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The partial pressure effect on the growth of YSZ film and YSZ buffered multilayers on silicon

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Abstract

YSZ thin film was deposited on native Si wafer without prior removal of surface amorphous SiO_x layer with pulsed laser deposition (PLD) technique by varying oxygen partial pressure during deposition. Initial oxygen partial pressure was about 10^{-6} mbar followed by 5×10^{-4} mbar. High quality YSZ thin film can be successfully fabricated without an amorphous interfacial SiO_x layer. The YSZ thin film grows epitaxially on silicon with commensurately crystallized YSZ/Si interface. Superconducting YBCO and ferroelectric PZT thin films deposited on the high quality YSZ thin film show excellent physical and microstructure properties.

Keywords: A. Films; B. Interfaces; D. Oxide superconductors; D. PZT

1. Introduction

Yttria stabilized zirconia (YSZ), prepared as thin film, is a potential candidate for buffer layer for the growth of high temperature superconductivity thin film, e.g. $YBa_2Cu_3O_{7-\delta}$ (YBCO) on silicon [1–5]. A buffer layer is used to prevent diffusion of Si from substrate into YBCO and to offer a better-matched lattice for epitaxial growth of YBCO thin film. To obtain high quality YBCO thin film, initial deposition of well-crystallized YSZ buffer layer is crucial.

It is well known that there is always a thin surface layer of amorphous SiO_x on top of native Si wafer. YSZ buffer layer deposited directly on native Si wafer has very poor physical properties as there is a layer of amorphous interfacial layer between YSZ thin film and silicon substrate. To improve physical properties of YSZ film, many researchers suggested that the amorphous SiO_x layer on top of native Si wafer to be removed before the deposition of YSZ. However, complex operating procedure and strict cleaning condition make the removal of amorphous SiO_x layer hard to be performed in most laboratories.

In this study, we found that high quality epitaxial YSZ thin film without amorphous interlayer can be successfully fabricated on Si wafer by varying oxygen partial pressure during deposition. We employed this new method to grow YSZ buffered YBCO thin film and YSZ buffered ferroelectrics $Pb(Zr_xTi_{1-3})O_3$ (PZT) thin film, with YBCO as electrode, on silicon.

2. Experimental

YSZ thin film and YSZ buffered multilayers were grown with pulsed laser deposition (PLD) technique on silicon. A KrF excimer laser, pulse duration 30 ns, wavelength 248 nm, was operated with a fluence of 1.5 J/cm^2 on the target surface. A single crystalline YSZ, commercially available YBCO and PZT ceramic targets were used to deposit YSZ buffer layer, YBCO and PZT thin films, respectively. Si(1 0 0) wafer of size 10 mm × 10 mm × 0.5 mm were cleaned in nitric acid, acetone, ethanol and distilled water with ultrasonic cleaner. This substrate was mounted to heater using silver paste. The chamber was evacuated to 10^{-7} mbar. Si substrate was heated to 730 °C in 10 min. Initial deposition of YSZ was carried out, with 5 Hz laser frequency, in a base pressure of 10^{-7} mbar for 3 min. Oxygen partial pressure was then increased to 5×10^{-4} mbar and deposition of YSZ was continued for another 15 min. Thickness of YSZ buffer was about 120 nm. Some of the as deposited YSZ thin film was cooled in oxygen. For the others, YBCO thin film was deposited for 30 min, with

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laser energy and frequency remained the same, substrate temperature at 730 °C, oxygen partial pressure of 0.2 mbar. Pure oxygen was filled immediately after the deposition. Films were annealed at 500 °C for 40 min. The substrate was then cooled down to room temperature slowly.

Well-crystallized PZT thin film was deposited onto YBCO and PZT coated Si wafer at a temperature of 600 °C. Laser fluence of 1.5 J/cm^2 and repetition rate of 5 Hz was chosen for PZT deposition at an ambient pressure of 0.25 mbar. A post-annealing of film at 600 °C, 1.0 atm of oxygen was carried out.

X-ray diffraction (XRD) θ–2θ scan and ω scan (rocking curve) were conducted to determine crystalline and orientation of YSZ, YBCO and PZT thin film deposited. Quantitative chemical composition, as well as micro structural analysis, was done by using Philips CM300 field emission gun transmission electron microscope (TEM) with energy dispersive X-ray (EDX) spectrometer operating at 300 kV. Cross-sectional TEM specimens were prepared by conventional method, i.e. polishing, mechanical dimpling and ion-beam milling. Secondary ion mass spectrometry (SIMS) depth profile analysis was carried out on a Cameca IMS6f instrument, using O_2^+ primary ions with impact energy of 5 keV.

3. Results and discussion

Fig. 1(a) shows a XRD pattern of 120 nm YSZ film on Si substrate deposited by varying oxygen partial pressure during deposition. The film is uniformly (1 0 0) oriented. It suggests that the epitaxial relationship between YSZ and Si is cube-on-cube. Lattice parameter of YSZ deduced from XRD data is 5.15 Å. The FWHM of rocking curve of YSZ(2 0 0) peak is about 0.8°, same as the reported value of YSZ thin film deposited on HF etched silicon substrate [6].

Fig. 2(a) is a cross-sectional HRTEM image of deposited YSZ thin film on Si(1 0 0) substrate with the corresponding electron diffraction pattern as inserted. The orientation relationship between YSZ and Si is YSZ(1 0 0)/Si(1 0 0) and YSZ[0 1 1]/Si[0 1 1]. It is obvious that YSZ grows epitaxially on Si with no amorphous interfacial oxide at the interface. Although we did not conducted any acid-etching process on native Si wafer prior to deposition, no amorphous SiO_x interfacial layer was observed. This phenomenon is believed to be due to the reaction of Zr ions with SiO_x on the surface of Si wafer under low oxygen partial pressure and high temperature conditions. The free energy of formation of ZrO_2 ($G_{800\,K} = -941.6$ kJ/kmol) is lower than that of SiO_2 ($G_{800\,K} = -734.2$ kJ/kmol) [7]. In our deposition process, initial deposition of YSZ was conducted in very low oxygen partial pressure condition (10^{-6} mbar). Due to shortage of oxygen in the chamber, Zr ions absorbed oxygen ions from SiO_x layer on the surface of Si wafer, reducing SiO_2 to SiO. Rubloff et al. [8] found that the critical oxygen partial pressure above which silicon oxide layer remains stable at

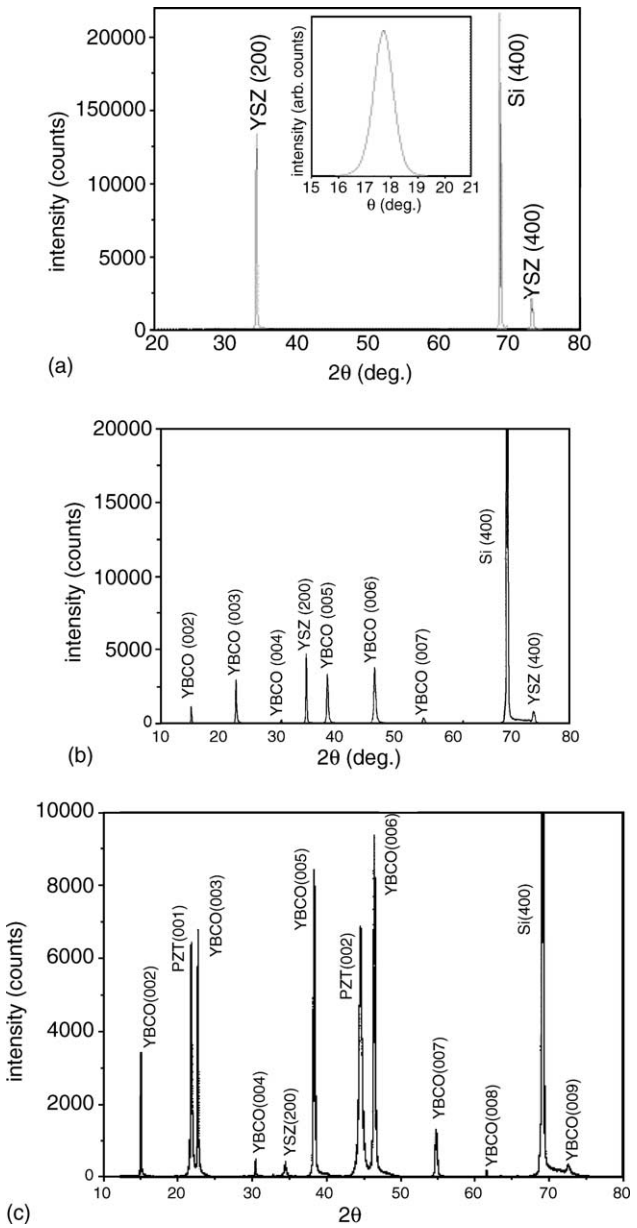

Fig. 1. (a) XRD pattern of YSZ thin film on Si(1 0 0) substrate. YSZ was deposited with initial oxygen partial pressure of about 10^{-6} mbar followed by 5×10^{-4} mbar. The insert is the rocking curve of YSZ(2 0 0) peak. (b) XRD pattern of YSZ buffered YBCO thin film on silicon. (c) XRD pattern of PZT/YBCO/YSZ/Si multiplayer.

730 °C is about 7×10^{-5} mbar. Therefore, SiO desorption is expected for lower oxygen partial pressure, 10^{-6} mbar during initial deposition process. As a result, thickness of SiO_x layer will be reduced or even eliminated. Fig. 3 shows the SIMS profile of the 120 nm YSZ film on silicon substrate. At the interface, the intensity of Zr atom decreases sharply while that of Si atom increases rapidly. This implies that there is no inter-diffusion of Zr and Si at the interface.

For comparison, we also deposited two YSZ thin films on Si(1 0 0) wafer under constant oxygen partial pressure of 5×10^{-6} mbar and 5×10^{-4} mbar, respectively, from initial

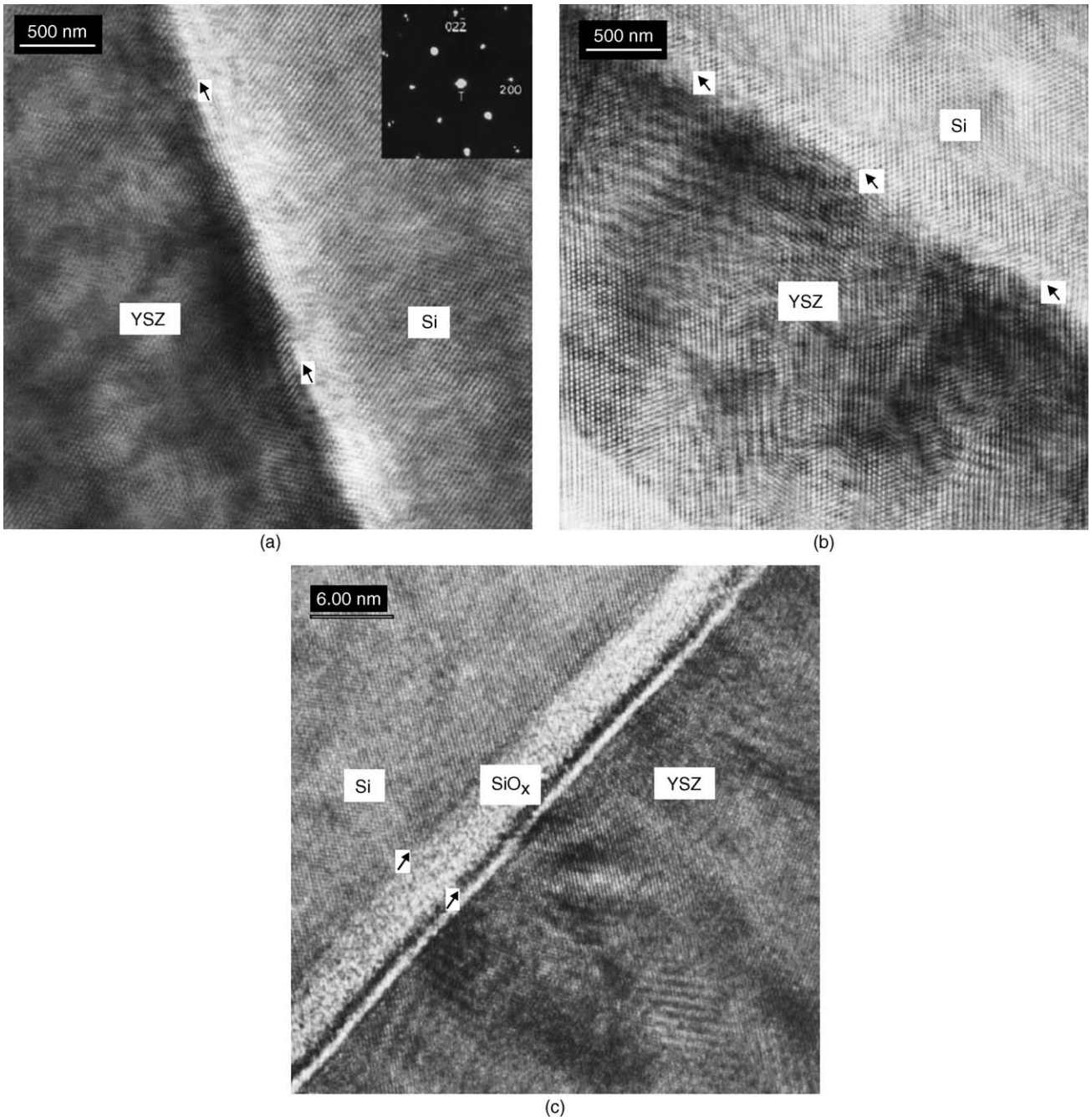

Fig. 2. Cross-sectional HRTEM image of YSZ thin film on Si(1 0 0) substrate. The YSZ thin film was deposited with (a) initial oxygen partial pressure of about 10^{-6} mbar followed by 5×10^{-4} mbar. The insert is the electron diffraction pattern of YSZ/Si interface, (b) constant oxygen partial pressure of 5×10^{-6} mbar, (c) constant oxygen partial pressure of 5×10^{-4} mbar.

stage. Fig. 2(b) and (c) shows cross-sectional HRTEM image of YSZ thin film deposited under constant pressure of 5×10^{-6} mbar and 5×10^{-4} mbar, respectively. We found that the former forms commensurately crystalline interface without any amorphous layer. The later has an amorphous interfacial oxide layer of about 4.5 nm. It demonstrates that the initial lower oxygen partial pressure is crucial for obtaining crystalline interface between YSZ thin film and Si substrate. However, due to shortage of oxygen, the YSZ thin film deposited in constant low oxygen partial pressure has more oxygen vacancies. The YSZ lattice parameters were enlarged and there were more defects in the film.

Having successfully fabricated high quality expitaxial YSZ thin film on native Si wafer, we deposited YBCO thin film, with the epitaxial YSZ thin film as buffer layer, on native Si wafer. Fig. 1(b) shows a XRD curve of YBCO/YSZ/Si thin film. It is found that only (0 0 1) peaks of YBCO are present suggesting that YBCO thin film is uniformly *c*-axis oriented. Fig. 4(a) is a low magnification TEM image of YBCO/YSZ/Si thin film. The interface

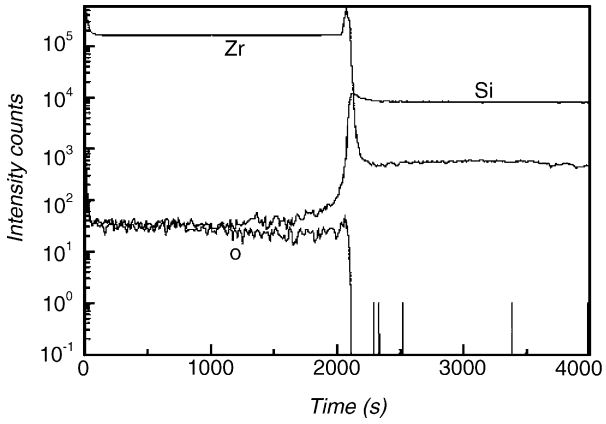

Fig. 3. SIMS depth profile of 120 nm YSZ thin film on silicon substrate. The YSZ thin film was deposited with initial oxygen partial pressure of about 10^{-6} mbar followed by 5×10^{-4} mbar.

between YSZ and Si, as well as between YBCO and YSZ, is sharp and commensurately crystallized. No amorphous SiO_x layer is observed.

We know that a crucial problem of fabricating epitaxial YBCO film on silicon substrate is the interfacial inter-diffusion between Si and YBCO. Even a small amount of Si diffusing into YBCO thin film will have detrimental effect on the physical properties of YBCO film [9]. Although YSZ is a good buffer for resisting Si diffusion, the strength of Si diffusion depends strongly on the deposition condition. To determine Si distribution, SIMS depth profile of YBCO/YSZ/Si, YSZ deposited using varied oxygen partial pressure was obtained, as shown in Fig. 5. The thickness of YBCO and YSZ are 300 and 120 nm, respectively. Interfaces of the multilayer can be clearly distinguished. Practically, no Si is observed to diffuse from Si substrate into the YBCO thin film. If we define diffusion length as distance that intensity counts of Si decrease from 2×10^6 to 2×10^3, the diffusion length of Si into YSZ buffer is about 40 nm. This indicates that the YSZ buffer layer can serve as a resisting media against diffusion of Si even after 30 min of YBCO deposition at 700 °C and 40 min of oxygen annealing at 500 °C. It is found that zirconia has a relatively wide penetration depth across YBCO/YSZ interface into YBCO film. The reason is still unknown. The method of varying oxygen partial pressure during deposition is beneficial for obtaining high quality YSZ thin film, which has strong chemical stability to resist Si diffusion in high temperature condition. The as deposited YBCO film shows excellent physical properties. The best transition temperature T_c(onset) and T_c(0) are determined to be 92 and 87 K, respectively.

We have deposited YBCO thin film with excellent physical properties and crystal structure on native Si wafer, with high quality epitaxial YSZ as buffer layer. Deposition process was continued, depositing PZT thin film on these layers. This is in parallel with recent development of using complex oxides such as YBCO as electrodes for ferroelectric thin

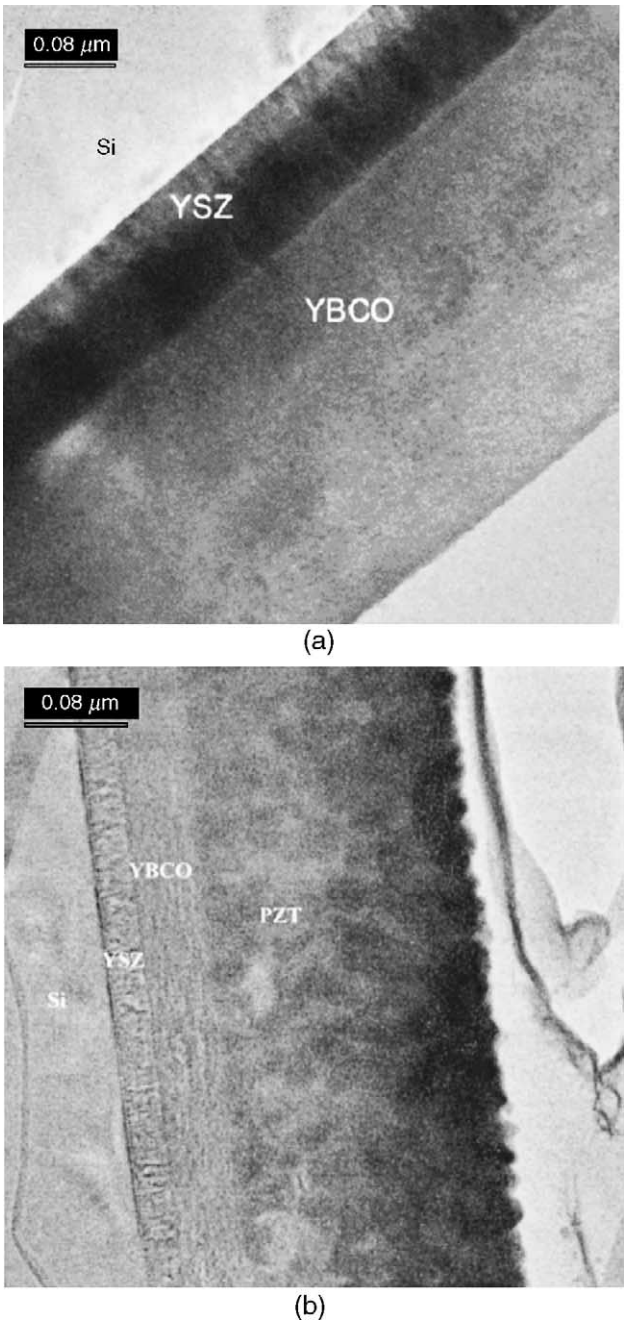

Fig. 4. Low magnification cross-sectional image of (a) YBCO (300 nm)/YSZ (120 nm)/Si, (b) PZT (1.2 μm)/YBCO (300 nm)/PZT (120 nm)/Si.

film capacitors and piezoelectric micro-mechanical system (MEMS). Interest in complex oxides electrodes is resulted from the fact that they have perovskite-based crystal structure with good lattice matching with PZT ferroelectric thin film. In addition, long fatigue life, fast switch speed and low resistivity are some superior properties of complex oxides over conventional metal electrodes.

Fig. 1(c) shows a XRD curve of PZT/YBCO/YSZ/Si multiplayer. For PZT, only (0 0 1) and (0 0 2) peaks are present. There is no peak associated with oxygen or lead deficient

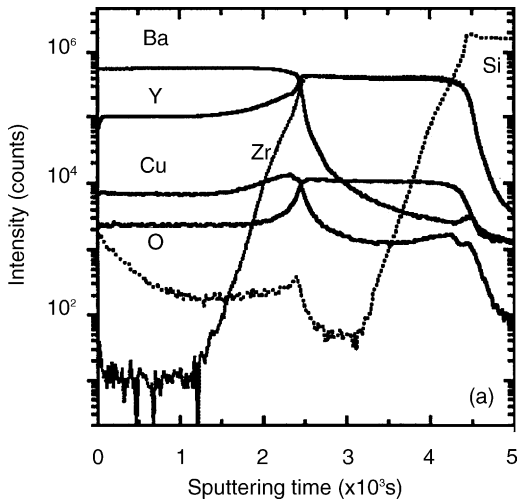

Fig. 5. SIMS depth profile of YBCO (300 nm)/YSZ (120 nm)/Si. The YSZ thin film was deposited with initial oxygen partial pressure of about 10^{-6} mbar followed by 5×10^{-4} mbar.

pyrochlore phase of PZT observed. The good structure of the deposited PZT thin film may be attributed to the similar perovskite structure and the high quality YSZ buffer layer on silicon substrate. Fig. 4(b) is a low magnification TEM image of PZT (1.2 μm)/YBCO (300 nm)/YSZ (120 nm)/Si. The interfaces between Si and YSZ, YSZ and YBCO, YBCO and PZT are sharp and there is no perceptible inter-diffusion across the boundary.

The electrical property evaluations of the PZT film deposited demonstrate good ferroelectric properties: the leakage current J is of 6×10^{-6} A/cm^2 at electrical field $E =$ 100 kV/cm, the ferroelectric hysteresis at a series of external fields for a 1.0 μm thick PZT film, the remnant polarization is about 30 μC/cm^2 and coercive field is about 35–40 kV/cm.

4. Conclusions

In summary, we investigated the partial pressure effect on the growth of YSZ thin films and YSZ buffered YBCO and PZT multilayers on Si wafer. Epitaxial YSZ thin film without an amorphous SiO_2 layer was successfully grown on natively oxidized silicon wafer by varying oxygen partial pressure during the deposition. HRTEM investigation shows that interface between YSZ film and Si(1 0 0) substrate is commensurately crystallized and without an amorphous layer. The commensurate crystalline interface is attributed to the low oxygen partial pressure at initial deposition stage, where the amorphous interface oxide is eliminated by Zr ions reacting with native silicon oxide on the surface of Si wafer. We suggest that our result can be used for fabrication of other high quality crystalline oxide thin films on Si wafers to integrate Si-based technology with new device, which utilize different physical properties of crystalline oxide thin films.

On native Si wafer, we successfully fabricated perfect (1 0 0) oriented crystalline YSZ buffer layer and subsequently *c*-axis oriented YBCO thin film. Silicon diffusion length in YSZ layer is 40 nm. As a result of perfect YSZ buffer layer and short diffusion length of silicon, YBCO thin film deposited shows excellent crystal structure and physical properties. We believe this method would shed lights on the fabrication of high quality perovskite thin film on YSZ buffered silicon, where diffusion of silicon into the as deposited film is strongly prohibited.

For YSZ buffered PZT film on silicon with YBCO as electrode, all layers show good epitaxial relationship and PZT film deposited demonstrates good ferroelectric properties.

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