High oxidation state at the epitaxial interface of γ -Al₂O₃ thin films grown on Si(111) and Si(001)

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High resolution synchrotron radiation x-ray photoelectron spectroscopy allowed us to identify the chemical bonding at the interface between epitaxial γ -Al₂O₃ and Si substrate. The experiments were performed on 1 nm thick epitaxial γ -Al₂O₃ layers grown on both Si(111) and Si(001) substrates. In both cases, the Si 2*p* core level decomposition recorded at photon energy of 160 eV provided evidence for the absence of Si²⁺ and Si³⁺ species and the presence of two different Si⁴⁺ species. A microscopic model is proposed for the interface obtained with two incomplete SiO₂ planes based on the Si 2*p*_{3/2} line shape. © 2010 American Institute of Physics. [doi:10.1063/1.3499280]

Nowadays, due to numerous promising applications in the microelectronic and nanotechnology fields, the growth of well crystallized oxide thin films on silicon is the subject of intense research activity.¹

To reach this objective, growth conditions must be found to obtain a high crystallographic quality of the oxide while maintaining a sharp interface with respect to Si.² Among the oxides of interest, Al₂O₃ presents some important advantages for interface engineering on silicon.³ Al₂O₃ is stable on silicon at temperatures and oxygen pressures up to 900 °C and 10⁻⁵ Torr, respectively.^{4,5} If combined with some high- κ oxides, this could provide an interesting way to reach small equivalent oxide thickness in complementary metal-oxide semiconductor devices.⁶

Moreover, the interest of studying and controlling the growth of alumina on silicon goes far wider because it could be part of complex oxide/semiconductor heterostructures and as a result, open the way to the integration of high performance micro-optoelectronic functionalities on Si wafers.⁷

Al₂O₃ grows on silicon with a spinel-like structure (γ -Al₂O₃), and a lattice parameter $a_{\text{Al}_2\text{O}_3}$ of 0.791 nm. Despite an apparently large lattice mismatch of -31% with silicon, epitaxy is possible and occurs due to the spontaneous onset of favorable indirect epitaxial relationships.⁴ On both Si(111) and Si(001) substrates, γ -Al₂O₃ is (111) oriented⁴ with two in-plane orientations⁸ and four in-plane orientations,⁵ respectively.

Although many interesting structural studies have been reported recently on the growth mode, orientation, and epitaxial relationship, little attention has been focused on the chemical nature of the heterointerface. Knowing if γ -Al₂O₃ is connecting via an oxygen sublattice or an Al sublattice with Si is highly crucial in semiconductor technology applications. However, the atomic structure connecting the crystalline γ -Al₂O₃ with the Si substrate remains unknown.

In this context, we have investigated the high resolution x-ray photoelectron spectroscopy (HRXPS) of the Si 2*p* core level induced by tunable synchrotron radiation to identify the chemical bonding at the epitaxial γ -Al₂O₃/Si inter-

face. In the past, this experimental technique has provided valuable information on the microscopic structure of the amorphous SiO₂/Si system. It has the advantage of resolving the oxidation states of Si atoms in the interface layer via the chemical shift in the Si 2*p* core level.^{9,10} In addition to the fact that the elemental silicon component Si⁰ was not bonded to oxygen, the Si 2*p* core level spectra showed four distinct peaks about 0.9 eV apart, which are characteristic of the interface region. The so-called suboxide states, denoted by Si¹⁺, Si²⁺, Si³⁺, and Si⁴⁺, thus correspond to a silicon atom surrounded by an increasing number of oxygen ligands, ranging from one to four. Recently two more components (denoted α and β) were required to obtain good agreement in the fitting procedures, α and β being located at the low and high binding energy tails of the bulk peak, with a binding energy shift of -0.25 eV and 0.2 eV, respectively.¹¹ These components were attributed to strained interfacial Si without any Si-O bonds, due to the presence of the SiO₂ film. Contracted bonds gave negative shifts and contributed to the Si ^{α} and elongations bonds caused shifts toward higher binding energies, at the origin of the Si ^{β} component.¹² The oxidation states of Si at the SiO₂/Si interface are by now well understood and it will be very useful to understand the connections at the interface between epitaxial γ -Al₂O₃ and Si.

The 1 nm thick epitaxial γ -Al₂O₃ layers studied here were grown on Si(111) and Si(001) in a Riber 2300 molecular beam epitaxy reactor equipped with a 30 kV reflection high energy electron diffraction (RHEED) system. The Al₂O₃ films were prepared by electron gun evaporation of single crystal Al₂O₃ under molecular oxygen. The growth rate of Al₂O₃ was followed *in situ* using a mass spectrometer. RHEED and atomic force microscopy studies have shown that high quality γ -Al₂O₃ layers are possible on both Si(111) and Si(001) substrates for growth temperatures above 900 °C and oxygen partial pressures around 10⁻⁵ Torr. Further details of the growth procedure are presented elsewhere.⁴

After growth, samples were transferred *ex situ* to the SOLEIL synchrotron. HRXPS were carried out on the soft-x ray beamline (TEMPO). The end-station is equipped with a high-performance SCIENTA-SES 2002 electron analyzer.

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In order to remove all carbon and SiO₂ contamination from the surface, caused by the *ex situ* transfer and sample cleaving, samples were annealed at 750 °C for 2 h under ultrahigh vacuum (pressure lower than 2×10^{-10} Torr in a preparation chamber connected in ultra high vacuum with the analyzer). As the annealing temperature was lower than 900 °C (growth temperature), any changes in the Al 2*p* and Si 2*p* core levels were observed before and after annealing; only the carbon component was completely removed. Measurements were performed at normal emission. A photon energy of 160 eV was chosen to achieve high interface sensitivity. Under these experimental conditions, the photon energy and electron energy resolutions were better than 40 meV.

The quality of epitaxial growth had previously been confirmed by x-ray photoelectron diffraction of Al 2*p* and O 1*s* photoelectrons performed on the same samples.⁵ Moreover, on the Al 2*p* core level there was only one sharp and strong peak at 75 eV, the binding energy characteristic of a completely oxidized alumina film, without any sign of alumina suboxide (Al₂O_x) or metallic bonds with silicon (Al–Si).⁵

Figure 1 displays the photoemission Si 2*p* spectra recorded on a 1 nm thick layer of γ -Al₂O₃(111) epitaxially grown on Si(111) (a) and Si(001) (b). To improve the resolution of the various Si 2*p* components, the Si 2*p*_{1/2} spin orbit contribution is numerically removed, after background subtraction; we assumed a spin orbit splitting of 0.6 eV and Si 2*p*_{1/2}:Si 2*p*_{3/2} ratio of 0.5.⁹ The Si 2*p*_{3/2} spectra are fitted by sums of Gaussians convoluted by a Lorentzian of 0.085 eV full width at half maximum (FWHM).

On Si(111) the line shape [Fig. 1(a)] consists of six resolved components that correspond to the electron signals (B) attributed to the interior bulk, (α) –0.33 eV, (β) +0.31 eV, (Si⁺) +0.8 eV, and two (Si⁴⁺) components centered at 3.22 and 4.00 eV. However, on Si(001) [Fig. 1(b)] we observe seven components (B), (α) –0.33 eV, (β) +0.31 eV, (Si⁺) +0.9 eV, (Si³⁺) 2.54 eV, and two Si⁴⁺ components, 3.25 and 4.00 eV. All the energy positions are calculated with respect to the bulk line shape (B).

The main result to be extracted from these spectra is the absence of the Si²⁺ and Si³⁺ components on Si(111) and that of Si²⁺ on Si(001). This is not common behavior in the oxidation of silicon surfaces. This is due to the extremely good epitaxy of γ -Al₂O₃ on Si compared to the amorphous growth of SiO₂/Si.

With respect to the SiO₂/Si system,¹¹ the energy distance of α and β contributions from the B component on both surface orientations is higher. This difference results from the biggest lattice mismatch between γ -Al₂O₃ and Si, which imposes larger Si–Si bond-length variations in the Si surface substrate than in the case of SiO₂/Si.

We attribute the two components around 4 and 3.2 eV to silicon surrounded by four oxygen ligands, Si⁴⁺, but in a different configuration with respect to the Al atoms at the interface. The component at the higher binding energy of ~4 eV is attributed to Si bonded to four oxygen as first neighbors and four Si–O as second neighbors. The component at the lower binding energy of ~3.2 eV is attributed to Si bonded to four oxygen as first neighbors but to Al–O as second neighbors.¹³ The overall intensity of both components is 26% on Si(111) and 15% on Si(001) of the spectral weight. Quantitative analysis of the Si 2*p* spectra, taking into account the electron mean free path,⁹ shows that the

FIG. 1. Si 2*p* (gray solid line) recorded on 1 nm thick of epitaxial γ -Al₂O₃(111) on Si(111) (a) and on Si(001) (b). The photon energy tuned at $h\nu = 160$ eV for both samples (surface sensitive mode), with an overall experimental resolution better than 40 meV. The curve resulting from the fitting procedure (dark solid line) is compared to the Si 2*p*_{3/2} intensity (dots). The binding energy shift for each component is indicated in the figure, in relation to the bulk (b), the corresponding Gaussian width (between square brackets). The Gaussian FWHM of B, α and β are 0.32 eV. The Lorentzian width is 0.085 eV.

equivalent of only one monolayer (0.5 ML) of silicon atoms is oxidized at the Si(111) [Si(001)] interface with alumina. The Si⁺ components on both surface orientations are equivalent to 0.5 ML, estimated by comparing the Si⁺ peak at H₂O-exposed Si(001) as a reference. The Si³⁺ on Si(001) is very weak and less than 0.3 ML.⁹

In order to understand this behavior a simple schematic diagram of an ideal epitaxial interface between Al₂O₃ and both Si(111) and Si(001) surfaces are presented in Figs. 1(a) and 1(b), respectively. This ideal interface is created taking into account the results of the fitting procedure on the Si 2*p* peak. On Si(111), the absence of Si²⁺ and Si³⁺ components can be presented as shown in Fig. 1(a). Si⁴⁺ atoms can be represented with two incomplete planes (denoted as plan A on the top, and plan B below) and residual Si⁺ species con-

nect the interface to the silicon bulk. On Si(001), two incomplete planes of Si^{4+} (plans A and B) followed by residual Si^{3+} and Si^+ similarly assure the connection with the Si bulk [inset Fig. 1(b)] of the interface layer.

The fact that not all the Si surface dangling bonds are satisfied at the surface is due to the large difference between the Si lattice (diamondlike) and $\gamma\text{-Al}_2\text{O}_3$ lattice (spinel-like). Our previous work on Si(111) has shown that an indirect epitaxial relationship between $\gamma\text{-Al}_2\text{O}_3$ and Si exists, formed by aligning two $\gamma\text{-Al}_2\text{O}_3$ unit cells with three Si unit cells. This leads to an effective lattice mismatch of -2.9% , much smaller than the cube-on-cube lattice mismatch that exceeds $+45\%$.⁴ The presence of interface defects and Si dangling bonds also correlates with electrical measurements taken on $\text{LaAlO}_3/\gamma\text{-Al}_2\text{O}_3(111)/\text{Si}(001)$ showing the presence of negative charges at the interface leading to a flat band voltage shift.⁶ The number of defects will be higher on Si(001) because of the lower stability of this interface during SiO_2 sublimation.¹⁴

In conclusion, we have presented experimental evidence of an extremely sharp interface between alumina and silicon for the two most common substrate orientations. HRXPS of the Si $2p$ core level does not show Si^{2+} and Si^{3+} coordination at the interface while only two Si^{4+} coordinated bonding at the interface originated in the equivalent of one ML of silicon atoms. The atomic configuration of the interface between Al_2O_3 and Si is obtained by two incomplete planes of SiO_2 .

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