Interface reactions of high-κ Y_2O_3 gate oxides with Si

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(Received 7 June 2001; accepted for publication 26 July 2001)

Ultrathin Y_2O_3 films were electron beam evaporated in an ultrahigh vacuum onto Si(100) and investigated by high-resolution medium energy ion scattering. Selected films were capped *in situ* with amorphous Si. Uncapped films that were exposed to air prior to analysis contained excess oxygen compared to a stoichiometric Y_2O_3 film, and showed a 6–8 Å interfacial layer. Si uptake from the substrate occurred in these films after a 700 °C vacuum anneal, presumably by reacting with the excess oxygen. Si-capped Y_2O_3 films on the other hand were stoichiometric, and the substrate interface was sharp ($\leqslant$2 Å), even after 900 °C vacuum anneals. No change was seen at the Y_2O_3 capping layer interface until $\geqslant$800 °C for vacuum anneals. These measurements indicate that control of the interface composition is not possible after exposure of ultrathin Y_2O_3 films to air.
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The aggressive scaling of device technology calls for identifying high permittivity (high-κ) dielectrics to replace SiO_2 and oxynitrides in gate and other applications.[1] During film growth and postprocessing of high-κ gate structures, formation of an interfacial SiO_2 (or silica rich) layer often results and is limiting the capacitance of the gate stack. Many high-κ metal oxides are permeable by oxygen, leading to interfacial SiO_2 growth.[2–5] For instance, rare earth oxides (e.g., Y_2O_3, La_2O_3, and Gd_2O_3) are known to absorb water under standard processing conditions. In addition, the interface between the high-κ film and the upper gate electrode (which for the first generation of high-κ devices will probably remain polycrystalline-Si)[1] must be well understood, as intermixing at this interface also leads to a variety of detrimental effects.

In this letter, we report on the composition and stability (after vacuum anneals) of the interfaces of electron beam (e-beam) deposited Y_2O_3 films ($\kappa = 16–18$) with the underlying Si substrate and with an amorphous Si (*a*-Si) capping layer. Y_2O_3 films were grown in a multichamber UHV system under conditions described in detail elsewhere.[6] To avoid oxidation of the Si surface, the packed ceramic powder Y_2O_3 e-beam source was extensively outgassed. A pressure in the low 10^{-9} Torr range could be achieved during deposition. Amorphous Si capping layers were deposited in the same UHV chamber from an effusion cell.

Physical characterization of the high-κ gate dielectric stacks was performed (after in-air transfer to another UHV system) with medium energy ion scattering (MEIS), a high-resolution variant of Rutherford backscattering spectroscopy, using a 100 keV proton beam.[7] Deconvolution of the experimentally obtained scattered ion energy spectra provides quantitative information on the depth profiles of the elements in the film, with a depth resolution of ~3 Å near the surface and ~8 Å at 30 Å depth.[5] MEIS can easily monitor relative SiO_2 compositional changes of 2 Å at the bottom interface of a 50 Å film. We complemented our MEIS studies by atomic force microscopy, which showed less than 2 Å root-mean-square roughness; thus, we assume that roughness is not relevant in our model of the films. Electrical characterization of these and similar Gd_2O_3 films, as well as the physical characterization with infrared absorption spectroscopy and scanning transmission electron microscopy, are discussed elsewhere.[6] An advantage of MEIS is that it yields accurate compositional profiles, key to the stoichiometric issues discussed in this letter.

Figure 1 shows MEIS results obtained from an uncapped Y_2O_3 film that was exposed to air prior to analysis. In Fig. 1(a), we compare the ion scattering spectra from the sample before and after vacuum annealing. After annealing, the Y concentration narrows and a loss of oxygen is clearly seen, consistent with desorption of oxygen containing species, probably H_2O. The resulting depth profiles [Fig. 1(b)] show that a SiO_x rich layer (6–8 Å thick) exists at the substrate interface. Such a layer also existed before annealing. The O:Y atomic ratio in the bulk of the film changes from 2.25 to 1.73 (a stoichiometric film is 1.5), leaving the uncapped film O rich even after 200 °C vacuum annealing.

Continued vacuum annealing up to 700 °C does not significantly change this ratio. However, silicon uptake from the substrate into the yttria film (extending to a 15 Å wide region) is observed from the changes of the silicon peak as shown in Fig. 1(c). At this temperature, the film becomes $(Y_2O_3)_x(SiO_2)_y$ in the region where Si uptake occurs, with the silicate more SiO_2 rich closer to the interface.

The amount of excess oxygen in the film depends on ambient and processing history. It is likely that the O is trapped as a hydrate (H_2O) or as a hydroxide, e.g., $Y(OH)_3$. Upon annealing, some fraction of this excess O desorbs, while another fraction reacts with substrate silicon forming the near-interfacial silicate. This behavior has been observed for e-beam evaporated La_2O_{3+x}.[8] Oxidation of Y metal de-

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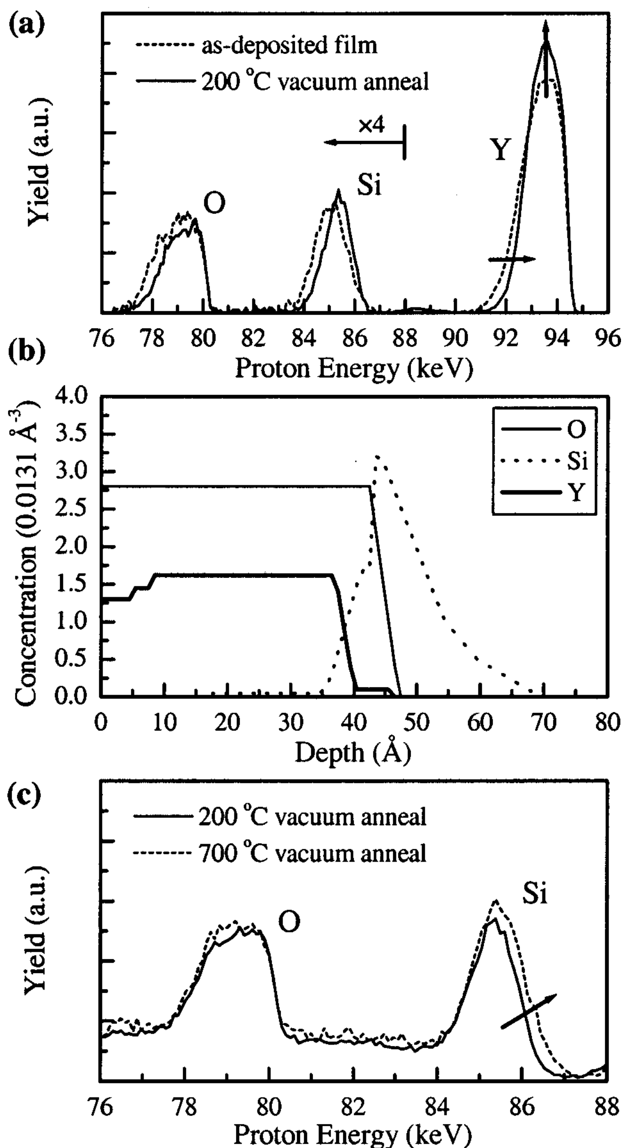

FIG. 1. Results for uncapped Y_2O_3 films on Si that were exposed to air prior to ion scattering analysis are shown. (a) Ion scattering data from an uncapped 40 Å Y_2O_3 layer before and after vacuum annealing at 200 °C. A loss of O is clearly seen. (b) Depth profile of the 200 °C vacuum annealed sample is shown. A SiO_x rich layer (6–8 Å thick) exists at the substrate interface. (c) Comparison of the O and Si regions of the ion scattering spectrum for vacuum annealing is presented at 200 °C and 700 °C. Si uptake from the substrate into the high-κ film is seen from the change in the Si signal.

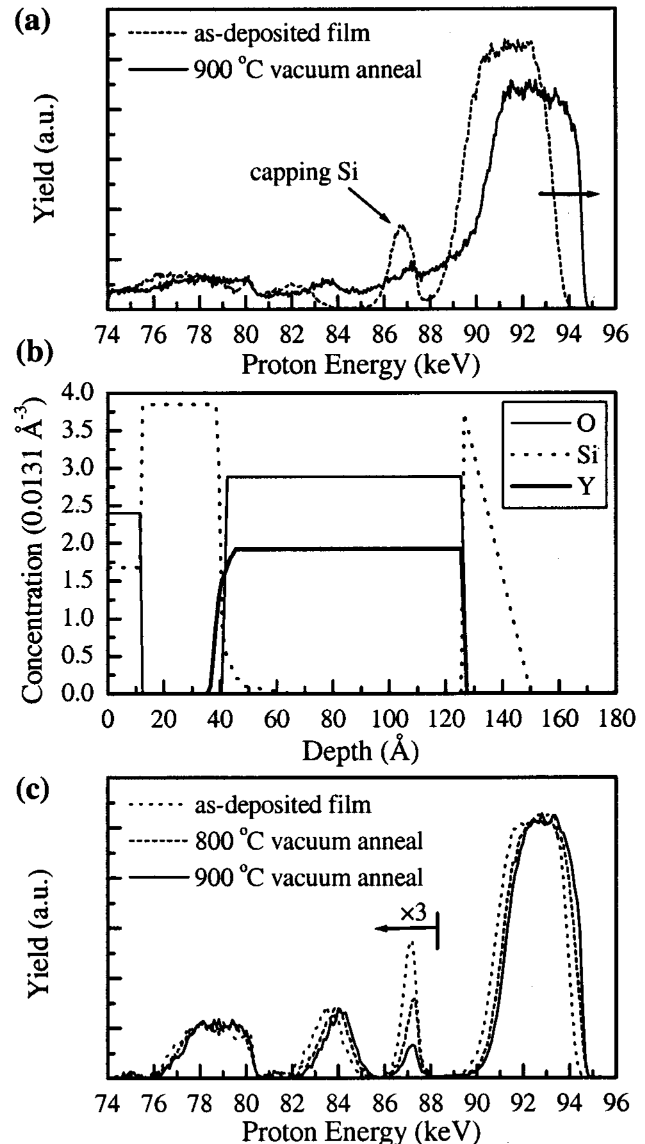

FIG. 2. Results for *in situ* a-Si capped Y_2O_3 films are shown. (a) Ion scattering spectra for the gate stack a-Si(40 Å)/Y_2O_3(90 Å)/Si before and after vacuum annealing are shown. At 900 °C, reaction with the capping layer Si has occurred resulting in the observed shift of the Y signal. (b) Depth profiles of the gate stack in (a) before annealing are shown. The interface to the substrate is abrupt (0–2 Å). No changes occur at the interfaces up to a temperature of 800 °C. (c) Ion scattering spectra for the gate stack a-Si(14 Å)/Y_2O_3(70 Å)/Si before and after vacuum annealing is shown. Reaction with the capping layer is observed here at lower temperatures, compared to the case of the thicker capping layer, and is accompanied by a loss of silicon and oxygen atoms. Little change occurs at the substrate interface at 900 °C.

posited on either Si or SiO_2(~10 Å)Si also leads to silicate formation.[9] Silicate formation in either case would result in a lower effective dielectric constant for that region of the film, although it may also provide chemical and electrical stability. It was previously observed that capacitor structures exposed to air prior to gate metal deposition showed adverse electrical behavior, such as frequency dispersion and hysteresis.[6] Forming gas anneals (either just before or after gate metal deposition) generally improved these conditions.

As we ultimately need to control the atomic composition (particularly the SiO_2 component) in the high-κ film to monolayer levels, capping the metal oxide before exposing the film to higher pressure and temperature conditions is a useful exercise. Using Si as the capping layer has the additional advantage that it will likely be used in the first generation of alternative gate stacks,[1] thus, its interface with the metal oxide must also be fully understood.

Figure 2(a) shows the MEIS spectra for a capped structure comparing results before and after vacuum annealing at 900 °C (1 min). Only slight changes in the energy spectrum occurred (not shown) for vacuum annealing up to 800 °C, indicating the stability of this yttria film in contact with both the a-Si capping layer and underlying substrate. By 900 °C, reaction of the oxide with the capping Si layer takes place as indicated by the shift of the Y signal in the MEIS spectrum towards higher energy. The large width of the Y signal demonstrates that either Y has diffused into the underlying substrate, or that Y–Si islands have grown. In addition, we have

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performed pure N_2 anneals to 850 °C on a similar sample, and found no observable difference in the energy spectrum compared to the as-deposited stack.

Depth profiles for the gate stack before annealing are presented in Fig. 2(b). Some overlap appears between Si and Y at the cap/oxide interface. This overlap could result from either roughness or a small amount of interdiffusion during the initial deposition. No additional change occurs at this interface for vacuum anneals up to 800 °C. In contrast to the uncapped case [Fig. 1(b)], the width of the oxide/substrate interface is abrupt (≤2 Å) for capped Y_2O_3 films. Furthermore [c.f. Fig. 1(c)], Si uptake from the substrate forming a silicate does not occur at temperatures ≤800 °C.

Ion scattering energy spectra for a Y_2O_3 film covered by a thinner silicon capping layer are displayed in Fig. 2(c) for the film before and after vacuum annealing at 800 °C (2 min) and 900 °C (1 min). As for the thicker capping layer, intermixing with the capping Si is observed. In this case, the reaction occurs at a lower temperature and is accompanied by a loss of Si and O, consistent with desorption of SiO species. Since a significant fraction of the thin *a*-Si capping layer becomes oxidized after exposure to atmosphere, one difference (upon annealing) between the thin and thick *a*-Si structures may be due to O present at the *a*-Si/Y_2O_3 interface in the thin-capped sample, permitting silicate formation. The thinner capping layer permits better depth resolution (in MEIS) for the oxide/substrate interface. In the thin-capped case [Fig. 2(c)], very little change is observed at the substrate interface up to 900 °C.

The primary difference between the capped and uncapped films is that the O:Y atomic ratio in the bulk of the Y_2O_3 region is significantly less in the capped films. Somewhat surprising for us was the observation that for the uncapped films, SiO_x (perhaps mixed as a silicate) forms at the substrate interface at room temperature, even though this requires oxygen transport through a 40 Å metal oxide film. The Si capping layer prevents this presumably detrimental ambient process by blocking the introduction of water or oxygen into the film. The ion scattering studies also revealed that *in situ* Si-capped yttria films behave differently from uncapped ones concerning their reactivity with the Si substrate.

We now discuss the aforementioned results in light of the various reactions that may be occurring. Films exposed to air show a clear increase in O content by MEIS both within the film and at the interface. In the metal oxide, it is not yet clear if the oxygen is in the form of a hydrate, a hydroxide, or another phase. Interfacial growth of SiO_2 proceeds via normal oxidation reactions; e.g., $Si+O \rightarrow SiO_2$, perhaps with silicate formation. (No attempt is made to write balanced reactions here, as we have no direct knowledge of the hydrogen content of the films.) Uncapped films show a loss of O upon low-temperature vacuum annealing by gas phase desorption and possibly interfacial SiO_2 formation: $Y_2O_{3+x} \rightarrow Y_2O_{3+y} + H_2O(g) + SiO_2$, with $y<x$.

Upon continued annealing, Si is drawn into the oxygen rich yttria layer forming a silicate, e.g., $Si+(Y_2O_3)_x[Y(OH)_3]_y \rightarrow (Y_2O_3)_{x'}(SiO_2)_{y'}$. For capped films, the reaction of the yttria layer with Si occurs preferably at the upper interface. This could result from either a higher local excess O concentration at the upper interface or differences in reactivity between amorphous and crystalline Si.

Two other mechanisms of O loss likely occur at higher temperatures in the layered (gate stack) structures studied here, both proceeding via SiO desorption. A clear loss of Si and O was observed from the capping layers for $T > 800$ °C; this, we assume, occurs via the SiO_2/Si decomposition reaction: $Si+SiO_2 \rightarrow SiO(g)$. Ultimately, the fate of most metal oxide thin films upon vacuum annealing is likely via a parallel process, $Si+MO_x \rightarrow SiM_y + SiO(g)$. We have previously observed this on other high-κ films when annealed in vacuum (reducing environments work as well) at >900 °C.[10] If Y indeed has a higher oxygen affinity than Si, the reduction of SiO_2 should happen at a lower temperature than that of MO_x.

An important implication of this study is that examining uncapped yttria films is questionable once exposed to even partially oxidizing atmospheres. The same should hold for La, Gd, and other related hygroscopic oxide films. Their silicates and aluminates, however, are known to be more stable (although with lower κ). The issue of oxygen uptake is less problematic for Zr- and Hf-based films, although rapid oxygen transport through such films remains an issue.[2–5]

In conclusion, this work demonstrates that atomic control of the dielectric/substrate interface for ultrathin Y_2O_3 high-κ films on Si is best realized by preventing exposure of the films to atmospheric conditions. Uncapped films absorb excess O (i.e., $Y_2O_{x>3}$, with excess O presumably trapped in the form of water or hydroxide), and grow a measurable interfacial layer of SiO_2 or silicate under ambient conditions. Upon vacuum annealing to 200 °C, some O desorbs, and by 700 °C Si uptake is observed from the substrate, likely due to a reaction between Si and the remaining excess O in the yttria layer. Si-capped yttria layers prepared in UHV displayed stoichiometric Y_2O_3 films, and exhibit an abrupt transition to the substrate (≤2 Å), even after vacuum anneal to 900 °C. Yttria layers are stable next to the initially amorphous capping Si up to 800 °C. The very sharp starting interface between capped Y_2O_3 films and the Si substrate suggests interesting future work to tailor overall dielectric stack properties through fine control of the interface composition.

The authors acknowledge the Semiconductor Research Corporation and the National Science Foundation for financial support. They also thank Mike Steigerwald (Agere Systems), and John Brennan (Rutgers) for their help and insight.

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