FABRICATION OF MO NANORODS ON SILICON WAFER USING GLANCING ANGLE DEPOSITION TECHNIQUE.

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Abstract

Array of silicon nanorods with a circular cross section onto Mo nanopillars arrangement were grown using glancing angle deposition (GLAD) on Si (100).Deposition technique was used to fabricate Mo thin film on silicon flat surface. Teflon deposited on the tips of Mo nanorods at normal incident evaporation ($\theta_{dep.}$is 0^{o}C) with deposition time of (5 min.) to study the hydrophoposity and hydroplilicity of the surface. Morphology of Mo and Mo/Teflon nanocomposite was carried out using scanning electron microscope (SEM) which indicates a (100 nm) of mo thin film and Mo nanorods on silicon substrate. Contact angle measurement on nanocomposite Mo nanorods with Teflon grown on their tips exhibited contact angle values as high as (116^{o}) indicating an increase in the hydrophopocity of original hydrophilic Mo nanostructures that had an angle of (40^{o}).

Key words: nanorods, molybdenum, Teflon, GLAD.

تصنيع قضبان المولبدينيوم النانوية على رقائق السليكون باستخدام تقنية الترسيب الزاوي الخاطف.

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الخلاصة

تم تحضير مجموعة من اسطح السليكون بالمستوى النانوي من خلال ترسيب شريحة دائرية من اعمدة المولبدينيوم النانوية على تلك الاسطح باستخدام تقنية (GLAD). استخدمت تقنية الترسيب الاعتيادي لصنع طبقة رقيقة من الموليبيديوم على اسطح السيليكون المسطحة. رسب التفلون على اطراف اعمدة الموليبيديوم النانوية والتي سقطت بزاوية تبخر اعتيادية مساوية للدرجة صفر وبزمن (5) دقائق .لدراسة اسطح السليكون الكارهة والمحبة للماء. مورفولوجية اسطح الموليبيديوم و الموليبيديوم/تيفلون تمت دراستها باستخدام المجهر الالكتروني الماسح والذي اشار إلى وجود (100) نانومتر كطبقة رقيقة من المولبدينيوم و كذلك اعمدة المولبدينيوم النانوية على اسطح السيليكون . قياس زاوية الاتصال بين قطرة الماء و اعمدة المولبدينيوم النانوية المغطية بطبقة التفلون على نهاياتها اظهرت زاوية عالية تصل الى (116) درجة مظهرة اسطح نانوية كارهة للماء مقارنة مع الاسطح النانوية بدون التيفلون المحبة للماء بزاوية (40) درجة.

1. Introduction:

In recent years, silicon nanorays have received considerable attention due to their unique properties and potential application in silicon based optoelectronic devices. Various patterning techniques have been employed to grow periodic nanostructures including colloidal self-assembly , e-beam lithography and laser interference lithography (Patzig, 2008). While the former is cost effective but limited to hexagonal close packing with a high packing density, the latter two techniques are capable of creating regular sub-100-nm patterns with various lattice geometries, but are limited by low processing speed, high cost, and incompatibility with large-area processing (Gish 2008).

Glancing angle deposition (GLAD) technique is a physical vapor deposition method to design three-dimensional nanostructures by programming the vapor incident angle and substrate azimuthal rotation. This method offers large area growth of aligned nanorod arrays with additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. With recent advance in a multilayer deposition procedure, one can design complex and multifunctional heterogeneous nanostructures.

Glancing angle deposition (GLAD), developed by Robbie and Brett exploits atomic shadowing effects during physical vapor deposition to create nanostructures with a wide range of engineering shapes including nanopillars, zigzags, nanospirals, and Y shapes (Zhoj,2007) with potential applications as photonic crystals, sensors, catalyst supports, magnetic storage media, and field emitters (Nang,2007). GLAD on flat substrates involves a stochastic nucleation process, yielding films consisting of randomly distributed nanorods. In contrast, periodic arrays are achieved by substrate patterning prior to deposition (Li,2007). In the latter case, the patterned surface mounds are the nucleation sites for the nanostructures, since film growth on the surrounding substrate is suppressed by atomic shadowing, that is, the atoms of the directional deposition flux are captured by the mounds and do not reach the substrate using physical vapor deposition (PVD) (Kosiorek, 2004). It is well known that films deposited by physical vapor deposition (PVD) commonly possess a columnar microstructure which affects many film properties. Glancing angle deposition (GLAD), which capitalizes upon this fact, has been developed as a technique to engineer the columnar structure of Molybdenum thin films on the nanoscale. Recently there has been an increasing focus on methods to produce surfaces with a varying topography on the nanometer length scale for applications in e.g. biotechnology, photonics, and catalysis, since the nanoscale surface topography is known to influence the performance in these areas (Kuo, 2003). When glancing angle deposition is combined with a continuous substrate rotation, the growth of nanostructures with various shapes such as vertical posts, spirals and screws is possible. The shape is controllable with the ratio $\rho = r/\omega$ of the deposition rate r to the rotational speed ω. Besides the control of ρ, other deposition parameters such as the deposition angle β between particle flux and substrate normal, or the substrate temperature can be used to alter morphology and density of the grown sculptured thin films (Kuo, 2003). Controlling the wet ability of surfaces is an important problem relevant to many areas of technology; In general, the wet ability of a solid surface is governed by both the chemical state and the geometry of the morphology (Boduroglu, 2007). However, to fully utilize the hydrophobic properties of nanostructure surfaces, it is necessary to study the fundamental relationship between the nanostructure and the hydrophobic behavior. Once the relationship is established, new materials with desired hydrophobicity can be designed and fabricated. Sputtering is a simple and useful technique for preparing thin films with a desired structure and properties (Wisam, 2009).

In this study, a novel glancing angle deposition (GLAD) technique was used to deposit MO thin film and MO nanostructures on silicon wafer. The GLAD technique provides a novel capability for growing 3D nanostructure arrays with interesting material properties. It is a simple, single-step process In addition, GLAD offers a cost and time efficient method to fabricate nanostructured arrays of almost any material in the periodic table as well as alloys and oxides. The GLAD technique uses the ‘shadowing effect,’ which is a ‘physical self-assembly’ process through which obliquely incident atoms/molecules can only deposit to the tops of higher surface points, such as to the tips of a nanostructured array or to the hill tops of a rough or patterned substrate. Also this work was studied the contact angle of the composite structure of MO nanorods with Teflon at the tips dramatically increases from hydrophilic values of uncoated nanorods to the highly hydrophobic values after coating with Teflon tips.

2- Experimental Work:

The vertically aligned Si nanorod array samples were prepared by glancing angle deposition method. Experiments were done in Nanotechnology centre/ Institute of Applied Engineering and science in University of Arkansas at Little Rock (UALR) in USA. The substrate was Si(100) wafer cleaned by a RCA-1 method (solution of deionized water /hydrogen peroxide/ammonium hydroxide with 5:1:1ratio was heated to 70 ^{o}C) for 10 min. followed by copious deionized water rinsing. A schematic of the custom-made GLAD experimental setup in the present study is shown in figure (1).

In our experiments, normal deposition technique was used to formulate Mo thin film onto a silicon substrate. A DC magnetron sputtering system was employed for the fabrication of Mo nanorods on Si is performed using GLAD technique. In all experiments, The depositions were performed on native oxide p-Si (100) wafer pieces (substrate size 3×3 cm2), using a 99.99% pure Pt cathode (diameter about 7.6 cm). The substrates were mounted on a sample holder located at a distance of about 18 cm from the cathode.. They were tilted so that the angle between the surface normal of the target and the surface normal of the substrate was about (θdep = 87◦).For the normal incidence (θdep = 0◦),The substrates were rotated around the surface normal with a speed of 2 RPM. The base pressure of about 1.5 × 10−6 Torr was achieved using a turbo-molecular pump backed by a mechanical pump. In all deposition experiments, the power was 200 W with an ultrapure Ar working gas pressure of 3.5 × 10−3 Torr. The substrate temperature during growth was below (85°C). The deposition time was 45 min. For the normal incidence 10 min. was used, For The deposition rate of the glancing angle depositions of Mo nanorods was measured utilizing quartz crystal microbalance (Inficon- Q-pod QCM monitor, crystal: 6 MHz gold coated standard quartz) measurements and SEM image analysis to be about 10 nm min−1. First, the deposition rate of Mo nanorods was monitored on the QCM. Since the distance between the target and the QCM is smaller than that of the substrate, the deposition rate of Mo nanorods on the substrate was determined by dividing the measured film thickness from cross-sectional SEM images by the deposition time. Then, a correction distance factor was calculated dividing the deposition rate on the substrate to that on the QCM. GLAD allows coating Teflon only on the tips of the Mo nanorods, resulting in a bi-layer nanorod structure (metal base and Teflon tip), while normal incidence results in a continuous Teflon thin film coating. A custom-made Teflon (Applied Plastics Technology) disk was used as the sputtering target. The target was 0.3175 cm thick and 5.08 cm in diameter. The substrates (arrays of Pt nanorods on a silicon wafer piece) were rotated around the surface normal with a speed of 2 RPM. The deposition was performed under a base pressure of about 2 × 10−6 Torr. During Teflon deposition experiments, the power was 150 W with an ultrapure Ar working gas pressure of 3.2 × 10^{-3} Torr.

In a similar fashion to the Mo nanorods, the deposition rates of the normal incidence and glancing angle depositions of Teflon nanopatches were measured using SEM image analysis and QCM measurements to be about 13 and 4 nm.min−1, respectively. The surface morphology of the nanocomposite (Mo/Teflon) and (Ag/Teflon) structures were analyzed using an SEM. The hydrophobic behavior was investigated by contact angle measurements using a VCA optima surface analysis system (AST Products, Inc., MA). Finally, the surface energy measurements were also performed using the two-liquid method to confirm the contact angle measurements.

3- Results and Discussion:

Figure (2a,b) shows a top and cross sectional views of molybodium thin films on silicon flat substrate using a phsical vapor deposition process. As can be seen, atomic shadowing of molyebodium islands and clusters of Mo on the Si substrate which leads to the growth of highly porous moeybodium thin film on silicon flat surface.

A scanning electron microsope (SEM) unit was used to study the morphology of Mo thin film and (Mo/Teflon) nanrod on silicon wafers. Figure (3a,b,c) is a typical SEM images of pure Mo nanorods and unique structure with Mo nanopillars growth. This morphology as a result of the stochastic nucleation process of moleybodeum on wafers. Glad technique result in growing the Mo with 100 nm in height as shown in figure (2) which the Mo deposition flux iminge on the substrate from glancing angle ($\alpha=87^o$) with a substrate rotation at (2rpm). The development of Mo nanorods which are separated on narrow pores is due to the growing clusters shadow unoccupied sites as well as smaller smaller clusters from the incident vpor flux, whle the limited a datom surface mobility suppresses the filling of voids by diffusion.

Figure (4) shows the SEM images of Teflon thin film deposited on Si and the composite structure Mo nanorods with Teflon tips which are deposited using the RF sputtering technique at normal incident times of 5 min. The normal incidence deposition of Teflon on Mo nanorods results in a contineouse Teflon capping thin film layer lying mainly at the tips of Mo nanorods.

Figure (5) presented contact angle measurement of conventional flat Teflon thin film deposited on Si wafer, Mo thin film deposited on Si substrate and Mo nanorods with normal incidented deposited Teflon film. The contact angle larger than 90^o denotes a hydrophic surface. Mo and Teflon exhibit different behavior when their surfaces get in contact with wter droplet. It is shown that from the figure (5) the contact angle of Mo thin film deposited on Si substrate was about 40^o givimg a hydrophilic behavior of the surface while the contact angle for the normal depositon flat Teflon thin film was about (109.3^o) indicating a hydrophobic surface. As it can be seen from figure (4) the contact angle measurement of composit (Mo/Teflon) was about 116.7^o reported a significant increase in the hydrophobicity of hydrophilic Mo nanostructures, this may be due to the presence of low energy teflon nanopatches with large surface energy teflon.

4- Conclusions:

Nanostructured Mo films were prepared by glancing angle deposition (GLAD) method which exhibit highly oriented nanostructure composite of (100 nm) pillars columns. Samples were characterized using scanning electron microscope (SEM) and our resultsshow a conventional Mo thin films exhibited a continuous surface and vertical Mo nanopillars on Si Wafer. It was have demonstrated that the hydrophilic property of Mo nanorod surface was shifted to hydrophobic by deposition of small amount of Teflon at the tips of Mo nanostructures. The contact angle measurement show high value as 116^o which give an indication of increasing in the hydrophobicity of originally hydrophilic Mo nanorods with contact angle (140^o).

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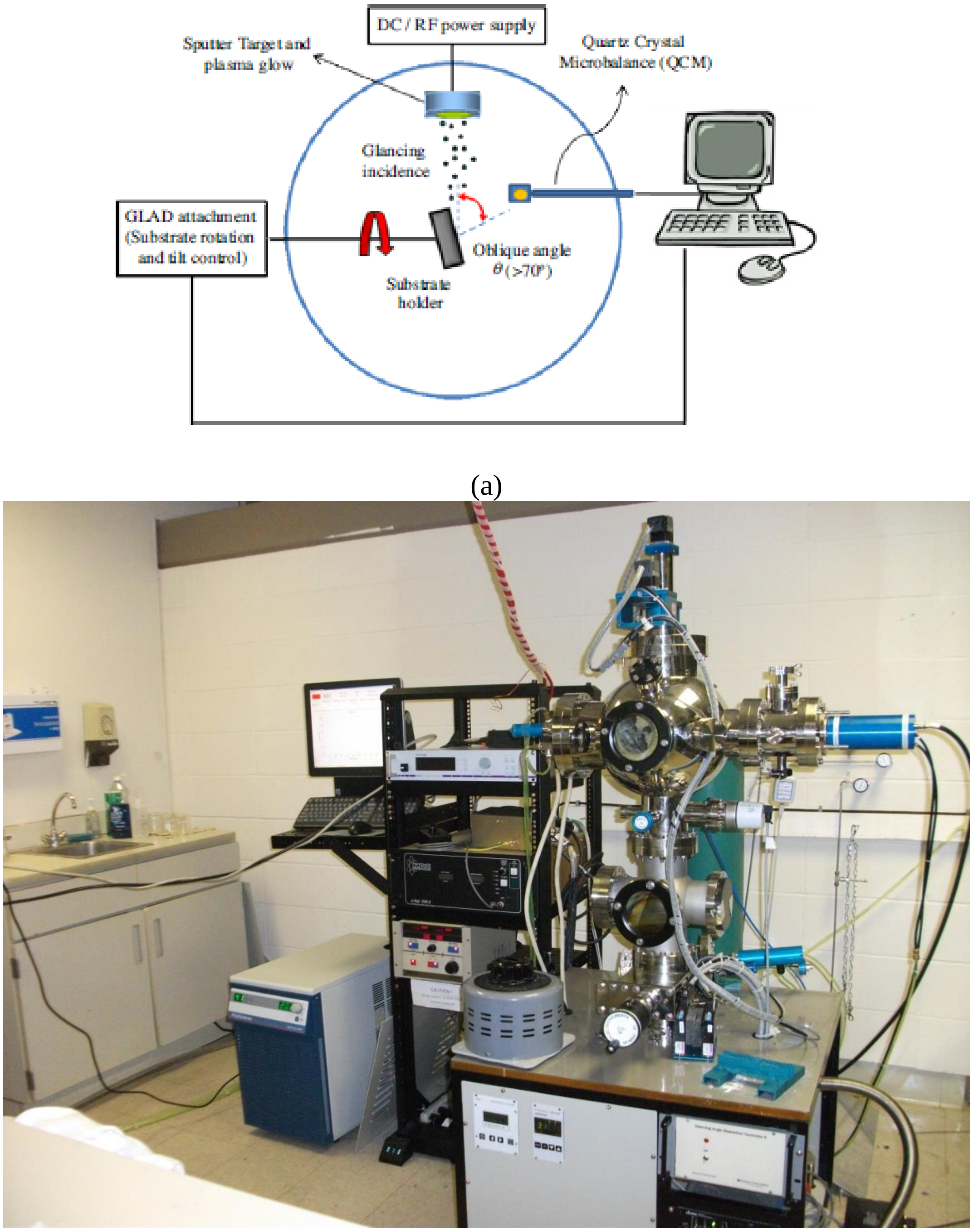


(a)

(b)

Figure (1)a- Schematic of GLAD Technique, b- Glancing Angle Deposition Device in the Lab.

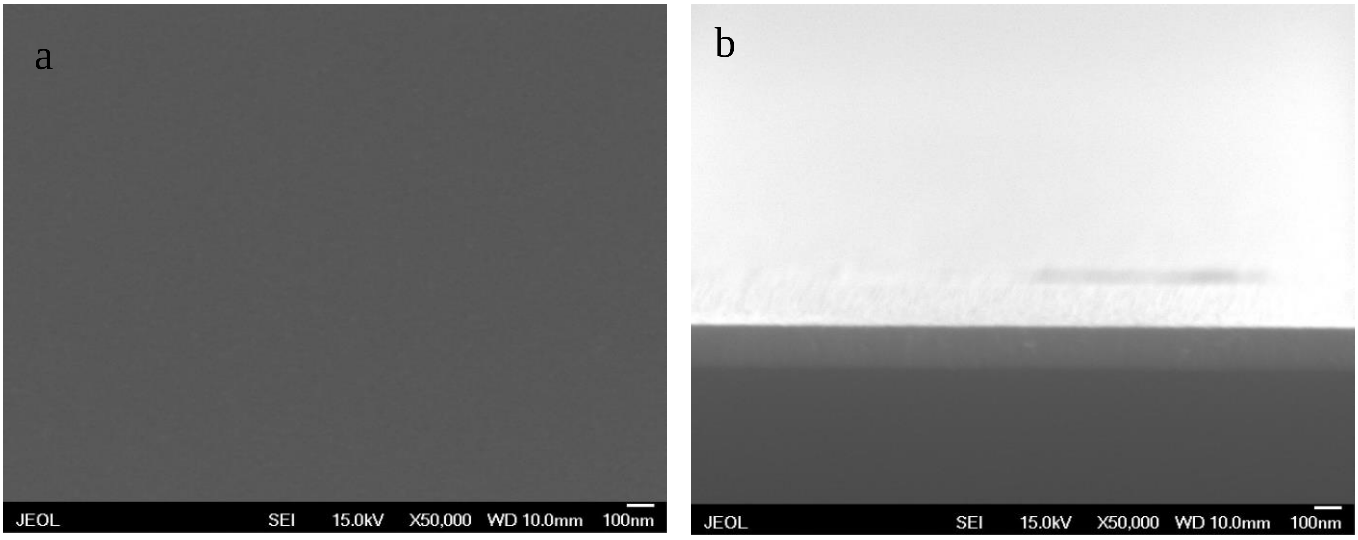


Figure (2)SEM Images of Mo Thin Films on Si Substrate.

- **Base pressure: 2 x 10e-06 mbar**
- **Operating pressure: 3.2 x 10e-03 mbar**
- **Power: 200 W**
- **Deposition time: 10 min**
- **GAS: Ar: 12.8 ccm**
- **Tilt: 0 degree**
- **Rotation: 2 rpm**

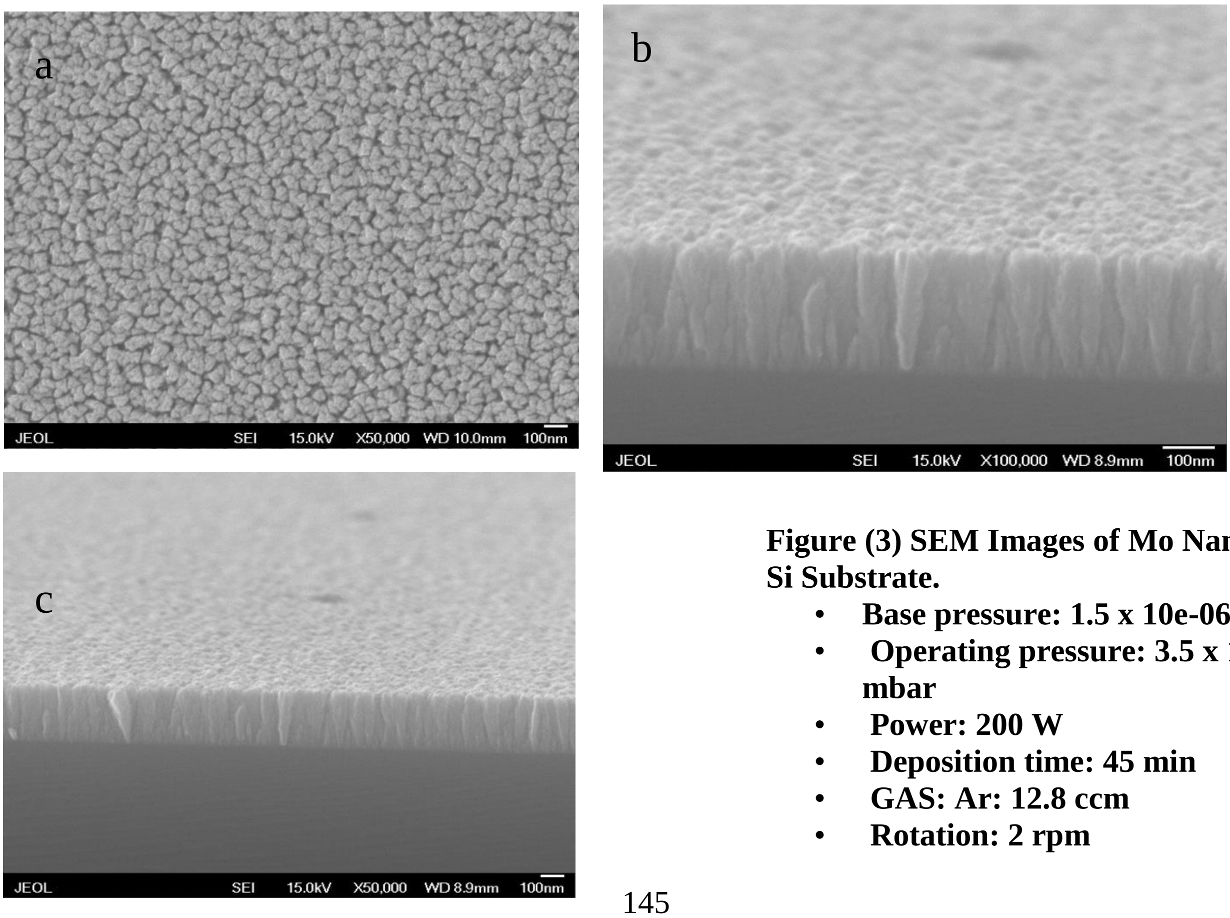


Figure (3) SEM Images of Mo Nanorods on Si Substrate.

- **Base pressure: 1.5 x 10e-06 mbar**
- **Operating pressure: 3.5 x 10e-03 mbar**
- **Power: 200 W**
- **Deposition time: 45 min**
- **GAS: Ar: 12.8 ccm**
- **Rotation: 2 rpm**

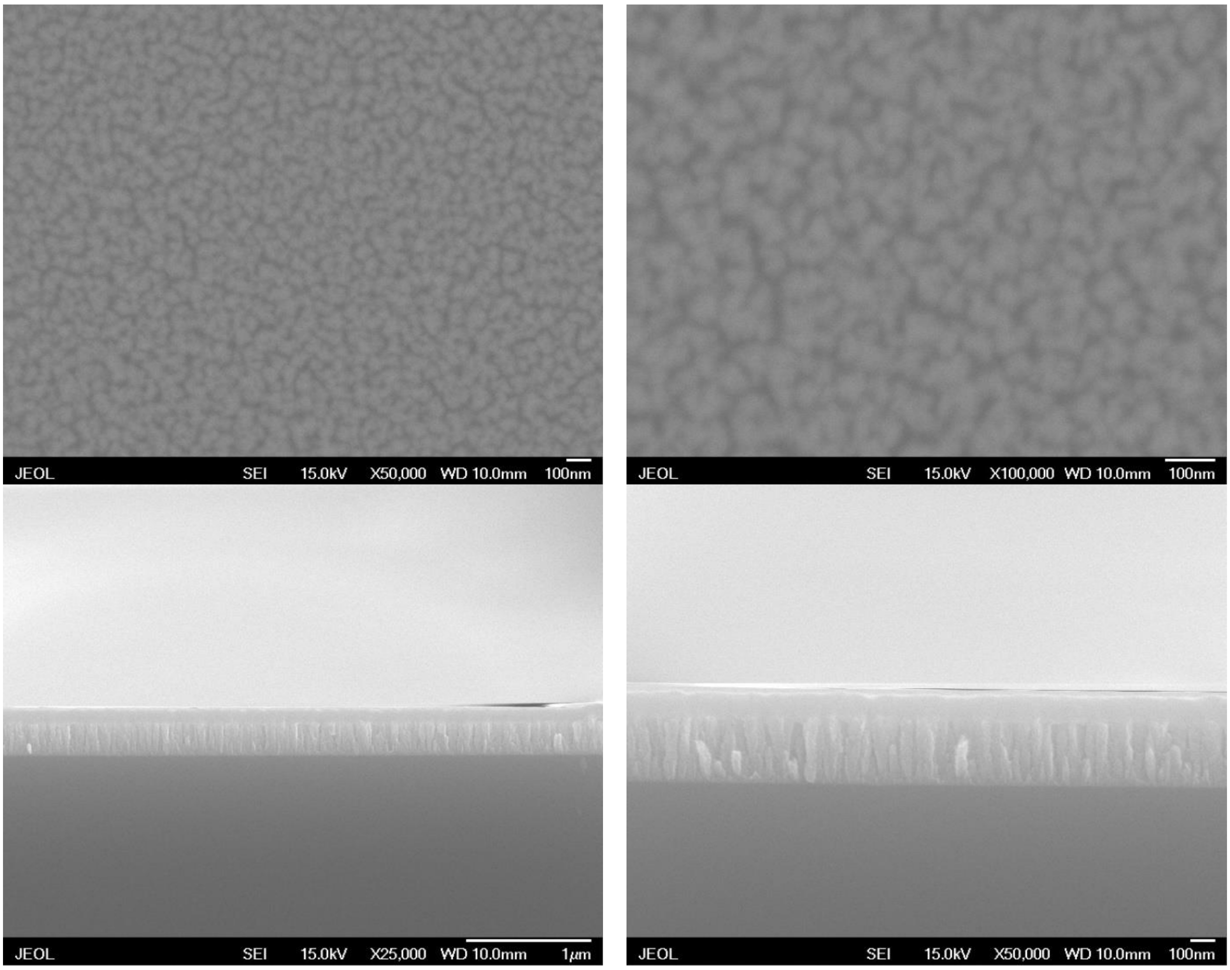
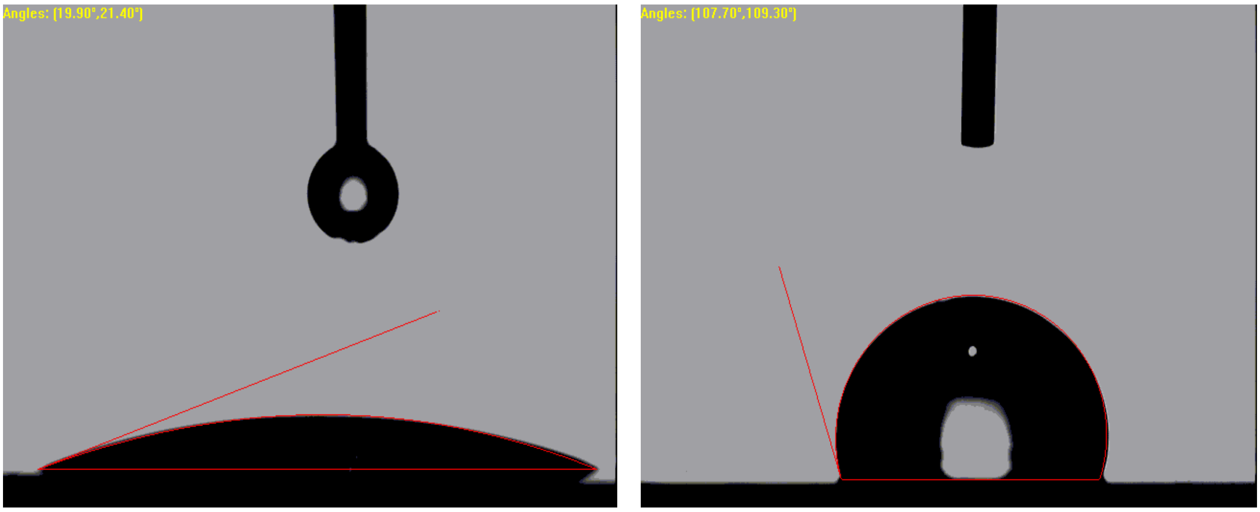


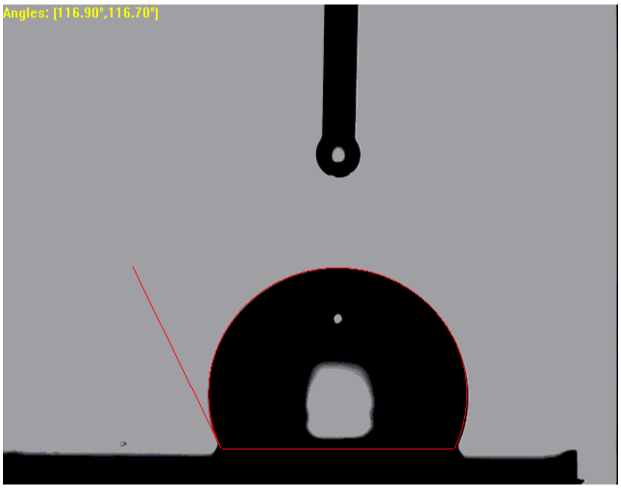
Figure (4) SEM Images of Teflon Thin Film on Mo Nanorods on Si Substrate.

- **Normal deposition of Teflon**
- **RF power supply**
- **Base pressure: 2 x 10e-06 mbar**
- **Operating pressure: 3.2 x 10e-03 mbar**
- **Power: 150 W**
- **Deposition time: 5 min**
- **GAS: Ar: 12.8 ccm**
- **Rotation: 2 rpm**
- **Tilt: 0 degree**



Mo Thin Film on Si Substrate.

Teflon Thin Film deposited on Si Substrate.



Teflon Thin Film deposited on Mo nanorod/Si Substrate.

Figure (5) Contact Angle Measurement.