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Phase stability and Morphology of high-k gate stack of $Si/SiO_2/HfO_2$ and $Si/SiO_2/ZrO_2$

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Abstract : Phase stability and morphological investigation on the $Si/SiO_2/HfO_2$ and $Si/SiO_2/ZrO_2$ stack are presented. Thermal stability of HfO_2 and ZrO_2 determines the quality of interface and subsequently the performance of device. The stacks have been fabricated and annealed at 1000 ^{O}C for various time. In evolution of crystalline phase and morphology (electrical and geometrical) of high-k materials, annealing time and process are observed to be crucial factors. The crystallization of some phase has been observed in the case of $Si/SiO_2/HfO_2$. The chemical environment around Zr and Hf in respective samples is observed to be different.

1. Introduction

As semiconductor device dimension continues to shrink, the semiconductor industry focus on replacing conventional SiO_2 based devices with that of high-k dielectric materials as a gate oxide. The rapid shrinking of the transistor feature size has forced the channel length and gate dielectric thickness to also decrease rapidly.

The gate oxide SiO_2 thinning has reached to the limit. The minimum thickness requires to exhibit a full band structure is observed to be close to 1.6 Å [1]. Counting interface, the distance required to have full band gap is in the range between 7 and 8 Å [2]. Considering the reliability issues, further scaling can only be achieved by using alternative high-k materials. The alternative materials that have shown great potential are HfO_2 and ZrO_2.

Formation of intermixed phase SiO_2-HfO_2 and SiO_2-ZrO_2 have also been suggested [3]. As a result of reaction between the SiO_2 and high-k materials, the dielectric properties, interface region, and traps or well formation also are modified.

Very recently, (1-x)(SiO_2)-x(MO_2) (M=Hf, Zr,), have also been suggested. The dielectric properties of such materials depend on the coordination metal and content of metal [4].

In this investigation, we have attempted to understand the thermal stability of these high-k dielectric materials and its effect on electrical property of gate stack. The detailed structural and electrical properties of $Si/SiO_2/ZrO_2$ and $Si/SiO_2/HfO_2$ will be presented.

2. Experimental

The gate stacks of $SiO_2/ZrO_2/SiO_2$ and $SiO_2/HfO_2/SiO_2$ were fabricated on a p-type (100) silicon wafer with 4nm thick thermally grown SiO_2 layer using dry oxidation process at 800°C. Subsequently HfO_2 and ZrO_2 dielectric material thin films were deposited on SiO_2 by RF sputtering of Zr or Hf target in the Ar ambient, respectively, where 30 W RF power was applied. The processing pressure was 0.8 mTorr and the flow rate of Ar inert gas was maintained at 16 sccm. Samples were subjected to the oxidation at 550 ^{O}C for 2 hrs followed by post deposition annealing in N_2 ambient at 1000 ^{O}C for 0, 5, 15 s. The samples were examined using I-AFM, XRD, and XPS. The electrical properties of gate oxide are measured.

3. Result and discussion

The XRD pattern for the $Si/SiO_2/ZrO_2$ and $Si/SiO_2/HfO_2$ are provided in Figs. 1 and 2. The stack of $Si/SiO_2/ZrO_2$ and $Si/SiO_2/HfO_2$ are not in amorphous form as desired. The thermal stability of these materials is an important issue to be addressed. However, the stack, $Si/SiO_2/HfO_2$ appears to very unstable and transforms to crystalline form on annealing for 5 and 15 s.

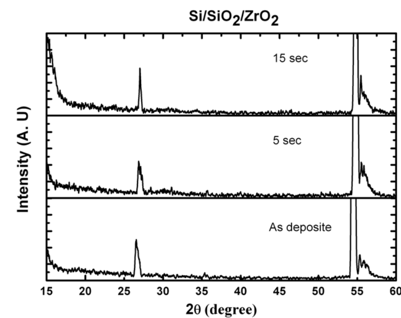


Fig. 1 XRD pattern for $Si/SiO_2/HfO_2$ gate stack.

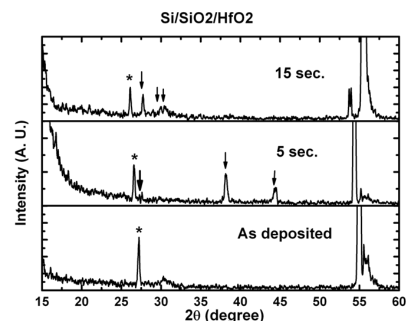


Fig. 2 XRD pattern for $Si/SiO_2/ZrO_2$ gate stack
* indicates substrate peaks while arrow indicates unknown phase of SiO_2-HfO_2 system.

The crystalline nature of the $Si/SiO_2/HfO_2$ is observed to be determined by the annealing time. In the case of $Si/SiO_2/ZrO_2$, no other than substrate peaks are clearly observed. However, in the case of 5 s annealed sample, the crystallization of some phase is evident. Very interestingly, when annealing time is increased by 10 s, peaks also disappeared. The XRD pattern for the $Si/SiO_2/ZrO_2$ is exhibited in Fig. 2.

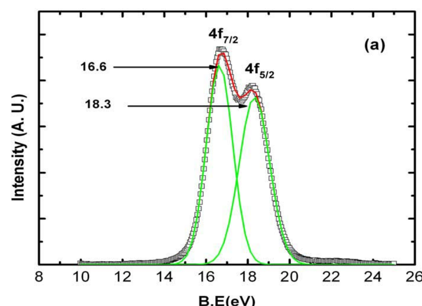
It is not wise to make any strong suggestion about the thermal stability of ZrO_2 and HfO_2. However, the results suggest that ZrO_2 forms a complete amorphous phase while in the case of SiO_2-HfO_2, it may exhibit composite nature i.e. crystalline and amorphous.

The nature of dielectric layer determines the device performance and hence, it is necessary to retain the dielectric layer. However, it has been observed that the ZrO_2 and HfO_2 react with SiO_2 resulting into formation of $(1\text{-}x)SiO_2\text{-}(x)ZrO_2$ and $(1\text{-}x)SiO_2\text{-}(x)HfO_2$. However, exact composition cannot be ascertained.

Apparently, the charge storing capacity, which depends on the dielectric properties of material, band offset, defects density at interface alters altogether, and the very interest to improve the performance is defeated.

The chemical and thermal stability of surface is determined by the surface band structure. The chemical environment of Zr, Hf and O is examined using XPS. The XPS spectra for Hf (4f) and O (2s) are provided in Figs. 3a and b. The peak position for the Hf ($4f_{7/2}$) in HfO_2 is generally observed in the range between 16.3 and 17 eV [5]. The binding energy for $4f_{7/2}$ and $4f_{5/2}$ are 16.6 and 18.3 eV respectively. The splitting is observed to be 1.7 eV, which agrees with literature. The binding energy for O (1S) is 530.3 and 531.4 eV. A doublet for the O (1S) is observed with a difference of 1.1 eV. For the metal oxide, photoelectron peak (singlet) for O (1S) is generally observed in the range between 528.1 and 531.1 eV. The doublet that has been visible in Fig. 3(b) is clear indication that chemical atmosphere for the oxygen differs. Similar effect has been observed for the O(1S) in ZrO_2 as deposited sample.

The shift of 1.8 eV is observed for ZrO_2 as deposited sample. The area under the curve and ratio give us the idea about the concentration of particular species under the similar chemical environment. In the case of HfO_2 sample, the ratio of area is 1.2 while in the case of ZrO_2 sample, the ratio is 1.4. The area under curve for the peak at higher BE is observed to be higher for HfO_2 sample. Thus the surface of HfO_2 sample appears to be more susceptible for chemical change relative to ZrO_2 surface.



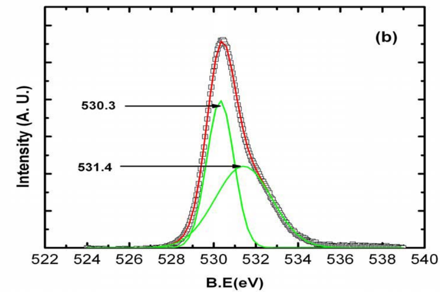


Fig. 3 XPS spectra for Hf (4f) and O (1s)

The photoelectron peak of O(1s) for SiO_2 occurs at relatively higher binding energy than that for metal oxide. Thus the shift in O(1S) may be attributed to the formation of Hf-O-Si and Zr-O-Si interfacial regions. The binding energy for O(1s) photoelectron peak for ZrO_2 sample has been observed at higher binding energy relative to HfO_2 sample. This is suggestive of the reactive nature of ZrO_2 and SiO_2 resulting into a glass like interfacial phase.

4. Conclusions

Thermal stability of high-k ZrO_2 and HfO_2 has been investigated and the stability of ZrO_2 is observed to be poor relative to HfO_2. The formation of crystalline amorphous $Si_{(1-x)}Zr_xO_y$ in case of SiO_2 and ZrO_2 is indicated while in case of HfO_2 sample some crystalline phase is observed.

Acknowledgements

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