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EELS study of oxygen superstructure in epitaxial Y_2O_3 layers

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Abstract

The superstructure found in epitaxial Y_2O_3 layers on (0 0 1)Si is examined by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). The oxygen K-edge is measured by EELS both on the superstructure and a defect-free region of the Y_2O_3 layers and they are compared to EELS spectra obtained from bulk stoichiometric and reduced Y_2O_3. It is shown that during epitaxial growth of Y_2O_3 on (0 0 1)Si in UHV, oxygen vacancies order into a superstructure creating non-stoichiometric regions in an otherwise stoichiometric Y_2O_3 layer. Furthermore it is shown that oxygen deficiency introduces a change of the density of states of the lower conduction band of Y_2O_3 and a decrease of its electronic gap by 0.8 eV.

Keywords: Y_2O_3; Epitaxy; EELS

1. Introduction

Recent work on Y_2O_3 films has been devoted on electronic applications as part of metal-oxide-semiconductor (MOS) heterostructures. Because of its relatively high dielectric constant κ (13–18), high conduction band offset ($\sim$2.3 eV) and thermal stability with silicon, Y_2O_3 is a promising candidate for replacing SiO_2 as a gate dielectric in MOS transistors [1–4]. Many of these interesting unique properties of Y_2O_3 depend critically on the presence of defects and their concentration [5]. In particular, the presence of oxygen vacancies in bulk Y_2O_3 has been proven to affect its electronic structure [6] and its electrical [7] and mechanical properties [8]. It should be noted that oxygen vacancies in candidate metal oxide high-k gate dielectrics generate a high density of fixed oxide charges. This is expected to cause intolerable variations (a few tens of meV) in the threshold voltage degrading the reliability of future transistors. In addition, charged defects in the metal oxide dielectric located near the interface could produce excessive Coulomb scattering of carriers decreasing the channel mobility of these devices. Despite their importance, detailed information about these defects in Y_2O_3 thin films is still lacking. In the course of previous work [9,10], we found that several regions of the Y_2O_3 layers produced by molecular beam epitaxy (MBE), contained a superstructure which we assigned to ordering of oxygen vacancies. A similar type of superstructure has been observed previously [11,12] for the Y_2O_3/Si system, but no explanation of its origin has been given.

In the present work, we provide concrete evidence of the existence of oxygen vacancies in epitaxial layers on (0 0 1)Si, grown by MBE. We furthermore show that these vacancies order into a superstructure. We use transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) in order to study the nature of these defects and clarify their origin. The oxygen K-edge is measured by EELS both on the superstructure and a defect-free region of the Y_2O_3 layers and they are compared to EELS spectra obtained from bulk stoichiometric and reduced Y_2O_3.

2. Experimental

Pure Y_2O_3 powder, commercially available, was annealed in oxygen ambient at 1400 °C for 24 h to remove any intrinsic oxygen vacancies, resulting in white powder stoichiometric samples. The same commercially available powder was annealed in vacuum ($\sim 10^{-7}$ Torr) for 1 h by electron beam bombardment in order to produce black, reduced samples for which a large number of oxygen vacancies are expected.

The Y_2O_3 layers were grown on (0 0 1)Si semi-insulating substrates by e-gun evaporation of a powdered target of yttria, in an UHV chamber (base pressure $\sim 2 \times 10^{-10}$ Torr). The thickness of the grown Y_2O_3 layer is 40 nm. Details of the growth procedure are given elsewhere [9,10].

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The EELS experiments were carried out in a Philips CM20 TEM equipped with a Gatan GIF200 post-column filter. The EELS experiments were carried out on regions of the samples thinner than 25 nm in order to avoid plural scattering effects. The spectra were recorded with an energy dispersion of 0.1 eV/channel and an energy resolution at zero loss peak of no more than 1.2 eV (full-width at half maximum). In order to avoid effects from specimen drifting, several spectra were accumulated correcting the specimen position in between measurements.

3. Results and discussion

Structural characterization of the layers, by X-ray diffraction and TEM, showed that they are epitaxially grown on (0 0 1)Si. However, the layer is made up of regions with two distinct crystallographic domains which both have (1 1 0)Y_2O_3//(0 0 1)Si while they are rotated by 90° with respect to each other, i.e. [0 0 1]Y_2O_3//[1 1 0]Si and [0 0 1]Y_2O_3//[$\bar{1}$ 1 0]Si. A superstructure with period 1.326 nm is also present in domains of the second orientation of the layers [9,10]. Fig. 1 is a bright field image of cross-sectional TEM showing the Y_2O_3/Si system and revealing this superstructure. In the inset of Fig. 1, the selected area electron diffraction (SAED) pattern of the sample is presented, showing the spots corresponding to the superstructure. Detailed analysis of the diffraction pattern is given in reference [9]. Fig. 2 is a HREM image of the superstructure region.

Fig. 3 shows the EELS oxygen K-edge after background subtraction, recorded from the defect-free region and the superstructure of an Y_2O_3 layer epitaxially grown on (0 0 1)Si. These regions are marked in the micrograph of Fig. 1. The experimental oxygen K-edge from the defect-free region contains two sharp structures a and b at 536.7 and 540.9 eV and a shoulder c at 545.3 eV. The shape of the spectrum from the superstructure is the same and the two peaks a and b are still present but their balance is reversed, while shoulder c is more pronounced. Furthermore, the threshold energy of this edge is shifted towards smaller energies by 0.8 eV. An estimate of the oxygen vacancies present in the superstructure region of the layers, is made by quantification of the spectra shown in Fig. 3. Assuming that the defect-free regions of the layers are fully stoichiometric, the superstructure regions contain approximately 7% less oxygen. Since the unit cell of Y_2O_3 contains 96 oxygen atoms, the unit cell in the superstructure regions has approximately seven oxygen vacancies.

These results are in very good agreement with previously published work [6]. The shape of the spectrum from the defect-free region is very similar to that obtained by EELS from pure bulk Y_2O_3 [13]. There is no published EELS data on non-stoichiometric Y_2O_3, however, X-ray photoelectron spectroscopy (XPS) measurements carried out on reduced bulk Y_2O_3 [6], produced results similar to those obtained from the superstructure.

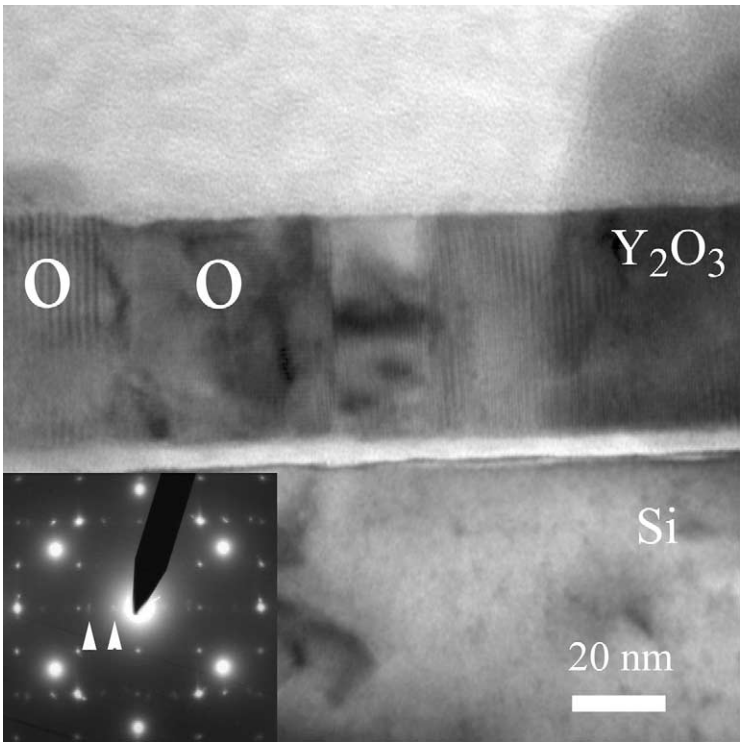

Fig. 1. Bright field image of cross-sectional TEM showing a Y_2O_3 layer grown epitaxially on (0 0 1)Si. Oxygen vacancy ordering is shown as superstructure in some regions of Y_2O_3 layer. The SAED pattern of the sample is shown in the inset. Diffraction spots corresponding to the superstructure are marked by arrows. Circles mark the regions from where EELS were recorded.

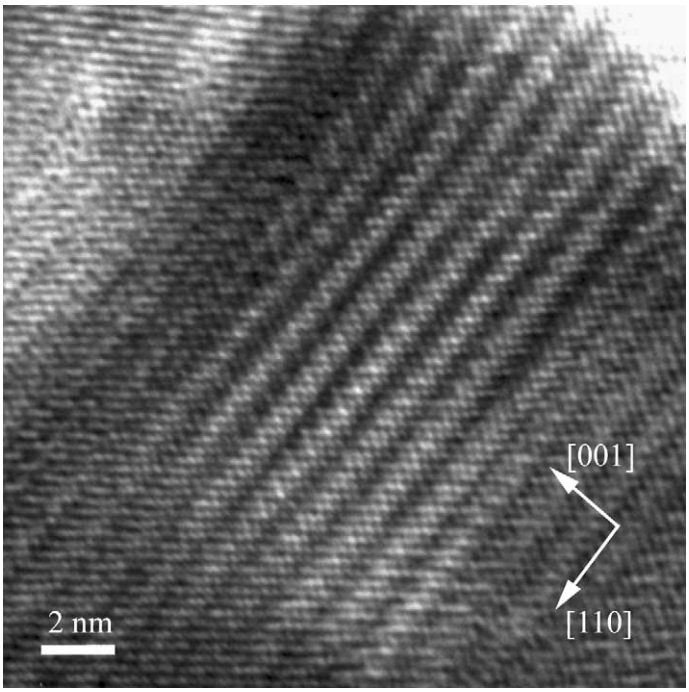

Fig. 2. HRTEM image of the superstructure of a Y_2O_3 layer.

The modulations in O K-edge shown in Fig. 3, reflect mainly the density of O 2p states which hybridized with Y orbitals form the Y_2O_3 conduction band. The two peaks a and b are said to be the signature of the tetrahedral arrangement of the oxygen atoms, while no explanation of the origin of peak c is reported [14]. Hence the similarity between the shape of the oxygen K-edge in Y_2O_3 and in various isoelectronic oxides, such as La_2O_3 and Gd_2O_3 [15] as well in ZrO_2 [16]. In the fluorite-like lattice of Y_2O_3, each yttrium atom occupies a strongly distorted octahedral site with oxygen atoms occupying six of the eight corners of a cube around it. It is expected that local crystal field splits the Y d-orbital into t_{1u} and e_g orbitals, which hybridized with O 2p orbitals give rise to the twin structure in the O K-edge [14,16]. Theoretical calculations [6,14], of the local density of states on the oxygen atoms both on stoichiometric and reduced Y_2O_3, reproduce quite well the shape of the O K-edge. Furthermore it is predicted [6], that the introduction of oxygen vacancies leads to a reversal of the balance of the two main peaks because of the disturbance of the octahedral symmetry of the yttrium atoms, in very good agreement with our experimental results shown in Fig. 3. It should be noted, however, that these theoretical calculations underestimate by almost 60% the width of the local density of states when compared with both, ours and previously published [6,13] experimental results.

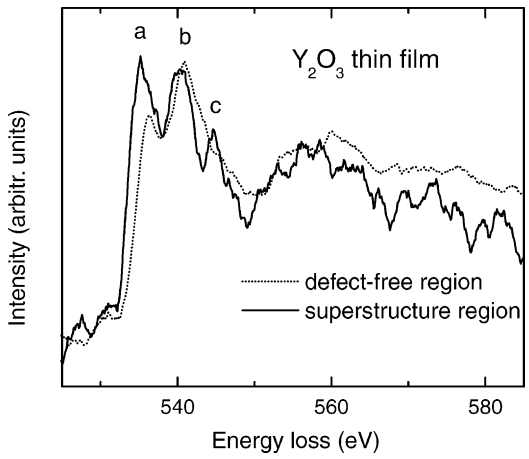

Fig. 3. EELS oxygen K-edge after background subtraction, of a defect-free region and a superstructure region of an Y_2O_3 layer epitaxially grown on (0 0 1)Si.

Finally, we comment on the shift of 0.8 eV of the K-edge of the superstructure compared with that of the defect-free region of Y_2O_3 layer as shown in Fig. 3. Theoretical calculations on the effect of oxygen vacancies on the ionic charge distribution in Y_2O_3 [6] show that there is a tendency toward a more covalent bond between oxygen and yttrium and a decrease of about 0.5 eV of the electronic gap, when oxygen vacancies are introduced. We, therefore, expect that the shift toward smaller energies we measure in the K-edge of the superstructure, is a manifestation of the decrease of the electronic gap induced by the non-stoichiometry.

Based on the above considerations, we opine that during epitaxial growth of Y_2O_3 on (0 0 1)Si, in UHV, oxygen vacancies are introduced into the layer and order into a superstructure creating non-stoichiometric regions in an otherwise stoichiometric layer.

The existence of oxygen vacancies in oxide layers deposited in UHV is expected since during evaporation, the oxide decomposes and some of the oxygen is pumped away.

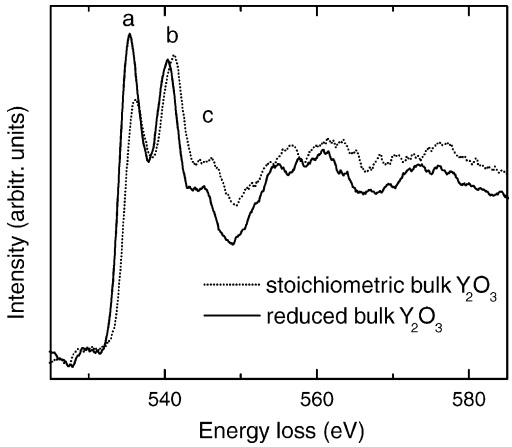

Fig. 4. EELS oxygen K-edge after background subtraction of stoichiometric and reduced bulk Y_2O_3.

The reason of ordering of the vacancies is not, however, clear. We believe that this ordering is related to the minimization of the stress due to the mismatch of the two lattices during the epitaxy of Y_2O_3 on (0 0 1)Si. Ordering of vacancies creates a superstructure with periodicity along the [0 0 1] Y_2O_3, of $a_{\text{sstr}} = 1.326\,\text{nm} = (5/4)a$, where $a = 1.06\,\text{nm}$ is the lattice constant of Y_2O_3. Moreover the minimum distance between Si atoms along this direction is $d_{220\text{Si}} = 0.192\,\text{nm}$. Hence, the mismatch with Si, calculated as $(7d_{220\text{Si}} - a_{\text{sstr}})/a_{\text{sstr}}$, is reduced from 8 to 1.3%. We note that the unit cell of Y_2O_3 is made up of $4 \times 4 \times 4 = 64$ minicubes, each containing one Y atom surrounded by six O atoms and therefore, the superstructure unit cell is made up of five minicubes along [0 0 1] Y_2O_3. Further evidence to the fact that vacancy ordering is induced by the epitaxy on (0 0 1)Si, is that no superstructure has been observed in bulk non-stoichiometric Y_2O_3. To further corroborate the above conclusions, we measured the EELS oxygen K-edge of stoichiometric and reduced bulk Y_2O_3, shown in Fig. 4, which is in agreement with previously published EELS and XPS results on Y_2O_3 [6,13]. By comparing Figs. 3 and 4, it is evident that the spectrum corresponding to the stoichiometric bulk Y_2O_3 has the same shape with that from the defect-free regions of the thin film, while the spectrum from the reduced bulk Y_2O_3 with the one obtained from the superstructure of the Y_2O_3 thin film. Consequently, it is verified that the oxygen stoichiometry determines the balance of the peaks a and b and that the superstructure of the Y_2O_3 thin film is oxygen deficient.

4. Conclusion

We have measured by EELS, the oxygen K-edge of stoichiometric and reduced Y_2O_3 both in bulk and thin film form. Our results show that during epitaxial growth of Y_2O_3 on (0 0 1)Si in UHV, approximately 7% oxygen vacancies are introduced into the layer, ordering into a superstructure and creating non-stoichiometric regions in an otherwise stoichiometric Y_2O_3 layer. We believe that this ordering is related to the minimization of the mismatch stress during the epitaxy of Y_2O_3 on (0 0 1)Si. The oxygen deficiency introduces a change of the density of states of the lower conduction band of Y_2O_3 and a decrease of its electronic gap by 0.8 eV, in agreement with previously published theoretical calculations.

Acknowledgements

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