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A Study of Impact of Incorporating Locations of Yttrium on the Properties of GeO_x/HfO_2-based/TiN Gate Stack Based on Material Reaction

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Abstract

In this paper, an influence of incorporating location of Yttrium (Y) into GeO_x interfacial layer (IL) with HfO_2-based/TiN gate stack on p-Ge was studied. Various incorporating Y processes presented contrasting electrical and material results. Depositing Y metal before IL formation improved interface quality, however, degraded the dielectric constant (κ) of the HfO_2. We found non-fully oxidized Y atoms would capture nearby O atoms in Ge-O and/or Hf-O bonds, which depended on the position of Y. A series of XPS analyses indicated that Y doped GeO_x (YGO) induced Hf-N bonds in HfO_2 with N_2 plasma treatment, which degraded the κ of HfO_2 .

1. Introduction

For further scaling MOSFET, Ge is one of high-mobility materials for enhancing the device on current. However, an essential challenge for Ge devices is how to form a high-quality interfacial layer (IL) on Ge. C. Lu *et al.* proposed a potential solution to solve the interface issue by doping Yttrium (Y) into GeO_2 (YGO) [1]. Based on the values of Gibbs free energy in Table I, Y-O bonds are more stable than Hf-O and Ge-O bonds. In fact, adding stable Y-O bonds into GeO_x benefits to improve thermal stability of IL and its quality [2]. However, the influence of YGO IL for HfO_2-based/TiN gate stack should be discussed in detail. In this paper, we demonstrated various processing conditions of incorporating Y into GeO_x ILs and presented a series of material analyses to deeply realize the material interaction as various processes.

2. Device Preparation

Fig. 1 shows the process flow and structures of p-Ge capacitors for various ILs processes of Y incorporation. Standard IL process used oxygen plasma oxidation (PO) for GeO_x formation [3]. Y-first/PO IL was formed by depositing a 0.6 nm Y metal followed by PO. PO/Y-later IL was formed by depositing a 0.6 nm Y after PO. High-κ layers were grown by PEALD and TiN metal was deposited by sputtering Ti with N_2 plasma.

3. Results and Discussion

In Fig. 2, equivalent oxide thickness (EOT) and interface trap density (D_{it}) of various ILs are shown. We found Y-first/PO case possessed lower D_{it} (4.9×10^{11} $eV^{-1}cm^{-2}$) and higher EOT (1.9 nm) values than those in PO/Y-later case. Surprisingly, the PO/Y-later case showed the highest D_{it} value. Fig. 3 shows the corresponding TEM images and EDX depth profiles. In fact, the IL of Y-first/PO case was only slightly thicker than the others. However, the EOT value was significantly degraded. The extracted dielectric constant (κ) of the HfO_2-based layers of Y-first/PO case was 10 only. For further investigating the difference between Y-first/PO and PO/Y-later cases, a simple test structures with various ILs under a 1 nm HfO_2 layer through a PDA of 500 ºC were used for XPS analysis (Fig. 4(a)). Corresponding XPS spectra of O *1s* and oxide composition are shown in Fig. 4. XPS spectra of Hf *4f* and O/Hf atomic ratio are shown in Fig. 5. We found the peak of Hf *4f* of Y-first/PO case was located at lower binding energy, which means the amount of Hf-O bonds in the HfO_2 of Y-first/PO case was less. We, thus, concluded that Y-first/PO case had more Y-O bonds than PO/Y-later case, however, which had a lower O/Hf atomic ratio ~ 1.403. This means pre-depositing Y followed by PO can form more Y-O bonds, nevertheless, the formation of stable Y-O bonds in the GeO_x layer might rob the O atoms from upper HfO_2 layer. Next, we transferred the test structures through a N_2 plasma treatment of TiN deposition. The XPS results of Hf *4f* are shown in Fig. 6, indicating the Y-first/PO case had more Hf-N bonds formed by N_2 plasma treatment. This phenomenon was consistent with our EDX results, which showed N pile-up near IL. Postulated material interaction models were proposed in Fig. 7. Pre-depositing Y before IL oxidation resulted in more Y-O bonds in IL, and then, if Y atoms were not fully oxidized, they would rob the nearby O atoms from the HfO_2 layer and induce oxygen vacancies in HfO_2. The oxygen vacancies would be filled by N atoms to form Hf-N bonds after N_2 plasma treatment. To further confirm the relation between Hf-N bonds and κ degradation, a pure Ti metal was used to substitute TiN metal of capacitors. Actually, we did observe the κ degradation of HfO_2 could be significantly improved.

3. Conclusions

In summary, the influence of incorporating Y into IL with HfO_2-based/TiN gate stack was investigated. Doping Y into IL could improve interface quality; however, it also induced oxygen vacancies in HfO_2 and indirectly formed Hf-N bonds as TiN deposition, which degraded the κ of HfO_2. If incorporating Y after the GeO_x formation, non-fully oxidized Y atoms would rob the O atoms of IL and further degrade the interface quality.

References

[1] C. Lu *et al*., VLSI, (2015) T18. [2] C. H. Chou *et al*., JSSST (2018), No.2. [3] Y. H. Tsai *et al*., EDL (2016), No. 37, 1379.

Acknowledgements

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Table I. Free Gibbs Energy values of thermal dynamic for conventional oxides.

Oxide	Gibbs Free Energy (kJ/mol)
GeO_2	-497.06
HfO_2	-1027.17
Y_2O_3	-1905.31

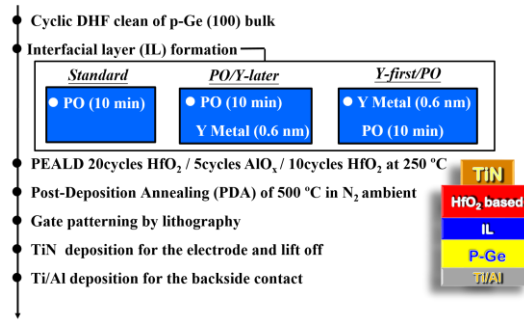

Fig. 1. Process flow and illustrative structure of p-Ge/IL/HfO_2-based/TiN gate stacks with three kinds of IL structures.

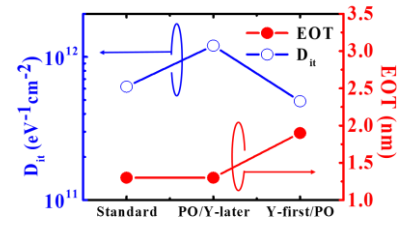

Fig. 2. Corresponding D_{it} and EOT values for various IL cases. Y-first/PO method could suppress D_{it} value; however, PO/Y-later method presented the highest D_{it} value.

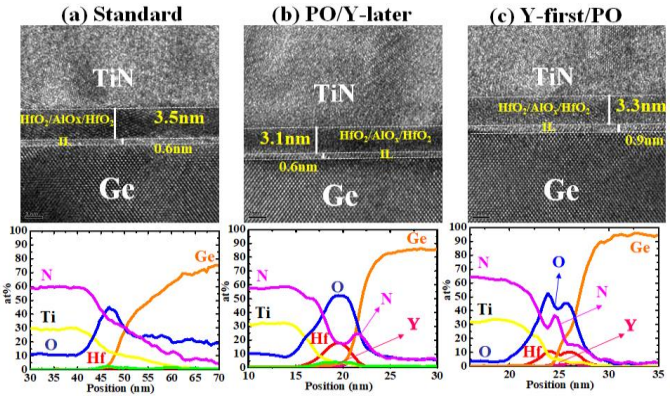

Fig. 3. TEM images and EDX depth profiles for (a) Standard, (b) PO/Y-later and (c) Y-first/PO cases. Especially, N pile-up could be found in Y incorporation cases. The extracted κ of the $HfO_2/AlO_x/HfO_2$ stacks of standard and Y-first/PO cases were 15 and 10, respectively.

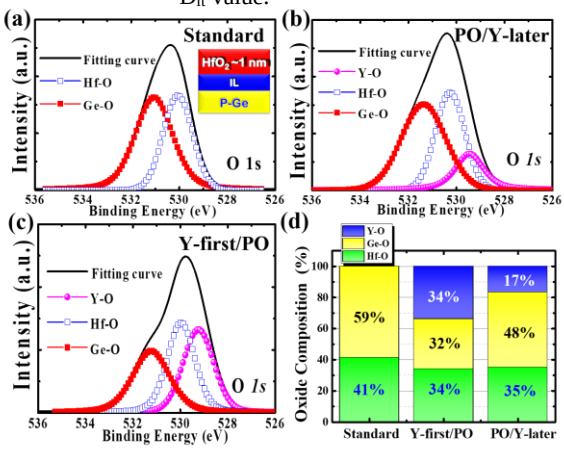

Fig. 4. XPS spectra of O *1s* for (a) Standard, (b) PO/Y-later and (c) Y-first/PO cases. (d) Oxide composition for various test structures. Y-first/PO case had more Y-O bonds than PO/Y-later case.

O/Hf (atomic ratio)	Standard	PO/Y-later	Y-first/PO
	2.36	2.08	1.403

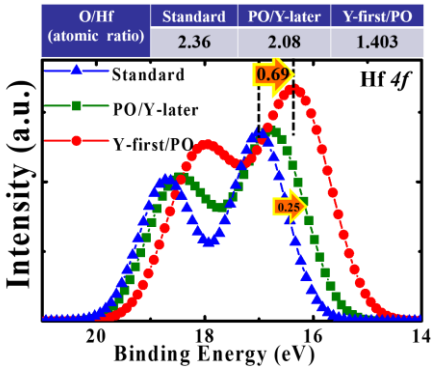

Fig. 5. XPS spectra of Hf *4f* for Standard, PO/Y-later and Y-first/PO cases. Corresponding O/Hf atomic ratio was extracted by XPS spectra of Hf *4f* and O *1s*. Y-first/PO case had less Hf-O bonds and lowest O/Hf atomic ratio ~ 1.4 (O-less HfO_2).

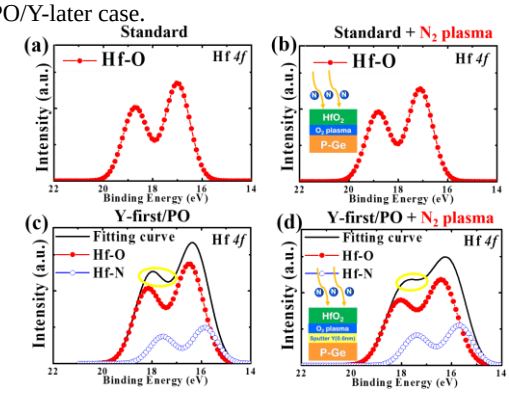

Fig. 6. Corresponding XPS spectra of Hf *4f* for (a) Standard and (c) Y-first/PO case, (b) Standard and (d) Y-first/PO case through N_2 plasma treatment. The Y-first/PO case had more Hf-N bonds formed by N_2 plasma treatment. It means more oxygen vacancies were filled by N atoms in Y-first/PO case.

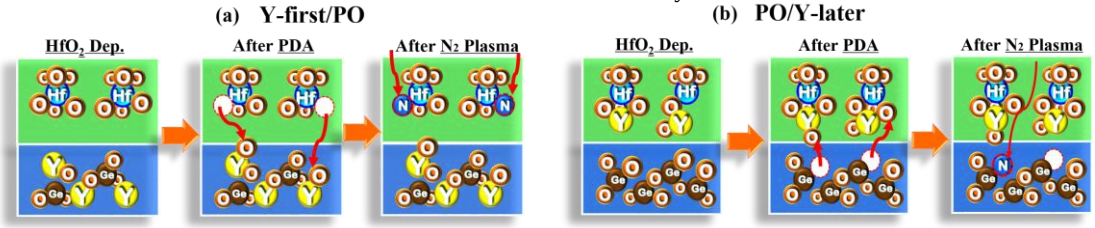

Fig. 7. Cartoons of the postulated sequential material interactions for Y-first/PO and PO/Y-later cases. (a) Pre-depositing Y before plasma oxidation was prone to make Y atoms located in IL. After HfO_2 deposition and PDA processes, non-fully oxidize Y atoms might rob the O atoms of upper HfO_2 and form oxygen vacancies in HfO_2. During a N_2 plasma treatment, Hf-N bonds were formed in HfO_2. (b) In the process of Y deposition after plasma oxidation, Y atoms oppositely located in HfO_2 layer. Hence, through a PDA process, Y atoms might rob the O atoms of under GeO_x layer. This mechanism would degrade the IL quality, even if through a N_2 plasma treatment.