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Local structure of oxygen-deficient Yttrium oxide *

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Abstract: Yttrium oxide thin films have been deposited on Si (100) substrate by using pulsed laser deposition (PLD) method. X-ray diffraction (XRD), hard and soft X-ray absorption spectroscopy (XAFS) are employed to investigate the origin of oxygen vacancies and their influence on the structure and atomic distributions. The XRD results indicate that the Y_2O_3 thin films strongly orient the (111) axis of the cubic structure. Analyses on the Y K-edge extended X-ray absorption fine structures reveal that the coordination number of Y atoms decreases and the bond length of Y-O contracts due to the loss of oxygen atoms. The X-ray absorption near edge structure analysis together with a theoretical approach further confirms the oxygen vacancies formation and their possible location.

Key words: X-ray absorption spectroscopy, oxygen vacancy

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1 Introduction

The demand of increased performance of the metal oxide semiconductor field effect transistor (MOSFET) calls for further scaling device sizes. This downscaling needs the high-k dielectric to replace SiO_2 as the future gate dielectric material in order to decrease the direct tunneling leakage current while maintaining the same gate capacitance [1–3]. Among the materials investigated, yttrium oxide thin film has aroused great interest due to its excellent thermal and dielectric properties, such as the wide energy band gap (5.5 eV), the relatively high dielectric constant (13–18), the relatively high band offset (2.3 eV) with silicon substrate, the good thermodynamic stability, and the well-matched lattice constant with Si (a=10.6 Å being approximately two times the Si lattice parameter $a_{\rm Si}$=5.43 Å) [4, 5]. Therefore, yttrium oxide thin films have found important applications as dielectric layers in electroluminescent devices, CMOS devices and high-density dynamic random access memory [6].

However, it has been reported that high-k oxide can suffer from higher defect densities than the conventional SiO_2 dielectric layer. These defects are arguably the main cause for the degradation of Si carrier mobility, threshold voltage hysteresis, leakage current, and flat-band voltage shifting, and finally, the degradation of transistors [2, 7]. In particular, the oxygen vacancies have been identified as one main source of intrinsic defects in the high-k oxide films [8–12]. Recently, some reports have discussed the effect of oxygen vacancies in Y_2O_3 films on the structural and electrical properties [13, 14]. Except for the dielectric layer, Y_2O_3 is also one promising host material for the rare earth doped luminescent materials and solid-state lasers. Thus, oxygen vacancy in these luminescent films would change their luminescence property. Therefore, the quality and functionality of the yttrium oxide thin films critically depend on the presence of defects and their concentration. As defects have remarkable influence on the properties of Y_2O_3, it is necessary to understand the origin of such defects and the defect-property relation. When a vacancy is formed, a relaxation process will be involved in order to reduce the total energy of the system. This relaxation process naturally involves the redistribution of charges and the local structure change around Y and O atoms. Therefore, we can investigate the local structure change in films to confirm and detect the origin of oxygen vacancies.

In the present work, we provide concrete evidence of the existence of oxygen vacancies in yttrium oxide epitaxial layers on Si(100), grown by the PLD method. The XAFS technique at both Y-K edge and O-K edge is employed to study the local structure of Y_2O_3 films. We

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will take advantage of the sensitivity of the XAFS spectroscopy together with a theoretical approach to detect the origin of oxygen vacancies. These results may be helpful in further understanding their structural and electrical properties.

2 The experiment

A set of Y_2O_3 thin films was deposited on p-type Si (100) substrates using pulsed laser deposition (PLD) method. Targets were prepared by standard ceramic techniques (at 1200 ℃ in air for 5 h). The substrate with ρ=0.6∼1.2 Ωcm was first ultrasonically degreased with acetone, ethanol, and deionized water respectively. Then the substrate was etched in 10% HF solution for 1 min. The distance between the target and substrate was fixed at 65 mm during the deposition. Prior to the film deposition, the PLD chamber was pumped down to the vacuum condition with a base pressure under 3.7×10^4 Pa. Then the target was pre-sputtered by laser for 30 minutes to remove the surface contamination, while the substrate was gradually heated to the desired deposition temperature. During the film growth, the target and the substrate were rotated respectively. In this experiment, a KrF excimer laser (248 nm, 10 Hz) was operated with fixed energy 200 mJ, the substrate temperature was kept at 200 ℃ and 400 ℃.

The X-ray diffraction measurement was performed with a Level Goniometer using the Cu K α radiation (1.5406 Å) to characterize the crystalline structures of the deposited films. The Y K-edge XAFS spectra of Y_2O_3 thin films were measured in a grazing-incidence geometry with a grazing-incidence angle 1° at Beamline BL13B1 of Photon Factory (PF, KEK) of High Energy Accelerator Research Organization, Japan. The electron-beam energy of PF was 2.5 GeV and the maximum stored current was about 450 mA. The water-cooled Si(111) plane double-crystal monochromator and a Ge pixel array detector with 100 segments were used. The energy resolution was better than 2 eV at 9 keV, calibrated from the near-edge features of copper metal at the Fermi energy, Ef (8980.3 eV). The O K-edge XANES spectra were measured at Beamline U19 of National Synchrotron Radiation Laboratory, China. The beam from a bending magnet was monochromatized with a varied line-spacing plane grating and refocused by a toroidal mirror. An energy range from 100 to 1000 eV was covered with a resolution of about 0.2 eV. The data were recorded in the total electron yield (TEY) mode by collecting the sample drain current under a vacuum better than 5×10^{-5} Pa.

3 Results and discussion

Figure 1 shows the XRD spectra of the Y_2O_3 films deposited on the Si (100) substrates at 200 ℃ and 400 ℃ in the vacuum condition (3.7×10^{-4} Pa). It is observed that only one (111) diffraction peak is shown in the spectra and with increasing substrate temperature, the intensity increases while the full-width at half-maximum (FWHM) decreases. This result indicates that the crystallinity of the film becomes better with higher deposition temperature.

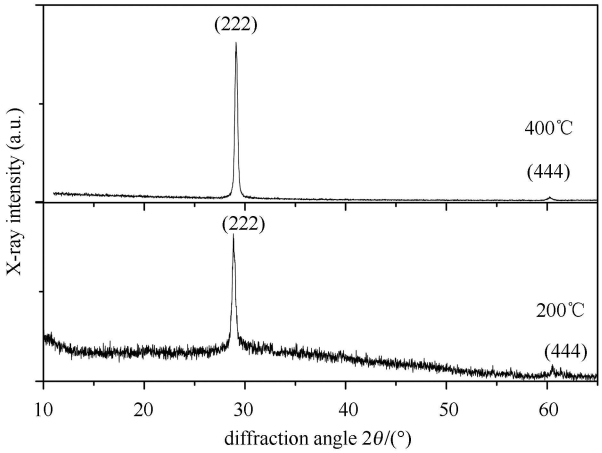

Fig. 1. The XRD patterns for Y_2O_3/Si (100) films grown at various substrate temperatures.

EXAFS has been accredited as one precise method for molecular structural characterization. This technology could provide detailed information on the local structure around a specific atom, such as the coordination number and the fluctuation in bond length. Such microcosmic information cannot be obtained by conventional XRD measurement [15, 16]. Therefore, the Y K-edge extended-XAFS (EXAFS) was used to investigate the local environment of Y_2O_3 films. The cube Y_2O_3 powder was also measured as a reference. The data were analyzed using the IFEFFIT program performed in the ATHENA and ARTEMIS packages [15, 16]. The EXAFS oscillations $\chi(k)$ weighted by k^3 are shown in the set of Fig. 2. Many differences can be obviously observed in their shape and amplitude between the powder and films, implying they have different local structures. A Fourier transform (FT) of all spectra is performed and the magnitude of the FT result is displayed in the main part of Fig. 2.

As mentioned above, Yttria has the cubic bixbyite structure, attributed to the Ia3d space group (No.206) with the lattice parameter a=10.60 Å [17]. In this cubic structure, Y is surrounded by the first coordination shell with six oxygen atoms, and has a range of interatomic distances with an average value of 2.295 Å. The second and third neighbors are Y atoms, each of which includes six Y atoms located at approximately 3.516 Å and 4.0 Å respectively [18]. As shown in Fig. 2, the Y_2O_3 powder and films exhibit three FT peaks located around 1.7

Å, 3.1 Å, and 3.8 Å, respectively. The first peak corresponds to the nearest neighbors of the absorber atom, a Y-O shell in the structures, while the second and third peaks correspond to the Y-Y shells. It can be clearly seen that both Y_2O_3 films have a similar signal to that of the Y_2O_3 powder. However, one remarkable change is that the intensity of film is gradually decreased and the Y-O peak gradually shifts to lower distances. This can be interpreted qualitatively like the local structure of films undergoes disordering.

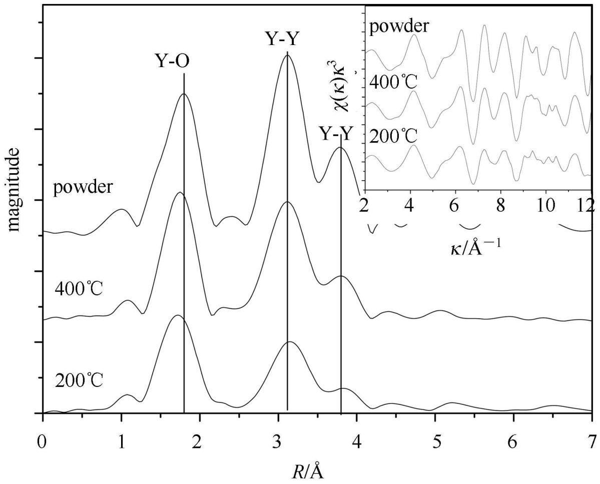

Fig. 2. Magnitude of the Fourier transform of the Y edge EXAFS for the Y_2O_3 films and yttria powder; Inset: the k^3-weighted EXAFS signal $\chi(k)k^3$.

In order to obtain quantitative structural information, the EXAFS datas are fitted in k space within a Kaiser-Bessel window from 1.1 Å to 2.2 Å, just including the first coordination Y-O shell. The scattering amplitudes and phase-shift functions used are extracted from the FEFF calculation [19]. A quantitative curve-fitting analysis is performed and the best fitting curves are obtained as illustrated in Fig. 3 (the solid lines). The fitting numerical results including the coordination number CN, the average interatomic distance R, and the Debye-Waller disorder factors σ^2 of the first coordination shell (Y-O) around yttrium atoms, obtained from the EXAFS data fitting, are summarized in Table 1.

Table 1. Structural parameters of the first (Y-O) coordination shell around yttrium atoms of samples obtained from the EXAFS data modeling.

sample	bond	CN	R/Å	σ^2/Å^2
powder	Y-O	6	2.286	0.0049
film-400 ℃	Y-O	5.33	2.254	0.0059
film-200 ℃	Y-O	5.15	2.267	0.0074

From the fitting results of Y_2O_3 powder, we can see that an yttrium atom is octahedrally coordinated with six oxygen atoms, which constitute the first coordination shell. All O atoms lie at an average distance of 2.286 Å, in agreement with the value 2.295 Å of standard cubic Y_2O_3 structure, as discussed above. For the Y_2O_3 film samples, the fitting results are similar to those of powder, indicating that they have a similar cubic structure, consistent with the above XRD results. However, the coordination number is less than 6 and the bond length contracts in film structure. The lower coordination number and shorter bond length obtained should be attributed to the loss of oxygen atoms, suggesting the oxygen vacancies formation around the Y atoms. Due to the lattice distortion derived from the local strain field, the presence of vacancies would in turn result in the decrease of the interatomic distance while in the increase of disorder factor. Therefore, it is reasonable to consider that the point defects associated with oxygen vacancies have been formed in the Y_2O_3 film when grown in the oxygen deficiency condition.

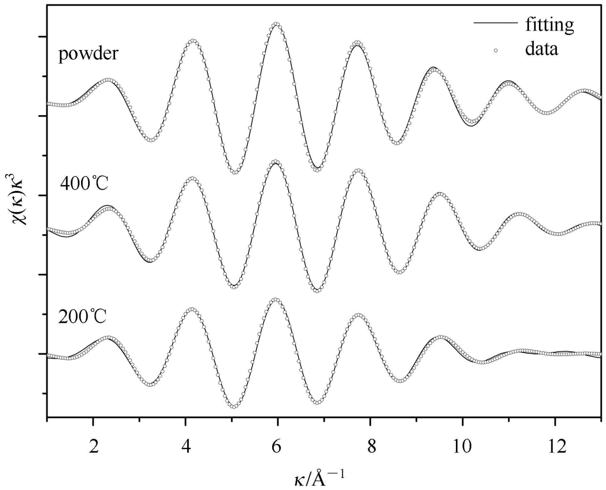

Fig. 3. The fitting results of the first Y-O shell in k space for the Y_2O_3 films and yttria powder, the dotted line: the experimental data; the solid line: the fitted curve.

It is well known that the XANES spectroscopy is more sensitive to the three-dimensional atomic arrangement and electronic structures around the absorbing atoms; probably it is able to provide more currently unavailable information on the defects [20]. For this purpose, we plot the O K-edge XANES experimental spectrum of Y_2O_3/Si (100) films in Fig. 4. One can clearly observe the fine structures a, b, and c at the threshold located at 531.2eV, 536.2 eV, and 540.4 eV respectively, already noted in the picture. Although the deposition temperature is different, both Y_2O_3 films exhibit quite similar XANES features, indicating they have similar local structures, in agreement with the results discussed above.

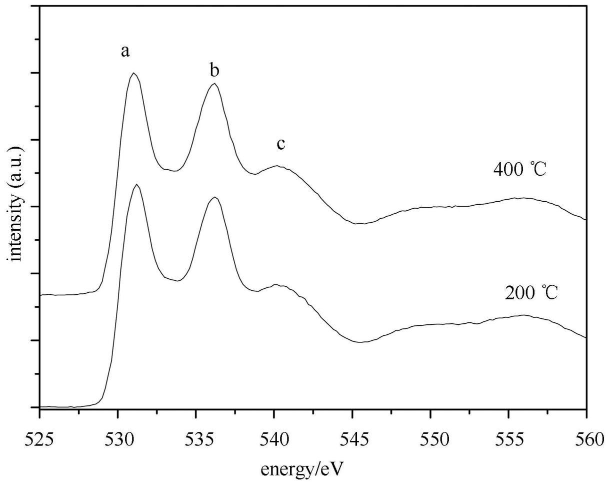

Fig. 4. The O K-edge XANES spectra for Y_2O_3 films.

In order to interpret the XANES features and investigate the origin of oxygen vacancies, one-electric real space full multiple scattering XANES calculations realized on a 37-atom cluster at O K-edge were performed using the FEFF 8.2 code [21]. To account for the experimental energy resolution, a Gaussian function (FWHM=0.3 eV) is performed during calculation, and the result obtained is illustrated on top of Fig. 5(a). It is observed that its main structures including a, b and c obtained from calculation agree well with the experimental data, which is also illustrated at the bottom of Fig. 5(c). The first two peaks a and b are the contributions from the tetrahedral environment of the oxygen atoms. It is reported that the local crystal field splits the Y d orbital into t_1u and e_g orbitals, which when hybridized with O 2p orbital give rise to the twin structure a and b in the O K edge [13]. However, one remarkable point is the reversal of intensity of the main structure a and b between the calculation (a) and experimental spectra (c). It has been reported by F. Pailloux, that two oxygen atoms located between 4.534 Å and 4.567 Å (N=28 and 29) play an important role in the relative intensity of these two peaks [22]. The introduction of oxygen vacancies would lead to a reversal for both main peaks, because of the disturbance of the octahedral symmetry. Therefore, another cluster introducing two oxygen vacancies is used to calculate under the same condition, and the result is plotted in the middle of Fig. 5(b). We can see that the balance of the two main peaks is reversed, and this curve obtained is in pretty good agreement with the experimental result (c). Furthermore, because two oxygen vacancies are introduced, the coordination number of yttrium atom in its first neighbor shell is less than 6, which agrees well with the EXAFS result mentioned above. Based on the above discussion, it is verified that the oxygen vacancies have been formed in Y_2O_3 films when grown in vacuum chamber condition.

When oxygen vacancies are formed, the strongly distorted local structure around the oxygen vacancy may give a shallow energy level, because the energy level of the vacancy state is shallower. Therefore, the existence of oxygen vacancies could greatly affect the physical properties originating from the change of the electron band structure. Furthermore, the oxygen vacancies will become one main source of intrinsic defects, which will degrade the carrier mobility, increase the leakage current and finally result in the transistors degradation [7–10].

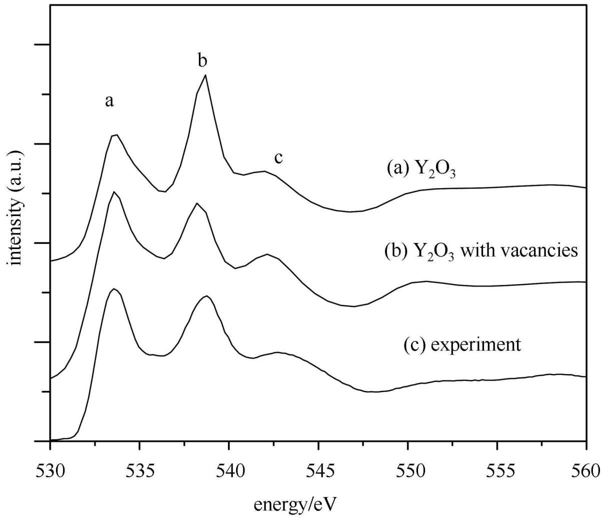

Fig. 5. Comparison between the experimental curve and the theoretical spectra with different models.

4 Conclusions

Yttrium oxide films were prepared by pulsed laser deposition in the vacuum condition. We have investigated the effects of oxygen vacancies on the structure and Y-O bonding environments by using XRD and Y K-edge extended-XAFS. XRD analysis shows that the Y_2O_3 thin films strongly oriented their (111) axis of the cubic structure. The EXAFS results confirm that the coordination number is lower and the bond length contracts around Y atoms due to the loss of oxygen atoms. The O K-edges XANES together with a theoretical approach is employed to study the local structure in Y_2O_3 films. The structure model in the best agreement with the experimental result further confirms that oxygen vacancies have been formed in the Y_2O_3 thin films.

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