Institution: Queen's University Belfast

Unit of Assessment: 9 (Physics)

Title of case study: Failure in Multilayer Ceramic Capacitors (MLCC's) for AVX Ltd.

1. Summary of the impact (indicative maximum 100 words)

The provision of professional analysis and advice has created an economic impact of $0.6M with AVX Ltd, a leading supplier of electronic components within the Kyocera Group. This information was pivotal to AVX Ltd retaining a major contract, for multi-layer ceramic capacitor (MLCC's) supply through to the automotive manufacturer Volkswagen Group. Our intervention addressed a reliability issue in the MLCCs and allowed them to improve processes and revise manufacture protocols. The impact drew on previous collaborative research with AVX Ltd and innovative methodologies for preparation of micro and nanoscale samples of materials in capacitors in academic research.

2. Underpinning research (indicative maximum 500 words)

In the mid-1990's, academic staff, Bowman and Gregg, initiated a research activity to map and understand the properties of micro- and nanoscale ferroelectrics. Ferroelectrics were receiving significant commercial interest in numerous capacitor applications/markets. A key element in the early research was the fabrication and functional characterisation of very simple thin film planar capacitor structures based on titanates. These were investigated in an attempt to elucidate fundamental reasons for the dramatic collapse in permittivity, that reduces device capacitance, with decreasing device thickness and which was not understood at the time [*Reference 1*]. This was of great importance as titanates are of principal use for both commercial ceramic capacitors (circa 10^{12} components manufactured p.a.) such as the X7R devices and for novel high-K perovskite-based Dynamic Random Access Memory (DRAM) systems conceptualised at the time.

While capacitor structures made in-house did allow useful insights [*Reference 2*], it soon became clear that ferroelectric (dielectric) properties were so sensitive to defects, introduced during thin film growth, that a radically new experimental approach was needed. Thus, from 2002, a wholly novel programme in which thin film capacitors were made from small slices of ferroelectric cut from high purity single crystals using Focused Ion Beam (FIB) milling [*Reference 3*] was initiated. Functional characterisation of these relatively unclamped defect-free systems demonstrated that the permittivity did not necessarily collapse with dielectric thickness decrease at all and that the effect could be engineered out in real devices. Such insights were published in a number of articles between 2004 and 2009 [*Reference 4, 5*].

At the same time as this FIB micro-machining work progressed that included further insights into damage mitigation [*Reference 6*] we commenced a Knowledge Transfer Partnership (KTP) with AVX Ltd. The three-year project from 2005-2007 worth £123K was titled "*Critical interfaces in currently produced capacitors*". The project engaged M.M. Saad, primary author of Reference 3, as the Knowledge Transfer Associate. The project combined precision micro-machining by FIB to isolate known and potential defects and regions of MLCCs for detailed chemical and structural analysis that would then be followed up via TEM (Transmission Electron Microscopy) and STEM (Scanning Transmission Electron Microscopy). In the programme the parts investigated covered X7R specifications for in consumer electronics applications through to those for high voltage automotive usage. This provided Bowman and Gregg with significant bilateral experience in handling of parts and establishing common terminological ground for the use of the research methodologies and results to be applied to evaluating the defects that arise in such commercial components.

We note that associated research in thin film capacitors remains an active area of endeavour, most recently via Technology Strategy Board (TSB) support of a project "*Advanced capacitors for energy storage*" with Syfer Technology worth £164K in 2010-12 and has received significant recent press attention http://goo.gl/p1kp12. Such collaborations have tapped various aspects of the ferroelectrics expertise developed in Queen's, but microscopy and FIB-processing knowledge has been crucial in all collaborative research to date.

3. References to the research (indicative maximum of six references)

For each reference we provide data on the journal ranking within ISI classification area/s by ISI Journal Impact Factor (IF), the actual Journal Impact Factor and the number of cites the article received on the ISI Web of Knowledge to September 2013.

References 1-3 illustrate both quality of the underpinning research and evidence to the impact, while references 4-6 provide the latter.

[1] *"Investigation of dead layer thickness in $SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3$/Au thin film capacitors"*, L. J. Sinnamon et al., Applied Physics Letters, **78**, 1724 (2001). http://dx.doi.org/10.1063/1.1356731 (17th of 125 in Physics – Applied, IF 3.8, 123 cites).

[2] "*Exploring grain size as a cause for "dead-layer" effects in thin film capacitors*", L.J. Sinnamon, et al, Applied Physics Letters, **81**, 703 (2002). http://dx.doi.org/10.1063/1.1494837 (17th of 125 in Physics – Applied, IF 3.8, 77 cites).

[3] *"Intrinsic dielectric response of ferroelectric nanocapacitors"*, M. M. Saad, et al, Journal of Physics: Condensed Matter **16**, L451 (2004). http://dx.doi.org/10.1088/0953-8984/16/41/L04 (18th of 69 in Physics – Condensed Matter, IF 2.55, 96 cites).

[4] *"Size Effects on Thin Film Ferroelectrics: Experiments on Isolated Single Crystal Sheets",* L. W. Chang, et al, Applied Physics Letters*,* **93**, 132904 (2008). http://dx.doi.org/10.1063/1.2990760 (17th of 125 in Physics – Applied, IF 3.8, 31 cites)

[5] "*Settling the Dead Layer Debate in Nanoscale Capacitors*", L. W. Chang, et al, Advanced Materials **21**, 4911 (2009). http://dx.doi.org/10.1002/adma.200901756 (4th of 125 in Physics – Applied, IF 13.9, 25 cites).

[6] "*Strategies for gallium removal after focused ion beam patterning of ferroelectric oxide nanostructures*", A. Schilling, et al, Nanotechnology **18**, 035301 (2007). http://dx.doi.org/10.1088/0957-4484/18/3/035301 (16th of 125 in Physics – Applied, IF 4.0, 16 cites)

4. Details of the impact (indicative maximum 750 words)

Through the longstanding interaction with AVX Ltd the company was aware of our unique academic research involving FIB micromachining allied to microscopy of ferroelectrics to reveal intrinsic behaviour and identify consequences of defects to capacitor behaviour.

In 2011, AVX Ltd encountered a reliability problem concerning specific MLCC product ranges. Through their Tier 2 customers Lear Corporation and Johnson Controls Inc. who on behalf of their Tier 1 customer Volkswagen Group (for VW and Audi) reported that the Volkswagen Group had revised the environmental specification for MLCC (case sizes 0603 and 0805) for automotive applications [*Source 1*].

Under revised environmental stress conditions at the customer site and subsequently replicated in the AVX Ltd. factory, of increased humidity and temperature, the supplied parts where exhibiting unacceptable failure rates. "*The automotive industry is one of the most demanding markets for MLCC with failure rates often pushed toward no more than 1:10^9 parts"* [*Source 1*]. This arises because both the owner and the public on the road perceives particular brand of vehicle to have broken down and to not associate the breakdown with failure of a supply chain component.

AVX Ltd made available a selection of operational and failed parts for our investigation along with a technical brief on their electrical testing to date on the basis that they "… *were aware of the research in ceramic capacitors and in particular the innovative focused ion beam methods applied to ferroelectrics and capacitors that had been developed at Queen's*" [*Source 1*].

With our previous research in more sensitive nanoscale capacitors allied to our expertise acquired via the KTP project "*handling 'green' and finished parts*" we were familiar at handling their commercial product and that was seen as '*beneficial*" [*Source 1*].

A MLCC is comprised of a stack of several hundred interleaved ferroelectric ceramic and nickel electrode layers. Electric contact to the device is then made via end terminations of two layers of nickel and tin. The tin layer provides the region for solder contact to be made. In the particular product that exhibited failure the electrode is connected to the MLCC via a stress relieving silver-polymer composite layer.

We were able to adapt and formulate a modification to our usual FIB based micromachining protocols used in the creation of nanoscale capacitors to develop a workflow that would allow us to extract representative sample pieces for evaluation and inspection. This adapted workflow meant that we were able to perform successional slicing of the MLCC's in a series of testing locations.

Electron microscopy imaging and associated chemical analysis was performed on slices extracted and in regions from where they had been removed. It became evident that the failure under humidity test was not arising from damage to or degradation of the more sensitive ferroelectric ceramic material, but instead it was originating at the interface of the electrode layers and the ferroelectric ceramic.

A major challenge, over the last fifteen or so years, in all research and engineering of ferroelectric capacitors has been the move away from noble metal electrodes and contacts to base metals such as nickel. Nickel will unfavourably oxidise at the interface with the oxide-based titanate ferroelectric. In this case of these failed parts further detailed examination on FIB machined sections led to an unexpected cause of the actual device failure. The final overcoat of tin was introducing additional stress due to a high deposition rate that was exacerbating the delamination of the nickel from the ferroelectric. That delamination then provided a path for the metal in the polymer composite to escape under application of voltage and caused part failure.

A report [*Source 2*] of the investigation and outcomes was prepared and a de-briefing meeting at AVX Ltd arranged and the findings presented. In addition to the technical staff of AVX Ltd at Coleraine also present were engineers from their subsidiary plant in the Czech Republic that undertakes the electro-plating of the metal electrode layers.

In addressing the reach and significance of this impact we note that while AVX Ltd is based in Coleraine, Northern Ireland (NI), they are part of AVX Corporation who are in turn part of Kyocera Electronic Devices in the Kyocera Group.

As of 2012 AVX Ltd. employed 317 people in NI and had a £108M turnover; no profit figures are available [*Source 3*]. The factory operates a subsidiary activity in the Czech Republic. Product development and principal manufacture in undertaken in Coleraine and then the parts are shipped to the Czech Republic for the plating and sample testing before supply to customers.

On the basis of our technical report and de-briefing meeting, informed by data acquired using our FIB micromachining protocols AVX Ltd were able to undertake timely revisions to their manufacturing program. This eradicated the part failures to an accepted tolerance level and thus allowed them to deliver on the contract to their Tier 2 customers Lear Corporation and Johnson Controls Inc. who then in turn supply to their Tier 1 customers VW and Audi [*Source 1*].

AVX Ltd. have confirmed that the value of the international contract was "*valued at $0.6M"*. [*Source 1*].

5. Sources to corroborate the impact (indicative maximum of 10 references)

1. Letter from Business Development Manager, AVX Ltd. Coleraine

2. Technical Report to AVX Ltd., 19 May 2011

3. Northern Ireland's Top 100 Companies – The Belfast Telegraph, 30 April 2013, http://www.belfasttelegraph.co.uk/business/top-100-companies/company-list/87-avx-29216579.html