Institution: University of Sheffield

Unit of Assessment: 13C - Electrical and Electronic Engineering, Metallurgy and Materials: Materials Science and Engineering

Title of case study: Development of a functional oxide based deposition technology allowing the introduction of new commercial products

1. Summary of the impact

Research undertaken by the University of Sheffield between 1999 and 2012 in functional oxide thin films was commercialised through knowledge transfer partnerships (KTP) with Ilika Technology. This directly led to over £1M in contracts and subsequent improvements in the commercial viability of the product base of blue-chip companies such as Toshiba, Toyota and Ceramtec and contributed to the increase in Ilika's turnover to ~£2M per annum and a growth in staff from 5 to 35 in 2012. In 2011, Ilika floated on the stock exchange with a valuation of ~£20M. The CEO has personally recognised the role Sheffield has played in establishing Ilika Technology as a limited company and in growing company revenue through contracts with leading multinationals.

2. Underpinning research

Ferroelectric thin films are used in the fabrication of non-volatile computer memories, pressure sensors and micromotors. The majority of these devices are based on the compound lead zirconate titanate (PZT), which has a unique combination of functional properties suitable for the above applications. The body of work on ferroelectric thin films that Reaney has published is recognised worldwide as having established the basic blueprint of how to control the microstructure and properties of PZT thin films deposited by sol-gel spin coating. Reaney was the first to establish directly the relationship between the use of excess PbO and the resulting microstructure/properties. He established the basic mechanism by which film orientation can be controlled and also determined how in thicker films (1 micron), porosity can result from the formation of metallic Pb particles during pyrolysis [R1, R2].

Reaney's background in ferroelectric thin film technology, his knowledge of structure and microstructure obtained from extensive studies using advanced transmission electron microscopy and his world renowned appreciation of solid state chemistry mean that he is one of a small handful of scientists capable of interacting with the SME Ilika Technology on the deposition of oxide films.

In 1999, Professor Ian Reaney (Department of Materials Science and Engineering, University of Sheffield, since 1994) was awarded an EPSRC grant, 'Multilayer sol-gel processing of thick PZT films for sensor and actuator applications' (GR/M33501/01) in which he developed an understanding of the crystallisation of sol-gel thin films. The work resulted in two papers published in international Journals [R1, R2]. Reaney has continued to study PZT thin films and has been awarded two further grants 'The effect of constraint and thickness on octahedral tilt transitions in perovskite structured thin films' (EP/D067049/1) and 'Domain wall-defect interactions in ferroelectric (EP/I038934/1) which have resulted in a number of publications in high impact factor journals.

In 2008, the Chief Scientific Officer (CSO) at Ilika Technologies and Reaney undertook a collaborative EPSRC funded proof of concept study (EP/F015259/1) to determine if compositions in the $PbO\text{-}Nb_2O_5$ phase diagram exhibit large dielectric tunability and low dielectric loss for potential applications as tuneable electronic filters. New highly promising tuneable dielectrics in the cubic pyrochlore phase field were discovered, which is now leading to optimisation and prototype device fabrication [R3, R4].

In 2004, Reaney was invited to participate in a Knowledge Transfer Partnership (KTP) with Ilika. The first KTP (No 862) entitled, 'To develop novel PbO-free piezo-electric ceramic compositions for industrial applications using Plasma Vapour Deposition (PVD) Technology', spearheaded the

development of methodologies to deposit oxide based films. Prior to this project, Ilika had expertise in metals and polymer thin films for catalysis but no background in functional oxides for piezoelectric, dielectric or ferroelectric applications. The deposition methodologies developed are described in detail in refs [R5, R6] but, in brief, a proof of concept stage was first attempted, based on the high throughput synthesis of lead zirconate titanate (PZT). After the initial experimentation, the most productive method of operation was determined to be at room temperature where deposition rates are maximised in an O_2 rich environment within the PVD vacuum chamber. This resulted in the formation of an amorphous oxide phase, which was then crystallised in a furnace to form the PZT perovskite structure, a process based on the sol-gel deposition method researched and optimised by Reaney. Compositional spreads of varying Zr:Ti ratio were obtained and structural phase boundaries determined by a combination of energy dispersive X-ray analysis, X-ray diffraction and Raman spectroscopy. Reaney's experience and understanding of amorphous to perovskite transformations in sol-gel thin film deposition was pivotal in establishing control over the microstructure and thus obtaining the desired functional properties. His appreciation of the role of excess PbO and the relationship between composition and grain structure were critical in understanding microstructure/structure/property relations leading to film optimisation. In 2009, Ilika and Reaney undertook a second KTP (No 7023), entitled: 'To develop PbO free, high remnant polarisation ferroelectric films suitable for the fabrication of non-volatile memories', which extended the collaboration for a further 3 years and extended the portfolio of complex oxides that Ilika were capable of fabricating.

3. References to the research

References that best indicate the quality of the research are indicated with asterisks (***):

R1*** Z.X. Zhou, I.M. Reaney, P.Y. Wang et al.TEM characterisation of single- and multilayer triol-based sol-gel PZT (53/47) thin films, *Journal of the American Ceramic Society*, **87(2)** (2004) 221-226. doi: 10.1111/j.1551-2916.2004.00221.x

R2*** Z.X. Zhou, I.M. Reaney, D. Hind et al., Microstructural evolution during pyrolysis of triol-based sol-gel single-layer $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films, *Journal of Materials Research*, **17(8)** (2002) 2066-2074. doi: 10.1557/JMR.2002.0306

R3 M. Mirsaneh, B.E. Hayden, E. Furman, S. Perini, M.T. Lanagan, I.M. Reaney, High dielectric tunability in lead niobate pyrochlore films, *Applied Physics Letters*, **100(8)** (2012) Article Number: 082901. doi: 10.1063/1.3687722

R4 M. Mirsaneh, B.E. Hayden, S. Miao, J. Pokorny, S. Perini, E. Furman, M.T. Lanagan, R. Ubic, I.M. Reaney, High throughput synthesis and characterisation of the $Pb_nNb_2O_{5+n}$ ($0.5 < n < 4.1$) system on a single chip, *Acta Materialia*, **59(5)** (2011) 2201-2209. doi: 10.1016/j.actamat.2010.12.023

R5 P.S. Anderson, S. Guerin, B.E. Hayden, I.M. Reaney et al., Optimisation of synthesis of the solid solution, $Pb(Zr_{1-x}Ti_x)O_3$ on a single substrate using a high-throughput modified molecular-beam epitaxy technique , *Journal of Materials Research*, **24(1)** (2009) 164-172. doi: 10.1557/JMR.2009.0008

R6*** P.S. Anderson, S. Guerin, B.E. Hayden, I.M. Reaney et al.Synthesis of the ferroelectric solid solution, $Pb(Zr_{1-x}Ti_x)O_3$ on a single substrate using a modified molecular beam epitaxy technique, , *Applied Physics Letters*, **90(20)** (2007) Article Number: 202907. doi: 10.1063/1.2738191

4. Details of the impact

Ilika Technologies Ltd focuses on three key markets, namely energy storage and capacity, materials for improving electronic component performance, and new materials that have interesting catalytic, electronic and magnetic properties. The company uses a high-throughput technology based on a modified molecular beam epitaxy system, developed by the CSO (who started the company). This is a case study demonstrating economic impact through the improved performance

of an existing business by the introduction of new processes and procedures. Specifically, the introduction of functional oxide based deposition technology into Ilika who had previously only focussed on metal and polymers. The CEO and CSO of Ilika have stated in the final reports of the KTP862 [S1] and 7023 [S2] that the know-how transferred to Ilika from Sheffield enabled Ilika to leverage contracts in excess of £1M with blue-chip companies such as Toyota, Toshiba and Ceramtec in the area of tuneable devices, piezoelectrics, and lithium-ion batteries which rely on oxide based films and ceramics [S3]. These and similar contracts constitute ~ 30% of the revenue generated by Ilika since 2008 [S3]. The contracts undertaken by Ilika using technology embedded by Reaney have led to improvements in the product base of a number of multinationals, broadly within the arena of 'materials for energy', such as micro-batteries, and illustrate the breadth of impact realised through his research.

The crucial role of the underpinning research in realising this economic impact both within Ilika and via their contracts with blue-chip multinationals, is summarised by the CEO as follows:

> "*Professor Reaney's research has been instrumental in the economic growth and stock market flotation of Knowledge Transfer Partner Ilika Plc. The knowledge he provided to the company allowed it to develop entirely new expertise in functional oxide based deposition technology and a more sophisticated approach to ceramics that has allowed it to access new markets and new customers, and grow existing relationships. For example, Prof Reaney's techniques are employed for the automotive hybrid and electronic car market and, in terms of impact since 2008, have generated revenue of £3m. IP has also been generated with Toyota in 2011, resulting in three patents (JP2011222415A, WO2011/128976A1, WO2011/128977A1), the opportunity to work further with Toyota, and also to exploit that patent technology in other markets."*

Another product opportunity that has arisen via the ability to design and produce micro-batteries is for the smart home market – to communicate and link up electrical devices. These batteries can be powered by a small PV type device, have long life, and low levels of leakage. This has resulted in Ilika filing for two patents themselves and for the Company to develop a whole new range of applications and markets.

The company has also expanded its workforce from 5 employees to 35 since 2004, and the CEO estimates that a quarter of staff are currently working on projects directly attributable to the new technology gained from Professor Reaney's research. Ilika's success has also benefited the UK and wider global economy. Since 2004, Ilika has spent an estimated £800k on consumables, infrastructure and equipment in the UK and a further £700k on equipment globally. Ilika floated on the London Stock Exchange with shares valued at £20M [S4]. The CEO has personally recognised that without Reaney's involvement it would have been considerably more difficult to develop the company in areas that rely on oxide based technology for their main applications and devices, as follows:

> "*Ian's knowledge and expertise is globally pre-eminent and has been an extremely important factor in the growth of the company*."

Reaney now acts as a consultant with Ilika to advise on future and current oxide based functional material programmes.

5. Sources to corroborate the impact

S1. Final report on Knowledge Transfer Partnership 862, submitted 2008.

S2. Final report on Knowledge Transfer Partnership 7023, submitted 2012.

S3. Information directly supplied by CEO of Ilika Technologies Ltd, which confirms the outputs from the work of the University of Sheffield brought new technology base to the business leading to new market capture. Letter on file.

S4. www.ilika.com