Stable Hydrophobic Surface of ZnO Thin Film by CBD Method

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ABSTRACT

This paper we report the formation of a stable hydrophobic surface of ZnO thin film by using chemical bath deposition method. Industrial Importance of hydrophobic surface and their applications. We can calculate the contact angle and surface energy by used drop – Shape Analysis technique. Contact angle measurement reveals that the ZnO thin film by CBD method is hydrophobic. Also study the wettability of the Zno thin film.

Keyword: - *Goniometer, Hydrophobic surface, Contact angle, Surface energy and wettability (ZnO thin film; CBD method; XRD)*

1. INTRODUCTION

Basically, Hydrophobic surfaces are described by contact angles greater than 90 degree. It is well known that the wettability of a solid surface is a function of two primary factors including surface roughness and surface chemistry. The chemical composition of the surface determines the surface energy, which has a great effect on its wettability. However, only changing the surface chemistry cannot determine the hydrophobic state, and these two factors must exist simultaneously. The surface topology also has a significant effect on the hydrophobic nature of the surface. Surface roughening by increasing the solid-liquid interface also increases the hydrophobic state.

Hydrophobic coatings have found many applications in industry including anti-fog coating, anti-freeze surfaces, oil and water separation, anti-bacterial surfaces, and medical applications. Improving corrosion resistance is one of the most important current problems of society causing large damages. In general, corrosion damage cannot be stopped completely, but there are many methods for decreasing it; e.g.,cathodic and anodic protection, using protective coating to reduce the corrosion rate. One of the important coating methods to reduce the corrosion rate of surfaces is to use super hydrophobic coatings.

The contact angle has received tremendous interest from both fundamental and applied points of view. It plays an important role in many industrial processes, such as oil recovery, lubrication, liquid coating, printing, and spray quenching. In recent years, there has been an increasing interest in the study of super hydrophobic surfaces, due to their potential applications in, for example, self-cleaning, nano fluidics, and electro wetting. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Small contact angles (90°) correspond to high wettability, while large contact angles (90°) correspond to low wettability. Here we used drop – Shape Analysis technique to measure contact angle and surface energy of ZnO thin film. Study hydrophobic surface most natural materials are hydrophobic. The contact angle is always greater than 90 degree for hydrophilic surface.

1.1 Hydrophobic Surface:

- Hydrophobicity comes also from the Greek word Hydro (water) and Phobicity (fear).
- Contact angle greater than 90^{o}.
- Examples: Waxes, Oils, Fats, etc.

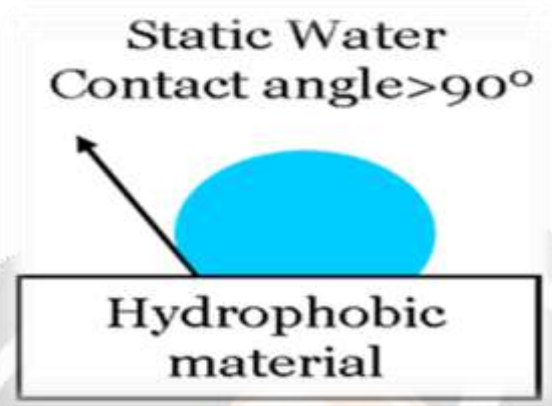

FIG: 1.1 (a) Hydrophobic surface

1.2 Superhydrophobic Surface:

- Contact angle greater than 150°.
- Example- Lotus leaf.

FIG: 1.2 (b) Superhydrophobic surface

1.3 Contact angle and Surface energy

Angle of Contact:-

The angle between the tangent planes at the solid surface and the liquid surface at the point of contact is called contact angle.

Surface Free Energy:

The energy associated with the intermolecular forces at the interface between two media is called surface free energy.

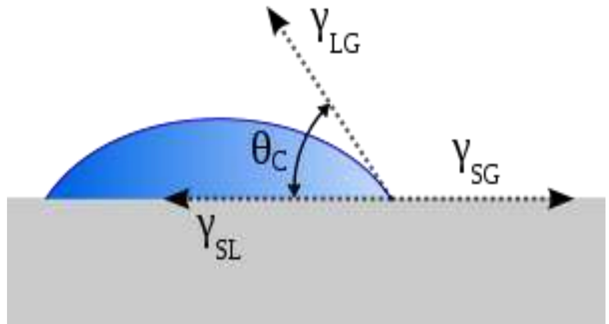

FIG: 1.3 (c) Contact Angle

Surface Tension:-

The force per unit length acting at right angle to an imaginary line drawn in the free surface of liquid is called as surface tension.

1.4 Wettability:-

- Ability of a liquid to wet a given solid.
- Results from intermolecular interactions.
- Higher the surface energy lower will be contact angle.
- High surface energy overcomes surface tension and liquid droplet spreads over surface.

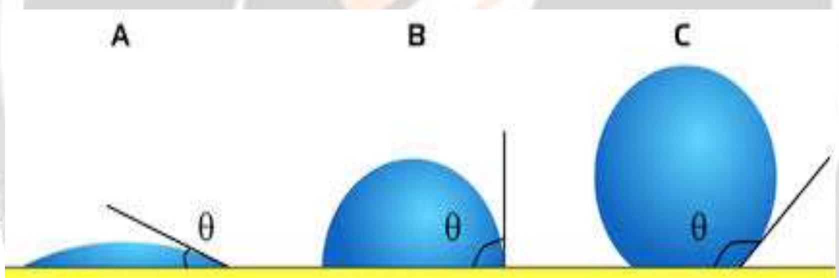

FIG: 1.4 (d) Wettability

1.5 Cohesive and Adhesive forces:-

- **Cohesive forces** - Intermolecular forces of attraction between molecules of same substance.
- **Adhesive forces –** Intermolecular forces of attraction between molecules of different substance.

Contact angle	Degree of wetting	Strength of:	
		Solid/liquid interactions	Liquid/liquid interactions
θ = 0	Perfect wetting	strong	weak
0 < θ < 90°	high wettability	strong	strong
		weak	weak
90° ≤ θ < 180°	low wettability	weak	strong
θ = 180°	perfectly non-wetting	weak	strong

TABLE : 1.4 Wettability

2. General Introduction of Hydrophobic Surface

Hydrophobic (Water hating) surfaces have little tendency to adsorb water and water tends to "bead" on their surfaces. Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water. The hydrophobic effect represents the tendency of water to exclude non-polar molecules. The effect originates from the disruption of highly dynamic hydrogen bonds between molecules of liquid water. If the droplet forms a sphere that barely touches the surface, the contact angle is more than 90 degrees, and the surface is hydrophobic, or water fearing. Many polymers exhibit hydrophobic surfaces. Highly hydrophobic surfaces made of low surface energy (e.g. fluorinated) materials may have water contact angles as high as ~120°. Some materials with highly rough surfaces may have a water contact angle even greater than 150°, due to the presence of air pockets under the liquid drop. These are called super hydrophobic surfaces.

Hydrophobic behaviour is generally observed by surfaces with critical surface tensions less than 35 dynes/cm. At first, the decrease in critical surface tension is associated with oleophilic behaviour, i.e., the wetting of the surfaces by hydrocarbon oils. As the critical surface tensions decrease below 20 dynes/cm, the surfaces resist wetting by hydrocarbon oils and are considered oleo phobic as well as hydrophobic. Active recent research on super hydrophobic materials might eventually lead to industrial applications. This requires micro-scale surfaces with typically Nano scale features on top of them. For example, a simple routine of coating cotton fabric with silica or titania particles by sol-gel technique has been reported, which protects the fabric from UV light and makes it super hydrophobic.

Similarly, silica nanoparticles can be deposited on top of already hydrophobic carbon fabric. The carbon fabric by itself is identified as inherently hydrophobic, but not distinguished as super hydrophobic since its contact angle isn't higher than 150°. With the adhesion of silica nanoparticles, contact angles as high as 162° are achieved. Using silica Nano-particles is also of interest to develop transparent hydrophobic materials for car windshields and self-cleaning windows. By coating an already transparent surface with Nano-silica with about 1% wt., droplet contact angles can raised up to 168° with a 12° sliding angle.

3. Industrial Importance of Hydrophobic Surface

In addition, an efficient routine has been reported for making polyethylene super hydrophobic and thus self-cleaning 99% of dirt deposited on such a surface is easily washed away. Patterned super hydrophobic surfaces also have the promises for the lab-on-a-chip, microfluidic devices and can drastically improve the surface based bio analysis. An example of super hydrophobic effect in live application is the team Alinghi in America's Cup using specially treated sailing jackets. The treatment is built up by micrometer size particles in combination with traditional fluorine chemistry. A recent application of hydrophobic structures and materials is in the development of micro fuel cell chips.

Reactions within the fuel cell produce waste**.** Gas CO_2 which can be vented out through these hydrophobic membranes. The membrane consists of many micro cavities which allow the gas to escape, while its hydrophobicity characteristic prevents the liquid fuel from leaking through. More fuel flows in to replace the volume previously kept by the waste gas, and the reaction is allowed to continue.

4. Applications of Hydrophobic Surface:

Some of the applications and industries that benefit from a better understanding of contact angle, surface energy, and surface tension of hydrophobic surface.

4.1. Plating and Printing and Inks:

Successful plating requires clean surfaces. Contact angle predicts adhesion and is used for quality assurance testing on surfaces that are be plated. New ASTM Standards (e.g., D7490 and D7334) use contact angle to determine wettability. Wetting is important to adhesion and the prevention of surface problems such as cratering, dewetting, and crawling. While wetting is important to adhesion, excessive wetting can cause inks to bleed and fail to perform properly. In the manufacture of inks, the contact angle formed by a drop of ink on paper determines the printing quality. It has been practically observed that it must be ideally between 90 degrees and 110 degrees. If it’s less than 90 degrees, the ink will spread on paper. If it’s more than 110 degrees, breaks will occur while printing.

4.2. Hard Disk Drives:

The processes involved in manufacturing a magnetic hard disk and the magnetic head slider are sensitive to surface cleanliness as well as surface wettability as it applies to loading the surface with a lubricant. Contact angle and surface energy play a critical role in helping engineers design and inspect hard drive products that overcome stiction, reduce flying height, and increase product reliability.

4.3. Metallurgy

Knowledge of contact angle behaviour of liquid metals on metal and oxide surfaces is essential in understanding the process of soldering, brazing, tinning and heat transfer. Contact angle is used to characterize surface roughness, oxidation, and wetting behaviour for all types of metals and metal finishing.

4.4. Insecticides

The efficiency of insecticide sprays also depends on their wetting behaviour on the surface of insects. Usually with most insecticides, an organic liquid having a low surface tension is used as a spray so that it spreads completely. Contact angle is therefore an essential parameter to be considered in any pesticide or insecticide spray formulation.

4.5. Oil and Petroleum

An important technological application that emerged out of contact angle studies is in the enhanced oil recovery from sand beds. Laboratory experiments on displacing petroleum by water in glass capillaries have demonstrated that a considerable fraction of the oil remains attached to the wall when the central space of the capillary is already filled with water. In a sand column, the amount of oil remaining in the sand when water appeared at the downstream end of the column is directionally proportional to the contact angle. Flooding the oil wells with surfactants along with water or steam reduces the pressure drop across each oil water meniscus, reduces the oil-water interfacial tension and changes the contact angle so that water displaces oil at the liquid-solid interface. The process is called 'tertiary oil recovery' and it is now possible by this method to recover more than 90% of oil from an oil well.

5. Experimental and Instrument

Contact angle goniometer ramé-hart Model 500-F1 is Advanced Goniometer with DROP image Advanced. It is goniometer with 21" rail system, fire wire camera, advanced 3-axis stage with fine and coarse vertical adjustment, micro syringe fixture assembly, needle, storage cover, fiber optics illuminator. Support automated dispensing system.

5.1 Materials/Instrument Requirements:

- Sample surface should be at least 0.5 x 0.5 cm in size.
- Liquids used with the plastic pipette tips need to be compatible with the plastic.
- If you don't know whether your material will work, contact NBTC staff before you use the solvent.
- The plastic 20µL micropipette tips can be used for contact angle measurements, not hanging drop measurements. The blunt metal syringe tips can be used for either contact angle or hanging drop measurements.

Fig. 5.1"Ramé-hart," – 500 Advanced Goniometer Set Up

6. Synthesis of ZnO Thin Film:

The ZnO thin films were prepared by chemical bath technique at room temperature. The reaction bath is composed of $ZnCl_2$, NaOH and TEA (tri ethanolamine) used as complexing agent. For deposition of the film, commercial quality glass microscope slides of dimension 16 mm 26 mm 1 mm are used. Prior to use, these glass slides were soaked in aqua regia, a mixture of concentrated HCl and HNO_3 in the ratio of 3:1. They were removed after 24 h and washed thoroughly in cold detergent solution, rinsed in distilled water and drip dried in air. The properly degreased and cleaned substrate surface has the advantage of producing highly adhesive and uniform film.

The substrate was immersed vertically at the centre of reaction bath in such a way it should not touch the walls of the beaker. Only one concentration of $ZnCl_2$ (0.04 M) and of NaOH (0.08 M) were used in this method. Tri ethanolamine was used either directly or as aqueous solution with varying concentration of TEA to prepare various samples.

At the end of the dip period, the films are washed and drip-dried in air. Post deposition annealing of the films expelled the water molecules resulting in the ZnO. The annealing temperature used in this study was 563 K.

6.2 Reaction Mechanism:

Reaction mechanics is as follow

$$ZnCl_2 + TEA \leftrightarrow Zn\,(TEA)^{2+} + 2Cl^-$$

$$Zn\,(TEA)^{2+} \leftrightarrow Zn2^+ + TEA$$

$$NaOH + OH^- \leftrightarrow Na^+ + 2OH^-$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$$

$$Zn\,(OH)_2 \leftrightarrow ZnO + H_2O$$

7. Contact Angle Measurement of ZnO Thin Film

Fig. below (7.(a)) shows the images captured during the measurement of contact angle as a function of time. These interior sites cannot sustain for the water wetting due to the annihilation process and surface shows the hydrophobic behavior. The results obtained from the measurement shows that the synthesized material characterized for the contact angle measurement shows the very low absorption as measuring the function of the time. Time treatment gives the very less decrease value in the measurement of the contact angle. These results indicate the stability of the result over the long period of the time. The stability of the result over the long period proves the highly potential of the ZnO thin film for the self-cleaning application of the material.

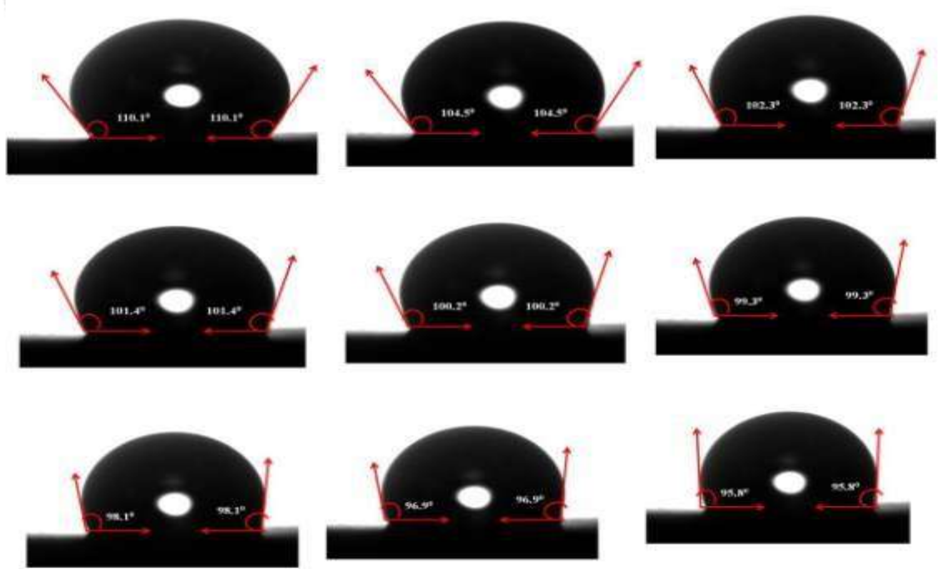

FIG. 7. (a) Contact Angle Measurement of ZnO thin film

As time passes this oxidation process starts to increases hence the value of the contact angle being decreased. This happens due to the increased surface energy with time due to the oxidation process. This work has provided evidence for air capitations between hydrophobic surfaces in inorganic material (ZnO). It was also shown that the range and magnitude of interaction forces could, to some extent, be predicted by looking at certain surface features like structure, roughness and the overall length scales. Force assumed by using super hydrophobic surfaces showed extremely long-range interaction distances of time treatment stability.

Sr. No.	Time (min)	Contact Angle (degree)	Surface Free Energy (mJ/m^2)
1	1	110.0	25.98
2	5	105.0	21.96
3	10	102.5	20.88
4	15	102.0	20.00
5	20	101.2	19.80
6	25	99.0	18.96
7	30	98.6	18.00
8	35	96.8	17.40
9	40	96.0	16.50

TABLE: 7. (b) Calculated values of CA and SE of ZnO thin film by using Contact Angle Meter.

Table;7.(b) shows that the decreasing trend of CA proves the materials ability to hold the water drop on the surface of the material. The graph plotted by using this data (Fig. 8. (c)) shows that the relation between the CA and SE. As time passes CA going to decreases and correspondingly SE of the material enhances. It means that materials become more wetable, which has the absorption coefficient high.

From this data it is easily remarkable that the lower angle material exhibit the good wettability property and found to application in the charge storage mechanism where it high absorption coefficient is required.

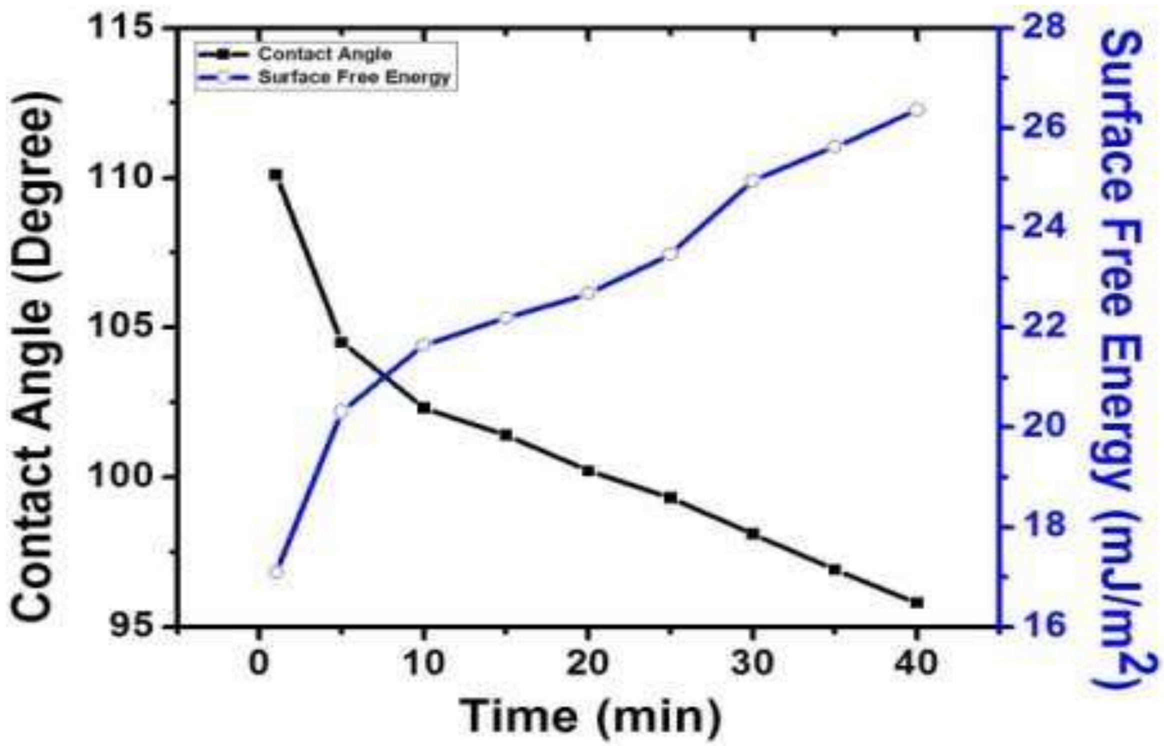

FIG. 7. (c) Contact Angle and Surface Energy relation with time

8. CONCLUSIONS

Through paper we report the formation of a stable hydrophobic surface of ZnO thin film by using chemical bath deposition method and we have discussed about surface and surface phenomenon such as surface energy, surface tension, angle of contact, wettability. General introduction of instrument and practical importance for industrial applications is mentioned. Measurement of contact angle, surface energy and work of adhesion. Also the measurement is done for hydrophobic thin films in addition to its time dependent wetting behavior.

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