Role of Nanoscale Topography on the Hydrophobicity:

A Study of Fluoro-Based Polymer Film on Silicon and Carbon Nanotubes

A.R. Phani*, L. Lozzi, M. Passacantando and S. Santucci

Department of Physics-University of L'Aquila and INFM-CASTI Regional Laboratory
Via Vetoio 10 Coppito 67010 L'Aquila ITALY, arp@net2000.ch

ABSTRACT

The unique electronic, mechanical and chemical properties of carbon nanotubes making them most promising candidate for the building blocks of molecular-scale machines, and nanoelectronic devices. On the other hand, highly hydrophobic films are being actively considered in silicon based micro-electromechanical systems, nanotechnology based devices, optoelctronic devices, or biomedical devices to reduce adhesion that may be encountered during wet processing. In order to fill the gap, and fulfil the requirements, it could be proved that morphological changes in the nanometer range influences the water contact angles and their hystersis of low-surface energy materials. Thin films of fluorine based block co-polymer itself forms nano-hemispheres (similar to lotus leaf) at and above 100°C favoring an increase in the water contact angle from 122° (25°C) to 138° (400°C). The structural, optical, mechanical and hydrophobic properties of fluorine based block co-polymer are also discussed. By applying nanolayered (5 nm) fluorine-based block co-polymer film on a aligned carbon nanotubes (CNT) morphology with a certain roughness, the advancing contact angle for water on fluoro-based polymer film on a nearly atomically flat Si wafer increased from 122 ° to 138° (close to super hydrophobicity) and 150° on the rough asparagus-like structure of CNT has been observed.

Keywords: carbon nanotubes, block-co-polymer, hydrophobicity, contact angle, nano-hemispheres

1 INTRODUCTION

It is well known, that the hydrophobicity of surface is strongly affected by the chemical composition and topographical appearance. Considering only the chemical factor, contact angles of around 120° can be obtained for materials with lowest surface energy (6.7 mJ/m^2 for a surface with regularly aligned closer-hexagonal packed $-CF_3$ groups) For achieving higher contact angles (super hydrophobicity), a certain topography is required. For the topographical modification of low-surface energy materials, in the last years two main approaches have been investigated. The first approach considers the structuring or texturing of the material itself during or after depositing on a smooth substrate through, e.g. varying the deposition conditions [1], post treatment with ion or electron beam, and plasma etching [2]. In other case, the low energy materials were deposited on substrate with certain structure or texture, which were obtained by methods like embossing or laser ablation [3] photolithography [4] or deposition of rough interlayer by thin film technology. It was proved that, by combining the chemical structure (by using sol-gel technique) with nano-topography (by using sputtering), one could achieve super hydrophobicity [5].

Many deposition techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD) or plasma polymerization, have been used to produce hydrophobic coatings on glass, silicon and other metallic substrates. Unlike PVD, CVD, or plasma polymerization techniques, with the sol-gel technique it is possible to modify the surface of any material (e.g. glass, metal, polymers) with organic polymers. This process is cost effective with easy operation at low or even at ambient temperature. One main advantage of the process is, the possibility to coat three-dimensional substrates (or irregular geometries) with high homogeneity in film thickness and good adhesion.

In the present work, a clean, and economic process is introduced to prepare temperature-resistant, hydrophobic thin films on Si (100) and CNT previous deposited on SiO_2/Si substrates. Keeping in view the necessity of the hydrophobicity on nanoelectronics made from carbon nanotubes, an attempt has been given to spin coat a nanolayer of (5 nm) of hydrophobic fluorine containing block-co-polymer poly [4,5- difluoro 2,2-bis (trifluoromethyl)-(1,3 dioxole)-co-tetrafluoroethylene] here after named as (TFD-co-TFE) on to bare Si (100) substrates as well as previously grown carbon nanotubes on SiO_2/Si substrates. Films deposited on quartz, glass surfaces [6] and polished AISI 440C steel surfaces [7] and their structural, chemical characterization, wettability properties have been reported. The basis of this work is the use of fluorine containing block-co-polymer namely poly [4,5- difluoro 2,2-bis (trifluoromethyl)-(1,3 dioxole)-co-tetrafluoroethylene] (TFD-co-TFE). Compared to perfluoroalkylsilane or hexamethyldisilazane, TFD-co-TFE exhibits higher mechanical strength, chemical durability, and temperature stability. The importance of the compound is the stability to high temperatures up to 400 °C, which could be due to carbon-oxygen link of the fluorine

containing block-co-polymer structure as depicted in the figure 1.

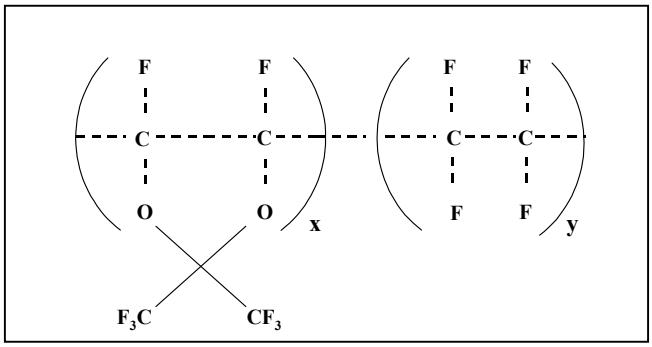

Figure 1: Structure of the fluorine-based block-co-polymer used as a precursor for the preparation of TFD-co-TFE films by sol-gel spin coating process

Sol-gel thin films based on this compound have been prepared by a spin coating technique followed by annealing at low temperatures. It was observed that as the annealing temperature increased from 100 °C to 400 °C, formation of nano-hemisphere-like structures were formed on the film surfaces of TFD-co-TFE coated on Si (100).

3 EXPERIMENTAL PROCEDURE

Calculated quantities (0.1 M) of poly [4,5 difluoro 2,2-bis (trifluoromethyl) - (1,3 dioxole) – co -tetrafluoroethylene] (amorphous copolymer: 65 mole % dioxole, T_g: 160 °C) were dissolved in special fluorinated solvent (Fluorinert FC-70) in a 100 ml round bottom flask. Both reagents were obtained from FLUKA Chemicals and used without further purification. To the above solution few drops of stabilizing agent was added and stirred at room temperature for about 6 hours in nitrogen atmosphere to prevent particle contamination. The contents were refluxed at 40°C for 4 h. The final solution was filtered in order to remove any particulates formed during the process. The obtained filtered stock solution was used for spin coating the substrates. A schematic flow chart diagram for the preparation of the hydrophobic thin films by sol-gel spin coating technique was shown in figure 2.

Polished Si (100) substrates and CNT grown on SiO_2/Si substrates with surface roughness R_a = 1.5 nm 36 nm, respectively and have been used in the present study. The deposition parameters for the growth of CNT on SiO_2 /Si substrates by radio frequency plasma chemical vapor deposition technique were described elsewhere [8]. Prior to spin coating, Si (100) substrates were rinsed with isopropanol and then placed in a trough containing isopropanol and subjected to ultrasonic cleaning for 15 min in order to remove any organic matter and dust particles present on the surface. Afterwards the substrates were again rinsed with isopropanol and then blown dry with high purity nitrogen gas (99.95%).

The clean substrates were immediately placed in the spin coating chamber. Using 50 microliters pipette 10-15 microliters of the stock solution was placed on the surface of the substrate and spun with 1000 rpm speed for 30 sec (cylce-1) to spread the solution on the entire surface of the substrate. This step was followed by 3000 rpm for 30 sec (cycle-2) in order to evaporate the solvent. The steps consisting of cycle-1 and cylcle-2 were repeated 10 times for the Si (100) substrates and one time for CNT / SiO_2 /Si substrates in order to get 50 nm thickness and 5-8 nm nanolayer thickness. At the end, the obtained xerogel films deposited on Si (100) were subjected to annealing for 1 hour at different temperatures ranging from 100 °C to 400 °C in argon atmosphere.

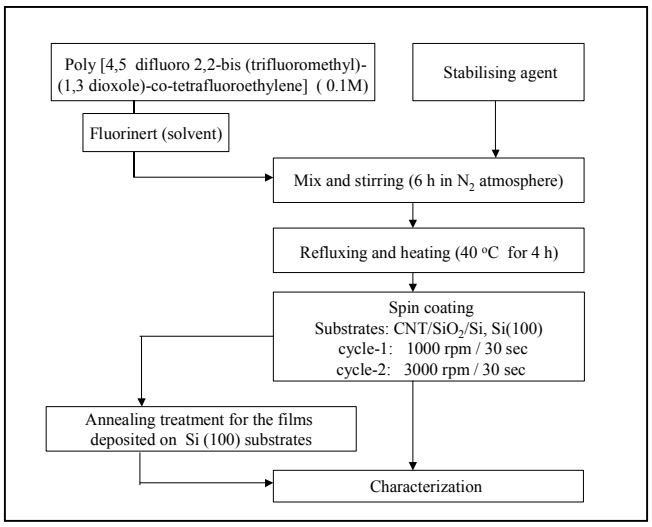

Figure 2: Flow chart for the preparation and deposition of TFD-co-TFE thin films by sol-gel spin coating process

The microstructure, elemental composition, and surface topography of the TFD-co-TFE xerogel films as well as annealed thin films were characterized by employing scanning electron microscopy (SEM) attached with energy dispersive X-ray (EDX) analysis, and atomic force microscopy (AFM) techniques, respectively.

4 RESULTS AND DISCUSSIONS

4.1 Scanning Electron Microscopy

SEM images and the corresponding energy dispersive X-ray (EDX) spectra of the TFD-co-TFE film deposited on Si (100) at room temperature and annealed at 400 °C for 1 h in argon atmosphere have been shown in figure 3 and 4, respectively. The xerogel (as deposited) films were uniform with flat and smooth structure.

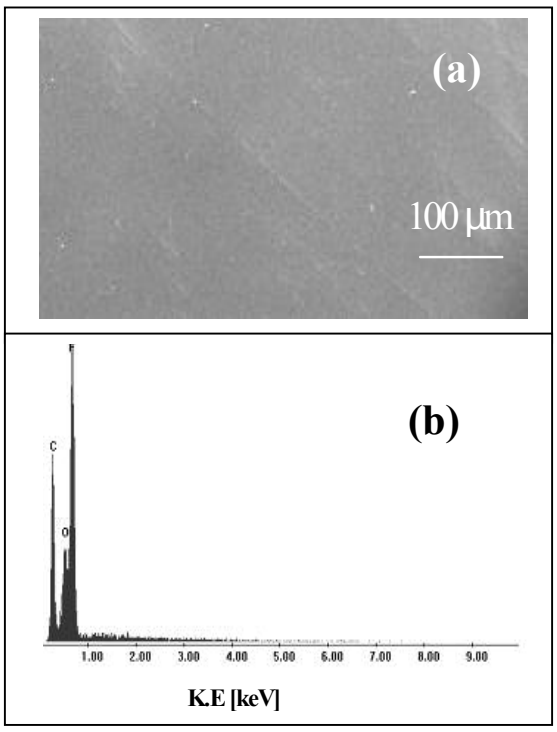

Figure 3: SEM image and EDX spectrum of TFD-co-TFE film deposited on Si (100) at room temperature by sol-gel spin coating process

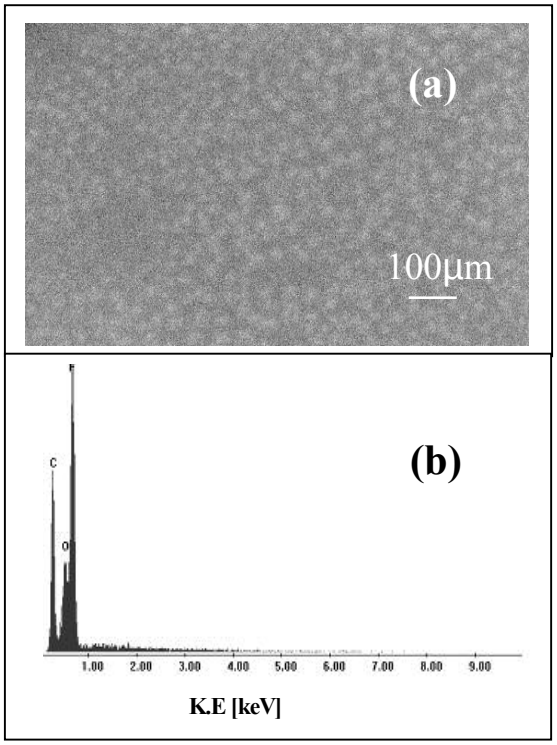

Figure 4: SEM image and EDX spectrum of TFD-co-TFE film deposited on Si (100) by sol-gel spin coating process and annealed at 400 °C for 1 h

It became difficult to take the SEM images because of the interaction of the high electron beam on the sample, which caused the film to leave with a small hole. No morphological changes in the surface were observed for the annealed samples at other temperatures except in the growth of the nano-hemisphere-like structures. Figure 3b and 4b represents SEM-EDX spectra of the TFD-co-TFE film on Si (100) for both xerogel film and xerogel film annealed for 1 h at 400 °C in an argon atmosphere. The X-ray pattern confirms the presence of carbon and fluorine along with oxygen content in the films. The weight percent of the C, F and O in the film were 40.2 wt.%, 42.3 wt.% and 17.5 wt.%, respectively. Similar behavior was also observed for the annealed samples as shown in figure 4b.

The as deposited carbon nanotube structure on SiO_2 /Si substrate grown at substrate temperature 650 °C has been shown in the figure 5. It is evident from the figure that the growth of carbon nanotubes is rough and asparagus-like structure.

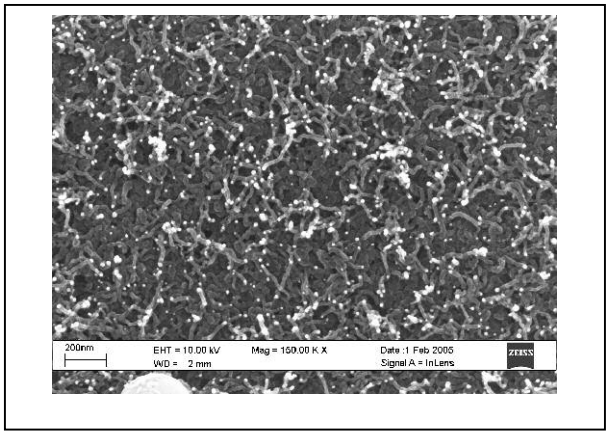

Figure 5: SEM image of roped CNT on SiO_2/Si substrate grown at 750°C by radio frequency pulsed plasma chemical vapor deposition technique

4.2 Atomic Force Microscopy

Figure 5a and 5b represents the topographical AFM images of the TFD-co-TFE films deposited on Si (100) substrates for both xerogel film and xerogel film annealed for 1 h at 400 °C in an argon atmosphere. The xerogel films have exhibited a flat like structure with little formation of nano-hemisphere like structures as indicated by the white circles (figure 5a). As the annealing temperature was increased from 100 °C to 400 °C, the growth of nano-hemisphere-like structures was increased as shown in the figure 5b, indicated by white circles.

The roughness of the films has been measured by AFM technique. The roughness of the films (R_a) deposited on Si (100) substrates has changed with annealing temperature from 8 ± 1 nm for xerogel film to 32 ± 1 nm for the film annealed at 400 °C as shown in the figure 6. The

growth size of the nano-hemispheres increased from 6 ± 1 nm for xerogel film to 26 ± 1 nm for film annealed at 400 °C.

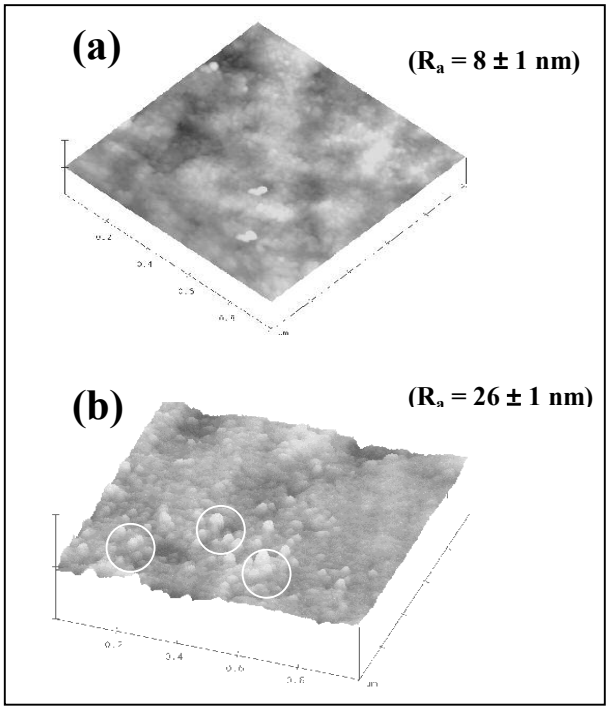

Figure 5: AFM topographical images of TFD-co-TFE thin films on Si (100) substrate by sol-gel spin coating process (a) As deposited (xerogel) film and (b) Xerogel film annealed at 400 °C / 1 h
(scan area 1μm × 1 μm, Z axis = 100 nm)

4.3 Hydrophobicity

Contact angle of the films deposited at room temperature and annealed at different temperatures as well as substrate heated at various temperatures have been measured by spheroidal segment method using a contact angle measurement system (Circular Curve Fit Option). The contact angle, θ, was derived from advancing contact angle, θ_a, and reducing contact angle θ_b, by the following equation: $\text{Cos}\ \theta = \theta_a + \theta_b / 2$ or $[(\gamma_{SV} - \gamma_{LV}) / \gamma_{LS}]$, where γ_{SV}, γ_{LV}, and γ_{LS} are free energies of solid-vapor, liquid-vapor and liquid-solid interfaces, respectively. Water contact angle versus annealing temperature for the TFD-co-TFE films on Si (100) substrates have been presented in figure 6a. From figure 6a, it was evident that TFD-co-TFE films on Si (100) as deposited have shown water contact angle 122° and as the annealing temperature increased from 100 °C to 400 °C the contact angle was increased from 122° to 138°. This could be due to the growth of nano-hemisphere like structures at 100 °C and above. The room temperature water contact angles of TFD-co TFE film deposited on Si (100) and CNT /SiO_2/Si were 123 and 150° as shown in figure 6b and 6c, respectively.

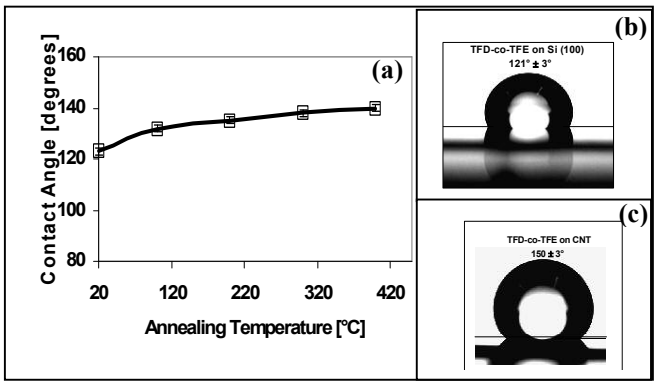

Figure 6: (a) Water contact angles *vs* annealing temperatures of TFD-co-TFE films deposited on Si (100). Water droplet pictures taken during measurement at room temperature (b) TFD-co-TFE film coated on Si (100) and (c) TFD-co TFE film coated on CNT/SiO_2/Si

5 CONCLUSIONS

Poly [4,5-difluoro 2,2-bis (trifluoromethyl)-(1,3 dioxole)-co-tetrafluoroethylene] (TFD-co-TFE) films have been deposited by sol-gel spin coating technique on Si (100) and CNTprevious grown on SiO_2/Si substrates. The xerogel (as deposited) films on Si (100) have been subjected to annealing for 1 h at different temperatures ranging from 100 °C to 400 °C in an argon atmosphere. SEM-EDX spectra confirmed the presence of carbon (~41 wt%), fluorine (~41 wt%) and oxygen (~18 wt%) in the deposited and annealed films. AFM topographical images revealed the formation of nano-hemisphere-like structures with increasing annealing temperatures. The size of the nano-hemispheres increased from 8 nm for xerogel film to 28 nm for film annealed at 400 °C on Si (100). The room temperature water contact angles of TFD-co TFE film deposited on Si (100) and CNT /SiO_2/Si were 123 and 150°, respectively.

REFERENCES

[1] G. Cicala, A. Milella, F. Palumbo, P. Favia, R. d'Agostino, Diamond and related Materials 12, 2020, 2003.
[2] Y. Inoue, Y. Aoshimura, Y. Ikeda, A. Kohno, colloids and Surfaces B: Biointerfaces 19, 257, 2000.
[3] D. Oner, T. J. McCarthy, Langmuir 16, 777, 2000.
[4] T. Uelzen, J. Muller, Thin Solid films, 434, 311, 2003.
[5] Y. Gerbig, A.R. Phani, H. Haefke, Applied Surface Science, 242, 251, 2004.
[6] A. R. Phani, M. Passacantando, S. Santucci, Materials Chemistry and Physics, 2005 (unpublished).
[7] A.R. Phani and H. Haefke, Materials Letters, 58, 3555, 2004.
[8] L. Valentini, J.M.Kenny, L. Lozzi, S.Santucci, J. Appl. Phys. 92, 6188, 2002