iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH
IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 6 Issue: III Month of publication: March 2018

DOI: http://doi.org/10.22214/ijraset.2018.3502

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

Synthesis of TiO_2 based Self Cleaning Superhydrophilic Thin Film Coating

Devarrishi Dixit[1], Yashpal Prajapati[2] Siddharth Verma[3], Saiyed Mohammad Iqbal[4], Rajeev Gupta[5]
[2]*Department of Material Science, University of Petroleum and Energy Studies*
[1,3,4,]*Department of Chemical Engineering, University of Petroleum and Energy Studies*
[5]*Department of Physics, University of Petroleum and Energy Studies*

Abstract*: The self cleaning properties can be introduced to the surface of a glass by engineering a thin film on it. This coating then comes in intimate contact with the surroundings and helps to keep the glass dust and dirt free. This paper proposes to synthesize TiO_2 based photocatalytic coating. The coating gets activated under the sunlight and breaks down the dirt during the daytime while during the night, the condensation of moisture drives out the dirt as the water droplets wet the surface thus cleaning it. The paper proposes synthesis of thin film and investigates the contact angle, morphology, surface roughness, thermal stability, transparency and maps XRD data.
Keywords*: Superhydrophilic, self-cleaning, photo catalytic, thin films, contact angle, sol-gel, spin coating, surface roughness.

I. INTRODUCTION

Study of surface wettability has been of high importance in recent years. The wettability is defined in terms of water contact angle (CA) i.e., the angle liquid or vapour makes with the solid surface. The contact angle greater than 90^0 is considered hydrophobic and that above 150^0 is considered superhydrophobic while that lies below 90^0 is hydrophilic and around 0^0 as superhydrophilic. Hydrophilic surfaces not always have self cleaning properties so it is necessary to impart these properties.

Due to increased cost of labour and time limitations it has become very necessary to switch to advanced technology. The technology which has a potential to effectively deal with the current problem is solely based on nanotechnology and surface engineering. The use of glass was one of the major boom for the craft industry but along with it came certain limitations. The limitations to make glass: water-repellent, water-loving, dirt free, self-cleaning, and transparent. The accumulation of dirt and dust over the surfaces takes toll on the transparency, integrity and beauty of the surface. The accumulation of dirt on the surface of solar panels has hampered the efficiency to a great extent. This issue became severe due to the deposition of bird beads. The cleaning of such surfaces required shutting down of the entire setup leading to increased down time and decreased production. Further, the cleaning of sticky bird beads if not done cautiously leads to scratches on protective surface as a result of which irradiance decreases. This reduces the power conversion efficiency.

The accumulation of dirt and dust on window panes is also a big issue. In sky scrappers the cleaning is very costly and sometimes fatal for the labours. Thus, here appears to be an area where superhydrophilic coatings can prove to be effective alternative. Anti-fogging property is also due to the application of superhydrophilic coatings. These coating prevent the micro water droplets to condense on the surface keeping it clean.[1][2]. Scientists have recently discovered the anti-biofouling properties of superhdrophilic coating, the property of a surface to prevent the accumulation of microorganisms, plants, algae, animals or contaminants on the wetted surface.[2]

These coatings find their way in anti-baterial, anti-stain [3][4], fingerprint resistant, non-toxicity, self cleaning, water purification, paint industry [5][6] and various medicinal applications. The applications of TiO_2 based coating are very extensive and only limited to our ability of thinking. The coating are very robust and can be prepared both by bottom up and top down approach.

The use of TiO_2 based coatings have gained a vary high interest because of their easy availability, corrosion resistance, phtocatalytic activity [7], low cost, and ease of activation. TiO_2 is both self cleaning and hydrophilic. The phenomena of photocatalysis in TiO_2 is directly proportional to the concentration of hydroxyl groups. As TiO_2 possesses both photocatalytic and pholostimulated superhydrophilic properties, the metal oxide on application of sunlight and moisture deals in self cleaning surfaces.

II. EXPERIMENTAL PROCEDURE

A. Materials and Reagents

Titanium isopropoxide (99.999%, Sigma Aldrich), Methanol (99.999%, Sigma Aldrich), Ethanol (99.999%, Sigma Aldrich), and Hydrochloric acid (37% conc.) were used to prepare the thin film coating.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

B. Preparation of sol-gel

Sol was prepared by mixing of Ethanol (25ml), distilled water (30ml) and HCl (3ml) and stirring it for 5 minutes at 200rpm. Titanium isopropoxide [$Ti(OC_2H_3)_4$] was then added drop by drop to the above solution. This was then stirred at 450rpm for 15 minutes and simultaneous keeping it at a constant temperature of 65^0C. Four samples were prepared by varying the amount of Titanium isopropoxide in the sol. Table I illustrates the variation of Titanium isopropoxide.

TABLE I
VARIATION OF TITANIUM ISOPROPOXIDE

Sample	Drops of Variation of Titanium isopropoxide
1	2
2	4
3	6
4	8

C. Mechanism

$TiO_2 + h\nu \longrightarrow TiO_2\ (e^- + H^+)$

$H_2O + H^+ \longrightarrow \bullet OH + H^+$

$O_2 + e^- \longrightarrow O_2^{\bullet -}$

$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$

$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$

$O_2^{\bullet -} + HO_2^{\bullet} \longrightarrow O_2 + HO_2^-$

$HO_2^- + H^+ \longrightarrow H_2O_2$

$H_2O_2 + h\nu \longrightarrow 2\bullet OH$

$H_2O_2 + O_2^{\bullet -} \longrightarrow HO^{\bullet} + OH^- + O_2$

$H_2O_2 + e^- \longrightarrow HO^{\bullet} + OH^-$

TiO_2 gets activated under sunlight due to photocatalytic activity. The metallic ions formed interact with atmospheric oxygen and water molecules giving hydroxyl ions as the end product. The hydroxyl ions breakdown the dirt particle which get wiped out on application of water, leaving the surface spotless.

D. Coating process

The glass slide was cleaned with methanol. The different concentration of prepared solution was spin coated to glass slide (1cm x 1cm) at 4000 rpm for 60 seconds. The coated glass slides were cured at 70^0C for 5 minutes.

E. Characterisation

1) *Hydrophilicity:* Hydrophilicity of the thin films was evaluated. The contact angles were measured in air by sessile-drop method. A micro injector was used for injection of a 10µl water droplet on the surface of coatings. The contact of all the samples was obtained using a contact angle goniometer at room temperature and pressure, under LED lamp light. The Drop Shape Analyzer software produced by Kruss was used to process the contact angle measurements.
2) *XRD analysis:* X-ray diffraction patterns for all samples were obtained using Eco D8 Advance XRD machine produced by Brukker with Cu Kά radiation (λ=1.54060 Å) at room temperature and pressure, operating at a voltage of 40 kv and 25 mA current. Coupled two theta SSD 160 detector was used for XRD analysis. Diffrac.Commander software was used to plot the graph between counts per second vs 2 theta.
3) *UV-Vis:* The UV-Vis transmittance of coated sample were investigated by taking the transmittance of glass slide as the base line using Lambda-35 UV/VIS Spectrometer produced by Perkin Elmer. UV Unilab software was used to map the readings.

4) *Atomic force microscopy(AFM):* The morphology of the thin film for all samples was mapped using Nanosurf Naio Atomic force microscopy produced by Nanosurf. The roughness of the surface was investigated at resolutions of 10nm and 100nm.
5) *Thermal stability:* Each sample was exposed to temperatures (45, 50, 55, 60, 65) and change in contact angle was studied. The differences were then tabulated and plotted over a graph. Hot air oven produced by Weiber was used to heat the samples to required temperatures.

III.RESULTS AND DISCUSSION

Titanium isopropoxide must be added drop by drop to the sol so as to allow proper mixing, facilitating a transparent coating. Bulk addition of Titanium isopropoxide results in agglomeration giving way to yellow colour sol-gel. This gel has poor transparency and high contact angle as compared to sol-gel prepared by adding drop by drop titanium isopropoxide.

A. Hydrophiliicity

The sessile drop method was used for measurement of contact angle between the coating and distilled water. The water contact angle on different samples was exhibited.

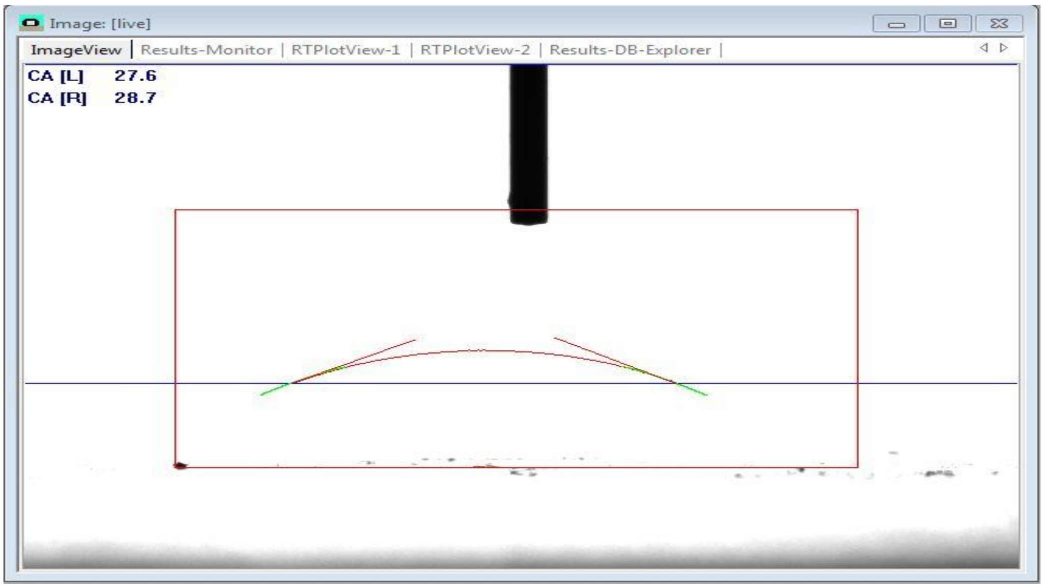


Fig. 1 2 drop titanium isopropoxide

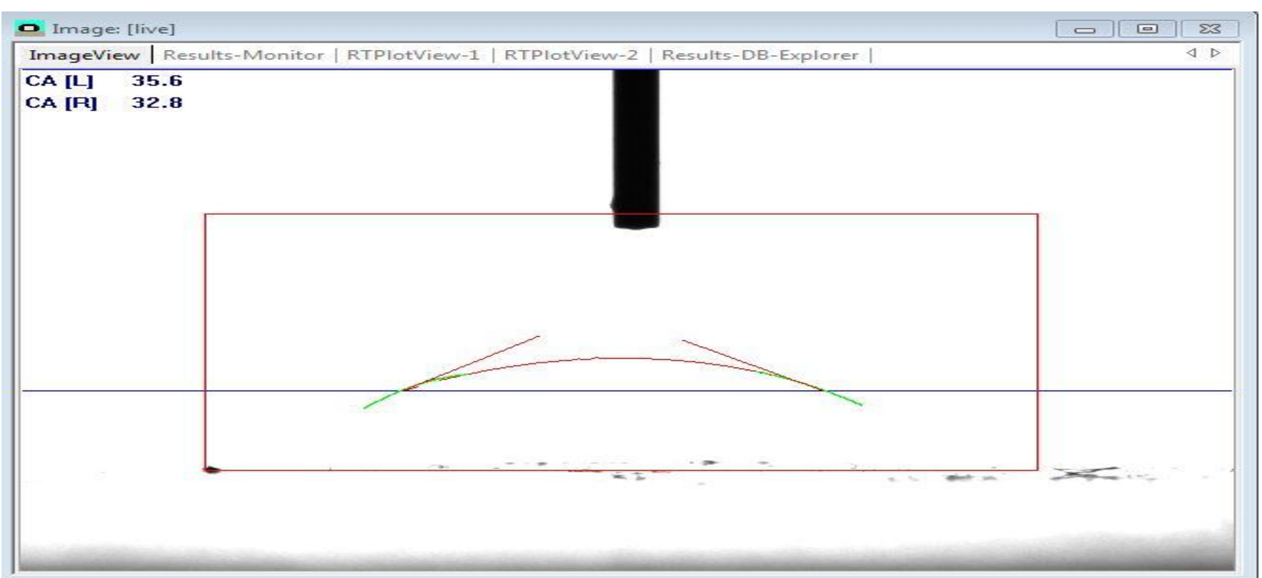


Fig. 2 4 drop titanium isopropoxide

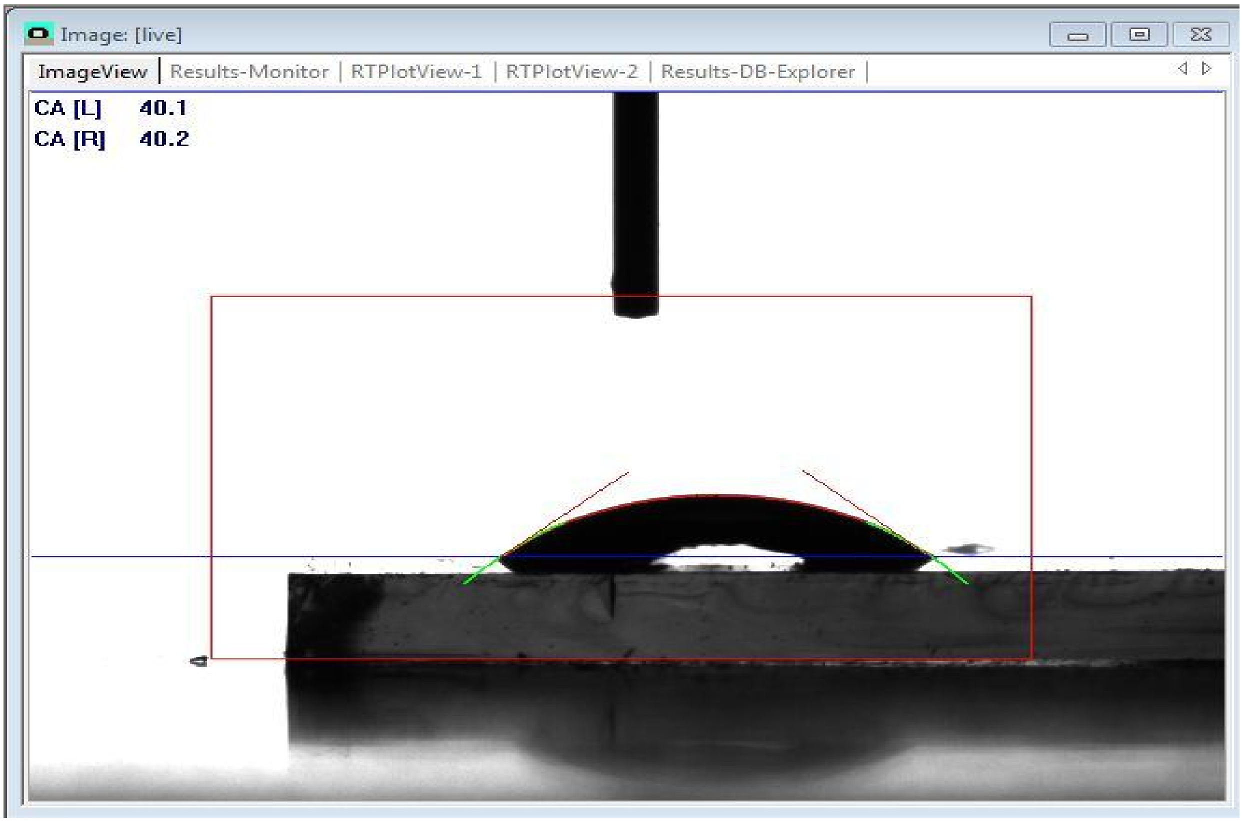


Fig. 3 6 drop titanium isopropoxide

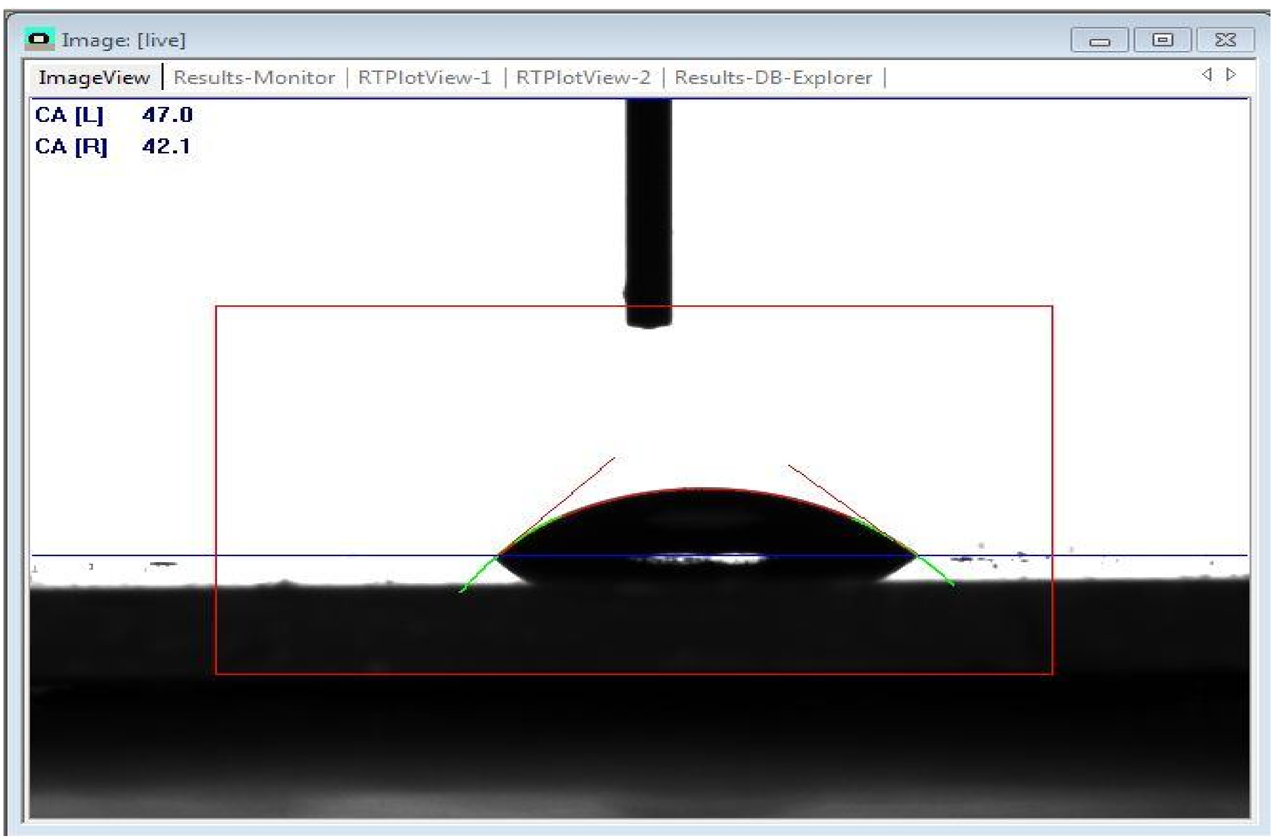


Fig. 4 8 drop titanium isopropoxide

TABLE III
VARIATION OF TITANIUM ISOPROPOXIDE AND CONTACT ANGLE

Sample	Drops of Variation of Titanium isopropoxide	Water contact angle	
		L	R
1	2	27.6	28.7
2	4	35.6	32.8
3	6	40.1	40.2
4	8	47.0	42.1

It is observed that with an increase in concentration of TiO_2 in the sol-gel the water contact angle increases significantly. The considerable increase in contact angle might be due to the presence of surfactant which has the ability to modify the surface energy and surface tension[8]. It can be seen from Table 2 that contact angle increases with increase in amount of titanium isopropoxide added.

B. XRD Analysis

The X-ray diffraction (XRD) pattern was employed to study the structure of nanostructured TiO_2 coating. The characteristic reflections of each sample is recognisable in Fig. 5-8. The characteristic reflections of TiO_2 thin film coating displayed the characteristic reflection of TiO_2 nanoparticles. As seen from results the characteristic reflection peak of TiO_2 nanoparticles appeared at $2\theta = 38.2070^0$.

The subsequent d value was calculated using the Bragg's equation:

$n\lambda = 2d \sin\theta$

d= 4.7073 Å

where n is an interger determined by given order, λ is the wavelength of X-rays, d is the interlayer space between the planes in atomic lattice, and θ is the angel between the incident ray and scattering plane.

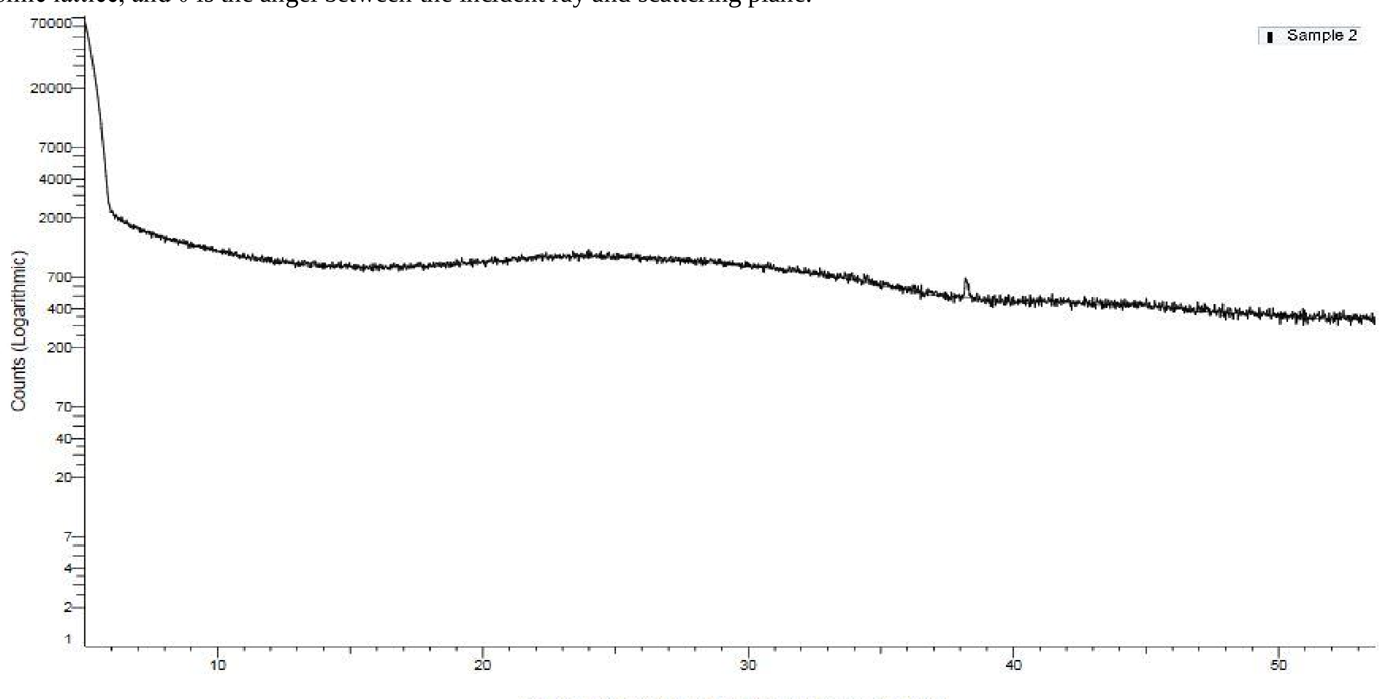


Fig. 5 XRD of 2 drop titanium isopropoxide

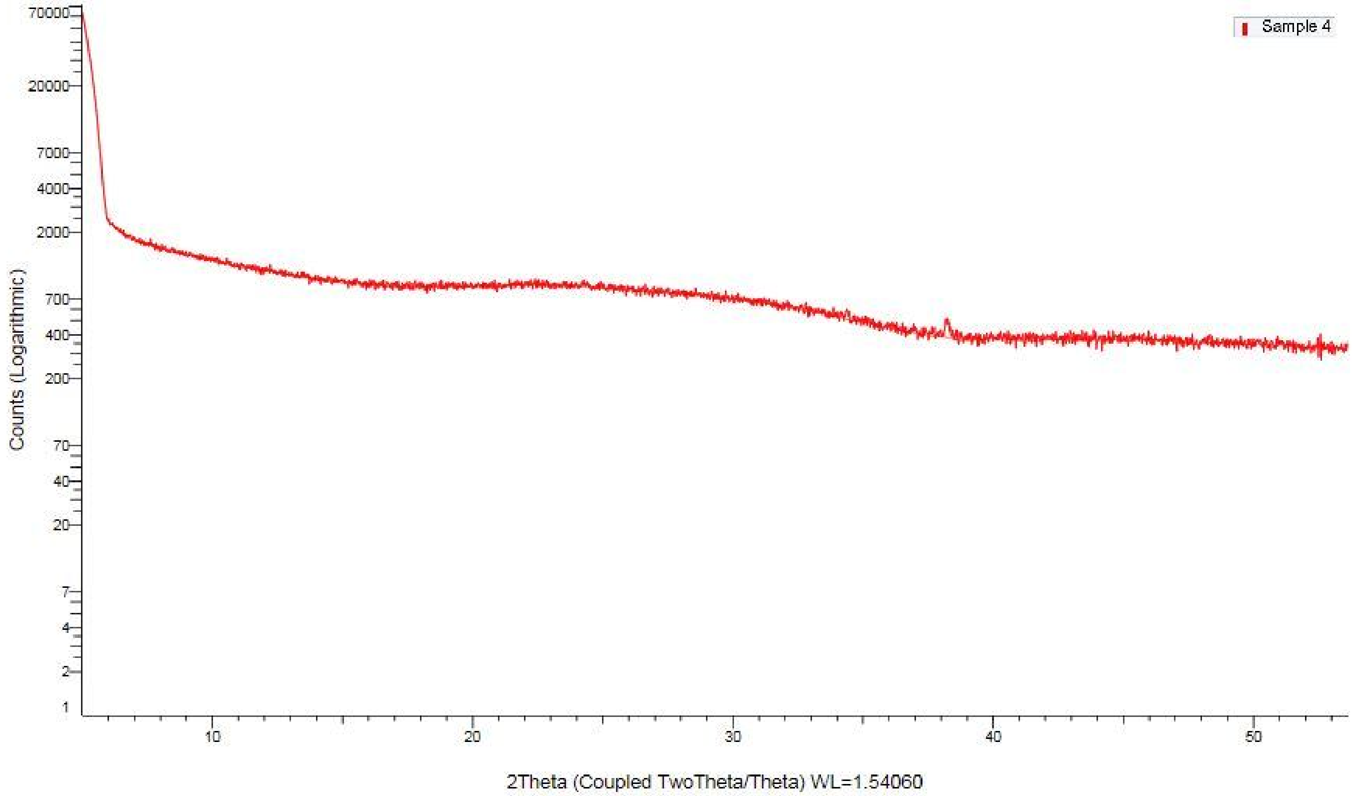


Fig. 6 XRD of 4 drop titanium isopropoxide

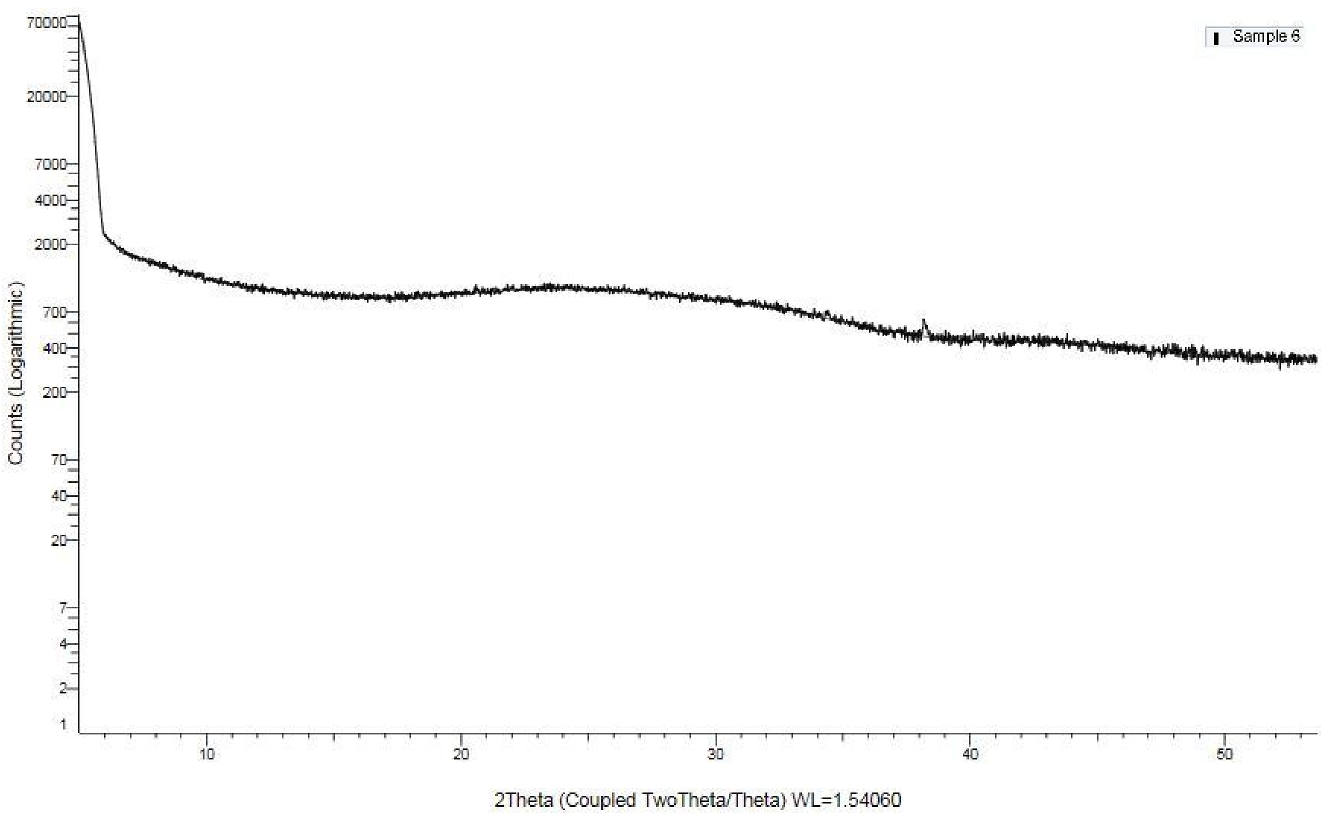


Fig. 7 XRD of 6 drop titanium isopropoxide

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

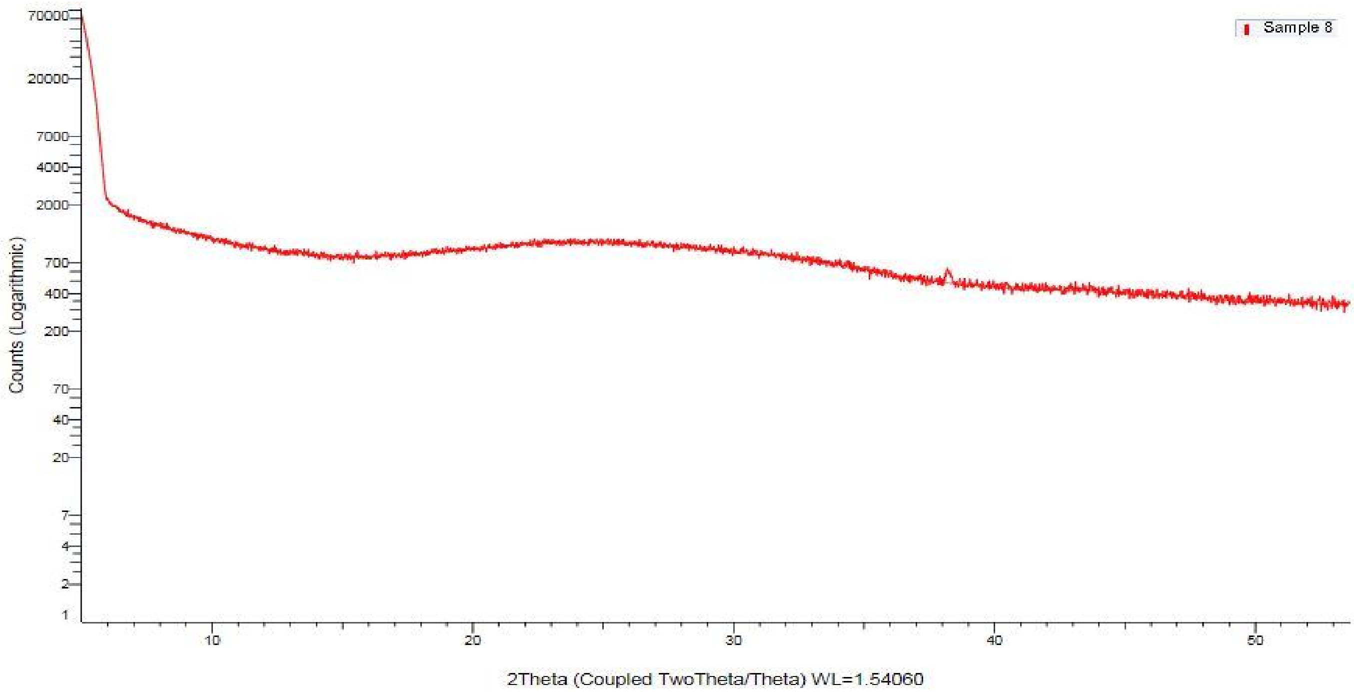


Fig. 8 XRD of 2 drop titanium isopropoxide

C. UV-vis

The transmittance spectra of each sample was observed for each sample for a wavelength range between 200nm – 800nm. The results from Fig. 9-12 converge to a conclusion that the coating showed an average transparency of 75% and peaked to 90% at 415nm wavelength. A high amount of varied transmittance and absorbance was observed between 320nm to 400nm wavelength. This could have been possible because of high transmittance of UV-rays or it could also be possible because of noise during the change from visible spectrum to UV spectrum. In deep UV spectrum an extremely high absorbance is observed which peaks at 200nm wavelength.

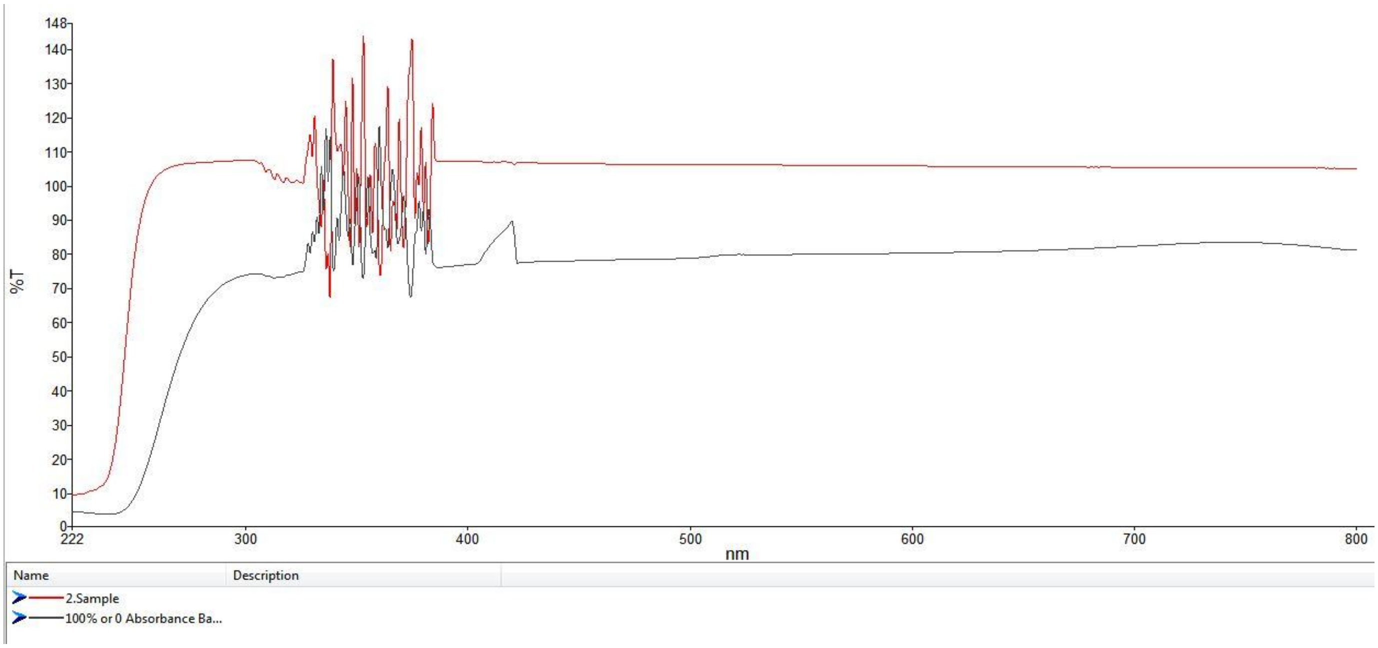


Fig. 9 UV-Vis of 2 drop titanium isopropoxide

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

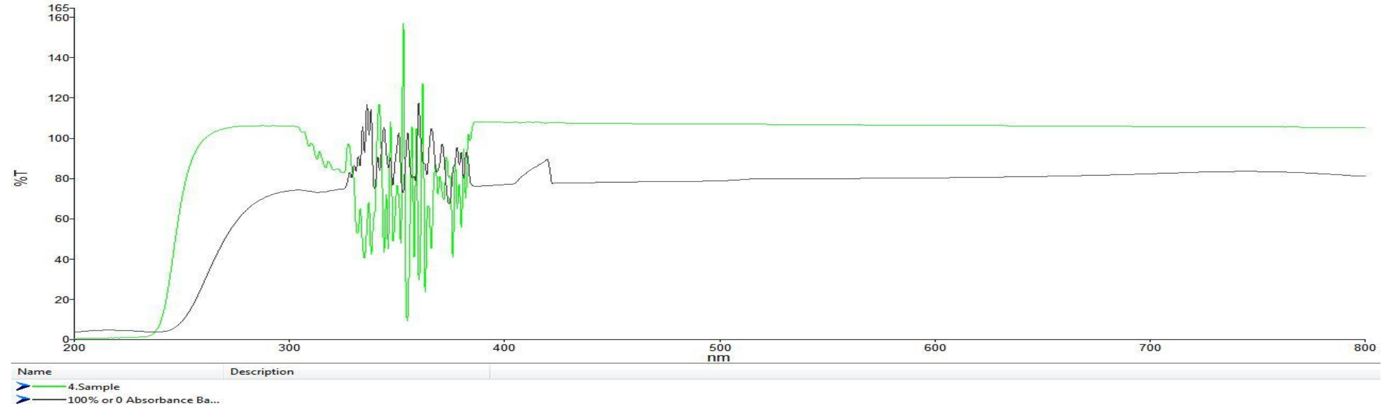


Fig. 10 UV-Vis of 4 drop titanium isopropoxide

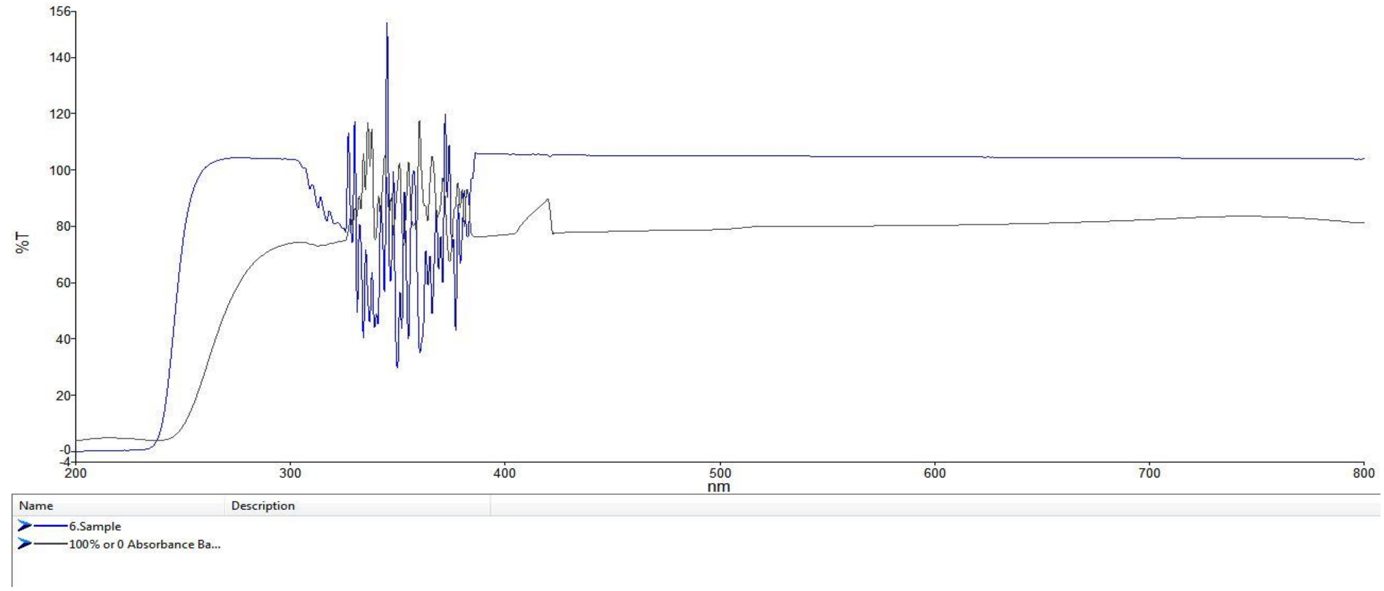


Fig. 11 UV-Vis of 6 drop titanium isopropoxide

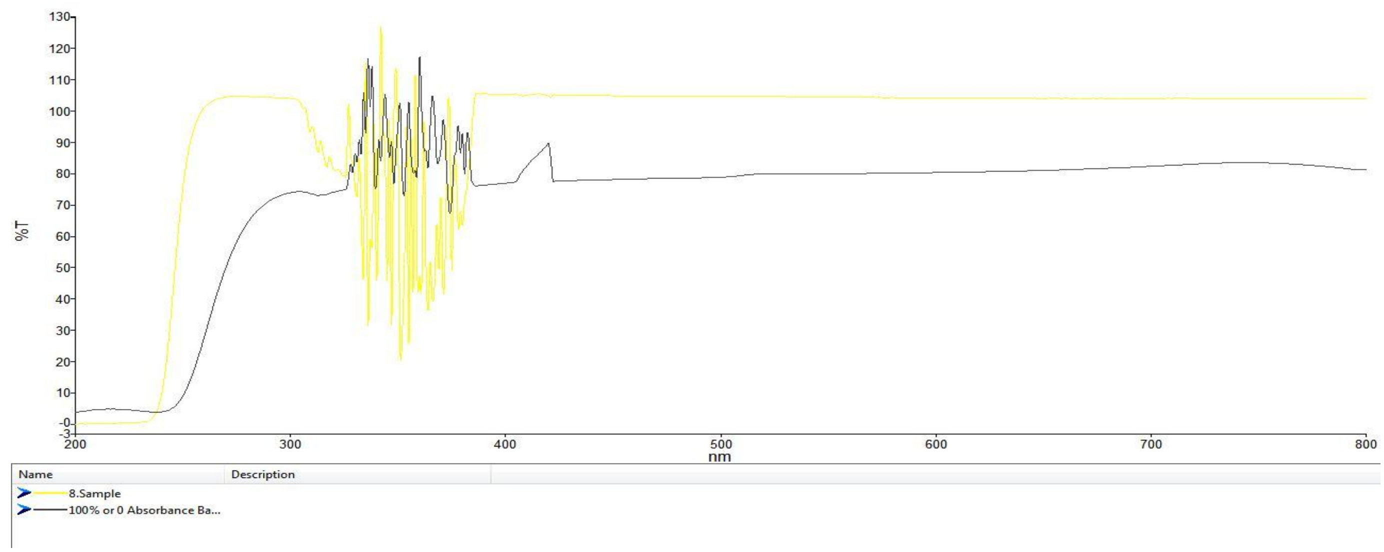


Fig. 12 UV-Vis of 8 drop titanium isopropoxide

D. Atomic force Microscopy(AFM)

The surface morphology was mapped at the resolution of 10nm and 100 nm for each sample and the roughness was investigated.

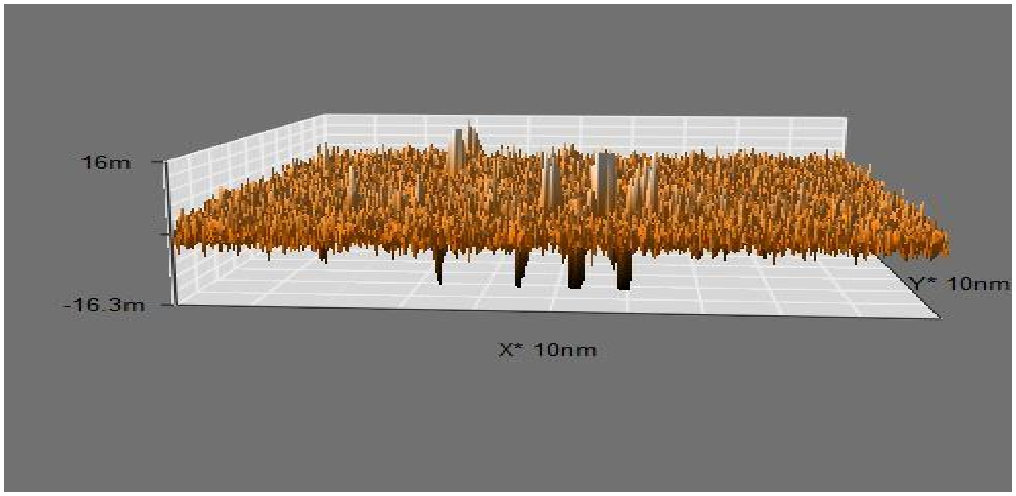


Fig. 13 Side view of coating

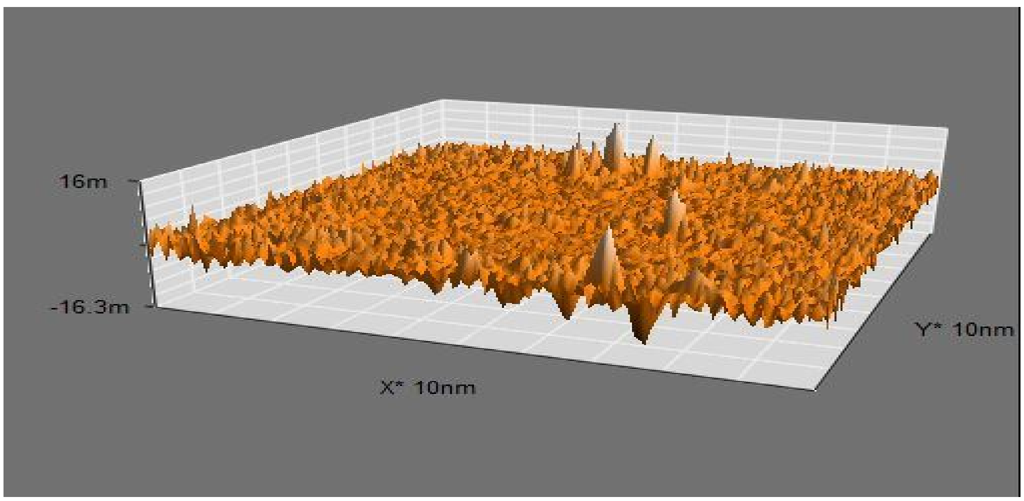


Fig. 14 Isometric view of coating

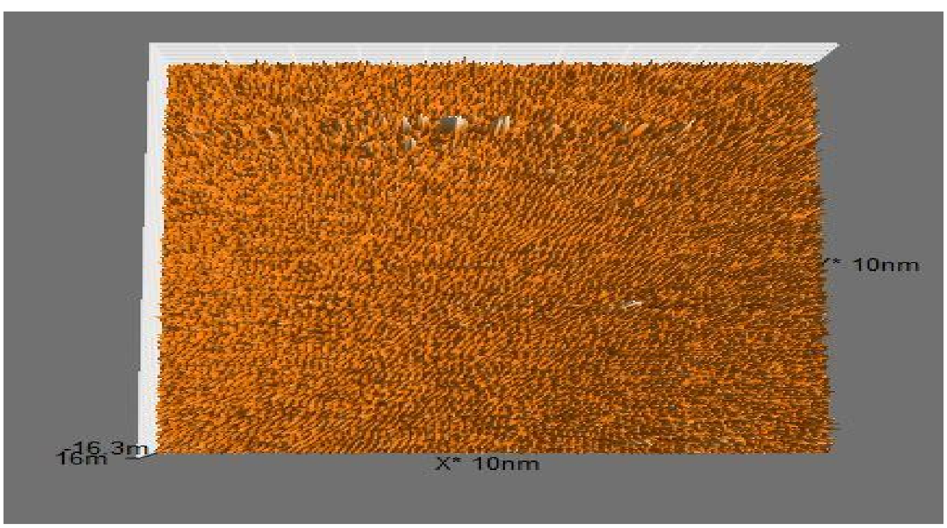


Fig. 15 Top view of coating

ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 6.887
Volume 6 Issue III, March 2018- Available at www.ijraset.com

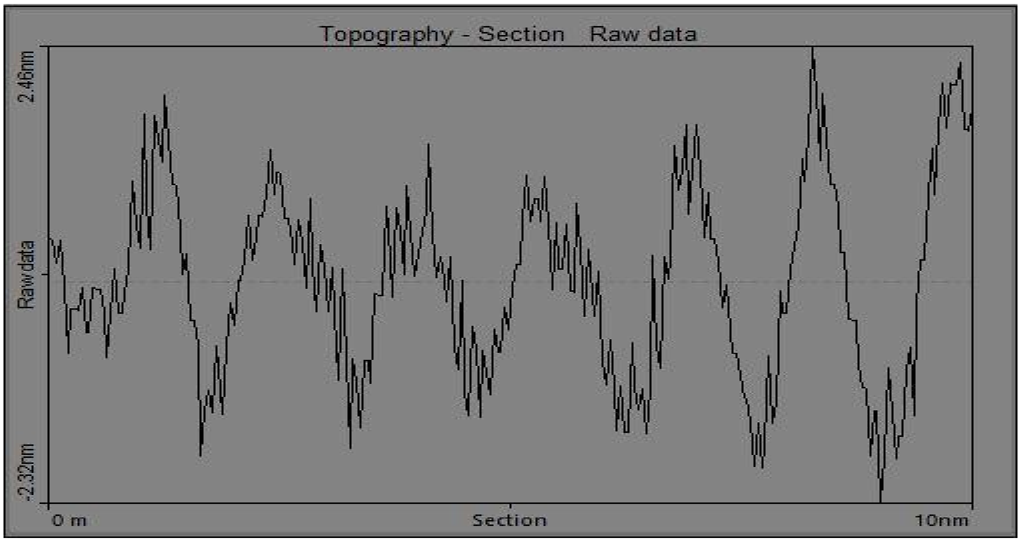
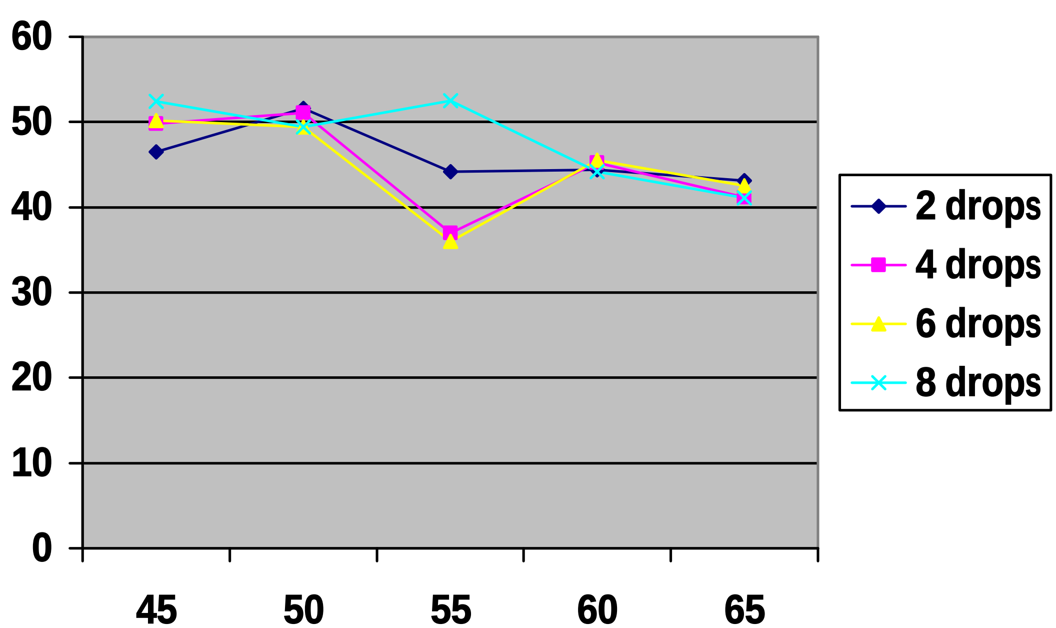


Fig. 16 Surface roughness of coating

It was concluded from Fig. 13-16, that surface roughness for the coating was very low compared to the size of water molecule. Thus, an extreme wetting of the surface was observed which was the reason for low water contact angle. The contact angle of surface is directly proportional to the surface roughness i.e., the density of nano-horns in a given cross-sectional area.

E. Thermal stability

Effect of temperature on contact angle for all samples was observed. From the Graph 1, it can be concluded that initially the water contact angle increased then dipped at 55^0C and gives the least value at 65^0C.



GRAPH III
THERMAL STABILITY OF THIN FILMS

The decrease in contact angle might have occurred due to redistribution of surfactant on the surface of glass. The thin-films were stable between temperature range of 45^0C to 65^0C. Thus, proving their stability in extremely hot conditions.

IV. CONCLUSIONS

The addition of titanium isopropoxide must be drop by drop to result in very low water contact angle coating. The contact angle of the coating increases with time due to decay of material on the surface and finally stablizes. On application of heat the surfactant redistributes on the surface and lower contact angles are observed at 65^0C. The thin film has 75% transparency within visible spectrum which peaks to 90% at 415nm. The coating has zero transmittance in deep UV spectrum. The AFM results give very low surface roughness as a result the coating is highly hydrophilic.

V. ACKNOWLEDGMENT

This research was carried out in University of Petroleum and Energy Studies under the research project 'Transparent superhydrophilic self cleaning coatings. The authors would like to thank this support.

REFERENCES

[1] Choi, M., Xiangde, L., Park, J. H., Choi, D., Heo, J., Chang, M., … Hong, J. (2017). Superhydrophilic coatings with intricate nanostructure based on biotic materials for antifogging and antibiofouling applications. Chemical Engineering Journal, 309, 463–470. https://doi.org/10.1016/j.cej.2016.10.052

[2] Olad, A., Nosrati, R., Najjari, H., & Nofouzi, K. (2016). Preparation and investigation of hydrophilic, photocatalytic, and antibacterial polyacrylic latex coating containing nanostructured TiO2/Ag+-exchanged-montmorillonite composite material. Applied Clay Science, 123, 156–165. https://doi.org/10.1016/j.clay.2016.01.022

[3] Paetz gen. Schieck, H. (2014). Medical Applications, 4, 321–326. https://doi.org/10.1007/978-3-642-53986-2_18

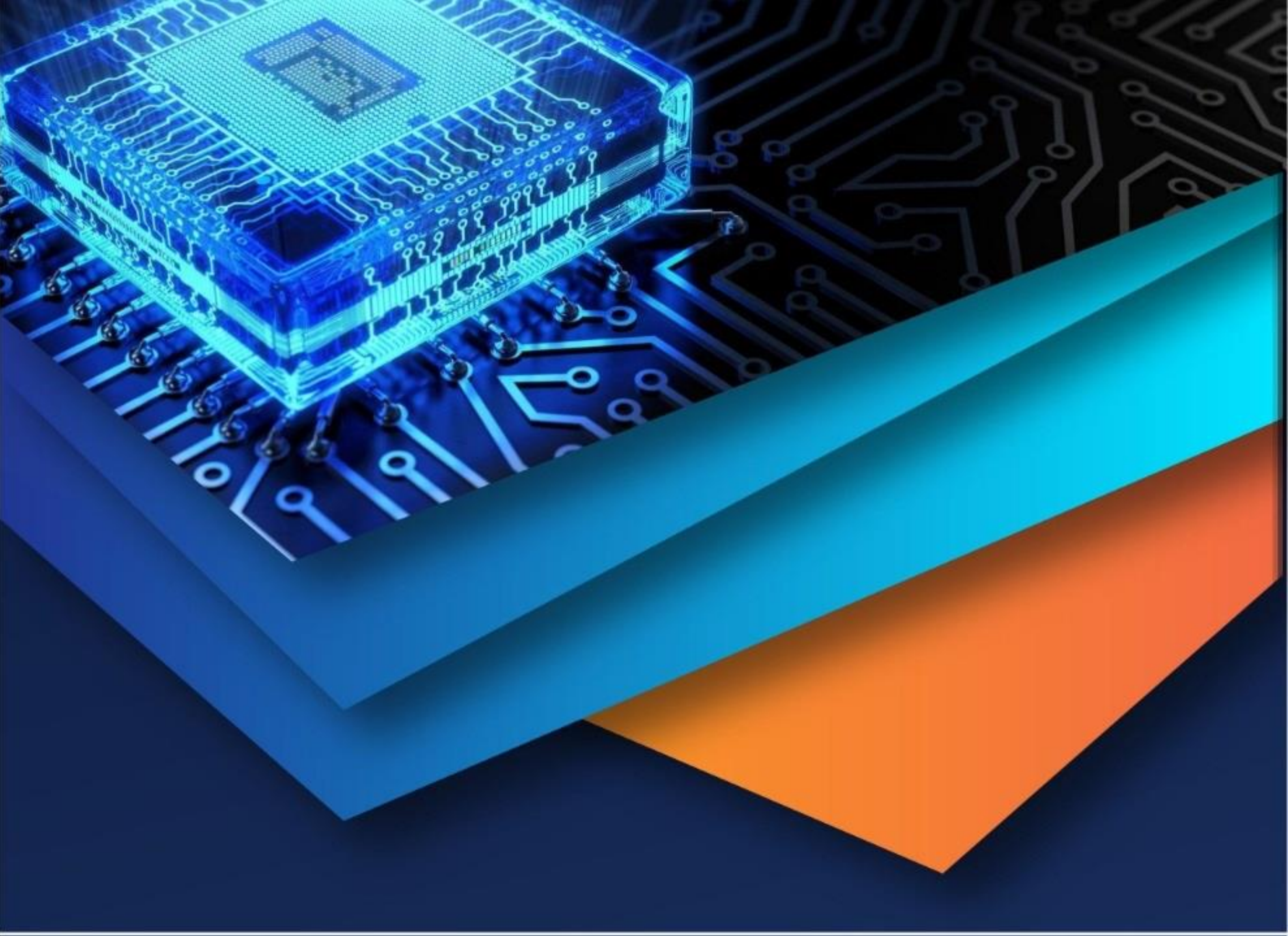
[4] Ragesh, P., Anand Ganesh, V., Nair, S. V., & Nair, A. S. (2014). A review on "self-cleaning and multifunctional materials." J. Mater. Chem. A, 2(36), 14773–14797. https://doi.org/10.1039/C4TA02542C

[5] Takeuchi, M., Sakamoto, K., Martra, G., Coluccia, S., & Anpo, M. (2005). Mechanism of Photoinduced Superhydrophilicity on the TiO_2 Photocatalyst Surface. The Journal of Physical Chemistry B, 109(32), 15422–15428. https://doi.org/10.1021/jp058075i

[6] Wang, F., Zhang, G., Zhao, Z., Tan, H., Yu, W., Zhang, X., & Sun, Z. (2015). TiO_2 nanosheet array thin film for self-cleaning coating. RSC Adv., 5(13), 9861–9864. https://doi.org/10.1039/C4RA13705A

[7] Zhang, L., Zhao, N., & Xu, J. (2014). Fabrication and application of superhydrophilic surfaces: A review. Journal of Adhesion Science and Technology, 28(8–9), 769–790. https://doi.org/10.1080/01694243.2012.697714

[8] Zhang, X., Jin, M., Liu, Z., Tryk, D. A., Nishimoto, S., Murakami, T., & Fujishima, A. (2007). Superhydrophobic TiO2 surfaces: Preparation, photocatalytic wettability conversion, and superhydrophobic-superhydrophilic patterning. Journal of Physical Chemistry C, 111(39), 14521–14529. https://doi.org/10.1021/jp0744432



10.22214/IJRASET

INDEX COPERNICUS
45.98

ISRA JIF
IMPACT FACTOR: 7.129

TOGETHER WE REACH THE GOAL
IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY