Ion Beam Deposition and Surface Characterization of Thin Multicomponent Oxide Films During Growth*

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A. R. Krauss¹, J. Im^{1,2}, V. Smentkowski^{1,†}, J. A. Schultz³, O. Auciello¹,
D. M. Gruen¹, J. Holocek³, and R. P. H. Chang²

¹Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439

²Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

³Ionwerks, Houston, TX 77130

[†]Present address: GE Corporate Research & Development Center, Schenectady, NY 12301

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^{sputter -} Ion Beam Deposition and Surface Characterization of Thin Multicomponent Oxide Films During Growth

A. R. Krauss¹, J. Im^{1,2}, V. Smentkowski^{1†}, J. A. Schultz³, O. Auciello¹, D. M. Gruen¹, J. Holocek³, and R. P. H. Chang²

¹ Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL 60439

² Northwestern University, Department of Materials Science and Engineering, Evanston, IL, 60208

³ Ionwerks, Houston, TX 77130

Ion beam deposition of either elemental targets in a chemically active gas such as oxygen or nitrogen, or of the appropriate oxide or nitride target, usually with an additional amount of ambient oxygen or nitrogen present, is an effective means of depositing high quality oxide and nitride films. However, there are a number of phenomena which can occur, especially during the production of multicomponent films such as the ferroelectric perovskites or high temperature superconducting oxides, which make it desirable to monitor the composition and structure of the growing film in situ. These phenomena include thermodynamic (Gibbsian), and oxidation or nitridation-driven segregation, enhanced oxidation or nitridation through production of a highly reactive gas phase species such as atomic oxygen or ozone via interaction of the ion beam with the target, and changes in the film composition due to preferential sputtering of the substrate via primary ion backscattering and secondary sputtering of the film. Ion beam deposition provides a relatively low background pressure of the sputtering gas, but the ambient oxygen or nitrogen required to produce the desired phase, along with the gas burden produced by the ion source, result in a background pressure which is too high by several orders of magnitude to perform in situ surface analysis by conventional means. Similarly, diamond is normally grown in the presence of a hydrogen atmosphere to inhibit the formation of the graphitic phase.

A surface analysis system incorporating pulsed beam ion scattering spectroscopy (ISS), direct recoil spectroscopy (DRS), and mass spectroscopy of recoiled ions (MSRI) with differentially pumped ion beam and detector lines has been integrated with a multi-target ion beam deposition system, permitting the characterization of the surface composition and structure of a thin film surface during growth at ambient pressures of several tens of milli Torr. A number of phenomena are observed which are not amenable to study in systems which require cessation of film deposition in order to study surface properties. In addition, it has been found that the positive-to-negative ion ratio of the MSRI signal provides a unique "phase fingerprint" which in a number of cases permits ready identification of the chemical phase of the growing film. Data will be presented showing representative applications in the area of multicomponent oxide film growth for which the in situ ion beam characterization methods described here provide a unique means for understanding thin film growth phenomena.

† Present address: General Electric Corporate Research & Development Center, Schenectady NY 12301

INTRODUCTION

As thin film materials, device structures, and processing conditions become increasingly more complex, there is a growing need for in situ, real-time, surface-specific analytical tools to characterize phenomena occurring at interfaces between layered structures and at the surface of thin films during growth. These analytical tools must not be destructive, should provide a wide range of surface compositional and structural information on a time scale which is commensurate with the deposition rate, and must be compatible with the geometric constraints of the deposition process and the temperatures and ambient gas pressures required by the thin film growth environment. A number of materials of growing technological importance for thin film applications present problems in terms of materials interactions and compositional instability of one or more components. Prominent among these materials are a series of multicomponent oxides such as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT), $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST), and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Each of these materials has (a) highly useful properties such as high ferroelectric polarizability, piezoelectric behavior and high temperature superconductivity, (b) a range of compositions and phases, with properties which are highly dependent on the phase and composition, (c) at least one constituent which segregates strongly to surfaces and interfaces in either vacuum or oxygen environments, and (d) at least one constituent which is kinetically stable in that the concentration in the film depends critically on the substrate temperature and ambient gas composition and pressure.

We have found that an appropriately configured combination of three low-keV ion beam spectroscopies can be used to provide an exceptionally wide range of surface compositional and structural information under conditions which are compatible with the growth environments typically associated with these multicomponent oxides. This paper will provide a background discussion of these surface analytical tools, describe the integration with an ion beam sputter deposition thin film growth chamber, and illustrate the application of the methods to the study of phenomena occurring during the growth of two ferroelectric oxide thin film materials.

BACKGROUND ON TIME OF FLIGHT LOW ENERGY ION BEAM SURFACE ANALYSIS METHODS

The basic concepts of the three analytical methods are illustrated in Fig. 1. An ion beam with a kinetic energy of several keV is incident upon the surface to be studied. At these kinetic energies, the collision kinematics are essentially those of classical two body elastic collisions. The three analytical methods differ in the direction of incidence of the primary beam relative to the sample normal, and the placement and characteristics of the detectors.

In low energy ion scattering spectroscopy (ISS), the mass of a surface atom is determined by measuring the kinetic energy loss of a primary ion of known mass which scatters from a single surface atom. This method may be thought of as a low energy equivalent of the widely used

Rutherford Backscattering Spectroscopy (RBS) [1]. ISS is a well-established surface analysis technique that has been used for many years to characterize the composition and surface structure of materials, [2-5], and is the most surface-specific of the surface analytical methods, with a depth sensitivity which can be limited to one atomic layer [2].

The kinetic energy of the backscattered primary particle can be measured either by using an electrostatic energy analyzer (ESA) or by pulsing the beam and using a time of flight (ToF) detection scheme. The ESA only detects the ion fraction, (typically 10^{-2} - 10^{-4}) of the scattered primary beam, and transmits only a narrow portion of the energy distribution of these ions. In contrast, the ToF detection scheme simultaneously detects the full energy range of both ions (which typically constitute a very small fraction of the backscattered primaries) and neutrals. Consequently, the required beam dose for ToF detection is 3-5 orders of magnitude smaller than that required by the ESA. A typical analysis beam dose for ToF detection is $\sim 10^{11}$ - 10^{12} ions/cm², removing or displacing 1 part in 10^3 - 10^4 of the near-surface atoms and making the ToF scheme essentially non-destructive [6-9]. However, Most commercial ISS instruments use electrostatic energy analyzers because they represent a relatively inexpensive modification to existing Auger and photoelectron analyzers.

Direct Recoil Spectroscopy (DRS) is not as well-known as ISS, but it has been in use in a number of laboratories for several years [10-13], and recent improvements [14-17] in time of flight instrumentation have carried over to DRS. DRS may be thought of as a low energy equivalent of Elastic Recoil Detection (ERD) [1] in that it employs relatively grazing entrance and exit angles to eject surface atoms via a single collision event with the primary ion. The ejected surface atoms have sufficiently high energy to be detected by a particle counter such as a channel plate multiplier, and the beam forming and detection hardware are very similar to that of ISS. The principal advantage of DRS compared with ISS is the ability of the former method to detect all atomic species, including those which are lighter than the primary ion.

Mass Spectroscopy of Recoiled Ions (MSRI) [8, 13-15, 17] can be thought of as a form of DRS in which only the ion fraction of the direct recoil spectrum is detected. It is similar to secondary ion mass spectroscopy (SIMS) except that the geometry is chosen to emphasize single collision ejection events, rather than the multiple collision cascade mechanism associated with the SIMS process. Consequently, the kinetic energy and ion fraction of the ejected surface atoms are much higher than is the case for SIMS. The consequences of the high kinetic energies of the MSRI ions will be discussed in the next section.

THEORY

In ISS, a primary ion with energy E_0 and mass M_1 is scattered by a surface atom of mass M_2 at an angle θ_1 relative to the direction of incidence (Fig. 2). The collisions are described by classical two body collision kinematics. The kinetic energy E_1 of the scattered primary ion is given by

$$E_1 / E_0 = (1 + \alpha)^{-2} [\cos \theta_1 \pm (\alpha^2 - \sin^2 \theta_1)^{1/2}]^2 \quad (1)$$

where $\alpha = M_2/M_1$. It should be noted that Eqn. 1 has real values only if $M_2 > M_1$, and that ISS is therefore not able to detect surface atoms which are lighter than the primary ion.

One of the unique features of ISS is the ability to determine local surface structure by varying the angle of ion beam incidence on the sample. The method of determining surface atomic structure by Angular-Resolved Ion Scattering Spectroscopy is referred to as ARISS. A plot of the locus of trajectories followed by each primary ion as a function of impact parameter, shows (Fig. 3a) that there is a region behind each target atom (shadow cone) from which the primary beam is excluded. Target atoms lying in this "shadow cone" are not seen by the primary ions, and consequently do not contribute to the ISS signal. As the angle of incidence (ψ) approaches the sample normal, as shown in Fig. 3b, there is a critical angle, ψ_c such that the shadowed "B" atom begins to be visible behind the "A" atom which is closer to the surface along the direction of the incident beam. The ISS signal then increases abruptly. The sharpness of the onset of the "B" atom signal provides a measure of the degree of surface disorder, which is in part due to the presence of point defects, and the temperature dependence of this signal is a consequence of the phonon characteristics of the surface atoms. The value of the critical angle varies from material to material, and from one crystal face and beam orientation to another of a given material, and can be quantitatively related to the bond distance and bond angle for specific atomic species within the first few atomic layers as indicated in Fig. 3b.

Equation 1 indicates that a primary ion scattered by a single collision with a surface atom into a specific angle θ_1 will have a well-defined kinetic energy E_1 , corresponding to a sharp, symmetric ISS peak. However, if the primary ion suffers a number of large impact parameter collisions, as when interacting with thick layers, the ISS peaks are broad and asymmetric with a long low-energy tail consisting of multiply scattered primary ions. It is therefore possible to differentiate between thick (more than 2-3 atomic layers), disordered layers, and single layer or aligned single crystal growth.

DRS is based on detection of direct recoil-sputtered surface atoms which are ejected as the result of a single collision between the primary ion and a surface atom. The kinetic energy E_2 of these atoms is given by,

$$E_2 / E_0 = 4 \alpha (1 + \alpha)^{-2} \cos^2 \theta_2, \quad (2)$$

where θ_2 is the angle of the recoiled particle's trajectory with respect to that of the incident primary ion. Equation 2 always has solutions for both $M_2 > M_1$ and $M_2 < M_1$, and DRS in fact is one of relatively few surface analytical methods to have good sensitivity for hydrogen and its isotopes [12].

By placing the detector at a position corresponding to a relatively small value of θ , (grazing incidence and exit angles) many of the detected atoms will be ejected as the result of a single collision with the primary ion, and the kinetic energy of the ejected atoms will be given by Eq. 2. In comparison, atoms ejected close to the sample normal are the result of a cascade of numerous small angle collisions, primarily between recoiling target atoms, rather than between the primary ion and a target atom, and have much lower kinetic energy than the value given by Eq. 2. By the time that a surface atom receives enough normally directed momentum from the cascade to be ejected from the surface, the kinetic energy has been degraded by the numerous collisions between the cascade atoms. The sputtered atoms are ejected with a typical kinetic energy of only a few eV, regardless of the primary ion energy. There is therefore a significant time during which charge exchange can occur between the surface and the departing atom, resulting in a high degree of neutralization of the sputtered atoms.

A general understanding of the charge state of atoms leaving a surface may be obtained by examining the model of ion-surface interactions developed by Hagstrum [19] to describe experimental results obtained by ion neutralization spectroscopy. In this model, the probability of survival as an ion by an atom leaving the surface is given by

$$P^+ \sim \exp (-a/V_{\perp}). \quad (3)$$

where the perpendicular velocity component $V_{\perp}$ is given by $V_{\perp} = V_2 \cos \psi_2$, V_2 is the velocity corresponding to E_2 , ψ_2 is defined by reference to Fig. 2, and a is a parameter which depends on the electronic character of the sputtered atom and the chemical state of the surface. For clean transition metal surfaces, the value of a is typically of the order of 2×10^4 m/sec [19].

The kinetic energy distribution of atoms ejected from a surface by ion beam impact is shown in Fig. 4 as curve (a). There is a large intensity at very low kinetic energies, corresponding to ejection by the random collision cascade. The peak of this distribution occurs at $E_b/2$ where E_b is the surface binding energy. There is another peak at higher kinetic energies which corresponds to ejection by the direct recoil process described above. The high energy side of this peak results from a single collision with no multiple scattering, and is given by Eq. 2. The low energy tail is the result of multiple scattering events.

Also shown in Fig 4 (curves b and c) are the probabilities of ion survival as a function of kinetic energy for two different values of α . The ejected ion kinetic energy distribution will be the convolution of the curve (a) with an ion survival probability as represented by curves b and c. The ion fraction of atoms ejected as a result of the random collision cascade process will be low (typically 10^{-2} to 10^{-5}) for most physically reasonable values of α . On the other hand, the ion fraction of the direct recoil atoms can easily exceed 10% and may in some cases approach 100%.

The three complementary pulsed ion beam surface analytical techniques ISS, DRS and MSRI are collectively referred to as time of flight ion scattering and recoil spectroscopies (TOF-ISARS). MSRI is a form of DRS which uses a time refocusing analyzer such as a Poschenrieder sector [13, 19] or reflectron [20,14], to eliminate the multiple scattering background of the direct recoil spectrum, obtaining much greater sensitivity (up to ~ 1 part per million) and greater mass resolution than the simple line of sight direct recoil detector.

MSRI is superficially similar to the more commonly used secondary ion mass spectroscopy (SIMS) except that:

- (1) the ion beam is incident on the sample at a grazing angle, and the detector is positioned at a grazing angle in the forward scattering direction. In this arrangement, surface atoms are largely ejected by direct impact of the primary ion.
- (2) The kinetic energy of the MSRI ions is much higher than that of the particles ejected by the collision cascade process characteristic of the secondary ion mass spectrometry (SIMS) technique. The low velocity of the SIMS ions results in very efficient neutralization of the sputtered atoms, and the typical ion fraction for inert gas bombardment is in the range 10^{-2} to 10^{-4} , although some signal enhancement can be obtained through the use of an oxygen or cesium ion beam. The high velocity of the MSRI ions on the other hand, leads to low neutralization probability, and ion fractions in the range 10-40% are achievable. The MSRI data are consequently much less subject to the large "matrix effect" which causes the SIMS ion signal to vary by 4-5 orders of magnitude as a function of target material and state of surface oxidation [21] and makes quantification of SIMS data very difficult.
- (3) Although the matrix effect is much smaller in MSRI than in SIMS (typically less than one order of magnitude for MSRI as opposed to 3-5 orders of magnitude for SIMS), it is not totally absent. Consequently, both positive and negative ions of most elements are present in the MSRI spectra and it is possible in many cases to determine the chemical phase of a surface simply by comparing the positive and negative MSRI ion signal ratio with that of a reference sample. Clear distinctions between the hexagonal and cubic forms of boron nitride, graphite, amorphous carbon and diamond [8], and the perovskite and pyrochlore phases of PZT have been observed as shown in Table I.

A unique characteristic of the TOF-ISARS techniques in any of the variations described above is the capability for *in situ*, real-time analysis of growing films in relatively high background

gas pressures such as the oxygen needed to produce the multicomponent oxide thin films of interest to this review.

At a given ambient pressure and kinetic energy, the number of energetic particles (scattered primary ions or recoil-sputtered surface atoms) which survive after traveling a given distance d through the background gas in the deposition chamber is given by

$$I = I_0 e^{-d/\lambda} \quad (4)$$

where I_0 is the primary beam intensity in vacuum and

$$\lambda = kT/p\sigma, \quad (5)$$

is the collisional mean free path, where k is the Boltzmann's constant, T is the temperature, p is the pressure and σ is the collision cross section between the energetic particle and the gas molecules.

Therefore the gas phase attenuation is given by

$$I = I_0 e^{-dp\sigma/kT}. \quad (6)$$

In general, the cross section is a function of the kinetic energy and mass of the energetic particle. Since the kinetic energy of the exit beam will always be less than that of the primary beam and, in the case of DRS and MSRI, the mass of the detected atom will also differ from that of the primary beam, eq. 6 becomes

$$I = I_0 e^{-p(d_1\sigma_1 + d_2\sigma_2)/kT} \quad (7)$$

where d_1 (0.2845 m) and d_2 (0.118 m) are the distances which are traversed through the high pressure region for the incoming and outgoing particles, respectively, σ_1 is the cross section which determines the flux of the primary beam (with initial kinetic energy E_0) arriving at the sample, and σ_2 is the cross section which determines the number of scattered primary ions (eq. 1) or direct recoil surface atoms (eq. 2) arriving in a small solid angle subtended by the detector. These cross section values are kinetic energy-dependent. The primary ion energy in the instrument at Argonne is typically 10 keV. The value of E_2 depends on the values M_1 and M_2 via Eq. 2, but for values of E_2 in the range 2 to 10 keV in an atmosphere of H_2 , N_2 or O_2 , the gas phase scattering cross section values lie in the range $\sim 2 \times 10^{-20} \text{ m}^2$ to $\sim 3 \times 10^{-19} \text{ m}^2$ [22].

By isolating the ion beam source and detectors from the sample chamber, it is possible to maintain the sample in an elevated pressure of active gas such as oxygen, while performing real-time surface analysis of e.g. a thin oxide film during growth. The means by which this is achieved experimentally, and a description of the system performance is presented in the following section.

The combined use of time-of-flight mass spectroscopy of recoiled ions, ion scattering, and direct recoil spectroscopies described above provides the means for measuring the surface composition [11, 6] with excellent sensitivity for trace elements [9], including hydrogen [15], and determination of the local surface geometry [4] and chemical phase. It is also possible to distinguish layer-by-layer growth in thin films from 2D and 3D island formation [23]. A relative measurement of the degree of surface disorder including the presence of point defects may be

obtained, and with sufficient care, it is even possible to measure the surface phonon dispersion. In summary, an extraordinarily rich set of data may therefore be obtained with the set of compatible diagnostic tools which are collectively referred to as ToF-ISARS.

Although the experimental work described in this chapter is focused on multicomponent oxide ferroelectric thin films and heterostructures, the TOF-ISARS technique has also been successfully used to study growth processes of other system materials such as high temperature superconductors [23], semiconductors [23] and diamond [16].

EXPERIMENTAL

A schematic of the current TOF-ISARS system is shown in Fig. 5, while a detailed description of the system is presented elsewhere [24,22]. In brief, the chamber is split into two sections. Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron (UPS) spectroscopy are included in the upper chamber to perform postdeposition surface analysis as a complement to the TOF-ISARS studies of growth processes. Thin film deposition is accomplished in the lower chamber by means of a 3 cm Kaufmann ion gun which is focused onto a target mounted on a rotatable carousel which holds four 75 mm diameter targets.

The primary beam for the TOF-ISARS analysis is produced by a telefocus ion source (Atomika W610). The highly collimated beam passes through two deflection regions, separated from each other by an apertured drift space. By controlling the time interval between the application of voltage steps to the two sets of deflection plates, a pulsed ion beam with pulse duration adjustable from ~ 10 to 1000 nsec is produced. A final set of dc deflection plates is then used to steer the beam to the desired location on the sample. The beam line is differentially pumped by turbomolecular pumps. Two channel electron multiplier detectors are positioned at angles of 165 and 25 degrees relative to the ion beam direction, and the reflectron for the MSRI analyzer is positioned at a scattering angle of 60 degrees (Fig. 5). Each detector is differentially pumped and views the sample through a 1 mm diameter aperture, either mounted on the end of a small ground potential tube which extends toward the sample, or at the end of the MSRI extraction optics. These structures are located sufficiently far away from the sample so that they do not block the deposition flux. By differentially pumping the space behind the apertures, it is possible to maintain a detector vacuum approximately three orders of magnitude lower than that of the sample environment.

The signal in principle, undergoes attenuation, broadening, and shift as a result of gas phase scattering in the region immediately surrounding the sample. However, as seen in Fig. 6 which shows the ISS signal intensity for a 10 keV Ne^+ beam scattering from an Au surface in an Ar atmosphere at a pressure ranging from 1×10^{-4} to 2.8×10^{-3} Torr, the high energy (short time of flight) edge which corresponds to single collision scattering does not in practice shift or broaden

with increasing pressure [16]. The intensity decreases uniformly, but it is possible to perform surface analysis up to pressures of several mTorr. The observed decrease in signal intensity with ambient pressure depends on the surface composition, primary ion mass and kinetic energy, but is generally consistent with gas phase collision cross sections found in the literature [26]. Similar results are obtained for DRS and MSRI [14]. For typical beam conditions [24], the loss in signal intensity limits ambient gas pressure and beam path length to a maximum of ~ 300 mTorr-cm [25]. This limit is high enough to permit in situ, real-time characterization of thin film growth for a large number of deposition methods, and even permits analysis during the growth of many materials requiring an ambient chemically active gas (O_2 , N_2 , H_2) for formation of the desired phase. Examples of such materials include multi-phase oxides and nitrides, as well as diamond, which is normally grown in an ambient hydrogen atmosphere. By comparison, conventional surface analytical methods such as x-ray photoelectron spectroscopy (XPS) require ambient pressures of 1×10^{-8} Torr or lower.

STUDIES OF FILM GROWTH PROCESSES RELEVANT TO FERROELECTRIC CAPACITORS AND RELATED LAYERED HETEROSTRUCTURES

Examples are given of TOF-ISARS analysis of several different materials, both as a means of illustrating previously discussed capabilities of the methods, and to demonstrate surface analysis for oxide growth processes.

In Situ Analysis of $SrBi_2Ta_2O_9$ Layered Perovskite and $Pb(Zr_{1-x}Ti_x)O_3$ Film Growth

Layered perovskite materials such as $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) are being investigated for application as ferroelectric layers in capacitors for non-volatile ferroelectric memories (NVFRAMs) [27-31]. It has been demonstrated that Pt/SBT/Pt capacitors exhibit long polarization retention, little tendency to imprint (i. e. to revert to a previous polarization state), relatively low leakage, and practically no polarization fatigue (tendency for the maximum polarizability to decrease with continued polarization switching), making SBT capacitors one of the strongest candidates for application in the first generation of NVFRAMs. The structure of SBT is shown in Fig. 7. The important structural features in relation to the TOF-ISARS studies discussed in this section are the perovskite O-Ta-O and O-Sr-O chains along the c axis which are interrupted by the $(Bi_2O_2)^{2+}$ layers, but form continuous chains along the plane perpendicular to the c axis [32].

Oxygen vacancies acting as trapping sites for electrons injected into the ferroelectric layer, during polarization switching, are believed to be the principal cause of polarization fatigue in ferroelectric capacitors [33]. It has been hypothesized [34] that the outstanding fatigue resistance exhibited by SBT is related to the formation of a $(Bi_2O_2)^{2+}$ terminated surface which provides an

oxygen-rich region at the ferroelectric/electrode interfaces, resulting in the annihilation of oxygen vacancies at those interfaces. However, systematic studies on the effect of various deposition methods and growth parameters on composition, microstructure and properties of SBT layers and SBT-based capacitors are needed. Such studies have recently been initiated [35]. In addition, studies of film growth processes are needed to understand electrode-ferroelectric layer interfaces which appear to control various NVFRAM properties.

In practice, an NVFRAM device will consist of a hybrid structure involving a ferroelectric capacitor and a silicon transistor array. Platinum is commonly used as the capacitor electrode material because of its high electrical conductivity and because it is an effective template for epitaxial growth of the ferroelectric layer. However, Pt interacts with silicon, forming PtSi. Titanium has been suggested as a diffusion barrier between these two materials. The experiments described in this section are focused on clarifying the role of interfacial reactions in determining the properties of ferroelectric layered devices, and elucidating the mechanism by which oxygen is incorporated in SBT and PZT films during growth via ion beam sputter-deposition.

Unlike most of the other ferroelectric materials, the axis of maximum polarizability for SBT is not along the c-axis. To date, the best SBT films for ferroelectric applications have been randomly oriented. It is suspected that the direction of maximum polarizability is close to the a-axis, but it has been very difficult to grow epitaxial a-axis SBT. A set of experiments was therefore conducted to investigate interactions between the layers which would be part of an integrated NVFRAM. The first experiment in the series was focused on studying the interactions between the electrode, buffer layer, and underlying silicon. Electrical isolation from the Si substrate was provided by a 200 nm thick SiO₂ layer. A 50 nm thick Ti layer was deposited on top of this, followed by 150 nm of Pt. This deposition was done at room temperature.

The next step in the device fabrication process would require deposition of SBT onto the Pt electrode. However, crystallization of the ferroelectric SBT phase requires heating to ~700°C in an oxygen atmosphere. For the ion beam sputter-deposition method discussed here, 5×10^{-4} Torr of oxygen appears to be sufficient. Therefore, an experiment was first done to determine the effect of heating in oxygen on the underlying layers. As shown in the MSRI spectrum of Fig. 8(a), the surface composition at room temperature is dominated by H, C, O, Pt, Ar (backscattered primary ions), and a small amount of Ti. It should be noted that the signal intensities in the MSRI spectra do not directly correspond to the surface concentration. Because of its relative chemical inertness and high mass, the sensitivity for Pt is lower than that for Ti, Si, and H. As the temperature increases (Fig. 8(b) and 8(c)), the Pt signal decreases and nearly disappears, while at the same time the Ti signal increases significantly and a large Si peak grows in. From the decrease in the Pt signal, it may be estimated that at least 80% of the surface consists of Ti and Si at 700 °C.

The effect of this modified surface on the incorporation of simultaneously deposited Sr, Bi and Ta sputtered from a stoichiometric SBT target onto a substrate at 700 °C in an oxygen atmosphere at 5×10^{-4} Torr can be seen in Fig. 9. As deposition continues (Fig. 9(b) and 9(c)), the Pt peak disappears, and the Si and Ti peaks diminish in intensity, but do not disappear. Sr and Ta peaks appear and increase significantly, but little or no Bi is seen at the 700 °C deposition temperature. As the substrate temperature is subsequently decreased, (Fig. 10), the Ti and Si signals disappear, the Sr signal undergoes little change, the Ta signal decreases, and the Bi signal increases until at 400 °C, the Ta and Bi signals are equal in magnitude.

One possible interpretation of this behavior would be to attribute the apparent complementarity between Ti, Si and Bi surface concentrations to a competition between Ti and Si on one hand and Bi on the other for the available oxygen (see for example the Ellingham diagram in ref. [36], which is required to stabilize Bi on the substrate surface at high deposition temperatures (600-700 °C). However, an ISS study (using a normally incident 10 keV Ar⁺ primary ion beam to monitor surface composition), during heating in oxygen up to 570 °C of a 44 Å thick SBT film deposited directly on a Ti layer on an MgO substrate suggests that some of the Bi atoms may be retained in the film. As shown in Fig. 11, Bi, Ta, and Sr are clearly seen at room temperature, although it is apparent that the resolution and sensitivity of ISS are not nearly as good as that of MSRI. As the temperature increases, first the Sr signal and then the Ta signal disappear, leaving a nearly constant Bi peak and an increasing broad background signal characteristic of multiple scattering from a low mass atom such as oxygen. The disappearance of the Ta and Sr peaks can be interpreted as due to the movement of Ta and Sr out of the surface layer into the positions corresponding to formation of the layered perovskite structure shown in Fig. 7. Clearly, the Ti layer underlying the 44 Å thick SBT film does not prevent Bi incorporation.

The apparent contradiction between the ISS and MSRI results is resolved by considering the 580 °C angle-resolved ISS (ARISS) data of Fig. 12. As the angle of incidence increases from 0° (along the substrate normal) to 22°, the Bi signal disappears, and the oxygen multiple scattering peak splits in two. Referring to the SBT structure presented in Fig. 7, the ARISS data is consistent with a c-axis oriented SBT film in which the uppermost Bi atom is missing at the surface. As indicated in Fig. 3, a Bi atom in the uppermost atomic layer would be visible for a wide range of incident angles. The Bi atom which lies below the oxygen plane of Fig. 7 however, would be visible only for primary ions which are close to the surface normal. For off-normal incidence, the oxygen atoms shadow the underlying Bi atoms. Again referring to Fig. 7, there are two types of oxygen atoms, depending whether the direction of oblique incidence is along the *a* or the *b* axis, resulting in a split multiple scattering peak. Since the primary ion for the MSRI measurement was incident at 60° from the substrate normal, it is to be expected that crystallization of a c-axis oriented film with the upper Bi atom missing would result in a spectrum with little or no Bi visible.

Since an incomplete Bismuth-oxygen plane with the outer Bi atom missing corresponds to an oxygen-rich surface, it is germane to ask whether the non-stoichiometric oxygen at the SBT surface is related to this material's fatigue resistance [27-31,37]. Figure 13 shows a comparison between DRS oxygen profiles of PZT and SBT during deposition onto a 1500 Å thick Pt film on an MgO (100) substrate. There is a clear oxygen deficiency in a 20-30 Å thick region at the PZT/Pt interface, whereas there is no such oxygen deficiency at the SBT/Pt interface. Although it is difficult at this time to make a conclusive statement, there is a clear inference that the oxygen-rich SBT/Pt interface can be correlated with a resistance to the formation of oxygen vacancies, while the oxygen-deficient PZT/Pt interface can be correlated with the presence of oxygen vacancies and is related to the relatively poor fatigue resistance of this electrode/ferroelectric material combination. It also appears that, at least for sputter-deposition of PZT films, the oxygen vacancies responsible for the fatigue mechanism may be introduced during the earliest stages of ferroelectric film growth, and not during subsequent thermal processing or electrical cycling. There is a further suggestion that more aggressive oxidation strategies during the initial growth of PZT/Pt may suppress the fatigue phenomenon.

CONCLUSIONS

In conclusion, we have demonstrated that TOF-ISARS is a powerful technique to perform *in situ*, real-time characterization of multicomponent oxide film growth processes. The three techniques which comprise TOF-ISARS (ISS, DRS, and MSRI) provide complementary information, which when combined, provide surface-specific compositional and structural data which few surface analytical methods can match. Studies of SBT and PZT film growth reveal that a number of complex interfacial phenomena occur that affect the behavior of the final device. Some of these phenomena, such as the non-stoichiometry which occurs at the surface of SBT may be beneficial, although many other phenomena, such as oxygen deficiency at electrode-ferroelectric interfaces, interlayer diffusion and gettering-induced destabilization of the more volatile components of the multicomponent oxide ferroelectric materials are detrimental. TOF-ISARS analysis during growth represents a unique means of understanding and controlling thin film growth phenomena of complex materials.

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Table I
Chemical Phase Fingerprint

+/- MSRI signal ratio for each elemental species

Sample	Element	+/- ion ratio
Hydrocarbon	C	3.0
Graphite	C	1.0
Diamond	C	1.5
hexagonal BN	B	20
cubic BN	B	12
PZT (pyrochlore)	Zr	150
	Pb	12
PZT (perovskite)	Zr	32
	Pb	5

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FIGURE CAPTIONS

FIGURE 1. Schematic of a binary collision process between a probing ion and an atom on the surface under analysis.

FIGURE 2. Schematic of the collision coordinates

FIGURE 3. (a) Illustration of the shadowing effect and (b) determination of the interatomic bond distances and bond angles from shadow cone shape analysis.

FIGURE 4. (a) Kinetic energy distribution of atoms ejected from a surface by energetic ion impact; (b) and (c) the probability of escaping as an ion for two different values of α as a function of kinetic energy.

FIGURE 5. Schematic of the TOF-ISARS system indicating the location of the IBSD system, ion beam line, and ISS, DRS, and MSRI detectors.

FIGURE 6. ISS signal intensity for a 10 keV Ne^+ beam scattering from an Au surface in an extended Ar pressure range.

FIGURE 7. Schematic of the SBT structure.

FIGURE 8. MSRI spectra for a 10 keV Ar^+ primary ion incident on Pt (150 nm) / Ti (50 nm) / SiO_2 (200 nm) / Si.

FIGURE 9. MSRI spectra during SBT deposition onto a Pt (150 nm) / Ti (50 nm) / SiO_2 (200 nm) / Si substrate at 700 °C in an oxygen background at 5×10^{-4} Torr.

FIGURE 10. MSRI spectra during SBT deposition onto a Pt (150 nm) / Ti (50 nm) / SiO_2 (200 nm) / Si substrate at various temperatures in an oxygen background at 5×10^{-4} Torr.

FIGURE 11. *In situ*, real-time ISS spectra of: (a) as-deposited Sr, Bi, Ta species on a room temperature Ti/MgO substrate and during heating at 530 °C (b), 545 °C (c), and 570 °C (d). The evolution of the Sr, Bi, and Ta peaks correlates with the expected formation of the SBT structure, where the Bi atoms remain close to the surface in an incomplete $(\text{Bi}_2\text{O}_2)^{2+}$ layer, while the Sr and Ta atoms move to the perovskite layer underneath the surface (see Fig. 1).

FIGURE 12. ARISS spectra of the SBT film after the annealing and ISS analysis shown in Fig. 8. The angle indicated in the figure is the angle of incidence of the TOF-ISARS ion beam with respect to the SBT film surface normal.

FIGURE 13. DRS oxygen signals obtained during the initial stages of PZT (a) and SBT (b) film growth on Pt layers, using an ion beam sputter-deposition technique.

Krauss et. al. Fig. 1

Krauss et al. Fig. 2

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Krauss et. al. Fig. 9

Krauss et. al. Fig. 10

Krauss et. al. Fig. 11

(a) $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ on Pt/MgO

(b) $\text{SrBi}_2\text{Ta}_2\text{O}_9$ on Pt/MgO