Chapter 6

Delamination Phenomena

This section discusses delamination phenomena of ferroelectric capacitors, as a function of hydrogen-induced degradation. The data will be published in the Japanese Journal of Applied Physics under the title "*Delamination Behavior of Pt in SiO_2/Pt/Pb(Zr_xTi_{1-x})O_3/Pt Ferroelectric Thin Film Capacitor*". The authors are Youngsoo Park, June Key Lee, Ilsub Chung, and Jai-Young Lee

ABSTRACT

Silicon dioxide was deposited on a Pt/Pb(Zr_xTi_{1-x})O_3/Pt capacitor by plasma-enhanced chemical vapor deposition (PECVD) method. We then investigated the mechanism of blister formation on the resulting PECVD SiO_2/Pt/PZT/Pt capacitor. The blisters were observed at a temperature of 325 ^oC in an O_2 atmosphere, while in a N_2 or an Ar atmosphere blisters were not produced even at 500 ^oC. Hydrogen evolution analysis from the PECVD SiO_2 layer showed a sharp peak near 320 ^oC. The results indicate that the accumulation of water vapor pressure, developed via a chemical reaction between oxygen and hydrogen could be the dominant mechanism for blister formation in the capacitors.

§1. INTRODUCTION

Recently, lead zirconium titanate (PZT) has been extensively investigated in terms of its applications in ferroelectric random access memory (FRAM). Although the PZT thin film has many desirable properties in terms of high remnant polarization (P_r) and low coercive voltage (V_c), several problems remain, which hinder the full integration of a PZT film into microelectronic devices. One of the problems is the degradation of ferroelectric properties in a reducing ambient. Under conventional CMOS processes using a hydrogen atmosphere, the degradation of PZT capacitors would be characterized by a decrease in P_r, a shift in V_c, and an increase in leakage current density [1-3]. The typical reducing ambient which would typically be encountered during the integration process would be the deposition of SiO_2 film for the interlayer dielectric (ILD) and the intermetallic dielectric (IMD) [4]. Since SiO_2 films are deposited using source gases that have hydrogen related bonds such as SiH_4 or TEOS ($Si[OC_2H_5]_4$), the atomic hydrogen from the source gases degrades PZT capacitors during the deposition of the SiO_2 film. In order to recover the electrical properties of hydrogen-damaged capacitors, an annealing process has been attempted in an oxygen atmosphere over the temperature of 450 ^oC [5,6]. However, the problem here is that the characteristic morphology of blisters are observed in PECVD SiO_2/Pt/PZT/Pt layered structure after the recovery annealing in an O_2 atmosphere.

In the present study, the blister formation of SiO_2 deposited PZT capacitors was investigated in terms of annealing atmosphere. We also deposited a sputter SiO_2 film on a PZT capacitor and the characteristic morphology of the annealed capacitor was investigated. Fourier transform infrared (FTIR) spectra have been used to examine Si-H or Si-OH impurities for both PECVD and sputter SiO_2 films. We describe herein the mechanism of blister formation with respect to the chemical reaction between atomic hydrogen from PECVD SiO_2 and oxygen atoms from the annealing atmosphere.

§2. EXPERIMENTAL PROCEDURE

We sequentially deposited Pt/TiO_2 (270/50 nm) on thermally grown SiO_2 (200 nm)/Si substrate using DC magnetron sputtering. $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin films of 250 nm were prepared by the sol-gel method. The sol-gel solutions for PZT film were deposited via spin coating at 2500 rpm for 35 sec onto the substrate. After drying at 200 , the films were crystallized at 650 ^oC for 30 min in oxygen atmosphere to form the PZT perovskite phase. The top Pt electrode of 150 nm was then deposited by DC magnetron sputtering method. The photoresist film was patterned with a size of 100x100 μm^2, and then top Pt and PZT film were etched by means of inductively coupled plasma (ICP) etcher. Finally, well-defined top Pt electrode and PZT film was formed on the exposed bottom Pt electrode. In addition, a recovery process was performed in the conditions of 550 ^oC for 15 min in an oxygen atmosphere to allow for the recovery from the etching damage. The SiO_2 film (100 nm) was deposited on the electrodes of Pt/PZT/Pt structure by rf-PECVD or sputter method. PECVD SiO_2 was deposited using a source gases of SiH_4 and N_2O at a temperature of 200 ^oC, total pressure of 400 mTorr and rf-power of 20 W. The schematic drawing of the test structure is shown in figure 6-1. After the deposition of SiO_2, the resulting SiO_2/Pt/PZT/Pt structured capacitors were annealed in different atmospheres of O_2, N_2 and Ar for 15 min.

Infrared absorption spectroscopy was used to characterize the bonding nature of the SiO_2 film over the spectral range of 700 to 1400 cm^{-1}. In order to investigate the behavior of hydrogen in the SiO_2 film, a hydrogen evolution measurement was performed using modified gas chromatography (GC, Hewlett Packard 5890 II) [7]. The as-deposited SiO_2 film was heated in a reactor of a constant heating rate of 10 K min^{-1}, and high purity Ar gas (99.999%) was used to carry the evolved hydrogen gas into the GC apparatus. The evolved hydrogen was detected by the thermal conductivity detector (TCD). Temperature-stress hysteresis of SiO_2 film was measured by a Flexus stress measurement system.

§3. RESULTS AND DISCUSSION

PECVD SiO_2 films of 100 nm are deposited on the PZT capacitors with different

SiH_4 flow rates. Figure 6-2 illustrates the optical micrographs of the PECVD SiO_2/Pt/PZT/Pt capacitors that were annealed at two different temperatures of 250 ^oC and 325 ^oC in oxygen atmosphere. As shown in figure 6-2, PZT capacitors which were annealed at 250 ^oC exhibit a smooth and featureless surface. Increasing the annealing temperature to 325 ^oC leads to dramatic changes in the surface image. Numerous blisters are observed on the area of top electrodes with the structure of SiO_2/Pt/PZT/Pt/TiO_2/Si. However, the bottom electrode with the structure of SiO_2/Pt/TiO_2/Si retains its smooth morphology with no obvious blister, even at 325 ^oC.

We also annealed the capacitors in N_2 and Ar atmosphere over 300 ^oC, and the optical micrographs of capacitors annealed at 500 ^oC are represented in figure 6-3. In contrast to the annealing in O_2 atmosphere, the surface exhibits clear and a featureless morphology even at temperature of 500 ^oC.

In order to compare blister formation with different types of oxide layers, a sputter oxide was deposited on the PZT capacitor. We annealed the capacitors of sputter SiO_2/Pt/PZT/Pt structure in an O_2 atmosphere at different annealing temperatures. Figure 6-4 shows the optical micrographs of sputter SiO_2/Pt/PZT/Pt capacitor annealed at 500 ^oC. Comparing figure 6-4 with figure 6-2, it is clear that different surface images of the annealed PZT capacitor occur with different types of oxide films. For the case of the PZT capacitor with sputtered SiO_2, the top electrode exhibits smooth morphology with no blisters even at a higher annealing temperature of 500 ^oC. From the above results, it is clear that the blister formation of PZT capacitor with a SiO_2 layer is closely related to annealing temperature, annealing atmosphere, and the types of SiO_2 layers.

The characteristic morphology of blisters in the PECVD SiO_2/Pt/PZT/Pt structure is shown in figure 6-5. Cross-sectional SEM micrograph of blister in figure 6-5(b) shows clearly that the top Pt film has delaminated from the PZT. Thus, the blister is thought to be developed by delaminating and expanding the Pt film as a hollow dome as shown in figure 6-5.

In order to investigate the reason for the different behavior in blister formation between the sputter and PECVD SiO_2 films, we examined the stress-temperature behaviors for two SiO_2 films on Si wafers, which is shown in figure 6-6. The PECVD SiO_2 film was deposited with SiH_4 at a flow rate of 4 sccm. It can be seen that the stress-temperature behavior of the PECVD SiO_2 is very similar to that of the sputter SiO_2. The initial stress for both SiO_2 films is compressive. During the thermal cycle of heating and cooling, a hysteresis is observed, with the final stress being more tensile. When the film is under severe stress, the system tends to release stress through peeling or crazing in the case of tensile stress, and blistering or wrinkling in the case of compressive stress. Therefore, it is possible to predict the sign of stress by observing the characteristic failure mode. As shown in figure 6-6, however, PECVD SiO_2 exhibits tensile stress during and after thermal cycle. The blistering morphology in the PECVD SiO_2/Pt/PZT/Pt capacitor is not the characteristic failure mode under the tensile stress. Furthermore, since the stacked layer of capacitor would be expected to follow the similar stress-temperature behavior irrespective of annealing atmosphere, it is difficult to explain the reason for why stress causes the capacitors to result in different behavior of blister formation with the nature of the annealing atmosphere. Thus, the stress does not seem to be a main factor in inducing blisters on PECVD oxide deposited PZT capacitors.

The important difference between sputter and PECVD SiO_2 is the existence of hydrogen impurities in SiO_2 films. Since PECVD SiO_2 films are deposited using SiH_4, hydrogen related bonds of Si-H and Si-OH are incorporated into the deposited SiO_2 film. However, sputter oxide, which is deposited using a quartz target, contains no hydrogen-related bonds in the deposited SiO_2. Figure 6-7 shows the IR absorption spectrum of a PECVD SiO_2 film. The IR spectrum displays absorption peaks near 3400, 3670 cm^{-1} which correspond to Si-OH groups and near 875, 2270 cm^{-1}, corresponding to Si-H groups, which represents a significant incorporation of hydrogen impurities in the PECVD SiO_2 film [8,9].

Hydrogen evolution from the PECVD SiO_2 is monitored as shown in figure 6-8. Hydrogen desorption begins above 200 ^oC and peaks at around 320 ^oC. This peak temperature for hydrogen desorption is consistent with the blister formation temperature as represented in figure 6-2. Thus, the evolution of hydrogen from PECVD SiO_2 is likely to be responsible for the blister formation of PZT capacitors with PECVD SiO_2.

Although the PECVD SiO_2 deposited PZT capacitors are annealed above 325 , the blisters are not formed in an N_2 or Ar atmosphere as shown in figure 6-3. Blisters are only observed after annealing at temperatures in excess of 325 ^oC in an O_2 atmosphere. Based on these results, we can suggest the following mechanism for blister formation in the PECVD SiO_2 deposited PZT capacitors. The hydrogen from the PECVD SiO_2 diffuses out of SiO_2 layer or diffuses into the Pt top electrode. In the O_2 atmosphere used in the annealing procedure, the oxygen diffuses into the PECVD SiO_2 and Pt film. This leads to a reaction between hydrogen and oxygen atoms at the interface of the stacked layers in the capacitor. At over 325 ^oC, the burst of hydrogen would greatly enhance the chemical reaction, which could lead to a high pressure of water vapor in the stacked layer of the PZT capacitor. In extreme pressure conditions, the delamination of the layer would occur at the interface of the poor adhesion, which would be manifested in the form of blisters as in figure 6- 5(b). From the cross-sectional SEM micrograph of a blister in figure 6-5(b), it can be seen that the adhesion strength between the top Pt and the PZT layer is not sufficient to endure the local stress developed by the pressure of the water vapor. In comparing the blister formation behavior between the area of top and bottom electrode, it can be seen that the blister is only observed in the area of top electrode (figure 6-2). In contrast to the top Pt electrode where Pt directly adheres to the PZT layer, the bottom Pt electrode uses Ti adhesion layer on the thermally grown SiO_2. Thus, the adhesion layer of Ti protects the bottom Pt from delamination. This is the reason for why the blisters are not observed in the bottom electrode area of annealed capacitors with PECVD SiO_2 film.

We exposed the sputter oxide to humid atmosphere to confirm the hypothesis that the hydrogen related bonds in SiO_2 are responsible for blister formation in the PZT capacitors. Since SiO_2 film absorbs water molecules from the atmosphere, silanols (Si-OH) are generated through the reaction of water molecules to Si-O-Si bond in SiO_2 [10,11]. Because of the variation of bonding environments for the silanols, the hydroxyl (-OH) stretching band appears as a broad peak, and the broad absorption band between 3000 and 3700 cm^{-1} is known to be attributed to the loosely bonded Si-OH [12,13,14]. Figure 6-9 shows the IR absorption spectrum for the sputter oxide after exposure to a relative humidity of 85 % for 3 days. It can be seen that the broad absorption band centered at 3450 cm^{-1} develops after exposing the sputter oxide to the humid atmosphere.

In the same manner, we exposed the PZT capacitor with the sputter oxide layer to a relative humidity of 85 % for 3 days and annealed this capacitor at 500 ^{o}C in an O_2 atmosphere for 15min. The surface image after annealing is shown in figure 6-10. As shown in figure 6-10, numerous blisters can be observed along the edge of top electrode, which is quite different from the image of figure 6-4. From the thermal desorption study on PECVD SiO_2, the Si-OH corresponding to broad absorption band in IR spectrum can be removed by annealing near a temperature of 300 ^{o}C [12,15]. Therefore, it might be supposed that for the case of the sputter oxide exposed to a humid atmosphere, hydrogen-related bonds, as observed in figure 6-9, are evolved during the annealing, which have a chance to induce a high water vapor pressure inside the stacked layer, thus leading to blister formation.

Annealing in an O_2 atmosphere over 450 has been recommended to recover PZT capacitors from hydrogen or plasma-induced damage [5,6]. However, as mentioned in our results, the annealing of PECVD SiO_2/Pt/PZT/Pt capacitors in an O_2 atmosphere causes the top Pt layer to delaminate from the PZT. Since the delamination of Pt layer is closely related to the bonded-hydrogen in SiO_2 layer, we annealed the PECVD SiO_2/Pt/PZT/Pt capacitor in a N_2 atmosphere over 600 ^{o}C to remove the bonded-hydrogen from PECVD SiO_2 layer, and then subsequently annealed in an O_2 atmosphere. Figure 6-11 shows changes in IR absorption spectra of Si-H and Si-OH bands with annealing temperature. As shown in figure 6-11(a), the intensity of Si-H band is drastically decreased by annealing at a temperature of 310 ^{o}C, and it completely disappears at an annealing temperature of 500 ^{o}C. This change in Si-H bands is consistent with the thermal desorption spectrum shown in figure 6-8. For the Si-OH band as presented in figure 6-11(b), distinct absorption bands at 3400 cm^{-1} and 3670 cm^{-1} are observed. The absorption band at 3400 cm^{-1} is derived from the hydrogen-bonded silanol and the absorption band at 3670 cm^{-1} is assigned to the silanol in the closed pore of SiO_2 due to a local dielectric field [8,14,16,17]. Because there are different bonding environments for the silanols, the thermal desorption behavior is different these materials. As shown in figure 6-11(b), annealing at 310 ^{o}C does not alter the Si-OH absorption band to any extent. However, by increasing the annealing temperature to 500 ^{o}C, the absorption band at 3400 cm^{-1} disappears and the absorption band at 3670 cm^{-1} reduces its intensity significantly. Note that although a 500 ^{o}C anneal removes the silanols from the PECVD SiO_2 film, isolated silanol at a higher wavenumber near 3750 cm^{-1} remains. This is in agreement with a previous report that the temperature in excess of 600 ^{o}C is required to remove the isolated silanol [18]. Therefore, if the annealing of the PECVD SiO_2/Pt/PZT/Pt capacitor is carried out in a N_2 atmosphere over 500 ^{o}C, the hydrogen-related bonds can be removed from the PECVD SiO_2 film. In addition, a subsequent O_2 anneal can be conducted to allow the PZT capacitors to recover from the process-induced damage without the delamination of Pt layer.

§4. CONCLUSIONS

The mechanism of blister formation in PECVD SiO_2/Pt/PZT/Pt capacitors caused by annealing in O_2 atmosphere has been studied. The PZT capacitors which are covered with a PECVD SiO_2 layer exhibit a blistered morphology on the top Pt electrode after annealing in an oxygen atmosphere at over 325 ^{o}C. From the hydrogen evolution test, the hydrogen evolves abruptly from PECVD SiO_2 near 320 ^{o}C, which corresponds to the blister formation temperature. This suggests that the oxygen from the annealing atmosphere and the hydrogen evolved from SiO_2 layer induces a high pressure of water vapor in the stacked layers, causing the delamination of the top Pt layer with poor adhesion to PZT. Therefore, it can be concluded that the blister formation of a Pt/PZT/Pt capacitor with PECVD SiO_2 layer during annealing is due to high gas pressure resulting from a chemical reaction between oxygen and hydrogen, and the low adhesion strength of the top Pt /PZT interface.

§5. REFERENCES

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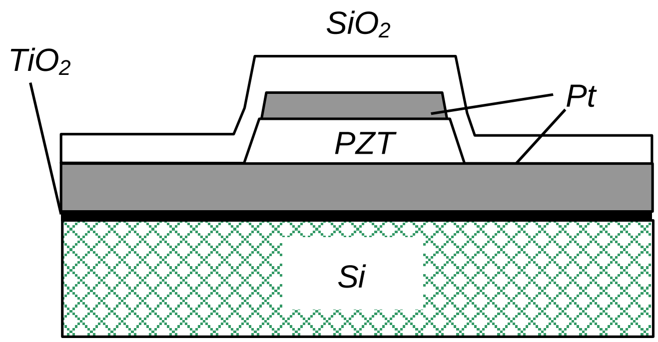

Figure 6-1. Schematic drawing of a PZT capacitor with PECVD SiO_2.

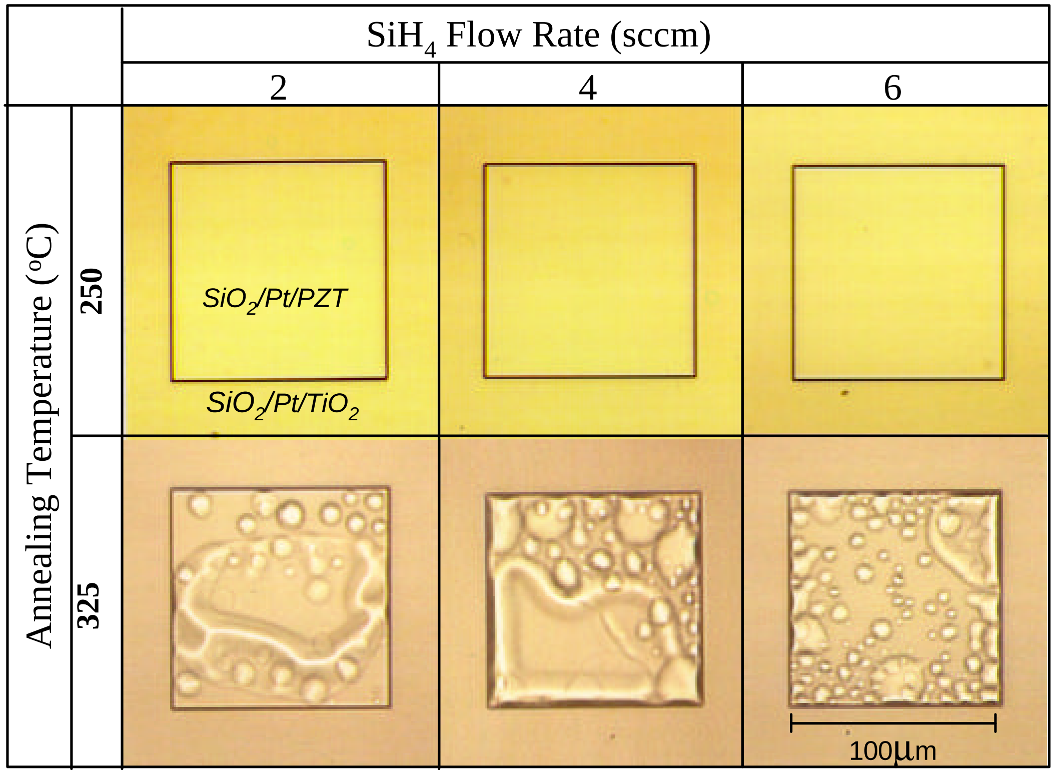

Figure 6-2. Optical micrographs of PZT capacitors annealed in an O_2 atmosphere.

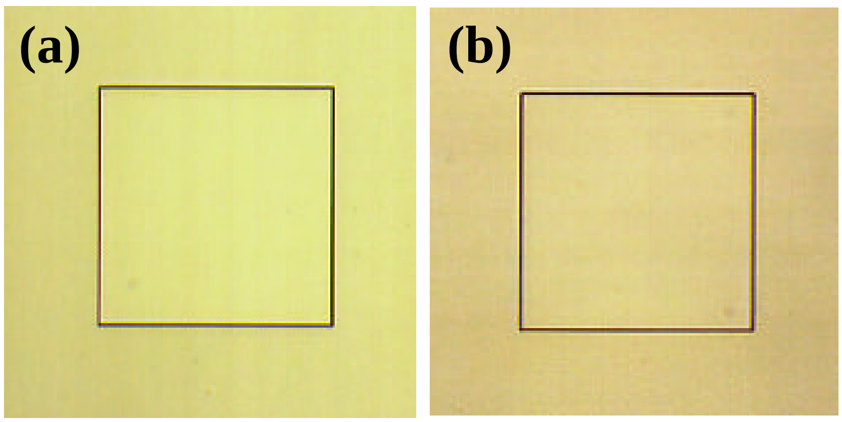

Figure 6-3. Optical micrographs of capacitors which were annealed at 500 ^{o}C in ambient (a) N_2 and (b) Ar. PECVD SiO_2 films were deposited using a SiH_4 flow rate of 4 sccm.

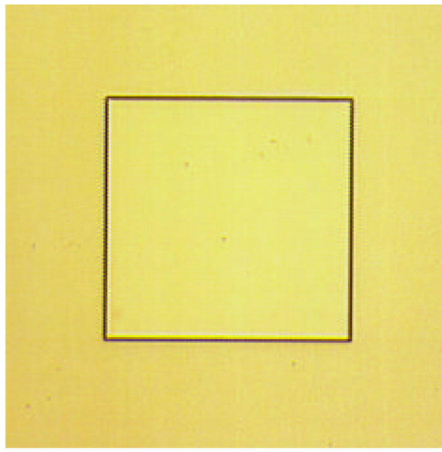

Figure 6-4. An optical micrograph of a capacitor with a sputter SiO_2 layer. The capacitor was annealed at 500 ^oC in O_2 atmosphere.

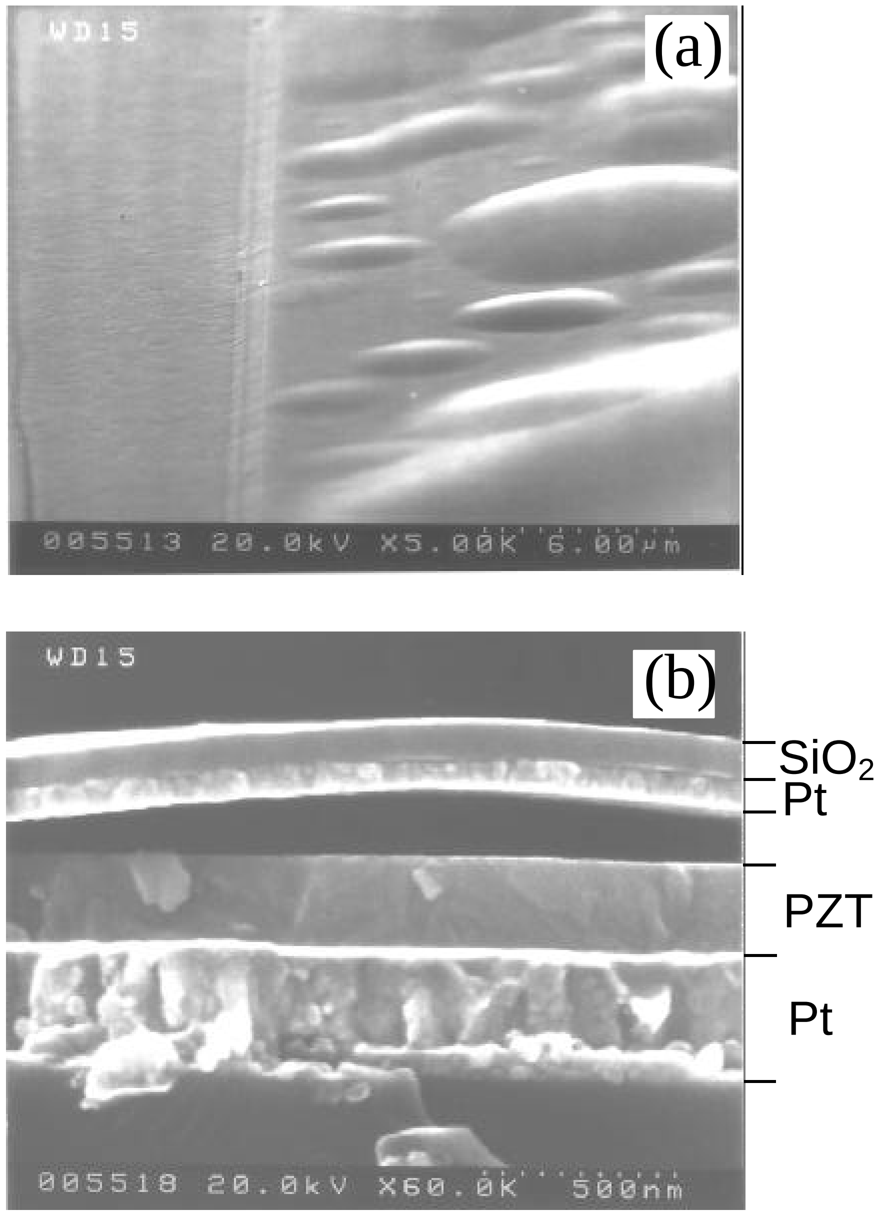

Figure 6-5. Scanning electron micrographs of blister: (a) surface of PZT capacitor and (b) cross-sectional micrograph showing delamination of top Pt from PZT film.

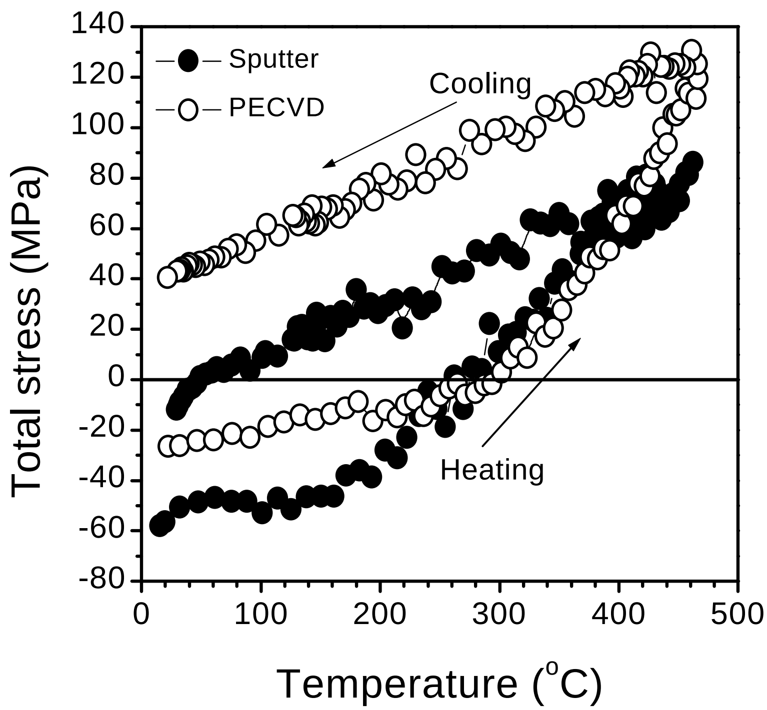

Figure 6-6. Stress-temperature behavior of sputter and PECVD SiO_2.

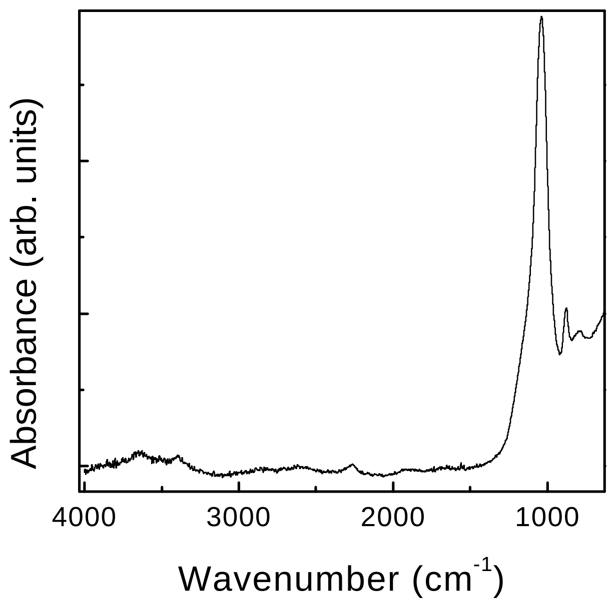

Figure 6-7. IR spectrum of PECVD SiO_2.

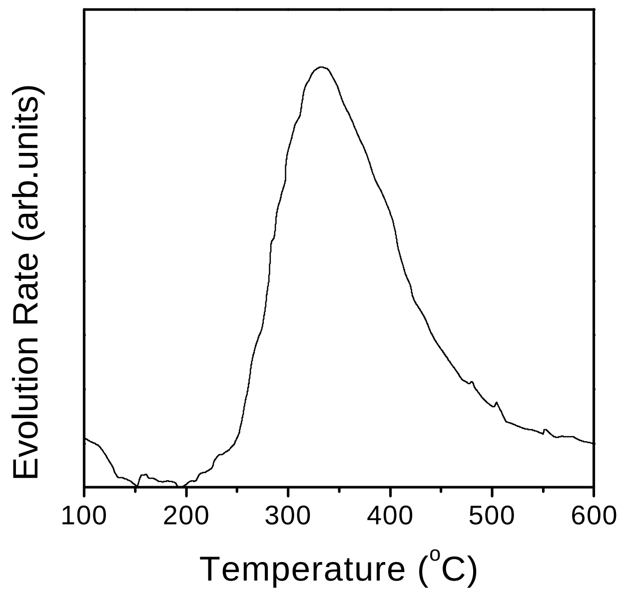

Figure 6-8. A hydrogen thermal evolution spectrum of PECVD SiO_2.

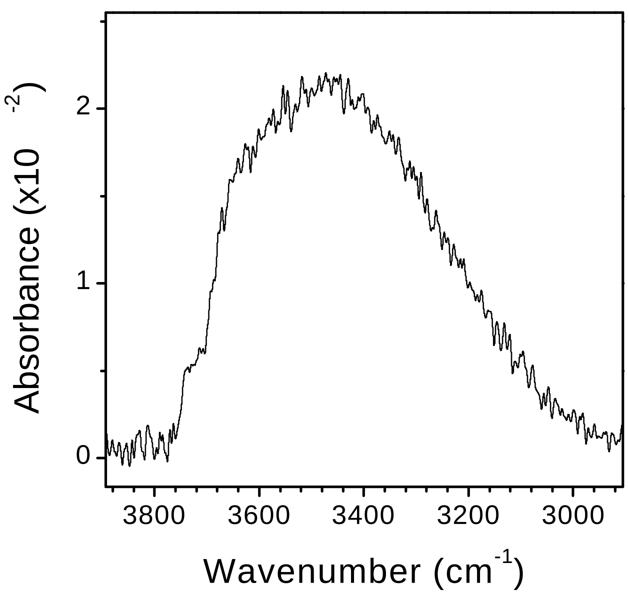

Figure 6-9. An IR absorption spectrum of Si-OH bands for a sputter SiO_2 film, which was exposed to a relative humidity of 85 % for 3 days.

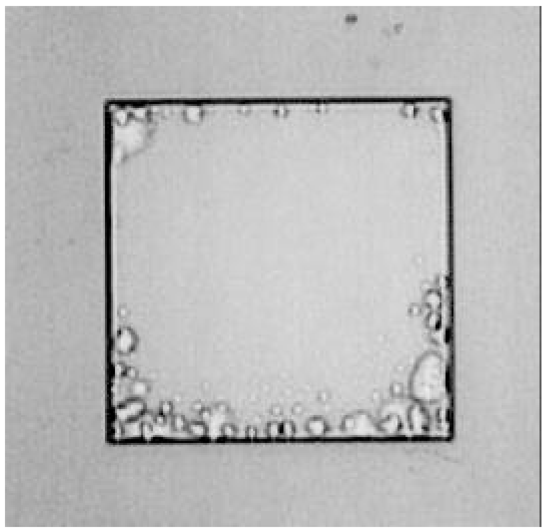

Figure 6-10. An optical micrograph of an annealed capacitor with sputter SiO_2, which was exposed to a relative humidity of 85 % for 3 days prior to annealing.

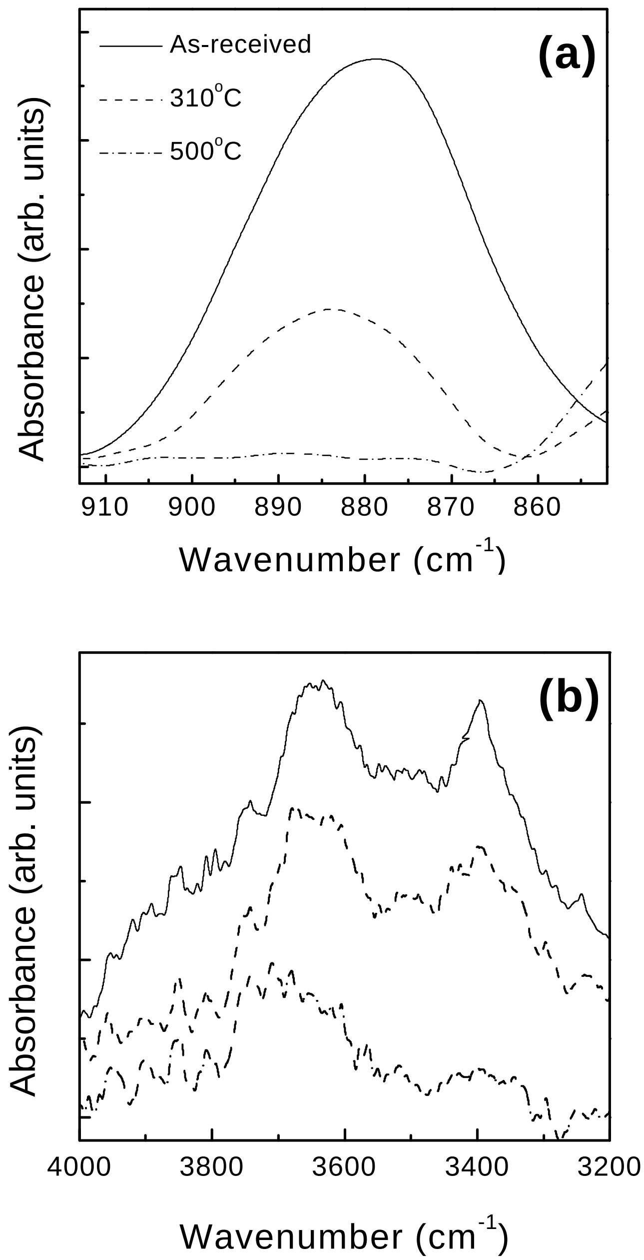

Figure 6-11. Changes in IR absorption spectra of PECVD SiO_2 with annealing temperature. (a) Si-H absorption band, and (b) Si-OH absorption band.