Waals). These two issues may be solved using a nanocomposite approach, in which high \( k \) nanocrystals are incorporated into a polymer host.

Polymer/ nanocrystal composites have received much attention because they take advantage of the high dielectric constant of the inorganic nanocrystal filler and high dielectric strength of the polymer host [4, 5, 8, 15, 36–42]. However, merely mixing nanocrystals and polymers at various volume fractions, and depositing them, may reduce the potential functionality of the resultant thin films. This reduction is caused by the agglomeration of nanocrystals, and the surface incompatibility between the nanocrystals and the polymer [8, 36–42], although surface-modified nanocrystals may facilitate the mixing with polymers [4, 36–42]. It has been reported that, for a nanoparticle or nanopowder filler, it is difficult to reach a high packing density in a polymer matrix (50–60% maximum) without generating porosity [4]. This can be attributed to the presence of polymer macromolecules that occupy a considerable portion of the volume fraction, and voids may persist within the composite, especially at high volume fractions of nanocrystals. In contrast, with conventional polymer/nanocrystal composites, we start by using aggregate-free nanocrystals as building blocks to make nanocrystal thin films and describe a strategy that uses a
precursor (such as a monomer with small molecular weight and size) that can easily infiltrate the thin film and fill up the voids. The void space is then occupied with the corresponding polymer after in situ polymerization of the monomer molecules (scheme 1).

Here, we report the preparation of a nanocrystal ink composed of aggregate free, highly crystalline BT or (Ba, Sr)TiO$_3$ (BST) nanocrystals used to successfully fabricate uniform and crack-free nanocrystal thin films via a low temperature solution processing technique (compatible with printing or spin-coating). Key to success is the ability to prepare wide area, pinhole-free films and minimize thickness, since $C = \varepsilon_r\varepsilon_0 A/\delta d$. To assess the effective dielectric constant of the film and analyze the effect of its constituents, a modified Kerner model (derived from Maxwell–Garnet theory) is used. Several distinctive methods are outlined and investigated for preparing dense nanocrystal/polymer thin films with enhanced dielectric performance. Specifically, furfuryl alcohol (2-furanmethanol, referred to by some vendors as furfural alcohol, abbreviated here as FA) is a versatile solvent that shows good affinity to BST nanocrystals and good compatibility with various solvents. FA can be used as an effective void filler as well as a polymerizable solvent to prepare densely packed nanocrystal/polymer composite thin films with increased dielectric properties over a wide range of frequencies and improved mechanical strength and adhesion.

2. Experimental details

2.1. Synthesis of Ba(Sr, Ti)O$_3$ nanocrystals and the self-assembled thin films

The synthesis of BST nanocrystals (preferentially Ba$_{0.7}$Sr$_{0.3}$TiO$_3$) is based on a solvothermal/hydrothermal process of a barium titanium metalorganic source in ethanol (EtOH)/H$_2$O solvent (water: 2.5–20 wt%). BT, Ba$_{1.0}$TiO$_3$ is prepared with the same method with no addition of Sr [27, 35]. For structural characterization see the supporting information (figures S1–S3 available at stacks.iop.org/Nano/24/415602/mmedia). Typically, stoichiometric barium isopropoxide (Aldrich), strontium isopropoxide (Aldrich) and titanium isopropoxide (Aldrich) are dissolved/mixed in 200-proof EtOH solvent. Then an EtOH/water solvent is added dropwise to the solution under stirring to form a transparent solution. The clear solution is transferred to a Teflon-lined stainless steel autoclave and heated at 190°C for 48 h. After the solvothermal treatment, the resulting precipitate is collected by centrifugation and thoroughly washed with EtOH. The BST nanocrystals that result are dispersed in EtOH or other solvents using ultrasonication to provide a stable and clear nanocrystal suspension.

2.2. Preparation of BST/polymer nanocomposite thin films

Three major procedures/formulations have been developed for thin film fabrication, namely: (1) FA (Aldrich) as a void filler for nanocrystal thin films based on an infiltration–polymerization process; (2) BT(BST)/FA solution (FA as the sole solvent), suitable for a printing process; (3) BT(BST)/EtOH + FA (EtOH or other alcohol, FA as co-solvents), with the ability to tune the surface tension of the solvent, providing a potential means for wetting a range of surfaces, and suitable for the spin-coating process. Further experimental details for procedures (1)–(3) are as follows:

(1) Nanocomposites by the infiltration–polymerization process

First, an EtOH solution of BST nanoparticles (20 mg ml$^{-1}$) is spin-coated onto a substrate to generate a thin film with a typical thickness of 200–400 nm. The film is dried at 80°C on a hot-plate to remove EtOH residue. Once dry, the film is immersed in FA for infiltration. After 30 min at room temperature, the film is withdrawn and dried on a hot-plate (60–90°C) for 0.5 h to gently initiate polymerization without evaporating the monomer, followed by heating at 120°C for 5 h for network polymerization.

(2) BT(BST)/FA (FA as the sole solvent)

BT(BST) nanocrystals are dispersed in FA solvent to a concentration of 20 mg ml$^{-1}$ using a regular sonicator to give a stable solution. FA has a higher surface tension (38.2 mN m$^{-1}$) and higher viscosity (4.62 mPa S) than EtOH solution (22 mN m$^{-1}$ and 1.074 mPa S, respectively), and a lower surface tension than water (72 mN m$^{-1}$). Thus, a dispersion of BST nanocrystals/FA is more suitable for drop casting or potential printing. Following deposition, the film is dried on a hot-plate (60°C) for 0.5 h to gently initiate polymerization without evaporating the monomer, followed by heating at 120°C for 5 h for network polymerization.
10 ml of FA is mixed with 250 µl of p-toluenesulfonic acid (or PA, 0.025 M in EtOH solvent) which is used as an acid catalyst (concentration 6.25 × 10⁻⁴ M). Then, 400 ml of BST nanocrystal solution (with EtOH as the solvent, 20 mg ml⁻¹) is mixed with 50–100 ml of the above FA solution. The mixture is shaken for 5 min prior to use.

Alternatively, a BST/FA/EtOH solution is prepared by simple mixing of a BST/FA solution (20 mg ml⁻¹, no acid catalysts) and EtOH solvent with a volume ratio of 4:1–2:1.

The final BST/FA(PA)/EtOH solution (EtOH and FA as co-solvents) shows good wettability and can disperse well on oxide substrate surfaces, such as glass or Si/SiO₂ wafers. A BST/FA/EtOH solution is prepared by simply mixing a BST/FA solution (20 mg ml⁻¹) and EtOH solvent with a volume ratio of 4:1–2:1. The BST/FA/EtOH solution (EtOH and FA as co-solvents) shows equally good wettability on similar substrate surfaces. Following deposition, the film is dried on a hot-plate (60–90 °C) for 0.5 h to gently initiate polymerization without evaporating the monomer, followed by heating at 120 °C for 5 h for network polymerization. The nanocrystals are self-assembled to a closely packed thin film with the evaporation of the low-boiling-point EtOH solvent (78 °C) while a suitable fraction of the high-boiling-point FA solvent (170 °C) remains trapped in the nanocrystal thin film.

### 2.3. Characterization

The x-ray powder diffraction (XRD) of nanocrystal samples was measured using a PANalytic x-ray diffractometer with Cu Kα radiation. Phase, crystallinity, stoichiometry and phase purity were determined by this method (see supporting information figure S1 available at stacks.iop.org/Nano/24/415602/mmedia). Transmission electron microscopy (TEM) was performed on a JEOL 100CX microscope. Particle size, uniformity and the discrete nature of the nanocrystals was verified (see supporting information figure S2 available at stacks.iop.org/Nano/24/415602/mmedia). Scanning electron microscopy (SEM) was performed on a Zeiss Supra55VP field emission SEM. Thin films were cross sectioned by cleaving and analysis.

To prepare metal–thin insulator (dielectric) film–metal devices (MIM capacitors) the dielectric measurement was performed on thin films sandwiched between two crossed Au or Al electrodes with a crossed area of 1 mm × 1 mm. The thin film was made on glass and flexible substrates (25 mm × 25 mm) with 16 electrodes. Multiple spin-coatings (two to six) can be applied to achieve layer structures in the 80–400 nm range. The frequency dependence of the capacitance, dielectric loss and ESR were measured using an Agilent 4294A Precision Impedance Analyzer. A comprehensive description of the dielectric performance measurement is given in [35].

### 2.4. Printing

Two methods, dispenser printing and spray coating, were used to fabricate capacitors with printed dielectric layers made from the aforementioned nanoparticle dielectric inks. For the dispenser printer, an EFD Ultimus V dispenser has been verified to work with inks with viscosities of 1 cP to 80 000 cP through a nozzle of known internal diameter and using air pressure to drive the process (pressures of up to 100 p.s.i. with 5 ms pulsing capability). The dispenser printer has 1 ml repeatability. The dispenser setup has a programmable x–y–z stage with an accuracy of 0.1 µm and two cameras to align the dispenser tip and to observe the dispenser tip during the printing process. For medium to high viscosity inks, off-the-shelf needle tips were used. For low viscosity inks, tips were made in-house using a micropipette puller, which makes tips down to 1 µm inner diameter. The complete printing process is programmed using the BASIC programming language. For the spray coating process, an Iwata airbrush, modified to enable precise servo control of the trigger position, was used to deposit nanoparticle dielectric thin films using the same EFD Ultimus V dispenser controller and programmable x–y–z stage to control the deposition. Nitrogen gas was used to transport nanoparticle ink droplets to the printed surface. The parallel plate capacitor test structures were fabricated on glass substrates using thermally evaporated Al electrodes and dispenser-printed or spray-coated nanoparticle dielectric films. The thermal evaporation of aluminum and subsequent formation of the electrodes was carried out using an Edwards Auto 306 or a Cressington 308 R thermal evaporator. Laser-cut stainless steel shadow masks were used to pattern the electrodes. The experiments conducted with the thermal evaporator produced aluminum electrodes that were 100–300 nm thick, with the electrode thickness controlled using a crystal monitor during deposition. Alternating layers of evaporated electrodes and printed dielectric were successively deposited to form three-dimensional (3D) multilayer capacitor structures. Preparation of the dielectric layer was followed in accordance with the experimental procedure described in 2.3.

### 3. Results and discussion

#### 3.1. Modeling of a self-assembled nanocrystal thin film and the importance of effective dielectric constant

The nanocomposite thin films studied herein can be considered as a 0–3 type composite of high k nanocrystal fillers (granular) distributed in a continuous dielectric polymer host matrix. It must be emphasized that for any capacitive or gating effect to be meaningful, the effective dielectric constant, ε_eff, of the dielectric thin film layer must be assessed as a whole. Particles with a very high dielectric constant embedded in a polymer matrix may sound appealing, but unless the volume fraction of the high k component is in the majority there will be negligible impact on ε_eff. An effective dielectric constant for the composite thin film can be predicted by a modified Kerner model with correction of the volume fraction from 0–1, expressed as [4]:

\[
\varepsilon_{\text{eff}} = \frac{\varepsilon_h \cdot \varepsilon_f + \varepsilon_f \cdot \varepsilon_v \cdot (A)(B)}{\varepsilon_h + \varepsilon_v \cdot (A)(B)},
\]

where \( A = \frac{3\varepsilon_h}{\varepsilon_f + 2\varepsilon_h} \) and \( B = 1 + \frac{3\varepsilon_f \cdot (\varepsilon_f - \varepsilon_h)}{\varepsilon_f + 2\varepsilon_h} \).

\[ (1) \]
where $\varepsilon_h$, $v_h$ and $\varepsilon_f$, $v_f$ are the dielectric constants and volume fractions of the host and filler, respectively. The modified Kerner model and variations were obtained from Maxwell electrostatic theories and related boundary conditions [43, 44]. The modified Kerner model takes into account the influence of the particle–particle dipolar interactions and their effect on the surrounding host medium, and is therefore a reasonable approximation for a high volume fraction of fillers. For a pure nanocrystal thin film, the host is the air that stays within the void space of the nanocrystal filler (schematic 1). The result shows that the effective dielectric constant of the composite thin film is independent of the size of the granular filler, i.e. the model is effective for predicting the dielectric constant of a continuous dielectric film with nanoscale fillers, while the size only affects the dielectric constant of each individual nanoparticle. Hence, for comparing the effects of the dielectric constants of filler and matrix with the volume fraction of the fillers, equation (1) can be expressed as:

\[
\frac{\varepsilon_{\text{eff}}}{\varepsilon_h} = \left[\varepsilon^2 + 4\varepsilon + 4 + 2v_f\varepsilon^2 + 2\varepsilon v_f\right]^{-1} - 4v_f + 9v_f^2(\varepsilon - 1)\left[\varepsilon^2 + 4\varepsilon + 4 - v_f\varepsilon^2 - \varepsilon v_f\right]^{-1} + 2v_f + 9v_f^2(\varepsilon - 1)^{-1},
\]

where $\varepsilon = \varepsilon_f/\varepsilon_h$. (2)

The corresponding results (figure 1) show that a more efficient way of increasing the effective dielectric constant, $\varepsilon_{\text{eff}}$, is to increase the volume fraction of the filler. However, it is well known that the limitation of closed packing of homogeneous hard spherical particles is about 0.74, i.e. there is a fundamental limitation for increasing the effective dielectric constant through increasing the packing density of spherical particles. Further, it has been reported that $\varepsilon_{\text{eff}}$ may reach a maximum at a volume fraction of 50–60% and decrease with further increasing the volume fraction, showing a departure from the modified Kerner model, most likely because the porous structure arising from nanocrystal packing cannot be filled up by a polymer with a large molecular volume [4]. With a host–filler composite model, consideration of an additional third phase—that of persisting void space—becomes increasingly important at high volume fractions. Even if void space is <3% of the volume fraction, the contribution to $\varepsilon_{\text{eff}}$ is far from negligible. Void space can be considered a second type of filler for the host–filler composite model. The equations which can be used to predict the effective dielectric constant of composited film with the presence of three phases can be expressed as follows [4]:

\[
\varepsilon_{\text{eff}} = \varepsilon_h + v_f (\varepsilon_f - \varepsilon_h) a_v + v_f (\varepsilon_f - \varepsilon_h) a_f - 4v_f + 9v_f^2(\varepsilon - 1)\left[\varepsilon^2 + 4\varepsilon + 4 - v_f\varepsilon^2 - \varepsilon v_f\right]^{-1},
\]

where $a_v$ is the electric field concentration factor for the corresponding $r$ phases (void and filler), $\varepsilon_v$ and $\varepsilon_f$ are the dielectric constant and volume fraction of the void, and $s$ is the depolarization factor (1/3 for spherical particles). Equation (3) is a recursive equation; hence while evaluating $\varepsilon_{\text{eff}}$ with the presence of some voids, the dielectric constant of void, filler and volume fraction of filler were set as constants. The results (figure 1) indicate that $\varepsilon_{\text{eff}}$ can be optimized by increasing the volume fraction and dielectric constant of the filler up to a point, but consideration of the dielectric constant and volume fraction of the host becomes highly significant, and equally effective a means to maximize $\varepsilon_{\text{eff}}$.

Based on the modeling study, it is concluded that an efficient approach to increase $\varepsilon_{\text{eff}}$ is to (i) increase the packing density of nanocrystals and (ii) replace the intercrystal void space with some inorganic or polymer species with higher dielectric constants. It is noted that improving $\varepsilon_{\text{eff}}$ is best achieved through a combination of (i) and (ii), rather than focusing solely on the dielectric constant of the nanoparticles. Improving interconnection/interaction between nanocrystals is also very important for enhanced properties because it can further increase the density of polarizable dipoles in thin films.

For conventional polymer/nanocrystal composites, it is difficult to mix polymer and nanocrystals so well that the packing density of nanocrystals can be increased up to 60 vol% without generating porosity because of the large volume of the macromolecules. Different from the conventional nanocomposites, a new strategy is explored that involves a monomer precursor such as FA with small molecular weight and size that can easily infiltrate the thin
after in situ uniform dispersion of BST nanocrystals in poly(FA) (PFA) microporous zeolite. The strong interactions also provide nanosized pore channels such as in mesoporous silica or voids. It was reported that FA can effectively infiltrate even solution, and also FA can effectively infiltrate the intercrystal nanocrystals can be readily dispersed in FA to form a stable of the nanocrystal surface and FA solvent/monomer: the interactions between OH groups alcohol. (2) FA molecules have strong affinity with BT(BST) with water and is soluble in common organic solvents such as advantages of FA include the following. (1) FA is miscible and is compatible with various solvents [46]. The main solvent because it shows good affinity with BST nanocrystals (FA) and polyfurfural alcohol (PFA). (b) Dielectric constant and loss behavior over a wide frequency range (100 Hz–1 MHz), as shown in figure 2. (5) FA is hydrophilic and has a particularly strong affinity with BT(BST) nanocrystals, which makes it an excellent solvent for the nanocrystal dispersion (stable for ~months with no sedimentation).

Uniform, continuous and crack-free BST nanocrystal thin films of variable thickness (60 nm–1 µm thick) were prepared on metal electrode-coated substrates (Si/SiO₂, glass, flexible plastic) by multiple spin-coatings of the nanocrystal suspension at room temperature followed by baking in air at 80°C to remove residual EtOH solvent (figure 3). It is known that identical hard spherical particles may reach maximum closed packing density at 0.74 (face-centered cubic or hexagonal close-packed); for the uniform BST nanocrystals, the spin-coated thin films were estimated to have a packing density of ~68% or a porosity of ~32% by comparing the change of film thickness before and after sintering at 950°C and by assuming 100% densification after the sintering (supporting information figure S3 available at stacks.iop.org/Nano/24/415602/mmedia). The void space in the porous thin film was normally occupied by air, which has a low dielectric constant (~1) and a low breakdown voltage (~3 V μm⁻¹). The nanocrystals may also take up moisture from the air due to their hydrophilic surface property, causing a dramatic change in dielectric constant and dielectric loss behavior over a wide frequency range (100 Hz–1 MHz), discussed in detail in this paper. For dielectric applications of the nanocrystal thin film, the nanocrystal surface requires passivation and the intercrystal void space needs to be filled.

3.2. Pure BST nanocrystal thin films created by evaporatively driven self-assembly

Typical synthesis of BST nanocrystals involves solvothermal processing of a mixture of barium isopropoxide, strontium isopropoxide and titanium isopropoxide in EtOH/water solvent. The XRD profiles show a high purity perovskite phase with no addition of other impurities such as BaCO₃ (supporting information figure S1 available at stacks.iop.org/Nano/24/415602/mmedia). The spherical nanoparticles are single crystals with a narrow size distribution and tunable sizes of 7–30 nm diameter based on TEM and SEM results. Larger sizes are also possible. Fourier transform-infrared (FT-IR) spectra of the nanocrystals clearly show a broad peak in the range of 3400–3500 cm⁻¹ associated with surface hydroxyl termination groups (~OH), indicating the hydrophilic property of the nanocrystal surface (supporting information figure S6 available at stacks.iop.org/Nano/24/415602/mmedia). The gel-like products can be easily redispersed in EtOH or FA solvent after a general ultrasonication treatment to provide a stable nanocrystal suspension (~20–40 mg ml⁻¹), which is suitable for thin film fabrication using a spin-coating or printing process. FA molecules have a particularly strong affinity with BT(BST) nanocrystals, which makes it an excellent solvent for the nanocrystal dispersion (stable for ~months with no sedimentation).

Figure 2. (a) Scheme of molecular structures of furfural alcohol (FA) and polyfurfural alcohol (PFA). (b) Dielectric constant and loss of a pure PFA thin film. The dielectric constant is calculated to be ~5@1 MHz.
Figure 3. SEM images of uniform and continuous Ba_{0.7}Sr_{0.3}TiO_{3} (BST) nanocrystal thin films prepared by spin-coating and evaporatively driven assembly: (a) top-view; cross-sectional views of (b) 140 nm film, (c) 250 nm film and (d) 400 nm film.

Figure 4. SEM images of a pure BST thin film before (a) and after (b) FA infiltration and polymerization. (c) Cross-sectional view of (b). Thin films with ~30 nm BST nanocrystals are shown (d) Tapping model AFM image of the BST/PFA thin film. (e) Room temperature piezoresponse phase images versus tip bias of a pure BST film (f) a BST/PFA composite film (b); the blue and red line are trace and retrace lines, respectively.

Figures 4(a)–(c) clearly show that the void space in the pure BST thin film is greatly reduced after the FA treatment. The polymer/nanocrystal vol% composition is estimated to be 30/70 (±4). The surface roughness can be improved after the FA treatment. Atomic force microscopy (AFM, tapping mode image; figure 4(d)) shows that the BST (30 nm)/PFA composite thin film (100–500 nm thick) has lower root mean square (RMS) crystal sizes (RMS = 16.2 nm) compared to that of a pure BST (30 nm) nanocrystal thin film (RMS = 22.6 nm). It indicates that the BST nanocrystal thin film becomes smoother, showing a reduced surface roughness after FA treatment. When compared to physical deposition of polymers on top of a nanocrystal thin film, such as the deposition of PVP [35] or the evaporation of parylene C [27, 45] (see supporting information figure S5 available at stacks.iop.org/Nano/24/415602/mmedia), the polymerized FA (PFA) resides primarily within the intercrystal space of a closely packed nanocrystal thin film. It can be shown that no additional top layer is formed, confirming that a 0–3 nanocomposite is produced as opposed to a layered 2–2 nanocomposite structure. A layered structure, while producing a useful barrier layer, tends to cause an overall decrease in the effective dielectric constant of the thin film [45].

FT-IR spectra (supporting information figure S6 available at stacks.iop.org/Nano/24/415602/mmedia) shows the decrease of OH vibration peaks (~3400 cm\(^{-1}\)) and the increase of CH vibration peaks (~2900 cm\(^{-1}\)) when BST nanocrystals were treated with FA, which strongly supports the notion that the FA molecules react with surface hydroxyl groups of the BST nanocrystals and become almost fully polymerized after in situ heat treatment (scheme 1).
The polarization behavior of nanocrystal thin films before and after FA treatment was studied by piezoelectric force microscopy (PFM) at room temperature. PFM measures the mechanical response when an electrical voltage is applied to the sample surface with a conductive tip of an AFM. In response to the electrical stimulus, the sample below the tip then locally expands or contracts, which can be detected and measured in terms of piezoresponse. Figures 4(e) and (f) shows that the piezoresponse phases and hysteresis loops are different for a BST nanocrystal thin film before and after FA infiltration/polymerization. No obvious piezoresponse can be observed for a pure BST film because there is neither coupling nor interactions between isolated single domain nanocrystals, and the asymmetric loop may be attributed to the pinning effect of space charges resulting from the intercrystal voids (figure 4(e)). On the contrary, a sharp 180° piezoresponse phase switching can be observed for the BST/PFA composite film with a very small hysteresis loop (figure 4(f)). It suggests that, after the FA treatment, the intercrystal void space is occupied with PFA and therefore interactions or coupling between individual nanocrystals have been established. The role of PFA can be approximated to a stress coupling medium between neighboring nanocrystals that are exhibiting a piezoelectric response. The resonance curve (figure 4(f)) is probably due to the electromechanical coupling effect of the composite film, suggesting a high level of homogeneity within the film. The result confirms that in situ polymerization of FA in the intercrystal void space occurs, and that interactions between previously isolated nanocrystals in the thin film can be achieved. Such a technique could have a great deal of potential for further increasing the macroscopic polarization in nanocrystalline BST. In addition, since there is negligible hysteresis in the BST thin film when the nanocrystal is <30 nm in diameter, the nanocrystal/PFA thin film is expected to present a stable dielectric constant and low dielectric loss in a wide temperature range.

Figure 5. Measured capacitance and dielectric loss (dissipation loss, tan δ) of thin films (a) before and (b) after FA treatment. FA treatment has the ability to dramatically reduce loss characteristics and prepare functional capacitors from self-assembled nanocrystal films. The FA is polymerized in situ, leading to a transparent network of PFA and creating a sealed nanocomposite 3–0 film in which the filler volume fraction is $0.68 > V_f > 0.62$.

3.4. Dielectric properties of BST/PFA nanocomposite thin films

A pure BST nanocrystal thin film may absorb moisture because of its porous and hydrophilic nature. Figure 5(a) shows dramatic changes of both capacitance (and therefore dielectric constant) and dielectric loss (also referred to as dissipation loss, tan δ) over the frequency range 100 Hz–1 MHz. Much higher capacitance (or dielectric constant) and dielectric loss are observed at low frequency (<100 Hz) due to the contribution from interfacial polarizations (space charges) and surface absorbents (e.g. water molecules), whose polarization direction cannot follow the frequency switching of the AC electric field. This causes a dramatic decrease in dielectric constant and loss with increasing frequency. The dielectric constant and dielectric loss ultimately smooth out at very high frequencies (>50 MHz), for which the intrinsic dielectric property of BST nanocrystals is dominant.

In contrast, the BST/PFA nanocomposite film shows a dielectric constant and dissipation loss that is extremely stable with respect to frequency (figure 5(b)), with a slight decrease in capacitance towards higher frequency, as expected. The slight increase in dissipation factor at higher frequencies is attributable to contact resistance, which typically increases to >0.1 MHz. The explanation for this marked change in performance is obviously to do with the role that FA molecules play in passivation of the nanocrystal surface and filling of the intercrystal void space through in situ polymerization. The FA molecules can easily infiltrate a BST nanocrystal thin film and fill up the majority of the intercrystal void spaces (due to the strong affinity between the nanocrystal surface and FA molecules, and possibly a favorable capillary effect). With in situ polymerization of FA upon heat treatment, the BST nanocrystal surface can be passivated and the void space can be filled up as well. The result (figure 5(b)) is a stable capacitance (or dielectric constant) and dielectric loss. In table 1, a typical capacitance density is 0.58 nF mm$^{-2}$ for a 300-nm-thick thin film (or an effective dielectric constant, $\varepsilon_{\text{eff}}$, of ~19.6) at a frequency of 1 MHz, while it is 0.45 nF mm$^{-2}$...
In addition to the aforementioned impact factors, there is a contribution from the order–disorder feature of the Ti cation [47–49], which can play a role in the dielectric constant. Although there are few reports of direct measurement of dielectric constants of individual BT(BST) nanocrystals, it is reasonable to estimate the dielectric constants using the modified Kern model (equations (1)–(3)). The crystal structure of BT(BST) nanocrystals has been postulated to be a structure containing a gradient lattice strain layer between an inner tetragonal core and a surface cubic layer with an independent thickness of 15 nm [48, 49], i.e. the nanocrystals with sizes <15 nm would likely be a pure cubic phase. Moreover, the single domain critical size of BT(BST) is calculated to be nearer 80 nm [50]. Although high effective dielectric constants of composite films and nanoparticles above thousands have been reported in a low frequency range, the high values likely originate from interfacial polarizations (space charges) due to the fact that the constants reduced to below 100 when the frequency of the applied field is higher than 100 Hz [51]. Moreover, most reported effective dielectric constants of 0–3 composite films with size of BT(BST) nanocrystal filler smaller than the critical size of single domain were not over 50 [52].

It is widely accepted that decreasing the grain size of a ferroelectric phase leads to a reduction of coherence length of the ferroelectric coupling between local dipoles and a diminished macroscopic polarization, causing a reduction in the dielectric constant. Although the crystal structure of fully grown nanocrystals appears cubic from x-ray diffraction data, Raman spectroscopy and pair distribution function analysis demonstrate the presence of non-centrosymmetric regions arising from the off-centering of the titanium atoms [53–55]. Room temperature polarization switching was also demonstrated down to ~5 nm in size for individual nanocrystals [56]. In terms of eigen-lattice vibrations and Raman active order–disorder of the cubic BT(BST) nanocrystals [15, 54, 57, 58], the dielectric constant of the room temperature cubic phase should be mainly due to the order–disorder feature and its coupling with A1 modes, i.e. c axis dielectric behavior resides in the cubic phase.

A reasonable interpretation, therefore, is that the cubic phase plays a significant role in the dielectric constant of these BT(BST) nanocrystals. The Curie–Weiss law is not applied to calculate the dielectric constant of the cubic phase attained at room temperature. An individual cubic phase at room temperature is calculated to be around 50 where the interface polarization was minimized by deactivating the interface of

### Table 1. Comparison of dielectric properties of BST nanocrystal thin films with different polymer modifications (taken at 1 MHz).

| Sample                          | Effective dielectric, \(\varepsilon_{\text{eff}}\), constant of thin film | Dielectric loss | Volume fraction of nanocrystals (%) |
|---------------------------------|------------------------------------------------------------------------|-----------------|-------------------------------------|
| A pure BST (8 nm) film (no polymer) | 15                                                                     | 0.24            | ~68                                 |
| BST (30 nm)/PFA (by spin-coating, and by infiltration/polymerization) | 34                                                                     | 0.05            | ~60*                                |
| BST 8 nm/PFA (by spin-coating, and by infiltration/polymerization) | 19.6                                                                   | 0.045           | ~68                                 |
| BST (8 nm)/Parylene (reference [27], comparison) | 10.4                                                                   | 0.039           | 2–2 structure                       |

\(\varepsilon_{\text{eff}} \sim 15\) for a pure BST thin film before the FA treatment. The increase in the capacitance density (or the effective dielectric constant) of BST nanocrystal thin film suggests that the intercrystal void space has been successfully infiltrated and occupied by PFA. In addition, the dielectric loss also remains low (~0.04–0.05) up to a frequency of 1 MHz as compared with a high loss for the pure BST thin film (see table 1), and the dielectric loss could be further reduced when the sample was well sealed to avoid moisture uptake. The corresponding experimental and simulation results can be found in the supplemental data (available at stacks.iop.org/ Nano/24/415602/mmedia).

Previously, and in direct comparison with the results reported here, we explored a technique that relies on parylene coating as a void filler as well as a moisture barrier [27, 45]. Parylene-C film can conform closely to surfaces (including edges, flat surfaces, and corners) when all sides of the surface are exposed simultaneously to a polymerizing gas (active monomer gas from decomposed precursor gas). Although parylene precursor (dimer) is decomposed to monomers and vaporized at a high temperature of 550°C, the coating process takes place at ambient temperature. SEM analysis shows limited capability to penetrate through the porous thin film and fill up the void space. It is likely that the parylene-C monomer is highly reactive and insufficiently hydrophilic to enable a process of intervoid penetration and coating, prior to formation of a polymerized network. Instead, parylene-C favors deposition on top of the film to form a dense and insulating top layer. This serves as an excellent barrier layer, produces interesting asymmetric performance of the dielectric constant. Although there are few reports of direct measurement of dielectric constants of individual BT(BST) nanocrystals, it is reasonable to estimate the dielectric constants using the modified Kern model (equations (1)–(3)). The crystal structure of BT(BST) nanocrystals has been postulated to be a structure containing a gradient lattice strain layer between an inner tetragonal core and a surface cubic layer with an independent thickness of 15 nm [48, 49], i.e. the nanocrystals with sizes <15 nm would likely be a pure cubic phase. Moreover, the single domain critical size of BT(BST) is calculated to be nearer 80 nm [50]. Although high effective dielectric constants of composite films and nanoparticles above thousands have been reported in a low frequency range, the high values likely originate from interfacial polarizations (space charges) due to the fact that the constants reduced to below 100 when the frequency of the applied field is higher than 100 Hz [51]. Moreover, most reported effective dielectric constants of 0–3 composite films with size of BT(BST) nanocrystal filler smaller than the critical size of single domain were not over 50 [52].

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nanocrystals and polymer matrix [58]. Using the Kerner model, we estimate the dielectric constant of individual 8 nm BST particles to be $\sim 57$, in reasonable agreement with previous estimates for single domain nanocrystals of BT or BST in this size regime.

To assess the mechanical strength/adhesion of the nanocrystal thin films, the standard test methods for measuring adhesion by the tape test was applied, in which Scotch tape was first applied on the film surface with force followed by being peeled off the surface. It was found that nothing was removed in the case of the BST/PFA film, but a thin layer could be peeled from a pure nanocrystal thin film. The result strongly suggests that PFA resins bond individual nanocrystals together, providing enhanced interactions between nanocrystals and between nanocrystals and substrate.

3.5. BST/PFA nanocomposite thin films from BST/FA and BST/FA/EtOH inks and printed capacitors

Since it has been shown that FA molecules have strong affinity with these types of BT(BST) nanocrystals, due to the abundance of surface hydroxyl groups, it was postulated and confirmed that BST nanocrystals could also be dispersed in FA, relying on the idea that the monomer alcohol could serve well as the dispersing solvent. The BST/FA mixture forms a transparent orange (or yellow) solution that can be stable for months without sediments (figure 6(e)). BST/PFA composite thin films can be prepared with the BST/FA ink solution in which FA is used as a solvent as well as a polymer precursor, and higher dielectric constant and low loss was attained from BST (30 nm)/PFA composite film. Since FA solvent has a higher surface tension (38.2 mN m$^{-1}$) and higher viscosity (4.62 mPa S) than EtOH solution (22 mN m$^{-1}$ and 1.074 mPa S, respectively), and a lower surface tension than water (72 mN m$^{-1}$), the BST/FA solution is a suitable candidate ink for chemical deposition or printing. The wettability of the BST/FA ink solution can also be tuned with mixed solvents of FA and EtOH (typically with a volume ratio of 4:1) for coating and spraying applications. When BST/FA/EtOH ink solution was drop-coated or spin-coated on a substrate, the nanocrystals were first self-assembled to a closely packed thin film with the evaporation of the low-boiling-point solvent EtOH (78°C) while the void space in the thin film traps the high-boiling-point solvent FA (170°C) that can eventually be converted into polymerized FA. The SEM images in figure 6 show that nanocrystal/PFA can form a close-packed, uniform thin film with thickness from nanometers to micrometers without any phase separation, and the nanocomposite thin film is denser than a pure BST thin film with intercrystal voids occupied with poly(furfuryl) alcohol, PFA (figures 6(a) and (b)).

Smooth BST/PFA nanocomposite thin films can be prepared by printing transparent BST nanocrystals/FA ink solution.
including the electrode preparation, remains the same. The rest of the process, instead of the drawing or painting that is characteristic of traditional methods like spin-coating because it allows us to pattern the deposition without masking, while using a minimal amount of material. The dispenser printing technique uses a 32-gauge (~100 µm inner diameter) dispenser tip, brought close to the surface of the substrate such that a droplet of material is formed connecting the surface to the tip. The tip is then rastered, leaving a film of material behind on the substrate. Backpressure is maintained on the needle to prevent increases or decreases in flow. For wider area capacitor devices, a spray coating technique for large-scale dielectric film deposition is also demonstrated. This method uses a flow of pressurized air to atomize the nanoparticle ink and eject it out a nozzle towards the substrate. This printing method occurs on a 3D heated stage as with the previous dispenser printing process. The primary difference is that material is deposited in droplets brought to the surface by flowing air, instead of the drawing or painting that is characteristic of the dispenser printing technique. The rest of the process, including the electrode preparation, remains the same.

Multilayer capacitor structures of up to six dielectric layers were fabricated using the spray coating process (figure 8) and interleaved electrode layers. The SEM cross-sectional view clearly demonstrates the ability of the method to prepare a multilayer capacitor. The evaporated aluminum electrode layers are approximately 300 nm thick, and spray-coated BST/PFA dielectric layers are approximately 1 µm thick. Measured capacitance normalized to area and dissipation factor for a representative sample of printed six-layer capacitors is shown in figure 8. The distribution, attributed to variations in the thickness of the layers, is observed to be narrow. An average capacitance density of 0.83 nF mm$^{-2}$ and an average dissipation factor of 0.06 was measured at 1 MHz for this set of devices.

4. Conclusion

Chemically synthesized nanocrystals, combined with a novel deposition–polymerization technique, afforded the ability to prepare nanocomposite films with an effective dielectric constant of the film that is tunable according to nanoparticle size, and with effective film dielectric constants of up to 34. Wide area and multilayer capacitors up to 8 cm$^2$ and 190 nF are reported, for which the building block is an 8 nm nanocrystal. The approach relies on evaporatively driven assembly of perovskite nanocrystals with uniform size distributions in a tunable 7–30 nm size range, coupled with the use of low molecular weight monomer/polymer precursor chemistry that can infiltrate the porous nanocrystal thin film network post-assembly. The intercrystal void space (low $k$ dielectric volume fraction) is minimized, while simultaneously promoting intercrystal connectivity and maximizing the volume fraction of the high $k$ dielectric component. Such a method supports well the model for optimization of the dielectric constant for a multicomponent system. We report a stable dielectric constant and low dielectric loss over a wide frequency range of up to 1 MHz. Furfuryl alcohol, showing good affinity to the surface of (Ba$_3$Sr)$_2$TiO$_7$ nanocrystals and miscibility with a range of solvents, is demonstrated to be ideal as both a carrier solvent and later intercrystal void filler for the production of nanocomposites with up to >60 vol% dielectric oxide. The nanocrystal/furfuryl alcohol dispersions are suitable for thin
Figure 8. Schematic of deposition steps for multilayer capacitor fabrication (top left); SEM cross-section of a six-layer capacitor (top right). Aerial capacitance density (left), and dissipation factor (right) for a representative sample of printed six-layer capacitors. Each color line is a multilayer capacitor with corresponding dissipation (same color).

film fabrication by chemical deposition techniques, including spin-coating, printing or a spraying process. Fabrication by spin-coating and printing allows variable capacitor device structures to be prepared.

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