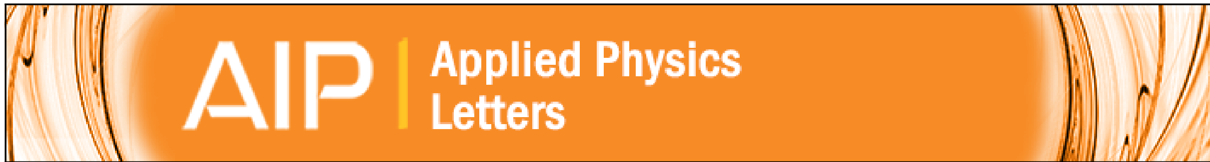

Composition, atomic transport, and chemical stability of $ZrAl_xO_y$ ultrathin films deposited on Si(001)

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Composition, atomic transport, and chemical stability of $ZrAl_xO_y$ ultrathin films deposited on Si(001)

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The stability of a $ZrAl_xO_y$ film sputtered on Si upon thermal annealing in vacuum or in O_2 was investigated. X-ray diffraction indicated that the as-deposited film was amorphous and remained so after annealing. Rutherford backscattering, narrow nuclear resonance profiling, and low-energy ion scattering provided the average composition of the film and the depth distributions of different elements. Chemical analysis of these elements was accessed by x-ray photoelectron spectroscopy. Annealing in vacuum produced thickness inhomogeneities and/or transport of very small amounts of Si from the substrate into the overlying film, with formation of Si precipitates. Annealing in O_2 led to oxygen exchange throughout the film, as well as Si transport in slightly higher amounts than in vacuum. Differently from the observed upon annealing in vacuum, Si was either incorporated into the Zr,Al–O framework or oxidized in SiO_2. © *2001 American Institute of Physics.*
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Replacing silicon dioxide as the gate dielectric material in standard Si-based complementary metal–oxide–semiconductor (MOS) technology constitutes an area of very lively research.[1] To reduce the concerns associated with leakage current at the gate in future high-performance commercial products, a material with a higher dielectric constant than that of SiO_2 (high-κ material) is required. Further requirements of gate dielectric materials are: (i) a sharp interface with the Si substrate, favoring a low density of interface states; (ii) a large band gap (comparable to that of SiO_2, 9 eV); (iii) a large energy barrier from the conduction band to the gate electrode (otherwise the leakage current will be unacceptably high despite the higher dielectric constant); and (iv) physicochemical and structural stability at both gate electrode/high-κ dielectric and high-κ dielectric/Si–substrate interfaces in further processing steps. For instance, most high-κ oxides follow an $E_g \propto 1/\kappa^2$ law,[2] according to which a higher dielectric constant is systematically accompanied by a smaller band gap. Al_2O_3 ($\kappa = 11$, $E_g = 8.9\,\text{eV}$) and ZrO_2 ($\kappa = 20$, $E_g = 6\,\text{eV}$) constitute exceptions to this rule as their dielectric constants are higher than that of SiO_2 and they still have large band gaps. Electrical characteristics, interface abruptness, and thermal stability of Al_2O_3 (Refs. 3 and 4) and ZrO_2 films[1,5–7] on c-Si have been addressed before, revealing very promising features. The synergistic use of the properties of Al_2O_3 and ZrO_2 films to engineer a candidate material for replacing SiO_2 has recently been proposed.[8] Ultrathin $ZrAl_xO_y$ films directly deposited on Si presented very low leakage currents as compared to SiO_2 films of the same equivalent oxide thickness, and other electrical characteristics were also very favorable.[8] It remains, however, the need for a detailed, atomic-scale understanding of the physicochemical characteristics of such gate structures as well as a description of their evolution upon thermal treatment. This is addressed here through ion-beam analysis and photoelectron spectroscopy.

In this work, a $ZrAl_xO_y$ film was deposited by reactive sputtering from a $Zr_{80}Al_{20}$ target in an oxygen-containing plasma onto a Si(001) substrate etched in a buffered HF solution. Independent, *ex situ* ellipsometry measurements indicated a thickness of approximately 8.3 nm for the as-deposited film. Postdeposition annealings were performed *ex situ* at 600 °C for 10 min, either in high vacuum ($\approx 10^{-5}$ Pa) or in 7×10^3Pa of dry O_2 enriched to 98.5% in the ^{18}O isotope ($^{18}O_2$). The use of O_2 enriched in the stable isotope of low natural abundance allows distinguishing oxygen eventually incorporated during annealing from that originally present in the film. X-ray diffraction using Cu $K\alpha$ radiation indicated that the as-deposited film was amorphous. The thermal treatments produced no detectable crystallization, as seen for ZrO_2 (Ref. 9) and Al_2O_3. We cannot rule out the existence of nanocrystallites, since the present x-ray diffraction method is not sensitive to nanocrystals of about 10 interatomic distances and less.

Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA) indicated the stoichiometry Zr_4AlO_9 for the as-deposited film. After annealing in vacuum, the amounts of Zr and O remained constant within experimental uncertainty ($\pm 5\%$). A small amount of Al was lost either by out-diffusion through the surface or in-diffusion into the Si substrate. After annealing in $^{18}O_2$: (i) the amounts of Zr and Al remained essentially constant; (ii) ^{16}O was substantially exchanged for ^{18}O, with net incorporation of oxygen into the film. RBS was also used to determine Zr profiles, showing rather uniform depth distributions and sharp interfaces with the Si substrate (within depth resolution).

Oxygen profiles were determined by means of nuclear resonance profiling (NRP) using the narrow and isolated resonance of the nuclear reaction $^{18}O(p,\alpha)^{15}N$ around 151

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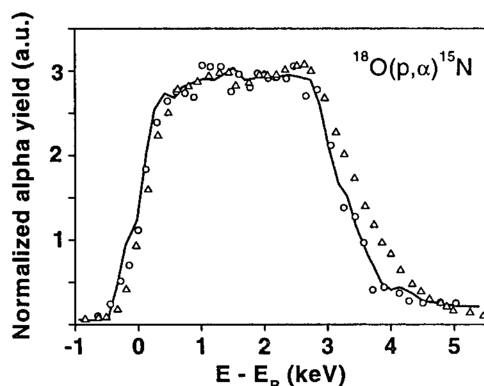

FIG. 1. (a) Normalized excitation curves of the nuclear reaction $^{18}O(p,\alpha)^{15}N$ around the resonance at 151 keV before and after thermal annealings. The line represents the as-deposited sample; circles and triangles correspond to the samples annealed in vacuum and in $^{18}O_2$, respectively.

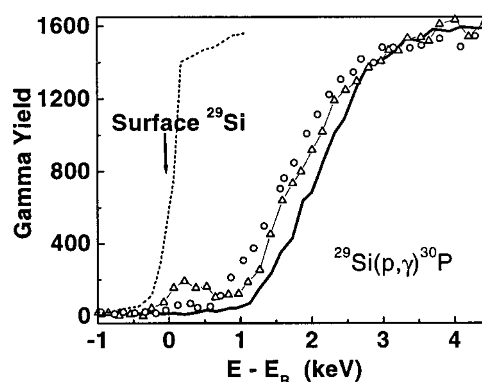

FIG. 2. Excitation curves of the nuclear reaction $^{29}Si(p,\gamma)^{30}P$ around the resonance at 414 keV before and after thermal annealings. Symbols are the same as in Fig. 1. Also shown is an excitation curve from a bare Si wafer, which establishes the energy position corresponding to Si at the sample surface (dotted line).

keV.[10] A 60° sample tilt was used in the present case, leading to a depth resolution of approximately 0.7 nm near the sample surface. Figure 1 shows normalized excitation curves, recalling that according to NRA results the ^{18}O concentrations in the as-deposited and vacuum-annealed samples are 0.2% of the total O concentrations, whereas in the $^{18}O_2$-annealed sample ^{18}O represents 67% of the total oxygen content. The excitation curves can be simulated using the program SPACES,[11] by assuming a certain depth distribution of ^{18}O. The ^{18}O profile for the as-deposited sample revealed an abrupt interface with the substrate within depth resolution. Simulations also indicated that annealing in vacuum did not significantly change the depth distribution of oxygen. ^{18}O incorporated during annealing in $^{18}O_2$ was evenly distributed within the whole film, evidencing a deeper and more diffuse interface with the substrate. According to Ref. 10, one can attribute the ^{18}O profile here observed to a mechanism whereby oxygen molecules from the gas phase diffuse through the oxide, either interstitially or by a simple diffusion mechanism, reacting with the Zr_4AlO_9 network and replacing ^{16}O atoms, which are released and can diffuse toward the surface passing to the gas phase. The even distribution of ^{18}O in the oxide indicates that diffusion-reaction rates are very high, leading to an equilibrium situation even for rather short annealing times in $^{18}O_2$.

Silicon profiles were determined by NRP using the narrow and isolated resonance of the nuclear reaction $^{29}Si(p,\gamma)^{30}P$ at 414 keV (Ref. 10) and a 60° sample tilt. Excitation curves are shown in Fig. 2, including an excitation curve from a bare Si wafer used to establish the proton energy showing Si at an outermost surface. Profiles obtained from simulations with SPACES revealed: (i) the absence of Si in the as-deposited film, consistently with an abrupt high-κ/Si interface; (ii) transport of a rather small amount of Si from the substrate into the high-κ film up to a region close to the surface upon annealing in vacuum; and (iii) transport of a larger amount of Si into the high-κ film up to the surface upon annealing in $^{18}O_2$. Transport of Si from the substrate across other deposited films during postdeposition annealing in oxygen has been reported.[3,12–16] This was confirmed here by a surface-selective, far more sensitive analysis using ion scattering spectroscopy (ISS),[17] as shown in Fig. 3. The ISS spectra of He^+ ions with incidence energy of 1.0 keV are shown for the as-deposited and $^{18}O_2$-annealed samples. The signal from Si is absent in the former, whereas it is clearly present in the latter.

Chemical analysis of the films was accessed by x-ray photoelectron spectroscopy. The Zr $3d$, O $1s$, Al $2p$, and Si $2p$ core levels were monitored with an overall resolution of 0.9 eV for 10 eV pass energy and using Mg $K\alpha$ x-rays. The great similarity between the Zr $3d$ photoelectron spectra of the as-deposited sample in the present work and of $ZrSiO_4$ (Ref. 18) indicates that the as-deposited film is a double oxide, namely, zirconium aluminum oxide (or Zr,Al–O), with an approximate composition Zr_4AlO_9, according to ion-beam analysis. Annealing in vacuum or in O_2 did not cause major changes in the Zr $3d$ core level. O $1s$ photoelectron spectra are shown in Fig. 4. The spectrum from the as-deposited sample has three components corresponding to O–Zr, O–Al, and O–Si bonding, centered at 531.0, 532.1, and 533.3 eV, respectively. Vacuum- and O_2-annealed samples display the same components, but in different proportions. Annealing in vacuum produced an increase in the intensity of O–Zr with respect to O–Al and O–Si, whereas annealing in O_2 led to

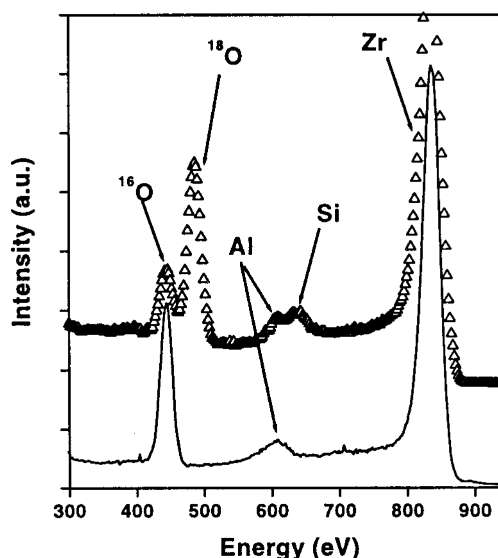

FIG. 3. Ion scattering spectroscopy (ISS) measurements for the as-deposited (bottom) and $^{18}O_2$-annealed (top) samples. The arrows indicate the position of the different atom species in the spectra.

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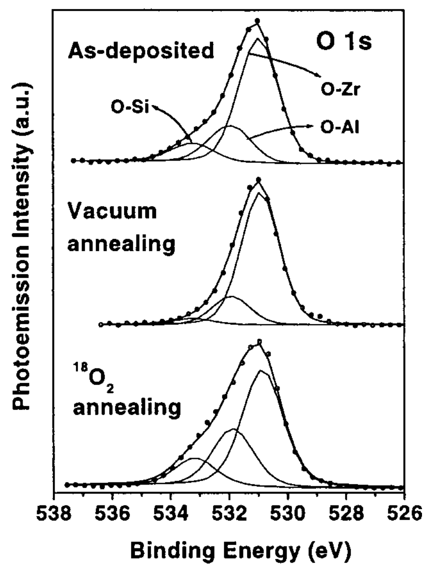

FIG. 4. O 1*s* photoelectron spectra for the as-deposited, vacuum-, and O_2-annealed samples. The components used in the fittings and the total fitting curve are also presented.

the opposite. Figure 5 shows Si 2*p* photoelectron spectra. From the as-deposited sample one notices the presence of Si–O bonding, centered at 102.8 eV binding energy (corresponding to SiO_2), and another component at 99.7 eV. This can be assigned to a silicate, either Si–Al–O or Si–Al–Zr–O at the near-interface region. A new component is observed in the vacuum-annealed sample (99.2 eV binding energy) that can be attributed either to the formation of Si–Si bonds or to thickness inhomogeneities.[16] The picture displayed by the Si 2*p* photoelectron spectra is consistent with that provided by O 1*s*: (i) annealing in vacuum reduces the proportion of Si–O bonding, while Si–Si bonding appears, indicating the formation of Si precipitates, and (ii) after annealing in O_2 the Si 2*p* photoelectron spectra can be fitted almost completely by the component corresponding to SiO_2.

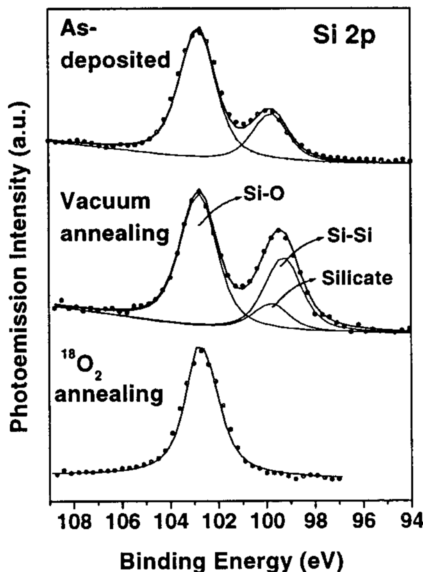

FIG. 5. Si 2*p* photoelectron spectra for the as-deposited, vacuum-, and O_2-annealed samples. The components used in the fittings and the total fitting curve are also presented.

In conclusion, when annealed in vacuum at the rather moderate temperature of 600 °C, Zr_4AlO_9 thin films deposited on *c*-Si display atomic transport of very small amounts of Si from the substrate into the oxide film, with formation of Si–Al–Zr–O alloys or Si precipitates. This may have deleterious consequences once a metal electrode is deposited on the film to form a MOS capacitor, as metal silicides and silicates form at the electrode/dielectric interface. Annealing in O_2 at the same temperature leads to oxygen exchange throughout the films, as well as Si transport from the substrate into the oxide. The moderate oxidation of the Si substrate here observed favors application of this material as a gate dielectric. Differently from the observed upon annealing in vacuum, the Si atoms that migrate to the near surface of the film are either incorporated into the Zr,Al–O framework or oxidized to SiO_2.

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