

MOLECULAR BEAM EPITAXY FOR THE GROWTH OF FERROELECTRIC THIN FILMS

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Abstract: Recent developments in the field of thin film ferroelectrics include also deposition by a molecular beam epitaxy process. It is anticipated that this will yield high quality epitaxial films and two-dimensional ferroelectric structures. Present paper discusses the requirements which have to be fulfilled for a successful and controlled deposition of ferroelectric thin films in an UHV environment and gives a comparison with the classical MBE. It describes the feasible methods to obtain stable low pressure molecular beams of different metals and briefly discussed the in-situ low temperature oxidation issue.

Rast tankih feroelektričnih plasti z molekularno epitaksijo

Ključne besede: mikroelektronika, plasti tanke, plasti feroelektrične, MBE rast molekularna žarkovna epitaksialna, nanašanje materialov, strukture 2 D dvodimenzionalne, UHV vakuum ultravisoki

Povzetek: Med dosežke najnovejšega razvoja feroelektričnih tankih plasti štejemo tudi rast le-teh s tehniko molekularne epitaksije. Predvidoma bomo s pomočjo te tehnike uspeli nanesti feroelektrične tanke plasti visoke kvalitete in izdelati dvodimenzionalne feroelektrične strukture. V pričujočem delu obravnavamo zahteve, ki morajo biti izpolnjene, če hočemo uspešno in kontrolirano nanesti feroelektrične tanke plasti v UHV okolju in hkrati jih primerjamo s klasično MBE metodo. Nadalje opisujemo ustrezne pristope, s katerimi dobimo stabilne molekularne tokove različnih kovin pri nizkih tlakih, kakor tudi na kratko obravnavamo nizekotemperaturno oksidacijo na licu mesta.

1. Introduction

1.1. Ferroelectric Thin Films

Ferroelectrics are a very complex class of materials which combine a large variety of useful properties in a single material; i.e., mechanical, optical, electrical, ferroelectric, piezoelectric, pyroelectric, electro-optic, non-linear-optic, acousto-optic... The sensitivity of these properties to external stimuli makes ferroelectrics interesting for a wide variety of applications in electronics, sensoric, micromachines and transducers, and in integrated and acousto-optics. Their main attribute is spontaneous electrical polarization (arising from the relative displacement of the ions within the unit cell) which has more than one possible equilibrium orientation and can be thus switched by the application of an adequate external electric field. In many ferroelectrics the polarization decreases with temperature and vanishes at the ferroelectric phase transition or Curie point T_C . Ferroelectrics crystallize in many crystal structures, however, the cubic perovskite structure, which is the high temperature form of many ABO_3 oxides, is probably the most important ferroelectric prototype. To this family belong technologically important ferroelectrics like $BaTiO_3$,

$PbTiO_3$, $SrTiO_3$, $PbZrO_3$, $NaNbO_3$, $KNbO_3$, or solid solutions of these materials. The other two technologically interesting ABO_3 compounds are $LiNbO_3$ and $LiTaO_3$ which have a similar coordination but a hexagonal structure. The ion displacements in the ferroelectric phase are for the latter two materials exceedingly large. Ferroelectrics have been most commonly used in a ceramic or crystalline bulk form. Their advantages in a thin film form have been recognized in the 80's and since then a variety of deposition techniques have been applied for their production. We can divide them into two large groups; with and without particle bombardment. While at the beginning of the ferroelectric thin film work the techniques with bombardment, like different kinds of sputtering, were very popular, today they seem to be fading out to give room to less expensive techniques, like sol-gel, or to advanced growth techniques like metallorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), where a high control over the growth process is available. Figure 1 shows a chart of the most commonly used deposition techniques. PZT and related ferroelectrics were probably the most popular materials grown in thin film form. Nevertheless, development of ferroelectric thin films with controlled properties at relatively low growth temperatures still

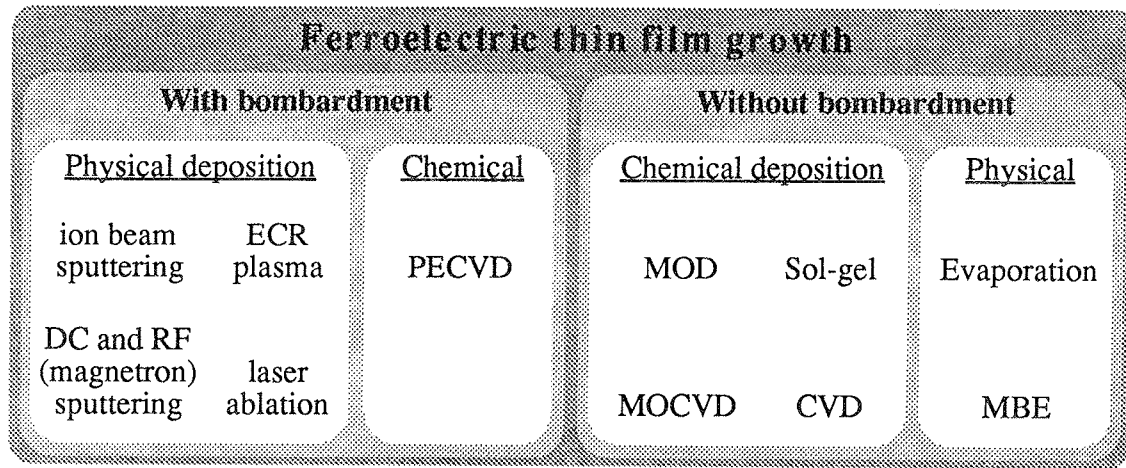


Fig. 1: Thin film deposition methods used for the growth and deposition of ferroelectric thin films

remains a major research task and among all deposition techniques being used today no single method seems to be a clear winner. While sol-gel method is widely used for the deposition of thicker films where the grain structure and high cycling temperatures do not matter, the growth of high quality epitaxial two dimensional structures will have to be performed by MOCVD or MBE.

1.2. Molecular Beam Epitaxy in Science and Technology

MBE has been developed over the last two decades as a response to the need for a thin film growth technique capable of depositing nearly perfect and contamination free semiconducting materials with very well defined thicknesses in the range of a single monolayer to several hundreds of monolayers. Since the pioneering work of J. R. Arthur and A. Y. Cho /1,2/ the technique has

matured into a sophisticated thin film growth tool which has been applied mainly to the growth of different compound semiconductors but is currently evolving also in the field of high T_C superconductors and dielectrics. It is not an exaggeration to say that MBE has not only made possible the fabrication of classical quantum mechanical structures but has extended the imagination of researchers and device physicist to design a whole new generation of devices based on new artificially structured materials. In general terms, MBE is a refined form of vacuum evaporation. The hardware system usually consists of two to three interconnected stainless steel chambers; a growth chamber, a load lock, and an optional surface analysis chamber. A load lock is essential for maintaining UHV conditions over many growth runs. In the MBE process molecular beams, directed beams of neutral molecules or atoms of a relatively low density produced by heating solid substances in effusion cells, impinge under the ultra high vacuum (UHV) conditions

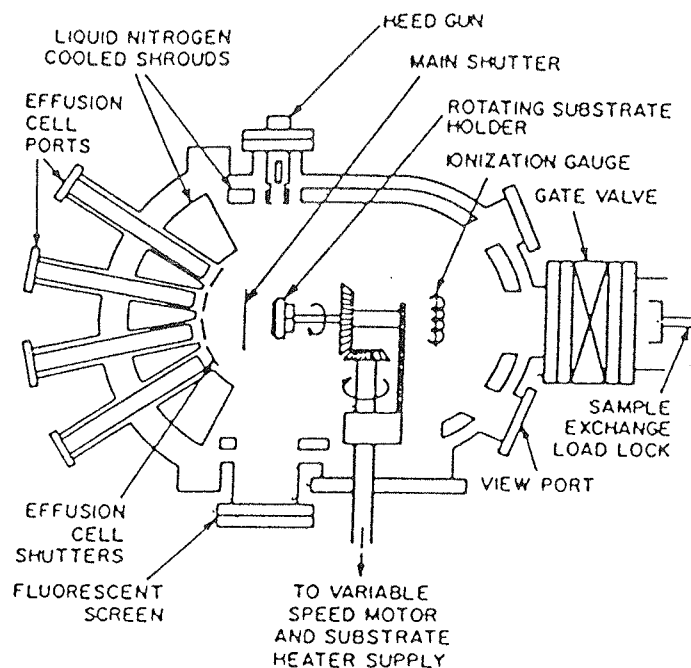


Fig. 2: Schematic of a solid source MBE chamber showing the arrangement of effusion cells, shutters, substrate manipulator, RHEED system, and cryo-panels.

on a heated substrate where they react and contribute to the formation of a thin film. Low background and beam pressures allow a line of sight process where the probability for collisions in the vapor phase is practically negligible. The beam fluxes are interrupted by mechanical shutters. A reflection high energy electron diffraction (RHEED) system is an invaluable tool for the in-situ quality and thickness control of the growing thin films. It allows observation of individual monolayers and through its help the growth of single quantum wells and superlattices has become possible. The growth chamber incorporates large area cryo-panels providing additional pumping and a trap surface for the molecules which did not successfully contribute to the growth. Figure 2 shows a typical layout of an MBE chamber used for the growth of III-V compounds, i.e., GaAs, AlAs, AlGaAs...

2. Issues to be Considered for MBE of Ferroelectrics

2.1. Materials

The beams of each individual specie to be deposited play in MBE a central role. It depends on the nature of material how easy or difficult it is to create these beams and maintain them stable over the whole deposition period which can take several hours to complete. Most materials used in MBE of semiconductors have to be heated to around 1300 K. This is a very comfortable temperature to work with; the radiation losses are high enough to allow a quick response to the control parameters and the temperature is still too low to cause any problems with containers (crucibles) or contamination. For the comparison let's consider now a few interesting ABO_3 ferroelectric materials and their components. An important parameter for the selection of the right source for the creation of molecular beams is materials vapor pressure. Figure 3 shows the vapor pressure curves of selected materials found in ferroelectric compounds mentioned at the beginning of the introduction. For

comparison, the curves for Ga and Al, the most commonly used materials in MBE, are also given. Data has been obtained from the work by R. E. Honig^{3/}. A perusal of Figure 3 shows that most of the materials found in ferroelectric compounds differ considerably in their properties from the respective III-V components; the "A"-site elements are very volatile and exhibit several orders of magnitude higher vapor pressures while the vapor pressures of the "B"-site components are normally several orders of magnitude lower than those of Al and Ga. Considering the extremes: potassium has a suitable vapor pressure slightly above the room temperature while Ta has to be heated to almost 3000 K. This shows clearly that A and B component molecular beams can not be obtained with the same kind of sources.

2.2. Material Sources - Suitability, Stability, and Control Issues

2.2.1. "A" component sources

Fluxes of different components normally have to be stable within a few percent over the whole range of operation and over longer periods of time. In standard III-V MBE systems this means that the effusion cells have to be stabilized to better than 0.5 K. This is quite routinely achieved at the operating temperatures of 1300 K and over. For materials like lead, barium, and lithium the same flux stability requires a temperature stability better than 0.2 K at operating temperatures around 700 K. Normal effusion cells are designed with extensive Ta shielding in order to minimize heat losses and can be therefore poorly stabilized at low temperatures. For this purpose specially designed low temperature effusion cells have to be used which allow radiative cooling and still maintain temperature uniformity over the whole volume. Potassium and sodium are two materials which are not suitable for the evaporation from effusion cells. There are many reasons for that: (1) The required temperature stability and uniformity would have

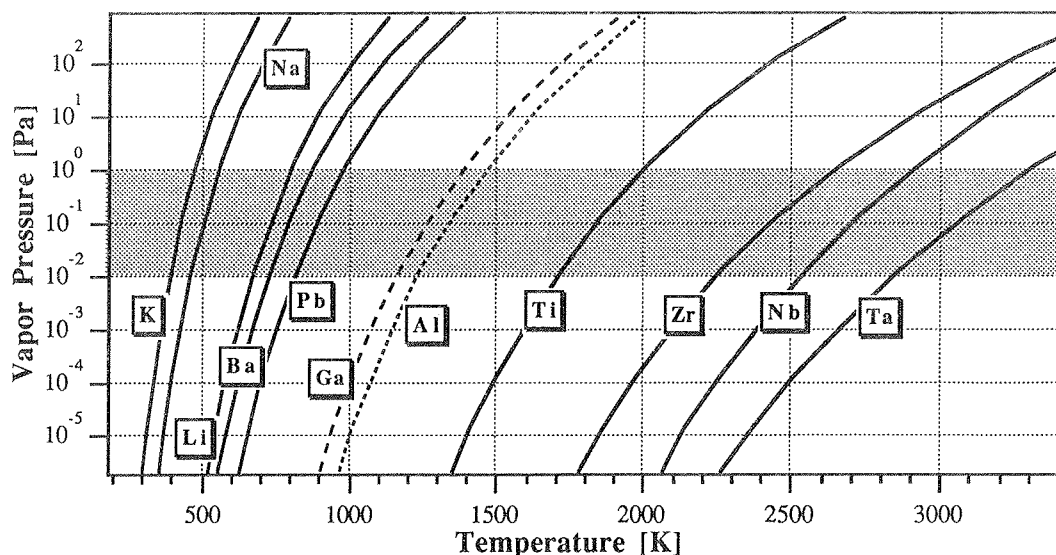


Fig. 3: Vapor pressure data of selected components of ABO_3 ferroelectric materials and Ga and Al. The shaded area shows the desired range of beam pressures which facilitate a growth rate in the range of 0.1 nm/s.

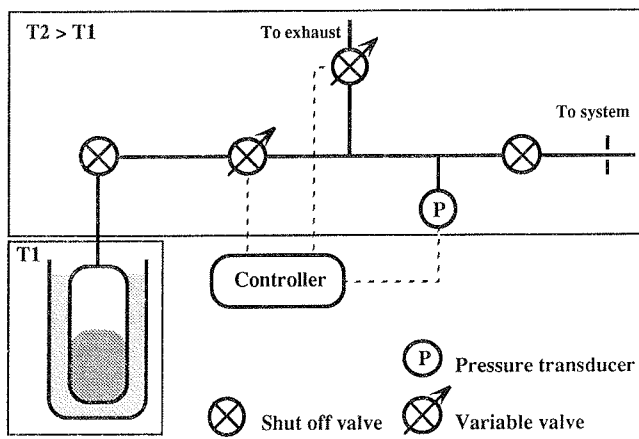


Fig. 4: External source useful for the high vapor pressure materials with active pressure control in front of the system orifice.

to be better than 0.1 K. (2) The operating temperature would be too low to achieve the required control parameters. (3) Due to the high vapor pressure already at the room temperature the materials would evaporate steadily until the depletion of the source, causing a high potassium background pressure (cooling of the source when not in use is not an option because this would condense also unwanted impurities on the source walls and on the material itself which would volatilize upon the warm up). (4) The conditioning of the chamber at high temperatures (normally around 500 K) in order to achieve UHV conditions would be impossible for it would result in total exhaustion of the material from the source. Figure 4 shows a feasible way of obtaining controlled and stable fluxes of materials like potassium and sodium. It consists of an ampoule containing the desired material which is placed externally in a thermally stabilized bath. The material is guided to the system through a thermalized tube which ends with an orifice. The ampoule is isolated from the vacuum system by a valve. System can be either temperature controlled or combine

temperature and pressure control. Two pressure controlled valves control pressure in front of the orifice by admitting more material from the ampoule when the pressure has dropped or by removing excess material through an exhaust line when the pressure has exceeded the desired value. Without this valve the excess pressure would have to be relieved through the front orifice which would result in a slowly reacting control system. The latter, more sophisticated approach, has a potential of achieving very stable fluxes even at the non equilibrium evaporation of the material.

2.2.2 "B" component sources

The transition metals have a low vapor pressure and are, with the exemption of maybe titanium, not suitable for the evaporation from classical effusion cells. These materials can be evaporated from e-beam evaporators which heat a small amount of material with a high current electron beam. E-beam evaporators have been successfully used for the production of optical metallic coatings where flux stability and thickness control on the monolayer scale are not important. For these applications sources run normally at a constant power level and are shuttered off once a desired film thickness has been achieved. The evaporation times are short so that long term stability is not a problem. Application of such a source to an MBE process with three to four orders of magnitude lower beam densities and hours, instead of minutes or seconds, long evaporation times is therefore not straightforward. The constant power approach proves to be useless due to long term drifting problems. In order to be used in MBE these sources require an active control loop which regulates the supplied heating power according to the changes in flux. In order to maintain controlled and stable deposition conditions the fluctuations of the flux in MBE should be on an average maintained within one to a few percent of the controlled value. Achieving this at the deposition rates of 0.01 nm/s is a real technological challenge. Three different control

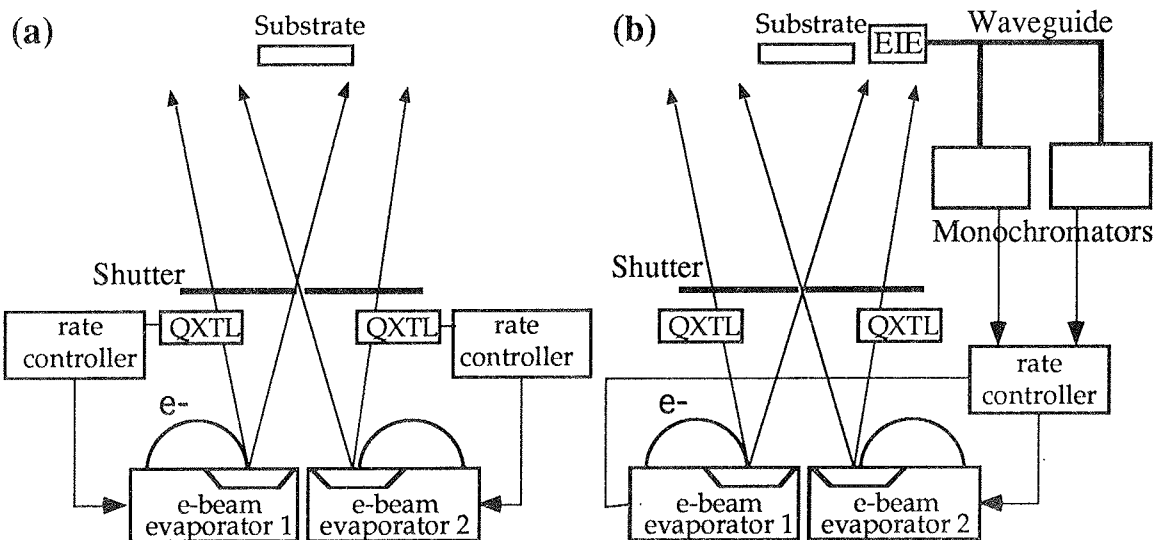


Fig. 5: Configuration of an active flux control system; (a) with quartz crystal oscillator, (b) with EIES.

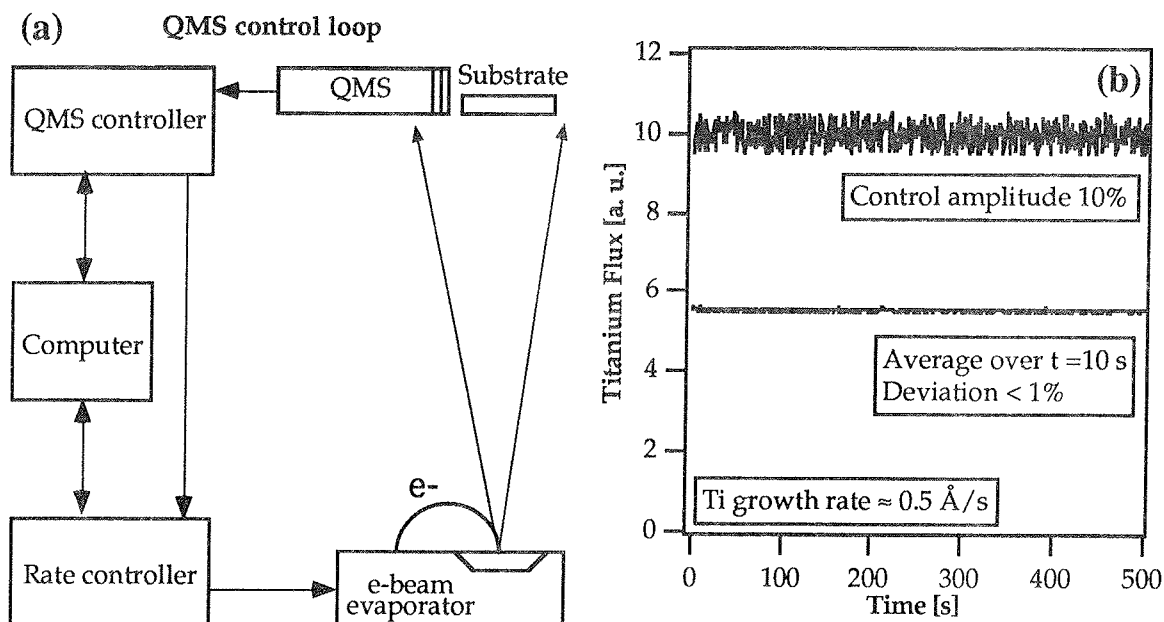


Fig. 6: Schematic of the principle of the flux control by QMS (a), and the measured Ti flux stability after the optimization of control parameters (b).

systems have been developed whose main difference is in the flux sensing device. The simplest and the least expensive variant is based on quartz crystal (QXTL) deposition rate monitors which sense the mass deposited on the crystal through the oscillation frequency change. In order to be able to control and stabilize the flux already before the shutter is opened they have to be positioned so that they see unperturbed flux of material all the time. The accuracy of such a system can be increased if the crystals are placed closer to the material sources where the flux density is higher. Such systems have been used relatively successfully but they have a few major shortcomings; they are heat sensitive (the problem increases with the proximity to evaporators), they have a relatively short lifetime (for the replacement of the quartz crystals the whole deposition system has to be exposed to the atmosphere), they are deposition rather than flux monitors, each e-beam evaporator requires its own quartz crystal monitor. Figure 5(a) shows a typical setup with two quartz monitors. A typical rate control resolution achieved by such a system is 0.02 nm/s.

The second control system uses an electron impact emission spectrometer (EIES) as the flux sensing device. It measures the characteristic light which atoms emit when being struck by electrons. In contrast to a quartz deposition monitor this is a real flux measuring device. The measuring head is placed close to the substrate and is not heat sensitive or of a deposit dependent lifetime. Commercial systems can control up to two e-beam evaporators with a rate control resolution of 0.01 nm/s (Leybold's specification). A schematic of a setup employing EIES is shown in Figure 5(b).

Both previous approaches have been developed for the alloy deposition control for a standard evaporation process and have been transferred to the UHV technology. The control system based on a quadrupole mass spec-

trometer (QMS) has been developed specifically for the UHV processes with low evaporation rates in mind. In order to prevent contamination by the direct flux the QMS has to be shielded and equipped with a cross-beam ionizer, which efficiently ionizes species flying orthogonal to the axis of the spectrometer. The operation principle is quite simple; a QMS scans over a desired number of masses and sends respective mass intensity signals to a computer or directly to a controller which controls the evaporator's power supply. A schematic of an experimental setup is shown in Figure 6(a). The control frequency is typically 100 Hz for a single mass and decreases with the number of controlled sources. A typical control amplitude at a deposition rate of 0.01 nm/s lays around 10% but the average over a few seconds shows a deviation of under one percent. Such a setup controls well even the flux of tantalum, as shown in Figure 6(b), that is a difficult material to evaporate.

Control system	QXTL	EIES	QMS
Manufacturer	Leybold	Leybold	Balzers
Lowest controllable rate [nm/s]	0.01	0.01	0.005
Control deviation at 0.01nm/s [%]	10	10	1
Control frequency [Hz]	4	8	100
Lowest measurable rate [nm/s]	0.02	0.0003 (Cu)	0.0000005

2.2.3. Oxygen sources

The limiting factor for the growth rate of the oxidic materials in an MBE environment is the oxidation process. Molecular oxygen is normally not sufficiently reactive and does not lead to a complete oxidation even at very low growth rates. Thin films grown under a flux of molecular oxygen have to be post growth annealed. This

action cancels the benefit of the low temperature processing offered by MBE. However, the amount of active oxidizing species can not be increased as easily as the flux of metals. A higher reactivity under UHV conditions can be achieved by the use of ozone or atomic oxygen.

Ozone has been successfully used for the growth of thin film high temperature superconductors. It is produced by passing O₂ through an electrical discharge followed by the separation of O₃ from O₂ in an LN₂ cooled container. Since ozone is toxic and liquid ozone explosive only a small amount of liquid (a few ml) is produced just prior to growth/4/. The hazard can be reduced significantly by adsorbing ozone into silica gel /5/ and then slowly releasing it. In this manner it can be stored over a week without significant deterioration. As found by many researchers, ozone offers significant improvements in oxidation capability over molecular oxygen, however, due to its hazard many people have been reluctant to use it.

For the use of plasma sources in an MBE environment the main challenge is to produce a sustained and stable plasma at low pressures (< 10⁻² Pa) governed by the line of sight process. In the past few years two different plasma sources have been developed for the application in MBE, a radio frequency (rf) radical source and a microwave electron cyclotron resonance (ECR) source. The former produces an rf discharge in a small volume which is maintained at a higher pressure than the rest of the deposition system. The active species are allowed to exit through several capillary holes. The upper limit for the cracking efficiency of this source has been estimated to be about 30%, /6/.

The ECR source creates a plasma through magnetic confinement of electrons. In this manner a stable plasma can be achieved at pressures even as low as 10⁻³ Pa, /7/. Because of this the source does not require an aperture which would impede the exit of active species. This type of source has been successfully used for the growth of nitrides and oxides, / 8/.

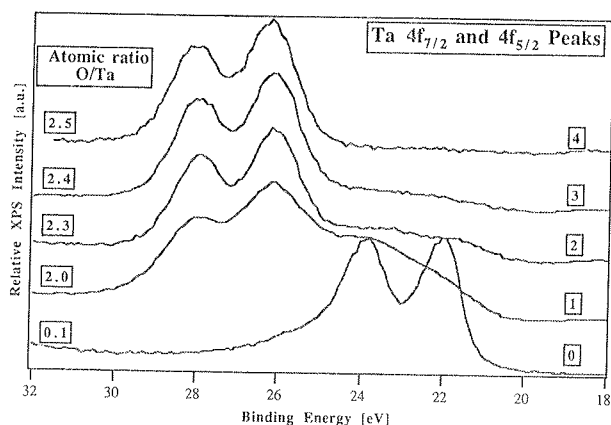


Fig. 7: XPS spectra taken from different samples exhibiting various degrees of oxidation of tantalum. Spectrum "0" - Ta, spectrum "4" -

To better understand the difference in the oxidation capability in different experimental conditions let us examine Figure 7 which shows the XPS results obtained during the evaporation of tantalum oxide. Pure tantalum exhibits a characteristic XPS 4f doublet peak located at the electron binding energy of 22 eV, as shown in the spectrum "0". In an oxidized state this peak shifts for over 4 eV toward the higher binding energies. As such, one observes four different peaks in a partially oxidized state, two shifted and two unshifted, and only two shifted peaks in fully oxidized samples. In order to determine the degree of oxidation one can simply compare the area under shifted and unshifted peaks. The calculated oxygen/tantalum ratio is given for each case on the left side of Figure 7. The results shown in spectrum "1" were obtained from a film deposited with a flux of molecular oxygen while other spectra represent different degrees of plasma excitation. From these results it is clear that the ECR plasma source plays an important role in the in situ oxidation process.

3. Summary

Molecular beam epitaxy of ferroelectrics can potentially create new thin film materials and enable the research of ferroelectric two dimensional structures. For this purpose it is important to achieve stable growth conditions by the application of suitable sources for different metals. The achievement of complete in-situ oxidation at low growth temperatures is of great importance and can be conveniently achieved by active species produced by a plasma source.

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