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Wettability of transparent conductive nanostructured ITO and ITO/Al_2O_3 coatings

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Abstract. In this paper, the water wettability of nanostructured ITO films, including those with Al_2O_3 protective layers, was studied. Nanostructured ITO films were deposited by magnetron sputtering and electron beam evaporation on the preheated surface of a glass substrate, after which they were additionally annealed in a nitrogen atmosphere for 10 min. Some samples were covered with an aluminium oxide layer with various thicknesses. The Al_2O_3 protective coating was fabricated by atomic layer deposition. To estimate the wettability, we measured the contact angles of water drops on the horizontal surface of the films. The results show that, depending on the deposition method and thickness, structured ITO films can be characterized both by hydrophilic and by hydrophobic properties. In the case of covering of the nanostructured ITO film deposited by the electron beam evaporation with a protective coating of aluminium oxide, the hydrophobic properties of structured ITO films can be significantly improved and a superhydrophobic coating can be obtained.

Keywords: transparent conductive films, indium-tin oxide, wettability, atomic layer deposition, aluminium oxide

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Смачиваемость прозрачных проводящих наноструктурированных покрытий ITO и ITO/Al_2O_3

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Аннотация. В данной работе исследовалась смачиваемость водой наноструктурированных пленок ITO, в том числе с защитными слоями Al_2O_3. Пленки структурированного ITO наносились методами магнетронного распыления и электронно-лучевого испарения на предварительно нагретую поверхность стеклянной подложки, после чего дополнительно отжигались в атмосфере азота в течение 10 мин. Сверху часть образцов была покрыта слоем оксида алюминия различной толщины. Защитное покрытие Al_2O_3 наносилось методом атомно-слоевого осаждения. Для оценки смачиваемости измерялись краевые углы капель воды на горизонтальной поверхности пленок. Результаты показывают, что в зависимости от метода нанесения и толщины пленки структурированного ITO могут обладать как гидрофильными, так и гидрофобными свойствами. В случае нанесения на пленку структурированного ITO, нанесенного методом электронно-лучевого испарения, защитного покрытия из оксида алюминия можно значительно улучшить гидрофобные свойства структурированного ITO и получить супергидрофобное покрытие.

Ключевые слова: прозрачные проводящие пленки, оксид индия-олова, влагостойкость, атомно-слоевое осаждение, оксид алюминия

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Introduction

Nanostructured coatings based on indium-tin oxide (ITO) [1, 2] can be used to produce displays and optical contacts of LEDs, which makes it possible to reduce reflection and the effect of display backlighting and to increase the quantum yield of LEDs. However, the rough surface of these films leads to a greater susceptibility to the chemical action of the environment [3], especially under conditions of high humidity or in contact with water, so the fabrication of hydrophobic nanostructured coatings would solve the problem of chemical degradation of the surface.

Generally, studies of wettability of different surfaces are of great interest due to the possibility of wide use in various fields. The wettability may vary depending on the properties of the surface, such as surface structuring, surface energy, porosity. Currently, depending on the field of application, numerous studies are being carried out in the field of manufacturing both hydrophilic and hydrophobic surfaces [4]. In [5], the possibility of modifying the surface of copper pipes coated with a copper oxide layer was studied to improve the efficiency of moisture collection, which is especially important for solving the global problem of drinking water shortage, especially in arid regions. In the paper [6], the authors consider the fabrication of a nanoporous material from iron with a controlled transition of wettability from superhydrophilic to superhydrophobic for the separation of oil and water for the water purification. Superhydrophobic surfaces are important components in many fields of cleaning applications and protective coatings; such coatings can be produced, e.g., from nanostructured ZnO films [7]. As can be seen from [8], the formation of a rough nanostructure on the material surface makes it possible to significantly change the material wettability, including imparting hydrophobic properties, which can be used to improve the chemical resistance of the material.

Materials and Methods

ITO films were deposited using a specialized combined electron-beam and magnetron sputtering system manufactured by Torr Int., USA. The formation of nanostructured self-organized ITO films formed by nanowhiskers was carried out by two methods: electron-beam evaporation and magnetron sputtering, in both cases, on a substrate preheated to 500 °C. The deposition rate in both cases was about 10 nm/min. After deposition, without turning off the heating, the chamber was filled with high-purity nitrogen to almost atmospheric pressure (800 mbar), and the samples were annealed for 10 min. Under these deposition conditions, the coating layer is formed according to the vapor-liquid-crystal (VLC) mechanism. The nature of the self-organization and shape of nanocrystals depend on the deposition mode and duration. Film formation begins with a denser layer, the refractive index of which is close to the refractive index of dense ITO, then separate whisker nanocrystals are formed, the effective refractive index of which decreases as the distance from the substrate increases. A more detailed description of the method and characteristics of the films are presented in [3]. Samples of unstructured ITO were obtained by magnetron sputtering; their thickness was ~ 170 nm. To form a protective coating on structured ITO films, an Al_2O_3 layer was deposited by atomic layer deposition using a PICOSUN P300B setup. This method consists in successive alternate treatment of the substrate with vapors of materials, namely, trimethylaluminum (TMA) and water, which react on the substrate surface.

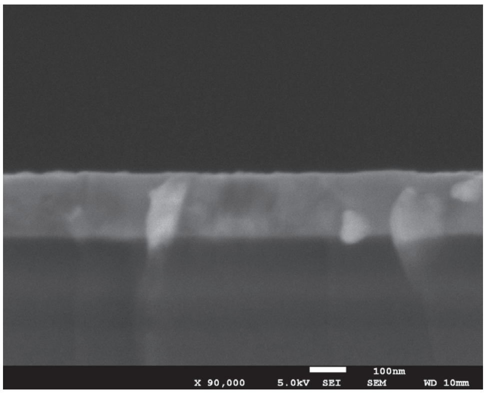
The thickness of the films obtained by electron beam evaporation was 50 nm in an equivalent of dense film, the thickness of the films grown by magnetron sputtering was 150 nm in an equivalent of dense film. The phrase “thickness x in an equivalent of dense film” should be understood that the mass of deposited material in the nanostructured film is the same as for a dense film with thickness x. This term was introduced because the calibration of a quartz sensor used to control the film thickness can only be carried out when a dense ITO film is deposited.

Drops were formed using a mechanical dispenser from Sartorius, the drop size was 3 μl. The drops were imaged using a Supereyes B011 digital optical microscope, the illumination was located on the side of the microscope. The substrate was placed horizontally, perpendicular to the camera direction, which resulted in the image of the drop from the side. SEM images of the films were obtained with a JEOL JSM-7001F scanning electron microscope.

Results and Discussion

The experimental results show that the unstructured ITO film (Film 1) (Fig. 1, *a*) are hydrophobic, the contact angle α = 100° (Fig. 1, *b*). The film was deposited by magnetron sputtering on a cold substrate. As a protective coating for the ITO layer, an aluminium oxide layer obtained by atomic layer deposition can be used. For planar Al_2O_3 film (Film 2) deposited on a glass substrate, the contact angle is α = 95° (Fig. 2). In the case of depositing a protective layer of Al_2O_3 on the planar surface of the dense ITO layer (Film 3) (Fig. 3, *a*), the results show no significant changes in the properties, the contact angle α = 100° (Fig. 3, *b*).

a)



b)

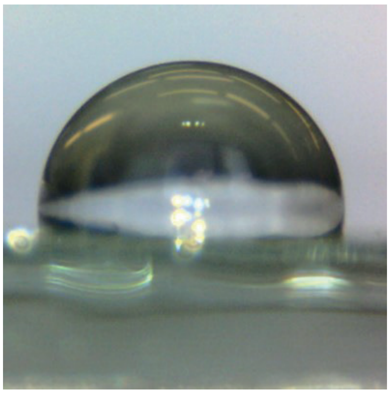


Fig. 1. SEM image of a planar dense 170 nm thick ITO film. (Film 1) (*a*). Drop profile on the film 1. Contact angle α = 100° (*b*)

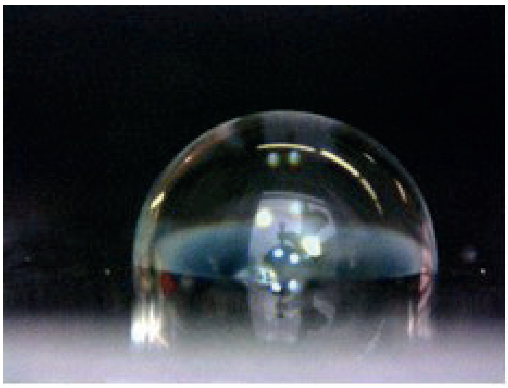


Fig. 2. Drop profile on an Al_2O_3 film 20 nm thick (Film 2). Contact angle α = 95°

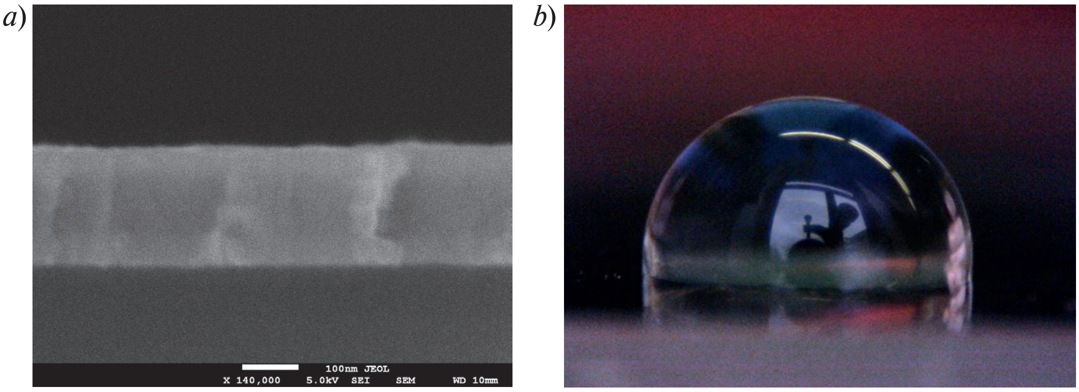


Fig. 3. SEM image of a planar ITO film coated with a 20 nm Al_2O_3 layer (Film 3) (*a*). Drop profile on the film 3. Contact angle α = 100° (*b*)

At the same time, the nanostructured ITO film, also deposited by magnetron sputtering but on a heated substrate with subsequent annealing in a chamber (Film 4), shows hydrophilic properties, and its contact angle α = 10° (Fig. 4, *b*). The SEM image of this nanostructured film shows a pronounced crystalline structure (Fig. 4, *a*).

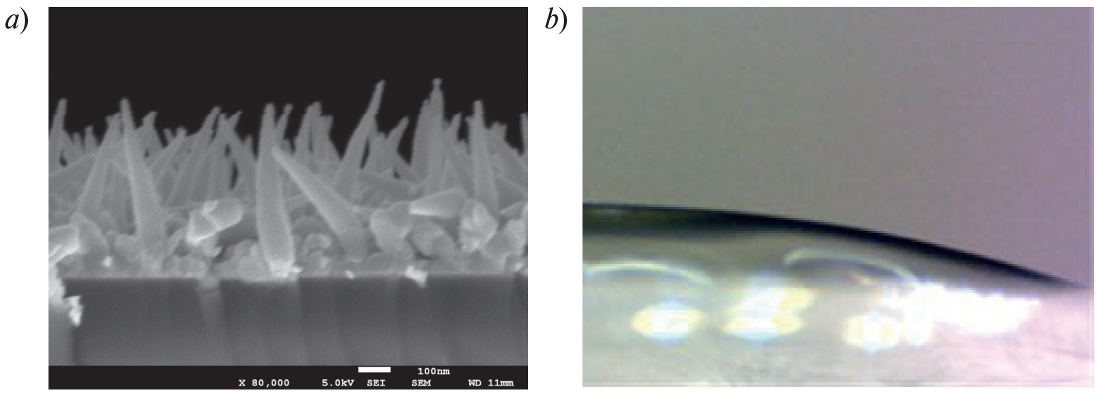


Fig. 4. SEM image of an ITO film (150 nm in equivalent of dense film) deposited on glass by magnetron sputtering on a heated substrate followed by annealing in a nitrogen atmosphere (Film 4) (*a*). Drop profile on film 4. Contact angle α = 10° (*b*)

If the deposition method of nanostructured ITO films is changed to electron beam evaporation on a heated substrate followed by annealing in a chamber, the wettability measurements turn out to be like planar ITO films. The film thickness in equivalent of dense film is 50 nm (Film 5) (Fig. 5, *a*). The contact angle of the film α = 101° (Fig. 5, *b*).

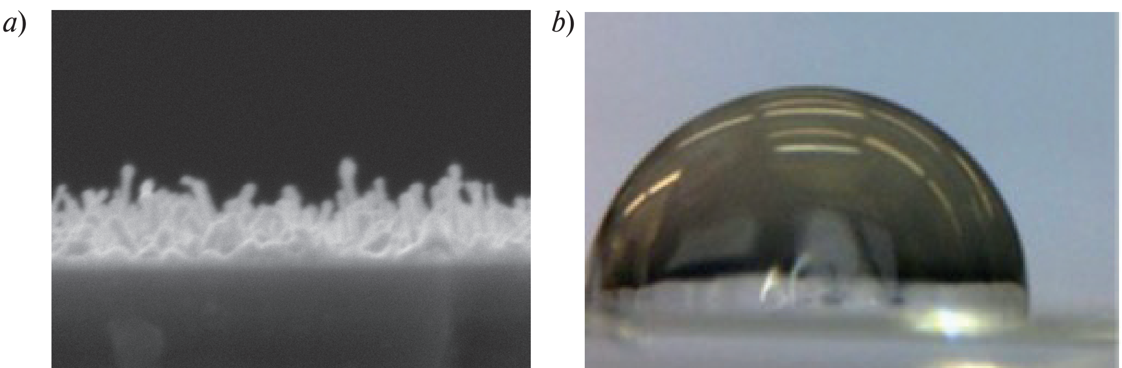


Fig. 5. SEM image of an ITO film (50 nm in equivalent of dense film) deposited on glass by electron beam evaporation followed by annealing in a nitrogen atmosphere (Film 5) (*a*). Drop profile on the film 5. Contact angle α = 101° (*b*)

In the case of nanostructured ITO film covered with a layer of aluminium oxide 1 nm thick (Film 6) (Fig. 6, *a*) used to improve the chemical resistance of the coating, the contact angle was α = 152° (Fig. 6, *b*), i.e., the film was superhydrophobic. Thus, the results show a significant enhancement of the hydrophobic properties compared to the structured and planar ITO films.

a) *b*)

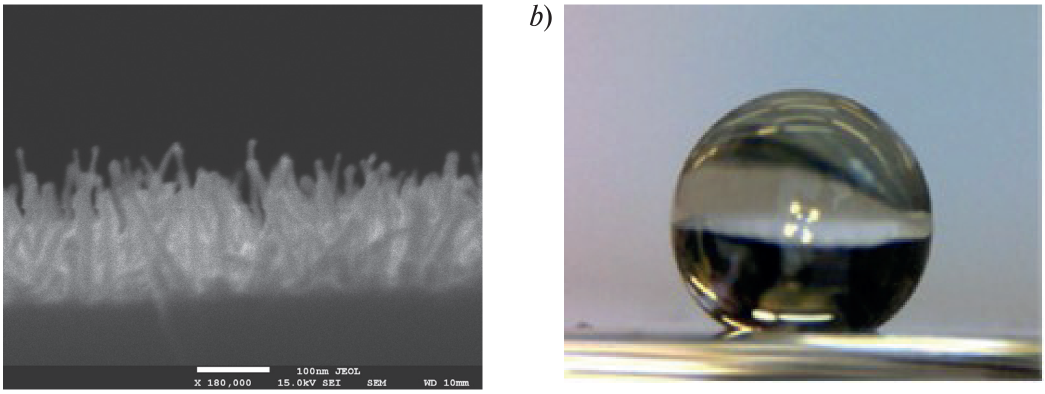


Fig. 6. SEM image of an ITO film (50 nm in equivalent of dense film) deposited on glass by electron beam evaporation on a heated substrate followed by annealing in a nitrogen atmosphere coated with 1 nm Al2O3 (Film 6) (*a*). Drop profile on the film 6. Contact angle α = 152° (*b*)

To study the dependence of contact angle on the thickness of the aluminium oxide layer deposited on the nanostructured ITO film, a nanostructured ITO film with a 10 nm thick aluminium oxide coating was fabricated (Film 7) (Fig. 7, *a*). The contact angle of contact of the film was α = 128° (Fig. 7, *b*),

a) *b*)

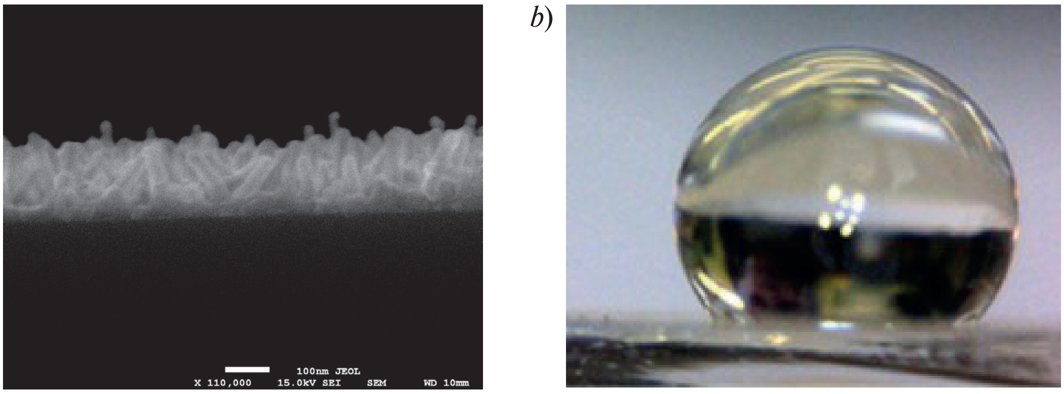


Fig. 7. SEM image of an ITO film (50 nm in equivalent of dense film) deposited on glass by electron beam evaporation on a heated substrate followed by annealing in a nitrogen atmosphere coated with 10 nm Al_2O_3 (Film 7) (*a*). Drop profile on the film 7. Contact angle α = 128° (*b*)

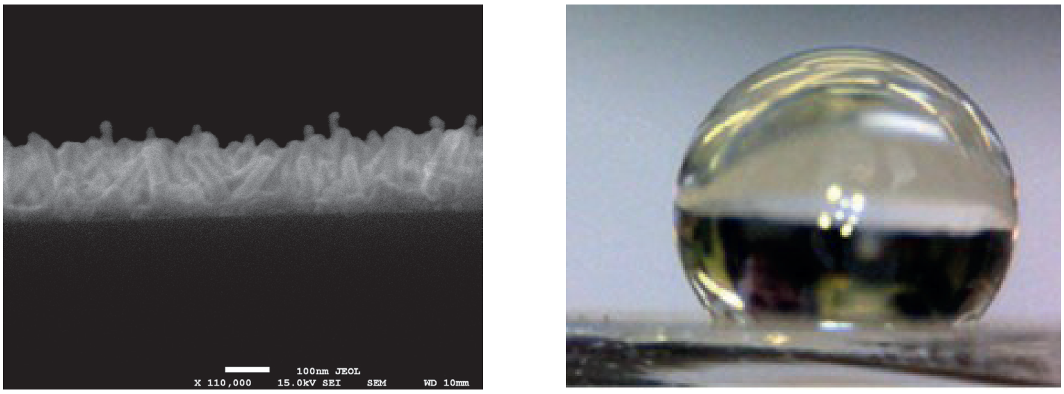


Fig. 8. SEM image of an ITO film (50 nm in equivalent of dense film) deposited on glass by electron beam evaporation on a heated substrate followed by annealing in a nitrogen atmosphere coated with 20 nm Al_2O_3 (Film 8) (*a*). Drop profile on the film 8. Contact angle α = 127° (*b*)

i.e., the film was hydrophobic. An increase in the Al_2O_3 layer thickness did not improve the hydrophobic properties of the combined film of nanostructured ITO and aluminium oxide; on the contrary, they deteriorated.

A nanostructured ITO film with a 20 nm thick aluminium oxide coating was also fabricated (Fig. 8, *a*). The contact angle of the film was α = 127° (Film 8) (Fig. 8, *b*), i.e., the film was hydrophobic. Thus, with an increase in the thickness of the Al_2O_3 layer, the hydrophobic properties of the combined structured ITO with an Al_2O_3 coating deteriorate, but a change in the Al_2O_3 layer from 10 nm to 20 nm had little effect on the contact angle.

Conclusion

In this work, we have studied the water wettability of nanostructured ITO films in various combinations with Al_2O_3 protective layers. ITO films were deposited by magnetron sputtering and electron beam evaporation on the preheated surface of a glass substrate, after which they were additionally annealed in a nitrogen atmosphere for 10 min. A protective Al_2O_3 coatings with various thicknesses were deposited by atomic layer deposition. To estimate the wettability, we measured the contact angles of water drops on the horizontal films surface. The experimental results show that it is possible to obtain coatings with pronounced hydrophilic properties ($\theta < 10°$), moderately hydrophobic coatings ($\theta \approx 130°$) as well as superhydrophobic coatings ($\theta > 150°$) by changing the deposition method of nanostructured ITO films and forming a protective Al_2O_3 layer.

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