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Integrated Powder-based Thick Films for Thermoelectric, Pyroelectric and Piezoelectric Energy Harvesting Devices

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Abstract—Energy harvesting devices based on piezoelectric, pyroelectric and thermoelectric materials offer an attractive solution for battery- and wire-less sensor nodes for a range of sensor applications. Current devices are typically fabricated using semi-manual approaches leading to higher costs and reduced yields as well as significant material wastage. Powder-based thick film devices have been shown to be capable of harvesting mW-levels of power while the associated printing technologies offer commercially attractive fabrication solutions.

This article provides a review of examples of recent piezoelectric, pyroelectric and thermoelectric powder-based thick film energy harvester devices and outlines potential fabrication techniques, ink compositions, and ways to reduce processing temperatures that can be used to create integrated thick film energy harvesting devices. The key to the creation of such devices is the management of thermal budgets and processing environments to ensure the functional properties of the thick films are maximised.

Index Terms—Energy harvesting, environmentally friendly manufacturing techniques, materials processing, piezoelectric devices, thermoelectric devices, thick film devices.

I. INTRODUCTION

The move to distributed wireless sensor networks is often heralded as a solution to ubiquitous monitoring and control of energy consumption (in offices, factories and homes), structural and vehicle health, manufacturing processes as well as human health and wellbeing. Without the need for hard wired data or power connections, distributed sensors would be installed with minimal disruption to operation while bringing significant savings through improved productivity. With this vision come new challenges; particularly those associated with the supply of power. While easy to implement, battery technologies have a finite life span and the need to maintain and replace the batteries represents a significant investment; especially where the sensor nodes are in remote or difficult to access locations such as offshore facilities, within vehicle structures or inside the human body. With the ever decreasing energy demands of sensor platforms and wireless communications technologies, coupled with improvements in power densities of energy harvesting (EH) there now exists the possibility of delivering prolonged operation without the need for regular battery maintenance and replacement.

The most abundant power sources for harvesting applications are solar, thermal and mechanical vibrations [1] with power densities of 100-1000 W/cm² available from direct sunlight and waste heat. The proportion of this that can be harvested quickly drops to μW/cm² levels with typical levels of 150-15,000 μW/cm² from outdoor solar, 5-100 μW/cm² from indoor lighting, 200-250 μW/cm³ from vibrations and 10-100 μW/cm² for thermal [2], [3], [4]. Photovoltaic (PV) devices are often viewed as the default solution, with a capability of generating mW/cm² power densities in bright sunlight and μW/cm² levels indoors [5], [6], yet there are numerous applications where PV harvesting may not be the most applicable solution. Engineering structures are typically housed indoors, operate both day and night and tend to be located in dusty locations. Furthermore sensors are often required within structures, airframes and vehicles and by their very nature such structures

tend to produce both heat and vibration. In industrialised societies up to 60% of the energy generated is wasted in the form of heat [7] while in automotive applications only 20% of the energy stored in the fuel is used to operate the car with 70-75% of the waste energy being dissipated as heat through the exhaust or radiator [8].

There exist multiple technologies to convert mechanical movement into electrical energy included magnetic induction, electrostatics, fluid flow, and piezoelectric effect. Of these piezoelectric devices are particularly attractive due to their ability to be scaled, limited moving parts, and no requirement for priming power.

Likewise there also exist a number of technologies to convert heat into electrical energy including turbine technologies, heat engines, thermionic emitters and thermoelectric generators. Of these thermoelectric generators offer the advantages of an absence of moving parts, quiet operation, light weight, scalability, and the ability to harvest energy from relatively low temperature sources [9], [10]. While frequently used for temperature control, thermoelectric generators (TEG) typically exhibit efficiencies around 10% making them attractive for EH and energy recovery applications despite being ill-suited for primary energy generation applications [11].

Like thermoelectric devices, pyroelectric devices possess the same range of advantages. These materials, related to piezoelectric materials, are capable of generating electrical energy when subjected to temperature fluctuations.

In all three cases, powder-based thick film technologies offer an attractive balance between power, price and manufacturability for commercial energy harvesting devices. This paper reviews examples of powder-based thick film technology applied to energy harvesting and outlines challenges and opportunities of fabrication.

TABLE I
EXAMPLES OF THICK FILM PIEZOELECTRIC AND PYROELECTRIC ENERGY HARVESTERS REPORTED IN LITERATURE

Architecture	Process	Active material thickness (μm)	Substrate thickness (μm)	Dimensions L x W (mm)	Power (μW)	Power density ($\mu\text{W}/\text{cm}^3$)	Operational frequency (Hz)	Ref
Bimorph	Screen	20 (x2)	n/a	6.5 x 5.5	33.2 @ 1 g	-	344	[3]
Bimorph	Screen	55	none	18 x 9	-	25-33@0.5 g	227	[12]
Unimorph	Screen	65 (x2)	250	20 x 8	400	-	230	[65]
Unimorph	Screen	22	12.3	(0.38-0.58)x 0.4	-	-	68-154 x 10 ³	[66]
Unimorph	PSG/spin	4	50	5 x 17	15.4 @ 1 g	97.9 @ 1 g	89	[4]
Unimorph	Aerosol	15	20	8 x 6	200 @ 1.5 g	137.5 @ 1.5 g	112	[14]
Unimorph	Tape cast	230	250	60 x 30	-	2083	8.2	[67]
Pyroelectric	Screen	60-100	500	-	-	-	$\sim 10^3$	[23]

II. ENERGY HARVESTERS

A. Piezoelectric energy harvesters

The majority of piezoelectric energy harvesting systems make use of one of four basic configurations [6]: extension, lateral, shear or hydrostatic. By their very nature, film based fabrication routes lead to the production of piezoelectric elements that have small dimensions through the thickness with respect to dimensions in the in-plane directions (fig 1) with the effect that film based energy harvesters are dominated by cantilever-like structures [12]. These typically exhibit low resonant frequencies, low structural volumes and produce a high strain in the piezoelectric material [13]. Piezoelectric materials and devices offer the advantages of high energy conversion efficiency and the ability to scale the device architecture. The power generated by such devices is proportional to the square of the coupling coefficient meaning that utilising high k materials such as PZT offers distinct advantages in terms of harvestable power [14].

Power extracted by mechanical harvesters is enhanced by maximising the mechanical energy transmitted to the piezoelectric element [6] with the effect that maximum power can be extracted

when large displacements ($P \propto d^2$) at high frequencies ($P \propto f^3$) occur. Large displacements necessitate large structures which in turn tend to oscillate at low frequencies. Given the greater importance of frequency there is a drive, from that perspective, of decreasing the size of the energy harvesting devices. However, as piezoelectric harvesters are scaled down in size their natural resonant frequency soon exceeds 1kHz which is significantly higher in frequency than the available environmental vibrations [4]. Reducing the scale of devices too far results in a reduction in this conversion efficiency as thin films often fail to match the properties exhibited by their parent material due to substrate clamping effects. In addition, the voltage generated by thinner films is lower [15].

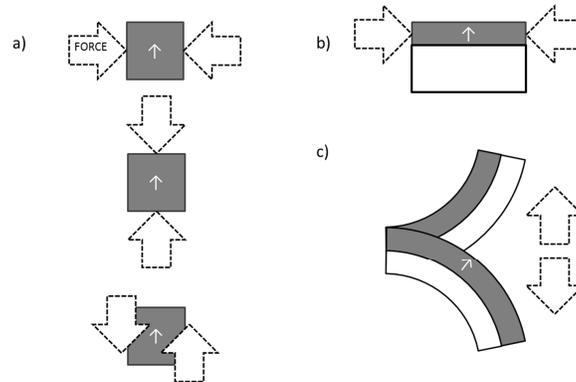


Figure 1 a) lateral, extension and shear modes of operation found in bulk piezoelectric materials, b) lateral excitation in film based devices utilized by cantilever structures (c)

This places a limit on the minimum appropriate size of a device which coincides with a requirement for thick films in the range 5-100 μm . The requirements for support materials pushes silicon and alumina (common substrate materials for PZT thick films) to the limit of performance due to their brittle nature and potential exposure to harsh environments [4]. There is an increased drive to move away from Si substrates due the relative high cost of materials, complicated and expensive process and inherent brittleness which may potentially limit applications in areas of high mechanical vibration [14] and lead to catastrophic, as opposed to safe, failure modes. Metallic substrates offer a viable alternative yet pose challenges due to their tendency to oxidise at high temperatures (as required for processing of the PZT films). Oxidation resistant substrates, such as stainless steel, WC-Co [16] and titanium [17], offer one route to overcome this issue while processing in an oxygen deficient environment is another. Care needs to be taken with this second route as reduction of the PZT may occur when the oxygen partial pressure is too low. For example, in the case of copper there exists a processing window ($10^{-7} < p\text{O}_2 < 10^{-11}$) where the copper remains unoxidised and the PZT is not reduced [15]. Further oxidation resistance can be accomplished by applying a thin protective layer such as ZrO_2 [18], [19], TiO_2 , [20] or high density sol gel active ceramic [21]. An alternative approach is to deposit a metal layer on top of the functional film before removing the sacrificial substrate [22]. This has the advantage of dramatically increasing the range of materials that can be combined. Conflicting requirements exist for cantilever-type harvesters. One the one hand positioning the piezoelectric layer far from the neutral axis of bending increases the power generated, while on the other hand the increased thickness of the cantilever increases its stiffness making it less able to interact with natural vibrations [12].

B. Pyroelectric energy harvesters

Related to piezoelectric materials, pyroelectric materials are able to generate electrical currents when subjected to a temperature change. While significantly less common than piezoelectric EH

devices the use of thick film pyroelectric materials also offers significant advantages over comparable bulk materials due to a much reduced thermal mass allowing higher duty cycles to be achieved. PZT thick films deposited by screen printing and sintered at 950°C were shown to generate currents of between 0.23 and 0.30 μA and voltages of 185-320V when subjected to a temperature fluctuation of 70K [23]. Despite the use of films only 60-100 μm thick the typical duty cycle was limited to 200 s due to the thermal mass of the films and the 500 μm thick alumina support wafer. Faster cycle times can be achieved by removing the substrate. However, pyroelectric energy harvesting will remain a niche application as thermal fluctuations tend to occur at relatively low frequencies, often at length scales of minutes and hours. In comparison, ambient mechanical vibrations often occur at frequencies of 100's of Hz.

C. Thermoelectric energy harvesters

Traditional thermoelectric generators (TEGs) are constructed from bulk materials that are shaped into small mm scale blocks and subsequently arranged into thermoelectric modules using semi-manual methods. The typical structure employed in these systems is a transverse, or π , architecture where the individual thermoelectric p- and n-type pairs are arranged thermally in parallel but electrically in series. A variation of this architecture is the unilayer approach [24] which uses either the n-type or p-type material. Here the individual thermoelectric elements are still linked thermally in parallel and electrically in series with the connecting electrical connections now running top-to-tail linking the hot and cold sides of the TEG. While such structures can be produced using thick film technologies, film based manufacturing techniques also open up the possibility of utilising in-plane, or lateral, architectures [25]. In such structures the thermal flux no longer passes from the top face to the bottom face through the device, but instead flows parallel to the film (fig 2). Significant losses [26] can be encountered if the thermal conductivity of the substrate is comparable to that of the thermoelectric materials. This loss can be mitigated by creating suspended beams (much like the cantilever-type structures found in piezoelectric harvesters) that reduce the parasitic transmission of thermal energy [27]. The disadvantage of such membrane structures is the reduced mechanical robustness and difficulty in mounting the devices against the heat source and radiator structures.

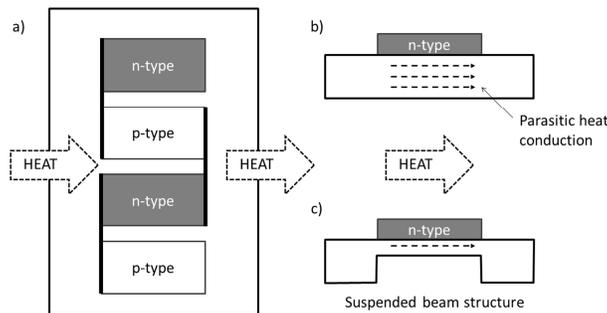


Figure 2 a) top view of in-plane film based thermoelectric generator, b) cross section, highlighting potential for parasitic heat conduction, c) suspended beam structure designed to reduce parasitic heat conduction.

TABLE II
EXAMPLES OF THICK FILM THERMOELECTRIC ENERGY HARVESTERS REPORTED IN LITERATURE

Architecture	Processing	Active material thickness (μm)	Elements	Seebeck coef. ($\mu\text{V/K}$)	ZT	Power factor ($\alpha^2\sigma$) mW/mK^2	Power density ($\mu\text{W/cm}^3$)	Ref
In-plane (n) $(\text{Bi,Sb})_2\text{Te}_3$ (p) $\text{Bi}_2(\text{Se,Te})_3$	Screen	80	5	123	-	0.06	-	[34]
In-plane (unimat) Bi_2Te_3	Dispenser	120	62	200 @ RT	0.31	0.27	130 (20 K ΔT)	[31]
Film only Bi_2Te_3	Screen	80	-	140	0.61 (@RT)	2.1	-	[29]
Film only $\text{Ca}_3\text{Co}_4\text{O}_9$	Aerosol	55	-	150-170 (@300- 700°C)	-	-	-	[36]
Film only ZnSb	Screen	-	-	355-365 (@ 330- 480K)	-	-	-	[30]
$\text{Bi}_{0.85}\text{Sb}_{0.15}/\text{epoxy}$	Screen	-	-	97	-	-	-	[70]
Ag-Ni	Screen	-	-	22-25 @RT	-	0.6-1.1 @ -RT	30 (200 K ΔT)	[71]
Multilayer (n) LaSrTiO_3 (p) Ni-Mo	Multilayer	(n) 100 (p) 25	50	(n) 20 @ RT (p) 153 @ RT	(n) 0.32 @623K (p) 0.04 @623K	-	450 (360 K ΔT)	[11]
In-plane (n) Bi_2Te_3 (p) Sb_2Te_3	Co- evaporation	-	8	(n) 248 (p) 188	(n) 0.93 @ 300K (p) 0.26 @ 300K	(n) 4.87 @ 300K (p) 2.81 @ 300K	-	[9]
Π Cu/Ni	Electro- plate	150	51	20.6	-	-	0.012 (0.12 K ΔT)	[27]

The majority of reports of film based energy harvesters have focused on $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ materials deposited by co-evaporating [9], [28], [25] thin films (1-1.5 μm thick) to create in-plane architectures or electroplating [27], [26] thick films (50-70 μm) to create π architectures. The values of ZT reported for the co-evaporated films were in the region of 0.26-0.97 [25], [9] and comparable to those of the corresponding bulk materials. There have been fewer reports of powder-based thick film processing techniques [29], [30], [31], [32], [33], [34] such as screen printing, being used due to the tendency of alloy films to oxidise during the high temperature processing used. With the increased interest in oxidation-resistant ceramic thermoelectric materials, powder based thick film processing technologies offer a commercially attractive route for low cost manufacture.

Multilayer fabrication technologies, as used in the construction of multilayer capacitor structures, can be used to create a third type of thermoelectric energy harvester architecture [11]. Here alternate p- and n-type materials are sandwiched together with interweaved electrodes that make alternate contact with the electroded hot and cold faces of the TEG. Heat flux passes along the length of the thermoelectric material, as with the in-plane structures, but in the absence of substrate materials parasitic heat loss is minimised occurring only through the thin electrode structures. Power densities of up to 450 mW/cm^2 were reported for SrTiO_3 based ceramic multilayer structures operating at a ΔT of 360K.

While $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ systems are the dominant choice of material for thermoelectric devices designed to operate near to room temperature there is much interest in thermoelectric materials that are more resistant to oxidation, chemical degradation, and that exhibit lower toxicity [35], [36]. Here materials such as doped ZnO [37], [38], doped SrTiO_3 [39], [40], $\text{Ca}_3\text{Co}_4\text{O}_9$ [36], and NaCo_2O_4 [41] materials have been investigated for bulk applications. Given the similarity between these materials and those typically used for piezoelectric applications there is a great deal of commonality between the requirements for, and approaches to, fabricating thick film piezoelectric and

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thermoelectric materials and devices.

The drive towards smaller scales and lower cost manufacturing techniques, both for piezoelectric and thermoelectric devices, means that semi-manual assembly routes are becoming progressively less viable [31] and automated printing type fabrication routes are becoming more commercially attractive. Tables I and II give details of some thick film based EH devices reported in literature.

To bring about this transformation in manufacturing it is necessary to manage the conflicting demands for high functional materials properties and material compatibility as high processing temperatures are typically required to ensure densification yet also lead to degradation of materials through oxidation, interactions and volatilisation of elements with an associated loss in stoichiometry. Screen printing is frequently used to create thick film structures as it offers a relatively quick and well established route to create films between 10 and 100 μm thick with relative ease. However there also exist a range of other film forming techniques, such as dip, spray, spin and electrophoretic coating, as well as rapidly advancing direct write capabilities such as ink jet, pad and pen printing which also offer viable routes to manufacture thick film devices. Direct writing technologies offer the advantages of reduced material wastage, flexibility in design and the ability to create complex shapes.

Irrespective of the fabrication route used a set of common requirements remain for creating powder based thick film devices. Due to the range of processes available only a brief review of the opportunities and challenges is presented here. Readers are directed to the more comprehensive textbook by the author on the subject [42] to gain a better understanding of the individual processes.

III. FILM INTEGRATION

A. Powder preparation

All thick film processing techniques are related through their use of a suspension of powder that is deposited onto the required substrate. Typically the powder used is that of the required final product, but in some cases this may not be necessary. Due to the low melting point of Bi/Sb-Te type materials ($\sim 425^\circ\text{C}$ for Be_2Te_3 [31]), and hence high interdiffusion rates of elements at moderate temperatures, it is not necessary to use powders of the final composition [30]. Instead the base elemental powders are blended and then reacted together during the thermal treatment used to process the films. Where this interdiffusion is incomplete and residual pure metallic phases remain in the structure the thermal conductivity of the film is increased resulting in reduced performance [30].

Where in situ formation is not possible or undesirable, mechanical alloying can be used to create the desired alloy materials before they are blended with the appropriate carriers to create a printable ink [31], [34]. In the case of metal alloy systems the appropriate metallic particles (e.g. Te, Sb, Bi) are milled in an oxygen free environment to prevent oxidation. With oxide materials [43] oxygen need not be eliminated during the milling process. A high proportion of milling media (15-30 times the weight of powder) is used to ensure that the starting powders are reduced in size through mechanical fracture and that sufficient energy is transferred to the powders to cause chemical blending.

The more common route to create complex ceramic materials is through mixed oxide calcination. Typically the starting reagents (usually metal oxides or carbides) are mixed together and calcined at temperatures between 700 and 900 $^\circ\text{C}$ to encourage interdiffusion of atomic species and the formation of the desired compounds. On cooling the powders are again milled to break up agglomerates and form the optimal powder size before being blended into the required inks for printing. The elevated temperatures used during mixed oxide processing may lead to a difficulty in controlling the composition of the powders due to the volatilisation of elements and inclusion of

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impurities.

TABLE III
EXAMPLES OF INKS AND PROCESSING CONDITIONS USED IN THE PRINTING OF THERMOELECTRIC, PYROELECTRIC AND PIEZOELECTRIC THICK FILM DEVICES

	Powder Synthesis	Powder	Carrier	Binder	Thickness (μm)	Temperature (°C)			Ref
						Drying	Burnout	Sinter	
Screen	Mech	76 wt% Bi-Te	22 wt% Toluene	2 wt% Polystyrene	80	60 (hours)	250/10m	-	[34]
Screen	In situ	75 wt% Bi-Te	20.3 wt%	-	-	120/15 m	200/5m	400/30m (N ₂) 550 (N ₂)	[29]
Screen	In situ	79.6% ZnSb	18%	None	171	150/10 m	330°C/20m	380/20m (N ₂)	[30]
Screen	Mech	36-64 vol% Bi-Te	64-36vol% epoxy resin	n/a	100-120	-	-	300 (Ar)	[31]
Screen	Calcination	80 wt% PZT	19.2 wt%	0.8 wt%	80-200	150	-	950	[68]
Screen	Calcination	PZT	Terpineol	Ethyl cellulose	20-40	120/30 m	550/1 h 700/30 m	900/60m	[56]
Screen	Calcination	PZT	-	-	30	120/10 m	-	925/30m	[19]
Screen	Calcination	PZT	Terpineol & ethyl acetate	PVB-PVAc	22	-	-	800/10m	[66]
Screen	Calcination	Complex perovskites	Terpineol	Ethyl cellulose	24-30	-	-	1000-1250/2 h	[69]
Tape	Calcination	PZT	-	PVB	30	vacuum	600/3 h	950-1150	[67]
PSG	Calcination	98 wt% PZT	4 wt% sol	None	4	450/3 m	700/10 m	700/15m	[4]
PSG	Calcination	60 wt% PZT	40 wt% sol	None	20	250/60 s	450/15 s	720/20m	[55]
EPD	Calcination	PZT	Acetic acid	None	25	-	-	900 (low O ₂)	[15]
EPD	Calcination	30 wt% Al ₂ O ₃	ethanol	PVB/PVAc	-	-	-	-	[62]

Note. Aerosol deposition annealing temperatures: Oxides 650-900°C [33], [59], Bi-Te 500-650°C [14]

Lower temperature synthesis routes include molten salt [44], [45], hydrothermal [46] and solution based processes such as sol-gel [47], [48], [49] [50] and metal salt reduction [51] which can offer better control over composition. These routes are also often favoured when high purity and small particle sizes are desired.

B. Inks

The most straightforward inks are those composed of the powder suspended in a suitable carrier fluid (e.g. water or alcohol) with the aid of dispersants or acidity control to ensure a stable suspension. Selection of appropriately small particles and narrow particle size distribution will ensure that the suspension remains stable during use and that large particles do not sediment out of the suspension over time. Often a glass frit is included in the ink to enhance bonding of the film to the substrate [29] or a sintering aid [52] to improve densification. Such additions can detrimentally affect the performance of the film material due to the presence of inactive or counter-productive, such as high thermal conductivity, second phases [30]. Examples of ink compositions and processing conditions for powder-based EH inks are given in Table III.

When processing temperatures are limited by low temperature stability substrates or electrode materials it is often not possible to bring about full densification of the powders or to cause a sol gel to decompose fully. Here powder-polymer inks may be employed to create a polymer composite film as curing temperatures need not exceed 150°C [53]. The polymer can be in the form of a thermally or UV curable thermoset such as epoxy [31], or a dissolved polymer [54], or a thermosetting polymer.

An alternative route is to use a sol gel carrier fluid (powder sol gel – PSG) which converts to the functional ceramic under moderate thermal treatments [55]. The sol-gel derived material acts to increase the density directly as well as enhancing sintering kinetics. In this case there is no undesirable second phase present and relatively high densities can be obtained through repeated

infiltration of the structure with the ceramic forming sol gel material.

C. Ink based printing

Inks containing powders suspending in liquid carriers can be deposited using a variety of techniques including screen printing [56], spin coating [55], pad printing [57], micro-moulding and spray deposition [58]. Following deposition the wet film is dried at a temperature where the carrier fluid will evaporate without boiling (60-150°C). If the carrier fluid boils the rapid release of gas will result in a highly porous film which will be very difficult to densify.

In cases where a dissolved polymer matrix ink is used the drying stage will often be the end of the process. Where thermosetting polymers are used the drying stage is used to remove any solvents added to control the viscosity while slightly higher temperatures (150-250°C) are used to cause the polymer to cure. Thermoplastic polymers require no elevated curing process, instead they are usually deposited at elevated temperatures when the matrix polymer is molten and set on cooling.

Where densification of the powder is required the film is heated to higher temperatures (300-450°C) following drying to burn out the organic binder or to convert the sol gel material into ceramic. Finally a high temperature treatment (700-900°C or up to $\sim 2/3$ melting temperature of the powder) is used to densify the film through sintering involving large scale atomic diffusion.

Direct write technologies, such as in jet printing, offer the advantages of minimising waste [31], facilitating automation [31] and allowing complex shapes to be created. The ink requirements vary depending on the printing technology employed but the components of the inks are broadly comparable to those used for screen printing.

Dispenser printing, or pen printing, uses a scanning pen-like stylus to directly deposit ink in the required locations. Powder loadings are still relatively high (36-64 vol%) [31] to ensure high green densities are achieved. Lower powder loadings are used for pad and ink jet printing due to the need to operate at slightly lower viscosities. Droplet based deposition techniques, such as ink jet printing, use inks of still lower viscosity that contain less powder. Furthermore due to the small diameter of the nozzles in the print heads, particle and agglomerate sizes are limited to below 200nm for high resolution printers. Pad printing or transfer printing inks are similar to screen printing inks.

D. Immersion based techniques.

Both electrophoretic deposition and dip coating are examples of immersion based techniques where the sample is inserted into a liquid suspension of powder particles. The creation of a stable suspension is critical to avoid time depended variations in film structure and properties. Stabilization through the control of pH (2-3 for PZT) has been successfully used to create a 25 wt% PZT suspension for dip coating. Due to the acidic nature of the suspension medium, prolonged exposure will result in leaching of Pb out of the PZT powder [15] reducing performance of the films. In such circumstances steric stabilization would be more appropriate.

In dip coating the viscosity of the suspension plays a significant role in determining the final thickness of the film [60] which is governed by the balance between the capillary, viscous drag and gravitational forces. Given that surface tension and fluid density are largely independent of powder loading the thickness of films deposited is proportional to the $2/3$ power of both viscosity and withdrawal speed. With the dependence on viscosity the thickness of the film can easily be increased without having to adjust the powder loading by adding a polymer to the ink. Using this approach it is possible to create films up to 100-200 μm thick.

The ability to create charged particles in a suspension is vital for electrophoretic deposition where an opposite electrical charge is applied to the substrate causing the suspended particles to be attracted to it [61]. The process is quick and allows complex shapes to be coated [62].

E. Aerosol deposition

High density films can be created using a high kinetic energy impacting process whereby appropriate

powders are suspended in air or nitrogen and directed at a surface at high speeds [32]. This approach has been used both for metallic and ceramic materials to produce films up to 2mm thick. Due to the ductile nature of metal alloys, such as Bi-Te, high density films can be achieved without thermal treatments. However, when used with ceramic materials [33] it is necessary to also sinter the structure to enhance densification and remove crystallographic defects due to the non-plastic nature of the ceramic powders. The exact temperature required depends on the sinterability and thermal stability of the individual ceramic; for $\text{Ca}_3\text{Co}_4\text{O}_9$ [33] this involves a heat treatment at 900°C in an air atmosphere while PZT [59] based materials can be processed at 700°C/1h in air.

Care needs to be taken to ensure the correct balance between particle size and gas velocity. The process relies on the deformation of the incident particles, due to the high speed impact, to prevent an overly porous structure from being obtained. Due to the corresponding higher kinetic energy of larger particles ($\text{KE} \propto r^3$) high impact speeds can cause the large particles to erode the substrate material. Integral to the need to establish the balance between particle size and gas velocity is the requirement to use a feedstock with a narrow particle size distribution. The underlying deformation process of the particle tends to result in a film with a textured structure and variations in material properties through the thickness. In the case of thermoelectric films the material close to the substrate exhibits an altered microstructure leading to lower electrical conduction while piezoelectric material close to the interface is often heavily clamped resulting in reduced piezoelectric properties. This near-interface region is typically 1-2µm thick such that films thicker than 5 µm exhibit no thickness dependence in properties [33].

F. Thermal treatments

With the exception of high kinetic energy impact methods, powder based deposition processes result in a porous green film that requires subsequent thermal processing to increase the density of the film. This thermal processing activates diffusion of atomic species and subsequent densification. Due to the tendency for non-oxide materials, e.g. Bi_2Te_3 , to oxidise it is necessary to use an inert shielding gas such as N_2 or Ar [29] to exclude the oxygen from the system. Thermal treatments at elevated temperatures may also have the effect of leading to the loss of volatile elements. This is evident in both thermoelectric and piezoelectric thick film materials. Bi_2Te_3 films were shown to lose mass through the loss of Te at temperatures in excess of 450°C [29]. Similar losses are observed in PZT and (K,Na)NbO₃ piezoelectric films at temperatures in excess of 700°C [19]. This loss of material can be mitigated by surrounding the film with powder of the same composition or deliberately formulating the starting powder with excess of the elements that are known to be lost. Due to the dynamic nature of sintering the thermal treatments are very time dependent, affecting both the microstructure and composition of the films.

Thermal treatments are also used to remove the carrier fluid and organic components (e.g. binders, plasticisers, dispersants) added to the inks to facilitate printing. Matters are complicated when materials with low sintering temperatures are used (e.g. metals) as sintering may commence before all of the organic components have been removed. This can lead to reduced sintering rates and trapped residual organic materials [63] that can adversely affect the properties of the the film. Long dwell times at lower temperatures can, in some cases, be used to overcome this issue by allowing more time for the organic components to be burned off.

G. Improving densities

The limitation of low processing temperatures (800-900°C) to ensure material compatibility and co-processing results in a relatively low film density when producing ceramic thick films due to reduced densification. Porosities up to 35 vol% are not uncommon in such films [3] and can be reduced through the incorporation of sintering aids [52], sol gel infusion [64] or external pressure during sintering [3], [15]. Pressure can only be applied where the substrate structure is sufficiently robust as

in the case of metallic substrates. Brittle ceramic or Si substrates, or those containing micromachined features, are generally unsuited for such treatments.

IV. CONCLUSION

Films within the thickness range of 2-200 μm have a great potential for energy harvesting applications involving piezoelectric, pyroelectric and thermoelectric devices due to their relatively high powder outputs, low materials wastage and potential to automate the manufacturing process. To achieve the required film thicknesses it is necessary to use powder based deposition processes which in turn requires the use of a thermal consolidation process. By managing the thermal budgets and processing environments it is possible to manufacture viable thick film piezoelectric and thermoelectric energy harvesting devices that exhibit potential power harvesting densities of 100-1000 $\mu\text{W}/\text{cm}^2$.

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