

Plasma processing techniques used at Caswell

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Abstract: The application of plasma based deposition and etching processes in materials research and device production at GMMT Caswell has been reviewed and is discussed briefly here. In particular the deposition of free standing and thin film diamond and ferroelectric films are areas of intense activity at GMMT. For diamond CVD techniques as diverse as microwave plasma and oxy - acetylene torch have been applied to date and aspects of deposition plasma chemistry are presented in relation to material properties. As the technology matures many complex problems emerge concerning the appropriate methods of increasing deposition rate, uniformity and area coverage towards the levels required for production. These are discussed and potential solutions are outlined. Finally the use of dual ion beam sputtering (DIBS) to prepare films of lead containing multi-component ferroelectric oxides for use in pyroelectric IR detectors and imagers is described. This process uses a new generation of ion guns relying on RF excitation of the plasma in the gun body. These have several advantages over the more conventional thermally driven Kaufman type ion sources in terms of materials processing.

Introduction

Plasmas play a key role in a multitude of advanced materials fabrication and engineering processes. However, despite this, the level of understanding of interactions occurring during plasma processes varies greatly. In some cases, plasma chemistry is studied in detail and related to the objective, be it film deposition, etching or surface modification. In other instances, the plasma is treated as entirely incidental as long as the final product meets the required specification. With this in mind, plasma processing at GMMT Caswell has been reviewed and is discussed in the first section of this paper. A rapidly developing area is the use of plasma deposition for thin films of materials such as diamond and ferroelectrics. Diamond is a unique material having an unmatched combination of mechanical, thermal and optical properties. The capability of low pressure diamond synthesis is giving rise to such as damage resistant IR windows and super-efficient heatsinks. The plasma processes of oxy-acetylene torch (OAT) and microwave plasma assisted chemical vapour deposition (MPACVD) are two leading diamond growth methods; the use of these two processes at GMMT is described here. Bulk ferroelectric ceramic materials are used in a wide variety of piezoelectric, pyroelectric and electro-optic devices and sensors. A particular example is the Prince of Wales Award for Innovation winning IR camera that uses an uncooled 100 x 100 pyroelectric detector array developed at Caswell. This is a hybrid device, relying on parallel processing of pyroelectric and silicon wafers followed by a flip-chip solder bump integration step. Full integration of the pyroelectric as a thin film deposited directly onto the silicon readout circuitry would bring enormous benefits in terms of enhanced detectivity and speed as well as reducing device size and cost. A range of plasma and non-plasma based film deposition techniques are at present vying for supremacy. At Caswell, the use of dual ion beam sputtering (DIBS) is described for integrated pyroelectric films on silicon.

Plasma Processing at GMMT Caswell

Caswell is part of GMMT Ltd and has approximately 370 employees, many with high level qualifications, and an annual turnover of order £17M (1991/2). There are three divisions, namely GaAs, Optoelectronics and Sensors. GaAs RF / microwave products include discrete FETs and a wide range of switches, attenuators and amplifiers. A recent development is the HEMT with a 0.6dB noise figure, 11dB gain device at 12GHz. A 75mm wafer fabrication line has recently opened to meet increased product demand. Optoelectronics produce lasers and broadband LED structures based on GaAs/AlGaAs, Optical Electronic Integrated Circuits (OEICs) and modulators based on GaAs, and a range of lasers, LEDs and detectors based on InP/InGaAsP. These are used in telecommunications, datalinks and in larger Caswell developed systems such as high speed coherent multichannel systems. Sensors maintain a leading edge in uncooled pyroelectric single element and arrayed IR detectors which are used for monitoring and surveillance in the automotive, military and security industries. Also, electronic packaging, piezoelectric devices and IR optical materials (particularly diamond) are under development.

Excluding trivia (e.g. plasma ashers), plasma processing in the three divisions has been surveyed. There are some 20 plasma based deposition systems and a similar number of etching systems corresponding to a similar number of materials processes, although more than one machine can be dedicated to a single process and vice versa. The split between R&D and production is not always easy to define; for GaAs and Optoelectronics this is approximately 50% but for Sensors the majority of processes are R&D. It is interesting that, although there has been a shift in emphasis towards production in recent years, R&D still remains a major activity at Caswell. Also, that GaAs and Optoelectronics devote more effort to (or, perhaps, are more critically dependent on) plasma diagnostics than sensors; most of their systems can use OES for plasma diagnostics or end-point detection. Optoelectronics have developed an acknowledged downstream mass spectrometry technique (including residual gas analysis and SIMS modes for quantification of layering during etching of III-V superlattice structures (1)). The plasma processes in both these divisions use exclusively PECVD and sputtering for deposition and RIE and IBE (including CAIBE and CARIBE) for etching. The majority of materials used are conventional in electronic fabrication lines, ie SiN, SiO₂, metals and polymers and use halide, argon, oxygen and hydrogen/ hydrocarbon etching chemistries. However there is also specialized knowledge of the etching of GaAs and multilayer III-V optical multilayers such as GaAlInAs and GaInAsP. On the other hand, sensors make use of more exotic plasma generation, eg, microwave at 2.45GHz in MPACVD diamond deposition systems, thermal in the OAT diamond system and filamentless RF ion guns for ion beam sputtering rather than thermally driven Kaufman type source. Sensors carry out less plasma diagnostics with only one system fitted with OES, partly because development is still at the materials rather than device stage.

A characteristic feature of recent GaAs MMICs has been a dry etched via hole through the 200 μ m thickness of the chip. This is subsequently metallized and allows direct grounding of circuit components to the metallized ground plane formed by the back surface of the wafer. The advantages of this feature are that any part of a chip may be grounded (reducing layout constraints), and also that bond wires to ground are reduced in length and number giving a reduction in parasitic inductance. The via holes are etched from the rear of the wafer to expose front-face metal pads and are aligned using infra-red optics to see through the wafer. In order to react with GaAs and form volatile etch products, a chlorine containing gas is necessary and Freon -12 (CCl₂F₂) has been found suitable. As this gas is a CFC, alternative gases are now being evaluated, with pure chlorine and silicon tetrachloride being considered as probable etchants. The anisotropic RIE process gives a steep sided etched hole without over - large apertures on the back surface of the wafer. Chemical selectivity prevents the etch penetrating gold based metals about 1 μ m thick on the front surface. A cross-section of a typical through via hole (before metallization) is shown in Fig. 1. The chemistry of the etch process is not well understood and is complicated by admission of air during loading if a load locked RIE system is not employed. The process will readily form polymers if not controlled which can totally inhibit etching. The anisotropic etch does cause problems to the mask, which can be eroded during the 200 μ m GaAs etch. Photoresist alone is not usually suitable and is used in conjunction with a metal mask. For chemical reasons the presence of nickel catalyses the GaAs etch and etch rates are approximately doubled by the presence of nickel. GaAs etched by wet or dry processes can show anisotropy as a result of crystallographic etching effects. This leads to some parts of the via hole exhibiting an undercut profile. It is essential to ensure that subsequent metallisation coats this feature and bias sputtering is a valuable technique for this process step. Size reduction is a desirable objective for future development of the process, but the deep features do pose problems in access of reactant gas to the via hole and etch rates diminish from 5 μ m/min to 2 μ m/min as etching proceeds. An extension of the technology (used in power MMICs) has been to etch recesses directly under the transistors (which generate heat), the recesses are 150 μ m deep and are subsequently filled with gold and act as heat-sinks.

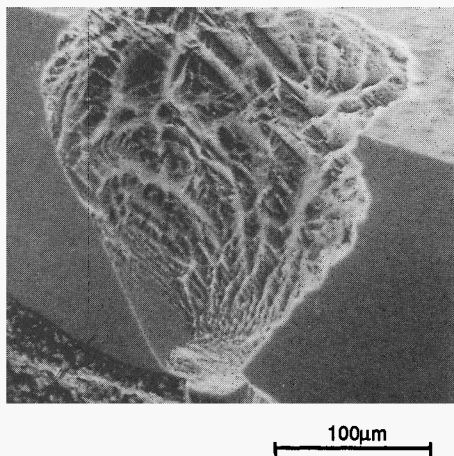


Fig. 1 Via hole through GaAs chip

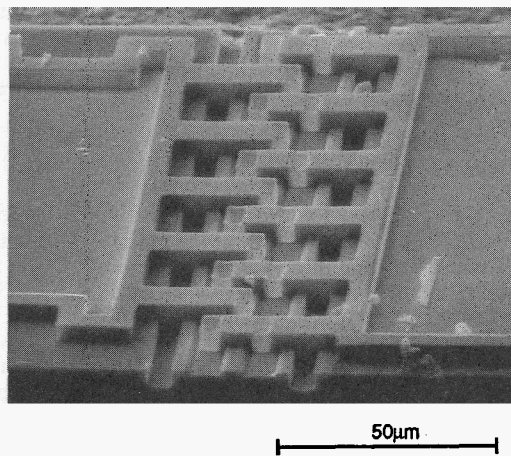


Fig. 2 Completed BR - DFB laser

A main thrust of Optoelectronics is the fabrication of devices and modules for optical communication in the form of OEICs, utilizing the optical and electrical properties of the III-V semiconductors. Fundamental to this aim is a high performance laser compatible with integration technology. The laser design developed at Caswell is a buried ridge distributed feedback (DFB) structure which allows precise control of the wavelength, a stringent requirement in transmission systems. The structures consist of InP and GaInAsP layers, incorporating quantum wells within the design. Pattern transfer into this type of material structure requires non-selective, precise etching with controlled profiles to achieve the designed architecture for optimum device performance. For these types of material structures a CH_4/H_2 process has been used. Figure 2 is an SEM view of a completed BR-DFB laser, illustrating the etched features. This process has been developed for the formation of isolation channels (2) in the DFB laser fabrication. By changing plasma parameters, it is possible to change the etch features to suit particular applications. This etch mixture has been tailored to our requirements to fabricate more advanced chips with several functions present on the same chip, such as duplexers (3) and narrow band filters (4).

Diamond Films by MPACVD and OAT

Interest in polycrystalline CVD diamond at GMMT stemmed from a desire to apply thin protective diamond films to conventional IR window materials for use in severe environments. Rapid improvements in growth rate and phase purity have opened up applications to include free standing diamond for multi-spectral windows, heat sinks and spreaders. These components will enable systems manufacturers in the aerospace and semiconductor industries to implement exotic designs that would previously have been unfeasible due to the limitations of existing materials or the cost of natural diamond. An illustration is the 3D multichip module (5), an attractive route for increasing IC packing density and reducing interconnect length, where theoretical comparisons have been made between diamond and AlN. For equivalent sized substrates in an edge cooled 500W circuit board, the use of diamond heat sinks would result in a 31°C temperature rise from semiconductor junction to heat sink, whereas with AlN, there would be an unacceptable rise of 367°C. Diamond would permit either higher power devices or increased reliability.

A myriad of techniques have been used to produce CVD diamond, and can be broadly categorized in ascending order of linear deposition rate viz. thermal decomposition, RF/DC glow discharge, hot filament, MPACVD, microwave plasma jet, OAT and local thermal equilibrium RF/DC plasma jets. This order corresponds with increasing neutral gas temperature (6). At GMMT, the OAT and MPACVD methods have been selected as both offer particular benefits although fundamentally different in concept.

The use of OAT for diamond synthesis was pioneered by Hirose (7) who demonstrated linear growth rates of more than $100\mu\text{m hr}^{-1}$ using a single nozzle burner. OAT utilises conventional welding torch apparatus but is run with an excess of fuel which modifies the flame chemistry. Studies of the flame structure have shown it to be composed of an inner core where the temperature may exceed 3000K, a reducing acetylene feather which is rich in C radicals and an oxidising outer region. Excited state CH , C_2 and OH species have been observed and a growth mechanism based on CH_3 has gained some acceptance. A single nozzle set up at GMMT confirmed that diamond films could be produced for little capital outlay, although area coverage was limited to a few tens of mm^2 . Continued development of OAT has resulted in the relatively sophisticated system shown in Fig. 3, but capital cost is still less than that of a microwave supply. The OAT is theoretically suitable for large area coverage but it has been observed that a scanned single nozzle does not maintain the diamond phase purity observed in the static case. A further problem is the significant thermal stress that can be produced by scanning a single point heat source leading to substrate buckling or even fracture. To overcome this problem, multi-flame nozzles have been developed in the form of single and dual linear arrays of growth flames surrounded by a ring of oxy-propane 'guard' flames. The guard flames serve the dual purpose of limiting the ingress of the atmosphere which can result in oxidation of Mo substrates and minimizing temperature variations across the substrate surface as they track the growth flames during raster scanning of the substrate. As OAT is an atmospheric process, thermodynamic considerations dictate the use of acetylene to achieve adequate flame temperatures thus flame chemistry investigations have centred on etch species. Unlike MPACVD, the OAT is not limited by deposition rate but by diamond phase purity, thus hydrogen addition and oxygen pulsing have been investigated to improve the crystalline quality. Atomic H is recognised as a crucial etchant of non-diamond carbon and is further believed to stabilise diamond with respect to graphite and even to convert non- sp^3C to diamond. The use of oxygen pulsing, where the oxygen flow is periodically increased, alters the nature of the flame from net deposition to etching. This permits the use of growth:etch cycles where the flame traverses the substrate at typically 0.1mms^{-1} under growth conditions followed by a reverse etch cycle at 0.4mms^{-1} . Both oxygen pulsing and hydrogen addition significantly reduce the degree of secondary nucleation observed on diamond crystallites and improve purity, as determined by SEM and Raman spectroscopy respectively. Films up to 20 x 20mm and $500\mu\text{m}$ thick have been produced by OAT, but to achieve the high purity and coat extended areas the growth rate has to be sacrificed to levels which are comparable to MPACVD. At this point, gas cost becomes a significant factor which can negate the low capital outlay as there is no potential for recycling gas and flow rates of several litres per minutes are necessary.

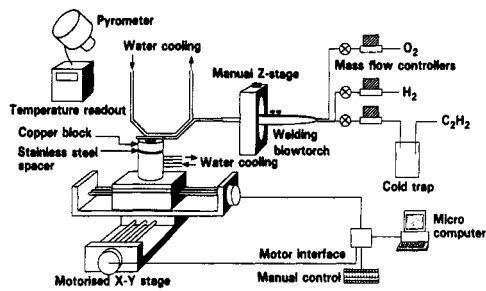


Fig. 3 Schematic of scanning oxy - acetylene torch system

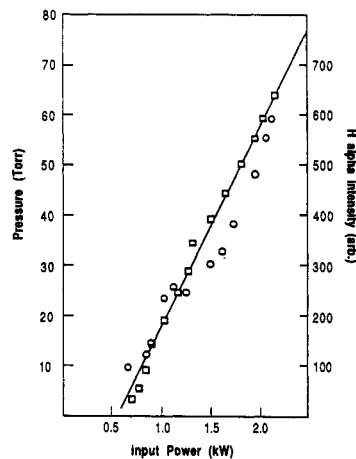


Fig. 4 Graph of plasma stability limit

MPACVD widely employed for diamond deposition and a variety of system have been developed. The use of microwave excitation is essential for diamond growth plasmas as electron energies of $\sim 9\text{eV}$ are required for significant H_2 dissociation to occur by electron impact. As average energies of $\sim 6\text{eV}$ have been measured in 2.45GHz (8) plasmas there are sufficient electrons in the high energy tail of the electron energy distribution function to generate an excess of atomic H; this requirement has largely precluded conventional low frequency RF parallel plate reactors. As the free space wavelength is comparable to the chamber diameter in microwave systems, some problems are evident in reactor design and typical films exhibit a pronounced non-uniformity in both thickness and morphology across the surface. Thickness non-uniformity is inconvenient and uneconomical as significant quantities of diamond must be removed to planarise a surface. Non-uniformity in morphology is, however, wholly unacceptable as this implies a variation in thermal and optical properties which will be detrimental in systems applications. In the case of optical windows, this could generate aberrations which would require corrective engineering and hence increased complexity and cost, thus even the growth of 150mm diamond plates would only represent a partial breakthrough if this non-uniformity persists.

The deposition rate is also a concern in MPACVD systems which have typically employed power supplies of less than 1.5kW and produced linear rates of a few $\mu\text{m hr}^{-1}$. The majority of work at GMMT has been performed with a simple bell jar system, which whilst capable of producing films of high crystalline quality, suffered from the aforementioned limitations. As a first step towards increased growth rate, a 6kW power supply was incorporated but plasma stability problems were apparent above 1kW. The cylindrical microwave cavity operates in TM_{012} mode, thus two points of maximum electric field strength exist in the unloaded cavity. (The presence of plasma may permit other modes to occur). In operation, this results in two positions which the plasma ball can occupy, in direct contact with the substrate ('stable') where the plasma is sustained by the lower half of the standing wave pattern. In the 'unstable' position, the plasma lifts towards the microwave antenna feed and, as the upper position of maximum electric field strength is coincident with the bell jar roof, this creates undesirable effects. At low powers, this may result in etching of the bell jar yielding Si contamination in the diamond film, whilst at high powers this can lead to rapid destruction of the bell jar. In order to confine the plasma to the substrate it is necessary to increment chamber pressure and microwave power sequentially to remain within the stability range shown in Fig. 4. The stability cut off is the minimum pressure required to confine a plasma of a given power to the substrate. This linear relation approximately corresponds with the intensity of the H_α emission of atomic H and holds for simple CH_4/H_2 mixtures. The addition of easily ionised noble gases results in instability at much lower powers. The use of high pressure to confine the plasma leads to a diminishing return in terms of growth rate. As the power is increased, with consequent pressure increases, the mean free path of the active species decreases until a growth rate plateau is reached and further power-pressure increases merely reduce the efficiency of the process. This limitation of the bell jar system for high power deposition has led to the adoption of an alternative design where the TM_{012} field pattern is bisected by a flat quartz window. As only the lower point of maximum electric field strength is exposed to the process gases, there is no potential for the type of gross plasma instability observed in the bell jar system but problems can still occur due to satellite plasma formation on any sharp, conductive edges present.

As diamond CVD moves towards production, it is useful to re-assess the prominent competing technologies. For the applications of direct interest to GMMT, namely windows, optical coatings and heatsinks, the hot filament method remains unattractive due to impurity contamination and the scale up complexities resulting

from filament embrittlement. The DC/RF plasma jet systems, while clearly advancing and producing high quality material still give rise to questions on economic grounds due to their carbon conversion efficiency and huge gas flow requirements. Recirculatory gas systems have been proposed but there are, as yet, no reports of their implementation. The scale up of OAT has been at a lower than anticipated rate and large area coverage has not been realised. These three methods are tied by the fact that no equipment vendors exist, which has resulted in individual companies/institutions undertaking equipment and process development programmes. This is in contrast to MPACVD where sub-assemblies such as microwave supplies and applicators are readily available and a company already exists which is largely dedicated to the provision of MPACVD diamond equipment. This may be a result of the universal acceptance of the original research type systems but recent developments indicate that a second generation of diamond MPACVD systems may have the capability of meeting the requirements of diamond growers who have identified their market and seek to commercialise new products. Notable examples are high power 2.45GHz monomode and multimode ball plasma systems, 2.45GHz microwave plasma jets (9) and 915MHz large area ball plasma systems. The high power (5-6kW) 2.45GHz monomode systems are largely extensions of the original designs with the necessary incorporation of substrate cooling due to increased plasma power densities. Deposition rates up to $15\mu\text{m hr}^{-1}$ have been achieved and detailed consideration of microwave cavity design have yielded uniformity improvements up to $\pm 5\%$ thickness variation across a 50mm wafer with no change in morphology. It is believed that this can be extended to 75mm with similar uniformity. Elegant designs exist for multimode 2.45GHz systems although it is not presently clear whether these have reached the hardware stage. The limited availability of 2.45GHz magnetrons larger than 6kW may restrict such multimode systems to coatings applications as the power density may be low for high growth rates over diameters up to 200mm. A further problem is their inability to uniformly coat complex geometry substrates such as domes. This facility is afforded by a remarkable, 2.45GHz microwave plasma torch system which can uniformly coat two 200mm diameter substrates simultaneously. The key to operation of this system is the use of high gas velocities to produce convective flow of reactant species as opposed to the diffusion limited transfer in conventional ball plasma systems. The provision of gas recirculation retains the efficiency of the MPACVD process and net gas consumption is comparable to monomode systems. As yet, large area coverage and high rate deposition (more than $10\mu\text{m hr}^{-1}$) do not co-exist at 2.45GHz, which has been a motivation for the use of lower excitation frequencies, notably 915MHz. Despite the anticipation of moderate drops in electron temperature and density from 2.45GHz the availability of power supplies up to 75kW provides the potential for high rate deposition over 200mm. Each system fulfils a specific role; the high power 2.45GHz monomode is suitable for advanced research and pilot production of bulk diamond components. The microwave plasma jet system is ideal for coating conventional IR windows and domes as well as volume manufacture of mechanical components such as cutting tool inserts. The 2.45GHz multimode system remains attractive due to anticipated similarity in plasma chemistry to original MPACVD systems. The 915MHz system must, however, represent the best hope for provision of large area bulk diamond components.

Integrated Pyroelectric Films on Silicon by Dual Ion Beam Sputtering

Ferroelectric oxide materials of the perovskite crystal structure possess a spontaneous switchable electric polarization that is the basis of many piezoelectric, pyroelectric and electro-optic devices. Successful integration of these materials as thin films would result in devices of greater speed and sensitivity as well as substantial cost reduction due to the elimination of expensive bulk ceramic production. Additional device possibilities arise due to the thin film geometry, the prime example of which is semiconductor ferroelectric random access memory (FERAM) which would be non-volatile, fast and radiation hard. FERAM has the potential to replace nearly all existing memory technology and has driven ferroelectric thin film development (10) and also stimulated the areas of sensors, transducers, actuators, optical switching and capacitors where thin ferroelectric films would offer significant benefits (11).

The key to achieving thin film devices is the availability of a deposition technique that produces high quality ferroelectric films with properties similar to bulk. Further, the technique must be compatible with conventional silicon wafer fabrication materials and processes. Due to these constraints thin film development has focussed mainly on established ferroelectric materials, in particular the perovskite titanates and zirconates. Pure and lanthanum doped lead titanate (PT and PLT) and lead zirconate titanate (PZT) offer the most for pyroelectric and other thin film ferroelectric applications. Unfortunately as these materials contain lead and require high processing temperatures (450 - 700°C) it is difficult to incorporate into silicon (and GaAs) processing. A range of techniques are vying for acceptance as a preferred route for thin film formation. These fall into three categories namely CVD, PVD and wet processes such as sol-gel. Each has advantages and disadvantages in terms of cost, process control and maximum required temperature (10). CVD includes MOCVD and PECVD which give good conformal large area coverage and ready variation of stoichiometry as long as suitable volatile precursors are available; for a heavy element like lead this is not always straightforward. In sol-gel liquid precursors are spun down at room temperature and then subjected to an annealing cycle to drive off the organic and crystallize the film. It is a simple low temperature technique that is cheap but, as yet, has not totally matched the quality of the films obtainable by CVD and PVD. PVD covers evaporation, sputter and laser ablation type approaches. Sputter based processes have been used for most of

the early ferroelectric thin film work due to the use of the technique for other thin film processes. Laser ablation, particularly using deep UV lasers, can produce stoichiometric multicomponent oxide films of exceptional quality from a small ceramic target as evidenced by ferroelectric and superconductor thin film work. However thickness nonuniformity in the deposit is a major problem which can only be overcome by complicated geometrical arrangements. At GMMT, MOCVD, laser ablation, sol gel, magnetron sputtering and DIBS have all been examined over the last ten years. Currently sol gel and DIBS are subject to intense development for the production of integrated pyroelectric imaging arrays for the long wave infrared. Such arrays have cost and size advantages over cooled photon semiconductor band-gap detectors and will allow penetration into domestic markets like security, fire detection and vision enhancement for motor vehicles.

Ion and multiple ion beam deposition techniques have been demonstrated to produce dense films with enhanced optical and mechanical properties (13). The primary advantage over competing PVD processes lies in the independent control that can be exercised over the energy and flux of the ions used for both sputtering of the target and bombarding of the depositing film. In conventional RF sputtering, and the laser ablation method, little direct control can be exercised over the wide distribution of particle energies in the plasma. The isolation of the plasma in an ion gun body not only removes a source of uncontrolled bombardment but also allows a lower process pressure since the gun extraction grids act as gas baffles. These characteristics result in a high degree of process control and flexibility.

The Nordiko 3450 dual ion beam sputtering (DIBS) system is composed of a cryo and turbomolecular pumped chamber, base pressure 5×10^{-8} torr, a target turret, an 700°C rotating heater platen and two 100mm diameter ion guns, Fig. 5. The ion gun plasmas are driven by RF (13.56MHz) and represent a significant advance from thermal plasma driven Kaufman-type sources. The RF driven guns obviate the need for a hot filament thus eliminating a source of film contamination and have been found to run continuously for hundreds of hours in pure oxygen. RF plasmas typically only require 100W input power to sustain the discharge resulting in cooler system operating conditions. The chamber also has filamentless electron sources for beam neutralization and Faraday cups for the measurement of beam current density. A two colour IR fibre pyrometer allows accurate measurement of the substrate surface temperature. Generally, a high energy Ar or Kr ion beam in the range 600-700eV, 80-100mA and beam current density (BCD) $1\text{-}5\text{mA}/\text{cm}^2$ is used to sputter material from a target while the substrate is immersed in a pure oxygen ion beam of 0-200eV, 0-40mA and BCD $0\text{-}0.2\text{mA}/\text{cm}^2$. More energetic ion beams can be used to pre - clean the target and substrate. A neutralization level of 110% of the ion beam current ensures stability during the deposition of insulating films. Deposition pressure is typically 10^{-4} torr. Thermally oxidized (100) Si, (1102) sapphire and (100) MgO with an e-beam deposited titanium/platinum electrode structure of thicknesses $50\text{\AA}/1000\text{\AA}$ used for the pyroelectric film deposition.

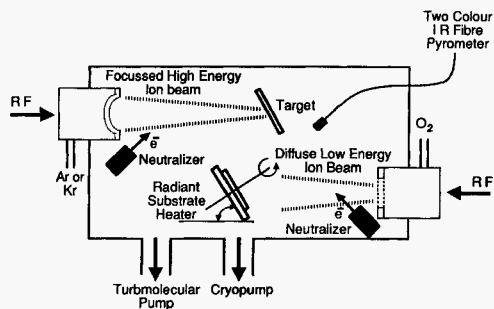


Fig.5 Schematic of dual ion beam sputter system

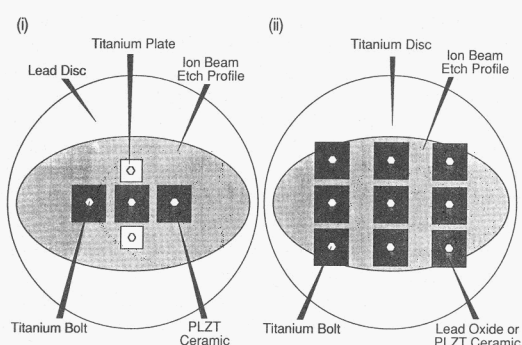


Fig. 6 Targets used for ferroelectric film deposition
(i) Metallic Ti / Pb (ii) PbO / PLT ceramic on Ti

For pure and lanthanum doped lead titanate deposition, adjustable composite targets have been developed as depicted in Fig. 6. In the first, pieces of titanium metal and/or PLT ceramic were bolted to a copper backing plate through a lead sheet using high purity titanium bolts. Two problems were encountered with this design in that the metallic lead was found to age rapidly making consistent stoichiometric control difficult and that high energy Ar neutrals reflected from the target impinge damagingly on the depositing film. To overcome this, the second target type composed of PbO secured on a titanium plate, has been developed and the

sputtering gas switched to Kr. The energy of Kr neutrals reflected from the target is reduced since the atomic weights are more closely matched and the absence of metallic lead eliminated target ageing anomalies. For stoichiometric control a better solution than a single segmented target would seem to be multiple targets and ion guns; however this is an expensive and complicated option. However, an interesting feature of the current single target process is the tolerance of the final film composition to the surface area of PbO and titanium exposed. Above a critical area coverage of PbO on the target the Pb/(Pb+Ti) ratio in the film settles at 0.57 independent of the growth temperature; the volatility of PbO is such that any further excess is not retained in the film. Why the ratio settles at 0.57 and not at the stoichiometric level of 0.5 is unknown. It may be an artefact of electron probe microanalysis although reference to a ceramic standard indicates this ratio to be real. Sol gel processes have been found to give improved crystallization for excess lead of typically 10% whilst DIBS films correspond to excess level of order 40% but still have high quality and good pyroelectric properties.

Generally, most PVD deposition processes produce amorphous lead titanate films up to 450°C, the pyrochlore phase between 450-500°C, the perovskite phase for the range 500-600°C and the lead deficient films above 650°C; in the 500-550°C regime, there exists a transitional mixed pyrochlore/perovskite structure (10). In the present study, use of the system in a single ion beam sputter (IBS) mode with merely molecular oxygen flowing through the secondary ion gun could not produce any perovskite material. Up to 500°C the films remained amorphous and beyond this temperature rapidly became totally lead deficient. Generation of an oxygen plasma in the secondary ion gun resulted in maximum retention of lead in the films even in excess of 700°C; in IBS mode 700°C gave a pure TiO₂ (rutile structure) film. It is intriguing that the generation of an oxygen plasma seemed to be the critical factor in this effect. The extraction of an oxygen beam of energy 50-100eV to bombard to growing film reduces the film lead content by a few % but did result in films with a slightly higher refractive index, indicating a higher density, but in all other respects they were identical to those grown with only an oxygen plasma present. Energies in excess of 100eV were detrimental to the film growth rate and rendered the films amorphous by preventing the formation of the perovskite structure although the ratio of Pb to Ti remained constant. This implies the bombarding beam resputters Pb and Ti equally at higher energies and inhibits crystallization by damaging the surface structure. It is apparent that the presence of active oxygen was the key element in enhancing the sticking coefficient of Pb. It is also significant that the oxygen plasma to substrate separation of 30 cm is close to the mean free path of order 50cm at the deposition pressure; this implies active species such as O₂⁺, O⁺ and O reach the substrate unimpeded. Probing of the region between the plasma and the substrate with the faraday cup did not reveal any (i.e. non-neutralized) spontaneous beam generation. In the DIBS mode, the PLT films were found to be amorphous up to 500°C, above which perovskite peaks began to appear in the X-ray diffraction (XRD) spectra, and were single phase perovskite at or above 550°C; no pyrochlore phase was seen at any temperature. Surprisingly, it has not been found that concurrent oxygen ion bombardment lowers the perovskite crystallization temperature, indeed the evidence is that it is raised, but it does create an extended temperature window within which the perovskite phase dominates and gives denser films.

Uniformity of film thickness, composition and pyroelectric properties of 2% over 60mm has been achieved. In all cases the PLT/PbO/Ti target and Kr gave the best uniformity and repeatability and a growth rate of 0.35µm/hour; for the Pb/Ti target and Ar the rate was only 0.08µm/hour. Higher rates could be achieved by depositing amorphous films and post annealing at high temperature to attain the perovskite phase; however the film properties were markedly inferior to in-situ grown perovskite films. Figure 7 shows bright field plan view TEMs of two lead titanate films detached from Si. One was grown by Ar ion sputtering of the Pb/Ti target and shows considerable texture due a high level of imperfection and defects in the film. It is likely that much of this disorder has been introduced by low flux high energy bombardment of the film by Ar atoms reflected from the target. Comparison to the Ar content of films deposited by RF sputtering with RF bias on the substrate places the energy of bombardment at 200-300eV. This is typically half the accelerating potential of the sputtering beam and is consistent with elastic recoil of Ar from the target. This energy level is sufficient for the Ar atoms to implant and damage the crystal structure of the lead film. The second was grown by Kr sputtering of a PbO/Ti target and shows greatly reduced levels of disorder and a larger grain size. Domains and twinning are visible in some individual grains but the overall film structure and grain texture is similar to that seen by TEM of doped lead titanate bulk ceramics manufactured at Caswell.

In general, it was found that films crystallized more readily on the Pt/Ti electrode than the bare substrate and that the Pt itself took up a highly preferred (111) orientation during PLT deposition. At elevated temperatures (>600°C) the orientation of the film was a strong function of the thermal expansion coefficient of the substrate. The low coefficient of Si ($3 \times 10^{-6} \text{K}^{-1}$) places the film in tension on cooling and at the cubic-tetragonal phase change confines the longer (001) c axis to the plane of the substrate giving a (100) film orientation. For MgO ($14 \times 10^{-6} \text{K}^{-1}$) the opposite occurs giving a (001) film and for sapphire ($7.5 \times 10^{-6} \text{K}^{-1}$) a mixed (100)/(001) orientation results. A (001) orientation is optimum for pyroelectric detection so for integrated devices on Si the films needs repoling or re-orienting. Fortunately, as the deposition temperature drops below 600°C a sudden switch to a (111) film orientation occurs for all three substrate materials. The hypothesis for this behaviour is

that during deposition the PLT film lattice matches to the (111) platinum structure. During cooling, thermal mismatch stresses build up which, for high deposition temperatures, become sufficient to overcome this lattice match and convert the film to (100) or (001) as appropriate.

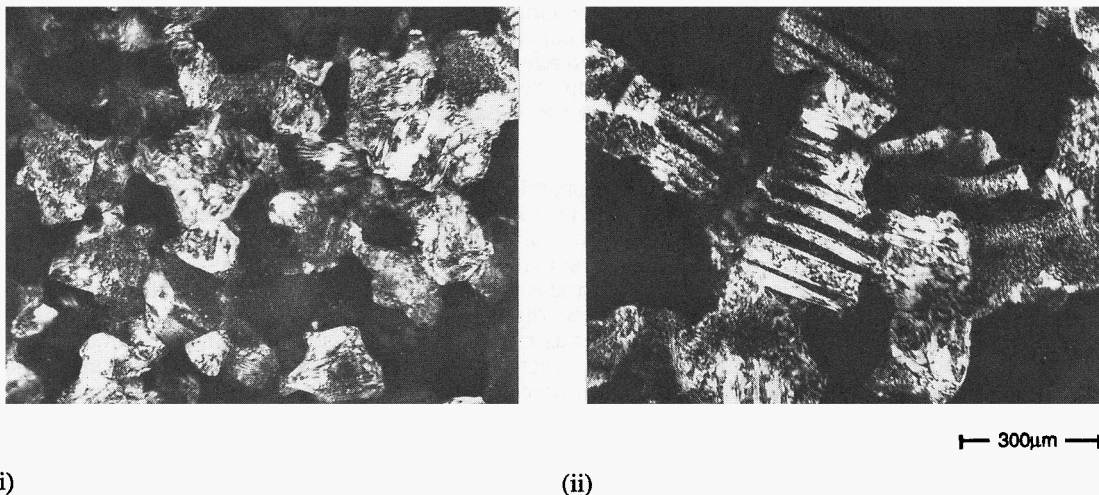


Fig. 7 Dark field TEM images of (i) PLT grown by Ar sputtering of metallic Pb/Ti target , and (ii) PLT grown by Kr sputtering of PbO / PLT ceramic on metallic Ti target

To examine electric and pyroelectric properties of the films 1mm diameter Cr/Au electrodes were evaporated onto the top surface. The 5-10 atomic% lanthanum doped films were found to be markedly better than the pure lead titanate. Pyroelectric coefficients for (001), mixed (001)/(100) and (100) films were typically 250, 100 and 50 $\mu\text{Cm}^{-2}\text{K}^{-1}$ for La doped lead titanate films on MgO, sapphire and Si respectively; the figures of merit, F_D , were 2.1, 1.5 and 0.6 $\times 10^{-5}\text{Pa}^{-0.5}$; $F_D = p C_V^{-1}(E_0 E_r \tan\delta)^{-0.5}$, p is the pyroelectric coefficient, C_V is the thermal capacity, E_0 the permittivity of free space, E_r the relative dielectric constant and $\tan\delta$ the dielectric loss. This illustrates the strong dependence of properties on film orientation and substrate. The (111) films gave 250 $\mu\text{Cm}^{-2}\text{K}^{-1}$ and 2.2 $\times 10^{-5}\text{Pa}^{-0.5}$ irrespective of substrate; these properties are viable for pyroelectric detector devices and it is interesting that they are better than for (001) films on MgO. This is because although the ceramic material used in the GMMT hybrid detector has an F_D of order 3-4 $\times 10^{-5}\text{Pa}^{-0.5}$, integration of films onto micromachined Si will give an order of magnitude improvement in thermal isolation and ultimate detectivity.

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