Aberration-Corrected HRTEM Analysis of Transition Layer Structure in ZrO_2 Ultra-Thin Film

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Yttria stabilized zirconia (YSZ) is an attractive material as a buffer layer for metal - insulator - semiconductor (MIS)-type Si devices such as ferroelectric gate transistors and superconductive devices [1,2]. One of the critical issues concerning YSZ is the instability of the threshold voltage of a MIS-field effect transistor (MIS-FET) due to the large hysteresis of their capacitance-voltage (C-V) characteristics. The hysteresis is ascribed to mobile ions or polarization caused by oxygen vacancy and related defects [3]. Furthermore, the diffusion of doping elements into the Si substrate increases interface-trapped charges. A pure ZrO_2 is effective to avoid the C-V hysteresis and interface-trapped charges attributable to the doped elements such as Y and oxygen vacancy. However, ZrO_2 has the monoclinic phase with large spontaneous strain, and thus makes a complicated domain structure with large roughness at surfaces and interfaces [4]. Therefore, the monoclinic ZrO_2 itself cannot be used to the gate dielectrics and buffer layers. ZrO_2 experiences the ferroelastic phase transition of cubic ($Fm\bar{3}m$) - tetragonal ($P4_2/nmc$) - monoclinic ($P2_1/c$). It was reported that ZrO_2 nano-particles have tetragonal phase due to the size effect [5]. This result indicates that the thinning of the ZrO_2 thickness would certainly make tetragonal phase stable. The objective of this study is to elucidate the size effect and the related nanostructure of ZrO_2 films using aberration-corrected TEM.

Un-doped ZrO_2 films were deposited on a p-Si(001) wafer with thin SiO_2 layers by Pulsed-Laser Deposition (PLD) technique [4]. The nanostructure of the films were investigated using the aberration-corrected transmission electron microscope (TITAN80-300, 300kV, FEI).

Figure 1 shows a plan-view image with diffractograms of each area of the image, where the precipitate (2) exists in the matrix (1). Diffractograms, which are two-dimensional Fourier transformed pattern of regions 1 and 2, indicate that the matrix is tetragonal or cubic phase and that the precipitate is monoclinic phase. The monoclinic phase has the coherent interface between tetragonal matrixes. Figure 2 shows a cross-sectional image with nano-beam diffraction patterns of the film projected in the $[\bar{1}10]$ direction. The region 1 is the monoclinic phase and the region 2 the tetragonal one from the diffraction patterns. Both of the phases have flat surface and interface, and are uniform along the out-of-direction. Figure 3 is (a) the HRTEM image around the tetragonal - monoclinic phase boundary and (b) the profile of the projected Zr-Zr distance across the phase boundary as a function of atomic columns in (a). The atomic columns of Zr (black column) and O (gray column) are clearly visible. The profile clearly shows the transition layer where the distance gradually changes between those phases. The width is c.a. 1.5 nm. The atomic displacement in the transition layer is understandable as the condensation of the ferro-distortive $E_g^1+E_g^2$ modes at Γ point in the

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reciprocal lattice of tetragonal phase [6]. These results indicate that the tetragonal-monoclinic phase transition was quenched due to a sort of size effect in the direction of film thickness. The balance of two type of stresses, (1) the tensile stress induced by the difference of the thermal expansion coefficient between ZrO_2 and Si and (2) the compressive stress induced by the dilative phase transition from the tetragonal to the monoclinic phases would contribute to the quench of the phase transition.

[1] C.Pellet, Thin Solid Films, **175** (1989) p23.
[2] A.I.Kingon, J.P.Maria, and S.K.Streiffer, Nature **406** (2000) p1032.
[3] T.Kiguchi, N.Wakiya, K.Shinozaki, and N.Mizutani, Mat.Res.Soc.Symp.Proc **748** (2003) p171.
[4] T.Kiguchi, N.Wakiya, J.Tanaka, and K.Shinozaki, Mater. Sci. Eng. B **148** (2008) p30.
[5] M.W.Pitcher, S.V.Ushakov, A.Navrotosky, B.F.Woodfield, G.Li, J.Boerio-Goates, and B.M.Tissue, J. Am. Ceram. Soc. **88** (2005) p160.
[6] K.Negita, and H. Takao, J. Phys. Chem. Solids, **50**, (1989) p325.

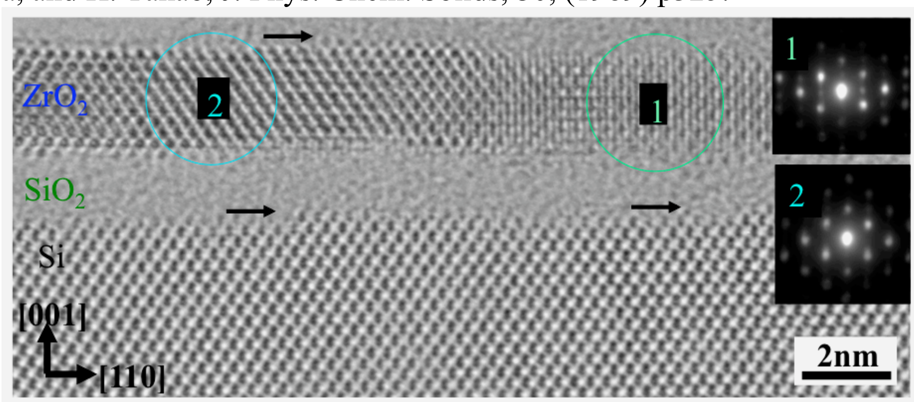

Figure 2. Cross-sectional image of ZrO_2 ultra-thin film.

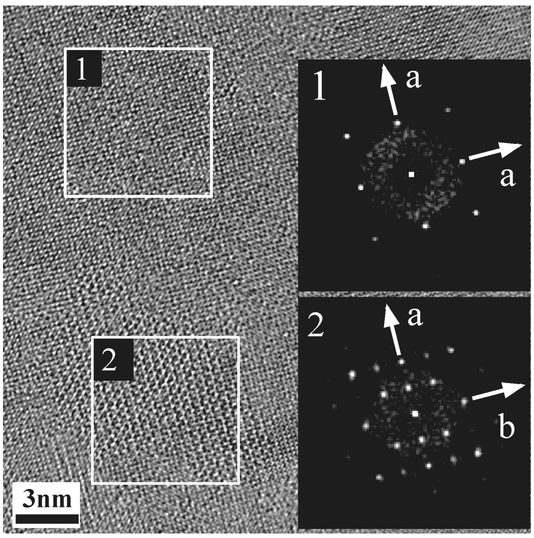

Figure 1. Plan-view image with diffractograms of each area of ZrO_2 ult thin film: the region (1) is matrix, and t region (2) is a precipitate.

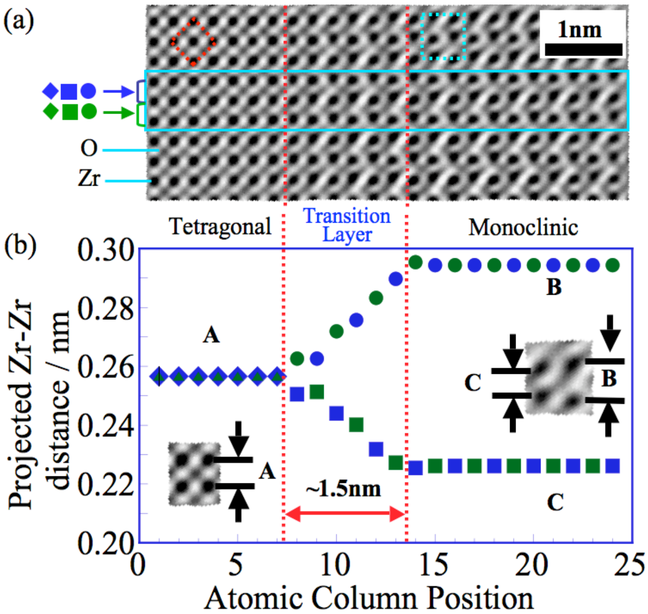

Figure 3. (a) HRTEM image around the tetragonal - monoclinic phase boundary and (b) the profile of the projected Zr-Zr distance across the phase boundary as a function of atomic columns in (a).

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