Evaluation of PZT Thin Films on Ag Coated Si Substrates

HONG-XUE ZHANG, PENTTI KARJALAINEN, ANTTI UUSIMÄKI,* and SEPPO LEPPÄVUORI*

Materials Engineering Laboratory, *Microelectronics and Material Physics Laboratory, University of Oulu, FIN-90570 Oulu, Finland

Fabrication characteristics of hybrid thin film components are investigated. Lead zirconate titanate (PZT) films, thickness 10 μm, are fabricated by using laser ablation on the Ag electrode (about 1 μm thick) which is deposited on 200 μm Si substrates by evaporation. Composition close to the target material is obtained in PZT films even in air and without substrate heating. Low surface energy in the Ag-Si system causes spheroidization of the Ag layer on the fresh Si substrate, but the surface can be modified by grinding and oxidization. Only some cavities exist at the interface. The interface between the Ag electrode and PZT layer is physically continuous, as revealed by electron microscopy. After annealing at 750°C for 2 h, the PZT layer consists of the rhombohedral perovskite phase with a fraction of the pyrochlore phase. Detrimental interdiffusion between Pb and Si occurs during annealing if the PZT thin film is directly on the Si substrate. This is retarded by the presence of the Ag layer.

Key words: Ag coated Si substrates, laser ablation, PZT piezoelectric films

INTRODUCTION

Lead zirconate titanate (PZT) is a well-known piezoelectric material which is widely used because of its excellent electromechanical properties.[1–7] In most applications, as for actuators, transducers, and sensors, in particular, the fabrication is in the form of thin films where high resolution and sensitivity coupled with compactness are essential. Conventional fabrication methods include sputtering,[8,9] chemical vapor deposition[10] and the chemical sol-gel process.[11] Among these, sputtering is the most frequently used because of its simplicity and convenience. However, deviation in the composition of films occurs from time to time, due especially to the evaporation of Pb. Even if an oxidizing atmosphere is used, the problem persists.[12–14] Furthermore, substrates have to be heated during deposition to obtain the desired crystalline structure.[15–18] This makes the sputtering procedure to depend, rather sensitively, on process parameters and the properties of the target materials.

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The laser ablation technique has been used for the fabrication of ferroelectric thin films only recently. The first report on laser ablation of PZT piezoelectric thin films was published by Otsubo et al.[19] in 1990. There it was stated that the compositional deviation in films could be avoided. This result has also been supported by Roy et al.[20] Even so, an oxidizing atmosphere or an elevated substrate temperature was employed in these studies.

Another important aspect concerning the application of piezoelectricity is the behavior of electrodes and substrates. Proper function of piezoelectric thin films depends largely on their properties, both physical and chemical. An example is the Si substrate on which the PZT film is deposited. As reported by Madsen et al.,[21] interdiffusion between the Si substrate and the PZT layer takes place during anneal-

Table I. Comparison of Compositions in Targets and As-Deposited PZT Films (at.%)

Elements	Target	As-Deposited Films
Pb	55	54
Ti	21	21
Zr	24	25

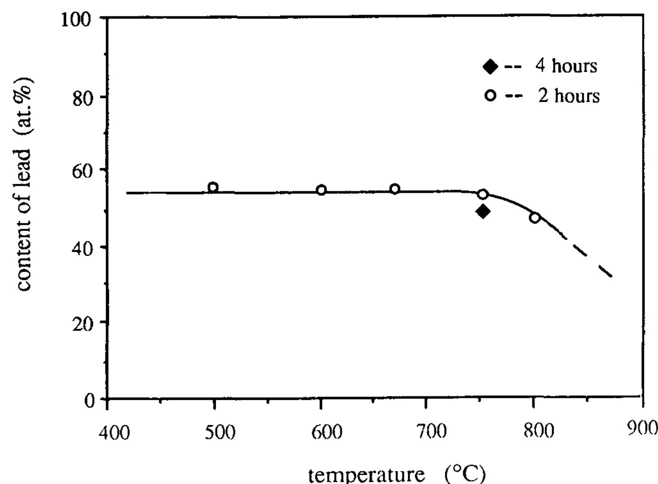

Fig. 1. Variation of composition in PZT films with annealing temperature.

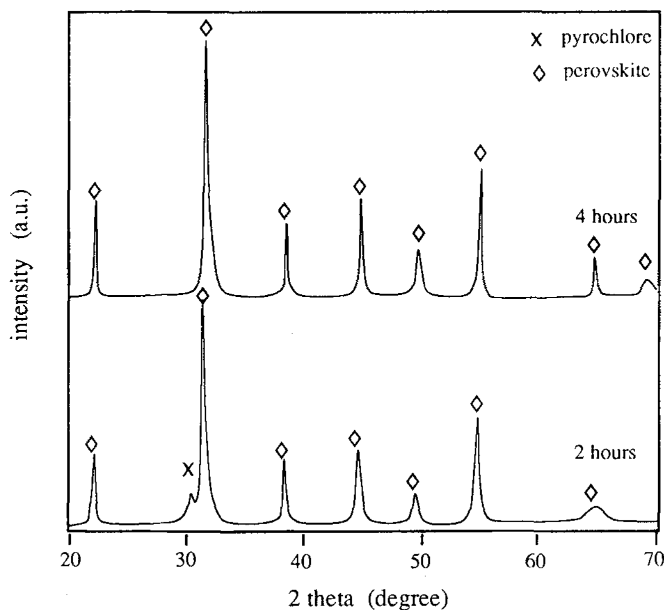

Fig. 2. X-ray diffraction spectra for the films annealed at 750°C for 2 and 4 h.

ing, which results in a Pb-rich SiO_2 at the interface and retardation of the formation of the perovskite structure. One way to solve this problem is the so-called direct bonding method, in which the active layers and electrodes are bonded together without any substrate.[22] Alternatively, the active layers can be annealed in advance and subsequently glued onto the substrate.[23] Both of these methods require that the active layers are thick enough for mechanical

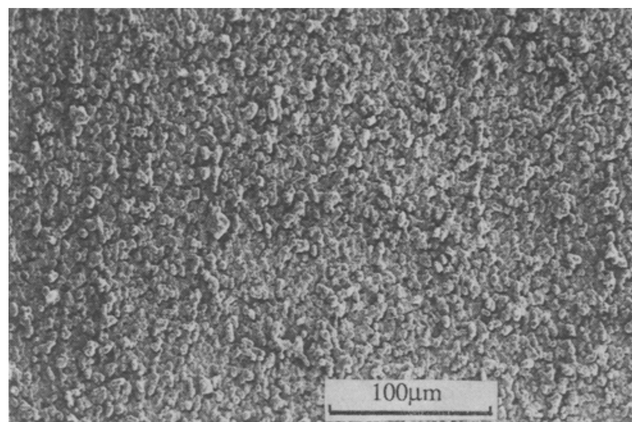

Fig. 3. Scanning electron micrograph of the film with Ag bottom electrode annealed at 750°C for 2 h.

handling so they are not suitable for thin films.

In a previous study, Zhang et al.[24] investigated the characteristics of PZT thin films on a sapphire substrate which were fabricated by laser ablation, and it was shown that the composition in the films was close to that of targets even on an unheated substrate. In this study, the deposition characteristics of PZT thin films in a non-oxidizing atmosphere on a Si substrate were examined. Simultaneously, the properties of a Si substrate coated with Ag electrodes and its effects on the crystalline structure of PZT films were investigated.

EXPERIMENTAL PROCEDURES

The starting material was the PZT ceramic powder fabricated by the mixed oxide route with the nominal composition $Pb(Zr_{0.52}Ti_{0.48})O_3$. An excess Pb was added to compensate for its loss during deposition and annealing. The target for laser ablation was made by cold-pressing the starting powder to a form of rod 10 mm dia and by sintering it at 900°C for 30 min to increase its mechanical strength. As substrate, Si slices 0.2 mm thick were cut into 5×15 mm^2 pieces. The bottom electrodes of Ag, 1 μm thick, were deposited on both sides of the substrate by evaporation. Subsequently, the PZT layers of 10 μm thickness were deposited by laser ablation using a Nd:YAG laser with a wavelength of 1064 nm and pulse fluence of 8 J/cm^2. Air at a pressure of about 5×10^{-3} Pa (5×10^{-5} mbar) was the working atmosphere in the chamber during the ablation process. The substrate was placed 30 mm from the target and was not heated. So the temperature was close to the ambient, although a slight temperature rise was likely due to ablation and deposition.

After deposition of the PZT active layers, the Ag top electrodes were deposited by evaporation. The fabricated elements were heated in an electric furnace up to 750°C and soaked for 2 to 4 h in air annealing atmosphere.

An x-ray diffractometer with the Cu-K_α radiation was used to investigate the crystalline structure of the films. Compositional analysis was carried out with the energy dispersive spectroscopy (EDS)

equipped with a scanning electron microscope (SEM, JSM-6400, Japan). Before measuring, the EDS system was calibrated with a standard Co specimen (accelerating voltage = 15 kV, beam current = 1.71 nA). Composition in the films was calculated by using the Link eXL-XAN 70 software system (Link Analytical Ltd., England). The accuracy of the analysis was evaluated to be 1 at.% and the spatial resolution about 1 μm. The topography of the layers on the surface and cross sections was also examined by SEM.

RESULTS AND DISCUSSION

Compositional Analysis of PZT Thin Films

As shown in Table I, the composition of the as-fabricated films is close to that of the target, except for the slightly lower Pb content. Considerable deviation in zirconium and titanium, which is often encountered in sputtering, was not found in the present experiments. This result is in agreement with those reported by Otsubo et al.[19] Accordingly, the absence of an oxidizing atmosphere did not affect the composition in films significantly. The slight deficiency of Pb that occurred in these experiments has also been observed in the laser ablation process with an oxidizing atmosphere, possibly originating from the decomposition of the target material during ablation.[22]

According to Otsubo et al.,[25] there exists two mechanisms of material ejection during laser ablation, explosive ejection and thermal evaporation. The former means that the target material is transferred in clusters of molecules. In the latter, the target material is evaporated, which is a process similar to the conventional thermal evaporation, and decomposition of the target material takes place. Which of these mechanisms dominate is dependent on the properties of the target material and the laser parameters employed. It can be concluded that in these experiments, the PZT was transferred from the target to the substrate predominantly by the explosive ejection mechanism. Thus, less decomposition occurred and the influence of the oxidizing atmosphere was weak.

The effect of annealing temperature on composition of films is shown in Fig. 1. As can be seen, the Pb content in the annealed films stayed constant when annealed below 750°C (soak time 2 h), even when annealed in air. Above this, the Pb content clearly decreased with increasing annealing temperature. This result showed that the evaporation of Pb was strongly temperature dependent. Following this, it was obvious that high substrate temperatures during the deposition stage were unfavorable for reproduc-

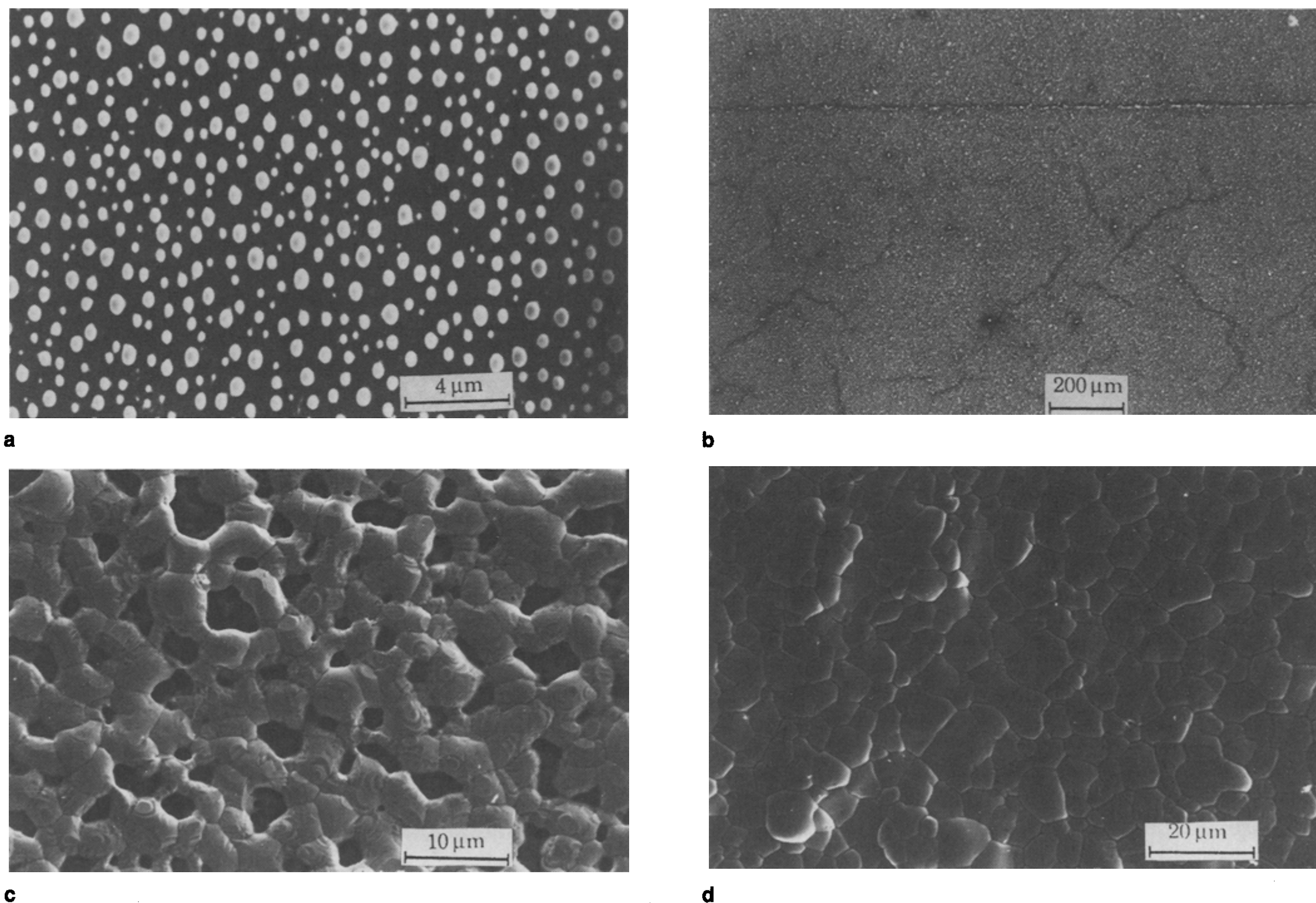

Fig. 4. (a) Ag layer on the Si substrate without surface treatments, annealed at 750°C for 2 h; (b) cracking caused by the spheroidization of the Ag layer during annealing at 750°C; (c) spheroidization of a Ag layer on the oxidized Si substrate during annealing at 750°C; and (d) Ag layer on the ground, oxidized Si substrate annealed at 750°C for 2 h.

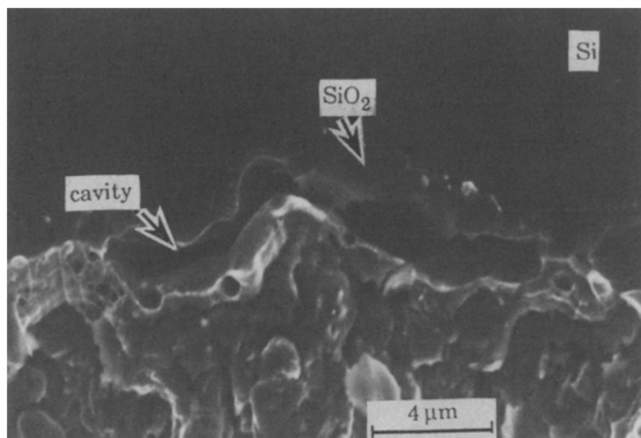

Fig. 5. Cross section of the element: PZT film/bottom Ag electrode/ground-oxidized substrate showing a perfect PZT/Ag interface and some cavities at the Ag/SiO_2 interface.

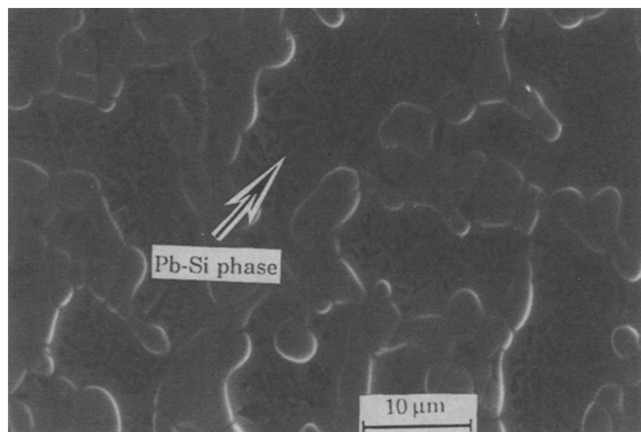

Fig. 6. PbO-SiO_2 compound formed at the PZT/SiO_2 interface during annealing.

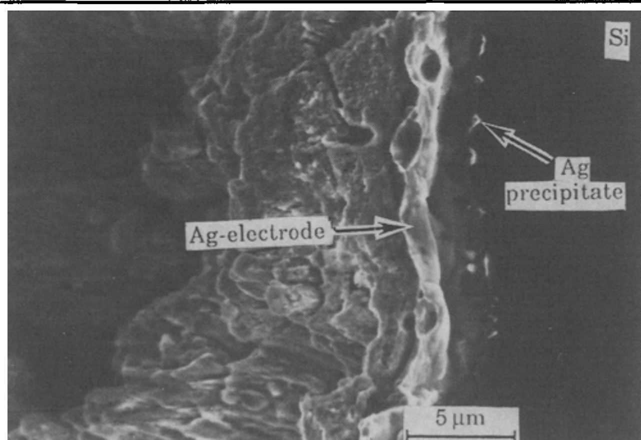

Fig. 7. Ag containing precipitates (white particles) at the SiO_2/Si interface indicating diffusion of Ag through oxide layer.

tion of the chemical composition. In particular, if the deposition is, as generally, carried out at reduced pressure, evaporation of Pb will increase.

Structure of PZT Thin Films

The as-fabricated films had an amorphous structure with the presence of microcrystallites. The x-ray diffraction investigation proved them to be the perovskite and pyrochlore phases. A similar result has been shown in previous paper.[24] The occurrence of microcrystalline perovskite is apparently related to the ejection mechanism and accordingly again supports the conclusion that the target material is transferred by the explosive mechanism during laser ablation. At higher annealing temperatures, the pyrochlore phase was converted to the perovskite structure gradually and the rhombohedral perovskite structure was obtained below 800°C even without Pb-rich atmospheres. This result is in good correspondence with the fact that the loss rate of Pb in films was lower below 750°C. The optimal annealing temperature was found to be between 700 and 800°C for a 2 h soak time, and a prolonged soak time was also favorable for the formation of perovskite (Fig. 2). Figure 3 is a surface SEM micrograph of the film annealed at 750°C for 2 h.

Modification of Interfaces

The first samples were fabricated using the following procedure. An Ag electrode layer with a thickness about 0.2 μm was deposited on the Si substrate by thermal evaporation. A 10 μm thick PZT layer was deposited on the Ag layer by laser ablation. Subsequently, the sample was annealed at 750°C for 2 h. After annealing, a top Ag electrode with a thickness of 0.2 μm was deposited by evaporation. The sample was subjected to an electric test which indicated an open circuit. Detailed inspection showed that the fault was related to the failure of the bottom Ag electrode. Figure 4a exhibits the post-annealing state of the Ag layer on the Si substrate. As can be seen, significant spheroidization of the Ag layer took place during the annealing. It apparently originated from the nonwettability of Ag on the Si substrate because of the low surface energy of Si. During spheroidization, the interface between Ag and PZT layers suffered significant distortion which was caused by the discontinuous shrinkage of the Ag layer and this induced internal stresses in the PZT layer. Its magnitude was higher than the strength of the thin film and this resulted in cracking problems (Fig. 4b).

In order to improve wettability and consequently the adhesion between the electrode and PZT layer, the Si substrate was subjected to the oxidizing treatment (wet oxidation with 500 mbar H_2O atmosphere, 1150°C for 2 h) before deposition of the Ag electrodes. However, the experimental results proved that oxidation was not effective in eliminating spheroidization. As shown in Fig. 4c, even if the thickness of the electrode was increased to more than 1 μm, spheroidization still took place and a net-like structure was formed during annealing. By trials, it was found that a procedure involving both mechanical grinding and oxidation improved surface wettability significantly. After that treatment, the Si substrate was completely wettable by Ag. As a result, the homogeneous, uniform Ag layer covered the Si substrate, as is shown in Fig. 4d.

The adhesion of individual layers was assessed by

SEM observations on cross sections. They gave the impression that the adhesion between the Ag layer and the PZT layer was superior to that between the Ag electrode and the Si substrate. In the former, a physically continuous interface was evident, which was believed to result from the diffusion of Ag across the Ag/PZT interface. But for the latter, a few local cavities existed in spite of the surface treatment (Fig. 5). These cavities were believed to have originated from contamination during the oxidation treatment. In the present experiment, the oxidation was carried out in a H_2O vapor atmosphere at a reaction temperature of about 1150°C. Finally, the Si substrate was cooled down and it was possible that some H_2O molecules may have remained in the surface layer. Those molecules could have been released from the oxide layer during annealing and trapped at the interface to form cavities.

Diffusion Across Interfaces and Interfacial Reactions

To further clarify the effects of the oxide layer, in some experiments the PZT was deposited directly on the oxidized Si substrate and the possible diffusion across the interface between SiO_2 and PZT was investigated. According to the EDS analysis, the interdiffusion of Si and Pb still took place during annealing, and a new phase was observed at the interface (Fig. 6). This phase consisted mainly of Pb and Si, and it is believed to be a PbO-SiO_2 compound.

This interdiffusion process was significantly modified by the presence of the Ag electrode layer. The EDS results showed that both the diffusion of Si to PZT and Pb to Si were suppressed and as a consequence there was no formation of the PbO-SiO_2 compound any more. This result firmly suggested that the Ag electrode layer had a denser structure and it could block the path of diffusion of Si and Pb. On the other hand, the diffusion of Ag into the SiO_2 layer was observed in these experiments, but it was seemly retarded at the Si/SiO_2 interface, as shown in Fig. 7. The significance of this result resides in its effect on cohesion strength. As well known, interface strength is an important factor in layered structures. The electrode layer acted not only as an electrical conductor, but also as an adhesive between the active layer and the substrate. Diffusion across the interfaces usually favors the establishment of strong adhesion, but it may also cause undesired effects, such as variation of crystalline structure in active layers or degradation of electrical properties. These detrimental effects can be reduced by restricting diffusion, i.e. constricting interdiffusion in a definite region. As shown in the present experiments, the oxide layer could be used for this restricted diffusion, because the diffusion of Ag was significantly limited in the oxide layer and diffusion depth was controlled by its thickness.

The restricted diffusion cannot apply to the Ag/PZT interface due to lack of an intermediate layer. In this case, the diffusion of Ag has to be controlled by annealing procedure. According to the present experiments, the films annealed at 950°C for 1 h showed that the diffusion of Ag extended to 3 μm with an average concentration of 4 at.%. For the films annealed at 750°C for 2 h, however, the diffusion of Ag into the PZT layer was not considerable (below the sensitivity limit of the EDS system). This result is in good correspondency with the earlier study, in which the measurements on the bimorph actuators showed that the effect of Ag diffusion was limited.[26] These results indicate that this diffusion was mainly controlled by annealing temperature.

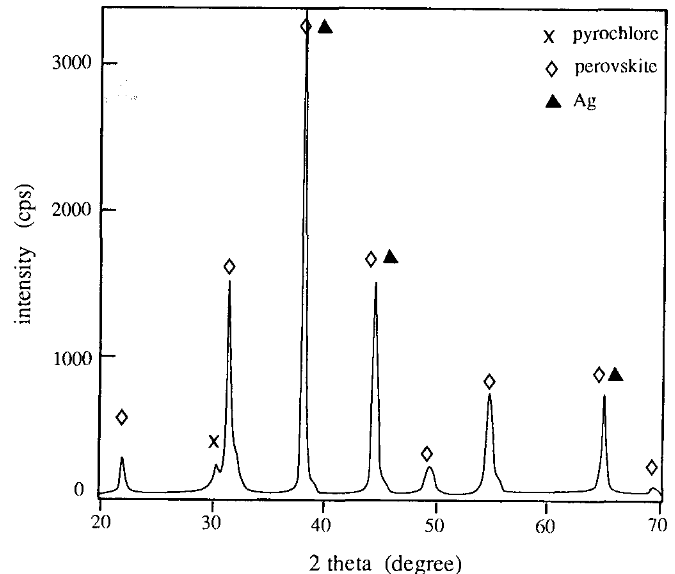

Fig. 8. X-ray diffraction spectrum for the film with both top and bottom Ag electrodes, annealed at 750°C for 2 h.

The PZT film with both top and bottom Ag electrodes was annealed at 750°C for 2 h. As can be seen in Fig. 8, the perovskite is the main phase in the film even though a small amount of the pyrochlore phase existed. When compared with Fig. 2, it is evident that the crystalline structure in the film with electrodes was the same as in the films without them. This result proves that a Ag electrode layer does not affect the crystalline structure of PZT films but that Ag diffusion can be considered as beneficial for interface strength.

CONCLUSIONS

Using laser ablation for deposition of PZT thin films, the composition close to that of the target could be obtained even without using an oxidizing atmosphere or heating the substrate. This supports the conclusion that the target material was transferred by the explosive ejection mechanism.

The evaporation of Pb during subsequent annealing depended strongly on temperature, but the rate was relatively low up to 750°C even in air atmosphere.

The wettability and adhesion of the Ag electrode, deposited by evaporation, onto the Si substrate could be improved by grinding and oxidizing the substrate surface. The detrimental diffusion of Si into the PZT layer, preventing the formation of perovskite struc-

ture, was retarded by the presence of the Ag electrode layer. The crystalline structure of the PZT layers was not affected by the existence of the Ag electrode layers.

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