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**IN SITU, REAL-TIME ANALYSIS OF THE GROWTH OF FERRO-
ELECTRIC AND CONDUCTIVE OXIDE HETEROSTRUCTURES
BY A NEW TIME-OF-FLIGHT PULSED ION BEAM SURFACE
ANALYSIS TECHNIQUE***

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IN SITU, REAL-TIME ANALYSIS OF THE GROWTH OF FERROELECTRIC AND CONDUCTIVE OXIDE HETEROSTRUCTURES BY A NEW TIME-OF-FLIGHT PULSED ION BEAM SURFACE ANALYSIS TECHNIQUE

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ABSTRACT

A new time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) technique has been developed and is now used to perform *in situ*, *real-time* analysis of ferroelectric and conductive oxide layers during growth. Initial results presented here show various major effects, namely: (a) RuO_2 films on MgO substrates appear to be terminated in O atoms on the top layer located in between Ru atoms lying in the layer underneath (This effect may have major implications for the explanation of the elimination of polarization fatigue demonstrated for $\text{RuO}_2/\text{PZT}/\text{RuO}_2$ heterostructure capacitors); (b) deposition of a Ru monolayer on top of a Pb monolayer results in surface segregation of Pb until a complete Pb layer develops over the Ru monolayer; and (c) a $\text{Pb}/\text{Zr}/\text{Ti}$ layered structure yields a top Pb layer with first evidence of the existence of Pb vacancies, which also may have major implications in relation to the electrical characteristics of PZT-based capacitors.

INTRODUCTION

The growth of ferroelectric thin films and integration with metal and metal-oxide conductive layers is currently being investigated for fabrication of electronic memory devices. The high dielectric permittivities of ferroelectric materials can be advantageously used in dynamic random access memories (DRAM),¹ and the large values of switchable spontaneous polarization are suitable for non-volatile random access memories (FRAM).²⁻⁵

Promising ferroelectric materials for application in memories are $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT)³⁻⁵ and a proprietary material named Y1.⁶ Although not much is known about the compositional and microstructural characteristics of Y1, a substantial amount of information exist in the literature about PZT.³⁻⁵ Both materials, however, have been used to fabricate capacitors with practically no polarization fatigue up to about 10^{12} polarization switching cycles, which is the maximum number of cycles normally tested.³⁻⁵ Fatigue-free Y1-based capacitors involve the use of Pt electrodes. On the other hand, PZT-based capacitors present large fatigue after about 10^6 - 10^7 switching cycles, when used in conjunction with Pt electrodes.³⁻⁵ However, the problem of fatigue in PZT-based capacitors has practically been solved by producing PZT-based heterostructure capacitors involving metal-oxide electrodes such as RuO_2 ⁷⁻¹⁰ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO).¹¹⁻¹³ The work on metal-oxide/PZT/metal-oxide heterostructure capacitors has shown that the electrode material and/or composition, orientation, and microstructure of the PZT layer and/or PZT / electrode interface have a strong influence on the electrical characteristics of the capacitor. For example, fatigue has practically been eliminated in the PZT-based heterostructure capacitors mentioned above, at least up to 10^{11} - 10^{12} polarization switching cycles.⁹⁻¹³

In addition to controlling the PZT/electrode interface, recent work has shown that the growth of the PZT layer needs to be controlled to avoid the formation of second phases such as pyrochlore, which also contribute to degradation of the electrical properties of PZT-based capacitors. For example, work on the synthesis of PZT films, using the sol-gel¹⁴ and ion beam sputter-deposition (IBSD)^{9,10} techniques, have shown that second phases such as pyrochlore or zirconates (in the case of IBSD^{9,10}) tend to be nucleated under certain conditions, when depositing PZT layers directly on bottom electrodes. The work mentioned above^{9,10,14} demonstrated that second phases can be practically eliminated from the PZT layer by growing a template PbTiO₃ (PT) layer on the bottom electrode prior to start the growth of the PZT film. An argument proposed¹⁴ to explain the effect of the PT layer in controlling the growth of PZT implies that the PT layer presents a lower energy barrier for PZT perovskite nucleation than the Zr-rich layers that may form when starting the growth directly on the bottom electrode.

The progress in producing PZT-based capacitors with controlled composition, microstructure, and electrical properties has been largely based on semiempirical considerations including thermodynamics and kinetic arguments. Missing from the work mentioned above are studies directed at obtaining valuable information on the film growth dynamics using *in situ*, real-time characterization techniques. For this purpose, we are now using a time-of-flight ion scattering and recoil spectrometry (TOF-ISARS) technique^{15,16} integrated with an automated ion beam sputter-deposition (IBSD) system,¹⁷ to perform *in situ*, real-time analysis of ferroelectric and conductive oxide films during growth in relatively high oxygen pressure environments.

This purpose of this paper is to report some of our initial studies on *in situ*, real-time characterization of growing PZT layers. The results reported here are focused on understanding the growth process of PZT on RuO₂, particularly the initial stages of nucleation and growth on the surface of RuO₂ layers used as bottom electrodes for PZT-based heterostructure capacitors.

EXPERIMENTAL TECHNIQUE

A schematic of the experimental system is shown in Fig. 1, while a detailed description of the IBSD and TOF-ISARS systems can be found in previous publications.¹⁵⁻¹⁷ Briefly, the integrated system consist of an UHV surface analysis chamber containing the TOF-ISARS and an Auger electron spectrometer, coupled to a multitarget IBSD system through a 6 mm differential pumping aperture. The base pressure of the analysis chamber is in the 10⁻⁹ Torr range. Oxygen can be introduced into the chamber through a leak valve for *in situ*, real-time characterization of adsorption of oxygen on surfaces and growth of ferroelectric and other oxide layers. A highly focused inert gas ion beam (normally 10 keV) is produced by an Atomika ion source and electronically processed into pulses 10-500 ns long by two sets of electrostatic deflection plates and four apertures (which can be adjusted over the range 0.125-4 mm diameter). The analysis beam impacts on the layer growing on the substrate, located on the axis of the analysis chamber, and is scattered at an angle of 165° into a channel electron multiplier detector located in a differentially pumped column (see Fig. 1). A second detector is positioned in the forward direction to detect direct recoil-ejected surface atoms when using the system in the direct recoil spectrometry mode.

The TOF-ISARS technique can be implemented in the ion scattering spectroscopy (ISS) mode, where ions, impacting at normal or oblique incidence angle, are scattered from atoms on the surface of the sample and the time of flight to the detector is measured; or in the direct recoil spectroscopy (DRS) mode, where atoms are ejected from the surface of the sample by direct impact of the analyzing ions (directed at grazing incidence angle to the sample surface) through binary collisions involving one ion and one atom, and the time of flight of the ejected atoms to the detector is measured. Both techniques are extraordinarily surface specific in that there is a "shadowed" region behind any surface atom exposed to the ion beam such that a second atom inside the shadow cone is invisible to the analysis beam.

Films are deposited using our automated IBSD technique, which involves a single ion beam directed at a localized place in space (Fig. 1), where different targets are positioned sequentially under the ion beam by means of a rotating holder driven by a computer-controlled stepper motor.

Figure 1 Schematic of the integrated IBSD / TOF-ISARS system used for this work.

Films with appropriate stoichiometry can be produced using a layer-by-layer deposition method, in which elemental (e.g. Pb, Zr, Ti) targets are sequentially sputtered and deposited on a heated substrate to induce the layer interdiffusion necessary to produce the compound film. The amount of material needed for each layer is controlled by measuring it with a quartz crystal resonator (QCR). A feedback signal from the QCR is provided to a computer driven by a custom made program that controls the deposition of each element, thus the film stoichiometry.

IN SITU AND EX SITU ANALYSIS OF RuO₂ LAYERS

In situ ISS analysis

In order to characterize the capability of the TOF-ISARS technique, we first studied the growth of a Pb/Ru layered heterostructure under relatively simple conditions. A layer of Pb (about 3.7 Å thick) was deposited at room temperature on a stainless steel substrate while performing *in situ*, real-time analysis. The sputtered flux was directed at 45° to the substrate normal, while the ISS ion beam was impacting normal to the growing layers. A peak appeared in the ISS spectrum at a time-of-flight of about 7.8 μsec (Fig. 2(b)), which is characteristic of Ar⁺ ions scattered from Pb atoms deposited on the substrate surface. The sharp structure of the Pb peak is indicative of a single layer-type distribution of Pb atoms on the surface. Following the Pb deposition, a Ru layer was grown (Fig. 2(c)). Instead of observing the Ru peak growing and the Pb peak decreasing, the ISS spectrum revealed that after depositing about one half monolayer of Ru the Pb peak was unchanged, while only a small Ru peak appeared (Fig. 2(c)). Finally, after deposition of slightly more than one monolayer Ru, the Pb peak decreased to approximately one half of its initial value, while the Ru peak intensity increased (Fig. 2(d)). These results can be interpreted as indicative of a layered structure where the Pb atoms initially segregate to the surface (Fig. 3 (b)), driven by a segregation energy of about 2.6 eV, determined by calculations using the Miedema model.¹⁸ Upon completion of a segregated monolayer of Pb on top of a remaining Ru layer (Fig. 3 (c)), further Ru deposition does not lead to more Pb segregation to the surface, since the Pb atoms are now sandwiched between two layers of Ru (Fig. 3 (c)), which equilibrates the driving force for segregation. Therefore, the intensity of the ISS Pb peak should decrease as the Ru peak increases, as observed in Fig. 2 (d).

Figure 2 In situ, real - time ISS spectra obtained with scattering of Ar^+ ions from growing layers of Ru and Pb.

Figure 3 Atomic scale model that correlates with the ISS spectra shown in Fig. 2.

Ex situ ISS analysis

A highly oriented (110) layer of RuO_2 (as determined by XRD) was deposited on a (100) MgO substrate at 500 °C using a separate IBSD system with a higher deposition rate than that available with the IBSD / TOF-ISARS integrated system. The layer was deposited by sputtering a Ru metal target while simultaneously introducing molecular oxygen into the film in the form of a jet that produced a 5×10^{-4} Torr background pressure in the deposition chamber. The RuO_2/MgO sample was subsequently transported in air to the TOF-ISARS system.

The surface of the RuO_2 layer was analyzed using the DRS mode of the TOF-ISARS technique. This mode is used to detect the presence of light atoms such as H, C, and O on the surface, since the ISS mode is unable to detect atoms which are lighter than the primary ions. The DRS spectra shown in Fig. 4, taken at 5×10^{-5} Torr of O_2 background pressure indicate that H, C and O are present on the surface of the RuO_2 layer. The presence of H and C was most probably due to the exposure of the RuO_2 film to air during transport to the analysis chamber, since a similar spectrum to that at 5×10^{-4} Torr of O_2 was obtained in vacuum at 10^{-7} Torr. The introduction of oxygen into the analysis chamber, as a jet directed at the film, resulted in a substantial increase of the H and C signals above that corresponding to O, which is most probably due H and C being carried as impurities in the oxygen stream and depositing on the surface of the RuO_2 layer to partially cover the O atoms of the RuO_2 . These results demonstrate the high sensitivity of our technique.

In situ heating while acquiring DRS spectra as a function of substrate temperature in the range 30-400 °C, revealed that the H and C species are desorbed from the surface until they practically disappear (Fig. 5). The spectra taken at 330 °C shows the presence of a Ru peak coexisting with the O peak, indicating that at this temperature some Ru atoms reside in the uppermost atomic layer. However, the Ru peak disappears for the spectra taken at 400 °C, which can be interpreted as resulting from an O layer covering the Ru surface. However, the O atoms appear not to be positioned on top of Ru atoms, since an ISS analysis done at 545 °C in 5×10^{-4} Torr of oxygen, with a 10 keV Ar^+ ion beam incident normal to the surface, shows an spectrum characteristic of a thick clean Ru layer (i.e., a sharp rise on the short time-of-flight side of the peak, and a long tail on the long time-of-flight side). The combined results of the DRS and ISS analysis described above indicate that the RuO_2 surface may consist of a single layer of O atoms positioned between Ru atoms located in an underlying atomic row.

Figure 4 DRS spectra at two different O_2 background pressures for a 1500 Å thick RuO_2 layer deposited on (100) MgO .

Figure 5 DRS spectra following those shown in Fig. 4. The spectra here were obtained in real-time as the sample was heated.

IN SITU, REAL-TIME ANALYSIS OF Ti/Pb/Zr LAYERED STRUCTURES

A Pb/Zr layered structure was deposited at room temperature on (100) MgO , followed by deposition of a Ti layer on top. Because of space limitations we present only a sequence of spectra corresponding to the *in situ, real-time* analysis performed while growing the Ti layer, and a subsequent angular resolved ISS (ARISS) analysis of the resulting three layer structure. The series of spectra shown in Fig. 6 illustrates the capability of the TOF-ISARS technique in providing new insights into the growth dynamics of layered structures. Upon depositing the Ti layer on top of the Pb/Zr layered structure, it was observed that the Pb peak started to grow very rapidly [Fig. 6 (50 sec)] and subsequently diminished slightly in intensity for longer Ti deposition times [Fig. 6 (3550 sec)]. Throughout the dynamic growth of the Pb peak, a small Zr peak was also seen to grow at a much lower rate (Fig. 6 (1400-3550 sec)). The interesting effect is that there was no evidence of Ti atoms on the surface, although these were the species being deposited.

Figure 6 ISS sequential spectra taken when depositing a Ti layer on top of a Pb/Zr layered structure previously grown on (100) MgO at room temperature.

Following the *in situ, real-time* analysis shown in Fig. 6, an ARISS analysis was performed (Fig. 7 (a)), which showed a rapid increase of the Pb peak at about 70° angle of incidence of the analyzing Ne^+ ion beam with respect to the surface normal, followed by a simultaneous increase of the Pb, Zr and Ti peak intensities at about 50° to a maximum value at about 33° . Following the

peak value of all three signals (at 33 ° polar angle) described above, the Pb intensity decreases to a value similar to that observed for polar angles in the range 50-70°, while the Ti and Zr peak intensities decrease to practically zero at normal incidence of the Ne⁺ ion beam.

Figure 7 (a) ARISS analysis of the sequentially deposited Ti/Pb/Zr layers (Fig. 6) at room temperature on (100) MgO; (b) atomic scale model that correlates with the ARISS data shown in (a).

The data presented in Fig. 7 (a) can be interpreted in terms of the atomic scale model shown in Fig. 7 (b), where it is proposed that Pb atoms may be positioned on the top two surface layers in such a way that those on the top-most layer are located on top of Zr or Ti, but not on top of Pb atoms in the layer underneath. On the other hand, the larger intensity of the Zr peak with respect to the Ti indicates that Zr atoms tend also to cover Ti atoms. This interpretation is supported by calculations of (vacuum) surface segregation which show that $\Delta E_{\text{seg}}(\text{Pb-Ti}) = -1.11 \text{ eV} > \Delta E_{\text{seg}}(\text{Pb-Zr}) = -0.83 \text{ eV} > \Delta E_{\text{seg}}(\text{Zr-Ti}) = -0.02 \text{ eV}$. The data presented in Fig. 7 may be the first evidence of the existence of Pb vacancies formed during deposition of PZT by the layer-by-layer IBSD deposition technique. After deposition is terminated, the surface composition slowly changes, resulting in a decrease of the Pb signal, the appearance of Ti on the surface, and a very strong enhancement of the Zr signal. This evolution is generally in accord with behavior expected for oxygen-induced segregation. However, further work is necessary to confirm this hypothesis, particularly involving analysis of films grown at high temperature in an oxygen atmosphere, which are the conditions used to synthesize PZT films.

CONCLUSIONS

A new time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) technique has been used to perform first *in situ*, *real-time* analysis of layered heterostructures relevant to the synthesis of ferroelectric PZT films, and conductive oxide layers, during growth. Initial results presented here show various major effects, namely: (a) RuO₂ films on MgO substrates appear to be terminated in O atoms on the top layer, which are located in between Ru atoms lying in the layer underneath. This effect may have major implications for the explanation of the elimination of polarization fatigue demonstrated for RuO₂/PZT/RuO₂ heterostructure capacitors, which indicates that fatigue may be eliminated because oxygen vacancies (considered as main contributors to fatigue through polarization domain pinning) at the PZT/metal electrode interface may be eliminated when used a conductive oxide such as RuO₂; (b) deposition of a Ru monolayer on top of a Pb monolayer results in surface segregation of Pb until a complete Pb layer develops over the Ru monolayer; and (c) a Pb/Zr/Ti layered structure yields a top Pb layer with first evidence of the

existence of Pb vacancies, which also may have major implications in relation to electrical characteristics of PZT-based capacitors. Further work involving deposition at high temperature in oxygen atmosphere, now in progress, will provide new insights into the growth dynamics of ferroelectric / metal oxide heterostructures under conditions used for the synthesis of capacitors by the IBSD deposition technique. Finally, it is relevant to point out that the TOF-ISARS technique can be applied to the *in situ*, *real-time* analysis of any film produced by vapor phase-deposition, and for *ex situ* analysis of films deposited with any other technique such as sol-gel or liquid phase epitaxy.

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