Energy band profile of Al /HfO_2 / p-Ge MOS structures by XPS and electrical characterization

M. A. Botzakaki[1*], G. Skoulatakis[2], G. Papageorgiou[1] and C. A. Krontiras[1]

[1]Dept. of Physics, University of Patras, 26504, Patras, Greece
[2]Dept. of Chemical Engineering, University of Patras, 26504, Patras, Greece

corresponding author: mpotzakaki@physics.upatras.gr

ABSTRACT

The construction of the energy band profile of MOS structures based on high-k dielectrics and high mobility substrates is critical for the understanding and optimization of their electrical response [1,2]. It is well known that some of the crucial criteria for an alternative to SiO_2 gate dielectric include a defectless interface (atomically flat with low rms roughness) exhibiting low Density of interface traps (D_{it}), a high value of permittivity (at least higher than SiO_2) as well as a sufficient barrier height that will effectively block electrons and holes. High quality HfO_2 constitutes one of the possible alternative high-k dielectrics mainly due to its chemical stability and high permittivity value (k=20-25) [3,4].

The aim of the present work is the construction of the interface band diagrams of HfO_2/ p-Ge combining two different experimental techniques i.e. X-ray Photoelectron Spectroscopy and electrical conductivity measurements. The implementation of these two methods gives a thorough insight of the electrical behaviour of MOS structures.

HfO_2/ p-Ge, up to 15nm, structures were grown via Atomic Layer Deposition (ALD) technique at 250°C. The precursor, used for the deposition of HfO_2 was Tetrakis(Dymethylamido)Hafnium while the co-reactant / oxidant was water. The chemical composition as well as the energy barrier height between 5nm HfO_2 / p-Ge interface were studied ex situ by XPS.

Al gate electrodes were deposited onto HfO_2 films, by thermal evaporation technique, resulting in Al / 15nm HfO_2/ p-Ge MOS structures. The structures were electrically characterized through the analysis of C-V, G-V and C-f measurements in order to evaluate the density of interfacial traps (D_{it}) and the EOT value. Furthermore, J-V measurements were performed and analyzed, for both positive and negative gate voltages with temperature as a parameter. Conduction mechanisms and energy barrier heights were verified / calculated for both negative and positive electric fields.

EXPERIMENTAL

(a) Sample preparation

- **5nm and 15nm thin films of HfO_2 grown by ALD onto p-Ge substrates.**
- **The substrates where properly cleaned prior to the deposition (HF 2% v/v and DI).**
- **Thin films were deposited by Atomic Layer Deposition, ALD (Savannah-100 ALD system by Cambridge-Nanotech/USA), through 160 alternating pulses of H_2O and Tetrakis (Dymethylamido) Hafnium. The deposition temperature was 250°C and the average growth rate of the films was 0.94 Å/cycle.**

(b) Chemical & Electrical characterization

- **XPS analysis.**

  The 5nm HfO_2/Ge interfaced samples were introduced in Ultra High Vacuum and characterized by XPS (non-monochromatized AlKα X-Ray source - 1486.6 eV-).

  Photoemission spectra were collected by a Leybold-Heraeus EA11 hemispherical energy analyser operating at constant pass energy of 100 eV.

  Adventitious carbon at 284.8 eV was used as a reference for electrostatic charging correction.

- **Formation of ~300nm top Al electrode by thermal evaporation. Patterned capacitors with gate area (4x4)mm².**
- **I-V characteristics by Keithley 2611A in the temperature range from 163K to 393K.**

CHEMICAL CHARACTERIZATION

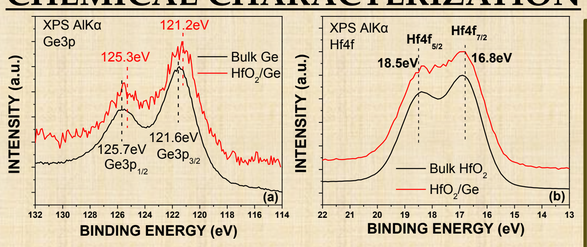

Figure 1: X-ray photoelectron spectra for (a) Ge3p (b) Hf4f

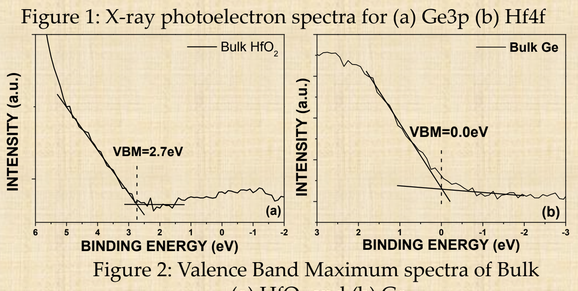

Figure 2: Valence Band Maximum spectra of Bulk (a) HfO_2 and (b) Ge

- The Ge3p XPS peak appears as a double peak, $Ge3p_{1/2}$ and $Ge3p_{3/2}$, due t spin-orbit interaction.
- The $Ge3p_{1/2}$ and $Ge3p_{3/2}$ peaks appear at the binding energies of 125.7 ± 0.1 and 121.6 ± 0.1eV respectively, characteristic of Ge^0 for Bulk Ge [5].
- For the HfO_2 (≈5nm) / Ge sample the $Ge3p_{1/2}$ and $Ge3p_{3/2}$ peaks appear at 0.4eV lower than the expected binding energy. This difference is attributed to differential charging.
- Two peaks appear, one located at 18.5± 0.1 eV ($Hf4f_{5/2}$) and the other at 16.8 ± 0.1 eV ($Hf4f_{7/2}$), with an energy difference 1.7eV and an area ratio 3:4 corresponding to HfO_2 [6].

- The valence band maxima of Bulk HfO_2 and Ge appear at 2.7 ± 0.1 eV and at 0.0 ± 0.1 eV respectively.
- According to Kraut's methodology [7] the VBO (ΔEV) and the CBO (ΔEC) value is determined by the following equations:

$$\Delta E_V = \left(E_{CL}^{Ge3p3/2} - E_{VBM}^{Ge}\right) - \left(E_{CL}^{Hf4f7/2} - E_{VBM}^{HfO2}\right) - \Delta E_{CL}$$

$$\Delta E_{CL} = E_{CL}^{Ge3p3/2} - E_{CL}^{Hf4f7/2}$$

$$\Delta E_C = E_g^{HfO2} - E_g^{Ge} - \Delta E_V$$

- The energy band diagram is constructed through the combination of XPS and I-V experimental data.
- The red values are calculated through XPS analysis, while the blue from the analysis of I-V measurements.
- The values pointed out in black are values taken from the literature.

ELECTRICAL CHARACTERIZATION

I-V CHARACTERISTICS

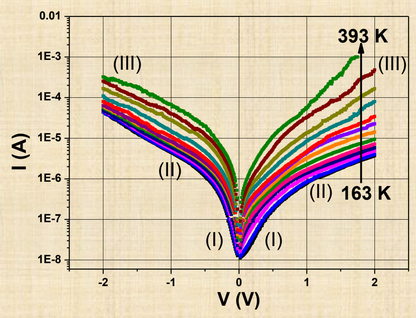

Figure 3: (a) I-V characteristics for Al/15nm HfO_2/ p-Ge under substrate (positive voltages) and gate electron injection (negative voltages) in the temperature range from 163K to 393K.

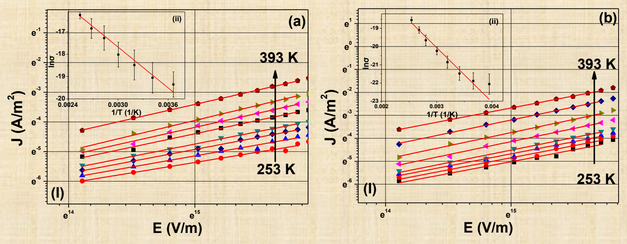

Figure 4: lnJ – lnE characteristics for gate voltages lower than 0.2 V in the temperature range between 253K and 393K for (a) substrate electron injection and (b) gate electron injection. Insets: Arrhenius plot for low (i) positive and (ii) negative voltages in the same temperature range.

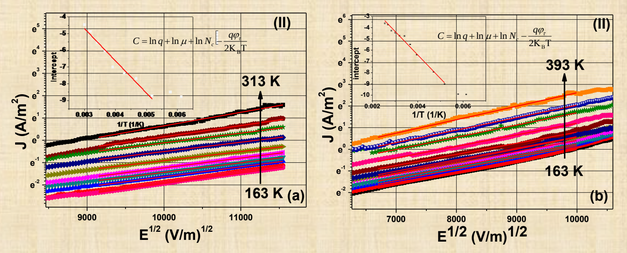

Figure 5: lnJ vs $E^{1/2}$ for (a) positive and (b) negative voltages. Inset: C vs 1/T

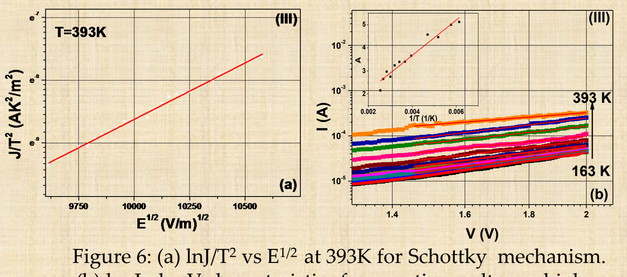

Figure 6: (a) lnJ/T^2 vs $E^{1/2}$ at 393K for Schottky mechanism. (b) logI - logV characteristics for negative voltages higher than 1,4V. Inset: Exponent A vs 1/T .

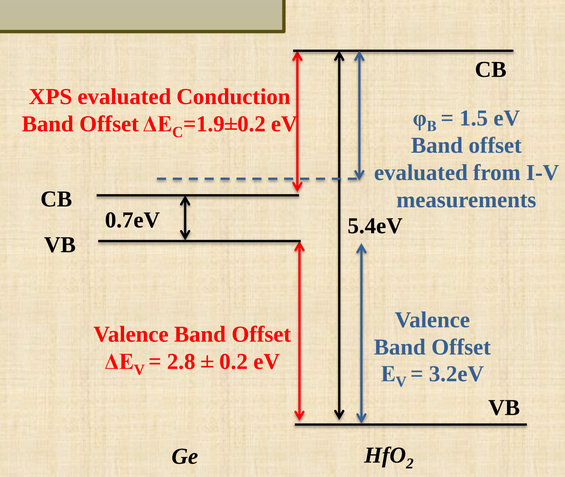

Figure 7: energy band diagram is constructed combining XPS and electrical characterization experimental data

VOLTAGE REGION I (V<0.2V)

- In the low voltage region at temperatures higher than 253K, the prevailing conduction mechanism both for substrate (positive voltages) and gate electron injection (negative voltages) is Ohmic (Fig. 4a,b).
- The activation energy of the Ohmic conduction mechanism, in both cases, is evaluated, according to eq. 1 [8],

$$J = \sigma E e^{\frac{-E_{act}}{KT}} \quad (1)$$

and equals to 0.28 eV (inset of fig.4a,b).

VOLTAGE REGION II ($0.6V<V_{app}<1.4V$)

- For positive, higher than 0.6V, applied voltages in the temperature range between 163K and 313K and for negative voltages between $0.6V<V_{app}<1.4V$ in the whole temperature range, the conduction is dominated by the Poole Frenkel mechanism.

$$J = q\mu N_c e^{\frac{-q(\varphi_T - \sqrt{qE/\pi\varepsilon\varepsilon_0})}{2K_BT}} \quad (2)$$

- The activation energy is calculated to be equal to 0.37 eV (inset of fig. 5a,b) [9].

VOLTAGE REGION III ($V_{app}>1,4V$)

- For temperatures higher than 313K, in the case of positive applied voltages, Schottky is the prevailing conduction mechanism.

$$J = A^* T^2 e^{\frac{-q(\varphi_B - \sqrt{qE/4\pi\varepsilon\varepsilon_0})}{K_BT}} \quad (3)$$

- Fitting the experimental data to eq. 3 (fig. 6a), the barrier height (ϕ_B) between HfO_2 / p-Ge, is evaluated to be equal to 1.5 eV.
- For negative voltages the dominant conduction mechanism is the trap controlled space charge limited (TSCLC) (fig. 6b)

$$J = \frac{8\mu\varepsilon_i}{9d^3} V^A \quad \text{where } A>2 \quad (4)$$

with $A=1+\sigma/kT$ and σ: the trap energy dispersion [10].

- The value of σ was calculated to be 0.1eV (inset of fig. 7a) indicating shallow traps, located near the coduction band [11].

- Calculated, through XPS and I-V analysis, values of ϕ_B differ of about 0.4eV.
- I-V measurements in a broader voltage and temperature range, have to be performed in order to get a better view of Schottky conduction mechanism and the evaluation of conduction band offset.

CONCLUSIONS

- The stoichiometry of HfO_2 deposited films has been identified by XPS.
- The valence band maxima of Bulk HfO_2 and Bulk Ge, as detected by XPS, appear at 2.7 ± 0.1 eV and at 0.0 ± 0.1 eV respectively.
- I-V analysis revealed that:
  - For both low positive and low negative applied voltages, Ohmic is the prevailing mechanism with an activation energy of 0.28 eV.
  - For positive applied voltages higher than 0.6V (i) in the temperature range between 163 and 313K, Poole Frenkel is the dominant conduction mechanism with activation energy equal to 0.37eV, while (ii) for higher temperatures, Schottky conduction mechanism is the prevailing one. The barrier height of HfO_2 / p-Ge is evaluated to be 1.5V.
  - For negative applied voltages (i) in the range of $0.6V<V_{app}<1.4V$, the prevailing conduction mechanism is Poole-Frenkel with an activation energy of 0.37eV, while (ii) for voltages higher than 1.4V the trap controlled space charge limited conduction is the dominant one.
- The energy band diagram is constructed combining XPS and electrical characterization experimental data. The calculated barrier heights from the I-V (1.5 eV) and XPS (1.9 eV) analysis, are in fair agreement.

REFERENCES

[1] H. Sung et al., Appl. Phys. Let. 105, 182101, (2015)
[2] Tahir et al., Applied Physics Letters 94, 212902, (2009)
[3] P. Svarnas et al. Thin Solid Films, 99, 49-53, (2016)
[4] M A Botzakaki et al. J. Phys. D: Appl. Phys., 49, 385104, (2016)
[5] Y. Zhu et al. J. Vac. Sci. & Techn. B 32, 011217 (2014)
[6] M A Botzakaki et al. J. Phys. D: Appl. Phys.49 385104 (2016).
[7] E. Kraut et al S. Phys Rev B 1983, 28, 1965
[8] M. T. Wang et. al J. Electrochem. Soc., Vol. 152, Issue 7 (2005)
[9] Frenkel, Physical Review, 54(8), 647–648.
[10] A. S. Sarkar and S. K. Pal, J. Phys. D: Appl. Phys. 48, 445501 (2015)
[11] R. Ramprasad, J. Appl. Phys. 94, 5609-5612 (2003)

ACKNOWLEDGMENTS

This/ The research/project is implemented through /has been co-financed by the Operational Program "Human Resources Development, Education and Lifelong Learning" and is co-financed by the European Union (European Social Fund) and Greek national funds.