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Electrical and Photonics Characteristics of Hftiero Thin Films Deposited at 673 K Substrate Temperature

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Abstract: Thin films of Ti and Er co-doped hafnium oxide (HfO_2) are deposited at 673K substrate temperature on Si (100) wafers by means of RF sputtering technique. The X-ray diffraction (XRD) has been performed to study crystal structure and surface morphology. Photoluminescence (PL) spectroscopy has been used to observe the photonics properties and defect levels of the thin films. The C-V measurements have been conducted to investigate electrical properties of thin films. The capacitance value of HfTiErO gate dielectric is higher as compared to pure HfO_2.

Keywords: HfTiErO, Thin films, substrate temperature, Photo luminous, RF Sputtering

1. INTRODUCTION

In our daily life, it has become essential to down scale the integrated devices, whereas keeping their circuit functionality and performance hasty at lowest costs. A large number of components per chip are needed in these devices as well as in bigger computers that increases the dimension as well as cost. In this study Si substrates have been selected to prepare these chips. To form good insulators from Si having mechanical, electrical and dielectric properties can be reacted with Oxygen or Nitrogen. Dielectrics are used as main components of complementary metal-oxide semiconductor (CMOS) as the transistor gate dielectric.

An extensive research has been conducted on substitute gate dielectrics to replace silicon oxide in the last few years. The continued scaling of CMOS transistors requires the alternate of the SiO_2 gate oxide, whereas the effective oxide thickness (EOT) of the classical silicon dioxide dielectrics to be smaller than 1 nm (Wu**,** *et al.* (2006). In the search of alternative high-*k* gate dielectrics various material candidates have been proposed and tested (Xiong, *et al.* (2005)]. Among all, Hafnium oxide and Hafnium based oxide material have got acknowledged their role in integrated electronics and optoelectronics devices (Deshpande**,** *et al.* (2006)]. Particularly, Er-doped HfO_2 is more interesting because of lowest ionic radii and highest electro negativities in lanthanide series (Wiemer, *et al.* (2010). Furthermore, Er-doped HfO_2 can also be applied in optical devices due to HfO_2 which has relatively wide band gap and/ or high refractive index Wang, *et al.* (2007). It has been also reported that higher k value as well as good photonics properties can be achieved by doping Ti and Er simultaneously into HfO_2 gate dielectric (Triyoso, *et al.* (2005), Khaskheli, *et al.* (2013).

Similarly we have also doped Ti and Er simultaneously into HfO_2 using RF sputtering method and compared the electrical and photonics properties with pure HfO_2 gate dielectric. In this attempt XRD, PL, SEM and C-V techniques were employed to investigate changes in the film microstructure and photonics properties. Metal Oxide Capacitors (MOSCAPs) with metal oxide electrode were fabricated to understand possible benefits of co-doped Ti and Er into HfO_2, such as increase in k value while maintaining reasonable leakage current and improve other dielectric properties. We present here the summary of investigated electrical and photonic properties of co-doped Ti and Er HfO_2 thin films.

2. EXPERIMENTAL METHOD

The Ti and Er co-doped HfO_2 Thin film were prepared by R.F magnetron sputtering on Single crystal Si (100) wafers at 673K substrate temperature with a constant sputtering power 100W. The chamber was initially evacuated to 3×10^{-4}Pa, Argon and Oxygen were induced during deposition. The ratio of O_2/Ar=0.4 remained same during the deposition. While sputtering time was 60 min and working pressure was 0.7Pa. Prior to deposition, the target was pre sputtered in an Ar atmosphere for 15 min in order to remove surface oxide from the target. Crystal structure of the film was characterized by X-ray diffraction (XRD) using CuKa radiation at 40kV and 40mA. By using SEM the thickness of the film was determined about 40nm using SEM. Film defects and photonic properties were

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analyzed using PL (laser at 100mW laser power) at room temperature under excitation wavelength of 532nm laser. GaAs photoelectron diode was used as the detector and the test system was Bruker IFS 120HR Fourier Transform Infrared Spectrophotometers. Ti and Er, two different contents doped into HfO_2 on thin films of about 40nm thicknesses have been used for Au/HfTiErO/Si/Aumetal–oxide–semiconductor (MOS) structures fabrication. The fabricated Au/HfTiErO/Si/Au structure has been used for extracting the CV measurements to determine the various electrical properties of the film.

3. <u>RESULTS AND DISCUSSION</u>

Fig.1 shows a typical XRD pattern of HfO_2 and HfTiErO deposited thin films. XRD was conducted to investigate the microstructure of HfTiErO film compared with pure HfO_2 film. The XRD peaks are very broad, suggesting mixed amorphous/ polycrystalline films or polycrystalline films with very small grains. The XRD measurements for HfO_2 thin film shows a broad peak 2θ = 28.35° h k l (−111) and along with several other smaller peak at 2θ = 31.64° h k l (111), 2θ = 34.27° h k l (002) and 2θ = 49.55° h k l (022) for pure HfO2.The peak positions are in good agreement with those of monoclinic phase (Ni, *et al.* 2008). While, the co-doped Ti and Er into HfO_2 sample shows a broad peak at 2θ = 29.77° h k l (111) having several weak peaks at 2θ= 49.64° h k l (220), 2θ = 58.97° h k l (311) and 2θ = 34.53° h k l (200). The peak position of HfTiErO films shows polycrystalline structure which may be due to mixing phase of monoclinic and cubic structure. However, most of the active Er ions exist with cubic structure as Er_2O_3 (Khaskheli, *et al.* 2012), hence, the broader peaks observed for the HfTiErO film may suggest that it has a greater amorphous fraction. **(Fig.1)**

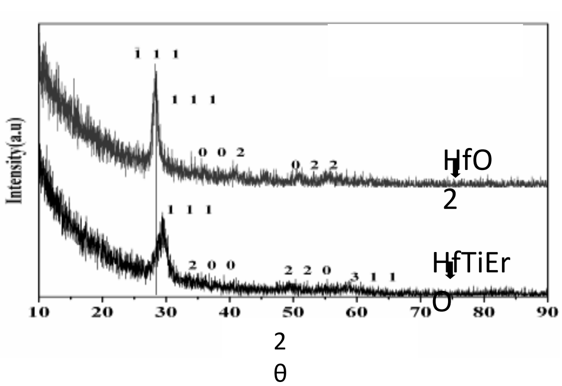

Fig.1. XRD spectra of HfO_2 and HfTiErO thin films deposited at 673 K substrate temperature.

Fig.2**;** PL spectra of Ti and Er co-doped HfO_2 thin film and a reference of pure HfO_2 thin film at room temperature under excitation wavelength of 532nm. The peaks at 382nm (3.24eV) and 403nm (3.08eV) are observed common peak of both samples. While additional peaks for HfTiErO at 415nm (2.98eV) and 438nm (2.98eV) are observed. It has been reported that the existence of O vacancy in the HfO_2 thin films introduces a series of states that lie from 2.70 to 3.80eV in the band gap, which provides recombination centers for excited e-h pairs (Xiong, *et al.,* 2005), (Wang, *et al.* 2007 and Ramo, *et al.* 2007). The energies of HfTiErO thin films observed peaks lie within this range. Thus, it can be concluded that PL peaks in both samples are due to defect levels in the middle of band gap formed by oxygen vacancies. It is well known that oxygen vacancies existed in thin film of oxides during growth or might be due to doping of Ti and Er element into HfO_2 (Foster, *et al.,* 2002), (Ni, *et al.,* 2008). We propose that both defects are dependable for creation of oxygen vacancies in samples. In pure HfO_2, the neutral vacancy is formed by removing a neutral oxygen atom from the regular site and leaving two electrons in the vacant site. The other charge states could be existed for zero, one, three, and four electrons in the vicinity of the vacancy (Xiong, *et al.,* 2005). Consequently, oxygen vacancies in HfO_2 thin film produce series defect level in the band gap. It can be seen from **(Fig.2),** that PL emission lifetime of pure HfO_2 is higher as compared to HfTiErO samples; whereas, number of peaks increased by doping Ti and Er into HfO_2. Moreover, we finally concluded that the Lifetime is higher in pure HfO_2 and decreases with doping Ti and Er, while number of different defects levels increases with doping.

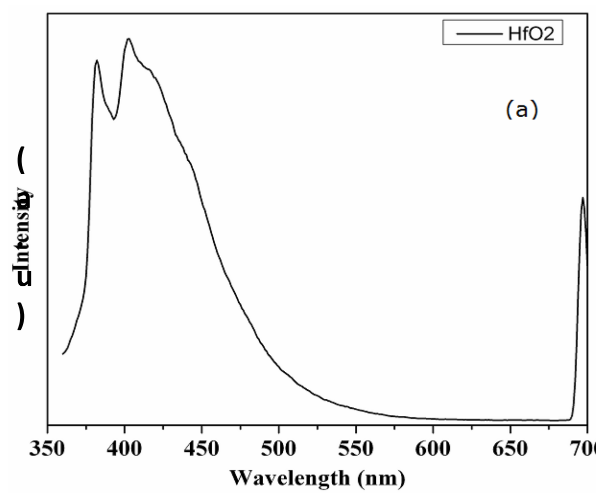

Fig.2. PL spectra of (a) HfO_2 and (b) Ti and Er co-doped HfO_2 thin films at room temperature under excitation wavelength of 350nm.

Fig.3 shows the typical C-V curves of HfO_2 and HfTiErO MOS Structure deposited at 673K temperature for 40nm thick film acquired on 1MHz frequency. The C-V curves indicated the oxide capacitor value Cox of Ti and Er co-doped HfO_2 film larger as compared to the curve of HfO_2 thin films. Whereas, an appropriate dielectric constant, low flat band voltage VFB and better interface state density (Dit=0.41× $10^{12}cm^{-2}eV^{-1}$) were observed.

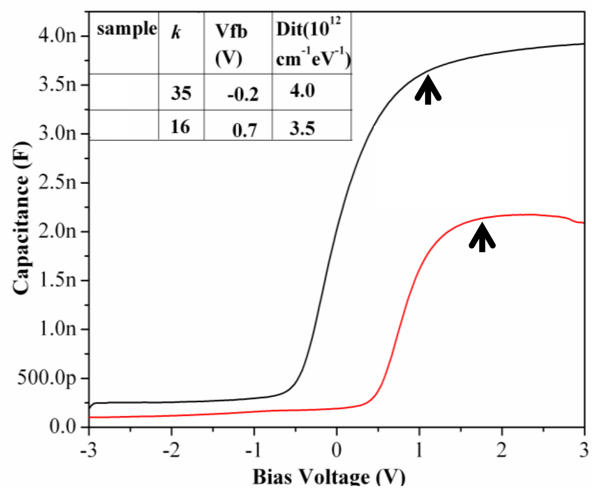

Fig.3. C-V curves of HfO_2 and HfTiErO MOS Structure deposited at 673 K temperature

4. CONCLUSION

An attempt has been made to investigate HfTiErO thin films deposited on Si (100) wafers using RF sputtering with thickness about 40nm. XRD spectra suggests existence of crystalline microstructure in HfTiErO thin film, which helps in enhancing the dielectric constant of deposited films. PL spectrum verified that the density of defect is higher in pure HfO_2 and decreases with doping Ti and Er, while number of different defects levels increases with doping. The C-V curves indicated the oxide capacitor value Cox of Ti and Er co-doped HfO_2 film larger as compared to the curve of HfO_2 thin film. Whereas, an appropriate dielectric constant, low flat band voltage VFB and better interface state density (Dit = 0.41 × $10^{12}cm^{-2}eV^{-1}$) were observed.

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