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Characterization of the static contact angle of zinc oxide nanowires synthesized by hydrothermal method

Caracterización del ángulo de contacto estático de nanocables de óxido de zinc sintetizados por método hidrotermal

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Abstract

The ability of a liquid to maintain contact with a solid is known as wetting, this is determined by the existence of a balance between the cohesive and adhesive forces. To study this property in materials it is required that the three phases of matter exist: liquid, solid and gas. The present work focuses its study on the characterization of the static contact angle that relates the cohesive and adhesive forces in the liquid-gas-solid system. Hexagonal zinc oxide nanowires were synthesized by the hydrothermal method on conductive glass substrates to which a zinc oxide seed was previously deposited by spin-coating and dip-coating. The results obtained show the change in the contact angles according to the growth of the nanostructures on the surface.

Static contact angle, Nanowires, Hydrothermal

Resumen

La capacidad de un líquido para mantener contacto con un sólido se conoce como humectación, está determinado por un equilibrio entre las fuerzas cohesivas y adhesivas. Para estudiar esta propiedad en los materiales se requiere que existan las tres fases de la materia: líquido, sólido y gas. El presente trabajo centra su estudio en la caracterización del ángulo de contacto estático, que relaciona las fuerzas cohesivas y adhesivas en el sistema líquido-gas-sólido. Se sintetizaron por el método hidrotermal nanocables hexagonales de óxido de zinc sobre sustratos de vidrio conductor a los que se les depositó previamente una semilla de óxido de zinc por spin-coating y dip-coating. Los resultados obtenidos muestran el cambio en los ángulos de contacto según el crecimiento de las nanoestructuras sobre la superficie.

Ángulo de contacto estático, Nanocables, Hidrotermal

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Introduction

Within nanotechnology, the shape, size and functionalisation of materials are topics of interest, as they have a significant impact on the properties of materials [1].

Zinc oxide is one of the materials with great potential for its applications in the development of permeable materials, transistors, sensors and UV laser diodes, thanks to its conductive, hydrophobic and hydrophilic properties [2].

Contact angle

The contact angle is used to quantify the wettability of solid surfaces. In an interacting system of a vapour, a solid and a liquid at a given pressure and temperature the angle should be in equilibrium reflecting the relative strength of the vapour, liquid and solid interactions [2].

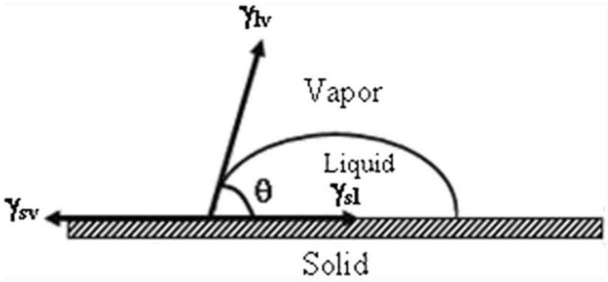


Figure 1 Schematic of contact angle and surface stresses

γLv	Vapour-liquid surface tension
γSv	Solid vapour surface tension
γSl	Solid-liquid surface tension

Table 1 shows the schematic of the relationship between surface stresses and contact angle (θ)

In the 20th century, Gibbs demonstrated the volumetric dependence of the contact angle by modifying the study carried out by Thomas Young in 1805, where he demonstrated the relationship between the contact angle and the surface tensions exerted on sessile droplets [3].
The relationship of surface tensions on flat surfaces proposes that there is a linear tension that limits the solid-liquid-gas phases and is explained by the following equation:

$$\cos(\theta) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} + \frac{k}{\gamma_{lv}}\frac{1}{a}$$

The above equation relates the linear stress (k) and the droplet radius (a) to the cosine contact angle taking into account the phase interface [3].

When the liquid droplet remains motionless on the solid surface the contact angle measured is the static (or sessile) angle, this is not the only stable type as there is a range of contact angles given by factors such as topography, chemical homogeneity and above all roughness [4].

The main contact angles are forward (measures liquid-solid cohesion) and backward (measures liquid-solid adhesion) since the difference between them generates the static angle which is defined by the angle hysteresis [4].

Contact angle hysteresis

Static contact angle measurements produce values depending on other parameters such as the way in which the liquid is deposited (velocity, angle, quantity) so hysteresis is used which encompasses the relationship between the dynamic angles (advance and retreat), it is analogous to the static friction term requiring a minimum amount of work to modify the contact line [5].

$$\theta = \theta_A - \theta_R$$

$\boldsymbol{\theta}$	Static angle
$\boldsymbol{\theta_A}$	Angle of advance
$\boldsymbol{\theta_R}$	Backward angle

Table 2

Relationship of roughness to the contact angle

Roughness plays a major role in the performance of the contact angle and wettability of the surfaces, since the more voids there are on the surface of the material, the more air pockets there are between it and the surface of the droplet. In relation to roughness, two phenomena are described: the first is the Wenzel effect, where the droplet homogeneously wets the grooves of the rough surface and the second known as Cassie-Baxter, where the droplet heterogeneously wets the surface of the material and stays above the grooves that encapsulate air [6] [7].

Methodology to be developed

By means of a chemical synthesis with zinc acetate and sodium chloride diluted in methanol, this mixture was kept under stirring for two hours at a temperature of approximately 60°C. Zinc oxide nanostructures were obtained and used as seeds on conductive glass substrates.

Seed deposition was carried out by spin-coating at a speed of 3,000 rpm for 40 seconds (3 samples) and by dip-coating by performing 20 dips at intervals of 5 seconds each (3 samples). Once the doped substrates were dried at room temperature, they were immersed in a solution of hexamethylenetetramine and zinc nitrate and baked for 2, 4 and 6 hours at a temperature of 90°C. At the end of this time, they were carefully washed with distilled water and left to dry at room temperature. Each sample was characterised for contact angle (seed and nanowires) and observed by scanning electron microscopy.

Results

The contact angles were measured by placing a drop of water on the surfaces. The first angle measured was that of the conductive glass without any modification, as can be seen in figure 2 without any modification the glass presents an angle of 63.064°.

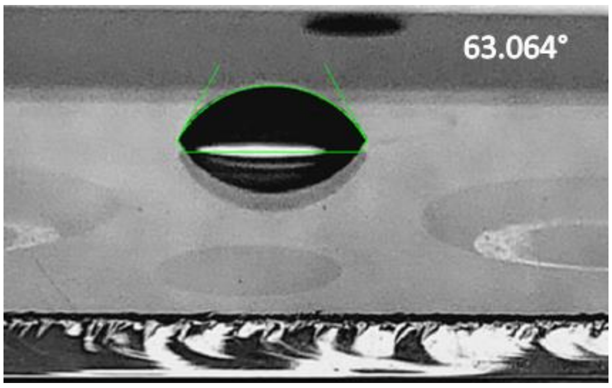


Figure 2 Contact angle of the conductive glass without modification

Since the parameters of the samples are the same before the synthesis of the nanowires, the contact angle was measured for Dip-coating and Spin-coating; as shown in figure 3, the seed deposition generates a change on the surface.

The contact angle decreased to 19.693° when the seed was deposited by the Dip-coating method, the same happened for the Spin-coating method, however, the decrease of the angle was not so drastic.

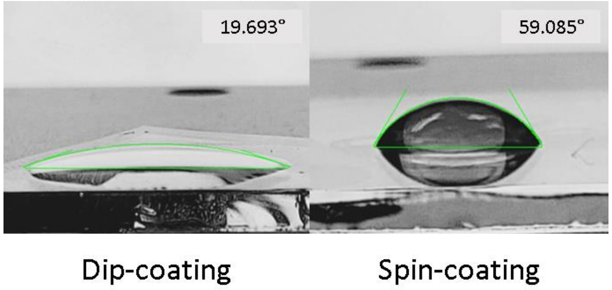


Figure 3 Contact angles of the seeds

EDS analysis was performed to validate the presence of zinc oxide on the surfaces, as shown in figure 4 by the characteristic peaks exist on the surface of the sample zinc and oxygen.

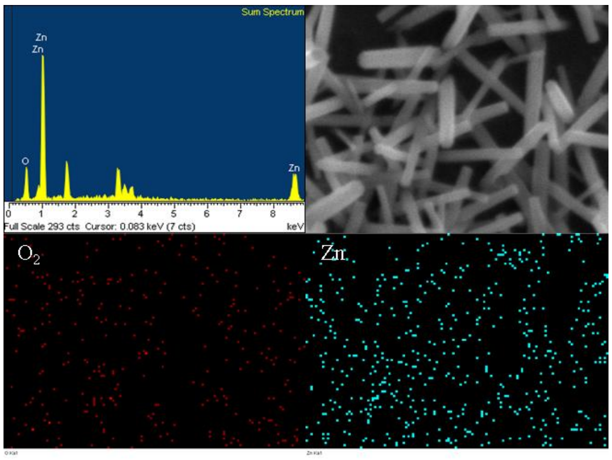
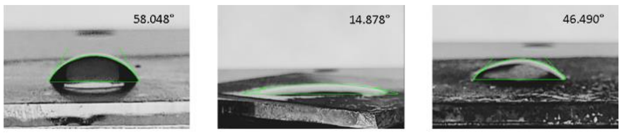


Figure 4 EDS of the surface of the zinc oxide nanowires

The characterisation of the contact angle of the dip-coated samples with the zinc oxide nanowires showed an unusual behaviour. As shown in figure 5, the first two hours increased the angle to 58.048°, but after two more hours the angle returned to a low angle, even smaller than with the seed. At the end of the experiment and after 6 hours of the hydrothermal method, the surface angle measured 46.490°, below the main angle (glass without modification) but exceeding the previous measurement.



Sample contact angle D2. Sample contact angle D4. Sample contact angle D6.

Figure 5 Contact angles of the dip-coated samples

To observe the possible causes of the effect presented in the samples, they were characterised by scanning electron microscopy. In figure 6a, belonging to the two-hour sample, the presence of small structures forming "bushes" can be observed, these are attributed to the increase in the contact angle due to the air that could have been trapped between them; in figure 6b, the structures are observed 4 hours after the hydrothermal method, it is possible to identify more clearly the hexagonal and long structures that come from the seed deposited on the surface. These structures are characteristic of the most stable structure of zinc oxide: wurtzite, the arrangement of the nanowires in this image exhibits gaps between them, therefore, water can penetrate between the structures thus decreasing the contact angle. The structures in figure 6c are long and thin, with an interlocking arrangement where air can be encapsulated.

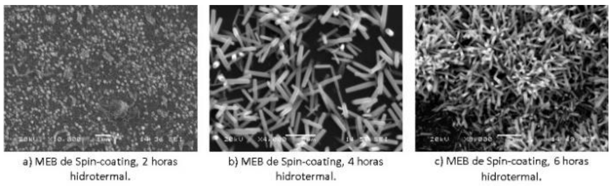
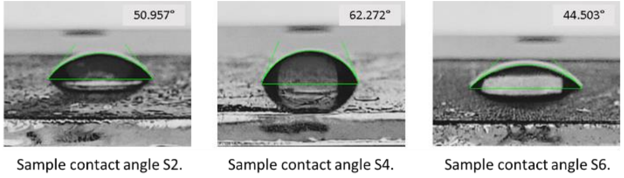

a) MEB de Spin-coating, 2 horas hidrotermal.
b) MEB de Spin-coating, 4 horas hidrotermal.
c) MEB de Spin-coating, 6 horas hidrotermal.

Figure 6 Scanning electron microscopy of the dip-coated samples

In the case of the spin-coating samples, the contact angle decreased a little, but remained in the same range after two hours of hydrothermal method, after 4 hours it increased reaching almost the main angle of the glass without modifications, however, after 6 hours the angle decreased again to 44.503°.



Sample contact angle S2.
Sample contact angle S4.
Sample contact angle S6.

Figure 7 Contact angles of the spin-coated samples

As with the dip-coated sample, the three substrates were characterised by scanning electron microscopy. Figure 8a shows small accumulations of material on the surface which could be the bases of the nanowires; in figure 8b, hexagonal structures are observed growing vertically and forming a type of "grass", the growth of the structures after 6 hours can be seen in figure 8c, a "bush" of vertical nanowires is formed.

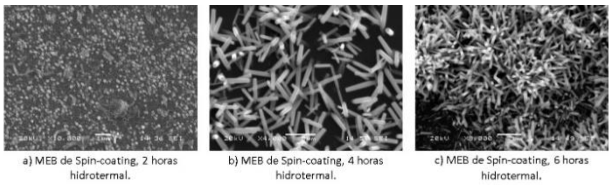

a) MEB de Spin-coating, 2 horas hidrotermal.
b) MEB de Spin-coating, 4 horas hidrotermal.
c) MEB de Spin-coating, 6 horas hidrotermal.

Figure 8 Scanning electron microscopy of the spin-coating samples

The decrease of the contact angle between the 4 and 6 hours samples could be due to the fact that, although these "bushes" are not sequential over the whole surface, they are located as if they were colonies, so the droplet could fall outside these structures decreasing the contact angle.

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Conclusions

The results obtained in the 6 samples show the growth of zinc oxide nanowires in relation to the time exposed to hydrothermal synthesis.

The samples with the seed deposited by dip-coating showed an accelerated growth since from the first two hours small linear structures were visible on the surface, which with the passage of time grew and intertwined.

The seed deposited by spin-coating maintained a progressive growth, after two hours the surface shows protrusions without any linear structure. After 4 hours of synthesis, hexagonal structures are observable, which adopt a bush-like shape after 6 hours.

The contact angles show varying values depending on the structures grown on the surface. Taking into account the description of hydrophobicity and hydrophilicity by the angles obtained on the surfaces not exceeding 90°, it is concluded that all the samples are hydrophilic.

Although the dynamic measurement of the droplets was not carried out, the static contact angle measurements show the behaviour between the growth of the zinc oxide nanowires and their contact angle.

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