

Electrostatic spray-assisted vapour deposition, first reported in *Materials World* in March 1998, is an innovative and cost-effective method for the fabrication of films and nanocrystalline powders. Here, the inventor of the process, Kwang-Leong Choy, describes further advances and applications for this novel process.

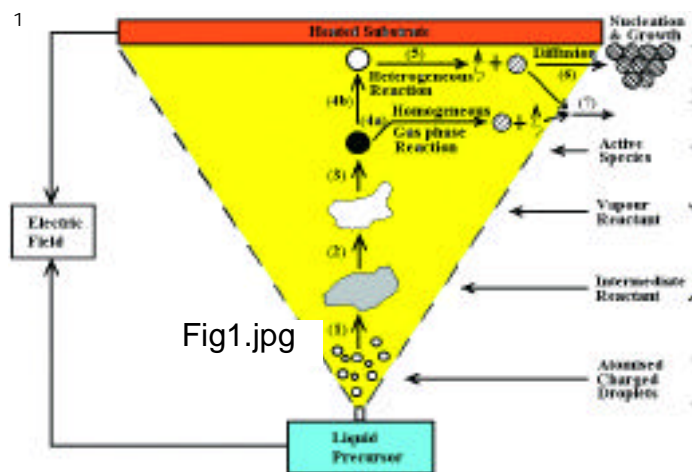
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Material manufacturers are under increasing pressure to reduce the cost of fabrication at the same time as improving the quality, reliability and performance of the manufactured materials. This is particularly the case where coatings are applied, although the electrostatic spray-assisted vapour deposition (ESAVD) technique, developed by Kwang-Leong Choy, offers the potential for a significant reduction in production costs. Moreover, it has the capability of increasing the material's efficiency and providing a microstructure that enhances its performance.

The process has natural advantages over conventional ceramic processing methods, such as tape casting, screen printing and calendring. These tend to have large shrinkage problems associated with the removal of polymeric binders and plastisers in subsequent sintering steps, so reducing the film quality for large area fabrication. Films also tend to crack during sol-gel processing and their thickness tends to be limited to about

one micron for each layer, with the process being repeated to obtain the required film thickness. Semiconducting routes, such as plasma spraying, tend to produce porous and splat-like structures, which limit the scope of applications.

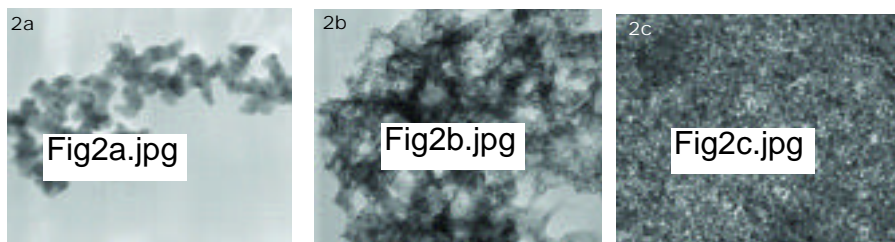
Fabrication based on the vapour phase deposition techniques seem to be the preferred processing route for producing materials of high purity with a controlled microstructure and stoichiometry at the atomic level, with CVD and PVD the two best-established commercial methods. However, CVD and PVD are expensive, time consuming and require large capital



A schematic diagram of the ESAVD process.

input on the reactor and vacuum system. Also, the PVD process also offers little flexibility in coating geometry owing to the line-of-sight nature of the process – consequently it is difficult to coat substrates of complex shapes.

The development of the low-cost, non-vacuum, open-air ESAVD method provides an alternative cost-effective processing method that addresses current limitations. Furthermore, the use of an electric field helps to direct the precursor towards the substrate, thus minimising loss to the surroundings and giving a high deposition efficiency (>90%), compared with CVD and PVD (which tend to be less than 50%). From the technical and economical viability evaluation, it is estimated that ESAVD provides high-performance coatings or nanopowders at a lower cost when com-



Transmission electron micrographs of $\text{Eu-Y}_2\text{O}_3$ in the form of (a) nanocrystalline powder (10–20 nm), (b) nanoporous thin film and (c) nanostructured thin film.

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pared to other processing technologies. Moreover, this simple and flexible technique allows the incorporation of the deposition technique into on-line processing, and the process can be scaled up for large areas and mass production.

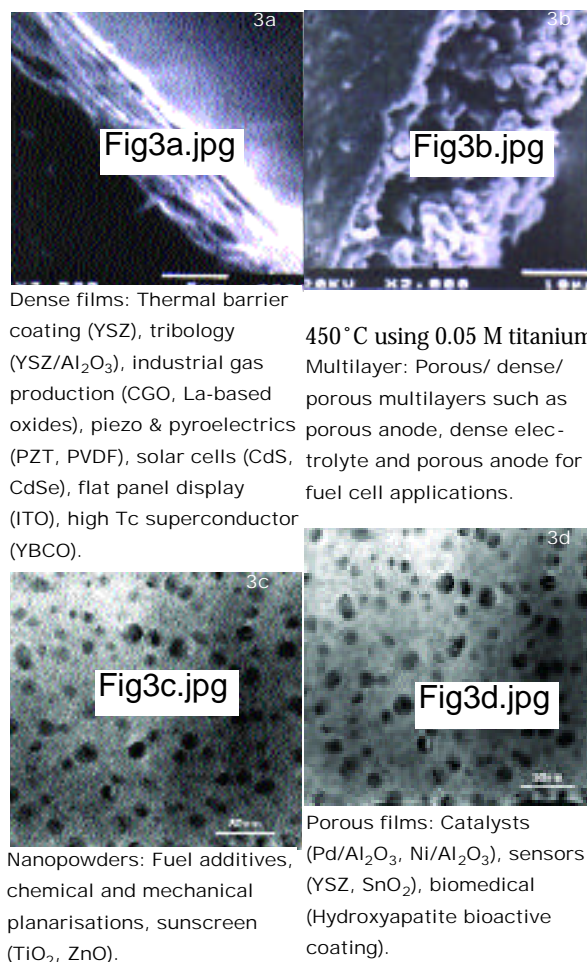
The ESAVD process involves spraying atomised charged precursor droplets across an electric field. Nanocrystalline ceramic powders or films can be deposited by tailoring homogeneous or heterogeneous chemical reactions in an open, heated atmosphere, figure 1. The underlying fundamental sciences of the ESAVD-based processes have been investigated and established - they include the criteria for the selection and formulation of the precursor solutions, the thermal decomposition behaviour and chemical reactions of the precursors in the vapour phase, electro-spraying patterns, processing maps and the deposition mechanism. This has led to the success of the technique for the fabrication of coatings with well-controlled structures, stoichiometry, crystallinity, texture and thickness, as well as nanopowders with a good control of particle size and distribution, surface area and composition.

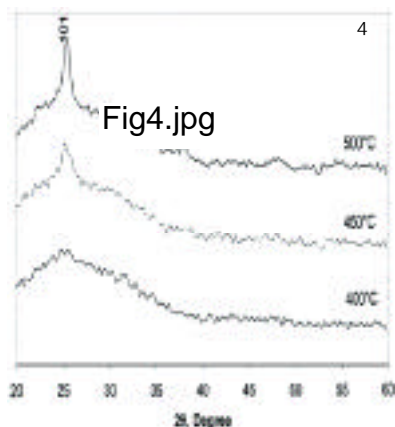
The ESAVD process can deposit a broad range of materials in the form of nanopowder, coatings, films, multilayer, functionally graded materials and nanocrystalline materials, figure.3. The deposition process can be performed in an open atmosphere, without the use of sophisticated reactor and expensive vacu-

um system, while the use of an electric field enhances the deposition efficiency. This rapid, flexible and cost-effective materials processing method has potential applications in almost all industrial fields. These include aerospace, power generation, electrical electronics, automotive, oil industry, biomedical and scientific instruments and consumer sectors. Simple oxides (e.g. TiO_2 , Al_2O_3 , ZnO and SiO_2), multicomponent oxides (e.g. PbTiO_3 , BaZrO_3 , $\text{La}(\text{Sr})\text{MnO}_3$, $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$), doped oxides (e.g. $\text{Y}_2\text{O}_3\text{-ZrO}_2$, $\text{Eu:Y}_2\text{O}_3$, $\text{In}_2\text{O}_3\text{-SnO}_2$), sulfides and selenides (e.g. CdS , ZnS , CdSe), metallic (e.g. Pt , Pd , Ni) as well as polymeric films (e.g. polyvinylidene fluoride) can all be deposited using ESAVD-based processes. The oxides and certain non-oxide materials that are not sensitive to oxygen can be deposited in an open atmosphere or controlled atmosphere. The process is an atomistic deposition method and can produce pure materials with structural control at nanometer-scale level and at low processing tem-

peratures.

How though do the resulting coatings behave in 'real-life'? Figure 4 shows the XRD of an adherent and optically transparent anatase TiO_2 film deposited at





The XRD trace of TiO₂ films deposited at different temperatures (350-400°C) using 0.05M precursor solutions.

alkoxide precursor, which had fully decomposed and reacted to form nanocrystalline anatase TiO₂ as indicated by the broad [101] peak in the XRD trace. The estimated crystal size from the Scherrer equation was about 10nm and the Raman spectroscopy analysis confirmed only anatase phase present in the deposited films. These films exhibited good optical transmission over a wavelength of 370nm. Anatase has the potential for photoelectrical applications in semiconducting electrodes in solar cells, photocatalysis and semiconductor field-effect transistors as well as many other applications.

In addition to the polycrystalline growth to produce nanostructured films, ESAVD is capable of depositing highly-oriented thin films and epitaxial films as illustrated in the deposition of ZnS films. ZnS has wide band gap (~3.8eV) and good luminescence characteristics that make it attractive for optoelectronics applications, such as light emitting diodes and flat panel electro-luminescent displays. Highly textured ZnS films are commonly deposited onto single crystal [e.g.

(100) Si] substrates using vacuum techniques such as molecular beam epitaxy and pulsed laser deposition. The viability of depositing highly textured ZnS thin films onto single crystals using ESAVD has been demonstrated using a mixture of 0.01-0.05 M of ZnCl₂ and (NH₂)₂CS precursor solutions. The deposition temperature was in the range 450-500°C. The XRD trace, figure 5(a), shows that the deposited films exhibit a strong cubic (200) peak. This means that ZnS has a preferred [100] growth orientation to the (100) Si substrate. Hence, there is a tendency towards epitaxial crystal growth in ZnS where the template crystalline structure is commensurate with the nucleating crystal face, in this case an epitaxial relationship of [100]Si//[100] ZnS. Such epitaxial growth behaviour has also been confirmed by TEM and HRTEM studies. Furthermore, the growth of textured ZnS thin films onto amorphous substrates has also been demonstrated using the non-vacuum ESAVD method, figure 5(b), which exhibited the [111] texture. Such unique texture or epitaxial formation or both, may be due to the alignment of bipolar units induced by the electric field during the decomposition and restructuring of the precursors in the deposition process, which results in the development of a preferred orientation or texturing in the films. The bandgap energy value for ESAVD-produced ZnS films is 3.30eV, comparable to those deposited using the vacuum techniques.

The ESAVD process can also be used to manufacture thick coatings. One of the most significant contributions of ESAVD to coating technology includes pioneering work on the ESAVD fabrication of thick thermal barrier coatings (>250nm) on gas turbine components. These have a columnar-like microstructure, which has been proven to be superior in terms

of erosion resistance, thermal shock resistance and thermal cycling behaviour, compared to those produced by commercial electron beam assisted physical vapour deposition and plasma spraying methods.

The technological impact of ESAVD-based coating technology has also been demonstrated successfully in the clean energy generation in solid oxide fuel cells and the direct deposition of Ni/Al₂O₃-based reforming catalysts for molten carbonate. The process offers a time-saving and feasible alternative to the existing laborious processing method.

Close collaboration with key players in corporate engineering companies to apply the ESAVD-based processes to the cost-effective manufacture of high-performance advanced materials for functional and structural applications has been established. A spinout company known as Innovative Materials Processing Technology Limited (IMPT) was founded in 1999 to exploit the ESAVD-based technologies and to bring about the successful incorporation of the innovative processes into all major areas of coating manufacturing and nanopowder production on a global scale. As a process, ESAVD has come of age and could well become the deposition method of choice for the twenty-first century.

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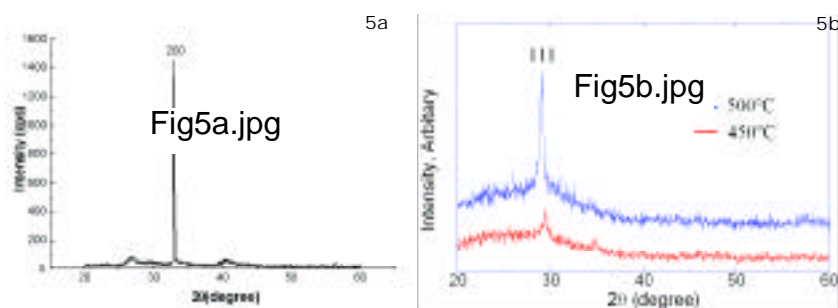
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Further reading

Further information about the ESAVD technology can be obtained from

1 K.L. Choy, *Progress in Materials Science*, 48 (2003) 57

2 Choy, K. L., 'Process principles and applications of novel and cost-effective ESAVD based methods', in *Innovative Processing of Films and Nanocrystalline Powders*, Choy, K. L. ed. (World Scientific Publishing Company), 2002, 15-69. ISBN: 1860943160



5a - XRD trace of the ESAVD of a ZnS thin film on a (100) Si Substrate. 5b - XRD trace of ZnS films deposited onto glass substrates.