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Synthesis and characterization of sol-gel derived CeO_2 dielectric thin films for CMOS devices

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We have prepared CeO_2 dielectric thin films using Cerium Chloride Heptahydrate, ethanol and citric acid as additive by sol-gel and deposited films were characterized for various properties. The micro-structural properties of these films were studied by XRD which reveals that the deposited film has amorphous structure which loweres leakage current. Chemical compositions of deposited thin films were analyzed by FTIR and EDAX which shows existence of CeO_2. The samples were optically characterized using Ellipsometry to find Refractive Index which is 3.615. This paper explores the properties of CeO_2 thin films to produce better promising gate dielectric in CMOS device applications.

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Keywords: High-K, CeO_2, Gate dielectrics, Thin film, Sol-gel

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1. Introduction

In present scenario of technology of new electronic materials and devices, one of the most important trends of nanoelectronics and technological research is scaling down devices to smaller physical dimensions, to follow Moore's law [1].

The decrease in device feature size results in higher speed, lower power consumption, and lower cost because of the increased density of devices per wafer [2]. But, this ability of semiconductor industry to continue scaling microelectronics devices to ever smaller dimensions is limited by the quantum mechanical effects as the thickness of conventional silicon dioxide (SiO_2) gate insulators is reduced to just a few atomic layers. Due to this effect, electrons can tunnel directly through the films and cause leakage currents resulting in enhancement of power dissipation, while heat radiations become critical issue. These factors significantly affect the device performance and reduce the device reliability [3]. In order to maintain low power consumption performance of complementary metal-oxide-semiconductor (CMOS) transistors, high dielectric constant (k) gate dielectrics must be employed to replace conventional SiO_2/SiON [4] as the scale of the channel length goes down to sub-0.1 μm feature size. An alternative gate dielectric needs stringent requirements for practical replacement of SiO_2/SiON. These requirements include high permittivity, thermal stability, high level film and interface quality, processing and materials compatibility with fabrication of devices, and long-term reliability [5].

Many materials have been investigated as candidates for the replacement of SiO_2/SiON. Among all the high-k dielectrics, such as metal-oxide of Al_2O_3 [6], CeO_2 [9-11], HfO_2 [10] and ZrO_2 [11]), rare earth metal oxide CeO_2 is one of the most promising insulating material with a lot of potential advantages such as its high dielectric constant (k = 16-52), large Bandgap (5.5 eV), good lattice constant (5.41A^o) i.e. lattice mismatch is only 0.35%, Along with this, it has thermodynamic stability on Si, good interface with Si substrate and good compatibility with modern processing techniques for the applications in Silicon-based devices[12- 19].

A wide range of growth and characterization techniques have been employed for depositing high-k dielectric thin films. One of these is the sol gel [20] processing which is now accepted technology for forming thin films and coatings. As it has proved to be technically sound alternative in some cases, as well as it has also been shown to be economical, safe, reliable, low temperature process, and meet the uniformity requirements for gate materials as compare to other deposition methods.

In this regard, the work is carried out to form CeO_2 thin film using sol-gel spin coating technique with citric acid as a catalyst. The second section of this paper describes the experimental procedure used for the deposition of thin film. The results are discussed in the third section and fourth section concludes the paper.

2. Experimental

Sol-gel derived CeO_2 films were deposited on commercially available p-type Silicon (100) wafers with resistivity ~10-20 ohm-cm, as follows: First substrates were cleaned using Trichloro-ethylene, Acetone and Methanol. Ceria sol was prepared by dissolving 2.5gm Cerium Chloride Heptahedra ($CeCl_3$:$7H_2O$) in 30 ml ethanol, followed by the addition of citric acid in 1: X [X=0.5, 1, 1.5, 2] mole ratio. Then solution with optimized viscosity range was spin-coated at a spinning speed of 2400 rpm for 30 seconds on Silicon substrate. These spin coated films were dried for 5 min in an electric furnace at 400^{0}C to remove undesired water molecules. The deposited films were characterized by Ellipsometer, XRD, FT-IR and EDAX for measurement of refractive index, structural and chemical composition of the film.

3. Results and discussion

The refractive index (RI) of the CeO_2 deposited film has been measured using the Ellipsometer (Philips SD-1000) at the visible wavelength of 632.8 nm is 3.615. The dielectric constant is frequency dependent property associated to electronic, ionic and orientation polarization.

$$\varepsilon_{total} = \varepsilon_{ele} + \varepsilon_{ion} + \varepsilon_{or} \tag{1}$$

The electronic polarization falls in visible range. Optical dielectric constant of the film has been calculated from the refractive index value measured with Ellipsometer. The theoretical formula used for the calculation is given as follows:

$$n = c / v = \sqrt{\mu \epsilon / \mu_o \epsilon_o}$$

$$n = \sqrt{\mu_r \epsilon_r}$$

where, ϵ_r is the material's relative permittivity, and μ_r is its relative permeability. For most materials, μ_r is very close to 1 at optical frequencies. Hence dielectric constant due to electronic polarization [21] is therefore, approximately equal to $\sqrt{\epsilon_r}$.

i.e. $$n = \sqrt{\epsilon_r}$$

$$\varepsilon_{ele} = \eta^2 \tag{2}$$

Theoretically calculated optical dielectric constant has the value 13.068 which is higher than that of SiO_2.

The IR analysis was carried out to obtain information about chemical bonding characteristics using the Nicollet 380 FTIR spectrometer. The Fig. 1 shows, the IR spectra of the deposited CeO_2 thin film. The spectra were recorded in the range 400-1200 cm^{-1} with 4 cm^{-1} resolution & 128 scans for both sample and background as reference.

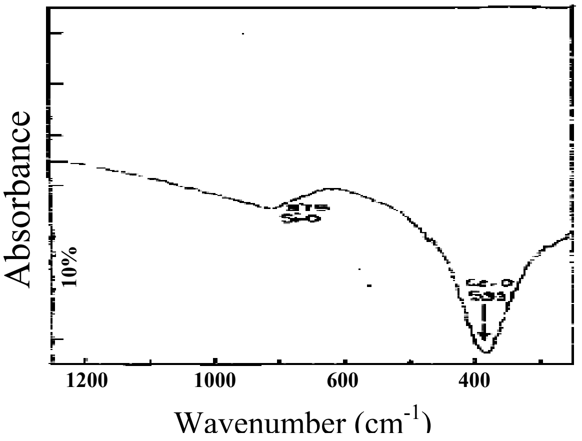

Fig.1. FTIR spectra of deposited CeO_2 film.

From Fig. 1, IR study of Si: CeO_2 oxide film showed the existence of both Ce- and Si-oxide phases. Un-bonded Si-O mode appears at 875 cm^{-1} together with Ce-O mode appears at 593 cm^{-1} in the IR spectra. In the sol-gel process of the CeO_2 film the O- H mode may be detected in the spectra at lower temperature. But in our case the O-H mode is completely absent due to the annealing at 400^OC temperature.

The deposited CeO_2 film crystal structure was observed by the Rigaku Miniflex make XRD instrument in which the X-ray source used was Cu-K of wavelength 1.54059 A^0. The X-ray pattern was recorded for the 2θ values range $20^0$to 60^0. The XRD spectrum recorded for deposited films is shown below.

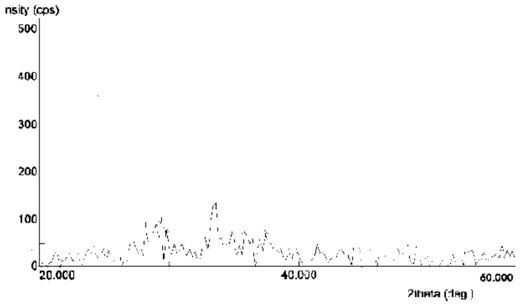

Fig.2. X-Ray diffraction pattern of CeO_2 film.

Fig. 3 shows X-Ray diffraction pattern of CeO_2 film annealed at 400^0 C. It reveals from the spectra that, the deposited CeO_2 film has amorphous structure. Even though, the polycrystalline films have higher k-value than the amorphous ones, however, the leakage current in polycrystalline films also reported to be higher than that of amorphous films [5]. Thus, this CeO_2 amorphous film is suitable to be used as gate dielectric in MOSFET.

The EDAX spectra of the deposited CeO_2 film is as shown in Fig. 3. The detailed chemical composition in the film is as given in the Table 1.

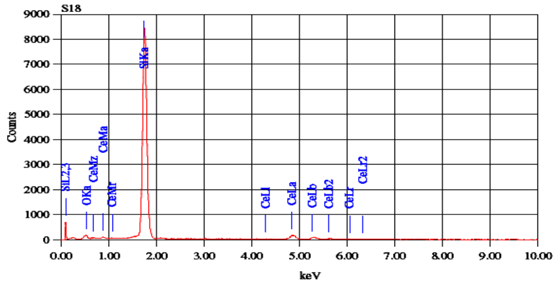

Fig. 3. EDAX spectra of the deposited CeO_2 film. (Magnification 1000 time, accelerating voltage= 20 kV, Probe current=1nA).

Table 1. EDAX spectra result of CeO_2 film deposited at 250^0C.

Element	Intensity	Mass%	Atomic%
Oxygen (O)	0.525	10.40	18.56
Cerium (Ce)	4.837	11.88	2.24
Silicon (Si)	1.739	77.72	79.02
Total	---	100.00	100.00

The EDAX spectra recorded clearly shows the presence of elements and their atomic wt% as listed in table 1. Since, the deposition was carried out at higher temperature; we have observed only desired species in the films. From aforementioned discussions, it clearly results that, the CeO_2 film has been grown successfully using sol-gel technique.

4. Conclusions

Amorphous CeO_2 thin films have been successfully deposited by the sol-gel spin coating technique using citric acid as catalyst. The dielectric constant of the film was observed to be 13.068. FT-IR and EDAX study reveals clearly the presence of the CeO_2 film. The result of XRD measurement shows that deposited CeO_2 film has amorphous structure. Therefore, based on the aforementioned observations, like higher dielectric constant, the desired structural and compositional properties, the deposited CeO_2 thin films can be a promising alternative candidate for the high-*k* gate dielectrics to replace conventional SiO_2 in CMOS device.

References

[1] G. E. Moore, Electronics**, 38**, 114 (1965).
[2] See online http://www.public.itrs.net/
[3] R. DeGraeve, IEEE Trans. Electron Devices, **45**, 904 (1998).
[4] M. L. Green, J. Appl. Phys.(Rev.), **90**, 2057 (2001).
[5] G. D. Wilk, J. Apl. Phys. **89**, 10 (2001).
[6] E. P .Gusev, Appl. Phys. Lett. **76**, 176 (1999).
[7] K. Karakaya, J. electrochem. Society, **153**(10), 233 (2006).
[8] Y. Nishikawa, Jpn. J. Appl. Phys. **41**, 2480 (2002).
[9] T. Inoue, Thin Solid Films, **343-344**, 594 (1999).
[10] G. D. Wilk, J. Appl. Phys. **87**, 484 (2000).
[11] H. C. Zhong, Appl. Phys. Lett. **78,** 1134 (2001).
[12] L. Yan, Semicond. Sci. Technol. **18**, 39 (2003).
[13] V. Grosse, J. Phys.D: Appl. Phys. **40**, 1146 (2007).
[14] T. Semikina, Semicond. Phys, Quantum Electronics and Optoelctronics, **7**(3), 291 (2004).
[15] S. Joumori, Jpn. J. Appl. Phys., **43** (11B), 7881 (2004).
[16] T. Inoue, Appl. Phys. Lett. **56**, 14 (1990).
[17] Y. Nishikawa, Appl.Phys. Lett. **81**, 4386 (2002).
[18] J. F. Kang et.al. Solid State Commun. **108**, 225 (1998).
[19] T. Ami, Mater. Sci. Eng. **B54**, 84 (1999).
[20] M. A. Aegerter, "Sol-Gel Technologies for Glass Producers and Users", Kluwer Aca. Pub.
[21] S. Altshuler, Y. Chakk, A .Rozenblat, A. Cohen, Microelectronic Engineering, **80**, 42 (2005).

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