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The role of ambient gas scattering effect and lead oxide formation in pulsed laser deposition of lead–zirconate–titanate thin films

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The angular distribution of lead in films deposited by pulsed laser irradiation of lead–zirconate–titanate and lead targets are studied as a function of ambient gas (argon or oxygen), gas pressure, and substrate temperature. When the substrate is kept in vacuum and at room temperature, a dip in the lead content attributable to the intrinsic resputtering of lead is observed at the position of the target surface normal. In the presence of an ambient gas, the dip disappears and the lead content increases at all angles. These results are attributed to a reduction of resputtering arising from scattering of the ablated species by ambient gas molecules. Under ambient oxygen and at high substrate temperature, the retention of lead content in the deposited films is largely due to the formation of lead oxide. © *1996 American Institute of Physics.* [S0003-6951(96)01140-0]

In a previous letter,[1] we presented experimental results that showed that intrinsic resputtering is responsible for the observed deficiency of Pb in lead–ziconate–titanate (PZT) films prepared by pulsed laser deposition (PLD) under vacuum condition and at room temperature. It is well known[2–6] that PZT films having the same stoichiometry as the target material can be prepared under 100–300 mTorr of ambient oxygen pressure at elevated substrate temperature (typically 550 °C). Therefore, it is of interest to study the role of ambient oxygen and substrate temperature in the PLD of PZT films. In the present work, we extend the study to films deposited in argon or oxygen under various ambient pressures and at various substrate temperatures. We will present experimental profiles of the spatial distribution of Pb in PZT films prepared under a gas pressure of 0.1–200 mTorr, and show that the resputtering effect is strongly affected by ambient gas pressure, in agreement with a resputtering model.[7,8] We will also show that ambient oxygen helps to preserve the Pb content in the films through the formation of PbO as suggested by Horwitz *et al.*[4] In order to elucidate the relative importance of PbO formation and ambient gas scattering effects, we have also measured the angular deposition profiles of Pb arising from excimer laser irradiation of a Pb target.

The experimental setup for the angular deposition studies in PLD was similar to that described in our previous report[9] except for the study of the substrate temperature effect, in which case a single strip of silicon wafer was used as the substrate and was adhered to the surface of a heating block. The wavelength of the excimer laser (XeCl) used was 308 nm and the pulse width was 10 ns. The target-to-substrate distance was 5 cm. The deposition was performed both at room temperature and at a substrate temperature of 550 °C. Experiments were carried out under 0.1, 50, and 200 mTorr of oxygen or argon. The deposited films were analyzed using an x-ray diffractometer and a scanning electron microscope equipped with energy dispersive x-ray analysis facility.

Figure 1 shows the angular distribution profiles of Pb in a PZT film deposited at room temperature by irradiating a PZT target at a laser fluence of 4 J/cm^2. It is clearly seen that under vacuum condition (0.1 mTorr) there is a dip in the Pb content at the target surface normal (0°), which is attributed to a resputtering effect. Similar profiles with a less prominent dip were observed at lower fluences of 2–3 J/cm^2. Also shown in Fig. 1 are the theoretical curves calculated according to the model of Zalm[7] and Hau.[8] In this model, the resputtering yield depends on kinetic energies of the impinging particles that have to be measured experimentally. The theoretical curves were obtained by using particle energies measured by the ion probe method and time resolved optical emission spectroscopy.[8] The number of energetic impinging particles was estimated from the charge collected by the ion probe. This number includes not only the positive ions but also the highly excited Rydberg atoms and fast moving neutrals.[10] Low energy neutrals, however, do not contribute significantly to the resputtering and are not included in the present model. As the ambient pressure increases to 200 mTorr, the kinetic energies of the laser ablated

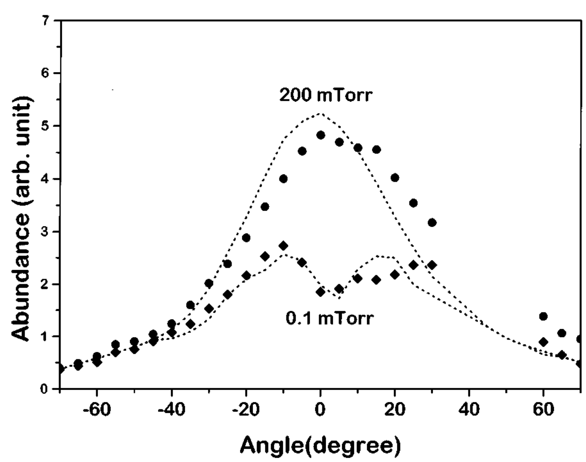

FIG. 1. Angular distribution profiles of Pb in PZT films deposited at room temperature by pulsed laser irradiation of PZT target at a laser fluence of 4 J/cm^2 under vacuum (0.1 mTorr) and 200 mTorr of oxygen. Solid diamond (0.1 mTorr) and solid circle (200 mTorr) denote the experimental data, while the dotted lines are the theoretical curves.

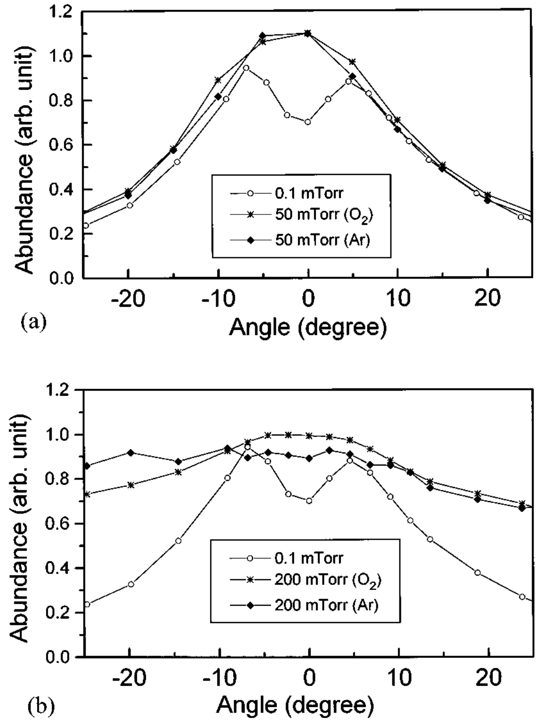

FIG. 2. Angular distribution profiles of Pb deposited at room temperatures by pulsed laser irradiation of Pb target at a laser fluence of 4 J/cm^2 (a) under vacuum and 50 mTorr of ambient gas and (b) under vacuum and 200 mTorr of ambient gas.

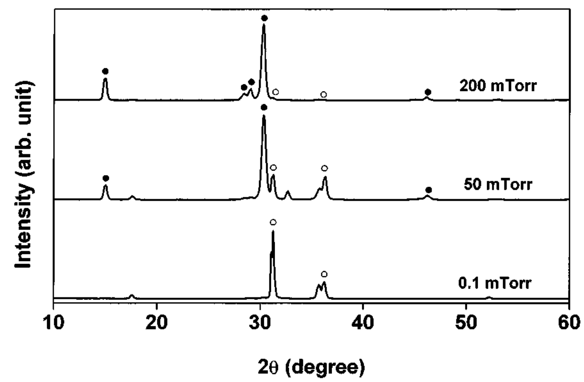

FIG. 3. X-ray diffraction spectra of films prepared at 250 °C by pulsed laser irradiation of Pb target under various oxygen ambient gas pressure. Solid circles (●) indicate PbO lines, while hollow circles (○) indicate metallic Pb lines.

species become smaller due to more frequent collisions with ambient gas molecules. This leads to a reduction of the resputtering effect, and consequently the disappearance of the dip at 0° and the increase in Pb content at all angles.

Figure 2(a) shows the spatial distribution profiles of Pb deposited on a substrate at room temperature arising from pulsed laser irradiation of a Pb target. Under vacuum condition (0.1 mTorr), a dip occurs at the target surface normal similar to the case for PZT target (see Fig. 1), indicating a significant resputtering effect. At a pressure of 50 mTorr, the angular distributions of Pb are almost identical whether the ambient gas is oxygen or argon. The dip disappears and the Pb content in the film is higher than that deposited under vacuum condition. Since PbO formation is unlikely under ambient argon, collisions with ambient gas molecules must be the dominant factor for reducing the resputtering effect, thereby resulting in an enhanced deposition of Pb. As shown in Fig. 2(b), when the ambient gas pressure increases to 200 mTorr, the spatial distribution becomes broader due to stronger scattering by ambient gas molecules. Near the target surface normal, the Pb content in the film deposited under ambient oxygen is slightly greater than deposited under ambient argon. Under such a high oxygen ambient pressure, PbO is readily formed. This result is later confirmed by x-ray diffraction study. Pb has a very large sputtering coefficient. For example, the sputtering yield[11] of Pb under the bombardment of 600 eV Ar^+ is 2.7. At present, we are unable to obtain the sputtering coefficient of PbO from the literature. However, most oxides have smaller sputtering coefficients than their corresponding elements.[11] We, therefore, expect the PbO thus formed is not so readily resputtered as Pb and more Pb content remains on the substrate in the form of PbO.

Figure 3 shows the x-ray diffraction spectra of films deposited at 250 °C by laser irradiation of Pb target under various oxygen pressures. PbO formation is observed at an oxygen pressure of 50 mTorr and becomes more prominent as the oxygen pressure increases. A substrate temperature of 250 °C is chosen for the x-ray study because it is high enough to give crystalline films and, hence, good x-ray diffraction spectra, and yet low enough to avoid substantial thermal evaporation of Pb. The x-ray diffraction spectrum of a film deposited at a substrate temperature of 550 °C under 200 mTorr of ambient oxygen is similar to that obtained at 250 °C, except that the oxide lines are even stronger, implying that PbO formation is important at higher substrate temperature.

Figure 4 shows the angular distribution profiles of Pb deposited at 550 °C under vacuum (0.1 mTorr) and at 200 mTorr ambient oxygen or argon. Under vacuum condition, the Pb film thickness was barely detectable. At a pressure of 200 mTorr, there was a much larger amount of Pb on the substrate when argon is replaced by oxygen as the ambient gas. Since the melting point of Pb is 327.5 °C, substantial thermal reevaporation of the deposited Pb occurs when the substrate is at 550 °C and under vacuum. For films prepared

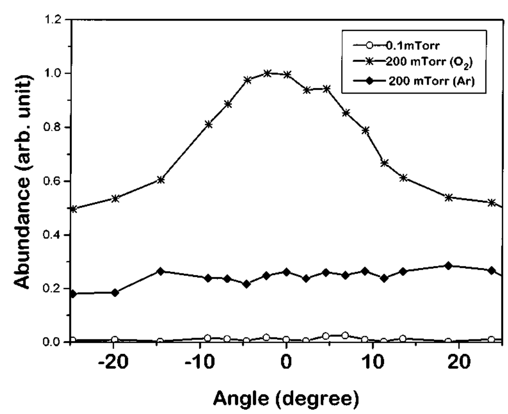

FIG. 4. Angular distribution profiles of Pb deposited at 550 °C by pulsed laser irradiation of Pb target under vacuum (0.1 mTorr) and 200 mTorr of argon or oxygen.

under 200 mTorr of argon, due to the partial pressure effect[4] and the lower surface temperature caused by gas convection, reevaporation of Pb is less severe, resulting in a significant amount of Pb on the substrate. Finally, under 200 mTorr of oxygen, there was a marked increase in Pb content because of the formation of PbO. With a higher melting point of 886 °C, PbO is not reevaporated. The above results show that oxide formation is the dominating factor in the preservation of Pb during PLD at high substrate temperatures and under ambient oxygen. Indeed, we are able to produce PZT films with the same stoichiometry as the target by PLD under 200 mTorr of oxygen and at a substrate temperature of 550 °C.

In summary, we have studied the spatial distribution of Pb when PZT or Pb target was irradiated by an excimer laser beam under various conditions. Under vacuum condition and with the substrate at room temperature, the resputtering effect gives rise to a dip in the Pb content at the target surface normal position. The reduction of the resputtering effect with increasing ambient pressure is due mainly to the lowering of the kinetic energies of the ablated species by scattering with ambient gas molecules. In addition, PbO is formed at high ambient oxygen pressure. Under ambient oxygen and at high substrate temperature, oxide formation is the dominating process and helps to retain Pb on the substrate even at temperatures well above the melting point of Pb. The above results provide an explanation for the success in the preparation of stoichiometric multicomponent oxide films containing Pb (such as PZT, PLZT, and PT) by pulsed laser deposition under several hundred millitorr of ambient oxygen at elevated substrate temperature.

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