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The growth-temperature-dependent interface structure of yttria-stabilized zirconia thin films grown on Si substrates

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Abstract
We report on the interface characteristics of yttria-stabilized zirconia films grown on silicon substrates. From x-ray reflectivity analysis we found that the film thickness and interface roughness decreased as the growth temperature increased, indicating that the growth mechanism varies and the chemical reaction is limited to the interface as the growth condition varies. Furthermore, the packing density of the film increased as the growth temperature increased and the film thickness decreased. X-ray photoelectron spectroscopy analysis of very thin films revealed that the amount of chemical shift increased as the growth temperature increased. Intriguingly, the direction of the chemical shift of Zr was opposite to that of Si due to the second nearest neighbor interaction.

(Some figures in this article are in colour only in the electronic version)

Due to recent efforts aimed at developing oxide based electronics, a large amount of research has been dedicated to studying high quality oxide films [1]. However, when oxide films are grown on non-oxide substrates, interface interdiffusion prohibits the formation of high quality oxide films. Furthermore, the existence of a lattice mismatch will also limit high quality films due to the interfacial strain effect. For oxide films on top of Si substrates there also exist a lattice mismatch and interface interdiffusion when the films are directly deposited on the Si surface [2, 3]. For example, when ZrO_2 or HfO_2 layers were deposited on Si to form metal-oxide semiconductors, the formation of a silicate layer at the interface plays a negative role [4]. To minimize the interface interdiffusion and lattice mismatch, and to avoid the extra effort required to remove the SiO_2 layer, the use of a proper metal-oxide layer as a buffer layer has been previously suggested [5, 6]. Among the potential metal-oxide layers that could be used for this purpose, yttria-stabilized zirconia (YSZ) has been identified as a good candidate for the growth of high quality $PbTiO_3$ [7, 8], Pb(Zr, Ti)O_3 [9], and YBCO [3, 10–12] films on Si substrates. Furthermore, YSZ itself can be used as an ionic conductor and solid electrolyte in thin film oxygen sensors and fuel cells [13, 14]. Therefore, it is important to investigate the details of interface interdiffusion between Si and YSZ films, since this can affect the physical properties of the films used for these applications [3, 5, 15–18].

In this paper we report the details of the interface chemical state and the interface structure of YSZ films grown on Si at different growth temperatures using pulsed laser deposition (PLD). Various YSZ thin films were deposited onto Si(100) substrates using a PLD system (λ_{KrF} = 248 nm, 2 Hz, 200 mJ, Nano-PLD-1000, PVD). For the target material, we used a 2-inch YSZ (8% yttrium doped) *single crystal* substrate[3]. The base pressure of the PLD system was maintained under 1.2×10^{-6} Torr. The chemical state and interface structure of the YSZ films were examined using an x-ray photoelectron spectroscope (XPS; monochromatic Al Kα, 1486.6 eV, ESCALAB250, VG Scientifics) and an x-ray reflectometer (PANalytical, X'pert PRO MRD), respectively.

X-ray reflectivity is a useful tool for measuring the buried interface structure of samples along with the chemical density and thickness of the individual layers. By comparing the measured reflected x-ray intensity and the calculated reflectivity profile from a proposed model structure as a

[3] Based on XPS quantification, we also verified that the most of YSZ films contained 66.1±2.4% oxygen, 7.2±0.8% yttrium, and 26.7±0.4% zirconium.

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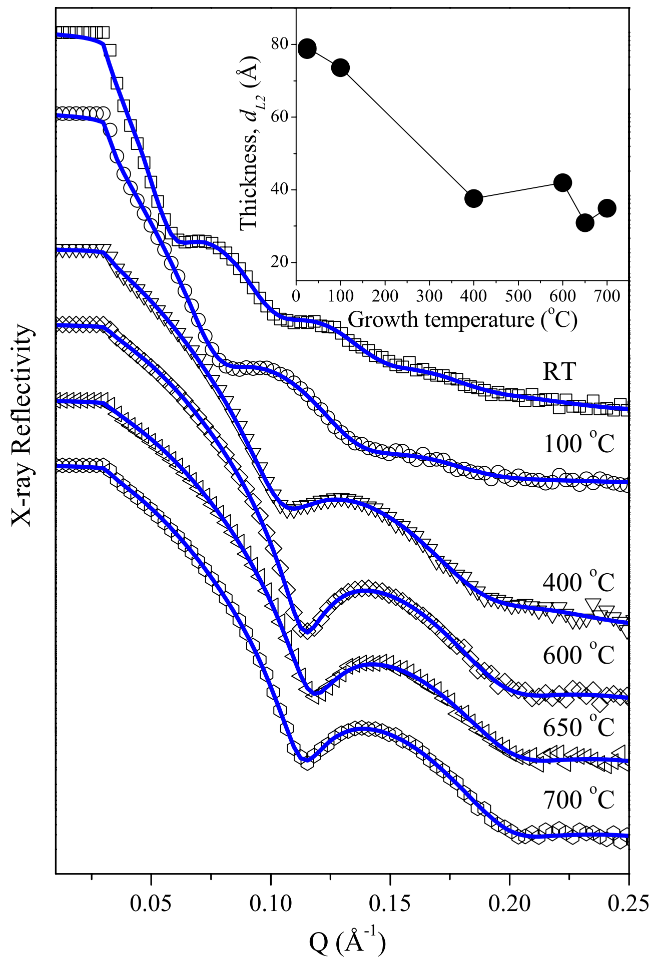


Figure 1. X-ray reflectivity profiles (symbols) and fitted results (solid curves) for the samples grown at different temperatures. The inset shows the growth-temperature-dependent fitted YSZ thin film thickness (d_{L2}). The lines in the inset were used to enhance the visual appearance of the figure. The deposition time was maintained at 10 min and a flow rate of 50 mTorr oxygen was used during growth.

function of wavevector transfer, $Q = 4\pi \sin\theta/\lambda$, where λ is the x-ray wavelength (1.54 Å) and θ is the angle between the incident x-ray beam and its projection on the sample surface, the chemical composition, amount of interface interdiffusion (roughness), and thickness of the YSZ thin film were quantified [19]. Furthermore, XPS is a tool for measuring the elemental composition, chemical formula and state, and electronic state of the elements that exist within a film under ultra-high-vacuum conditions [20]. However, the limited photoelectron escape depth allows only the top surface of the film to be analyzed. By combining two tools, we want to analyze the interface structure from x-ray reflectivity and the chemical state from XPS, which can provide details about the initial growth mechanism of YSZ on Si.

Figure 1 shows the measured x-ray reflectivity profiles (symbols) and best fitted profiles (solid curves) of YSZ films grown for 10 min at different temperatures under an oxygen flow (50 mTorr). Quantitative information was obtained using a two layer model structure even though only a single YSZ layer was deposited. The additional top layer (L1) was inserted

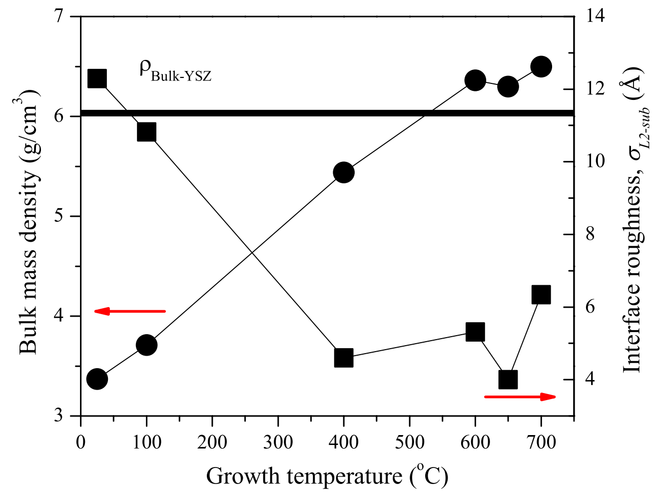


Figure 2. Fitted bulk mass density of YSZ films and interface roughness between of the YSZ films and Si substrate at different growth temperatures. The horizontal line represents the known bulk YSZ mass density. The lines connected data points were used to enhance the visual appearance of the figure.

to accommodate the effect of surface oxidation since the samples were exposed to air. Without any constraints, the x-ray scattering length density[4] (ρ), thickness (d), and roughness (σ) of each layer were determined based on simple least squares minimization using the dynamical (optical) formalism of Parratt [21] with the Parratt32 software package. The YSZ film thickness (d_{L2}) obtained from the numerical analysis as a function of the growth temperature is shown in the inset in figure 1. In general, as the growth temperature increased, the film thickness decreased. On the other hand, the mass density obtained from the scattering length density (ρ) of the YSZ film increased and reached a bulk mass density value[5] when the temperature was above 600 °C (shown in figure 2). The increases in mass density and the decreases in film thickness at higher growth temperatures occurred because the packing density of the films increased as the growth temperature increased[6]. Since the mass density obtained from the scattering length density of YSZ films represents the average surface density of the films, it is plausible that the YSZ forms islands (clusters) at the lower growth temperature. As the growth temperature increases, the YSZ clusters formed may have enough surface mobility to form the flatter films. The decrease of interface roughness between the YSZ layer (L2) and Si substrate (σ_{L2-sub}) as the growth temperature increases (shown in figure 2.) also supports the notion that the growth mechanism of the YSZ films changes as the growth temperature varies.

[4] The x-ray scattering length density is given by $\rho = \frac{r_e \rho_m N_A Z}{A}$, where r_e is the classical electron radius (2.82×10^{-5} Å), ρ_m is atomic density (g cm^{-3}), N_A is Avogadro's number (6.022×10^{23} atoms/mole), Z is the number of electrons, and A is the mass number (http://www.ncnr.nist.gov/resources/sldcalc.html).

[5] The atomic mass density of bulk YSZ ($Y_{0.08}Zr_{0.92}O_{1.96}$) is 6.033 g cm^{-3} (JCPDS-ICDD PDF no. 480224 (2002)). The corresponding x-ray scattering length density (ρ_{YSZ}) is $4.46 \times 10^{-5} + i2.5 \times 10^{-6}$ Å^{-2}. The scattering length density is calculated from http://www.ncnr.nist.gov/resources/sldcalc.html.

[6] The areal density obtained based on the x-ray reflectivity analysis showed the 10% variation of the total amount of YSZ among the samples.

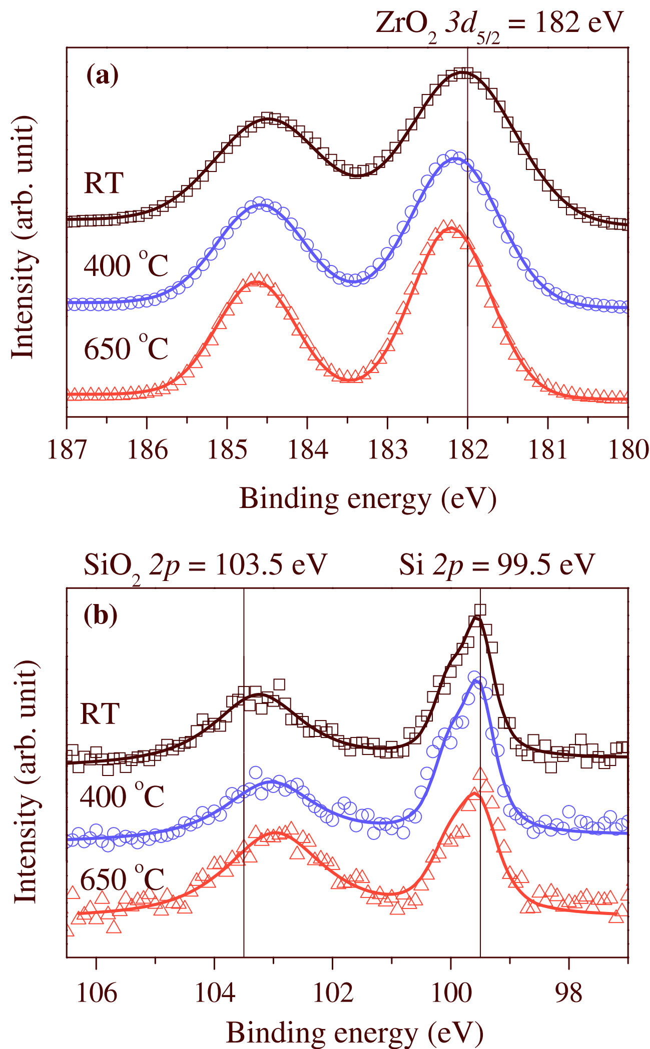
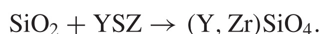


Figure 3. XPS spectra of (a) Zr-oxide 3d and (b) Si-oxide 2p for the samples grown at RT, 400 and 650 °C. The vertical lines indicate the reference XPS peak positions and the solid curves are the fitted results.

It is well known that the existence of surface oxygen on the top of the Si substrate plays an important role in forming high quality YSZ films [17] since it prohibits silicide formation. XPS was used to investigate the details of the interface chemical structures as a function of the growth temperatures. The samples used in the XPS study were deposited for only 3 min under an oxygen flow of 50 mTorr due to the detection limit of the photoelectrons (2–10 nm). When the YSZ film was deposited on the SiO_2 surface, the following chemical interdiffusion mechanism could be considered:



$$SiO_2 + YSZ \rightarrow (Y, Zr)SiO_4.$$

Since the room temperature ($\simeq$298.15 K) standard molar enthalpy (heat) of formation (ΔH^{o}) [22] of Y_2O_3 ($\Delta H^{o} = -1905.3$ kJ mol^{-1}) and ZrO_2 ($\Delta H^{o} = -1100.6$ kJ mol^{-1}) was lower than that of the SiO_2 ($\Delta H^{o} = -910.7$ kJ mol^{-1}), we expected that the reduction of oxygen from Si oxide to form the metal oxide complex and the extra oxygen will most likely react with Y and/or Zr ions. Figure 3 shows the growth temperature dependence of Zr-oxide 3d and Si-oxide 2p XPS spectra for the YSZ films grown on Si(100) substrates. The solid curves represent the fitted results, which were used to determine the proper peak position of the spectra[7]. For the sample grown at room temperature, the oxidized Zr $3d_{5/2}$ peak appeared at ~182.1 eV which was shifted by 0.1 eV to a higher binding energy compared to the bulk binding energy of ZrO_2 (Zr-$3d_{5/2}$ at 182.0 eV, the vertical reference line in figure 3(a)) [4][8]. This shift was attributed to the small chemical reaction between the YSZ layer and the Si substrate. As growth temperature increased, the binding energy shifted to higher energies. For the sample grown at 650 °C, the Zr-oxide binding energy increased by ~0.2 eV compared to the room temperature sample due to the increase of interface chemical reactions between the YSZ layer and the Si substrate. The chemical state of Si-oxide 2p when grown at different growth temperatures is shown in figure 3(b). For the sample grown at room temperature, the binding energy of the oxidized Si 2p peak appeared around 103.3 eV which was smaller than the reference binding energy of SiO_2 (103.5 eV). The oxidized Si binding energy was also reduced to 103.0 eV (0.3 eV less than that of oxidized Si 2p at room temperature) when the samples were grown at 650 °C. It is worth noting that the shift in binding energy due to the higher growth temperature can be used as a parameter to estimate the amount of metal fraction [4][9]. The growth temperature dependence of the binding energy shift for the YSZ samples grown on the Si substrate might be associated with the interface chemical reaction during growth. This opposite trend (increase of Zr-oxide binding energy and decrease of Si-oxide binding energy with respect to the increase in growth temperature) in the binding energy shift was attributed to the fact that the second nearest neighbor interaction of Si and Zr was different for oxidized Si 2p and/or oxidized Zr 3d, respectively [10]. It is worth pointing out that even though the binding energy shift is small, the trend of binding energy shifts is noticeable.

As the growth temperature increased, the number of Zr–O–Si bonds increased due to the increased interface interdiffusion. The electrons on the Zr side experienced a stronger bond due to the larger electron affinity energy of Si (1.90 eV for Si) [22]. The larger electron affinity energy of Si induced a shift in the electron configuration of the system. On the other hand, the electrons on the Si side experienced a weaker bond since the electron affinity energy of Zr (1.30 eV for Zr) [22] is smaller than that of Si. Therefore, the shift in the Zr-oxide binding energy was attributed to the effect of the second nearest neighbor interaction since the first nearest neighbor (Zr–O and Si–O bonding) does not change. It is worth noting that since yttrium behaves in a similar way to Zr, our discussion was limited to only the chemical state of Zr-oxide

[7] XPSPEAK 4.1 was used to analyze the measured XPS data (http://www.phy.cuhk.edu.hk/~surface/XPSPEAK/).

[8] It is worth noting that all the XPS peaks shown in this paper were properly corrected by setting the C 1s peak at 285 eV.

[9] Based on reference [4], we estimated the amount of metal fraction in the silicate to be 25% for the samples grown at 650 °C. For the samples grown at the lower temperature, the binding energy shift was also smaller, indicating the reduced interfacial reaction.

and Si-oxide. We also examined the film-depth-dependent binding energy shift using angle-resolved XPS (Theta300, VG Scientific) and found that the binding energy shift occurred over the entire depth range. Furthermore, a similar behavior was also observed for the samples annealed under vacuum.

By combining XPS and x-ray reflectivity, we were able to systematically examine the interface characteristics of YSZ films grown on an Si substrate. From the x-ray reflectivity analysis, we found that the packing density of YSZ films increased, the film thickness (d_{L2}) decreased and the bottom interface roughness (σ_{L2-sub}) decreased as the growth temperature increased, indicating that the YSZ film grows islands at lower temperatures and layer-by-layer growth occurs at higher temperatures. By examining the details of the chemical structure at the interface using XPS, we showed that as the growth temperature increases, the chemical shift of Zr-oxide and Si-oxide increases in the opposite direction due to the second nearest neighbor interaction between Zr and Si through oxygen. Using both XPS and x-ray reflectivity analysis, we found that the chemical reaction between the YSZ film and Si substrate was limited to the surface and forms a (Y, Zr)SiO_4 structure as the growth temperature increases.

Acknowledgments

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