



SURFACE MODIFICATION OF ALUMINIUM COATED GLASS SUBSTRATE BY TRI-AMINOSILANE

Megha A. Deshmukh, Harshada K. Patil, Sumedh D. Gaikwad, Arti D. Rushi, Gajanan A. Bodkhe, Mahendra D. Shirsat*

Intelligent Material Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (MS) – 431 004

*Email: mdshirsat.phy@bamu.ac.in

ABSTRACT:

Surface modification of Aluminium coated glass substrate by tri-Aminosilane is reported in the present communication. The coverage of 3-Aminopropyltriethoxysilane (3-APTES) on Aluminium (Al) Coated Glass (Al/Glass) substrate has been accomplished by dip coating method. Al was deposited on glass substrate by thermal evaporation technique. During deposition of 3-APTES various process parameters viz. solvent (toluene) concentration, deposition time and concentration of silane were optimized. The surface modification of Al/glass substrate with silane molecules was confirmed by ATR-FTIR study. Surface morphology of 3-APTES coated Al/glass substrate was investigated by Scanning Probe Technique viz. Atomic Force Microscopy (AFM).

KEYWORDS: Al Coated Glass Substrate, surface modification, Aminosilane, dip Coating

1. INTRODUCTION

The surface treatment of various metal and nonmetal substrates with silane groups has improved the performance of the metals and glass surfaces [1, 2]. Recent studies of the formation of monomolecular assemblies on various solid surfaces attracted the growing attention of world [3]. Organosilane molecules functionalized solid surfaces have vital industrial applications viz. catalysts advanced composite materials and chromatographic supports [4,5,6,7]. Mechanism of Aminopropyltriethoxysilane (APTES) adsorption on glass surfaces has been widely studied [8-12]. In recent era, researchers are taking more keen efforts towards the potential application of silane self assembled monolayer's which play significant role in attracting large molecules [13-16]. Functionalities of organic molecules allow the control of the hydrophobicity and hydrophilicity [17].

The interaction of the self assembled monolayer's coupling agents with the substrate surface may depend on the composition and the type of substrate surface [18], whether it is metallic or nonmetallic. Many investigations have been

proposed to explain the function of silane group agents [19]. Silane monolayer's play role of isolator and densely packed having number of applications in various fields [20]. The metal oxides and silicates surfaces naturally in balance with atmospheric moisture consist of surface hydroxyl groups. Thus, the surface hydroxyl and oxide group play significant role in the formation of each type of bonding [17]. The reactivity of surface immobilized groups totally depends on chemical accessibility.

In The functionalization of monolayer on solid surfaces provides the suitable functional groups viz -SH, -CN -COOH, -NH₂ and silanes [21]. In addition, the amino group itself acts as a catalyst and improves the adsorption rate of 3-aminopropyltriethoxysilane molecules on the glass surface [22, 23]. These surfaces can be most useful in various Nanotechnology applications and architecture [24]. The schematic of the 3-APTES modified surface is shown in Fig. 1, where C₂H₅O is serve as head group, Si (Silane) act as tail group and NH₂ as functional group.

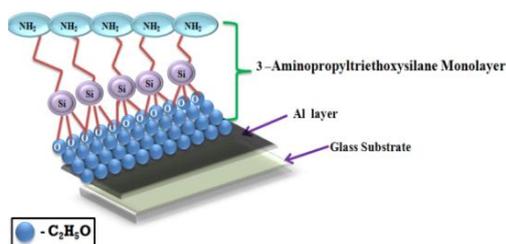


Fig. 1 Formation of 3-Aminopropyltriethoxysilane monolayer on Al coated glass substrate.

Aim of this investigation is to modify the surface of thermally evaporated glass substrate by 3-aminopropyltriethoxysilane. Dip coating method was used for the surface modification of Al/Glass substrate. The properties and structure of the silane-coating layer was characterized using atomic force microscope (AFM) and FTIR spectroscopy.

2. RESULTS AND DISCUSSION

Al coated glass substrates were prepared by thermal evaporation method by optimizing various parameters. Molybdenum filament was used to heat evaporant (Aluminium). Ultimate chamber pressure was 1×10^{-6} Mbar. Typical filament current was 12 Amps. Al deposition thickness achieved was 100nm.

Al /Glass substrates prepared by thermal evaporation method were soaked in acetone for about two minutes, and then dried under dry air stream. This assures that the slides are free from any trace of oil or water.

The preparation of 3-aminopropyltriethoxysilane on Al /Glass substrate was done by dipping slides in solution containing 1ml of silane with 50ml toluene for 5hrs. Obtained slides were rinsed through anhydrous toluene to remove any excess reagent. Finally the 3-APTES coated substrates were heated in oven at 120°C for 20min. The obtained substrates were stored in desiccator under vacuum until further use.

FTIR ANALYSIS:

In order to investigate the terminal amino groups in 3-APTES on Al /Glass substrates FTIR characterization was carried out (Fig. 2), which gave a broad peak in between 1640-1550 cm^{-1} due to -NH stretching. The spectra of 3-APTES modified substrate show peak at 1028.73 cm^{-1} for Si-O stretching of the silane group which are playing vital role in compounds for anchoring in organic layer to surface. A broad peak appears around 2400 cm^{-1} due to the existence of stronger hydrogen bonding of the SiOH group.

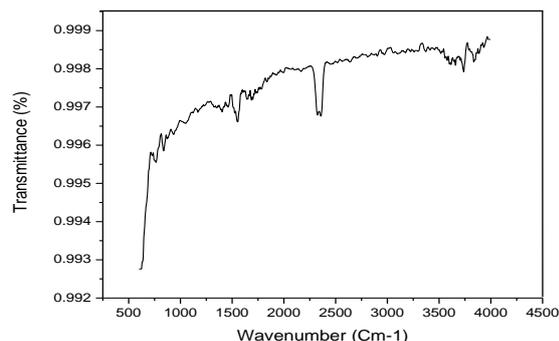


Fig.2 FTIR spectra of 3-Aminopropyltriethoxysilane monolayer on Al/glass substrate

2.1 SURFACE MORPHOLOGICAL STUDY

Atomic force microscopy was used to characterize structure of modified surface at molecular level and to understand the nature of adsorbed layer. It also offers the force difference between a tip and surface. AFM measurements were collected for 3-APTES coated substrate by Park XE-7 model. Area of $5\mu\text{m} \times 5\mu\text{m}$ was scanned at different spots to ensure representative areas. All scans were done in non-contact mode. AFM image of 3-APTES modified surface is shown in fig. 3(a). The average roughness of the surface was 42.00nm; histogram of the roughness was shown in fig 3(b)

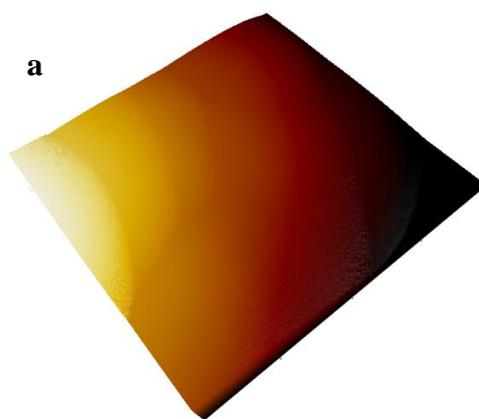
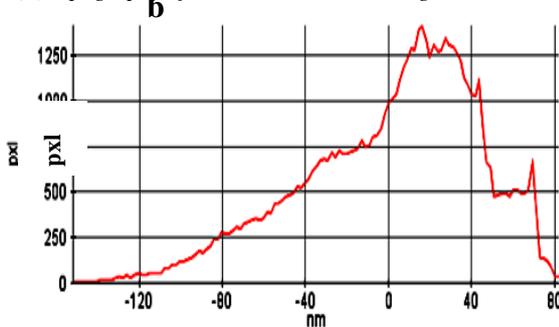


Fig. 3 NC-AFM image of grown APTES monolayer (a) topography of 3-APTES on Al coated glass substrate,



(b) Histogram of the roughness of grown monolayer.

AFM contributes very effectively in the investigation of adhesion force of SAMs by observing adhesion interaction between different functional groups which determined from force-

distance (F/D) spectroscopy. This is comprehended by obtaining force-distance curve (fig. 4). Nature of F/D spectroscopy curve conform the soft nature of modified surface. The viscoelastic properties of closely packed 3-APTES monolayer obtained by AFM had suggested Young's modulus of about 1.84GPa. It also confirms the adhesion force of monolayer consisting the chemical bonding force, Vander walls and elastic force [17].

Adhesion energy of material is $4.97517 \times 10^{-15} \text{J}$, which confirm the adhesion between of 3-APTES. Adhesion is one of the most important factor which helps to determine force between two different materials together. Pull-off force is considered as adhesion force [18]. For 3-APTES monolayer the AFM- measured pull-off force become $437.045 \times 10^{-9} \text{N}$ it is determined from retracting part of cycle corresponds to adhesion between functional groups on tip and sample surface.

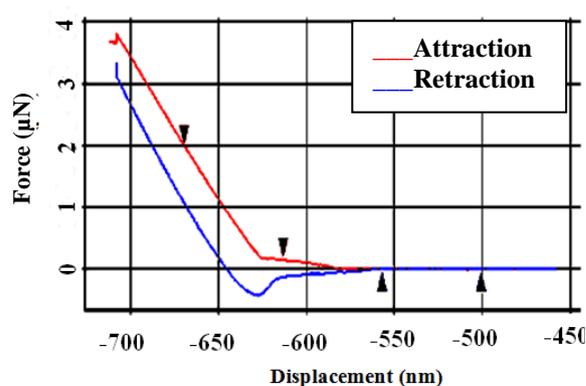


Fig. 4 F/D spectroscopy curve of 3-APTES on Al/ Glass Substrate

3. CONCLUSIONS

In present investigation we have successfully carried out surface modification of Al/Glass substrate with 3-APTES by dip coating method. The properties and structure of tri-aminosilane treated surface was investigated using surface characterization technique and spectroscopic technique viz. AFM, F-D spectroscopy and FTIR which confirms the APTES undergoes surface reactions. The F/D spectroscopy shows effective adhesion of 3-APTES and formation of soft nature surface. The morphological study confirms the distribution of 3-APTES molecules on substrate surface.

ACKNOWLEDGEMENTS

The authors are grateful to Department of Science and Technology (DST)-SERB, New Delhi, India (Project No. SB/EMEQ-042/2013).

REFERENCES

- [1] Joana F. Cabrita, Ana. S. Viana e Luisa M. Abrantes, *copper protection by phosphonic acid self-assembled monolayers*, *Corros. Prot. Mater.*, Vol. 29, N° 4 (2010)
- [2] J. Christopher Love, Lara A. Estroff, Jenna K. Kriebel, Ralph G. Nuzzo, and George M. Whitesides, *Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology*, *Chem. Rev.* 2005, 105, 1103-1169
- [3] Bain, C.; Whiteside, *Modelling Organic Surfaces with Self-Assembled Monolayers*, *G.M. Adv. Mater.* 1989, 28,506
- [4] L.A. Chrisey, G.U. Lee, C.E. O'Ferrall, *Covalent Attachment of Synthetic DNA to Self-Assembled Monolayer Films*, *Nucleic Acids Res.* 24 (1996)3031.
- [5] A.J. Aznar, E. Ruiz-Hitzky, *Mechanism of the grafting of organosilanes of mineral surfaces. IV. Phenyl derivatives of sepiolite and poly(organosilanes)* *Colloid Polym. Sci.* 270 (1992) 165.
- [6] Zhihong Nie, Alla Petukhova & Eugenia Kumacheva, *Properties and emerging applications of self-assembled structures made from inorganic nanoparticles*, *Nature Nanotechnology* 5, 15 - 25 (2010)
- [7] D. Mislovicova, I. Novak, M. Pasteka, *Coated silica and its behavior in dye-affinity chromatography*, *Journal of Chromatography A*, 1991 – Elsevier J. Chromatogr. 543 (1991) 9.
- [8] E. Metwalli, D. Haines, O. Becker, S. Conzone, C.G. Pantano, *Surface characterizations of mono-, di-, and tri-aminosilane treated glass substrates*, *Journal of Colloid and Interface Science* 298 (2006) 825–83
- [9] M. Child, M. Heywood, S. Pulton, G. Vicary, G.H. Young, *Structure and dynamics of amino functional silanes adsorbed on silica surfaces*, *J. Colloid Interface Sci.* 89 (1982) 203.
- [10] K.M.R. Kallury, P.M. Macdonald, M. Thompson, *Effect of Surface Water and Base Catalysis on the Silanization of Silica by (Aminopropyl)alkoxysilanes Studied by X-ray Photoelectron Spectroscopy and ¹³C Cross-Polarization/Magic Angle Spinning Nuclear Magnetic Resonance* *Langmuir* 10 (1994) 492.
- [11] F.M. Fowkes, D. Dwight, D. Cole, *Acid-base properties of glass surface*, *J. Non-Cryst. Solids* 120 (1990) 47.
- [12] J.R. Schallenger, E. Metwalli, C.G. Pantano, F.N. Tuller, D.F. Fry, *Adsorption of polyamides and polyamide-silane mixtures at glass surface*, *s Surf. Interface Anal.* 35 (2003) 667.
- [13] J.B. Brzoska, I.B. Azouz and F. Rondelez, *Silanization of Solid Substrates: A Step Toward Reproducibility* *Langmuir* 10, 4367-4373 (1994).
- [14] S. Flink, F.C.J.M. van Veggel and D.N. Reinhoudt, *Functionalization of self-assembled monolayers on glass and oxidized silicon wafers by surface reactions*, *J. Phys. Org. Chem.* 14, 407-415 (2001).
- [15] L.A. Chrisey, G.U. Lee and C.E. O'Ferrall, *Covalent attachment of synthetic DNA to self-assembled monolayer films*, *Nucleic Acids Research*, 24, 3031-3039 (1996).
- [16] A. Katz, P. Da Costa, A.C.P. Lam and J.M. Notestein, *The first single-step immobilization of a calixarene onto the surface of silica*, *J. M. Chem. Mater.* 14, 3364-3368 (2002).
- [17] Gulsin ARSLANI, Mustafa OZMENI, Beniz GUNDUZ1, Xunli ZHANG2 and Mustafa ERSOZ, *Surface Modification of Glass Beads with an Aminosilane Monolayer*, *Turk, J Chem* 30 (2006), 203 - 210.
- [18] S. Naviroj, S. Culler, J.L. Koenig, and H. Ishida, *Molecular structure of an aminosilane coupling agent as influenced by carbon dioxide in air, ph, and drying conditions*, June 9, 1982
- [19] S. varatharajan, sheela berchmans and v yegnaraman, *self-assembled monolayers at the electrochemical interface*, *J. Chem. Sci.*, Vol. 121, No.5 September 2009,
- [20] Sigma aldrich, *Preparing Self-Assembled Monolayers (SAMs) A Step-by-Step Guide for Solution-Based Self-Assembly*, Technical Bulletin AL-266.
- [21] N.K. Chaki, M. Aslam, J. Sharma and K.Vijayamohanam, *Application of self assembled monolayers in materials*

- chemistry, Indian Acad. Sci (Chem. Sci), 113, 659-670 (2001).
- [22] J.J.P. Blitz, R.S. Shreedhara Murthy, D.E. Leyden, *The role of amine structure on catalytic activity for silylation reactions with Cab-O-Sil*, J.Colloid Interface Sci. 126 (1988) 387.
- [23] P. Trens, R. Denoyl, J. Rouquerol, *Adsorption of (Q aminopropyl) triethoxysilane on silica from aqueous solution: A microcalorimetric study*, Langmuir 11 (1995) 551.
- [24] J. Sagiv, J. Am. Organized monolayers by adsorption. 1. *Formation and structure of oleophobic mixed monolayers on solid surfaces*, Chem. Soc. 102, 92 (1980).