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Layered Functional Ceramics via Misted Chemical Solution Deposition

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Abstract. A review is given of "misted" CSD deposition. This technique uses stoichiometrically correct sol-gel solutions but is not a spin-on process. Instead a monodisperse mist of droplets as large as 3 microns in diameter or as small as 0.3 microns is deposited on a substrate. This technique has the great advantage over sol-gel spin-on processing in that it is suitable for non-planar structures, including nanotubes and nano-wires. One could coat a variety of objects with this technique, including anything from non-planar flash-goggles to a parabolic mirror or focal-plane array of pyroelectric detectors. Yet it is much simpler and less expensive than conventional chemical vapour deposition (CVD). We illustrate its use with functionally graded layers on platinised silicon wafers, on nanotubes of piezoelectrics, and most recently [Pollard, Gregg, et al.] on 100 Gbit/cm2 arrays of Pt nanowires on Si substrates (the latter are 30-nm diameter, spaced 50 nm apart, embedded in porous alumina and capped with lead zirconate titanate capacitors).

Introduction

Our research focuses both on the fundamental physics, chemistry and material science of thin films functional oxides which are deposited here in our lab, and also on extrinsic effects caused by novel geometries and processing required for integration of such oxides into commercially available microelectronic devices. Here we describe recent results from a number of ongoing projects including:

- novel deposition techniques for HfO_2 and ZrO_2 gate oxides and $SrBi_2Ta_2O_9$ (SBT) ferroelectrics (FEs)
- novel nanoscale FE structures in the form of nanotubes
- mechanisms of dielectric leakage in ferroelectric thin films
- geometry effects in FeRAM memory cells and their wider implications for commercial nanoscale high-density memory devices of the future.

Misted Liquid Source Chemical Deposition

The technique involves deposition of a liquid layer of stoichiometrically correct organometallic precursor which is typically converted to the appropriate oxide film by thermal treatment. The liquid precursor is introduced to the substrate as a mist of submicron droplets, Fig 1. Uniform layers as thin as 70 nm have been prepared using this technique.

The first-generation misted deposition machine was the HDF-6000 from Samco Corp.[1,2] Its aerosol was generated with ultrasonic transducers at 1.65 MHz and resulted in 1.0 micron diameter liquid droplets at ca. 10 nm/minute deposition rate with horizontal flow across the substrate (usually a platinized Si wafer). This is the machine in use in our laboratory in Cambridge; it will handle a full 8” wafer. Later a more expensive mist system (Primaxx-2F) was manufactured by SubMicron Systems Co. in the USA, suitable for industrial use.[3] It uses charged droplets and a biasing

voltage on the substrate and a vertical flow. The Samco HDF-6000 usually is set up to provide micron-diameter droplets, but both it and the Primaxx-2F can operate with submicron delivery. The latter unit had typically 40 million droplets ccm of mean diameter 0.21 microns and a Gaussian size distribution with standard deviation of ca. 0.10 microns. This is a rather mono-disperse aerosol. Other operating parameters are typically: 1.5-3.0 liters/minute atomizer gas flow; pressure 50 Torr under ambient (n.b., not a high vacuum system); wafer rotation at 15 rpm; dep rate of 10-20 nm/minute. A step coverage of 78% on a 500 nm step height was reported in [3] for thermal ferroelectric SBT on platinized SiO_2.

The misted chemical solution deposition has many advantages as a deposition technique such as:

- excellent step coverage compared with spin-on
- precise composition control
- inexpensive, simple process
- ability to coat 3D substrates

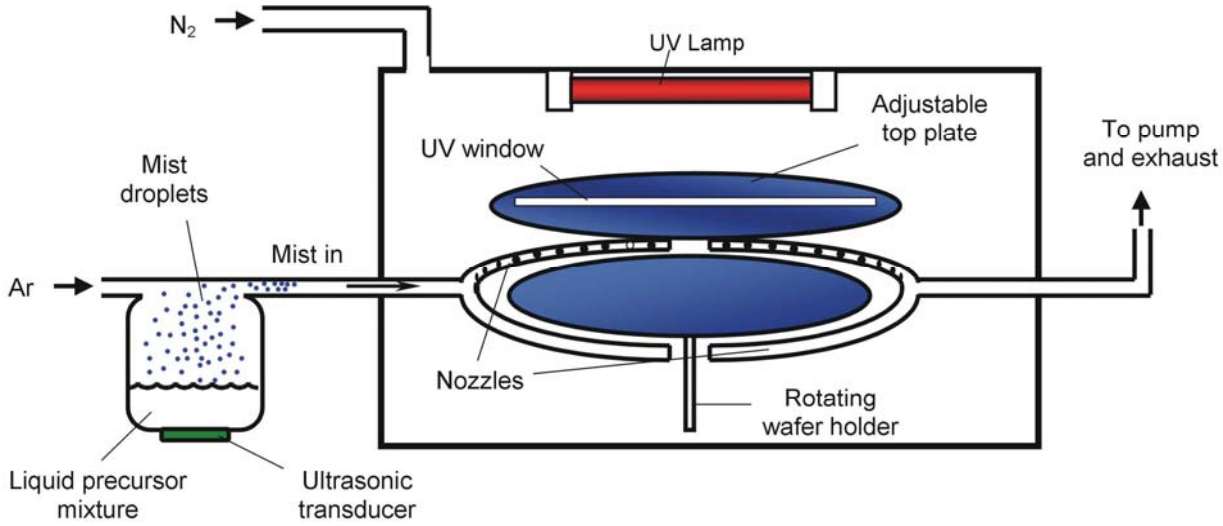

Fig 1 Schematic representation of the misted liquid source chemical deposition apparatus

Deposition of Gate Oxides

Unacceptable leakage characteristics of SiO_2 gate oxides in Field Effect Transistors (FETs) has resulted in the search for more suitable dielectrics. Hafnia and zirconia are believed to be the prime candidates because of their high permittivity (*ca*. 25) and chemical stability on Si.
Three novel hafnia precursors were investigated for HfO_2 thin films:

- Hafnium tertiary butoxide
- Hafnium (Bis-THD)
- Hafnium (Tris-THD)

The extent of crystallisation of the films was studied by Raman spectroscopy. Hf bis-THD has a significantly higher crystallisation temperature. This may have a potentially large commercial impact in the microelectronics industry, because the gate oxide must withstand a front-end processing step at 800-1000 °C for *ca*. 7 seconds without crystallisation.

Ferroelectric Films and Nanotubes

Using the misted deposition technique it is possible to produce uniform ferroelectric $SrBi_2Ta_2O_9$ thin films exhibiting excellent FE hysteresis, Fig 2. We have also prepared [3D] FE structures in the form of tubes [4]. These tubes are made from FE (SBT) and have geometries of 100 μm in length, diameters between 400 nm and 2 μm, and wall thickness 40 nm, Fig 3. These have a number of potential applications in both embedded ferroelectric devices (e.g. FeRAMs) and microelectromechanical devices (MEMs):

Data Storage (FE-response)
• High density 3D FeRAMs c.f.existing planar structures
• High aspect ratio coatings (trenching) for DRAMs
MEMs (piezo-response)
• Ink jet printers
• Drug delivery implants
• Micropositioners/movement sensors
• Composites

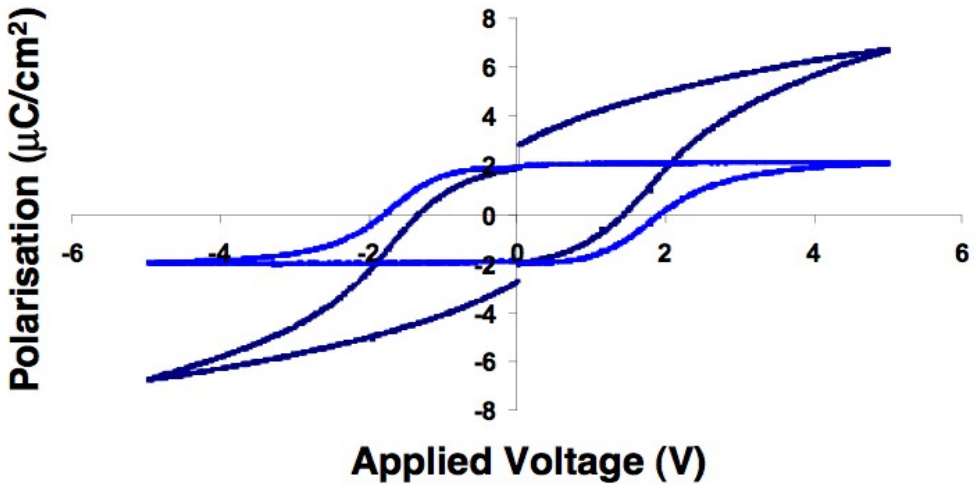

Fig 2 Ferroelectric hysteresis of a 600 nm thick SBT film annealed at 800 °C.

Electroding

With a small modification of the mist system, it has been possible to carry out in situ CVD on the ceramic films in order to put down metal electrodes on them. We have used Ru-DER, and organic ruthenium precursor available from Tosoh Corp. in Japan.[5] Earlier efforts with Pd-acetate failed to achieve good wetted interfaces between dielectric film and electrode.

Nanoscale FE Devices: Geometry

Manufacture of small cell FE capacitors for high density FeRAMs typically involves plasma etching or exposure to chemically reducing forming gases. We have recently shown that this degrades the exposed edge of the FE, leading to increased leakage. The activation energy of the additional leakage response (0.2 eV), figure 4, indicates the presence of H-O dipoles due to hydrogen reduction [6]. This has severe implications for switching of FE devices as the edge/area ratio increases during miniaturisation of FeRAM cells.

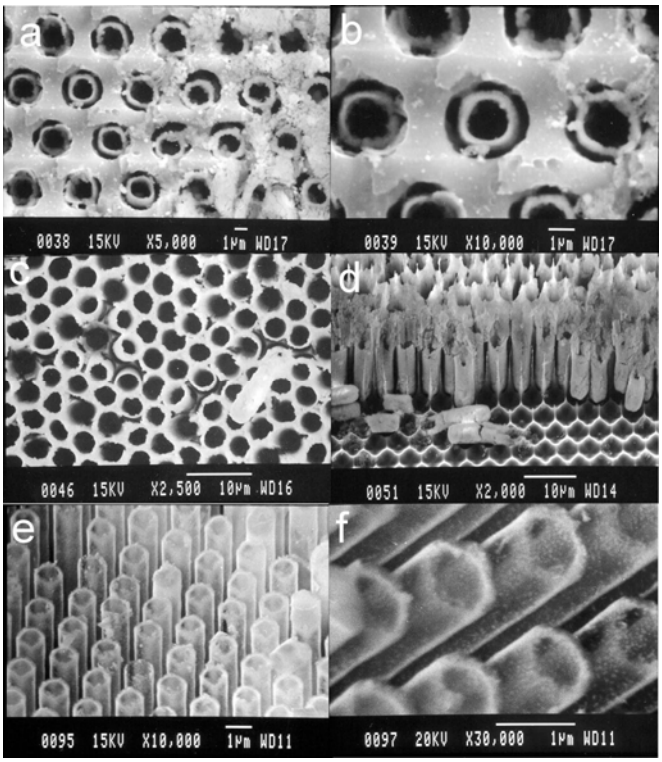

Fig 3 SBT tubes (a) with Ø *ca*. 2 μm and thickness *ca*. 200 nm (b). Larger Ø SBT (c) and cross sectional view (d). Array with Ø = 800 nm (e) and wall thickness < 100 nm (f).

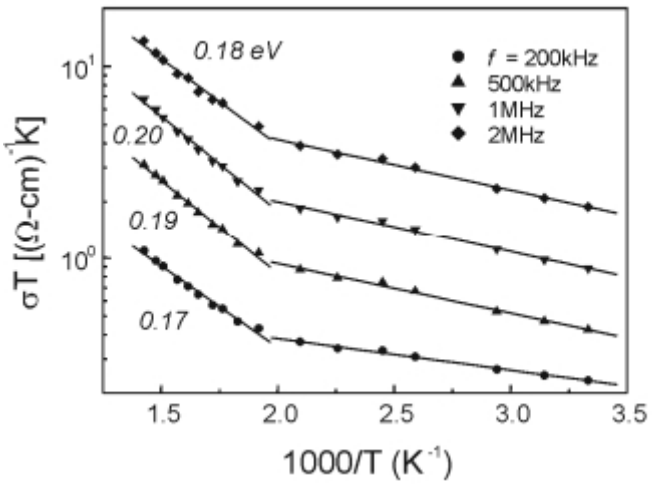

Fig 4 Arrhenius plot of additional leakage response in nanoscale PZT capacitor.

Functionally graded planar structures

LG Electronics Corp. in Korea has utilized the misted system deposition system described above for DRAM capacitor deposition, with (Ba,Sr)TiO_3 as the capacitor dielectric. Typically 150 nm of dielectric is deposited in three separate 50-nm layers. In this way the outer layers can be functionally graded to compensate for oxygen vacancy gradients near the electrodes. They found [7] that a carrier gas of N_2O improved performance, compared with a more standard O_2/Ar mix.

Summary

A misted deposition system is described that appears superior to flash MOCVD [8,9]. It provides functional gradients in dielectric films and it gives excellent conformal coverage of non-planar devices. It is an ideal laboratory R&D tool, with one-man operation, low cost, and quick turnaround (several different precursors can be used each week, unlike most CVD systems). It is also scalable to industrial production because dep rates and through-puts are high, and because it takes standard 8” wafers.

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