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Selective laser sintering of barium titanate–polymer composite films

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Abstract A selective laser sintering process has been used to consolidate electro-ceramic thin films on silicon substrates. Methods of forming pre-positioned layers of barium titanate were investigated by spin-coating the feedstock powder mixed with a commercial polymer photo-resist. The ceramic–polymer composite was deposited directly onto a nickel film which was evaporated onto a silicon substrate, pre-oxidised to form an electrically insulating layer. A range of laser processing parameters was identified in which consolidated barium titanate layers could be formed. The laser power was found to be more influential in forming sintered microstructures than laser exposure time. The microstructure of barium titanate films is sensitive to the SLS laser-processing conditions, with the optimum laser powers for the processing of the $BaTiO_3$–polymer found to be in the range 17–20 W. This article highlights the possibility of using 'direct write' techniques to produce piezoelectric materials upon silicon substrates.

Introduction

Recent developments in the field of selective laser-sintering (SLS) and -melting (SLM) have promoted the emergence of new manufacturing and design methodologies. These processes allow the rapid manufacture and testing of component geometries, made from a wide range of materials that may not have been possible using more conventional manufacturing methods. The new design freedoms born out of theses techniques have given rise to functional parts that cannot be realized by other methods [1].

SLS and SLM technologies allow a rapid design turn-around with zero or minimal tooling and secondary processing. Consequently they have reduced the timescale of concept-to-prototype transition that is the essence of rapid prototyping [2]. In the continuous selective laser sintering process, a succession of individual part cross-sections predetermined with computer-assisted design, are created from powdered materials by sintering them with an ytterbium fibre laser. A layer of the feedstock powder is pre-deposited and spread uniformly by a wiper blade; this ensures correct packing to allow optimum consolidation of the processed material. The laser 'writes' the layer pattern in the powder bed sintering the material and joining it to the previously formed build structure. Using this technique, between 25 μm and 200 μm thicknesses of material can be deposited in each layer depending upon powder morphology. This method has been applied to the rapid prototyping of a range of components from functional materials including metal heat exchangers [3], prosthetic implants [4] and shape memory actuators, amongst others [5]. 'Direct-write' methodologies such as ink-jet printing and SLS [6, 7] were recently developed to manufacture micro-electro-mechanical systems (MEM) component structures. These are complimented by polymer-based rapid manufacturing techniques such as digital light processing (DLP). Processes such as these may incorporate a 'smart' material feedstock to deliver an electromechanical response to a given change in the environment enabling mechanical or electrical actuation without the need for signal processing or an external power supply [5, 8].

Ceramic-ferroelectric materials of various types are technologically important in wide-range electrical and electronic applications. Barium titanate ($BaTiO_3$) one of the

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most technologically important ferroelectric materials and has been the subject of intense research [9]. It possesses a variety of useful properties that have the potential to be exploited in thin or thick film devices [10], such as non-volatile memory devices, electro-optic devices, thin film capacitors and pyroelectric detectors [11–13]. Therefore, a great deal of effort has been made to investigate the preparation and characterization of $BaTiO_3$ films in recent years. A variety of methods, such as sputtering [14, 15] metal organic chemical vapour deposition [16, 17], Pulsed Laser Deposition (PLD) [18–20] and hybrids of furnace/laser sintering [21] were applied to prepare such films. The manufacture of bulk or three dimensional discrete functional components and composites can be achieved using powder based fabrication routes such as conventional partial pressure furnace sintering. High shear mixing techniques have proved suitable for producing homogeneous and de-agglomerated powder/binder/solvent pastes which can be processed into net shape 3D components and devices such as discs, fibres, helices and cylinders. Selective laser sintering offers the potential of rapid prototyping ceramic components spanning geometries from films to 3D structures without the need for moulding or consolidation in the green stage.

The shape and size characteristics of feedstock powders are important in the SLS process, as it is required to flow easily when the powder is delivered to the build platform. This is of especial importance when the layers are to be 'recoated' in successive build layers to ensure uniformity through the cross-section of a part. Particles with smooth surfaces flow more readily within the powder bed leading to a higher 'loose' density. Particle shape is also an important factor as symmetrical particles pack more efficiently and consequently spherical grains are preferred due to their more efficient packing [22]. These surface and granulometry parameters of the powder are closely related to the powder material and its production process. For insulating ceramic materials, the issues of static charge and reactions with atmospheric moisture are further complications in achieving the appropriate flow-ability for this type of processing. In order to overcome these problems, one strategy is to mix the feedstock powder with surfactants, binders and solvents to make a two-phase 'ink' for printing processes. An alternative for films is to process the ceramic powder via the formation of a pre-positioned powder bed of the appropriate thickness.

This study investigates the SLS of $BaTiO_3$ in patterned powder/photo-resist pads on metallised silicon substrates shown schematically in Fig. 1. Although it has been demonstrated previously that the SLS/SLM processes can be used to manufacture functional MEMS parts in metallic materials [23], SLS has not yet found its way into the mainstream of MEMS ceramic fabrication technologies, which is the motivating factor for the present work.

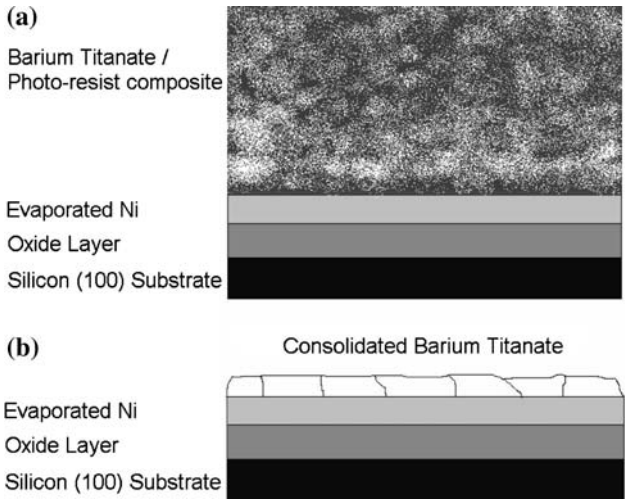

Fig. 1 Process schematic for sintering $BaTiO_3$ within a photo-resist matrix (**a**) the 'lay up' (**b**) post laser processing in the MCP Realiser™

Experimental

Prior to the SLS processing, the silicon substrate was processed using conventional clean room photolithography techniques. A SiO_2 insulating layer was grown by thermal oxidation on Si(100) wafers (10 h at 1,000 °C in air resulting in an oxide layer ≈ 200 nm in thickness) and then metallised with a thin film of Ni (250 nm) evaporated under high-vacuum conditions to serve as a bottom electrode, adhesion layer and provide additional heat sinkage.

A commercial photo-resist (Shipley 1828) was loaded with $BaTiO_3$ powder. The maximum loading was identified when spinning no longer resulted in a uniform thin film, which was found to be 75% (by weight). The maximum loading was required to ensure that a continuous layer of $BaTiO_3$ that was available to be sintered. The mixture was then ultrasonically homogenised and spin coated on wafers of 100 mm diameter. The wafers were spun in a ramped programme for 30 s at 2,000 rpm and then 90 s at 4,000 rpm. The spun-on films were then soft baked at 120 °C for 90 s, and patterned onto the Si (100) wafer with a 20 s UV exposure and developed. The protected Ni film was patterned using a 7:3 HNO_3/H_2O wet etch. The ceramic–polymer thin film was then hard baked at 140 °C for 5 min (Fig. 1a). The resulting uniform thickness of the $BaTiO_3$–polymer was measured by SEM cross-section micro-analysis.

Laser processing of the spin-coated $BaTiO_3$ thin films was performed using SLS (Fig. 1b). This is a layer-based solid freeform fabrication process. SLS is similar to SLM which involves scanning of a laser over a material interaction surface. The main difference is the partial sintering/surface melting of the powder in SLS compared full melting and resulting flow in SLM. An MCP Realizer™ was employed which is a commercial SLS/SLM workstation

with a 100 W continuous wave ytterbium fibre laser (IPG, Germany) operating with a wavelength of 1,068–1,095 nm. The scanning system used is a dual-axis mirror positioning system (Cambridge Technology) and a galvanometer optical scanner, which directs the laser beam in the x and y axis through an F-theta lens. The variable focussing optics are Sill 300 mm focal length lenses, which produce a focussed beam spot size of 60 μm diameter at 80 watts power. The sintering process was performed in an argon ambient environment. The build is controlled using the propriety control software Fusco and was programmed to write small discs with a diameter of 5 mm in the $BaTiO_3$ composite film at different laser powers ranging from 15 to 30 W, while the laser dwell time remained constant at 600 μs.

Characterisation of the laser processed $BaTiO_3$ thin films was performed using X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) with Energy Dispersive X-ray microanalysis (EDX). The crystalline phases of the films were identified by XRD (Rigaku) using CuKα radiation (0.154051 nm, 40 kV, 50 mA). The microstructures of the surface and cross-sections of the laser-processed films were investigated by electron microscopy and EDX using an S-4000 Hitachi SEM. Raman spectra were recorded using 514.5 nm radiation from an argon ion laser. The power incident on the sample was set at 17 mW. A Jobin-Yvon LabRam spectrophotometer with subtractive pre-monochromators coupled to the third spectrograph/monochromator with a 1,800 grooves mm^{-1} grating was used for recording the spectra. A Peltier-cooled charge-coupled device (80 K) detector was employed to detect the Raman signals. All of the spectra were recorded in backscattering geometry with a 50 times microscope objective.

Results and discussion

The effect of powder/photo-resist composition on spin coating of the ceramic–polymer was studied prior to laser processing. Figure 2 shows the influence of increasing the weight % of $BaTiO_3$ powder in photo-resist on the thickness of the spin-coated $BaTiO_3$ layer. From Fig. 2 it is apparent that the thickness, and maximum incorporation of ceramic powder in the spin-coated ceramic–polymer is at a maximum, when the formula is 75% (by weight) $BaTiO_3$ to photo-resist. Increasing the powder content further results in non-homogeneous films which do not yield uniform sintering properties through the film cross-section. Films with a weight-content of more than 75% $BaTiO_3$ resulted in an observable loss of homogeneity of the spin-coated layer due to agglomeration. This resulted in radial streaks in the spun resist, aggregation of powder clumps on the wafer surface and uneven spreading became more

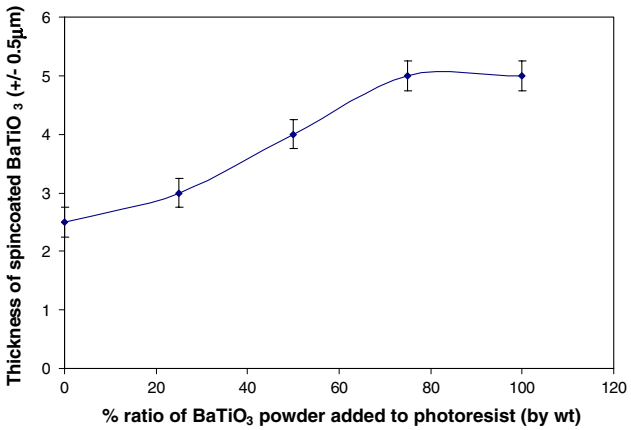

Fig. 2 Influence of increasing the wt% of $BaTiO_3$ in photo-resist on the thickness of the spin-coated $BaTiO_3$ layer due to (spin cycle at 4,000 rpm)

apparent as the relative weight of the powder increased. The optimum speed of the spin cycle was determined to be around 4,000 rpm for the 75% $BaTiO_3$ loaded photo-resist. Slower spin speeds of 2,000 and 3,000 rpm produced uneven and less homogeneous spin-coated layers. Spin speeds higher than 4,000 rpm were not possible using the spin coating unit used in this study. The first layer metallization or bottom electrode evaporated onto the SiO_2/Si(100) substrate used in this study was 250 nm thick nickel. Attempts at spin coating the ceramic–polymer formula directly onto the silicon oxide proved unsuccessful, suggesting that the metal is also required to promote adhesion between the spin-coated ceramic–polymer and silicon substrate.

Figure 3 shows SEM cross-sectional images of a series of consolidated films processed at varying laser powers. The influence of the laser power on the microstructure of the selectively laser sintered spin-coated $BaTiO_3$ powder was measured with a constant laser dwell time of 600 μs for all laser powers used. Varying the dwell time was found to have an insignificant effect on the consolidation of the powder bed over the range of laser powers investigated. It can be seen that laser powers below 15 W have little effect in sintering the $BaTiO_3$ particles in the powder bed (Fig. 3a). Laser powers in the region of 17–26 W yielded the most homogeneous laser sintered microstructures with some large spherical aggregates. No degradation of the thin nickel bottom electrode (Fig. 3b) is apparent. Laser powers of 30 W or above tend to remove or 'ablate' large regions of the spin-coated ceramic powder from the surface of the nickel causing significant damage to the planarity of the film which can be clearly seen in Fig. 3c.

Energy Dispersive X-ray micro-analysis (EDX) a cross-sectioned sample processed at a laser power of 20 mW is shown in Fig. 4. The EDX scan area of the cross-section

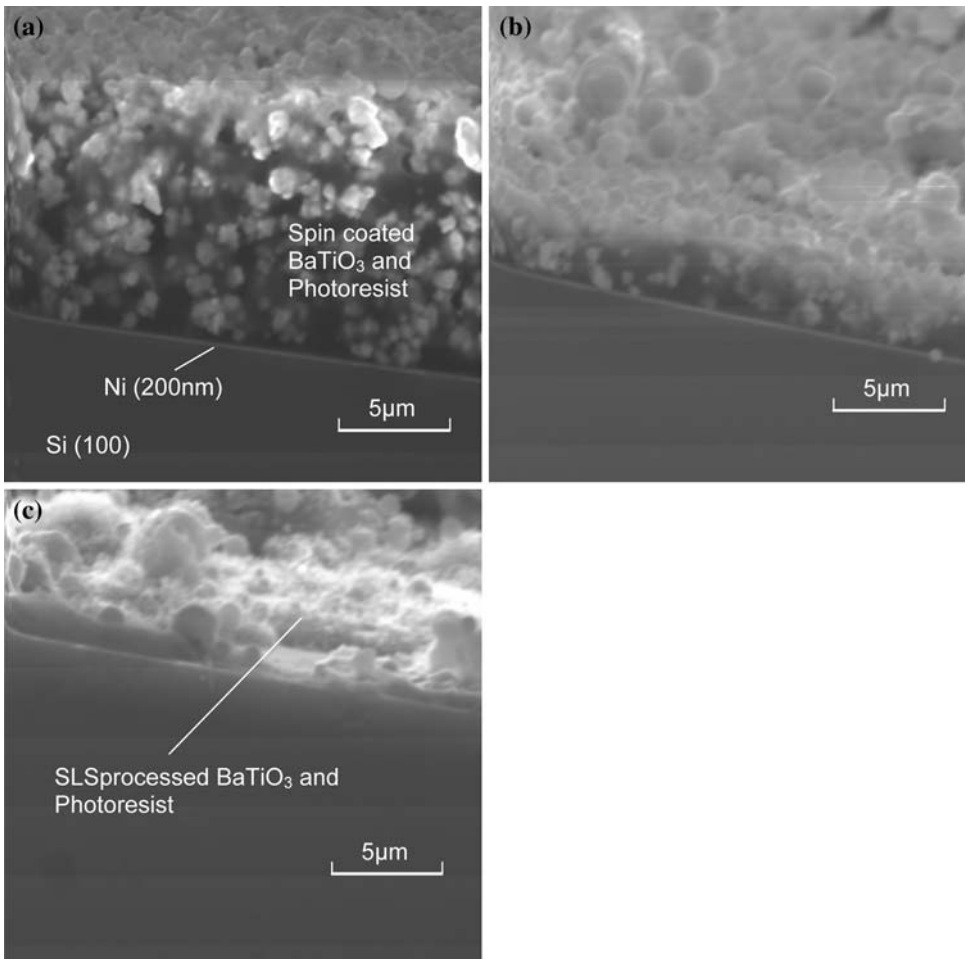

Fig. 3 SEM cross-sectional images showing the influence of laser power on the microstructure of thin film spin-coated $BaTiO_3$ powder on metallised Si(100); (**a**) 15 W, (**b**) 20 W and (**c**) 30 W

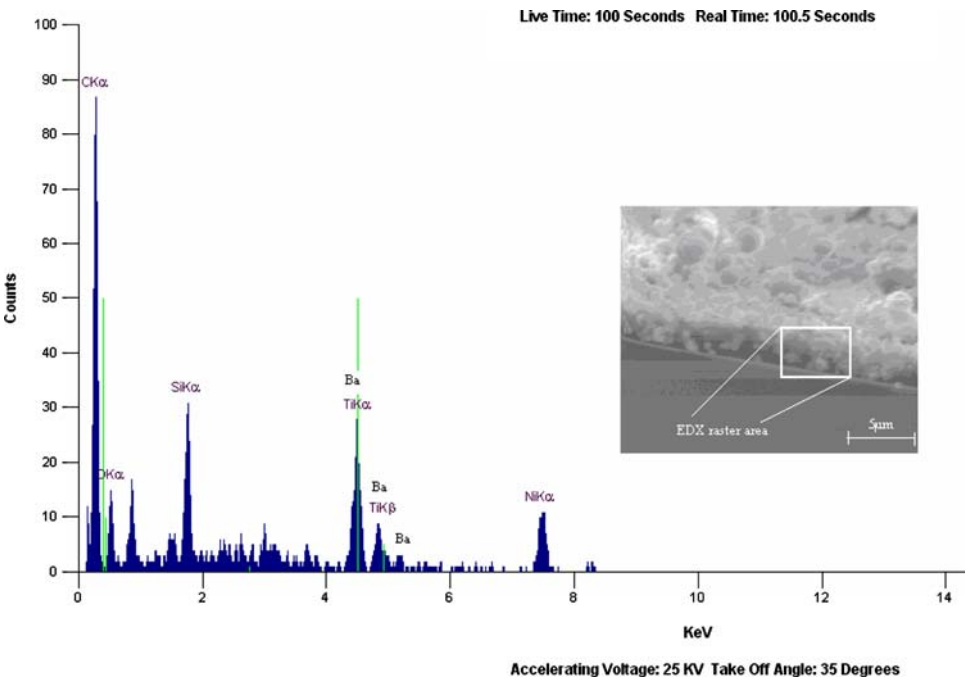

Fig. 4 Energy Dispersive X-ray micro-analysis (EDX) mapping of a cross-sectional area of SLS processed $BaTiO_3$ powder bed spin coated on a first layer (Ni) metallised SiO_2/Si(100) substrate

(inset of Fig. 4) shows the composition of the SLS processed material consists of Ba, Ti and O (0.5 keV). The data suggests that the elemental composition is not significantly modified by the SLS processing. X-ray signals are observed from the silicon substrate at 1.8 keV and the nickel metal layer (7.5 keV). The Ba and Ti peaks at 4.465 keV and 4.508 keV cannot be deconvoluted due to the inherent limited energy resolution of the EDX spectrometer used.

After SLS processing, the resulting films showed visible signs of discolouration suggesting some degradation of the original feedstock material that was white. However, the X-ray diffraction data shown in Fig. 5 indicates that the consolidation processing does not significantly degrade the bulk composition or phase of the spin-coated ceramic material. The diffraction pattern of the consolidated material shows the characteristic (100), (110), (111), (200), (210) and (211) features of $BaTiO_3$ powder (JCPDS 89-2475). Subsequent annealing of the ceramic films at 1,000 °C for 1 h in air restored the white colour of the films, but the θ–2θ reflections from the barium titanate are unchanged. The appearance of peaks at 2θ values of 37° and 43° are related to the presence of NiO in the post annealed films that would indicate undesirable oxidation of the metal film. These observations appear to indicate that the discolouration caused by sintering arises from some surface reduction or degradation of the powder particles and that post annealing can reverse the process. This assignment is not unequivocal, as it is plausible that the ablation of the photo-resist could leave residual carbon, which would be burnt away after oxidation. Figure 5b shows the diffraction patterns of $BaTiO_3$–polymer composite films sintered over a range of laser powers from 17 to 26 W followed by the same post-sintering annealing process. The diffraction patterns are characteristic of $BaTiO_3$ across the power range.

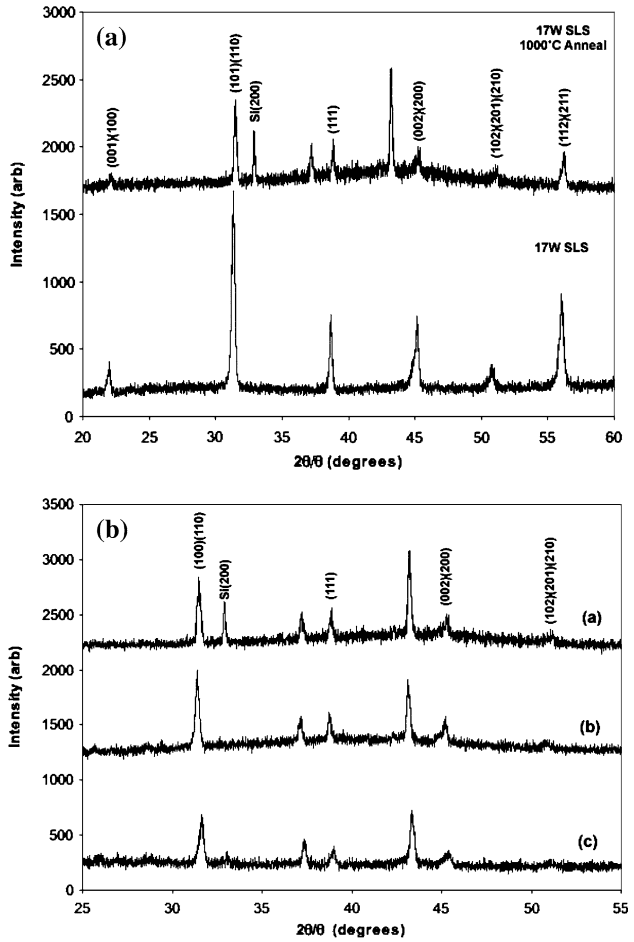

Fig. 5 XRD showing the influence of SLS laser powers and post annealing treatment on laser processed spin-coated $BaTiO_3$ films on first layer metallised Si(100)/SiO_2 substrates. (**a**) Shows the effect of post annealing treatment (1,000 °C for1 h) on SLS processed film at 17 W. (**b**) Shows the effect of increasing SLS laser powers (a) 17 W, (b) 20 W, (c) 26 W, on the spin-coated $BaTiO_3$ films on first layer metallised Si(100)/SiO_2 substrates

Barium titanate adopts a cubic phase above 393 K with the space group $Pm3m(O_h^1)$. At temperatures below 393 K it is ferroelectric with the P4mm (C_{4v}^1) structure, which further transforms to orthorhombic and rhombohedral structures at 278 and 183 K, respectively. Figure 6 shows the Raman spectra of the $BaTiO_3$/resist composites in the as-spun film (a) which exhibits a large fluorescent background arising from the polymer matrix and weak peak intensities which can be attributed to the A_1 (TO_2), E (TO_2) and A_1 (TO_3) modes of the room temperature P4mm phase.

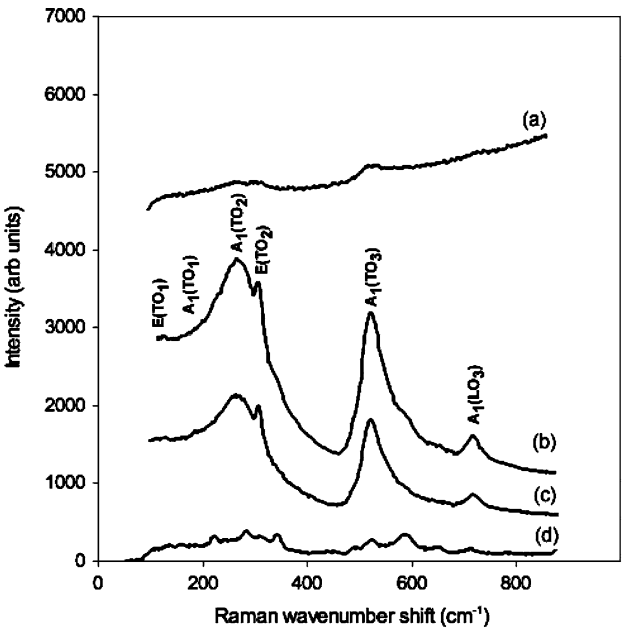

Fig. 6 Raman spectra showing (**a**) the as-spun $BaTiO_3$/resist coating; 1,000 °C post-annealed $BaTiO_3$/resist coatings exposed to laser powers of (**b**) 17 W; (**c**) 20 W; and (**d**) 26 W

After selective laser sintering of the spun film and subsequent annealing at 1,000 °C the polymer matrix is effectively burnt out leaving the crystalline $BaTiO_3$ film. The A_1 (TO_2), E (TO_2), A_1 (TO_3) and A_1 (LO_3) modes were observed at 270, 308, 525 and 725 cm^{-1} respectively. The asymmetric A_1 (TO_3) mode couples weakly with the A_1 (TO_2) mode [24, 25] and the phonon wave vector directions are randomly distributed with respect to the crystallographic axes in ceramics. This allows mode mixing and quasi-phonon modes in the spectrum. The influence of increasing the sintering laser power combined with post-annealing appears to be a reduction in the grain size. The resulting confinement of phonons in small grains materials leads to the breakdown of long-range order, activating phonons away from the center of the Brillouin zone ($k \sim 0$) and resulting in broadening and wavenumber shifts of the Raman modes. At laser powers of 26 W and above, the resulting films loose most of the characteristics of the feedstock $BaTiO_3$ powder and show some interactions with the underlying oxidized nickel have resulted. These observations indicate that only a limited range of laser powers is feasible for the formation of sintered barium titanate films from pre-positioned spin-coated barium titanate–polymer composite films.

Conclusions

The selective laser sintering process has been investigated as a method for the fabrication of electroceramic thin films on silicon substrates. Methods of forming pre-positioned layers of barium titanate have been investigated by spin-coating the feedstock powder mixed with a commercial polymer photo-resist. The composite film was deposited directly onto a silicon substrate coated with a nickel film which served to promote adhesion and uniformity during the spin-coating process. A range of laser power processing conditions were identified in which barium titanate layers could be consolidated. The microstructure of barium titanate films is sensitive to the SLS laser processing conditions, with the optimum laser powers for the processing of the $BaTiO_3$–polymer found to be around 17–20 W. Laser powers above 30 W tended to ablate areas of the film resulting in undesirable cracks and holes. These results suggest the potential for applying SLS in the consolidation of electro-ceramic films on silicon substrates. As SLS is a 'direct-write' process it has the capability of rapid-prototyping of complex structures without the need for lithographic masks and techniques. Further work is ongoing to investigate the use of other combinations of ceramics–polymer composite films including lead zirconium titanate and polyvinylidene–trifluoroethylene copolymer.

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References

1. Gebhardt A (2003) Rapid prototyping. Hanser Gardner Publications, pp 29–50
2. Venuvinod PK, Ma W (2004) Rapid prototyping-laser based and other technologies. Kluwer Academic Publishers, pp 1–21
3. Tsopanos S, Sutcliffe CJ, Owen I (2005) In: Proceedings of the fifth international conference on enhanced, compact and ultra-compact heat exchangers: science, engineering and technology, CHE
4. Hunt JA, Callaghan JT, Sutcliffe CJ, Morgan RH, Halford B, Black RA (2005) Biomatertials 26(29):5890
5. Chalker PR, Clare AT, Davies S, Sutcliffe CJ, Tsopanos S (2006) Mater Res Soc Symp Proc 890:93
6. Li X, Choi H, Yang Y (2002) Thin Solid Films 420–421:515
7. Polotai A, Breece K, Dickey E, Randall C, Ragulya A (2005) J Am Ceram Soc 88(11):3008
8. Kasai T, Ozaki Y, Noda H, Kawasaki K, Tunernoto K (1989) J Am Ceram Soc 72(90):1716
9. Wang Z, Miao J, Zhu W (2007) J Eur Ceram Soc 27:3759
10. Bihari B, Kumar J, Stauf GT, Van Buskirk PC, Hwang CS (1994) J Appl Phys 76:1169
11. Kim DH, Kwok HS (1995) Appl Phys Lett 67:1803
12. Lines ME, Glass AM (1977) Principles and applications of ferroelectrics and related materials. Clarendon Press, Oxford
13. Thony SS, Lehmann HW, Gunter P (1992) Appl Phys Lett 61:373
14. Huang CHJ, Rabson TA (1993) Opt Lett 18:811
15. Kaemmer K, Huelz H, Holzapfel B, Haessler W, Schultz L (1997) J Phys D: Appl Phys 30:522
16. Beckers L, Schubert J, Zander W, Ziesmann J, Eckau A, Leinenbach P (1998) J Appl Phys 83:3305
17. Huang CHJ, Rabson TA (1993) Opt Lett 18:811
18. Lu HA, Wills LA, Wessels BW, Lin WP, Zhang TG, Wong GK, Neumayer DA, Marks TJ (1993) Appl Phys Lett 62:1314
19. Gill DM, Block BA, Conrad CW, Wessels BW, Ho ST (1996) Appl Phys Lett 69:2968
20. Shu N, Kumar A, Alam MR, Chan HL, You Q (1997) Appl Surf Sci 109/110:366
21. Lin M-H, Lu H-Y (2002) Mater Sci Eng A 333(1–2):41
22. Morgan R, Sutcliffe CJ, O'Neill W (2004) J Mater Sci 39(4):1195
23. Ragulya AV (1998) Powder Metall Metal Ceram 37(7–8):137
24. Sanjurjo JA, Katiyar RS, Porto SPS (1980) Phys Rev B 22:2396
25. Begg D, Finnie KS, Vance ER (1996) J Am Ceram Soc 79:2666