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Formation of a silicate layer between lead oxide and a silicon-wafer surface during heat treatment

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PbO thin films were deposited on a silicon substrate by plasma-enhanced chemical vapour deposition (PECVD) using $Pb(C_2H_5)_4$ and oxygen at 250 °C. The interdiffusion reaction phenomena between the PbO thin film and the silicon substrate during heat treatments were investigated in a horizontal furnace in the temperature range between 350 and 650 °C under a nitrogen ambient for 1 h. The PECVD PbO film deposited on the silicon substrate at 250 °C, was amorphous and contained carbon-related contaminants which could almost be removed by heat treatment at 350 °C. The PbO on the silicon substrate initially participated in the interdiffusion reaction in the temperature range between 400 and 450 °C. This produced a silicate layer containing lead components. The lead content in the film varied with the depth of film and heat-treatment temperature. Metallic lead was observed as a cluster in the specimen heated at 550 °C. This cluster was produced by the agglomeration of metallic lead originating from PbO decomposition. The oxygen source for silicate formation was not ambient oxygen coming from the decomposition of Pb–O bonding. The metallic lead clusters dissolved as weakly bound metallic lead or as an unbound nanosized metal particle in the silicate layer at 650 °C.

1. Introduction

Lead-based ferrroelectric oxides, such as $PbTiO_3$, $Pb(Zr,Ti)O_3$ (PZT) and (Pb, La) $(Zr,Ti)O_3$ (PLZT), have been studied extensively in terms of their electronic applications. Lead oxide, as a major component of ferroelectric materials, has a high volatility at relatively low temperature [1]. Reliable fabrication of stoichiometric ferroelectric thin films such as $PbTiO_3$ is difficult owing to the high volatility of PbO in comparison with that of TiO_2. The stoichiometric control of $PbTiO_3$ thin films is very important, because the crystal structure of $PbTiO_3$ thin film is changed from the pyrochlore to the perovskite, and subsequently to the PbO phase with increasing Pb/Ti atomic ratio [2].

Generally, excess PbO in lead-based ferroelectric materials should be required to control the precise stoichiometry of the desired ferroelectric materials. However, the amount of excess PbO required should be varied with the type of substrate and the processing temperature [3, 4]. It was found that no excess lead was needed for films to form perovskite PZT on a sapphire substrate. This might be partially attributed to the absence of any interdiffusion of lead in the film with a sapphire substrate. Also, only a slight excess of lead was required in the case of platinum-coated silicon substrates to induce the perovskite phase. However, a large amount of excess lead was needed to produce the perovskite phase on a silicon substrate involving deposition and annealing processes. This result could be explained by the high reactivity of silicon substrates with lead.

The layer formed by the interfacial reaction is known to be a silicate containing a lead component [5, 6]. Such a silicate layer should reduce the applicability of ferroelectrics on silicon substrates in silicon microelectronics technology. Therefore, it is necessary to understand the interdiffusion reaction phenomena between lead oxide and a silicon substrate to avoid or decrease silicate formation; however, no previous studies on the behaviour of the interdiffusion reaction at the PbO/Si interface have been reported.

In this study, PbO thin films were deposited on a silicon wafer by plasma-enhanced chemical vapour deposition (PECVD) using tetraethyl lead and oxygen. To evaluate the interdiffusion reaction phenomena between PECVD PbO and a silicon substrate, heat treatments were performed in the temperature range between 350 and 650 °C under a nitrogen ambient for 1 h. The heat-treated specimens were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform–infrared spectroscopy

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(FT–IR) and X-ray photoelectron spectroscopy (XPS) in order to understand the interdiffusion reaction.

2. Experimental procedure

The PbO films on the silicon substrates were deposited by PECVD using $Pb(C_2H_5)_4$ (TEL, 99.999% purity) and oxygen. The PECVD apparatus consisted of a source delivery system with the bubbler of TEL, a vacuum system and a cold-wall reaction chamber equipped with parallel electrodes. The TEL bubbler was heated to 21 °C and the TEL vapour was carried by 99.999% pure argon. TEL vapour and oxygen were mixed before flowing into the reaction chamber. Gas mixtures were distributed through the upper-electrode via a shower head structure. An r.f. power of 20 W at 13.56 MHz was delivered to the upper electrode. The chamber pressure was 300 mtorr and the substrate temperature was fixed at 250°C. The flow rate of carrier gas was 80 standard $cm^3 min^{-1}$ and the oxygen flow rate was 8 standard $cm^3 min^{-1}$. P-type silicon substrates, (1 0 0) oriented, 4–5 Ωcm, were cleaned in a hydrogen peroxide sulphuric acid mixture, dipped in hydrofluoric acid, rinsed in deionized water, and blown with nitrogen. The thickness of the as-deposited PECVD PbO film on the silicon substrate was about 300 nm, as measured by scanning electron microscopy.

To investigate the interdiffusion reaction between the PECVD PbO thin film and the silicon substrate, heat treatments were performed using a horizontal furnace in the temperature range between 350 and 650 °C under a nitrogen ambient for 1 h. The reason for using a nitrogen ambient instead of an oxygen ambient or air was to prevent the ambient oxygen from participating in the interface layer formation and interdiffusion reaction. The interdiffusion reaction between PbO and the silicon substrate after the heat treatments was analysed by X-ray diffraction (XRD, Rigaka, copper target, nickel filtered), scanning electron microscopy (SEM), Fourier transform–infrared spectroscopy (FT–IR, Bomem-102) and X-ray photoelectron spectroscopy (XPS, Leybold, LHS-10, MgK_α; XPS spectra was calibrated using the binding energy of Au(4f), 84.0 eV, as determined by the *in situ* analysis with gold dots on specimens.

3. Results and discussion

The chemical constituents of thin films deposited directly on a silicon substrate can be easily analysed by FT–IR analysis. Fig. 1 shows the infrared spectra of an as-deposited film and the heat-treated PECVD PbO thin films on a silicon substrate. In the case of as-deposited PbO film, only one absorption band at 1420 cm^{-1} is clearly discernible in the FT–IR spectra as shown in Fig. 1a. This band can be assigned to the carbonate ion as a contaminant which may be produced by the incomplete reaction of TEL with oxygen species in the plasma [7]. Upon heat treatment at 350 °C, this carbonate band disappeared. The extent of the interdiffusion reaction between the PbO and the silicon substrate could be monitored from the infrared spectra as a function of treatment temperature. There were no noticeable absorption peaks in the infrared spectra of samples heated at 350 and 400 °C. This indicates that the carbonate ions could be decomposed in the PECVD PbO thin film and there was no significant interdiffusion reaction between the PbO and the silicon substrate below 400 °C. However, a broad infrared peak at 916 cm^{-1} appeared after heat treatment at 450 °C. This peak might be assigned to the stretching bond of Pb–O–Si generated by the initial reaction at the interface between the PbO and the silicon substrate. After heat treatment at 550 °C, the peaks at 466, 950, 1002 and 1121 cm^{-1} appeared. These peaks are consistent with the infrared spectrum typical of SiO_2. Hence, these peaks could be assigned to that of silicate containing lead. After heat treatment at 650 °C, the intensities of these bands increased and the locations of the peaks were shifted to higher energy in comparison to those of bands after heat treatment at 550 °C, indicating the consolidation of the silicate layer. From these results, it can be concluded that a silicate layer containing lead was the main product of the interdiffusion reaction between the PbO and the silicon substrate and that the initiation temperature for the inter-diffusion reaction was between 400 and 450 °C.

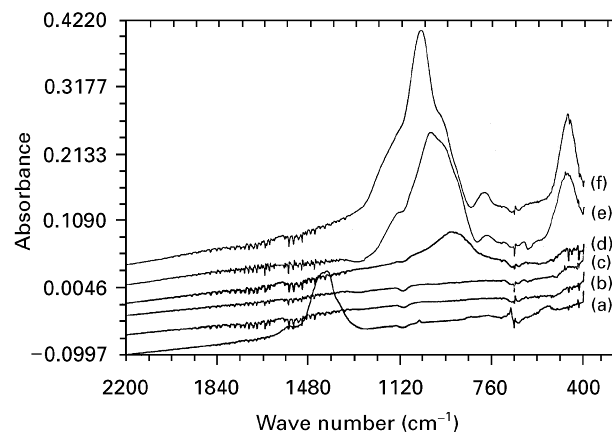

Figure 1 FT–IR spectra of PECVD PbO thin films on a silicon substrates heated at various temperatures under a nitrogen ambient for 1 h; (a) as-deposited, (b) 350 °C (c) 400 °C (d) 450 °C (e) 500 °C (f) 550 °C (g) 600 °C and (h) 650 °C.

The phase structure of the heat-treated PbO thin film on the silicon substrate was determined from the XRD patterns as shown in Fig. 2. The specimen heated at 450 °C showed diffraction peaks of polycrystalline PbO at $2\theta = 28.69°$, $31.85°$, $35.87°$ and $46.04°$ associated with the (1 0 1), (1 1 0), (1 0 2) and (2 0 0) directions, respectively [8]. In contrast the peaks related to the metallic lead at $2\theta = 31.21°$ and $36.34°$ appeared in the XRD pattern of the specimen after heat treatment at 550 °C [9]. The broad peaks from an amorphous silicate phase were also observed at $2\theta = 10°–15°$ and $24°–30°$. Hwang and Kim reported the formation of metallic lead during the PZT deposition process on a silicon substrate using metallorganic chemical vapour deposition [10]. Two reasons for the segregation of lead at the lead silicate/silicon interface were proposed. One was that lead has a

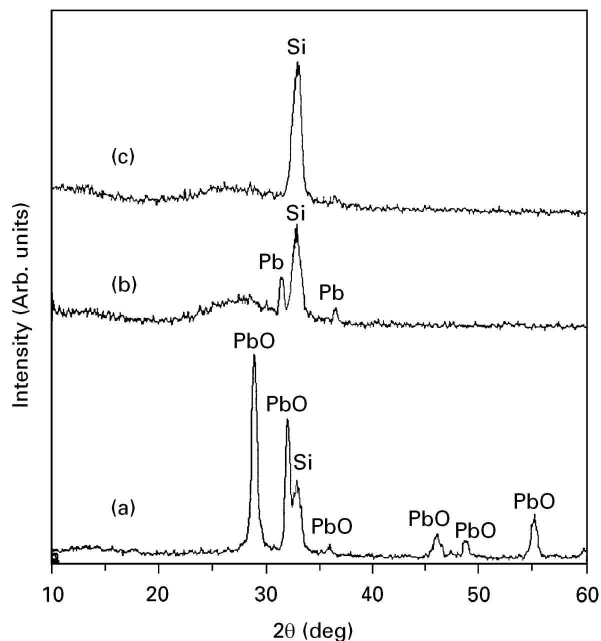

Figure 2 X-ray diffraction patterns of PECVD PbO thin films on a silicon substrate heated at various temperatures under a nitrogen ambient for 1 h; (a) 450 °C, (b) 550 °C and (c) 650 °C. The diffraction peak typical of the Si (1 0 0) substrate is shown.

larger diffusion coefficient than oxygen in the lead silicate layer. The other is that activity of lead might be increased in the deposited layer containing zirconium. However, they could not observe lead segregation in the case of $PbTiO_3$ thin film. After heat treatment at 650 °C, only the amorphous phase was detected, as shown in Fig. 2c.

From these results, it can be seen that PECVD PbO formed a polycrystalline structure at 450 °C. At 550 °C, PbO was partially decomposed to metallic lead and active oxygen ions and metallic lead might be agglomerated to clusters. The active oxygen ions then reacted with the silicon substrate to form an amorphous silicate layer. Hence, metallic lead clusters, PbO solid solutions and the silicate-containing lead elements coexisted in the specimen at 550 °C. During the heat treatment at 650 °C, metallic lead clusters diffuse into the silicate layer, resulting in the enrichment of lead in the silicate layer around the former sites of the clusters. Normal silicon oxidation cannot produce a silicate layer thicker than 10 nm at 650 °C under a nitrogen ambient for 1 h. It seems that the abnormally rapid growth of the silicate layer might be due to the high reactivity of the active oxygen ions generated by the decomposition of PbO.

The heat-treated specimens were dipped into acetic acid, in which only the uncombined PbO was soluble [11]. Fig. 3 shows the surface morphologies of these specimens. A specimen processed at 450 °C was fully stripped and some particles which did not contain a lead component remained on the surface, as shown in Fig. 3a. There was no significant reaction in the interface region. The surface morphology of a specimen processed at 550 °C showed both a smooth surface and holes, as shown in Fig. 3b. The smooth surface, without grain boundaries, suggested that the polycrystalline PbO was changed into another

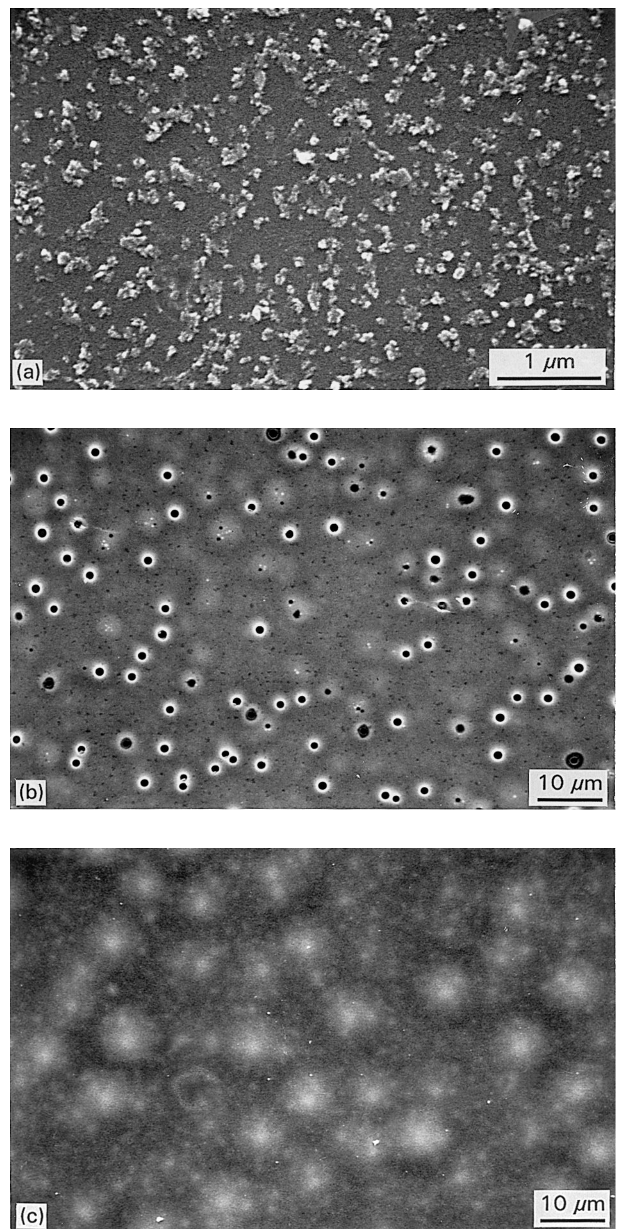

Figure 3 Surface morphologies of PbO thin films on a silicon substrate heated at various temperatures under a nitrogen ambient for 1 h (a) 450 °C, (b) 550 °C and (c) 650 °C. After heat treatment, each specimen was dipped into acetic acid to remove uncombined PbO.

amorphous layer identified as the silicate. The open holes might be the sites of metallic lead clusters, as predicted from Fig. 2b. The surface morphology of the specimen at 650 °C showed a smooth surface without holes. The smooth surface was divided into relatively white or relatively black sites. The white sites might be generated by the diffusion of metallic lead clusters during the rise in temperature from 550 °C to 650 °C. This is in agreement with the results of Fig. 2.

Cross-sectional views of the heat-treated specimens without surface etching are shown in Fig. 4. As the treatment temperature was increased from 450 °C to 650 °C, the thickness of the upper layer was increased from 330 nm to 460 nm. The cross-sectional view of a specimen treated at 450 °C shows a PbO layer of granular shape and a very thin layer at the interface between PbO and the silicon substrate. The thin interface layer was determined to be silicate-like from the

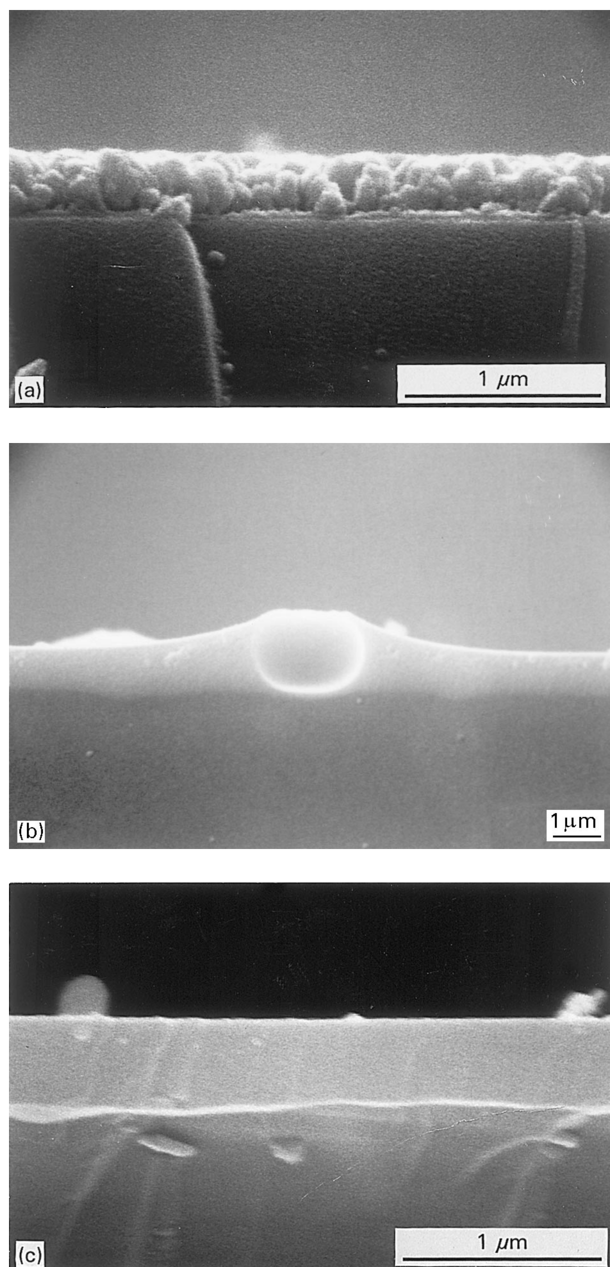

Figure 4 Cross-sectional SEM views of PECVD PbO thin films on a silicon substrate treated at (a) 450 °C, (b) 550 °C and (c) 650 °C under a nitrogen ambient for 1 h.

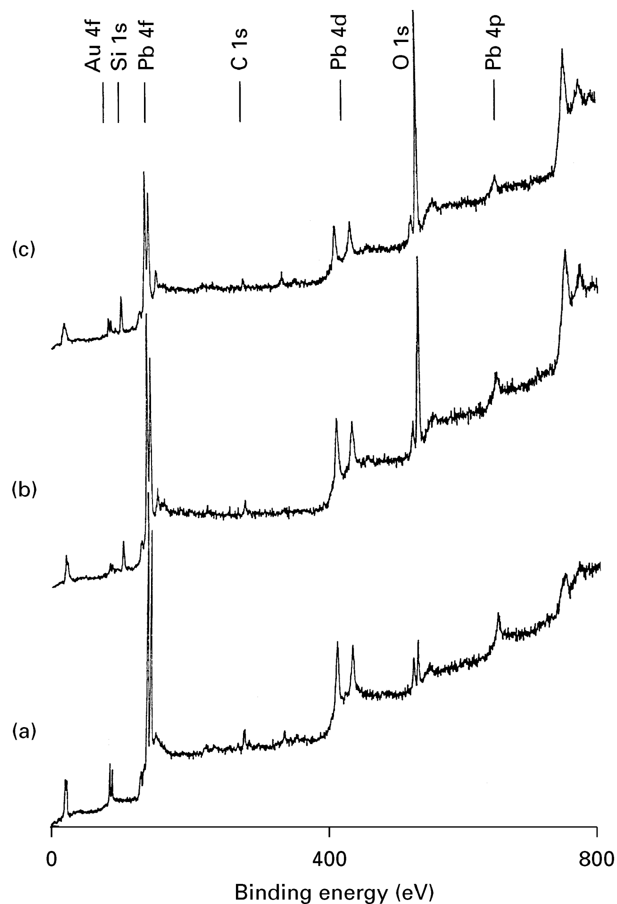

Figure 5 XPS spectra of PECVD PbO thin films on a silicon substrate treated at 450 °C, (b) 550 °C and (c) 650 °C under a nitrogen ambient for 1 h. The binding energy of Au(4f) was taken as reference.

results shown in Fig. 1d. The view of the specimen heated at 550 °C apparently showed a homogeneous amorphous layer and the open holes which were previously occupied by metallic lead clusters. The specimen heated at 650 °C had an amorphous layer without any traces of metallic lead clusters.

Preliminary XPS spectra of the heat-treated PbO thin films on the silicon substrate are shown in Fig. 5. The XPS spectra were obtained after argon ion sputtering with the ion energy of 3 keV for 1 h. As the treatment temperature increased, the relative amount of lead on the surfaces of the film decreased and that of oxygen increased. The XPS spectra of the specimen heated at 450 °C did not show any silicon-related peaks, because the PbO thin film covered the silicon substrate. However, the spectra of the specimens heated at 550 and 650 °C showed the silicon-related peak which was also observed in the spectra of as-received samples, indicating that the formation of silicate occurred on the outermost surface of the film.

A complementary approach to monitor the chemical transformation of the heat-treated specimens was provided by XPS. Fig. 6 shows a set of representative photoemission-spectra of the specimens heated at 450, 550 and 650 °C where the Pb(4f) binding energies were monitored. The conditions of specimens before obtaining the photoelectron spectra were as follows: the specimen heat treated at 450 °C (a) as-received, (b) argon-ion sputtered for 1 h; the specimen heated at 550 °C, (c) as-received, (d) argon-ion sputtered for 10 min, (e) for 1 h; the specimen heated at 650 °C, (f) as-received, (g) argon-ion sputtered for 10 min, (h) for 1 h. Fig. 6a and b show two Pb(4f) peaks at 138.6 and 143.5 eV, respectively, assigned to the PbO phase. The specimen heated at 550 °C has two kinds of doublet representing the oxidized and the metallic lead state for which the relative sizes of these peaks varied with the depth of film (increasing sputtering time) as shown in Fig. 6c–e. This result indicates that the decomposition of PbO occurred readily at the interface due to the reaction of active oxygen ions with silicon. The peaks of metallic lead were located at the lower binding energies of 136.6 and 141.5 eV by deconvolution and curve-fitting. The existence of metallic lead as clusters was confirmed by the XRD analysis and SEM result as shown in Figs 2 and 3. Desu and Kwok have reported that the ionic bombardment during etching

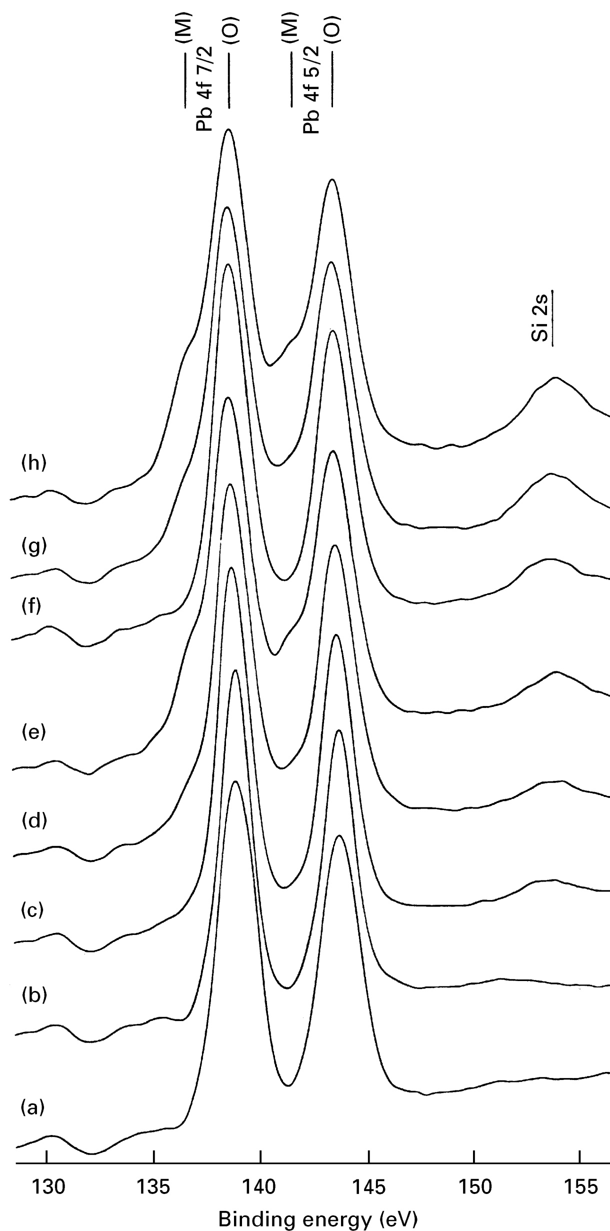

Figure 6 XPS spectra corresponding to the Pb(4f) peaks of PECVD PbO thin films on a silicon substrate treated at 450 °C, (b) 550 °C and (c) 650 °C under a nitrogen ambient for 1 h. The conditions of the specimens before obtaining photoelectron spectra were as follows: the specimen at 450 °C, (a) as-received, (b) argon-ion sputtered for 1 h; the specimen at 550 °C, (c) as-received, (d) argon-ion sputtered for 10 min, (e) for 1 h; the specimen at 650 °C, (f) as-received, (g) argon-ion sputtered for 10 min, (h) for 1 h. The peak of Si(2s) is also shown.

yielded the reduction of Pb^{2+} to metallic lead as evidenced in the XPS spectra of a PZT film before and after ion etching [12]. However, in the PbO film on a silicon substrate, the reduction of Pb^{2+} was not observed, as shown in Fig. 6b obtained after argon-ion sputtering for 1 h. In the specimen treated at 650 °C, the XPS spectra show the same trend as that of a specimen heated at 550 °C. This indicates that metallic lead components produced from PbO decomposition in the specimen heated at 650 °C exist as a metal phase dispersed in a silicate layer which could not be detected by the XRD analysis.

Fig. 7a and b show the infrared spectra of a PECVD $PbTiO_3$ thin film on a silicon substrate treated at 650 °C for 1 h under oxygen and nitrogen ambients,

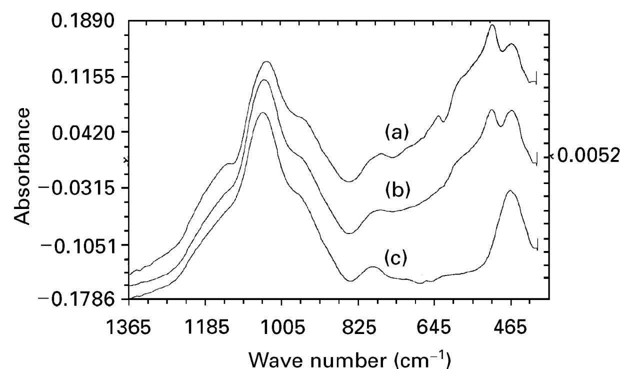

Figure 7 FT–IR spectra of PECVD $PbTiO_3$ thin films on a silicon substrate treated at 650 °C for 1 h under (a) an oxygen ambient and (b) a nitrogen ambient, and (c) that of PECVD PbO thin film on a silicon substrate treated at 650 °C for 1 h under a nitrogen ambient.

respectively. The peaks at 506 and 590 cm^{-1} could be assigned to the titanium octahedral coordinated in $PbTiO_3$. The other peaks could be assigned to the silicate. There was no difference between these two spectra, indicating that oxygen species participating in silicate formation might be supplied from the active oxygen ions coming from the decomposition of PbO instead of ambient oxygen. This could be confirmed by comparison with the infrared spectrum of PbO annealed under a nitrogen ambient, as shown in Fig. 7c, hence we conclude that PbO and $PbTiO_3$ follow almost the same pathway in the reaction with the silicon substrate during the thermal treatment.

Thus PECVD PbO deposited at 250 °C on a silicon substrate was amorphous and contained carbon-related contaminants. When the treatment temperature was 400 °C, this amorphous PbO film changed to the expected polycyrstalline phase without a significant interdiffusion reaction with the silicon substrate and the carbon-related contaminants were almost decomposed. The polycrystalline PbO on the silicon substrate participated initially in the interdiffusion reaction in the temperature range 400–450 °C. A rapid interdiffusion reaction between the PbO and the silicon substrate occurred over the temperature range 450–550 °C. The sequence of the interdiffusion reaction can be proposed as follows: (1) decomposition of the PbO into metallic lead and an active oxygen ion, (2) the diffusion of oxygen ions and metal lead into the silicon substrate with the formation of silicate-containing metallic lead, (3) metallic lead aggregated as clusters which were detected by XRD or SEM. The oxygen source for silicate formation was not ambient oxygen, but the active oxygen ions coming from the decomposition of the Pb–O system. Metallic lead clusters dissolved into the silicate layer, sequentially formed as weakly bound metal lead or unbound nanosized metal particles at the high temperature of 650 °C. The decomposition of Pb–O bonds might also be simultaneously on-going at 650 °C.

4. Conclusion

A comprehensive description of the sequence of the interdiffusion reaction occurring during the heat treatment of PECVD PbO thin films on a silicon substrate

has been provided. The interfacial layer was formed initially by the interdiffusion reaction between the PbO and the silicon substrate at the temperature range between 400 and 450 °C as the silicate layer containing lead elements. The silicate was amorphous. The lead content in the film varied with the depth of film and the heat-treatment temperature. Metallic lead was observed in the form of clusters in the specimen heated at 550 °C. These arose from the agglomeration of metallic lead originating from PbO decomposition. At 650 °C, the metallic lead clusters diffused into the silicate layer to form smaller-sized metallic lead particles which could not be detected by XRD but were detected by XPS. The major source of oxygen for silicate formation was the active oxygen ions coming from the decomposition of PbO.

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