The control of thin film deposition and recent developments in oxide film growth

Zoe H. Barber*

This review describes just some of the recent developments in thin film deposition technology which have led to improved understanding and control of film growth. The first part is concerned with the development of sputter deposition methods offering control of the energy of depositing species, and the use of structure zone models, which describe the link between film deposition parameters and film structure. Other deposition techniques are then introduced, including examples of the wide range of chemistry-based techniques currently being developed, to illustrate the fabrication of complex multi-component materials and the application of non-vacuum-based methods. The current level of control which may be achieved through application of some advanced *in situ* methods for monitoring film growth is also described.

Introduction

Thin film deposition was once considered a black art. Evaporation, sputter deposition and chemical vapour deposition were routinely used, but there was very little understanding of the link between deposition parameters and the final film structure. Most film deposition was of single elements or simple compounds, and there had been little research into the growth of even simple alloy films. Over the last two decades there has been a vast increase in the range of material types which can be deposited, the complexity of thin films which are possible, the ability to deposit precisely controlled heterostructures, and the reproducibility of film deposition. There is now a much greater understanding of the link between film deposition parameters and film structure, as well as the link between film structure and film properties. Such advances in the understanding and control of film deposition have come about through the development of deposition techniques, of methods for monitoring and controlling the deposition environment, and also through advances in materials characterisation techniques for both *in situ* monitoring during film growth as well as *ex situ* characterisation of thin film structures.

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Zoe Barber has been based in the Materials Science Department at Cambridge University, where she is currently a Senior Lecturer, since working for her PhD on the sputter deposition of alloy films. Her research interests are based around thin film deposition techniques (including ionised magnetron sputtering, pulsed laser deposition and sol gel coating), the control of the deposition environment, and hence of film structure and properties.
Current projects include ferroelectrics, thin film shape memory metals, the study of coatings and surface textures for biomedical implants, and heterostructure deposition for spintronics.

Thin film characterisation

Thin film characterisation poses particular problems of signal strength due to the small quantity of material, and signals are often hard to separate from those due to an underlying substrate. Electron microscopy is widely used for structural characterisation, but high resolution transmission techniques are often required, and sample preparation is an important consideration. The availability of focused ion beam systems for site specific specimen preparation has led to real advances here, but such techniques are extremely specialised as well as destructive. Atomic force microscopy, a technique which is now becoming widely available, can provide information about the nucleation and growth of film structures through high resolution characterisation of film surfaces (see Fig. 1).

Relatively recently, X-ray reflectivity and diffraction techniques have been developed and adapted specifically for thin film geometry.[1,2] Such methods are non-destructive and generally less expensive than using neutrons or electrons. Whilst the standard Bragg–Brentano geometry, measuring a simple θ–2θ scan, only gives information on crystallographic planes parallel to the film plane, grazing incidence X-ray techniques use a low angle of incidence (*e.g.* <0.6°, close to the critical angle for total external reflection) to give high intensity specular reflection[3] as well as diffraction from planes perpendicular to the film plane.[4] Intensity versus incident angle plots (Keissig fringes) can give a relatively quick, accurate measure of layer thickness and density, and the decay of these fringes yields information on interface and surface roughness.[3] This method has been demonstrated to
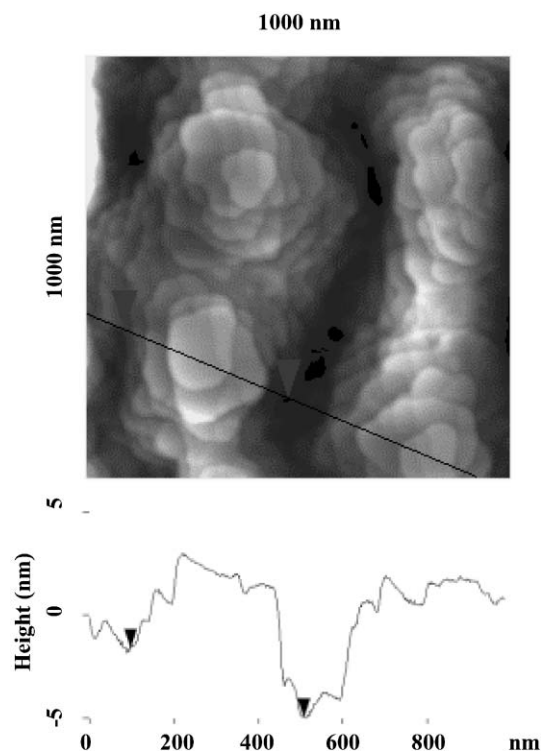
Fig. 1 Island nucleation and growth, as illustrated by atomic force microscopy of a (001) oriented 200 nm thick $SrBi_2Ta_2O_9$ film deposited onto single crystal (001) $SrTiO_3$. The step heights are approximately 1.2 nm, which is $1/2 \times$ the *c*-lattice parameter, *i.e.* 1/2 of the unit cell dimension.

give a valuable insight into the evolution of device structures (layer thickness and roughness) by application of a 'built-up sample technique', in which successive layers of a spin valve structure were deposited and individually characterised (see Fig. 2).[5] Grazing incidence also gives information on surface layers whilst avoiding complications due to the substrate and, by varying the incidence angle, one can effectively scan through the depth of the film.

Film complexity

In addition to incremental advances in thin film deposition and characterisation techniques, there have also been significant developments resulting from the demand for more complex materials. In particular, there was a step change on the discovery of the high temperature superconducting (HTS) oxides in 1986. Not only was there great demand for thin films for device applications, but in many cases thin film deposition was the only technique available for the production of high quality (pure, low defect) single crystal samples for fundamental studies of materials properties. These four and five component compounds require strict control of stoichiometry and oxygenation level, and represented a tremendous challenge to the film growth community. Many developments in film deposition technology may be traced back to this time: for example, the widespread application of pulsed laser deposition[6,7] and off-axis sputter deposition.[8]

Not only do HTS thin films require precise control of structure and composition, but these compounds are extremely
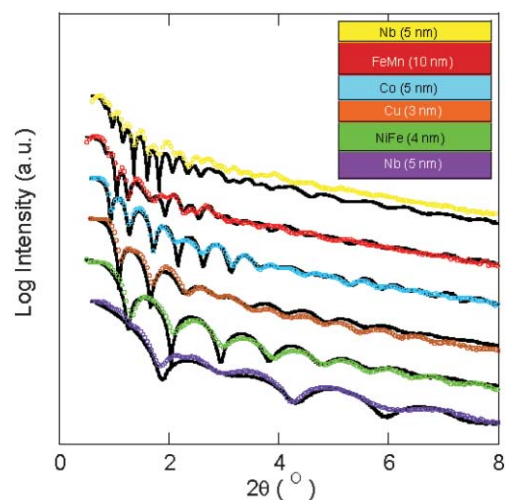

Fig. 2 Specular X-ray reflectivity plots for a spin valve structure built up sequentially and characterised following each additional layer. Curves are displayed with an artificial offset; coloured symbols represent experimental data and black lines simulated data. In each case the colour corresponds to the topmost layer in the sequence, as illustrated in the inset. Samples with fewest layers were probed first, and results used for simulations of the more complex structures. [Reprinted from reference 5, copyright 2004, with permission from Elsevier.]

anisotropic, and crystalline orientation is also critical. For example, in conductor applications high angle grain boundaries severely limit critical currents and must be avoided. Hence the standard wire drawing or tape fabrication methods previously used for superconducting cable manufacture proved unsuitable and much work has gone into the development of new techniques for fabricating highly textured conductors. Many of these solutions are based on thin film technology: for example, the growth of strongly textured buffer layer–HTS composite structures on textured metal tapes.[9–11] Similar strong anisotropy is exhibited by the ferroelectric Aurivillius phases, placing stringent demands on film orientation for device applications.[7,12]

It is now clear that structurally compatible oxides can exhibit the full spectrum of electronic, magnetic and optical behaviour (insulating, semiconducting, metallic, super-conducting, ferroelectric, piezoelectric, ferromagnetic),[13] as well as ion transport effects. In addition, these properties can be coupled, *e.g.* magnetoresistance, coexistent ferro-magnetism and superconductivity, and multiferroic pro-perties (simultaneous ferroelectricity, ferromagnetism and/or ferroelasticity). In order to be able to exploit these materials and to understand fully the relation between structure and properties it is essential to be able to produce high quality thin films with known compositions and structures, complete homogeneity (or controlled inhomogeneity) and, ideally, full functionality in the thinnest layers. This has led to the concept of oxide nano-engineering,[13] *i.e.* precise tailoring of material properties through the development of growth procedures which match the control currently offered for the fabrication of the highest quality semiconductor heterostructures and devices.[14]

Requirements of a deposition method

There are many demands to be met when deciding upon an appropriate film deposition technique for a particular application. For example, is the technique compatible with underlying device structures, or with the necessary substrate? This generally limits the maximum temperature available for film growth, and a compromise may have to be reached between crystalline quality and processing requirements. Often smooth surfaces and sharp interfaces are demanded (*e.g.* for device applications), but there is also great current interest in the intentional production of rough surfaces, with specific topography and chemical properties, for applications including cellular engineering.[15] Other factors which must be considered include coverage (*e.g.* uniform coating of sub-micron, high aspect ratio features or large areas), the presence of film strain (which may lead to substrate curvature or band gap shifts in semiconductors) and through-thickness uniformity. Commercial issues include costs, scalability, environmental impact, control, automation, and factors such as process flexibility (*e.g.* adjustment of the film composition).

Films may be produced in a single deposition sequence, forming the required phase and structure during the deposition (*in situ* growth), or the appropriate components may be deposited on the substrate followed by an annealing step in which the correct phase and structure are formed (*ex situ* processing). For device applications the former process is generally preferred, as *ex situ* processing may require prohibitively high temperatures. The fabrication of complex, multicomponent materials may require painstaking control. It is not sufficient to produce a depositing flux of species with the required elemental composition: transport of this flux to the growing film must be considered, as well as sticking coefficients at the substrate. In the case of oxide films, control of the oxygen level is often achieved in a subsequent oxygenation sequence.

Even for single component materials, film structure is critically dependent upon film growth parameters. Thin film deposition enables the tailoring of chemical and structural properties of materials through control of the deposition parameters, *if* we understand this link.

Physical vapour deposition (PVD) and structure zone models

PVD refers to the production of a vapour flux of the required film species (*e.g.* in simple thermal evaporation, by heating a source) which travels to a substrate, at which film growth proceeds. Structural development of the film requires migration of arriving species on the growth surface and there is a need to balance arrival rate with this surface mobility, allowing time for adatoms to reach equilibrium sites. On the one hand we might consider molecular beam epitaxy (MBE), in which high substrate temperatures and low deposition rates promote the formation of high quality single crystal films whilst, on the other hand, one may use a high rate deposition source on an unheated substrate to quench in disorder, for example in the fabrication of amorphous materials.

In order to be able to generalise, the concept of homologous temperature, T/T_m, is used, where T is the growth temperature and T_m is the melting temperature of the film material. The first structure zone model, SZM,[16] linked the microstructures observed in thick ($\gg 100$ μm) evaporated coatings to this parameter. However, in addition to its control with substrate temperature, adatom mobility can be increased with energy input from the depositing flux and other energetic species during film growth.

Sputter deposition

Sputtering is the ejection of species from a solid surface (the target) which is subjected to ion bombardment, and this is the source of the vapour flux in sputter deposition. These sputtered species have a range of energies dependent upon their atomic mass, the nature of the target and the type and energy of the bombarding species. Typical energies on leaving the target may be of the order of several tens of eV or more, *i.e.* very significantly higher than the thermal energy of the vapour flux during evaporation ($\ll 1$ eV).

Diode sputtering requires the presence of a sputtering gas (typically a few Pa of an inert gas) in order to maintain a discharge in front of the sputtering target, which is held at a high negative potential (*e.g.* >100 V). Positively charged gas ions from the discharge bombard the target surface to produce the sputtered flux. Some of these bombarding gas ions may be neutralised and reflected at the target surface and join the energetic flux of depositing film species impinging on the growing film. The depositing flux and reflected neutrals pass through the sputtering gas before reaching the substrates, undergoing collisions with gas species which reduce their energy and randomise their directions in a process termed thermalisation (the reduction of high energy species towards thermal energies).[17] A sputtering gas pressure axis was added to the earlier SZM to account for observations that lower sputtering gas pressures lead to higher quality, more dense film structure through enhanced adatom mobility.[18–20] Conversely, gas scattering at higher pressures reduces the energy of the flux and results in higher arrival angles at the growing film surface, promoting poor quality, low density film structures due to low mobilities and geometric shadowing effects.[21]

Whilst ion bombardment of a surface with a known ion dose, ion energy and direction may be effectively characterised through modelling and simulations, the complexity of the film growth environment makes this situation extremely difficult. The flux of depositing and other impinging species typically includes different particle types (atomic, ionic, molecular and even clusters) with a broad energy distribution, arriving from a range of angles. Reduction of the sputtering gas pressure in order to improve adatom mobility by increasing the average energy of the depositing species may lead to bombardment induced damage (*e.g.* formation of residual lattice defects and trapping of gas atoms) by the highest energy species. Although there may be few of them, particles with the highest energies persist (they are less likely to suffer energy reducing collisions in the sputtering gas) and can have a large influence upon film growth.
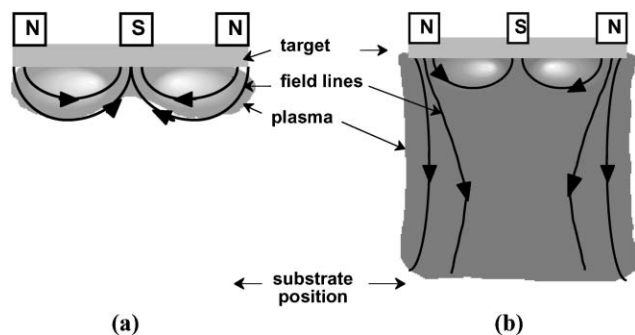
Fig. 3 (a) Balanced, and (b) unbalanced planar magnetron sputtering targets.

High energy bombardment of a surface is often harnessed to promote film adhesion: the first layers of a film may be deposited at a low sputtering gas pressure to clean the substrate surface and promote a degree of intermixing at the film/substrate interface. Conversely, higher pressures are used to limit bombardment-induced damage of an underlying substrate, device structure or of the growing film itself. The spread in arrival angle through sputter deposition at relatively high pressures can promote film coverage of shaped substrate surfaces (in contrast to line-of-sight deposition in a vacuum environment). However, it is important to realise that improved coverage through gas scattering is only relevant for coating features which are large relative to the mean free path of the scattered depositing species, making simple diode sputter deposition unsuitable for coating sub-micron structures in semiconductor wafer manufacture.[22]

Energy input can also be used to control film stress, which may vary from tensile in poor quality, low density film structures (those produced at low growth temperatures and/or high sputtering gas pressures) to compressive in full density, high crystalline quality films formed at low pressures. This stress transition (which also depends upon deposition geometry) has been shown to accompany a more general transition in film properties (*e.g.* density, reflectivity and electrical conductivity).[23,24] Electrical bias at the substrates can also control film density, structure and stress through energetic bombardment by ionised species.[25]

Improved control of film growth is achieved through access to low sputtering gas pressures (<1 Pa) using magnetron sputtering, in which a magnetic field confines the sputtering discharge close to the target surface (see Fig. 3a), limiting the loss of secondary electrons required to maintain the discharge. Unbalanced magnetrons have a field configuration designed such that a charged particle flux reaches the substrates[26] (see Fig. 3b). An increase in plasma density and still lower pressure operation can be achieved by electron confinement within grooves or holes in a target[27–29] or an additional hollow cathode structure around the target.[30] Direct gas feed into such structures enhances this hollow cathode effect, and a pressure differential results in extremely low pressures at the substrates (<0.03 Pa).[31] The SZM may be extended to include such very low pressure sputter deposition:[29] the energy delivered by condensing and bombarding particles leads to non-equilibrium atomic scale heating, which can promote the growth of bulk-like material at low substrate temperatures, and offers the possibility of fabricating films with novel structures and properties.

Further advances in the application and control of energetic particle bombardment at the growing film include multiple magnetron arrays, variable field strength magnetrons and pulsed magnetron sputtering.[32] An important research area for the further understanding and development of all of these plasma-based techniques is that of *in situ* plasma diagnostics (see Fig. 4) and the measurement of particle energies.[33–36]

Another technique for increasing control of the depositing flux is the addition of an independent ionisation source, for
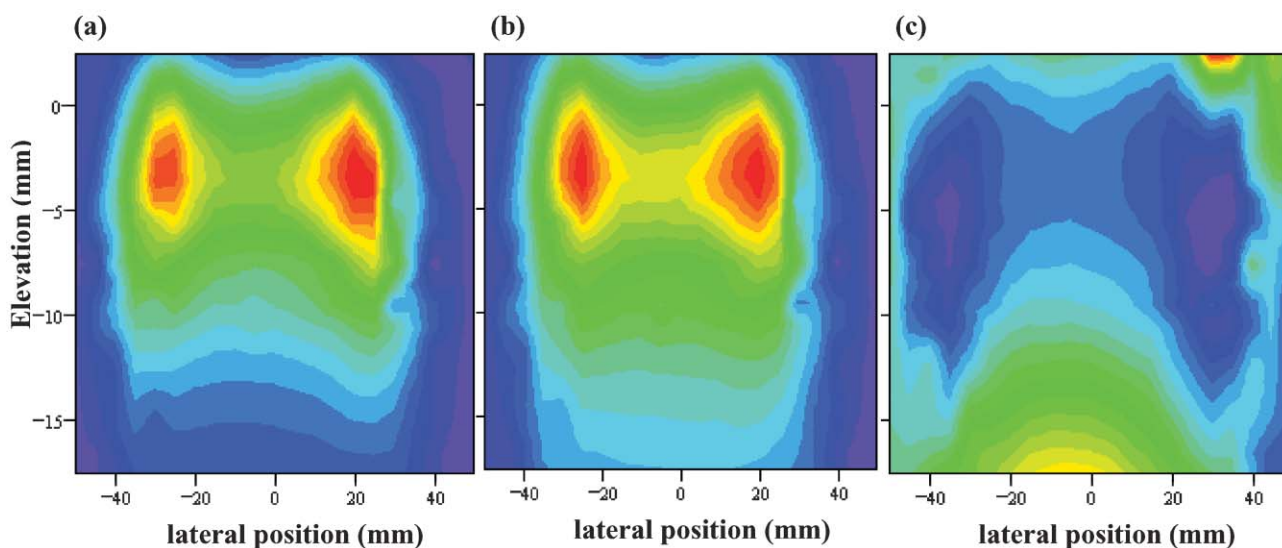

Fig. 4 Two-dimensional maps of spectral emission in front of a titanium planar magnetron target (the face of the target is at elevation = 0 mm): (a) Ti atomic emission, and (b) ionic emission, showing enhanced intensity (red/yellow) in the high density plasma regions corresponding to strongest magnetic field; (c) the ratio of ionic to atomic emission, with the region of highest relative ionisation pushed out in front of the target face.[35]
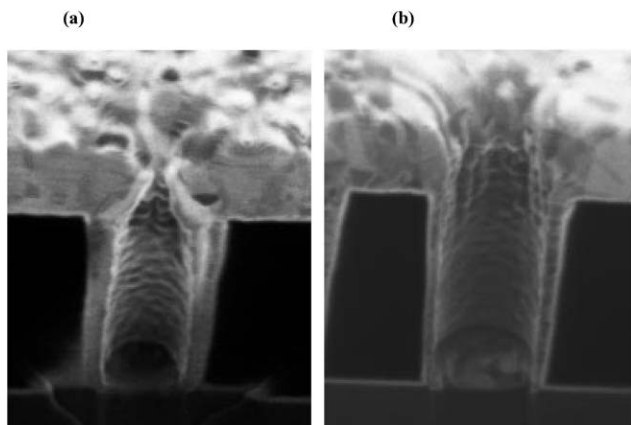
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Fig. 5 Silver-coated 500 nm wide vias in silicon, shown in cross-section. The silver film has been deposited by magnetron sputter deposition (a) without, and (b) with additional ionisation of the depositing flux using a radio-frequency discharge. [Reprinted from reference 38, copyright 2003, with permission from Elsevier.]

example, a radio-frequency coil located between the sputtering target and substrates.[37] The energy and direction of ionised film species may then be controlled with an electrical bias at the substrates. High energy directional deposition using this technique has been shown to offer control over the coverage of sputtered films on sub-micron features[22,38] (see Fig. 5). The ion flux and ionisation fraction (the proportion of the depositing flux which is ionised) may be controlled *via* the power inputs to the rf coil and to the sputtering source. High ionisation fractions at relatively low ion energies can lead to high energy input without bombardment induced damage. Efficient momentum and energy transfer between film species and energetic depositing film ions (as opposed to sputtering gas species) leads to relaxation and recrystallization of the growing film and high structural quality with neutral film stress.[39]

This illustrates that film structure cannot simply be defined in terms of average energy per depositing atom, and a SZM has been developed in which coating structure is related to T/T_m, bias voltage and ion-to-atom ratio,[40] allowing ion energy and ion flux to be considered independently. However, the influence of different energetic species (*e.g.* film or sputtering gas) is also very important and the 'ultimate' SZM must account for the growth temperature and adatom surface mobility, the arriving flux (defining the species, their relative proportions, energies and arrival directions), film growth rate, impurity level and, ideally, film/substrate variables such as surface and strain energy.

Multicomponent films and the control of stoichiometry

Alloy or compound films may be fabricated by simultaneous sputter deposition from several elemental targets, which can give good control over the film composition, although uniformity over the area of a substrate may be a problem. Alternatively films may be deposited using alloy or compound targets, or 'composite' targets constructed from appropriate relative areas of the different elements (often the most flexible approach). In these cases we must consider the transport of the depositing flux through the sputtering gas, which can lead

to significant deviation from target stoichiometry (lighter elements are preferentially scattered by the intervening gas). In addition, there may be preferential re-sputtering of elements due to energetic bombardment of the film during growth. Reactive sputtering is the deposition of compound films (*e.g.* oxides, nitrides) from elemental targets by adding a reactive gas (*e.g.* oxygen, nitrogen) to the sputtering environment. Some level of stoichiometry control may be achieved by control of the reactive gas partial pressure, which may be anything up to 100% of the sputtering gas.

Oxide film growth and *in situ* monitoring

Advances in film deposition capability following the appearance of the HTS oxides have contributed to tremendous progress in the development of many other oxide systems, *e.g.* ferroelectric materials in thin film form, including the layered Aurivillius phases,[12] and the mixed valence manganites.[41–44] These manganites show large changes in electrical resistance in the presence of a magnetic field (colossal magnetoresistance) and offer great potential for memory applications, as sensors and read/write heads, as well as promising completely new device concepts. They are chemically flexible, with the scope to control ion substitutions, charge exchange, and hence electrical, magnetic and transport properties, and are highly sensitive to strain effects, offering the possibility of controlling film properties through strain. A review of the structure/property relations, growth and applications of these materials is given by Prellier.[45]

During the development of sputter deposition for HTS oxide film growth, it was found that the presence of oxygen led to severe problems. Negatively charged oxygen ions are accelerated away from the (negatively charged) sputtering target, attaining high energies before reaching the growing film surface where they may re-sputter film material, damage the growing crystal structure or promote unwanted re-nucleation in epitaxial films. This led to the development of off-axis growth,[8] in which the substrates are placed with their faces perpendicular to the face of the sputtering target. A relatively high sputtering gas pressure is required in order that the depositing flux is scattered and deposited onto the substrates, and any species arriving at the growing film must have been scattered at least once *en route* from the target. An alternative method is high pressure sputtering, in which the target and substrates are parallel, but gas pressures of, for example, >100 Pa lead to energy reducing collisions for the energetic ions.[46] Although solving the problem of high energy film bombardment and stoichiometry control, these methods result in a rather inefficient process, very slow film growth and are often difficult to monitor and control. Alternatively, or in addition, stoichiometry may be achieved through the use of compensated target compositions, although the precise composition is a function of so many deposition variables that this is not only very difficult to predict, but locks the process into a single set of deposition parameters.

Molecular beam epitaxy

MBE is an evaporation technique which uses highly specialised sources to provide precisely controlled vapour fluxes.

Deposition is typically performed in an ultra high vacuum environment onto heated substrates (e.g. $T/T_m > 0.5$) at very low deposition rates (e.g. 1 nm min^{-1}), allowing significant surface mobility and hence promoting the formation of high quality crystalline structures. MBE is generally thought to offer the best controlled film growth, by supplying incident species in the desired sequence with sub-monolayer control, and this method has been demonstrated for building very fine scale heterostructures and new materials by atomic-layer engineering.[13,47]

In situ monitoring is generally required for this level of growth control and, specifically, it is the technique of reflection high energy electron diffraction (RHEED) which has contributed to recent advances in compound thin film growth. RHEED was, until recently, the tool of only MBE technicians—most text books state that it requires a UHV environment to give sufficiently long electron mean free paths and filament lifetimes. However, oxide film growth requires oxygen (and therefore reactive MBE), and techniques for overcoming this very low pressure constraint have recently appeared. These include differential pumping systems,[48] and the use of activated gas supplies (e.g. ozone, or plasma discharges)[49] in order to form fully oxygenated films at the lowest possible oxygen pressure.

The supply of incident species in precisely the correct proportions may not be sufficient to produce exactly the required film stoichiometry, even in the low pressure MBE environment. In particular, there are problems with species which have very low sticking coefficients (e.g. Bi and Pb in ferroelectric films). One solution to this uses "adsorption controlled conditions":[13] excess volatile component is supplied, but desorbs if not incorporated into the growing film structure, and hence growth is controlled by the supply of the low volatility species (e.g. Ti in bismuth titanate). However, this is clearly a severe limitation if one wishes to produce a non-equilibrium compound composition.

Pulsed laser deposition (PLD)

PLD is a physical vapour deposition technique in which the vapour flux is formed by the ablation of material from a target which is hit with a series of high energy laser pulses. It is widely used for complex oxide film deposition due to its versatility and flexibility: the deposition environment (gas type and pressure) can be used to control the energy and extent of the depositing laser plume (which includes activated species) and subsequent film development. Oxides are generally deposited in the presence of oxygen from stoichiometric targets, although some compensation may be required for components with low sticking coefficients.

The use of RHEED during oxide deposition by PLD, with a differential pumping system to maintain a good vacuum at the electron source (sometimes called laser-MBE)[48] has been adopted by several groups.[50,51] RHEED can be used to produce detailed surface maps during film growth in order to understand surface reconstruction and structural development,[49] and has been used to illustrate the change in growth regime due to different adatom mobilities and sticking coefficients on different surfaces and termination layers during

heteroepitaxial growth.[49,52] In combination with PLD, it has been used to demonstrate the production of high quality, very fine scale epitaxial oxide heterostructures with interface roughness corresponding to only one unit cell.[6] However, RHEED is often simply used to monitor cycles of monolayer completion through observation of the periodicity of the specular intensity.[48,50,51] An incomplete surface layer leads to a reduction in intensity (due to scattering by adatoms and islands), and monolayer completion (to create a perfectly smooth surface) restores intensity. Any cumulative roughening of the surface will lead to a decay in amplitude of this periodicity,[53] an effect which has been countered by use of *in situ* annealing steps.[48,51] (Lack of RHEED intensity oscillations may also signify ideal step flow growth,[54,55] in which there are no cycles of nucleation and coalescence.) The periodicity of the specular intensity due to layer-by-layer film formation generally corresponds to complete unit cell growth. However, if a unit cell consists of several molecular layers, sub-unit cell intensity oscillations may be observed. For example, $SrTiO_3$ growth *via* alternating deposition of charge-neutral layers of SrO and TiO_2 leads to two RHEED oscillations per unit cell, whilst simultaneous supply of all components gives a single oscillation per cell.[51]

The application of RHEED monitoring during PLD has led to major advances in the understanding and control of film growth by this technique. RHEED intensity oscillations corresponding to monolayer completion are overlaid with finer scale oscillations representing the laser pulses[48,50] (see Fig. 6a). This fine scale oscillation illustrates the high arrival rate on the film surface immediately after the laser pulse, as the plume reaches the substrate and two-dimensional nucleation leads to a drop in RHEED intensity. Between laser pulses, surface species organise into larger islands, giving an intensity increase. Optimisation of laser pulse frequency has been achieved through following RHEED oscillations:[53] the decay in intensity due to surface roughening can be avoided by the supply of one complete monolayer of material in a short period of high frequency pulses (e.g. 10–100 Hz), separated by a relaxation interval (which may be a few seconds) for surface reorganisation, during which the specular intensity of the RHEED signal recovers (see Fig. 6b). The remarkable level of control achievable is illustrated by the observation of a slight decay of intensity after each relaxation interval due to the fact that an integer number of laser pulses does not correspond precisely to one monolayer. A correction factor to account for this (in the example given,[53] periodic use of 42, rather than 43, laser pulses between relaxation intervals), can fine tune the amount of deposited material and lead to maintenance of single layer-by-layer growth.

Chemical deposition techniques

Chemical vapour deposited (CVD) films are produced by the chemical reaction of vapour phase precursors at the substrate surface. A great advantage of such film growth is the ability to coat large areas, complex shapes (even re-entrant shapes) and the semiconductor device structures previously mentioned, since film deposition can be achieved at any site reached by the flux of gas phase precursors. In comparison, any PVD
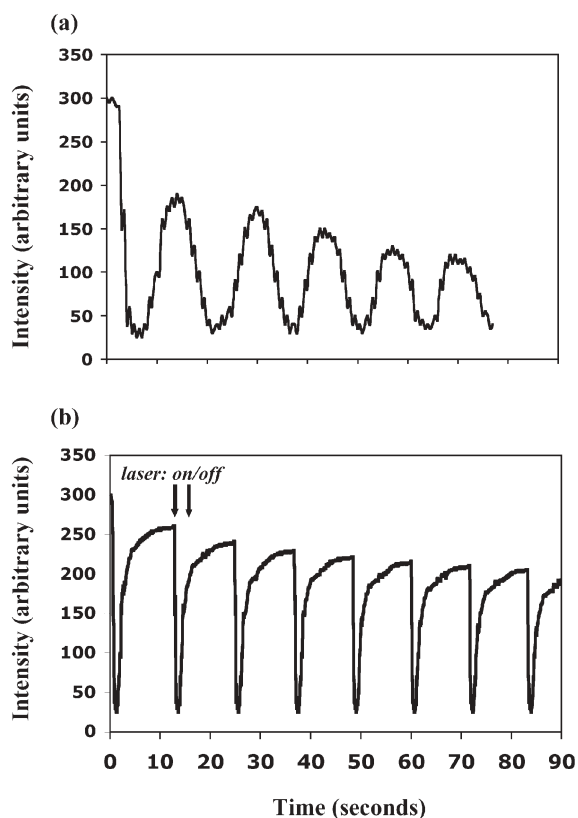
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(a)

(b)

laser: on/off

Fig. 6 Representation of the specular RHEED intensity of a growing film during pulsed laser deposition; (a) 1 Hz pulsing, showing five cycles of monolayer growth overlaid with intensity variations due to the arrival of material from each laser pulse; (b) high frequency deposition (10 Hz) interspersed with relaxation intervals, during which intensity partially recovers.

technique comprises a source and a substrate, and there is a basic geometrical limitation (although there are specific geometries for film deposition onto complex structures, *e.g.* cylindrical magnetron sputtering, these are rather specialised and often inflexible). In order for the film formation reaction to occur there is a limitation on the available growth temperatures for CVD, and often rather high temperatures are necessary (although a reduction can be achieved by the addition of some source of activation, *e.g.* plasma enhanced CVD). Chemical deposition techniques offer precise control of film composition *via* control of chemical precursors, and this extends to the ability to control very low dopant additions. Such methods are currently very widely used to deposit all types of coatings[56,57] and functional materials (*e.g.* optical coatings,[58] superconductors,[59] dielectrics[60] and ferroelectrics[61]), and CVD is the principal deposition technique used in the semiconductor industry. High vapour pressure metal-organic (MO) precursors are used for the extremely precise growth of the highest quality semiconductor structures: MO-CVD.[14]

A direct *in situ* atomic-scale structural probe which is compatible with the high pressure, reactive environment of MO-CVD is real time X-ray synchrotron scattering, or surface X-ray diffraction (SXRD).[62,63] Oscillations in the intensity of crystal truncation rods, CTR (which arise due to abrupt

termination of the crystal), can be used in an analogous way to RHEED intensity oscillations.[64] Layer-by-layer, step flow growth, and the switch to 3D growth have been followed as a function of temperature, precursor supply and oxygen pressure. An overall reduction in amplitude of these oscillations, due to surface roughening, may be overcome by growth pauses (stopping the precursor supply) of a few minutes. In-plane diffuse scattering around the CTRs arises from small angle scattering by islands in a partially complete layer, providing a means for characterisation of the spatial distribution of island and nucleation density.[64]

Another, very different, chemistry-based film deposition technology is chemical solution deposition, in which precursors are mixed in the form of solutions and applied to substrates using methods such as spin- or dip-coating.[65,66] Subsequent heat treatments are necessary to form the film material, making this an *ex situ* technique. For those familiar with vapour deposition this may seem like "bucket chemistry", but techniques are advancing, the control of stoichiometry can be high, and the advantages of cost (no need for a vacuum system) are giving a significant push to further developments (see Fig. 7).
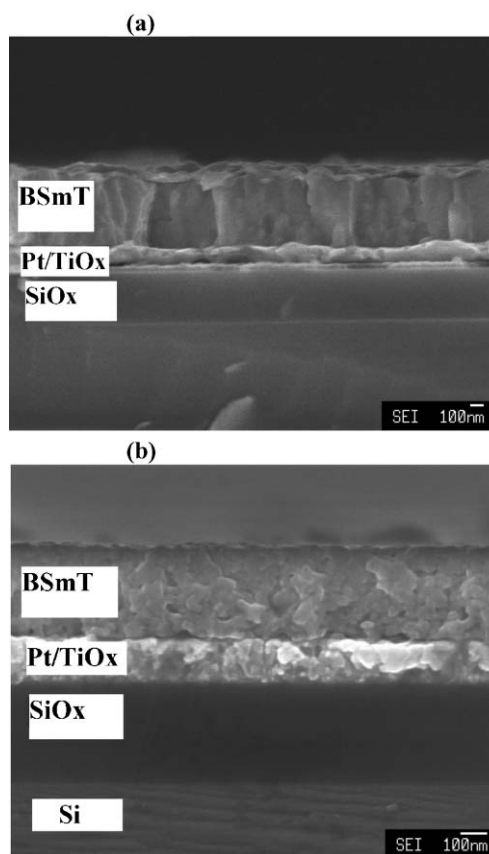

(a)

BSmT
Pt/TiOx
SiOx

SEI 100nm

(b)

BSmT
Pt/TiOx
SiOx
Si

SEI 100nm

Fig. 7 Cross-sectional scanning electron micrographs of Sm-doped bismuth titanate (BSmT) films deposited onto Pt-coated silicon by (a) pulsed laser deposition (a physical vapour deposition technique), and (b) chemical solution deposition, both annealed at 700 °C. This illustrates a dense, columnar growth by vapour deposition in contrast with the isotropic 'grainy' structure of chemical solution deposition. [Reprinted from reference 66, copyright 2005, with permission from Elsevier.]

There is much current interest in the development of non-vacuum techniques for film growth stemming from the requirements for HTS conductors,[9–11] for which a cheap, rapid, scalable and environmentally friendly method is needed. One such technique is high temperature spray pyrolysis, in which a film is deposited by spraying precursor solutions onto a heated surface where the constituents react to form a compound.[67] This places the method in the general category of chemical deposition, and it certainly offers much greater control than the more familiar, but fundamentally very different thermal spray coating and plasma spraying,[68] which are purely physical processes. The addition of an ultrasonic nebuliser leads to a controlled depositing mist of very small droplets: ultrasonic spray pyrolysis.[10,11,69,70] Film growth may occur *in situ* on high temperature substrates to form the film material in one step;[10,11,69–71] constituents may reach the surface in the form of liquid droplets, a dry solid (if the solvent evaporates) or as a vapour (in which case the technique becomes equivalent to CVD). Reaction to form the film material may occur heterogeneously on the substrate surface, may take place in the vapour state, or some combination of the two. Substantial progress has recently been made to bring this technique to a level of control which is comparable with vacuum methods, although a specific problem is the ability to know and control the growth surface temperature.[67] This can differ very significantly from the temperature measured on the back of a substrate, and is affected by the arriving flux of precursors and transport gas. Very high growth rates are achievable (*e.g.* 1 μm min^{-1}, or 10–100 times faster than conventional vapour deposition techniques), high quality epitaxial films may be fabricated and many groups are now working on the application of this method for a range of technologically important oxides.[71]

As with other chemistry-based techniques, spray pyrolysis is a convenient method for trials of new alloy compositions, *e.g.* ternaries and quaternaries, since the stoichiometry of the product can be tailored through the supply of reactants. However, film stoichiometry does not generally correspond on a one-to-one basis with chemical precursor mix![10,69,72] Particularly at high growth temperatures, different reactivities and sticking coefficients lead to very significant variations between the composition of the precursor supply and the resultant film. A detailed knowledge of the link between precursor and film composition is required, and there is a need to maintain the deposition parameters (precursor concentrations, transport gas flow and deposition temperature) in order to maintain this link.

It is often useful to consider film growth in terms of the thermodynamic driving force for formation of solid film material from either a vapour or liquid flux, *i.e.* in terms of the supersaturation of the arriving flux. For example, liquid phase epitaxy (LPE), in which a film forms from a liquid flux or melt,[73] is a process very close to equilibrium and the thermodynamic driving force for film formation is several orders of magnitude lower than that for PVD.[74] Hence a 'seed' is generally required, since there is insufficient energy to overcome a nucleation barrier. This technique is widely used to produce structurally perfect materials with extremely flat surfaces, *e.g.* high purity bulk single crystal semiconductors.

In terms of thin film growth, low supersaturation implies layer-by-layer growth (or step flow growth on vicinal substrates[54,55]), although nucleation may occur at high energy defect sites such as dislocations, leading to the appearance of growth spirals through continuous growth at screw dislocations[75] (see Fig. 8). As supersaturation increases there is a transformation to two-dimensional island nucleation and, ultimately, severe surface roughening through three-dimensional nucleation.[76] Crystallographic film texture may also be controlled in this way: low supersaturation results in greater kinetic control, which can promote in-plane aligned grains or epitaxy.

Epitaxial thin films of complex compounds such as HTS have been prepared by LPE, often using a seed film prepared by another technique.[77] Growth rates can be high (*ca.* 1 μm min^{-1}), but the very high melt temperatures lead to limitations. Reduction of melt temperature in the HTS rare earth–Ba–Cu–O system has been demonstrated through reduction of the oxygen partial pressure, use of a mix of rare earths (Y, Er, Yb) and the addition of Ag (a low supersaturation ensures that Ag is not incorporated into the growing film).[78]

Crystal growth from a thin liquid layer is a well established process, with much current interest, for example, in the growth of nanowires and whiskers.[79–81] It has been shown that, with several vapour deposition techniques, a thin liquid layer may exist on a growth surface even well below the bulk melting temperature, presumably through additional interface energy. For example, an abrupt change in film growth morphology at a specific substrate temperature during MO-CVD has been explained in terms of the formation of a quasi-liquid surface layer at the higher temperatures, leading to a change from conventional vapour growth to something termed vapour–liquid–solid growth.[82] This concept has been extended in a technique called tri-phase epitaxy, in which components are supplied to a liquid layer on a growing film surface.[83] Such growth by diffusive transport across a thin liquid flux layer has also been termed hybrid LPE.[76] It reduces the drawbacks of a large quantity of hot, aggressive flux as well as overcoming the problem of maintenance of supersaturation at the growth interface during conventional LPE (due to limited solubility of components and the difficulty of diffusion across a stagnant layer). The level of supersaturation of this liquid layer is controlled by feeding with new components (*e.g.* by pulsed laser ablation or a flame sprayed particulate flux) and a self consistent adjustment of the growth rate occurs to give a steady state supersaturation. A high supersaturation at the growth interface means that films can be deposited onto non-lattice-matched substrates without the need for seed layers.

Concluding remarks

Thin film deposition offers the potential for constructing materials and heterostructures with extremely precise control, even atom-by-atom control, although this requires a detailed knowledge of the growth mechanisms and the influence of the deposition environment. An example of the application of such precise control is the strong interplay between structural and electrical/magnetic properties in the manganites and other
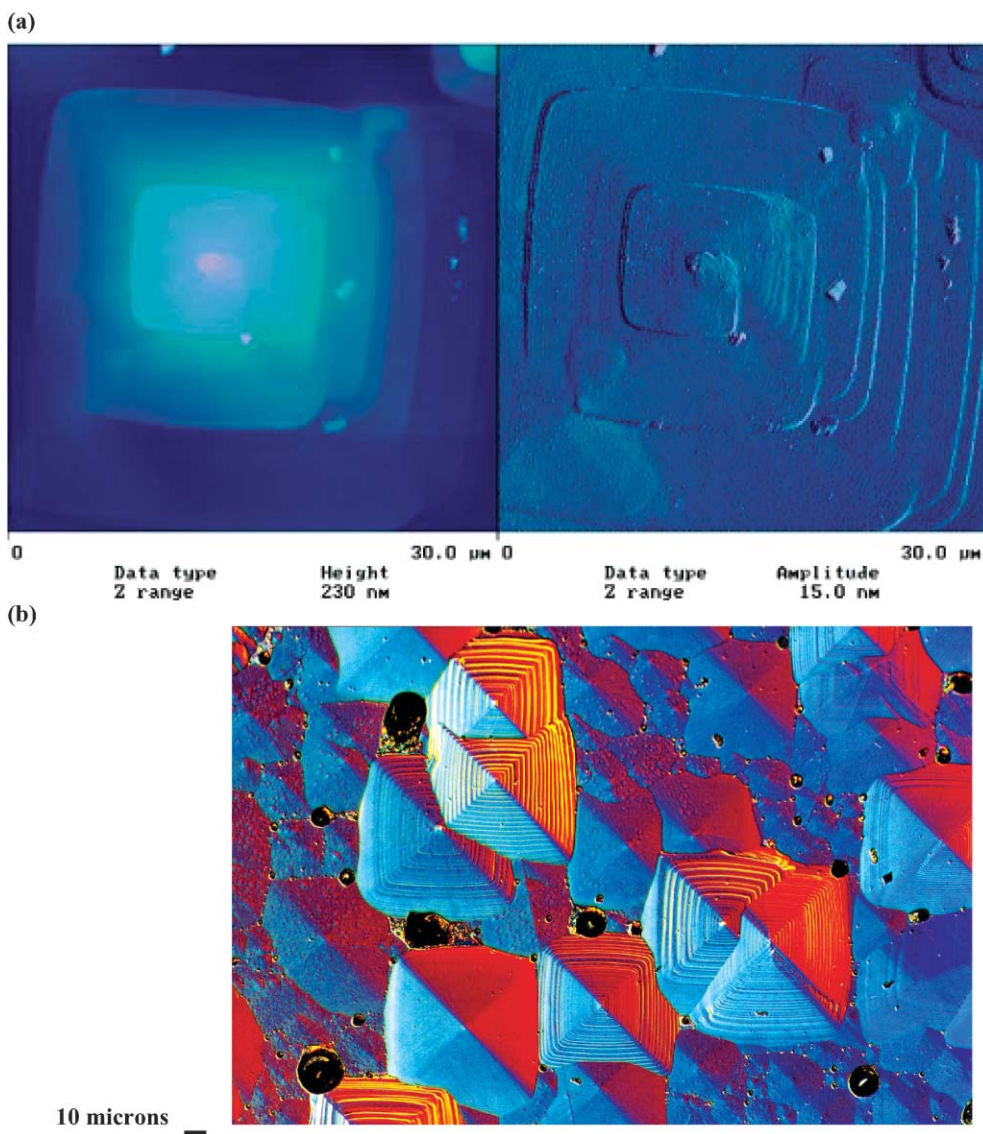
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Fig. 8 (a) AFM, and (b) optical micrographs of a 25 μm HTS film of Y–Ba–Cu–O grown by liquid phase epitaxy on a NdGaO$_3$ substrate, showing spiral growth around dislocation cores.

oxides, meaning that film properties can be tailored through film growth. Structural distortion through ion substitutions,[41,42] and interfacial strain through heteroepitaxy and lattice mismatch in thin film systems[44,84,85] provide powerful means of materials property control. Another option is the fabrication of nano-composite film structures in which two (or more) separate phases are coupled through heteroepitaxy, *e.g.* manganite/MgO[86] and multiferroic BTiO$_3$–CoFe$_2$O$_4$.[87]

This article has touched upon some of the recent developments in thin film technology which have contributed to the remarkable progress in this field, although it has necessarily been selective. Developments in magnetron design are leading to increased control over the depositing flux during sputter deposition, and the understanding of the link between the nature of the depositing flux and film structure is advancing with further developments of structure zone models. However, the complexity of the deposition environment, its characterisation and its relation to the deposition parameters, mean that

there remain many challenges. Whilst the direct measurement of the energy of depositing species is a rather specialised technique,[34] *in situ* monitoring of the deposition environment is now often achieved using plasma characterisation methods such as optical emission or absorption spectroscopy.[33,35,36]

The fabrication of complex multi-component materials, including the precise deposition of functional oxides, is currently being performed using a range of physical and chemistry-based techniques, and this article has described just a selection of these. MBE and PLD are specialised deposition methods which are contributing to advances in the understanding and development of film growth processes, as well as allowing the assessment of novel material structures, but they are limited by both cost and scalability issues. In contrast, MO-CVD is currently being used as a cost effective method for the deposition of many film materials, in addition to its major position in the semiconductor industry. This, and other chemical-based methods, offer great flexibility and control

over film composition through control of the precursor supply, although a detailed knowledge of the link between them is required. This link, and the overall optimisation of such film growth, is often investigated through extensive modelling and use of simulations, although practical trials are invariably necessary. Non-vacuum chemical growth methods such as spray pyrolysis, LPE and solution deposition offer even greater cost and scalability advantages. Their application in the growth of high quality functional materials is relatively novel, but is advancing very rapidly.

In this article, specialised *in situ* film and surface characterisation techniques (RHEED in combination with PLD, and SXRD) have been described. These enable optimisation of deposition parameters for the highest quality layer-by-layer growth of the required crystalline phases and for the development of novel materials and structures. Other techniques, such as emission and absorption spectroscopy are now quite widely used for *in situ* monitoring of film deposition parameters[46,88] and for feedback control. In addition, there is a wide range of *in situ* optical monitoring techniques (*e.g.* reflectivity, interferometry and ellipsometry) which are routinely used in production facilities for the precise control of film structure, thickness and uniformity.

This review has included some widely varying themes, from developments in high rate commercial sputter deposition techniques to growth of the most precisely controlled oxide film structures (which may be some years from eventual application). However, it can be valuable to take such an overview in order to be able to benefit from an understanding of some of the issues that are common to all thin film deposition. This is a rapidly expanding area, with methods and applications spanning many disciplines and set to have a major impact in fields from medicine and health care, through computing and communications, to energy generation and conservation, manufacturing and transport.

Acknowledgements

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