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Oxygen exchange and transport in thin zirconia films on Si(100)

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The composition and atomic depth distributions of ultrathin zirconia films (~ 30 Å) deposited on Si(100) have been investigated using medium-energy ion scattering (MEIS). Reoxidation in $^{18}O_2$ permits the oxygen incorporation, exchange, and mobility to be followed due to the isotope sensitivity of the MEIS technique. These quantitative studies showed that significant interfacial SiO_2 growth results when reoxidizing samples at temperatures as low as 500 °C, and that this growth saturates in time and pressure but increases with temperature. Substantial isotope exchange was also observed under various experimental conditions. The results are discussed taking into account published data on the bulk and grain boundary diffusion of O in monoclinic and tetragonal zirconia, the diffusivity of O in SiO_2, and the nanocrystallinity of the films.

I. INTRODUCTION

According to the 1999 International Technology Roadmap for Semiconductors,[1] an equivalent silicon oxide thickness of less than 15 Å will be needed for the gate dielectric in sub-0.1 μm complementary-metal-oxide-semiconductor (CMOS) devices. The critical problem with such aggressive scaling is that leakage currents due to direct electron tunneling across the SiO_2 will become prohibitive. To increase the gate capacitance while reducing the tunneling loss, alternative higher dielectric constant (high-K) materials are currently under intense investigation. Zirconia films (with dielectric constant $\epsilon = 12-25$ (Refs. 2 and 3)] satisfy many of the requirements needed to replace SiO_2 in future generation CMOS devices.[4,5] For instance, ZrO_2 and Zr silicates are thought to be stable on Si substrates at temperatures as high as 900 °C,[4] or in some cases even higher.[3] The high-temperature stability is necessary if high-K dielectrics are incorporated into a conventional CMOS process flow. The electrical characteristics of ZrO_2 and Zr silicates, demonstrating for example low leakage currents, have been discussed elsewhere.[3,5,6]

In order to minimize interface state defects and to optimize electrical characteristics, it is desirable to have at least one monolayer of SiO_2 at the interface to the substrate. SiO_2 formation at the interface has recently been discussed by Kawamoto *et al.*[7] in the framework of first-principles calculations, which indicated that the formation of an interfacial layer cannot be completely avoided. A consideration of Zr (and Hf) bond energetics indicated that tetragonal bonding to O is more favorable than silicidelike bonding, which would occur if no interfacial SiO_2 layer were present. However, since the total capacitance of a multilayer stack is dominated by the material with the lowest ϵ, it is desirable to minimize the thickness of any low-ϵ SiO_2 layer between the high-ϵ gate dielectric film and the Si(100) substrate.

A feature of metal-oxide gate dielectrics that has to be addressed is the compositional stability during thermal processes. For instance, annealing in an oxygen-containing atmosphere is a crucial step in forming the sidewalls of a CMOS gate. Accordingly, the annealing behavior of ZrO_2 films has been investigated by other research groups using electrical measurements,[5,6] ion scattering techniques,[4] and x-ray photoemission spectroscopy (XPS).[8] Heating in oxygen may be beneficial for the electrical properties of metal oxides (especially for films deficient in oxygen). A low oxygen partial pressure anneal may stabilize the films against decomposition.

Some phases of ZrO_2 and of many other metal oxides are excellent ionic conductors (of oxygen ions), possibly offering a supply of oxygen to the interface ultimately forming SiO_2. This paper presents the first direct measurements of the oxygen mobility in ultrathin ZrO_2 gate dielectrics demonstrating both oxygen exchange in ZrO_2 films and interfacial SiO_2 growth.

II. EXPERIMENTAL

Thin zirconia films (~ 30 Å) were produced at the University of Texas at Austin by magnetron sputtering under experimental conditions described elsewhere.[5] The samples were reoxidized at Rutgers in a single-walled electronics-grade quartz tube to investigate oxygen exchange and interfacial SiO_2 growth. The system had a base pressure in the 10^{-10} Torr range. The quartz tube could be heated up to 1100 °C. The standard processing procedure to clean the quartz tube before performing the reoxidation was to evacuate the system to $\sim 10^{-9}$ Torr using a turbo pumping stage, and bake the quartz tube to ~ 900 °C for several hours. During the baking, a few Torr of oxygen was added for ~ 1 h. We found that this procedure helped remove residual hydrocarbon contamination. A LN_2 cold trap further reduced water traces. Samples were oxidized in either dry $^{16}O_2$ or 98% isotopically enriched $^{18}O_2$. The temperature ramp-up time of the quartz tube was typically 3–6 min for processing temperatures up to 800 °C. ZrO_2 films were reoxidized with a range of temperatures (300–800 °C), pressures

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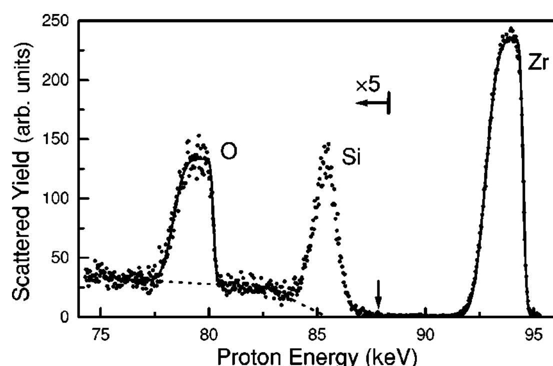

FIG. 1. MEIS proton backscattering spectrum from the as-deposited ZrO_2 film on Si(100). Signals from O, Si, and Zr are clearly resolved. The solid lines show the simulation for the film described in the text. The dashed line represents the background subtraction. The arrow near 88 keV indicates the energy where surface Si would be detected.

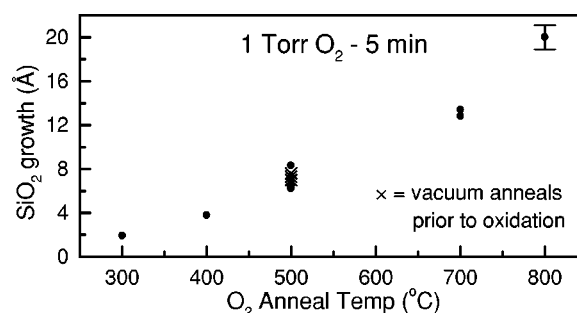

FIG. 2. The amount of interfacial SiO_2 growth observed versus temperature for re-oxidation in 1 Torr of O_2 for 5 min. Crosses indicate samples which were annealed in vacuum to 600–800 °C for ~10 min prior to reoxidation at 500 °C.

(0.3–8.5 Torr), and times (5–20 min).

Compositional depth profiles were obtained using medium-energy ion scattering (MEIS).[9] This technique is essentially a high-resolution, low-energy version of Rutherford backscattering spectroscopy. Instead of operating at MeV energies, MEIS experiments are performed using protons in the 100 keV range. The lower energy permits the use of high resolving power ion detection equipment, in our case an electrostatic energy analyzer.[10] An additional benefit is that the ion energy loss per unit distance traveled (the stopping power) for protons has its maximum in the range 50–100 keV.[11]

Depth profiles of elements were obtained by performing computer simulations of the backscattered ion energy distributions.[12] Quantitative depth profiles for different species with a resolution as high as 3 Å in the near surface region could be extracted. Due to the statistical nature of the ion-solid interaction (ion straggling), the depth resolution deteriorates for deeper layers. For the case of ZrO_2 films, the calculated resolution at a depth of 30 Å is ~8 Å. An advantage, relative to complementary profiling methods, is that MEIS does not rely on hydrofluoric (HF) acid back-etching or sputtering of the sample. One should consider, however, that MEIS data represent averages over a sample area of about 0.1 mm^2, making it difficult to distinguish between near interface compositional gradients and interface or surface roughness. Therefore, surface roughness was monitored by atomic-force microscopy, which revealed rms values of less than 2 Å for both the as-deposited and reoxidized films. MEIS results are further corroborated with TEM imaging.

III. RESULTS

Figure 1 shows a proton backscattering energy spectrum from the as-deposited ZrO_2 film. The position of the Si peak indicates that there is no or little Si diffusion to the solid-vacuum interface. The simulation yielded a stoichiometric $ZrO_{2.04\pm0.05}$ film with thickness of about 30 Å. A silica/silicate layer was identified at the interface to the Si substrate. Some intermixing (silicate) is likely present within the ~10 Å transition region between the nominally pure ZrO_2 film and the Si substrate. Details of the composition in the interface region can only be discerned with a depth resolution of ~8 Å using the applied simulation. However, the total amount of SiO_2 in that region can be determined with higher accuracy (as the areal densities of Si and O are known from the MEIS yield) and corresponds to about 6 Å of pure SiO_2.

Reoxidation of the ZrO_2 films leads to an increased amount of SiO_2 in the interfacial region over the entire investigated temperature range (300–800 °C). MEIS reveals this growth in different ways. The width of the O peak increases, shifting towards lower energy (indicating growth at the interface), while the Zr peak remains essentially unchanged (showing that the thickness and composition of the Zr containing layer does not change). The Si peak position shifts towards lower energies, and the width increases on the higher energy side, consistent with SiO_2 growth above the substrate. In addition, the areas of the O and Si peaks increase in the ratio 2:1, consistent with formation of amorphous stoichiometric SiO_2.

Utilizing these indicators of interfacial growth, the thickness of newly formed SiO_2 was measured for various oxidation conditions. Figure 2 shows the additional SiO_2 thickness as a function of the annealing temperature at an O_2 pressure of 1 Torr ($t=5$ min). A significant amount of growth of additional SiO_2 (~7 Å) has already occurred at temperatures as low as 500 °C. A further increase in the amount of SiO_2 is seen at higher temperatures. At $T=500$ °C, the oxidation pressure and time were varied. No significant change of the amount of SiO_2 growth was observed for pressures ranging from 0.3 to 8.5 Torr, and times from 5 to 20 min. Reoxidation at 500 °C was repeated several times under nominally identical conditions. Within the accuracy of the measurements, the growth was reproducible. Annealing of the films in vacuum to 600–800 °C for ~10 min prior to reoxidation at 500 °C also led to the same amount of SiO_2 growth (Fig. 2).

Annealing the as-deposited ZrO_2 films in dry $^{18}O_2$ gas was used to directly study oxygen exchange and growth behavior. We found that ^{18}O readily incorporates into the film, replacing ^{16}O, while retaining the same overall ZrO_2 stoichiometry (i.e., oxygen exchange). For temperatures $\geqslant 400$ °C, the ^{18}O distribution was essentially uniform throughout the film. Figure 3 shows a plot of the fraction of ^{18}O incorporated $[^{18}O/(^{16}O+^{18}O)]$ as a function of the annealing temperature. Annealing of the films in vacuum to

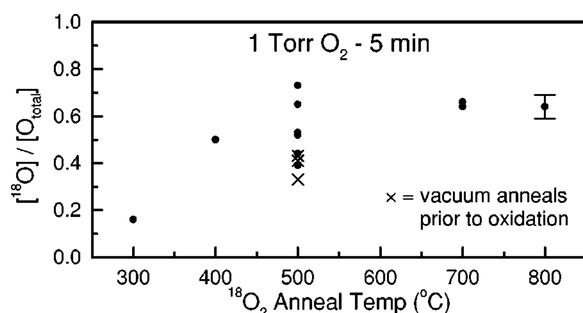

FIG. 3. The fraction of incorporated ^{18}O observed versus temperature for reoxidation in 1 Torr for 5 min. Crosses indicate samples which were annealed in vacuum to 600−800 °C for ∼10 min prior to reoxidation at 500 °C.

600−800 °C for 10 min prior to oxidation at 500 °C had a marked effect on the ^{18}O distribution, leading to a significant reduction in the amount of O exchange.

IV. DISCUSSION

In order to maintain the high capacitance of the gate dielectric stack, the formation of a thick interfacial SiO_2 layer is undesirable. Our work shows that O transport through nominally pure ZrO_2 is fast, and significant interfacial growth appears at temperatures as low as 500 °C (in agreement with previous XPS studies[8]). This may not be surprising given that stabilized cubic and tetragonal-ZrO_2 are well known to be fast ion conductors.[13] Such solids have doping-induced oxygen vacancies, and the oxygen conduction readily proceeds via a very mobile O sublattice. Grain-boundary diffusion, however, should also be considered for oxygen transport in thin films.

Aside from demonstrating the oxygen transport, an important result is that the interfacial growth saturates quickly in time (no change seen after 5 min at 500 °C) and in pressure (no change seen from 0.3−8.5 Torr). A possible explanation for this is as follows. Oxygen transport through the ZrO_2 film is likely as atomic oxygen, whether in a vacancy sublattice or grain-boundary diffusion mode. The growing SiO_2 film should have a much lower diffusivity towards oxygen than the metal-oxide layer, and this becomes the rate-limiting step. In this model, the ZrO_2 film is a source of oxygen (atomic, not molecular), and the SiO_2 growth that does occur becomes strongly inhibiting towards further SiO_2 growth. Only at temperatures sufficiently high to allow Si-O-O-Si exchange hopping (to bring additional O in), or Si suboxide outward transport, will growth continue (at a rate that decreases continuously with SiO_2 thickness).

One way to define a high-K film is by its relative dielectric thickness, using the thickness of an SiO_2 film of equivalent capacitance (the equivalent oxide thickness, EOT) as a metric. EOT values should be as low as possible while maintaining a physical thickness large enough to prevent leakage currents. The degradation (increase) of the EOT can be calculated from our measurements of the SiO_2 growth, and compared to the electrically measured values.[5] Electrical measurements resulted in EOT values of 14.5 and 17 Å for films annealed in oxygen at 550 and 650 °C, respectively. Using dielectric constants for ZrO_2 and SiO_2 of 25 and 3.8, estimating the dielectric constant of the 10 Å silicate transition region to be given by the average, and interpolating the SiO_2 thickness values from Fig. 2 to 550 °C and 650 °C, the EOT values calculated from MEIS data are 15 and 18 Å, in excellent agreement with the electrical measurements.

Quantitative studies of oxygen diffusion should ideally be performed on thicker and/or *in situ* grown amorphous, nanocrystalline, polycrystalline, and crystalline films. Surface or impurity effects may dominate the exchange processes observed in ultrathin films. Nonetheless, an attempt has been made to understand the mechanisms of O transport in these thin films. Two possibilities are considered, grain-boundary diffusion and the presence of multiple zirconia polymorphs.

Recently, Brossmann *et al.*[14] studied the bulk and grain-boundary diffusion of O in ultrafine grained, undoped monoclinic ZrO_2. Volume and interface (grain-boundary) diffusivities were directly measured from ^{18}O diffusion profiles obtained with secondary ion mass spectroscopy on samples with different crystallite sizes. At all temperatures studied, grain-boundary diffusion is faster than diffusion in the bulk of the crystallites by approximately four orders of magnitude. For instance, at 500 °C, the grain-boundary diffusion coefficient is 3×10^{-14} cm^2/s, but in the bulk it is only 1×10^{-18} cm^2/s. The relevance of their work to our study is that it is known that pure ZrO_2 films can have various degrees of crystallinity depending on the preparation temperature and film thickness.[15–17] Furthermore, their observed grain-boundary diffusivities are 3–4 orders of magnitude lower than the diffusivity of O in cubic and tetragonal stabilized zirconias,[14] which are fast ion conductors. Undoped monoclinic ZrO_2, on the other hand, is not a fast ion conductor, and has a higher activation energy for vacancy formation.[14] Since the monoclinic structure is the stable low-temperature phase of ZrO_2, a possible O transport mechanism in the case of these sputter-deposited thin ZrO_2 films is diffusion along grain boundaries, and not fast ionic conduction in the bulk of the crystallites. The volume fraction of grain boundaries then determines the degree of oxygen exchange.

Previous TEM images of ALCVD grown ZrO_2 films reveal that besides monoclinic, the tetragonal phase of ZrO_2 is also present.[4] The existence of the metastable tetragonal phase at low temperatures (without stabilizing dopants) is due to crystal size effects.[15,17] Since these polymorphs have very different O ion diffusivities (by approximately eight orders of magnitude), the metastable tetragonal phase may contribute to the oxygen transport. The volume fraction of the tetragonal phase then determines the exchange fraction.

Unlike the situation for the amount of interfacial SiO_2 growth, the amount of oxygen exchange varied significantly at 500 °C (0.39–0.73) when the reoxidation was repeated several times under nominally identical conditions (Fig. 3). Although a precise explanation for this observation is lacking, we can suggest some possibilities. Since the transported oxygen species is atomic oxygen, the availability of atomic oxygen at the surface is a factor influencing the degree of exchange. The amount of available atomic O depends on the rate of dissociation of O_2 on the surface, the diffusivity of the sample, and the amount of oxygen containing impurities (such as H_2O and CO) in the oxidizing atmosphere. Experiments to verify the affect of the oxygen exchange on the

dryness of the oxidizing gas gave no significant trend in the results, indicating that atomic oxygen incorporation at the ZrO_2 surface is probably not the rate-limiting step under these conditions.

An explanation for the fluctuations in the degree of oxygen exchange may come from sample-to-sample variation in the size distribution of crystallites. Since the grain-boundary diffusion is fast, we expect complete exchange of O at the grain interfaces. The volume fraction of the grain-boundaries can be computed from $f=2\delta/d$,[14] where δ is the grain-boundary width, and d is the crystallite size. For $\delta=5$ Å,[18] and a typical crystallite size observed in TEM,[4] $d=20$–30 Å, one finds $f=0.3$–0.5. This is consistent with the measured exchange values ($f=0.39$–0.73), and may explain why the exchange varies from sample to sample. Finally, since vacuum annealing should lead to an increase in the size of the crystallites, it is apparent that with the fractional volume occupied by the grain boundaries decreasing, the degree of oxygen exchange decreases too. The transformation of the tetragonal to the monoclinic phase during annealing (as has been observed previously[13,16]) may also lead to reduced exchange for samples first annealed in vacuum.

Further studies of the detailed nanocrystallinity (using TEM for example) are necessary to better understand the O dynamics in ultrathin ZrO_2 films.

V. SUMMARY

Substantial oxygen exchange has been directly observed for thin ZrO_2 films under various annealing conditions. To explain the oxygen exchange, diffusion along the grain boundaries of monoclinic crystallites has been considered. Additionally, the presence of metastable tetragonal crystallites (which show a high ionic conductivity) may contribute to the oxygen exchange. The observed interfacial SiO_2 growth exceeds the thermal growth rate of SiO_2 in O_2. This strongly suggests that the growth is initiated by the mobile atomic oxygen species in the ZrO_2 film.

Our results imply some boundaries on what are acceptable post-growth oxidation conditions when using ZrO_2 in gate dielectric applications. In particular, if it is necessary to anneal under oxidizing conditions, the temperature should be kept below 500 °C in order to avoid detrimental SiO_2 growth. For higher temperature processes, the oxidant partial pressure has to be kept extremely low. An alternative to low temperature or pressure annealing could be the formation of a barrier layer such as SiN. In addition, a poly-Si or other gate electrode on top of the high-K oxide should significantly diminish the interfacial SiO_2 growth rate during anneals.[5]

ACKNOWLEDGMENTS

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[1] Semiconductor Industry Association, International Technology Roadmap for Semiconductors: 1999 Edition (http://public.itrs.net/).

[2] T.S. Kalkur and Y.C. Lu, Thin Solid Films **207**, 193 (1992).

[3] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **87**, 484 (2000).

[4] M. Copel, M. Gribelyuk, and E. Gusev, Appl. Phys. Lett. **76**, 436 (2000).

[5] W. J. Qi, R. Nieh, B. H. Lee, L. Kang, Y. Jeon, K. Onishi, T. Ngai, S. Banerjee, and J. C. Lee, *Technical Digest International Electron Device Meeting* (IEEE, 1999), p. 145.

[6] Y. Ma, Y. Ono, L. Stecker, D. R. Evans, and S. T. Hsu, see Ref. 5, p. 149.

[7] A. Kawamoto, J. Jameson, P. Griffin, K. Cho, and R. Dutton (unpublished).

[8] Y.-M. Sun, J. Lozano, H. Ho, H. J. Park, S. Veldman, and J. M. White, Appl. Surf. Sci. **161**, 115 (2000).

[9] J. F. van der Veen, Surf. Sci. Rep. **5**, 199 (1985).

[10] R. M. Tromp, M. Copel, M. C. Reuter, M. H. von Hoegen, J. Speidell, and R. Koudijs, Rev. Sci. Instrum. **62**, 2679 (1991).

[11] J. F. Ziegler and J. P. Biersack, SRIM-*The Stopping and Range of Ions in Matter* Ver. 9, IBM, 1998.

[12] E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, Phys. Rev. B **52**, 1759 (1995).

[13] S. P. S. Badwal, Solid State Ionics **52**, 23 (1992).

[14] U. Brossmann, R. Wrschum, U. Sdervall, and H. E. Schaefer, J. Appl. Phys. **85**, 7646 (1999).

[15] M. A. Schofield, C. R. Aita, P. M. Rice, and M. Gajdardziska-Josifovska, Thin Solid Films **326**, 106 (1998).

[16] A. Gulino, G. Compagnini, R. G. Egdell, and I. Fragala, Thin Solid Films **352**, 73 (1999).

[17] R. C. Garvie, J. Phys. Chem. **82**, 218 (1977).

[18] R. Nitsche, M. Rodewald, G. Skandan, H. Fuess, and H. Hahn, Nanostruct. Mater. **7**, 535 (1996).