ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **23**, Number 1, 2020, 105–112

Synthesis of SiO_2Nanoparticles by Sol-Gel Method and Their Optical and Structural Properties

S. SARAVANAN and R. S. DUBEY

Advanced Research Laboratory for Nanomaterials & Devices,
Department of Nanotechnology, Swarnandhra College of Engineering & Technology,
Seetharampuram, Narsapur-534 280, West Godavari (A.P.), India
E-mail: shasa86@gmail.com

Abstract. This paper focuses on the sol-gel synthesis of SiO_2 nanoparticles for solar cells. The prepared samples were characterized by *Fourier transform infrared* (FTIR) spectroscopy, *dynamic light scattering* (DLS), fluorescence (FL) spectroscopy and *scanning electron microscopy* (SEM). Fourier transform infrared spectroscopy studies revealed the presence of Si-O-Si stretching vibration bonding at 1093, 798 and 459 cm^{-1}. SEM micrograph showed nearly irregular SiO_2 nanoparticles. The calculated average particle diameter was 192 nm by DLS technique. The FL spectrum shows an emission band at 644.8 nm in the visible range and two broad excitation peaks at 359 and 718 nm. The optical and morphological properties of the as-prepared SiO_2 nanoparticles are presented.

Key-words: Sol-gel, SiO_2 nanoparticles, scattering, fluorescence, morphology.

1. Introduction

In solar cells, enhancement of photon absorption and generation of charge carriers are the primary needs. Therefore, nanomaterials (such as nanorods, nanoparticles, ultrathin film and gratings) have been demanded due to their significant properties which can boost the conversion efficiency of the solar cells [1-4]. Similarly, the oxide materials are useful in the various applications such as piezoelectric devices, fuel cells, fabrication of electronic device, antireflection coating, sensors and catalysts [5]. In *photovoltaic* (PV) technology, nanomaterials have been found promising for the light harvesting in the visible spectral region, a fact which is due to the improved electron mobility as a result of fast charge carrier generation [6-9]. TiO_2 nanoparticles have been used in solar cells applications owing to their unique physical and chemical properties. Besides the TiO_2 nanoparticles, SiO_2 nanoparticles have also been used in solar cells as anti-reflection coating materials. This materials is also known to have excellent electrical and optical properties and, therefore, was used in the fabrication of sensors, piezoelectric device,

fuel cell, antireflection coating, catalysts as well [10]. Mahyar *et al.* [11] have prepared SiO_2-TiO_2 mixed nanoparticles by sol-gel method and studied their photocatalytic activity. They have demonstrated the a high thermal stability, larger specific surface area, crystallite stability and large energy band gap. Compared with pure TiO_2, these mixed oxide showed higher thermal stability (without phase transformations), specific surface area, band gap as well as smaller crystallite size. The prepared SiO_2-TiO_2 nanoparticles were studied for the photo-catalytic activity and their capability of fuchsin and amaranth photo-degradation has been compared. Kao *et al.* [12] have synthesized and characterized SiO_2 nanoparticles for chemical mechanical polishing on of steel substrate. The slurry of SiO_2 nanoparticles with their size in the range of (58-684) nm was found suitable as abrasive for the steel substrate. Theuring *et al.* [13] have compared Ag and SiO_2 nanoparticles to improve the light harvesting in amorphous silicon thin film solar cells. No difference was found, the current density being almost identical (SiO_2-12.7mA/cm^2 & Ag-12.5mA/cm^2) [13]. Minh *et al.* have investigated the optical performance of white light emitting diode (W-LED) with various nanoparticles including SiO_2 as the scattering material and reported improved performance due to the unique properties of the nanoparticles [14]. Farzaneh and Fourozune [15] have synthesized binary TiO_2 and SiO_2 nanoparticles by sol-gel method. The prepared nanoparticles were found in the range of 8-60 nm and the authors further explored the effect of the solution pH, reaction time, temperature and solvent on the nanoparticle properties. Finally, using the prepared nanoparticles, their photocatalytic activity was performed for the dehydrogenation of 1,4-dihydropyridines [15]. Gao and Yang [16] have reported the preparation of nanoscale SiO_2 particles by sol-gel method using *tetraethyl orthosilicate* (TEOS). They have studied the optimal experimental conditions, such as temperature, catalyst, etc. on the gel time, gel morphology and particle size [16]. Chen and Yan [17] have synthesized two different kinds of core-shell Au@SiO_2 and SiO_2@Au by chemical route. The prepared nanoparticles demonstrated enhanced surface plasmon effect. The integration of Au nanoparticles of various size and at different positions played a significant role in the performance of polymer solar cell. For instance, the integration of 40 nm Au nanoparticles with ZnO yielded a 10% increase in the conversion efficiency, which was enhanced from 3.2 to 3.52%. The integration of core shell nanoparticles with ZnO yielded a remarkable improvement of up to 3.99% (for the case of Au@SiO_2) and 4.2% (for the case of SiO_2@Au) [17]. N. Tiautit *et al.* [18] have studied the effect of SiO_2 and TiO_2 nanoparticles on the performance of dye-sensitized solar cells (DSSCs) by employing polymer gel as electrolyte. With 0.25 wt% of TiO_2 and 0.5wt% of SiO_2 nanoparticles added to the gel, the cells efficiency increased to 2.7% and 3.1%, respectively. The improved conversion efficiency was attributed to the higher viscosity of the nanocomposite gel, and phase separation of nanoparticles and polymer matrices [18]. Wardiyati *et al.*[19] have synthesized and characterized SiO_2 microstructure using sol-gel method. They have demonstrated that the SiO_2 coating on electromagnetic materials were useful to overcome the leakages of electromagnetic waves as compared with other materials. To this purpose, an economic process was used to fabricate SiO_2 nanoparticles. Using TEM and SEM morphological studies, amorphous SiO_2 nanoparticles with the particle size 15-20 nm and 298 m^2/g specific surface area were observed [19]. Dogan and Dag [20] used liquid SiO_2 nanoparticle solutions to coat textiles surface at room temperature by spray method. Contact angle and morphological analysis of the SiO_2 nanoparticle coated textile samples showed that they are hydrophobic [20].

In this work, SiO_2 nanoparticles were prepared by a simple sol-gel process using tetraethyl orthosilicate, acetic acid and methanol as starting materials. This work aims to study the structural and optical properties of synthesized SiO_2 nanoparticles. Section 2 presents the experimental

steps used for the preparation of nanoparticles. The results are presented in section 3 and concluded in section 4.

2. Experimental Approach

The chemicals used as starting materials, such as tetraethyl orthosilicate ($Si(OC_2H_5)$), acetic acid (CH_3COOH), methyl acetate ($C_3H_6O_2$) and methanol (CH_3OH), were purchased from Sigma-Aldrich. Silicon dioxide (SiO_2) nanoparticles were synthesized by sol-gel method as illustrated in fig. 1. Initially, 20 ml of methanol were dissolved in 2.3 ml of acetic acid, and stirred for 5 minutes at room temperature. Partially, the water molecules evaporated, and methyl acetate was produced. Further 1.5 ml of TEOS was added drop-wise at the same time interval. After 90 minutes of stirring, a homogeneous transparent solution was obtained.

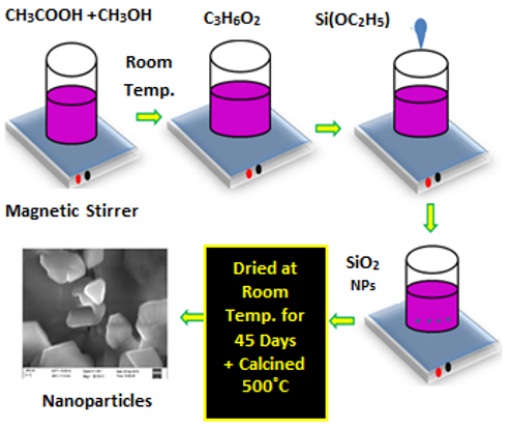

Fig. 1. Synthesis process of SiO_2 nanoparticles.

The chemical reactions involved in the SiO_2 nanoparticle synthesis are as follows:

$$\mathbf{C}H_3COOH + CH_3OH \rightarrow C_3H_6O_2 + H_2O \uparrow C_3H_6O_2 + Si(OC_2H_5)_4 \rightarrow SiO_2 + C_{11}H_{26}O_4 \uparrow$$

Finally, the prepared SiO_2 solution was and dried at room temperature. After drying, SiO_2 product was grinded and calcined at 500C and grained to obtain fine nanoparticles.

After calcination, the prepared samples were characterized using UV- visible spectroscopy (Perkin Elmer-Lambda 35), Micromeritics (Nano Plus- particle size analyzer), Fourier transform infrared spectroscopy (Perkin Elmer- Spectrum 2), Ffluorescence spectroscopy (Perkin Elmer - LS 45) and scanning electron microscopy (Carel Zeiss-Evo 18).

3. Results and discussion

According to the Rayleigh scattering, the synthesized nanoparticles elastically scatter light because of the presence of bigger particles. There are many factors that determine the optical properties of nanoparticles, such as incident/scattering angle, refractive index, wavelength, distance between the particles etc. However, particle size and incident wavelength are significant

parameters for their absorbance. The nanoparticles' absorbance is highly dependent on the wavelength range. After calcination, the SiO_2 nanoparticles were studied by UV-Vis spectroscopy. Fig. 2 shows the UV-Vis absorption in the wavelength range from 190 nm to 1100 nm. One can see that the intensity of the absorption spectrum of pure SiO_2 nanoparticles continuously decreases with the wavelength without any peaks [21-22].

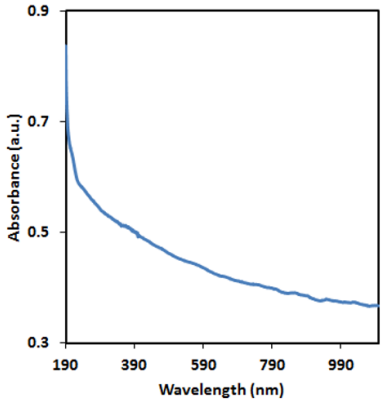

Fig. 2. UV-vis absorption spectrum of pure SiO_2 nanoparticles

The particle size studies revealed the distribution of SiO_2 nanoparticles according to the intensity by using DLS (particle size analyzer) technique. Fig. 3 depicts the intensity distribution of the prepared nanoparticles with particle size analyzer, the calculated average particle size being of 192 nm. Furthermore, the polydispersity index (PDI) is dimensionless and scaled at 0.405, indicating that the particle has small size distribution, being suitable for the DLS technique. Initially, ultra-sonication was used to break-up clumps for 5 minutes. DLS study showed the random movement of the particles within the liquid velocity of the scattered particle movement by using Brownian motion (dynamic fluctuation) and the diameter of the particles were estimated by Stokes-Einstein equation [23].

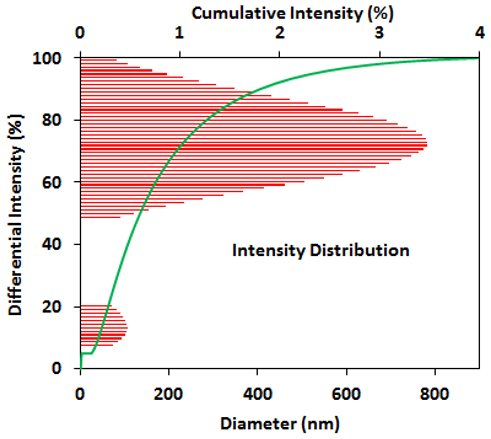

Fig. 3. Size distribution of SiO_2 nanoparticles according to intensity

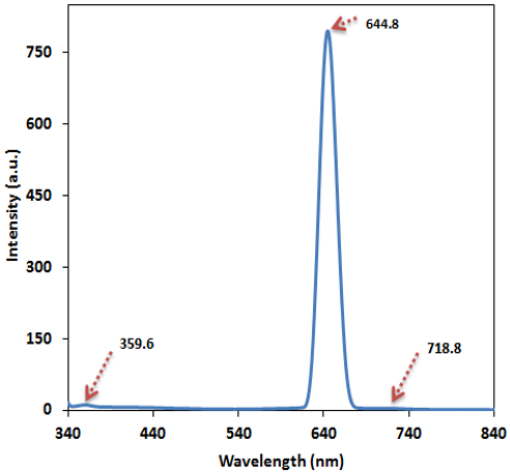

Fig. 4. Fluorescence spectra of SiO_2 nanoparticles calcined at 500°C

Fig. 4 shows the fluorescence (FL) emission spectrum of the prepared SiO_2 nanoparticles. This type of characterization was done to validate the UV-visible result, *i.e.* whether the material is getting excited or not at specific wavelength, as evaluated by the results. Normally, the luminescence structure depends on several parameters, like, solvent, atmosphere, calcination temperature, synthesis process condition etc. The FL spectrum shows the emission band at 644.8 nm (corresponding to sharp excitation) in the visible range and the broad excitation peaks at 359.6 and 718.8 nm [23]. The increment of fluorescence depends on the size of the particles and is playing an important role for various applications, such as to enhance the mechanical strength using nanoparticles [24-28].

As shown in fig. 5, FTIR transmittance spectrum (400 to 4000 cm^{-1}) confirms the presence of synthesized SiO_2 nanoparticles. The broad peak from 3000 to 3700 cm^{-1} was assigned to the presence of O-H group. Similarly, a peak corresponding to vibration bending can be noticed at 1649 cm^{-1}, which indicates the presence of O-H stretching bond [29-31]. Usually, the water molecules removed completely at higher annealing temperature, as suggested by Adam and Chua [32-33]. Moreover, the strong bands at 1093, 459 and 798 $^{-1}$ were associated to the asymmetric and symmetric Si-O-Si stretching vibration bondings [34].

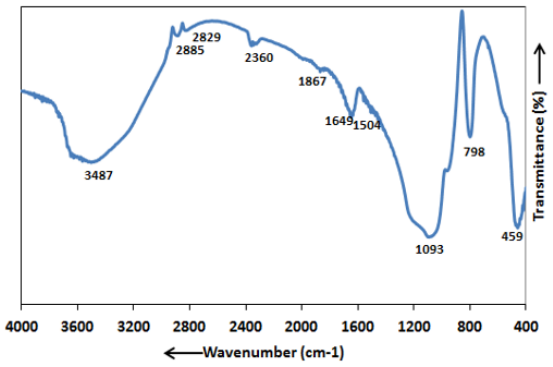

Fig. 5. FTIR spectra of silicon dioxide nanoparticles

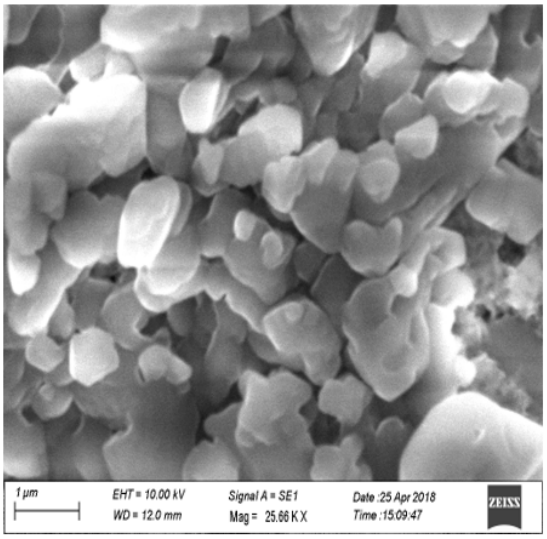

Fig. 6. SEM image of SiO_2 nanoparticles calcinated at 500°C

4. Conclusion

In this work, we have presented the synthesis of SiO_2 nanoparticles using sol-gel process and studied by using UV-visible spectroscopy, DLS, FL, FTIR and SEM. The FL study showed a sharp excitation peak at 644.8 nm in the visible range with broad excitation peaks at 359 and 718 nm. By using FTIR, the vibration peaks of Si-O-Si and Si-O were confirmed. SEM investigation evidenced the nanoparticles with little agglomeration. The particles size was found to be 192 nm by DLS study. Furthermore, the optical and structural properties of SiO_2 nanoparticles can be tailored by using synthesis process parameters for the respective applications.

Acknowledgements. We thank Mr. Vincent Sagayaraj, ACIC, St. Joseph's College (Autonomous), Trichy (T.N.), for the access to the characterization facilities. The authors are also thankful to Mr. V. Krishna Prabhu, Kalasalingam Academy of Research and Education, Krishnankoil (T.N.), for FTIR measurement.

References

[1] LEE K., YOON C.M., NOH J., JANG J., *Morphology-controlled mesoporous SiO_2 nanorods for efficient scaffolds in organo-metal halide Perovskite solar cells*, Chemical Communications **22**, pp. 1-4, 2016.

[2] TIAUTIT N., PURATANE C., PANPINIT S., SAENGSUWAN S., *Effect of SiO_2 and TiO_2 nanoparticles on the performance of dye-sensitized solar cells using PVDF-HFP/PVA gel electrolytes*, Energy Procedia **56**, pp. 378-385, 2014.

[3] DUBEY R. S., GANESAN V., *Reflectance modulation using SiO_2/TiO_2 multilayer structures prepared by sol-gel spin coating process for optical applications*, Superlattices Microstructures **111**, pp. 1099-1103, 2017.

[4] DUBEY R. S., JHANSIRANI K., SINGH S., Investigation of solar cell performance using multilayer thin film structure (SiO_2/Si_3N_4) and grating, Results in Physics **7**, pp. 77-81, 2017.

[5] NANDANWAR R., SINGH P., HAQUE F. Z., *Synthesis and characterization of SiO_2 nanoparticles by sol-gel process and its degradation of methylene blue*, American Chemical Science Journal **5**(1), pp. 1-10, 2015.

[6] RATHOD B., NEMADE K. R., WAGHULEY S. A., *Improvement in photovoltaic performance of TiO_2 nanoparticles by decoration of graphene nanosheets with spherical TiO_2 nanoparticles*, Materials Letters, 10, pp. 118-121, 2016.

[7] DAS K., DE S.K., *Optical properties of the type-II core-shell TiO_2@CdS nanorods for photovoltaic applications, Journal of Physical Chemistry C* **113**, pp. 3494-3501, 2009.

[8] MYUNG Y., JANG D. M., SUNG T. K., SOHN Y. J., JUNG G. B., CHO Y. J., KIM H. S., PARK G., *Composition-tuned ZnO-CdSe Core-Shell nanowire arrays*, ACS Nano **4**, pp. 3789-3800, 2010.

[9] GREENE L. E., LAW M., YUHAS B. D., YANG P. D., *ZnO-TiO_2 core-shell nanorod/P3HT solar cells*, Journal of Physical Chemistry C, **111**, pp. 18451-18456, 2007.

[10] GLEITER H., *Nanostructured materials: state of the art and perspectives*, Journal of Nanostructured Materials **6**, pp. 3-14, 2001.

[11] MAHYAR A., BEHNAJADY M. A., MODIRSHAHLA N., *Characterization and photocatalytic activity of SiO_2-TiO_2 mixed oxide nanoparticles prepared by sol-gel method*, Indian Journal of Chemistry **49A**, pp. 1593-1600, 2010.

[12] KAO M. J., HSU F. C., PENG D. X., *Synthesis and characterization of SiO_2 nanoparticles and their efficacy in chemical mechanical polishing steel substrate*, Advances in Materials Science and Engineering, pp.1-8, 2014.

[13] THEURING M., WANG P. H., VEHSE M., STEENHOFF V., MAYDELL K. V., AGERT C., BROLO A. G., *Comparison of Ag and SiO_2 nanoparticles for light trapping applications in silicon thin film solar cells, Journal of Physical Chemistry Letters* **5**(19), pp. 3302-3306, 2014.

[14] Minh T. H. Q., Nhan N. H. K., *Influence of $CaCO_3$, CaF_2, SiO_2 and TiO_2 scattering particles concentration on color rending index and color quality scale of the conformal packaging multi-chip white LEDs*, International Journal on Electrical Engineering and Informatics **9**(1), pp. 139-146, 2017.

[15] FARZANEH F., FOUROZUNE L. J., *Synthesis and characterization of TiO_2-SiO_2 nanoparticles as catalyst for dehydrogenation of 1,4-dihydropyridines*, Bulletin of material science **37**(1), pp. 1-8, 2014.

[16] HUI GAO, JUNLING YANG, *Nanoscale silicon dioxide prepared by sol-gel process*, Modern Applied Science **4**(9), pp. 152-156, 2010.

[17] CHEN X., YAN L., *Application of Au, SiO_2@Au, and Au@SiO_2 nanoparticles in PTB7:PC71BM polymer solar cells*, Journal of Materials Science: Materials Electronics **28**(18), pp. 13698-13704, 2017.

[18] TIAUTIT N., PURATANE C., PANPINIT S., SAENGSUWAN S., *Effect of SiO_2 and TiO_2 nanoparticles on the performance of dye-sensitized solar cells using PVDF-HFP/PVA gel electrolytes*, Energy Procedia **56**, pp. 378-385, 2014.

[19] WARDIYATI S., ADI W. A., DESWITA, *Synthesis and characterization of microwave absorber SiO_2 by sol-gel method*, Materials Science and Engineering **202**, pp. 012059-1-9, 2017.

[20] DOGAN O., DAG R., *Application of nano coating (SiO_2) on textile products*, Journal of Chemistry and Chemical Engineering **11**, pp. 82-85, 2017.

[21] REN Y., ZHAO Y., ZHANG Y., TANG W., XIN X., SHEN J., WANG L., *Facile synthesis of Au@SiO_2 core-shell nanoparticles with multiple Au nanodots by a reverse microemulsion (water-in-oil) method*, Colloids and Surfaces A: Physicochemical and Engineering Aspects **486**, pp. 14-20, 2015.

[22] VEERANARAYANAN S., POULOSE A. C., MOHAMED S., ARAVIND A., NAGAOKA Y., YOSHIDA Y., MAEKAWA T., KUMAR D. S., *FITC labeled silica nanoparticles as efficient cell tags: uptake and photostability study in endothelial cells*, Journal of Fluorescence **22**, pp. 537-548, 2011.

[23] KRAJNIK B., RACZKA M. G., PIATKOWSKI D., NYGA P., JANKIEWICZ B., HOFMANN E., MACKOWSKI S., *Silica nanoparticles as a tool for fluorescence collection efficiency enhancement*, Nanoscale Research Letters **8**(146), pp.1-7, 2013.

[24] SILVA E. D. S., RIBEIRO L. A., *Rheological and mechanical characterization of poly (methyl methacrylate)/silica (PMMA/SiO_2) composites*, Materials Research **17**(4), 926-932, 2014.

[25] FU S. Y., FENG X. Q., LAUKE B., MAI Y. M., *Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulatepolymer composites*, Composites Part B: Engineering **39**(6), pp. 933-961, 2008.

[26] NAKAMURA Y., YAMAGUCHI M., OKUBO M., MATSUMOTO T., *Effects of particle size on mechanical and impact properties of epoxy resin filled with spherical silica*, Journal of Applied Polymer Science **45**(7), pp. 1281-1289, 1992.

[27] REYNAUD E., JOUEN T., GAUTHIER C., VIGIER G., VARLET J., *Nanofillers in polymeric matrix: a study on silica reinforced PA6*, Polymer **42**, pp. 8759-8768, 2001.

[28] MURDOCK R. C., STOLLE L. B., SCHRAND A. M., SCHLAGER J. J., HUSSAIN S. M., *Characterization of nanomaterial dispersion in solution prior to in vitro exposure using dynamic light scattering technique*, Toxicological Sciences **101**(2), pp. 239-253, 2008.

[29] ARUN KUMAR D., MERLINE SHYLA J., FRANCIS P. XAVIER., *Synthesis and characterization of TiO_2/SiO_2 nano composites for solar cell applications*, Applied Nanoscience **2**, pp. 429-436, 2012.

[30] AZIZ R. A., SOPYAN I., *Synthesis of TiO_2-SiO_2 powder and thin film photocatalysts of sol-gel method*, International Journal of Chemistry **48**, 951-957, 2009.

[31] MOHAN J., *Organic spectroscopy principles and applications*, 2nd edn. Narosha Publishing House Pvt. Ltd, New Delhi, pp. 28-95, 2009.

[32] SHAHROKH ABADI M. H., DELBARI A., FAKOOR Z., BAEDI J., *Effects of annealing temperature on infrared spectra of SiO_2 extracted from rice husk*, Journal of Ceramic Science and Technology **6**(1), pp. 41-46, 2015.

[33] ADAM F., CHUA J. H., *The adsorption of palmytic acid on rice husk ash chemically modifiedwith Al(III) ion using the sol-gel technique*, Journal of Colloid and Interface Science **280**, pp. 55 61, 2004.

[34] SHOKRI B., ABBASI FIROUZJAH M., HOSSEINI S. I., *FTIR analysis of silicon dioxide thin film deposited by metal organic based PECVD*, Proceedings of 19th International Symposium on Plasma Chemistry Society, Germany, 27-31st July, 2009.