Stabilization of a very high-k tetragonal phase in Ge-doped ZrO_2 films grown by direct doping with Germanium

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1. Introduction

High-k oxides are good candidates for the replacement of SiO_2 at CMOS devices since there is a great demand for downscaling. ZrO_2 (zirconia) is a promising dielectric because it has good electrical properties and can withstand transistor processing. Zirconia has the following three low-pressure structural phases, monoclinic $P2_1/c$, cubic Fm3m and tetragonal $P4_2/mmc$. From these three phases, the tetragonal phase exhibits the higher k value (k~47) after theoretical calculations [1]. Therefore the idea is to stabilize the higher-k tetragonal phase in ZrO_2 without reducing band offsets, which is beneficial for gate leakage [2].

We have recently reported the stabilization of the tetragonal ZrO_2 phase in $ZrO_2/GeO_2/Ge$ stacks grown by molecular beam epitaxy [3]. This was done during the deposition process where an unintentional finite GeO_2 decomposition takes place followed by the incorporation of Ge into the growing ZrO_2 layer which subsequently stabilizes the tetragonal zirconia phase. In this paper we show that by intentionally incorporating Ge into ZrO_2 films grown on SiON/Si substrates at very low temperatures (225 ^{0}C) and low Ge contents of a few at. %, a high-k tetragonal zirconia phase is stabilized. This tetragonal phase remains stable after post deposition N_2 annealing up to 1050 ^{0}C.

2. Experimental details

We have deposited thin Ge-doped ZrO_2 films on SiON/pSi substrates by atomic oxygen beam deposition at 225 ^{0}C. Ge was evaporated at the same time as Zr during ZrO_2 growth. The Ge atomic fraction x (x=Ge/[Ge+Zr] at. %) was estimated from Rutherford back scattering (RBS) measurements in the range of 3-19.3 at. %. The thickness of Ge-doped ZrO_2 was estimated by x-ray reflectivity (XRR) measurements at ~20 nm. X-ray diffraction (XRD) and grazing incidence XRD (GIXRD) measurements were performed in order to record data for crystallographic phase analysis. Metal-insulator-semiconductor (MIS) capacitor structures were fabricated using shadow mask and Pt deposition. Post deposition annealing at N_2 ambient up to 1050 ^{0}C and at forming gas (N_2: 95%, H_2: 5%) ambient up to 450 ^{0}C was performed. Finally, electrical measurements such as capacitance-voltage (C-V) were done in order to study the electrical properties of the MIS capacitors.

3. Results and Discussion

Figure 1 shows GIXRD spectra for Ge-doped ZrO_2 films grown at T_g=225 ^{0}C on SiON/pSi substrates at Ge concentrations ranging from 0 up to 19.3 at. %. It is clearly shown at the diffraction pattern that from the undoped ZrO_2 (x=0 at. %) which appears to be a mixture of the monoclinic and tetragonal phase, there is a phase transformation into the pure tetragonal phase for the Ge doped ZrO_2 (x=3 up to 6.2 at. %.) [4]. The tetragonal phase is the dominant one up to x=6.2 Ge at. %. This is also indicated by the enhancement of the distortion ratio $c/\sqrt{2}a$ (Table 1) and by the shift of the dominant tetragonal (001) reflection to higher diffraction angles (Figs 1(b)-1(d)). For higher Ge doping (x=19.3 at. %) the structure of ZrO_2 becomes amorphous. Fig. 2 depicts the effect of the post deposition annealing temperature to the tetragonal zirconia phase. As shown at the XRD data of a 6.2 Ge at. % doped ZrO_2 film, the tetragonal dominant phase is stable and is retained up to 1050 ^{0}C N_2 anneal.

The capacitance-voltage (C-V) characteristics of a 6.2 at. % Ge doped ZrO_2/SiON/pSi MIS capacitor after forming gas anneal is illustrated in Fig. 3 taking into account the Rs correction (Rs=270 Ω) [5]. It is observed that the CV characteristics of the capacitor are close to ideal in terms of hysterisis, frequency dispersion in accumulation and stretch-out. This allows for an estimation of the equivalent oxide thickness (EOT) and k value using MISFIT model [5] taking into account a nominal thickness for SiON IL of 1.5 nm. Fig. 5 presents the variation of k value of a Ge doped ZrO_2 capacitor with respect to the Ge at. % concentration. It is observed that the k value increases as the tetragonal zirconia phase increases having a maximum value of 37.7 for x=6.2 Ge at. %. These data are in agreement with the results presented in Fig. 1. A summary of the structural and electrical characteristics of the as-deposited Ge-doped ZrO_2/SiON/Si stacks is presented in Table 1.

4. Conclusions

We have demonstrated that by incorporating Ge into ZrO_2 films on SiON/Si substrates at low deposition temperature (225 ^{0}C), the ZrO_2 tetragonal phase stabilizes and remains stable after post deposition N_2 anneal up to 1050 ^{0}C. This leads to a k value enhancement of the stacks obtaining a maximum k value of 37.7 for a 6.2 at. % Ge doped ZrO_2 film on SiON/Si substrates.

References

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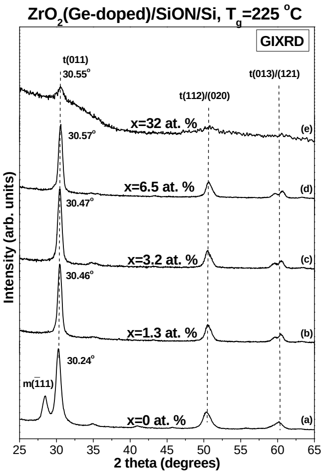

Fig. 1 GIXRD patterns for as-deposited Ge-doped ZrO_2 films deposited on SiON/Si substrate grown at 225 ^{0}C with respect to Ge content (x). The nominal ZrO_2 thickness is 20 nm. The monoclinic (m) and tetragonal (t) phases are shown in (a) for x=0 at. %, whereas the tetragonal (t) is shown in (b)-(d) for x=3-6.2 at. %. In (e) ZrO_2 structure becomes amorphous.

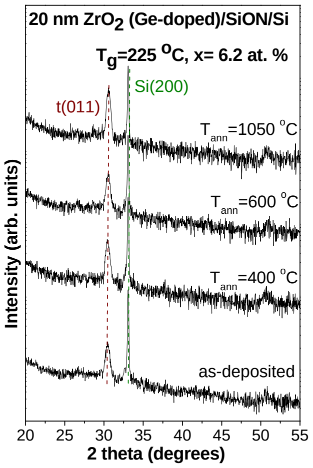

Fig. 2 XRD spectra of a 6.2 at. % Ge doped ZrO_2 film deposited on SiON/Si substrate grown at 225 ^{0}C with respect to the post deposition annealing temperature.

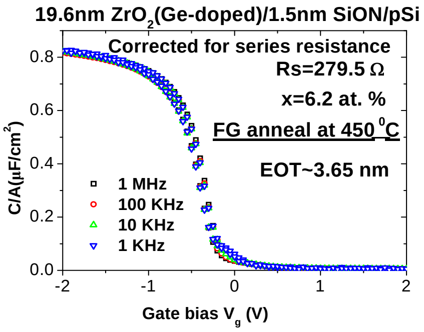

Fig. 3 C-V characteristics of a Ge doped (6.2 at. %) ZrO_2/SiON/Si stack after FG anneal at 450 ^{0}C.

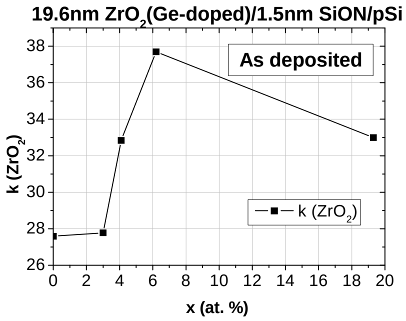

Fig. 4 k value of ZrO_2 as a function of Ge concentration (x) in as-deposited ZrO_2 films.

Ge content (at. %)	Crystal structure	$c/\sqrt{2}a$ - t-ZrO_2	k
0	t+m ZrO_2	1.01239	27.6
3	t ZrO_2	1.01902	27.8
4.1	t ZrO_2	1.0209	32.8
6.2	t ZrO_2	1.02177	37.7
9.3	amorphous		33

Table 1 Summary of the crystallographic phases, $c/\sqrt{2}a$ ratio and k values for the samples studied in Fig. 1. ($c/\sqrt{2}a$=1 for the cubic ZrO2 structure).