UGC-MRP Project Completion Report

"Deposition and Electrical Characterization of Rare Earth Oxide Doped High-k Thin Films on Si Substrates for Nanoscale MOSFETs"

File No.: 43-302/2014 (SR)

(1st July 2015 to 30th June 2018)

Submitted to

UNIVERSITY GRANT COMMISSION

(UGC-MRP NEW DELHI)

By

Prof. Ashok M. Mahajan

(Principal Investigator)

Department of Electronics

School of Physical sciences

Kavayitri Bahinabai Chaudhari

North Maharashtra University

Jalgaon– 425001

KAVAYITRI BAHINABAI CHAUDHARI

NORTH MAHARASHTRA UNIVERSITY

JALGAON -425001

(August 2018)

Annexure - III

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. **Name of Principal Investigator:** Prof. Ashok M. Mahajan
2. **Department of Principal Investigator:** Department of Electronics,
   University/~~College~~: North Maharashtra University, Jalgaon (MH)
3. **UGC approval Letter No. and Date:** F. No. 43-302/2014 (SR) dated 9th Aug 2015
4. **Title of the Research Project**: "Deposition and electrical characterization of Rare Earth Oxide doped high-k thin films on Si substrates for Nanoscale MOSFETs"
5. **Effective date of starting the project**: 1st July 2015
6. **a. Period of Expenditure: From** 1st July 2015 to 30th June 2018

   b. Details of Expenditure:

Sr. No.	Item Description	Amount Approved in Rs.	Grant Being Released 1st Installment Year 2015-2016 in Rs.	Expenditure Incurred in Rs.
1	**Books & Journals**	-	-	-
2	**Equipment**	10,50,000/-	10,50,000/-	10,43,369/-
3	**Contingency**	-	-	-
4	**Field Work/Travel (Give details in the proforma at Annexure-IV).**	30,000/-	7,500/-	5,350/-
5	**Hiring Services**	-	-	-
6	**Chemicals & Glassware**	15,000/-	15000/-	15,000/-
7	**Overhead**	3,000/-	3,000/-	3,000/-
8	**Any other items (Please specify)**	-	-	-
Total		**10,98,000/-**	**10,75,500/-**	**10,66,719/-**

A. Unutilized Amount= Rs. 8,781/-

B. Interest Amount = Rs. 15,458/-

Amount to be Refunded to UGC (A+B) = Rs. 24,239/-

c. Staff : NA

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. If as a result of check or audit objection some irregularly is noticed at later date, action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the grant of **Rs. 10,75,500/- (Rupees Ten Lakh Seventy Five Thousand Five Hundred only)** received from the University Grants Commission under the scheme of support for Major Research Project entitled **"Deposition and electrical characterization of rare Earth Oxide doped high-k thin films on Si substrates for Nanoscale MOSFETs"** vide UGC letter No. F. No. 43-302/2014 (SR) dated 9th Aug 2015has been utilized **Rs. 10,66,719/- (Rupees Ten Lacs, Sixty Six Thousand, Seven Hundred and Nineteen Only)** period of expenditure from **1st July 2015 to 30th June, 2018** for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Signature

(Prof. A. M. Mahajan)
Principal Investigator

Signature

(Mr. B. B. Patil)
Registrar of University
REGISTRAR
North Maharashtra University
Jalgaon

Annexure - IV

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

STATEMENT OF EXPENDITURE INCURRED ON FIELD WORK

Name of the Principal Investigator: Prof. Ashok M. Mahajan

Sr. No.	Name of The Place Visited	Duration of Visit		Mode of Journey	Expenditure Incurred (Rs.)
		From	To		
1	Mumbai	16/02/2017	18/02/2017	Bus	1,005/-
2	Mumbai	04/01/2017	06/01/2017	Bus	1,940/-
3	SRM University, Chennai	07/08/2017	13/08/2017	Train	1,535/-
4	SP Pune University	10/07/2017	16/07/2017	Train	870/-
	Total: Five Thousand Three Hundred and Fifty Only				**5,350/-**

Certified that the above expenditure is in accordance with the UGC norms for Major Research Projects.

Signature

(Prof. A. M. Mahajan)
Principal Investigator

Signature

(Mr. B. B. Patil)
Registrar of University
REGISTRAR
North Maharashtra University
Jalgaon

NORTH MAHARASHTRA UNIVERSITY • JALGAON-425001 •

Annexure - V

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Utilization certificate

Certified that the grant of **Rs. 10,75,500/- (Rupees Ten Lakh Seventy Five Thousand Five Hundred only)** received from the University Grants Commission under the scheme of support for Major Research Project entitled **"Deposition and electrical characterization of rare Earth Oxide doped high-k thin films on Si substrates for Nanoscale MOSFETs"** vide UGC letter No. F. **No. 43-302/2014 (SR)** dated **9th Aug 2015. Rs. 10,66,719/- (Rupees Ten Lacs Sixty Six Thousand Seven Hundre d and Nineteen)** has been utilized period of expenditure from **1st July 2015** to **30th June 2018** for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Signature	Signature	Signature
(Prof. A. M. Mahajan)	(Mr. B. B. Patil)	
Principal Investigator	Registrar of University	Statutory Auditor

REGISTRAR
North Maharashtra University
Jalgaon

NORTH MAHARASHTRA UNIVERSITY • JALGAON-425001 •

A. I. Kothari & Associate's Chartered Accountants FRN 112022W

AS PER OUR REPORT ANNEXED
M/s. A. I. Kothari & Associate's
Chartered Accountants
CA Anil Kothari-Partner
FRN-112022W M. No.-045352
28/08/2018

A.I.KOTHARI & ASSOCIATES
CHARTERED ACCOUNTANTS
Head Off :-245/I, V.V.Market,
(Golani Mkt) At- Jalgaon.425001
Email: aik1991@gmail.com

ALPHABETS OF TRUST

Branch Correspondence Address
201, Aditya Chembers, 2Nd Floor
Above Corporation Bank -
Navi Peth ,At- Jalgaon.425001
CA Anil Kothari 98230 07773

Ref :- NMU/CERT/131 Date:-28/08/2018

North Maharashtra University, Jalgaon
Department of Electronics,

Utilization Certificate

Certified that the Expenditure of the **"Deposition and electrical characterization of rare Earth Oxide doped high –k thin films on Si substrates for Nanoscale MOSFETs" Funded by Universit Grant Commission , New Delhi,** for the Period of 1st July-2015 to 30th June-2018 in respect of the **Prof. Ashok M. Mahajan Department of Electronic, North Maharashtra University, Jalgaon** have been audited by us with reference to the vouchers and the norms of Expenditure and relevant guidelines thereto, The statement of account Major Research Project duly signed by us is enclosed.

It is therefore hereby certifies that the grant received from North Maharashtra University, Jalgaon of **Rs. 1075500/- (Rs. Ten Lakhs Seventy Five Thousand Five Hundred)** and actually expenditure is **Rs. 1066719/- (Rs. Ten Lakhs Sixty six Thousand Seven Hundred Nineteen)** had been utilized by college for implementation of the above activities, in accordance with the terms and conditions and procedures, norms and guideline laid down for the purpose.

A. I. Kothari & Associates,
Chartered Accountants

CA Anil Kothari - Partner
Membership No 045352
Firm Registration No 112022W

A. I. Kothari & Associates Chartered Accountants FRN 112022W

Annexure VIII

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI –110 002.

Final Report of the work done on the Major Research Project.
(Report to be submitted within 6 weeks after completion of each year)

1. Project report No. **Final**

2. UGC Reference No.F. **43-302/2014 (SR) dated 9th August, 2015**

3. Period of report: from **1st July, 2015** to **30th June, 2018**

4. Title of research project: **"Deposition and Electrical characterization of Rare Earth doped High-k thin films on Si substrates for Nanoscale MOSFETs"**

5. (a) Name of Principle Investigator: **Prof. Ashok M. Mahajan**

(b) Deptt.: **Department of Electronics**

(c) University/college where work has progressed: **North Maharashtra University, Jalgaon**

6. Effective date of starting of project: **1st July, 2015**

7. Grant approved and expenditure incurred during the period of the report:

a. Total amount approved: **Rs. 10,98,000/-**

b. Total expenditure: **Rs.10, 66, 719/-**

c. Report of the work done: (Please attach a separate sheet):

i. Brief objectives of the project:

- To develop the novel process of passivation of interface layer between high-k and semiconductor substrate.
- To deposit the rare earth oxide high-k materials by sol-gel/EB evaporation technique on Si substrate.
- To develop the novel post deposition annealing (PDA) immediately after the deposition of high-k, to get the high-k film with various desired properties in order to cope up with the future technology node.

- To develop the novel Metal gate/high-k stack structure/MOS capacitors by depositing Metal electrodes through shadow mask by EB evaporation technique.
- Characterize the film composition and surface structure.
- Post metallization annealing in FGA and characterize interfacial structures at atomic scale.
- To carry out the electrical characterization (CV & IV) of the fabricated stacks or MOS capacitors to check the suitability for advanced CMOS technology (22 nm & beyond).

ii. Work done so far and results achieved and publications, if any, resultingfrom the work (Give details of the papers and names of the journals inwhich it has been published or accepted for publication:

Work done so far: Enclosure I

Published:

1. Khushabu S. Agrawal, Vilas S. Patil, Anil G. Khairnar, and Ashok M. Mahajan "Structural and Electrical Properties of Sol-gel CeO_2 Thin Films on Si (100) Substrate" J Mater Sci: Mater Electron (2017) 28:12503–12508 (IF: 2.324)
2. Khushabu S. Agrawal, Vilas S. Patil, and Ashok M. Mahajan "ALD-HfO_2 Ultra-thin Films Deposited on Different Crystallographic Orientation Ge for CMOS Applications" Thin solid Films, 654, 30-37 (2018) (IF: 1.939)
3. Viral Barhate, KhushabuAgrawal, Vilas Patil, SumitPatil and Ashok Mahajan"Spectroscopic study of La2O3 thin films deposited by indigenously developed plasma-enhanced atomic layer deposition system" International Journal of Modern Physics B, Vol. 32 1840074 (5 pages) (2018) (IF: 0.7)

Submitted:

4. Viral N. Barhate, Khushabu S. Agrawal, Vilas S. Patil, Sumit R. Patil and Ashok M. Mahajan, "Post deposition microwave assisted annealing effect on lanthanum doped cerium oxide thin films", submitted to Bulletin of Material Science (IF: 0.899)
5. KhushabuAgrawal, Viral N. Barhate, Vilas Patil and Ashok M. Mahajan, "La_2O_3 ultra-thin films grown by Low Power Plasma Enhanced Atomic Layer Deposition on Si and 6H-SiC substrates" submitted to Journal of Vaccum (Revision uploaded) (IF: 2.067).
6. Vilas S. Patil, Khushabu S. Agrawal, Viral N. Barhate, Sumit R. Patil and Ashok M. Mahajan, "XPS study of Homemade Plasma Enhanced Atomic Layer

Deposited La_2O_3/ZrO_2 Bilayer Thin Films", submitted to special issue of Semiconductor science and technology (IF: 2.280)

iii. Has the progress been according to original plan of work and towards achieving the objective? If not, state reasons.

YES

iv. Please indicate the difficulties, if any, experienced in implementing the project.

NA

v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet.

NA

vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission.

Enclosure II

vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a)Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any

(a) Trained Manpower No. 4

1. Mr. Vilas Patil
2. Ms. Khushabu Agrawal
3. Ms. Viral Barhate
4. Mr. Sumit Patil

(b) PhD Awarded:

1. Mr. Vilas Patil(Thesis Submitted)
2. Ms. Khushabu Agrawal (Pre Ph.D. Thesis Submitted)

(c) Publication of results:

Published

1. Viral Barhate, Khushabu Agrawal, Vilas Patil, Sumit Patil and Ashok Mahajan "Spectroscopic study of La_2O_3 thin films deposited by indigenously developed plasma-enhanced atomic layer deposition system" International Journal of Modern Physics B, Vol. 32 1840074 (5 pages) (2018) (IF: 0.7)
2. Khushabu S. Agrawal, Vilas S. Patil, Anil G. Khairnar, and Ashok M. Mahajan "Structural and Electrical Properties of Sol-gel CeO_2 Thin Films on Si (100) Substrate" J Mater Sci: Mater Electron (2017) 28:12503–12508 (IF: 2.324)
3. Khushabu S. Agrawal, Vilas S. Patil, and Ashok M. Mahajan "ALD-HfO_2 Ultra-thin Films Deposited on Different Crystallographic Orientation Ge for CMOS Applications" Thin solid Films, 654, 30-37 (2018) (IF: 1.939)

Under Review

4. Khushabu Agrawal, Viral N. Barhate, Vilas Patil and Ashok M. Mahajan, "La_2O_3 ultra-thin films grown by Low Power Plasma Enhanced Atomic Layer Deposition on Si and 6H-SiC substrates" submitted to Journal of Vaccum (Revision uploaded) (IF: 2.067)
5. Viral N. Barhate, Khushabu S. Agrawal, Vilas S. Patil, Sumit R. Patil and Ashok M. Mahajan, "Post deposition microwave assisted annealing effect on lanthanum doped cerium oxide thin films", submitted to Bulletin of Material Science (IF: 0.899)

6. Vilas S. Patil, Khushabu S. Agrawal, Viral N. Barhate, Sumit R. Patil and Ashok M. Mahajan, "XPS study of Homemade Plasma Enhanced Atomic Layer Deposited La_2O_3/ZrO_2 Bilayer Thin Films", submitted to special issue of Semiconductor science and technology (IF: 2.280)

(d) Other impact:

- RTP system procured and installed, the process parameters optimized, and technical competence of research team enhanced, through its usage in lab
- Laboratory enriched by Rapid thermal annealing system and that will helps in fabricating entire MOS devices in the MDLN laboratory.

Signature of Principal Investigator

Registrar
(Seal)

REGISTRAR
North Maharashtra University
Jalgaon.

Enclosure I

Detailed report of the work carried out, Results and Details of Publication

a. Work done so far:

1. Procurement of Rapid thermal annealing system.

The Rapid thermal annealing system (Fourvac Make) used for the post deposition annealing purchased through this project is shown below.

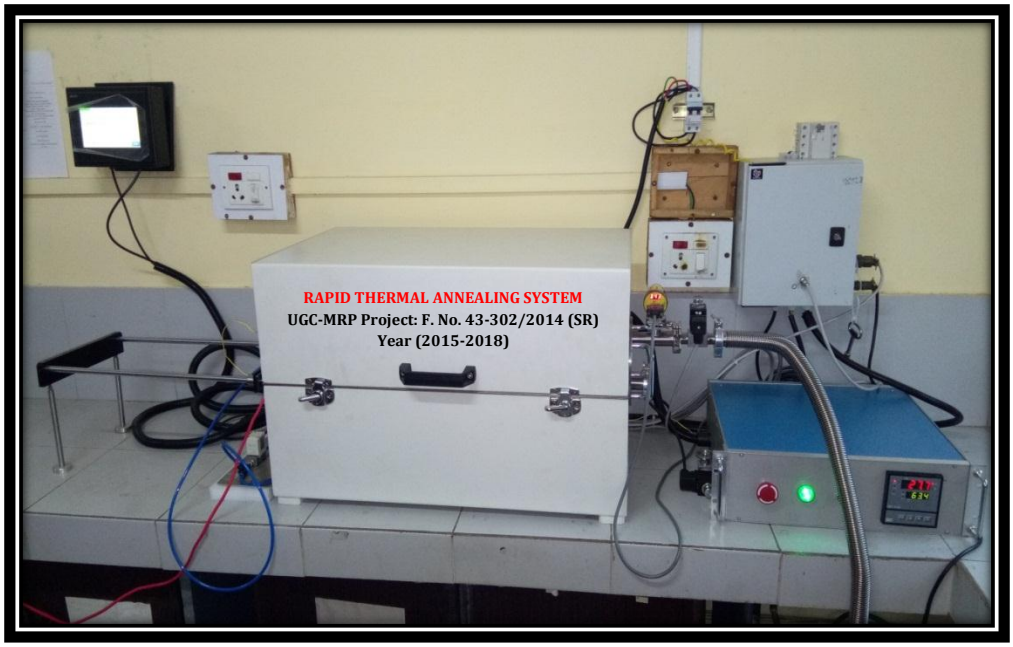

Figure 1: Rapid Thermal Annealing System

2. In situ passivation procedure:

The in situ passivation of Si and SiC were performed by using PEALD system in N2 plasma environment. Further, the passivation can also be done by using procured RTP system with the help of different gaseous environment and time variation. The effects of passivation were confirmed through FTIR and XPS. Figure 2 shows the XPS spectra of La_2O_3 films deposited on surface nitrided Si.

3. Methodology:

The rare earth doped high-k thin films were deposited by using sol gel and PEALD system. In PEALD, the in-situ passivation was performed by using N_2 and O_2 plasma for different timing. After passivation of the surfaces, the La_2O_3 films were deposited at various cycles. After deposition, the post deposition annealing is carried out in RTP. The metal electrodes were formed to check the electrical properties of the thin films. The flowchart for method adopted for fabrication of MOS devices in this work is shown in figure 3.

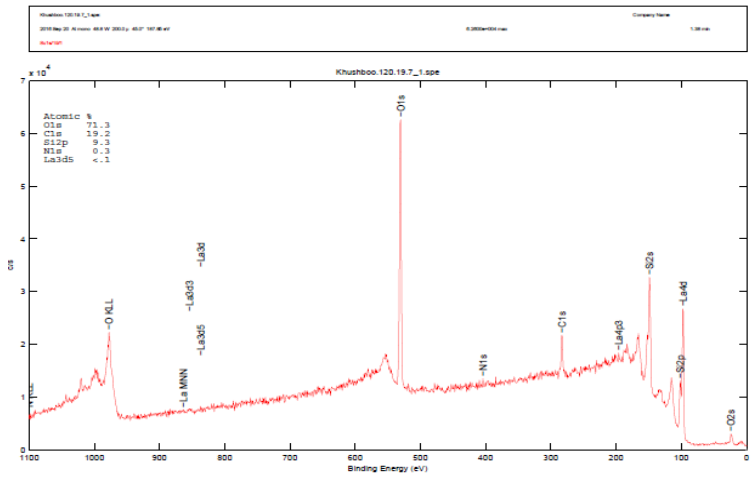

Figure 2: XPS spectra of La_2O_3 films deposited on surface nitrided Si

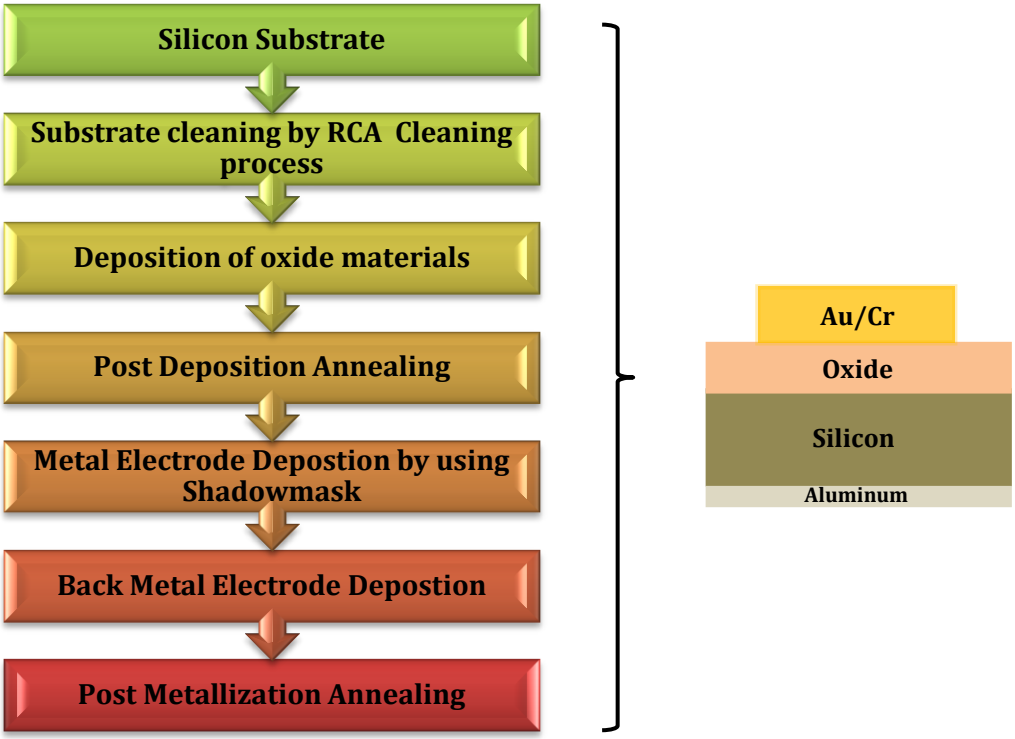

Figure3: Schematic illustration of the basic fabrication steps of MOS device

4. Results of the fabricated MOS devices:

4.1 The metal Work function engineering of Fabricated Au/Ti/CeO_2/Si MOS devices:

The ITRS projected that, the metals with higher work functions are the boosters for high performance of the devices. To meet the off current specifications, the increment in gate work function is required. However, the integration of metal gate

electrode and high-k dielectric suffers from the Fermi level pinning which causes difficulty in controlling the effective metal work function (EMWF) of the gate electrode.

The Metal induced gap states (MIGS) theory is widely used to explain these differences occurred at metal/high-k interface related to control of threshold voltage as it should be determined by metal work function since, the threshold voltage determines the on and off factor of the MOS switches. Further, it is noticed that the EMWF obtained through electrical measurement is different than the work function in vacuum. Many approaches have been studied to increase the work function of the devices. Han et al. [1] has been made the use of ion implantation to modulate the effective work function. Mustafa et al. [2]. Used the double gate Fin FET structure to modulate the effective work function and hence the threshold voltage performance of the device. Channel doping can be used to vary the EMWF [3]. Further, the variation in the thickness of underlying metal layer (by keeping the thickness of top metal layer unchanged) is one of way to change the metal work function of the gate electrode [4–7].

Overall, the use of metal gate electrode with suitable work function is the key to fabricate the devices with low V_{th} and drive currents. In this work, the bilayer metal gates were used to manage the drive currents and low V_{th} by enhancing the work function of the gate electrodes. The Ti is considered for lower work function (4.2–4.33 eV) and Au is considered for the high work function (5.1–5.3 eV) to deposit over annealed CeO_2 films. Here, the thickness of both layers is kept constant. After the deposition of Ti/Au bilayer, post metallization annealing has been carried out at 300 °C for 20 min in FG environment. The EMWF has been calculated by using metal induced gap state (MIGS) theory [8]. The relationship between equivalent oxide thickness (EOT) and flat band voltage determined from the C–V curves is given by the following Eq. [1]:

$$qV_{FB} + \varphi_{sub} = \varphi_{m,eff} + \frac{Q_{CeO2/IL}}{\varepsilon_0 \varepsilon_{IL}} EOT_i - \frac{Q_{CeO2/IL}+Q_{IL/sub}}{\varepsilon_0 \varepsilon_{IL}} EOT \ldots\ldots\ldots (1)$$

where, φ_{sub} is the work function of the substrate material, $\varphi_{m,\,eff}$ is the effective work function due to both metal layers ($\varphi_{m,eff1} + \varphi_{m,eff2}$), ε_0 and ε_{IL} are the permittivity of free space and the dielectric constant of the IL respectively, EOT_i is the physical thickness of the interfacial oxide, Q_{CeO2}/IL is the charge at the interface between the high-gate dielectric and IL. $Q_{IL}/_{sub}$ is the charge at the interface between the IL and substrate. From eq. 1 the y-intercept and slope of the fitted line in the Figure 4 gives the effective metal work function and the magnitude with sign of oxide fixed

charge density, respectively. By considering no interfacial layer (IL = 0) between high-k and substrate the y-intercept gives the value of effective metal work function. By calculation, the effective metal work function for Ti/Au bilayer metal gate stack annealed at 300 °C is to be 5.36 eV which is higher than the work function value in vacuum of both metals. The change in value of EMWF is due to interstitial hydrogen atoms with positive charge introduced by the FG annealing compensate negatively charged dipoles associated with the FLP of Si [8].

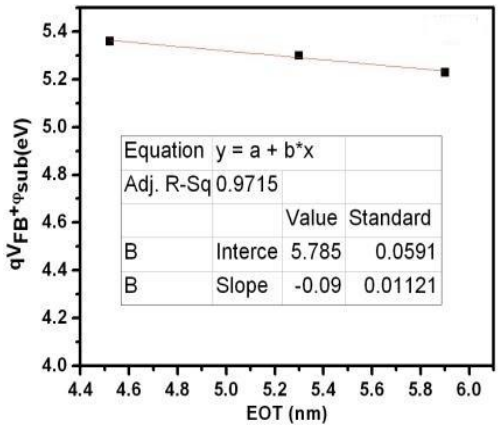

Figure 4: Plot of $qV_{FB}+ \varphi_{sub}$ verses EOT of Au/Ti/CeO_2/Si gate stack annealed at 400 °C

Again the post metallization annealing in forming gas environment helps to modulate the effective work function of top metal layer [9]. Figure 5 shows the curve of leakage current density (J) as a function of the gate voltage (V_G). The value of J is calculated by using eq. $J=I/A_G$. A_G is the gate area formed by depositing Ti/Au over CeO_2 as circular electrodes of 150 μm diameters. The notable value of leakage current density has been extracted from the curve at 1 V is $\sim 1.18 \times 10^{-5}$ Acm^{-2}.

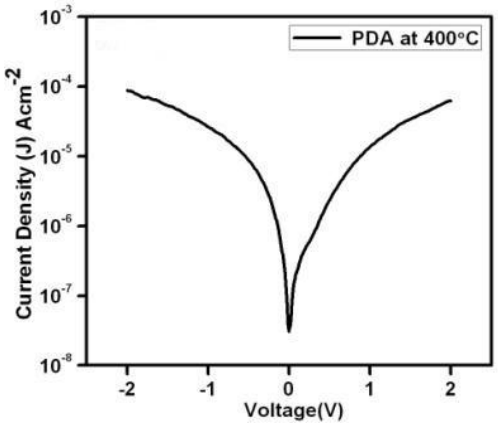

Figure 5: I-V characteristics of Au/Ti/CeO_2/Si gate stack annealed at 400 °C

The work has been published in Journal of Materials Science: Material in electronics (Springer IF: 2.23)

4.2 Effect of post deposition annealing on roughness of sol-gel deposited LaCeO films:

Three dimensional (3D) surface topographies of the $LaCeO_2$ thin films annealed in different ambience were examined using AFM with a scanning area of 3×3 μm shown in figure 6(a), 2(b), 2(c), 2(d) for as deposited, high frequency microwave annealed, low frequency microwave annealed and hot plate annealed at 400°C, respectively. The root-mean square (RMS) surface roughness of 2.9 nm, 2.4 nm, 2.3 nm, and 2.25 nm, measured for as deposited sample, high frequency microwave annealed sample, low frequency microwave annealed sample and hot plate annealed sample (at 400°C), respectively. Further, the film topography shows the smooth and crack free surface as observed from the AFM images.

In general, the post deposition annealing improves the film quality and it is found that observed RMS roughness are lower than that of as deposited sample and do not reveal significant difference in the film roughness for hot plate annealed and microwave annealed samples. Further, the 2D AFM micrographs show the uniform, homogeneous distribution of the grains over entire film.

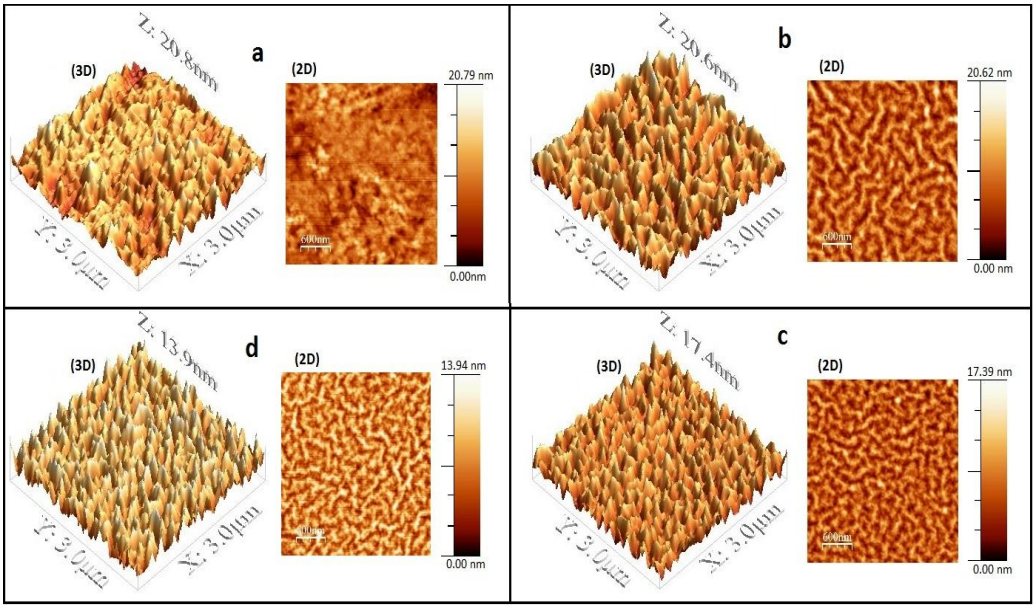

Figure 6: AFM micrographs of sol gel deposited LaCeO films on Silicon

The work has been submitted to Bulletin of Material Science (Springer IF 0.709)

4.3 In situ passivation of Si surfaces by PEALD:

The chemical composition of La_2O_3 films grown on Si were analyzed by means of XPS. The measurements were carried out at 45° take off angle with Al Kα monochromatic source of 1486.6 eV and deconvolution was performed by Gaussian fit method in Casa XPS. Figure 7 (a) shows the Si2P core level spectra of La_2O_3 films deposited on Si. The peaks centered at the binding energy of the 99.19 eV corresponds to the bulk Si and the less intense peak centered at the 103.5 eV shows the Si4+ oxidation state reveals the lanthanum silicate formation at the interface, which leads to a high-k/Si direct-contact interface without any low-interface layer [10, 11]. The binding energy centered at 834.5 eV and 848.75 eV corresponds to La3d5/2 and La3d3/2 states of the lanthanum and confirms the sub-oxide state of the lanthanum that indicates the presence of the La-OH bonds at the surface as shown in La3d core level spectra of figure 7 (b), this observation is identical with those reported by Lee et. al [12]. Figure 7 (c) shows the core level spectra of O1s. The peak centered at the energy of 530.50 eV corresponds to the La-O-Si bonds [13]. Figure 8 shows the graph of peak intensity as a function of number of cycles for the O1s spectra of Si samples.

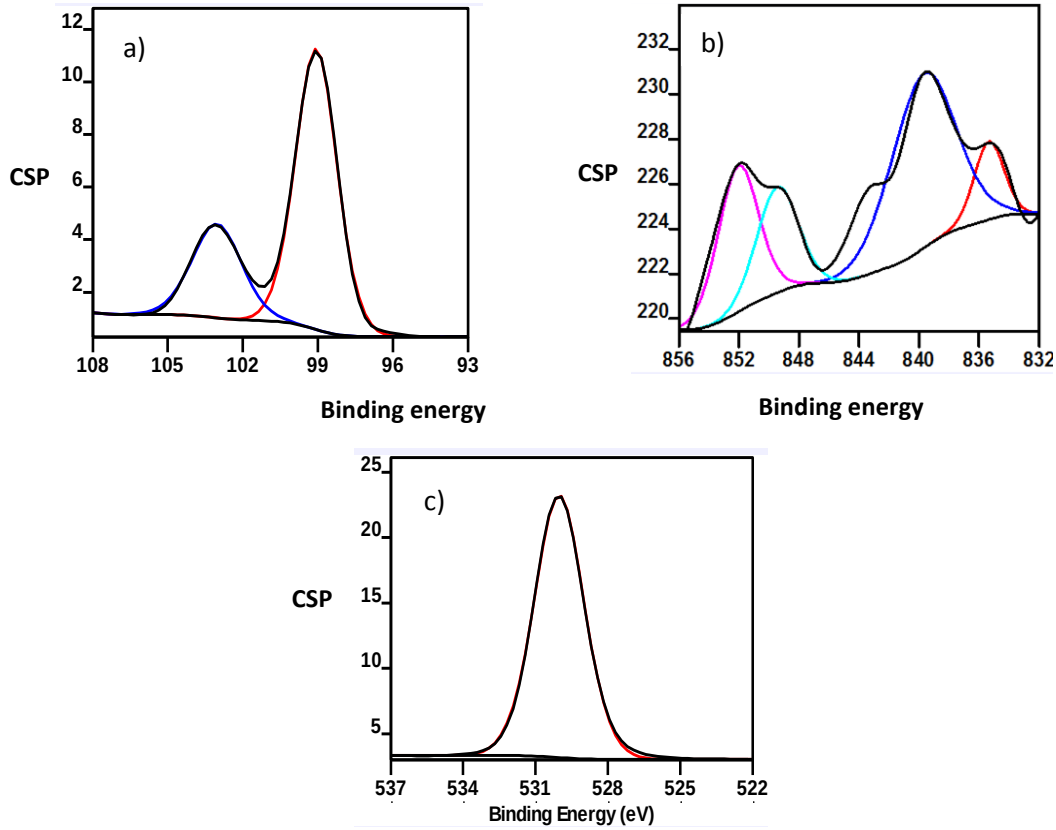

Figure 7: XPS core level spectra of (a) Si2p, (b) La3d and (c) O1s for the films deposited over Si.

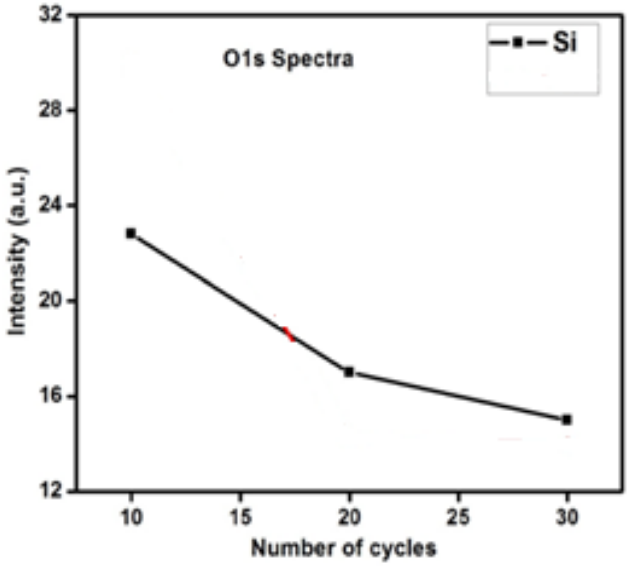

Figure 8: The graph of peak intensity of O1s spectra for La_2O_3 films deposited on Si verses number of cycles.

The intensity observed to be varying for the sample for 10 cycles thereafter; it is going to be constant on Si. Overall, these experimental observations can be attributed to the successful growth of the La2O3 thin films on Si by PEALD system, the variation in the chemical states of lanthanum, oxygen and silicon as observed in the core level spectra La3d, O1s and Si2p may indicate the changes in the structural properties of the deposited thin films therefore, to know more about the deposited films the HRTEM and XRD were performed.

- ✓ ***HRTEM with Energy Dispersive Analysis (EDS):***

Figure 9 (a) shows the cross section HRTEM image of La2O3 thin films deposited on Si for 30 ALD cycles captured at the resolution of 2 nm. The figure confirms the ~1.5 nm thick amorphous La_2O_3 layer over single crystal silicon for 30 cycles of ALD attributes to ~0.5 ± 0.05 Å/cycle growth rates for the substrate temperature of ~150oC and there is no formation of any interfacial layer between Si and La_2O_3.

Further, the elemental confirmation of the La_2O_3 thin films deposited on Si has been investigated by using the energy dispersive analysis (EDS). The EDS spectra confirm the La and oxygen elements over the films for 10, 20 and 30 cycles as shown in figure 9 (b). The percentage of La and O was observed to be increased as the number of cycles increased. The elemental percentage of La and O is given in table 1.

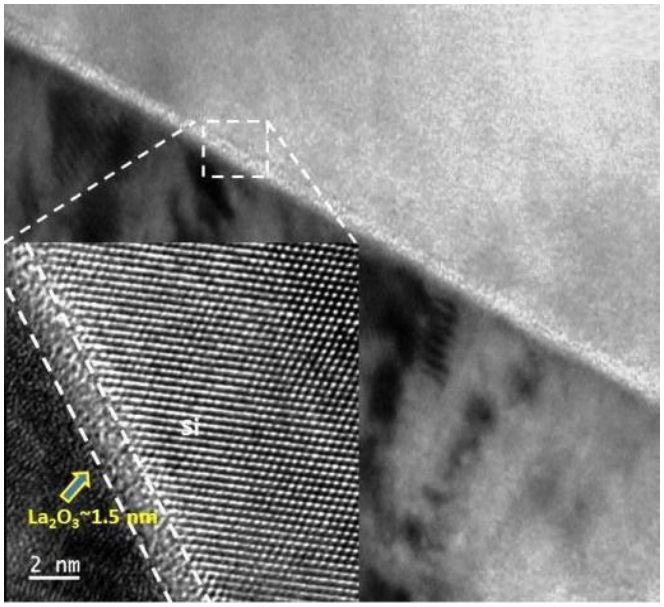

Figure 9 (a): Cross sectional HRTEM image of Si/La_2O_3 stack for 30 ALD cycles performed on silicon

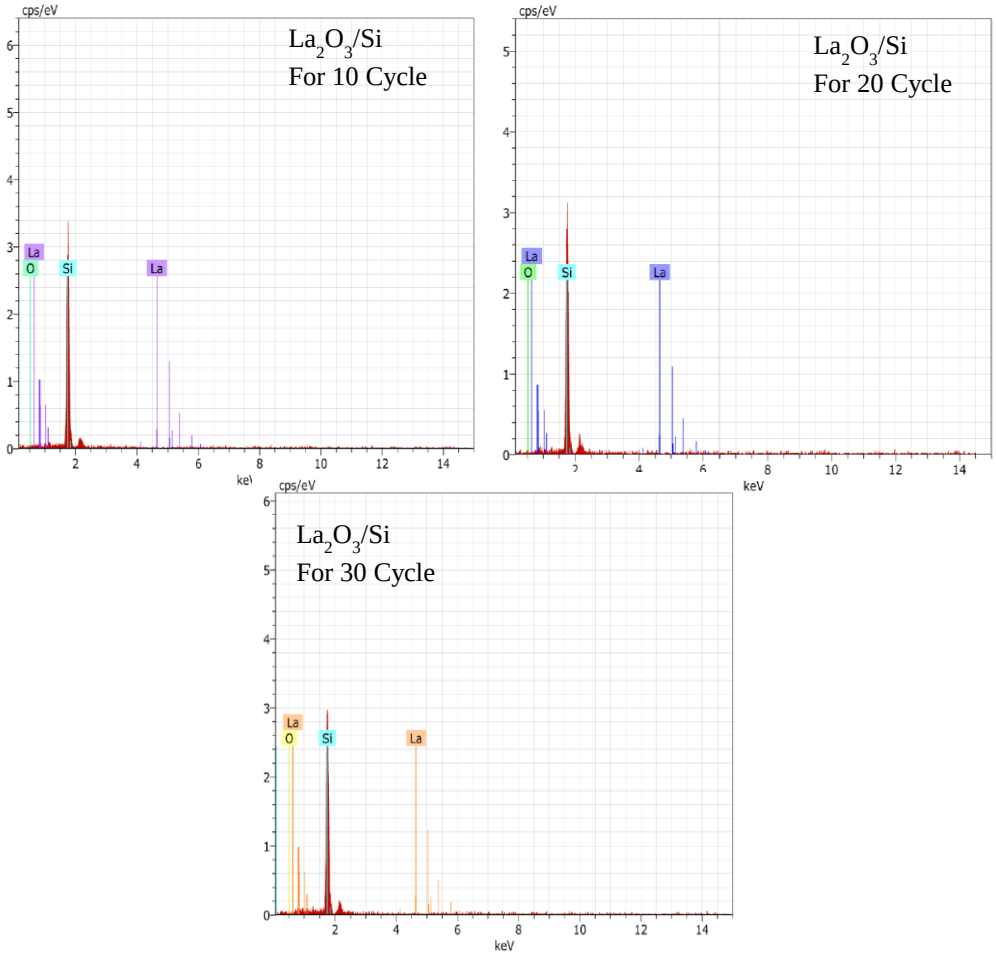

Figure 9 (b): EDS spectra of La_2O_3 thin films for 10, 20 and 30 ALD cycles performed on Si.

Table 1: Elemental percentage of the La and O over Si for 10, 20 and 30 ALD cycles.

Substrate/Material Composition	La (%)			O (%)		
	10 ALD Cycles	20 ALD Cycles	30 ALD Cycles	10 ALD Cycles	20 ALD Cycles	30 ALD Cycles
Si	0.75	1	1.58	1.36	2.05	2.65

The work has been submitted to Journal of Vacuum (Elsevier IF 1.98) Revision uploaded

4.4 Deposition of La_2O_3/ZrO_2 bilayer:

As we know the La2O3 is highly hygroscopic in nature which affects the device properties deeply. The ternary oxides can help to dissolve this problem. The other way to shout this problem is to form bilayer structure over the substrate which includes the formation of buffer layer on the La_2O_3. In this study, we have used ZrO_2 as the buffer layer, to study the interface property of this bilayer, the structure has been swapped and characterizations were performed. Ellipsometry measurement was carried out to know the physical thickness of the deposited films. The interfacial properties were investigated mainly by XPS. The AFM was performed to check the surface properties.

The thickness of La_2O_3/ZrO_2 gate stack was measured by using Sentech SE800 Ellipsometer having the variable spectral wavelength range of 280-850 nm. The measurements were carried out by using full spectral wavelength and R.I value constant at 1.42. The Ellipsometry shows average thickness of ~4.8 nm for La_2O_3/ZrO_2 stack deposited on Si. The average growth rate of 0.08 nm was achieved by using the process parameters given in section 3.7 of chapter 3. The stack calculated by dividing the measured thickness by total number of cycles.

X-ray photoelectron spectroscopy:

To study the interface composition of the $ZrO_2/La_2O_3/Si$ and $La_2O_3/ZrO_2/Si$ gate stack XPS measurements were performed with Al Kamonochromatised source of X-rays having energy of 1486.6 eV and take-off angles(TOA) of 45^oC.

$ZrO_2/La_2O_3/Si$ gate stack:

Figure 10 shows the elemental core level spectra of La3d, Zr3d, Si2p and O1s for $ZrO_2/La_2O_3/Si$ gate stack. The peak centered at the 831-852 eV corresponds to the

$La3d_{5/2}$ line spectra. The spectral lines of Zr3d were recorded at 181-184 eV, Si 2p in the range of 97.8-101.9 eV, O1s at 531 eV.

La_2O_3/ZrO_2/Si gate stack:

Figure 11 shows the core level spectra of La3d, Zr3d, Si2p and O1s for La_2O_3/ZrO_2/Si stack. The spectral lines of $La3d_{5/2}$ recorded at 831-851 eV, for Zr3d at 184 eV, for Si 2p at 98-102.5 eV and finally for O1s at 531.0 eV.

If we observed spectra's of both the stack, the peak centered at 102.5 eV of Si 2p corresponds to La_2O_3/ZrO_2/Si stack shows the formation of silicate at the interface, while no such silicate peak were observed in ZrO_2/La_2O_3/Si stack. Further, the shift in B. E. of bulk Si was also observed in Si 2p of both spectra.

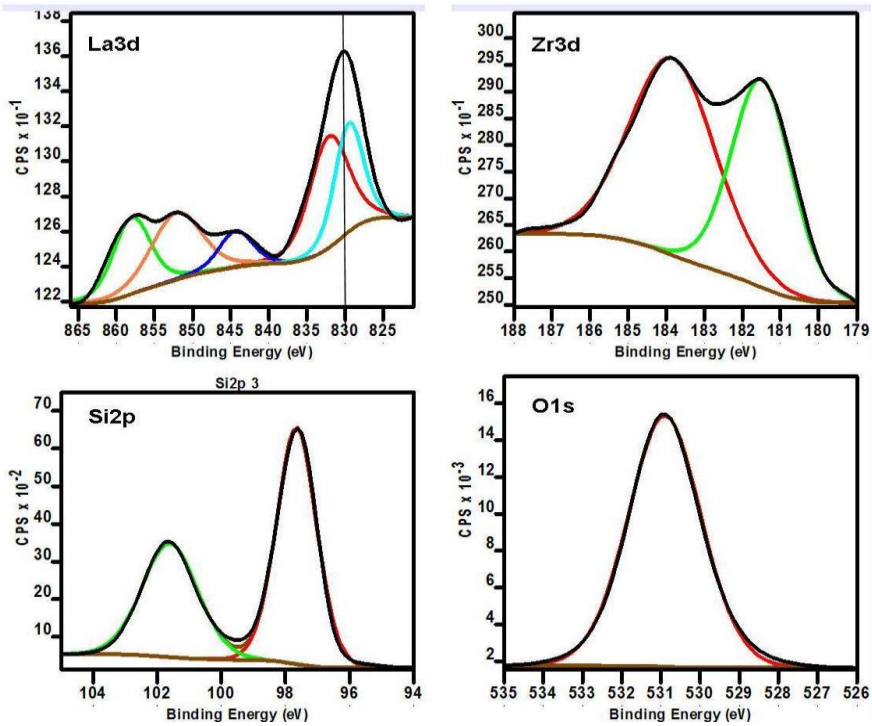

Figure 10: Core Level spetra of La3d, Zr3d, Si2p and O1s for ZrO_2/La_2O_3/Si stack

- ✓ ***Atomic Force Microscopy:***

The surface properties of La_2O_3/ZrO_2 bilayer thin films on Si were examined by using AFM. Figure 12 (a) and (b) shows the AFM micrographs of ZrO_2/La_2O_3/Si and La_2O_3/ZrO_2/Si samples, respectively scanned in the range of 3 ×3 μm. The RMS roughness of 0.35 nm and 0.48 nm was measured for ZrO_2/La_2O_3/Si and La_2O_3/ZrO_2/Si gate stack, respectively.

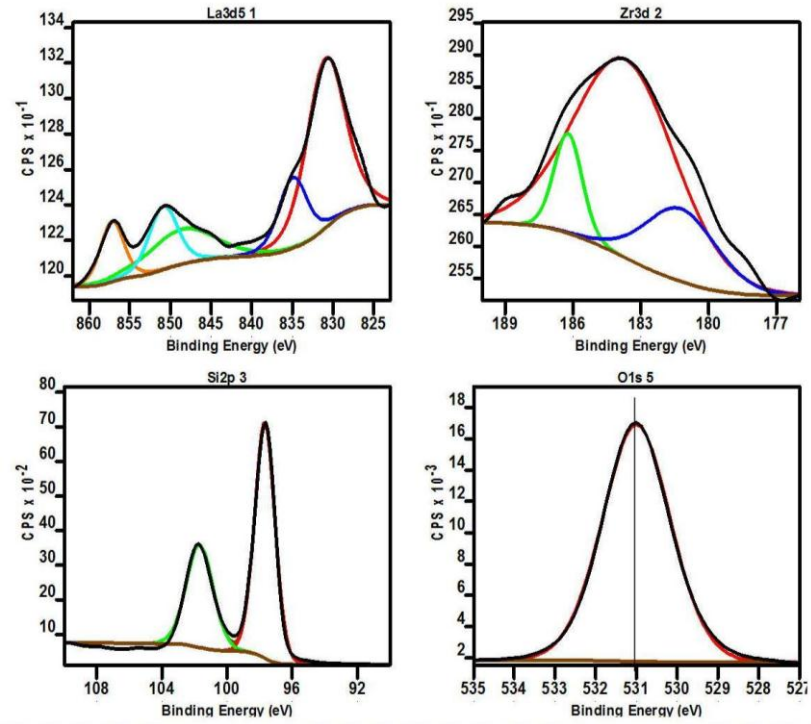

Figure 11: Core Level spetra of La3d, Zr3d, Si2p and O1s for $La_2O_3/ZrO_2/Si$ stack

The manuscript is submitted to Journal of semiconductor Science and technology.

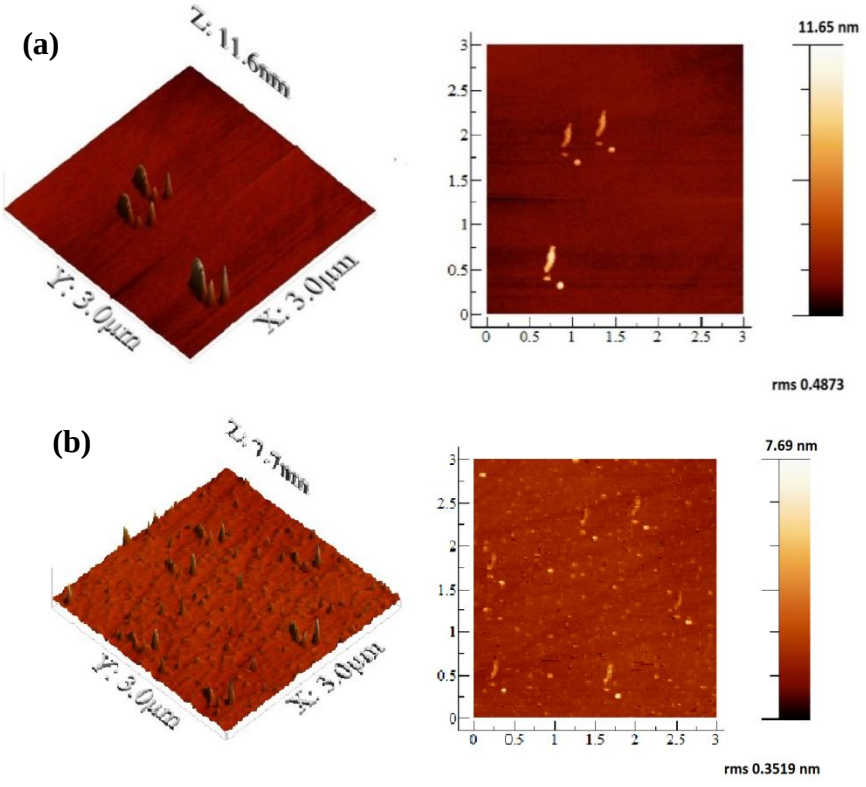

Figure 12: AFM Micrograph of a) $ZrO_2/La_2O_3/Si$ and b) $La_2O_3/ZrO_2/Si$ gate stacks

As all the details of the results are given in the published papers, the summary of the work done and results is tabulated in table 2.

Table 2: Summary of all the findings of the work carried out

Gate Stack	Method of Deposition	Annealing conditions	Characterization performed	Work submitted or published to the journal
Au/Ti/CeO_2/Si	Sol-Gel	Muffle Furnace 400^oC for 10 min	Ellipsometry, XRD, FTIR, AFM, IV-CV	Journal of Material Science: Materials in Electronics
Au/Cr/La_2O_3/Si	PEALD	In situ N_2 plasma annealing for 1 min	XRD, AFM, IV, HRTEM	Journal of Vaccum
$LaCeO_2$/Si	Sol-Gel	Microwave assisted annealing at different frequencies (High, Low)	XRD, FTIR, AFM	Bulletin of Material Science

Stack	**Results obtained**			
	Thickness	AFM Roughness	K value	Leakage current density
Au/Ti/CeO_2/Si	60.11 nm	0.6 nm	39	1.18×10^{-5} Acm^{-2}
Au/Cr/La_2O_3/Si	~ 3 nm	0.25 nm	-	9.58 mA/cm^{-2}
$LaCeO_2$/Si	-	2.3 nm	-	-

5. References:

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Outcomes of projects:

1. **Rapid Thermal Annealing System Installed at MDLN Laboratory, Department of Electronics, North Maharashtra University Jalgaon**
2. **Manpower Trained:**

- Mr. Vilas Patil
- Ms. Khushabu Agrawal
- Ms. Viral Barhate
- Mr. Sumit Patil

3. **Publications**

List of Publications through this project and acknowledges UGC:

Published:

7. Khushabu S. Agrawal, Vilas S. Patil, Anil G. Khairnar, and Ashok M. Mahajan "Structural and Electrical Properties of Sol-gel CeO2 Thin Films on Si (100) Substrate" J Mater Sci: Mater Electron (2017) 28:12503–12508 (IF: 2.324)
8. Khushabu S. Agrawal, Vilas S. Patil, and Ashok M. Mahajan "ALD-HfO2 Ultra-thin Films Deposited on Different Crystallographic Orientation Ge for CMOS Applications" Thin solid Films, 654, 30-37 (2018) (IF: 1.939)
9. Viral Barhate, KhushabuAgrawal, Vilas Patil, Sumit Patil and Ashok Mahajan"Spectroscopic study of La2O3 thin films deposited by indigenously developed plasma-enhanced atomic layer deposition system" International Journal of Modern Physics B, Vol. 32 1840074 (5 pages) (2018) (IF: 0.7)

Submitted:

10. Viral N. Barhate, Khushabu S. Agrawal, Vilas S. Patil, Sumit R. Patil and Ashok M. Mahajan, "Post deposition microwave assisted annealing effect on lanthanum doped cerium oxide thin films", submitted to Bulletin of Material Science (IF: 0.899)
11. Khushabu Agrawal, Viral N. Barhate, Vilas Patil and Ashok M. Mahajan, "La_2O_3 ultra-thin films grown by Low Power Plasma Enhanced Atomic Layer Deposition on Si and 6H-SiC substrates" submitted to Journal of Vaccum (Revision uploaded) (IF: 2.067).
12. Vilas S. Patil, Khushabu S. Agrawal, Viral N. Barhate, Sumit R. Patil and Ashok M. Mahajan, "XPS study of Homemade Plasma Enhanced Atomic Layer Deposited La_2O_3/ZrO_2 Bilayer Thin Films", submitted to special issue of Semiconductor science and technology (IF: 2.280)

Annexure – IX

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1. **Title Of The Project: "**Deposition and Electrical characterization of Rare Earth doped High-k thin films on Si substrates for Nanoscale MOSFETs"
2. **Name And Address of The Principal Investigator**:
   Prof. Ashok M. Mahajan,
   Professor of Electronics, Department of Electronics,
   North Maharashtra University, Jalgaon
3. **Name And Address Of The Institution**:
   North Maharashtra University, Jalgaon
   P.O. Box No.80, Umavi Nagar, Jalgaon-425001
4. **UGC Approval Letter No. And Date:**
   43-302/2014 (SR) dated 9th August, 2015
5. **Date of Implementation:** 1st July, 2015
6. **Tenure of The Project**: 3 Years
7. **Total Grant Allocated:** Rs. 10,98, 000/-
8. **Total Grant Received**: Rs. 10, 75, 500/-
9. **Final Expenditure:** Rs. 10, 66,719/-
10. **Title of The Project**: "Deposition and Electrical characterization of Rare Earth doped High-k thin films on Si substrates for Nanoscale MOSFET's**".**
11. **Objectives Of The Project:**
    - To develop the novel process of passivation of interface layer between high-k and semiconductor substrate.
    - To deposit the rare earth oxide high-k materials by sol-gel/EB evaporation technique on Si substrate.
    - To develop the novel post deposition annealing (PDA) immediately after the deposition of high-k, to get the high-k film with various desired properties in order to cope up with the future technology node.

- To develop the novel Metal gate/high-k stack structure/MOS capacitors by depositing Metal electrodes through shadow mask by EB evaporation technique.
- Characterize the film composition and surface structure.
- Post metallization annealing in FGA and characterize interfacial structures at atomic scale.
- To carry out the electrical characterization (CV & IV) of the fabricated stacks or MOS capacitors to check the suitability for advanced CMOS technology (22 nm & beyond).

12. Whether Objectives Were Achieved (GIVE DETAILS):

Yes, aforesaid objectives (point 11) have been achieved successfully.

13. Achievements From The Project:

- ✓ The Rapid thermal annealing system used for the high temperature annealing of thin films has been procured through this project, now available for the use.
- ✓ My research team members have been trained through this project: become expert now in device fabrication, characterization and statistical analysis.
- ✓ The 2 students have been completed their PhD work, contributed in this project equally.
- ✓ The 6 research papers published (3)/submitted (3) on the objectives given in this project in international journal of high repute.

14. Summary of the Findings (IN 500 WORDS):

Enclosure II

15. Contribution to The Society (Give Details):

- The rapid thermal annealing (RTP) system has been procured through the project, which was not available earlier in the laboratory and in university. Now, the facilities developed through this project are/will be made available to the students and the researchers from self/other department or of university at free of cost.
- The semiconductor device fabrication is being done at the North Maharashtra University successfully.

- Manpower trained through this project will contribute certainly to the society by developing novel electronics gadgets/ASICS/MEMS etc.

16. Whether Any Ph.D. Enrolled/Produced Out Of The Project:

Yes.

1 Produced: Mr. Vilas S. Patil (Thesis Submitted)

2 Enrolled: Ms. Khushabu S. Agrawal (Pre Ph.D. Thesis Submitted)

3. Ms. Viral N. Barhate: Enrolled

4. Mr. Sumit Patil: Enrolled

17. No. Of Publications Out of the Project: 6

(Published- 3 & Under Review- 3)

Published

1. Khushabu S. Agrawal, Vilas S. Patil, Anil G. Khairnar, and Ashok M. Mahajan "Structural and Electrical Properties of Sol-gel CeO_2 Thin Films on Si (100) Substrate" J Mater Sci: Mater Electron (2017) 28:12503–12508 (IF: 2.324)
2. Khushabu S. Agrawal, Vilas S. Patil, and Ashok M. Mahajan "ALD-HfO_2 Ultra-thin Films Deposited on Different Crystallographic Orientation Ge for CMOS Applications" Thin solid Films, 654, 30-37 (2018) (IF: 1.939)
3. Viral Barhate, Khushabu Agrawal, Vilas Patil, Sumit Patil and Ashok Mahajan "Spectroscopic study of La_2O_3 thin films deposited by indigenously developed plasma-enhanced atomic layer deposition system" International Journal of Modern Physics B, Vol. 32 1840074 (5 pages) (2018) (IF: 0.7)

Under Review

4. Viral N. Barhate, Khushabu S. Agrawal, Vilas S. Patil, Sumit R. Patil and Ashok M. Mahajan, "Post deposition microwave assisted annealing effect on lanthanum doped cerium oxide thin films", submitted to Bulletin of Material Science (IF: 0.899)
5. Khushabu Agrawal, Viral N. Barhate, Vilas Patil and Ashok M. Mahajan, "La_2O_3 ultra-thin films grown by Low Power Plasma Enhanced Atomic Layer Deposition on Si and 6H-SiC substrates" submitted to Journal of Vaccum (Revision uploaded) (IF: 2.067).

Layer Deposition on Si and 6H-SiC substrates" submitted to Journal of Vaccum (Revision uploaded) (IF: 2.067).

6. Vilas S. Patil, Khushabu S. Agrawal, Viral N. Barhate, Sumit R. Patil and Ashok M. Mahajan, "XPS study of Homemade Plasma Enhanced Atomic Layer Deposited La_2O_3/ZrO_2 Bilayer Thin Films", submitted to special issue of Semiconductor science and technology (IF: 2.280)

(Principal Investigator)

(Registrar)

(Seal)

REGISTRAR
North Maharashtra University
Jalgaon

Annexure – X

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

ASSESSMENT CERTIFICATE

It is certified that the proposal entitled **Depostiton and Electrical Characterization of Rare Earth Oxide Doped High-k ThinFilms on Si Substrate for Nanoscale MOSFETs** by **Prof Ashok M Mahajan (PI), Department of Electronics North Maharashtra University Jalgaon** has been assessed by the **External Experts** committee consisting the following members for submission to the University Grants Commission, New Delhi for financial support under the scheme of Major Research Projects:

Details of Expert Committee:

1. Prof. M. A. More **Savitribai Phule Pune University, Pune**	**External Expert**
2. Prof. K. M. Jadhav **Dr. B. R. Ambedkar Marathwada University Aurangabad**	**External Expert**

Observations: The proposal is as per the guidelines.

Project duration: 1st July 2015-30th June 2018

Project Outcomes:

a. Procurement and Installation of Rapid Thermal annealing system in lab

b. Trained Manpower No. 4

1. Mr. Vilas Patil
2. Ms. Khushabu Agrawal
3. Ms. Viral Barhate
4. Mr. Sumit Patil

c. PhD Awarded:

1. Mr. Vilas Patil (Thesis Submitted)
2. Ms. Khushabu Agrawal (Pre Ph.D. Thesis Submitted)

d. Publication of results: 06 (Published: 03**, Under Review:** 03)

Remarks:

The P.I. has achieved set objectives. The P.I. has utilized funds for equipment very efficiently in setting up indigenously designed and fabricated systems. Moreover the research output evidenced by publications in journals of international repute justify the research potential of these units and the P.I. During the research project human resource development has been achieved (02 - Ph.D. thesis submitted). In nut-shell, the research project has been executed efficiently. The committee unanimously congratulates the P.I. for successful completion of the major research project.

(Prof. M. A. More) 06/08/2018

(Prof. K. M. Jadhav) 6/8/18

(REGISTRAR)
(Seal)

REGISTRAR
North Maharashtra University
Jalgaon

Place : JALGAON
Date: 06/08/2018

NORTH MAHARASHTRA UNIVERSITY JALGAON-425001