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Intrinsic resputtering in pulsed-laser deposition of lead-zirconate-titanate thin films

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Pulsed-laser deposition (PLD) of lead-zirconate-titanate $[Pb(Zr_x,Ti_{1-x})O_3]$ (PZT) thin films under low ambient pressure has been investigated by studying the angular deposition distributions of the constituent elements of the films. Nonstoichiometric profiles are observed and a dip occurs near the target surface normal of the deposition profile of lead. Experimental results show that intrinsic resputtering of the film is important in the PLD process and is responsible for the anomalous distribution of lead. © *1995 American Institute of Physics.*

Pulsed-laser deposition (PLD) is a widely used method for producing good quality ceramic thin films because of its ability to retain the stoichiometry of the target material. However, in our previous studies on PLD of $Pb(Zr_{0.48},Ti_{0.52})O_3$ (PZT) film at a low ambient pressure of 10^{-4} mbar, a prominent Pb deficiency at positions around the target surface normal (TSN) was observed.[1] Several recent reports on PLD of multicomponent targets including $YBa_2Cu_3O_7$ (YBCO), $PbTiO_3$ (PT), and PZT also indicated a relative enrichment of the lower mass elements around the TSN.[2–4] Saenger[5] has proposed a qualitative explanation for the observed angular dependence on species mass and laser fluence in pulsed-laser deposited films derived from multicomponent targets. The observed compositional nonuniformities in YBCO depositions were also numerically simulated by Singh *et al.*[6,7] using a model in which the laser plume was treated as an initially isothermal plasma that subsequently undergoes adiabatic expansion. These approaches, however, cannot account for our observed anomalous angular deposition profile of Pb in PLD of PZT films under low ambient pressure.

It is generally recognized that in the sputtered deposition of thin films, resputtering of the deposited materials by intentional or inadvertent bombardment of energetic particles during deposition is a rather common process.[8–10] For compound materials such as PZT whose constituent elements have large differences in sputtering coefficients, resputtering may play a major role in governing the sputtered film growth rate and the film stoichiometry. PLD is a process well known to produce a relatively large proportion of energetic neutrals and ions, therefore resputtering of the deposited film materials is expected to be important. To our knowledge, no report has explicitly addressed this resputtering effect in PLD of multicomponent thin films. There are, however, a few reports suggesting that some of the materials did come off the substrate during PLD of thin films. For example, in the ArF excimer laser deposition of $YBa_2Cu_3O_{7-x}$ (YBCO) films, Okada *et al.*[11] observed Ba atoms coming off a Si substrate directly using laser induced fluorescence (LIF) spectroscopy. In a later study,[12] they found that the ablated particles were reflected and became stagnated in front of the substrate, and were then transported by diffusion onto the substrate under a high oxygen pressure. Geohegan[13] has also observed reflection of the emitted species from the substrate during KrF laser ablation of YBCO using high speed photography. No substantiated explanation in regard to their originating mechanism was suggested. In this report, experimental results are presented to elucidate the important role of resputtering in PLD of PZT film. In particular, we show that resputtering of the PLD film is primarily responsible for the observed anomalous deposition profile of Pb.

The experimental setup for the angular deposition studies in PLD is similar to that mentioned in our previous report.[1] The target was placed on a rotating holder and ablated by a focused XeCl excimer laser in a vacuum chamber evacuated by a diffusion pump system. The XeCl excimer laser (Lumonics, series TE 860-4) which generates light pulses at 308 nm with 10 ns pulse width was focused at an incident angle of 45° onto the target by a quartz lens ($f=25$ cm). The size of the focused spot, as measured from a burnt pattern on a Polaroid film, was 2.2×0.5 mm^2. The laser irradiation fluence was 4 J/cm^2 and the repetition frequency was 10 Hz. A silicon wafer was used as the substrate. The pressure in the chamber was kept at 1×10^{-4} mbar for all the experiments described. The deposited films were analyzed using a scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) analysis facility.

Figure 1(a) shows the amounts of Pb, Zr, and Ti in a film deposited at various angles with respect to the TSN from a PZT target. While the deposition profiles of Zr and Ti are narrow and sharply peaked, the deposition profile of Pb is relatively broad and has a dip in the direction around the TSN. A substantial deficiency in Pb with respect to Zr and Ti is clearly seen in this region. The ratios of Pb to Zr and to Ti in the film around the TSN are both 1:2. This is in marked contrast to the stoichiometric ratio of 2:1 of the target. Figure 1(b) shows the angular deposition profile of the film deposited from a pressed pellet of the pure PbO target. It is found that the deposition profile of Pb is broad and smooth. No dip around the TSN is observed. The above results suggest that the presence of the other two elements, Zr and/or Ti leads to the occurrence of the dip in the deposition profile of Pb in PLD of PZT films. To demonstrate how the presence of Zr and/or Ti affected the deposition profile of Pb, we carried out a PLD experiment in which the target was composed of two half discs of equal size. One half disc was PbO and the other was ZrO_2. It was mounted onto the rotatable target holder as usual. The laser beam was focused onto one side of this split

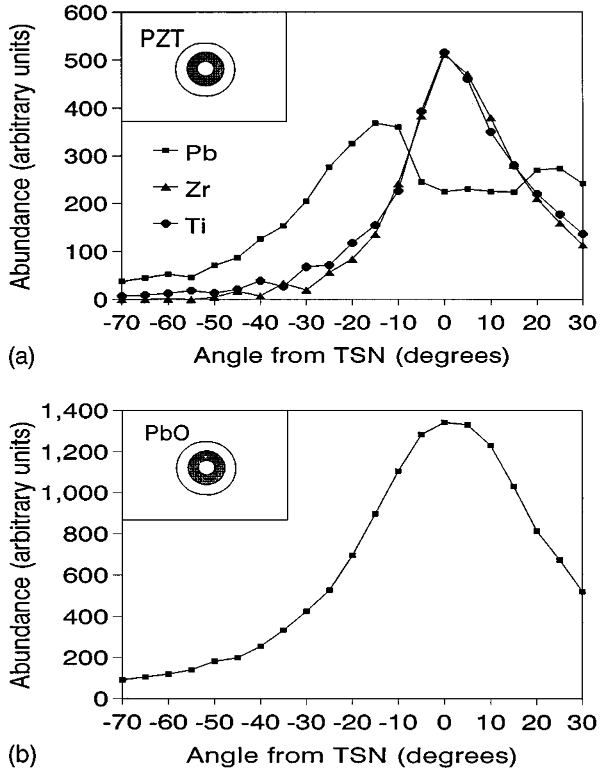

FIG. 1. The angular deposition profiles of (a) Pb, Zr, and Ti in a film from a PZT target, and (b) Pb in a film from a PbO target deposited at a laser fluence of 4 J/cm^2 and a base pressure of 10^{-4} mbar. Note that the data in the range $+30°–+70°$ are affected by the laser beam and are not included. The insert in each figure shows the appearance of the target after the experiment. The shaded region represents the area irradiated by the focused laser.

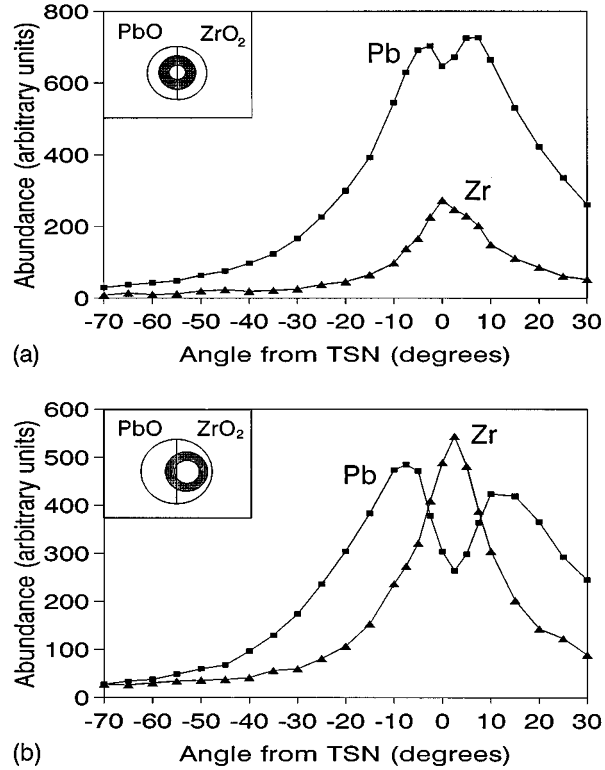

FIG. 2. The angular deposition profiles of Pb and Zr in films deposited from the PbO and ZrO_2 split target at a laser fluence of 4 J/cm^2 and a base pressure of 10^{-4} mbar. The laser irradiated area ratio of PbO portion to ZrO_2 portion are (a) 1:1, and (b) 1:2, respectively.

target. The rotational frequency was 5 Hz, half of the laser repetition rate. Therefore, only one half disc was irradiated by the laser each time the laser was fired. In this way, the materials from the two half discs were deposited alternately shot by shot onto the substrate. Figure 2(a) shows the amount of Pb and Zr in the deposited film at various angles with respect to the TSN from such a target. It is found that the angular deposition profile of Pb also has a dip around the TSN. However, the dip is much smaller than that observed in PLD of PZT target [Fig. 1(a)]. Similar effect is also obtained when ZrO_2 is replaced by TiO_2 in the split target. Note that the amount of Zr in the film is relatively small compared with the amount of Pb in the film. This is probably due to the difference in the desorption rate of PbO and ZrO_2 under the irradiation of the pulsed-excimer laser. In order to study the change in the deposition profile of Pb when the amount of Zr in the film is increased, the rotational axis of the split target was displaced towards the ZrO_2 half disk so that the area irradiated by the laser was larger in the ZrO_2 portion than in the PbO portion. The irradiated area ratio of PbO to ZrO_2 was 1:2. The rotational frequency of the target was adjusted to 3.3 Hz, which was about one-third of the laser repetition rate. In this way, the pulsed-laser ablated the ZrO_2 portion twice for every ablation of the PbO portion. Figure 2(b) shows the corresponding angular deposition profiles of Pb and Zr. The amount of Zr in the film is indeed doubled as expected. It is also seen that the dip in the deposition profile of Pb becomes significantly larger.

The above experiments show that the occurrence of the dip does not require the simultaneous presence of Pb and Zr or Ti in the gas phase as required by the models suggested by Saenger[5] and Singh *et al.*[6,7] The results suggest that Pb, indeed, came off the substrate during the PLD process. To verify this definitively, an experiment was setup to collect the materials that came off the substrate during the deposition of PZT film. A small piece of silicon wafer collector (0.75×1.5 mm^2) was placed near the TSN at a distance of 20 mm in front of the target surface. The collecting surface was parallel to the target and facing a direction away from the target. The ablation of the PZT target was carried out with and without the presence of a silicon substrate. The amount and the composition of the materials collected on the collector were then compared for the two cases. In the absence of the substrate, the amount of materials collected on the collector was barely detectable. This suggests that neither the scattering of the emitted species by the ambient gas molecules at such a low pressure nor the backscattering between the emitted species was important. In the presence of a substrate at 5 mm in front of the collector surface, a large amount of materials coming off the substrate was collected. The collected material amounted to more than one-sixth of the film materials that was deposited on the substrate. EDX analysis of the collected materials revealed a substantial enrichment in Pb (75%) with respect to the sum of Zr and Ti (25%).

The above observations can be understood by recognizing that particles are emitted from the target at high kinetic energies during PLD. Depending on the desorption processes which can be thermal or nonthermal, particle energies can range from a fraction of eV to several hundred eV. As is well-known, the desorption of the Pb component from the target is largely a thermal process resulting in a lower energy distribution and a broad spatial profile, whereas the desorption of Zr is largely nonthermal and hence resulting in a more energetic distribution and a much sharply peaked spatial profile.[1,14] Due to the relatively large sputtering coefficient of Pb,[15] resputtering of Pb will certainly be much more prominent than either that of Zr or Ti. The experiments of the split target clearly showed that Pb was sputtered by bombardment of energetic Zr atoms and ions, causing a larger dip as the Zr content is increased [Fig. 2(b)]. In a separate study, Eisenmenger-Sittner and co-workers[16] have also observed the resputtering phenomenon in the preparation of copper-lead tribological coatings by magnetron sputtering. They suggested that the strong deficiency in Pb found in the deposited film at low pressures was due to the resputtering of the Pb atoms from the substrate surface by the Cu atoms.

In conclusion, we have demonstrated that the Pb deficiency in PZT thin films prepared by PLD under vacuum is caused by resputtering. The experiment with a split target shows that the resputtering of Pb by Zr or Ti occurs even after Pb has been deposited on the substrate by a previous laser shot, suggesting that the collision in the gas phase during transport from the target to the substrate is not the major reason for the anomalous deposition profile of Pb. The collection of the materials coming off the substrate directly confirms this picture. We have also investigated the resputtering phenomenon in the PLD of PZT films under the deposition conditions of the ambient oxygen environment and elevated substrate temperature. Details of the results will be presented in another report. The resputtering mechanism identified in the present work is expected to be especially relevant to PLD of thin films in band-gap engineering.

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