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AES and XPS study of PZT thin film deposition by the laser ablation technique

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Abstract

$Pb(Zr_{0.52}Ti_{0.48})O_3/YBa_2Cu_3O_{7-x}$(PZT/YBCO) heterostructure is grown by the laser ablation technique using a 10% PbO-enriched PZT target. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) show that the PZT thin film grown by this method is nominal and that a target of PZT + 10% PbO is a proper target for growing nominal PZT thin films.

Keywords: Ferroelectrics; Thin films; Deposition

1. Introduction

In recent years, thin films of ferroelectric materials have been attracting the attention of the microelectronics community in view of their wide applications such as memories, ultrasonic sensors, infrared detectors and electro-optic devices [1–5]. Essentially, the memory element consists of a thin-film ferroelectric capacitor, in which the remnant polarization within the ferroelectric thin film plays the role of the storage. With the progress in the technology to deposit thin films, ferroelectric nonvolatile memories are now well into their development phase.

Reliable performance of the device made from such ferroelectric materials requires good quality thin films. There are a variety of techniques for thin film deposition. Some of these techniques are sputtering, evaporation, epitaxial deposition, chemical vapour deposition, sol–gel processing and laser ablation [6–9]. The last two methods are relatively new for the fabrication of ferroelectric films. In some of the these methods, such as sputtering and evaporation techniques, problem occurs in stoichiometry, orientation and uniformity of the film during the growth. Therefore, tedious annealing processes follow the growth of thin films by such techniques. Epitaxial deposition requires high technology and expensive equipment. In chemical vapour deposition (CVD), while the process is extremely reproducible and efficient, one limitation is the difficulty associated with the control of stoichiometry of the complex compositions like ferroelectric materials.

The sol–gel and laser ablation techniques developed in recent years seem to meet the quality requirements for device applications. The sol–gel method is widely used for its excellent homogeneity, ease of composition control, film uniformity over large area, and simple and inexpensive equipment. Processes using the sol–gel technique are described by various authors [10–12].

In this paper, the thin film fabrication by laser ablation technique is discussed. In particular, a $Pb(Zr_{0.52}Ti_{0.48})O_3/YBa_2Cu_3O_{7-x}$(PZT/YBCO) heterostructure prepared by this method is studied and characterised by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

2. Laser ablation technique

A schematic configuration of the laser ablation chamber is shown in Fig. 1. The laser used in this chamber was a Lambda Physik's LPX 100 excimer laser with the wavelength 248 nm. The laser is used to ablate the ceramic materials of a rotating target. The substrate is mounted onto a cylindrical heater for the purpose of epitaxial film growth. The base pressure of the vacuum

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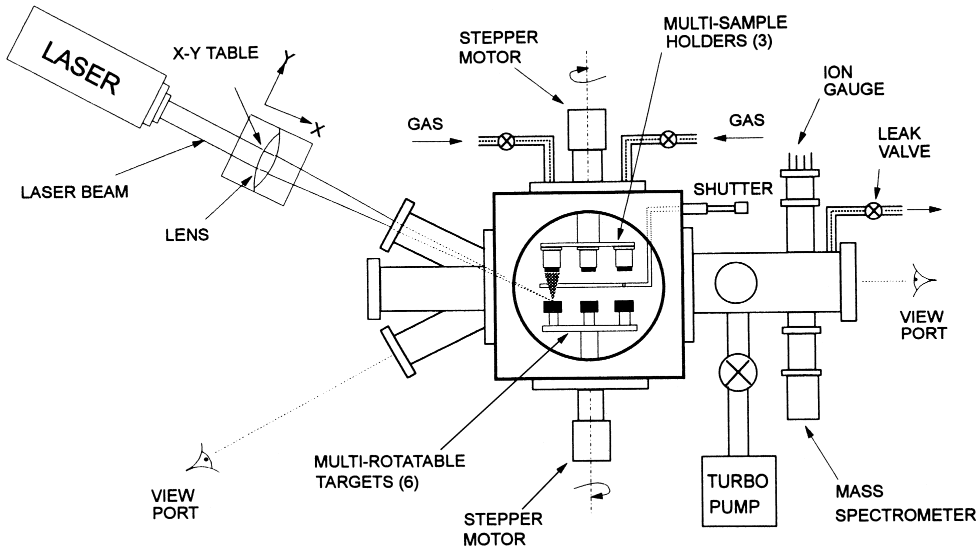

Fig. 1. Schematic diagram of the laser ablation system.

chamber is in the 10^{-6} torr range. Depending on the material used for thin film fabrication, the chamber can be filled with proper gas to compensate for the deficiency of that particular gas in that film deposition. The pressure in the chamber is monitored by a capacitance manometer.

One of the important factors in thin film deposition by this technique is the selection of the substrate material. For a specific film, the substrate should be a single-crystal material, chemically compatible to the film, and the thermal-expansion coefficient and its lattice should match up to the film with nearly the same lattice parameter [6,13].

3. PZT/YBCO heterostructure

A thin film of YBCO was deposited on $LaAlO_3$ to make the bottom electrode of the capacitor device. The $LaAlO_3$ is a proper substrate for the growth of YBCO thin films because of its highly matched lattice parameter. The growth of PZT thin films was realized from a target of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ containing a 10% excess of PbO. The 10% PbO in the target material was used to compensate for the decrease in lead in the film as the temperature of the substrate is increased. Such variations in Pb content are dramatic above 630°C, have been widely reported [14,15], and are attributed to the poor sticking coefficient of lead at high temperatures.

4. Results and discussion

The XPS spectra of both PZT target and PZT thin film sample are shown in Fig. 2. The curves are

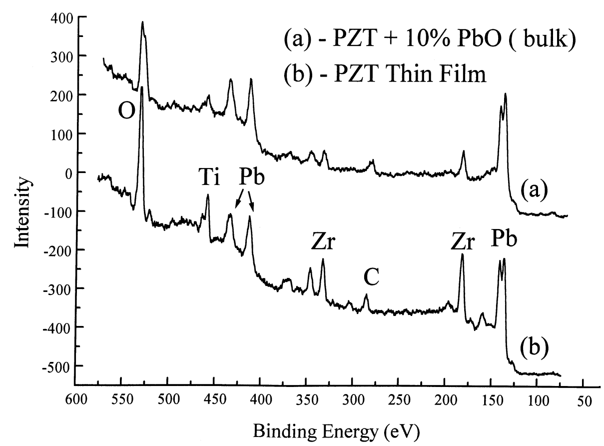

Fig. 2. XPS spectra of a 10% PbO-enriched PZT pressed powder sample and the PZT film made from the same material.

normalized to the Pb peak for a qualitative comparison of the elements in the samples. As expected, the spectrum of PZT thin film shows less Pb than observed in the PZT target [4]. This is clear by comparing the heights of the Ti, Zr and O peaks that are more dominant in PZT thin film sample. The AES spectrum of PZT thin film is shown in Fig. 3. In the thin film, AES and XPS show the same ratio of Pb:Zr:Ti:O to be 1:0.54:0.44:2.95 that is close to the elemental ratio for nominal PZT (1:0.52:0.48:3). In extracting the elemental ratio of the elements from AES spectrum, the sensitivity of Auger signals for different elements has been considered and incorporated in the calculation. Therefore, the composition of the ferroelectric thin films made by the laser deposition technique is nominal PZT when using a PZT target with 10% excess of PbO. In other

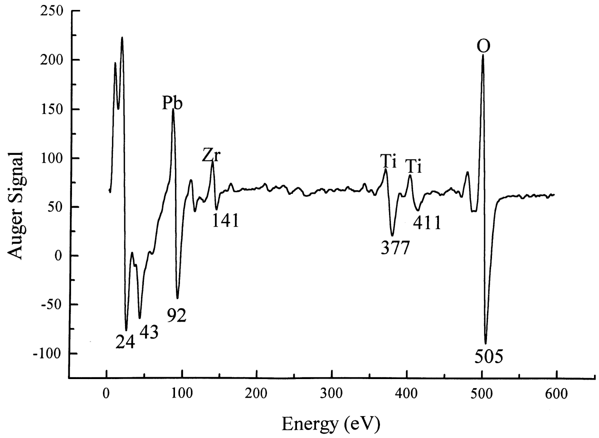

Fig. 3. AES spectra of the PZT film.

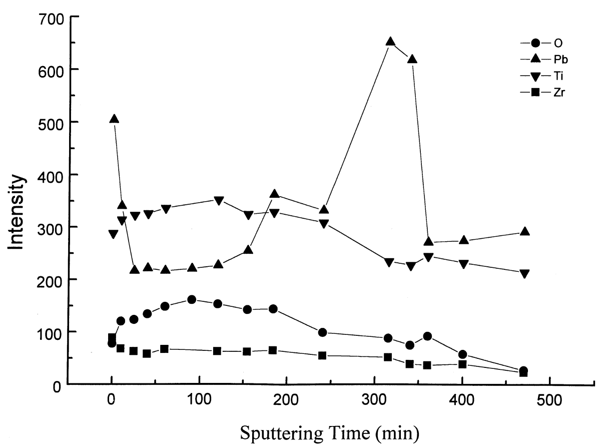

Fig. 4. Depth profile of PZT thin film, 1 min sputtering is 0.2 nm depth).

words, the excess lead in the target moves the film composition towards the stoichiometric composition.

Another feature worthwhile to be considered from Fig. 2 is the double peak of oxygen and the different feature of the Pb peak in the target sample as compared to the thin film sample. This is due to the 10% excess of PbO in the target. The details of these features are discussed in Ref. [16].

The depth profile of the PZT film is shown in Fig. 4. In this figure the ordinate represents the intensity of different elements in PZT in arbitrary unit. The horizontal axis is the depth into the sample down to the PZT/YBCO interface. One minute sputtering time corresponds to 0.2 nm depth into the sample. The depth profile of the sample shows excess amount of Pb near the surface and also in the interface area. The predominant amount of Pb near the surface is due to the segregation of Pb outward toward the surface of the PZT and oxidizing to form PbO. As it was mentioned earlier, due to the poor sticking coefficient of Pb, it can easily diffuse through channels created by defects during thin film preparation [17]. As the film is sputtered, the depth profile indicates nominal PZT thin film down to the interface.

At the interface, however the ratio of lead species to those of the other elements in the PZT is relatively high. This is probably due to the better match of PbO lattice parameter ($a = 0.39$ nm) with the perovskite YBCO ($a = 0.38$ nm, b = 0.39 nm) in our films. Therefore, it is favourable for PbO to be formed at the interface first and for the PZT ($a = 0.48$ nm) to grow on it [6].

5. Conclusion

We have discussed the growth of epitaxilal YBCO and PZT thin films by the laser ablation technique to make a PZT/YBCO heterostructure. AES and XPS data of these thin films indicates that during the growth of PZT there is Pb deficiency in the thin film that can be compensated by using a target of PZT with 10% excess of PbO. Therefore, a target of PZT + 10% PbO is a proper target for growing nominal PZT using the laser ablation technique.

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