Physics of the Solid State, 2022, Vol. 64, No. 11

14

Unoccupied electronic states of ultrathin phenolphthalein films on the ZnO surface formed by atomic layer deposition

© A.S. Komolov[1], E.F. Lazneva[1], N.B. Gerasimova[1], V.S. Sobolev[1], E.V. Zhizhin[1], D.A. Pudikov[1], R. Sodylev[1], S.A. Pshenichnyuk[2], N.L. Asfandiarov[2], B. Handke[3]

[1] St. Petersburg State University,
St. Petersburg, Russia
[2] Institute of Molecule and Crystal Physics, Ufa Federal Research Centre, Russian Academy of Sciences,
Ufa, Russia
[3] AGH University of Science and Technology, Faculty of Material Science and Ceramics,
Al. Mickiewicza 30, 30-059 Kraków, Poland

E-mail: a.komolov@spbu.ru

Received June 6, 2022
Revised June 6, 2022
Accepted June 12, 2022

The results of a study of the unoccupied electronic states of ultrathin films of phenolphthalein molecules on a ZnO surface formed by atomic layer deposition technique are presented. The atomic composition of the ZnO layer was determined by X-ray photoelectron spectroscopy (XPS) and its crystallinity was characterized using X-ray diffraction. The predominance of the content of O atoms by 5−10%, compared with the content of Zn atoms, was found. The electronic characteristics of the ZnO/phenolphthalein structure were studied using total current spectroscopy (TCS) in the energy range from 5 eV to 20 eV above E_F during thermal vacuum deposition of phenolphthalein films up to 8 nm thick. Phenolphthalein molecules contain two hydroxyl functional groups. The TCS results on the phenolphthalein films are compared with the TCS results obtained from films of molecules that represent the backbone of phenolphthalein molecules without hydroxyl groups. The TCS fine structure maxima of phenolphthalein films located in the energy range from 5 eV to 8 eV above E_F can be associated with the boundaries of the π^* bands of electronic states. The work function of the ZnO surface formed by the ALD method were 4.2 ± 0.1 eV. The deposition of a phenolphthalein film led to a decrease in the work function of the surface by 0.1 eV.

Keywords: Phenolphthalein, ultrathin films, ZnO, atomic layer deposition, electronic properties, low-energy electron spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy.

DOI: 10.21883/PSS.2022.11.54212.399

1. Introduction

Organic films based on phthalide molecules demonstrate the property of switching from dielectric state to conductive state [1,2]. This is of interest for the development of molecular electric switches — an actual direction of organic electronics [3,4]. It is supposed, that the increase in electrical conductivity in phthalide films is associated with a break of the C−O covalent bond within the five-membered ring in the molecule (Fig. 1) [5,6]. This process can be activated by electron capture by the phthalide molecule under a direct impact of incident electron beam [5], as a result of introduction of electroactive substituents into the molecule [7,8], or as a result of electron charge transfer through the interface on the boundary of organic material and solid-state surface [9,10]. Semiconductor metal oxides, such as ZnO, in the form of layers or as part of a hybrid of organic and inorganic materials demonstrate wide opportunities for use in photovoltaic devices [10–12]. To explain the physical-chemical interaction at the interface between metal oxide and organic material, a mechanism of integer charge transfer is proposed, assuming ionization of the organic molecule in the near-interface region, and mechanisms of charge transfer with the participation of boundary electronic states [13–15]. Promising for the application of organic films are surfaces of two-dimensional (2D) inorganic semiconductors, for example, ZnO, prepared by the method of atomic layer deposition (ALD) [16,17]. It is shown, that at temperatures of 150−200°C continuous ZnO coatings can be formed on the initial silicon substrate with a thickness from several nm to several hundreds of nm. The ZnO coatings prepared by the ALD method have a bandgap of 3.4 eV, i.e., typical for these semiconductor materials. The use of ZnO layer in organic photovoltaic cell made it possible to improve characteristics of electron transport in a mock-up of organic photovoltaic device [17].

Earlier we have studied unoccupied electronic states in films of substituted phthalides using techniques of resonance electron capture [5,18] and total current spectroscopy (TCS) [18,19]. We have found limits of maxima of unoccupied electronic states in diphenyl phthalide films and shift of these maxima as a result of addition of −COOH functional groups to molecules of diphenyl phthalide. In this work we have presented results of TCS-studying of unoccupied

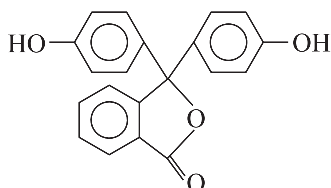

Figure 1. Structure formula of phenolphthalein molecule.

electronic states in the conductivity band of ultrathin films of phenolphthalein — the molecule, that is double –OH substituted diphenyl phthalide (Fig. 1). A special attention is paid to the description of properties of the ZnO substrate prepared in the course of work by the ALD method.

2. Experiment

The substrate used for the application of organic material was the surface of a ZnO semiconductor prepared by the atomic layer deposition (ALD) method. The synthesis was implemented using diethyl-Zn and deionized water as reagents. Temperature during the synthesis was maintained at a level of 200–250°C and layers of O and Zn atoms were applied one by one on the surface of silicon substrate [20]. Taking into account the applied number of layers, the estimate thickness of ZnO films was 100 nm. The atomic composition of ZnO coatings was studied in detail by the X-ray photoelectron spectroscopy (XPS) method, while the thickness and structure of ZnO coatings were determined using the X-ray diffraction (XRD) method. XPS-measurements were carried out using the Escalab 250Xi combined photoelectron spectrometer (by Thermo Fisher Scientific Inc.) with an energy of incident photons $\mathrm{Al}K_\alpha = 1486.6$ eV. The studies were conducted in conditions of ultrahigh vacuum of about 10^{-7} Pa at a room temperature. The possibility to clean the sample surface with a beam of Ar^+ ions was provided. The measured XPS-spectra were analyzed using the library of standard XPS-spectra of the equipment manufacturer, taking into account atomic factors of signal recording sensitivity [21]. XRD-measurements were carried out using the D8 Discover diffractometer (by Bruker) equipped with a source of $\mathrm{Cu}K_\alpha$ radiation energy (0.15406 nm).

Organic films were formed on the ZnO surface using a phenolphthalein reagent, which is commercially available from Sigma-Aldrich (Fig. 1). The reagent was degassed by soaking in vacuum at a basic pressure of 10^{-6} Pa at a temperature of 100°C for 2–3 h. The phenolphthalein film was thermally deposited on a ZnO substrate prepared in the process of work and cleaned by a beam of Ar^+ ions with an energy of 500 eV for 300 s. Current through the sample during this operation was about 1 μA. In the process of organic film depositing the substrate was at a room temperature. The distance from the source of organic material to the substrate was about 8 cm. The rate of depositing was about 0.1 nm/min, which was controlled using a quartz oscillator. In the process of film depositing the pressure in the vacuum chamber was increased by an order of magnitude from the basic pressure.

Electronic properties of phenolphthalein films on the ZnO surface were measured by the method of total current spectroscopy (TCS) [22,23] for a series of successively applied films with an increase in the sum thickness of the organic coating up to 8–10 nm. With an increase in coating thickness the spectral features caused by the substrate were attenuated and a new structure of maxima was formed that reflected the electronic properties of the formed films. In the TCS-experiment the incident electron beam was directed along the normal to the surface under study and a lock-in amplifier was used to record the derivative of total current S(E) through the sample with respect to energy. The energy of electrons in the testing beam was varied in a range from 0 to 25 eV relative to the vacuum level (E_{vac}) of the surface under study. The energy position E_{vac} relative to the Fermi level of the system (E_{F}) can be determined taking into account the calibration of the TCS-tool [22]. The calibration was performed using the surface of highly oriented pyrolytic graphite (HOPG). It is known, that alkaline earth films of HOPG surface are characterized by well reproducible work functions of about 4.6 eV [24]. The thin structure of total current spectra (TSTCS) contains information on positions of the DOCUS (density of unoccupied electronic states) function features of the studied material [22,25].

3. Results and discussion

The use of the ALD method allows forming of a thin-film layers of ZnO with well reproducible properties [16,17,20]. However, insignificant changes in the temperature mode of ALD or changes in precursor dosing modes can result in some deviations of structural and electronic properties of the prepared 2D-semiconductors. Therefore, in this study the diagnostics of the atomic composition and structure of the formed ZnO layers was carried out. In XPS-spectra of samples placed into the analytic vacuum chamber after holding in the air clearly distinguished maxima are found that correspond to core levels of Zn_{2p}, O_{1s} and C_{1s} (Fig. 2, curves *1*). Relative concentrations of these atomic components were determined taking into account relative intensities of measured XPS-maxima and sensitivity factors of their recording [21]. Thus, the relative concentration of C atoms was approximately 25%, while the content of O atoms was about 10% higher than the content of Zn atoms. It is known, that the carbon atoms, as well as some percentage of oxygen atoms found on the metal oxide surface is attributable to the adsorption of doping from the air [26,27]. To remove the adsorbates from the surface under study we used treatment with Ar^+ ions with an energy of 500 eV for 300 s (Fig. 2, curves *2*). As a result of cleaning the relative concentration of C atoms decreased down to 1%, and the predominance of O atoms content by 5–10%

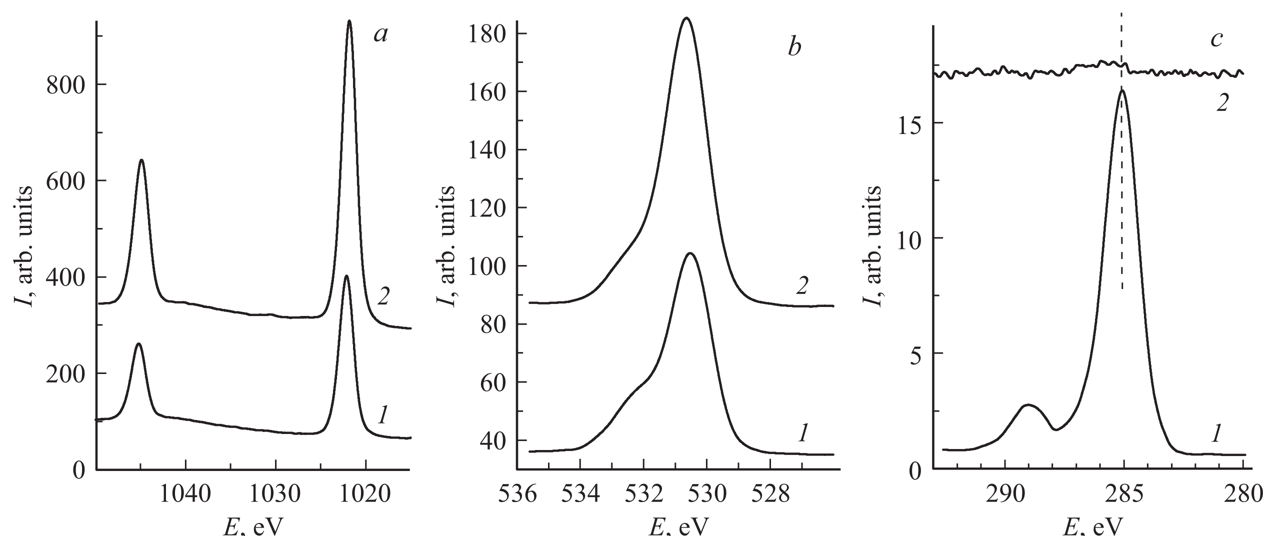

Figure 2. X-ray photoelectron (XPS) spectrum of ZnO surface formed by the ALD method in the region of maximum of the core level of Zn_{2p} (a), O_{1s} (b) and C_{1s} (c). Curves 1 — without pre-processing, curves 2 — after 300 s processing by Ar^+ ions with an energy of 500 eV.

over the content of Zn atoms was kept. As a result of Ar^+-cleaning the XPS-spectrum of the core level of Zn_{2p} remained almost unchanged (Fig. 2, a). XPS-maximum of O_{1s} demonstrates two main components: O_{1s} (530.5 eV) and O_{1s} (532 eV). Energy position of the first component is typical for suboxide, and the position of the second component is typical for stoichiometric ZnO [10]. As a result of Ar^+-cleaning the relative intensity of the O_{1s} component (532 eV) has decreased by about 2 times.

Diagnostics of structural features of the formed ZnO layers was carried out by the XRD method. The diffraction pattern obtained in the „$\theta/2\theta$" experiment geometry (Fig. 3) demonstrates four characteristic maxima in a range of 2θ angle from 20 to 60°. Observed reflections (Fig. 3): 32, 34.5, 36.5, and 57° correspond to well-known ZnO reflections of a Wurtzite type: (0 0 1), (0 0 2), (1 0 1), and (1 1 0) [17]. As a result of XRD-studying in the „$2/\Omega$" experiment the geometry thickness of the formed ZnO layer was found to be 104 nm and its roughness was not more than 5 nm. The roughness of the underlaying silicon substrate was not greater than 1 nm.

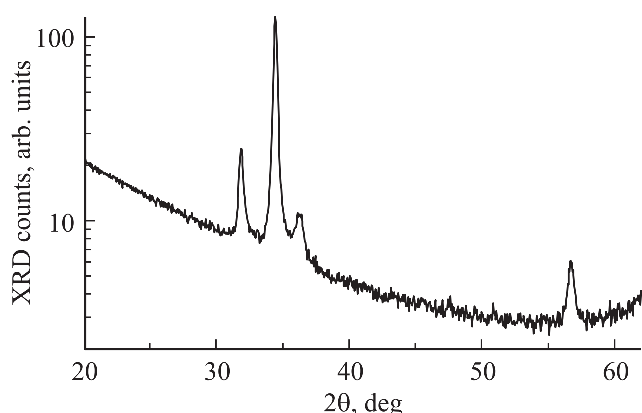

Figure 3. XRD-diffraction pattern of the ZnO film formed by ALD method.

The thin structure of total current spectra (TSTCS) is a series of maxima and minima attributable to the change in intensity of incident electrons reflection from the surface under study depending on the energy of incident electrons. Low reflection of incident electrons at a certain energy can be interpreted as a presence of allowed electronic states in the studied sample at the given energy. Usually, the energy range for TSTCS recording is located within 5 to 25 eV above the E_F. The series of TSTCS measured in the process of depositing of phenolphthalein films on the ZnO surface by ALD is shown in Fig. 4. With a thickness of organic coating equal to 0 nm, TSTCS corresponds to the surface of ZnO substrate before the application of the organic coating. TSTCS of ZnO demonstrates several clearly distinguished maxima, including those at energies of 8.0, 11.0, and 16.0 eV. Similar TSTCS was observed by us earlier from the crystalline surface of ZnO(0 0 0 -1) [14].

As the organic coating of phenolphthalein was deposited up to a thickness of 8 nm, TSTCS of the substrate was attenuated, and simultaneously the intensity of new maxima of TSTCS was growing (Fig. 4). A newly formed maxima of TSTCS P_1-P_5 should be associated with electronic properties of phenolphthalein films. Molecules of phenolphthalein are different from molecules of diphenyl phthalide, the films of which were studied earlier [19], by the presence of two hydroxyl (−OH) functional groups. Therefore it is reasonable to compare locations of P_1-P_5 maxima (Fig. 4) with locations of maxima of diphenyl phthalide TSTCS-films reported in [19]. Energy positions of the TSTCS maxima P_3-P_5 of phenolphthalein films correspond to energy

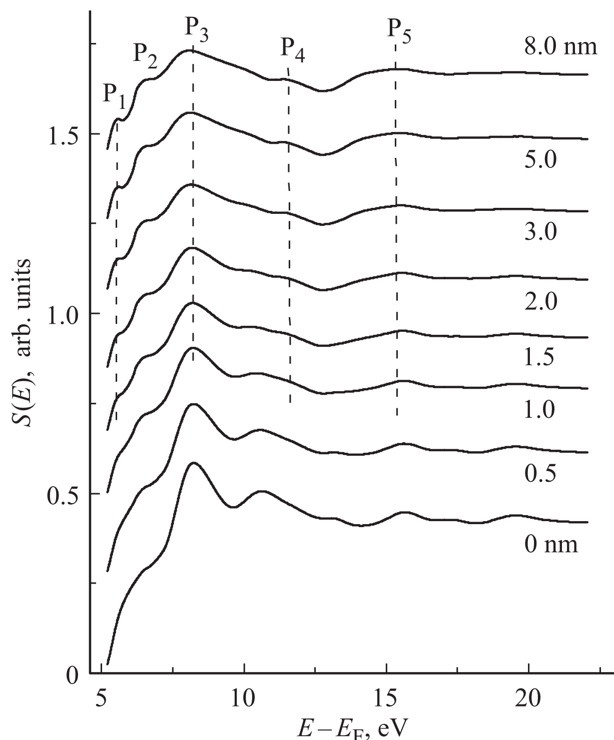

Figure 4. TSTCS in the process of depositing of phenolphthalein films on the surface of ZnO formed by the ALD method. Captions near curves specify the corresponding thickness of organic coating from 0 to 8 nm. Typical maxima P_1-P_5 for phenolphthalein films are specified. Vertical dashed lines are shown for convenience of maxima comparison.

positions of three maxima in TSTCS-films of diphenyl phthalide. At the same time the P_3-P_5 maxima are shifted by 0.2−0.4 eV towards higher electron energies. The TSTCS maxima P_1 and P_2 of phenolphthalein films are formed in the region of energies of 5−7 eV above E_F. In the case of diphenyl phthalide films only one TSTCS maximum is found in this energy region. It is reasonable to determine π^* or σ^* character of the observed P_1-P_5 maxima of TSTCS-films of phenolphthalein taking into account TCS-results obtained for the films of diphenyl phthalide and using the results of theoretic calculations of lower π^* orbitals of diphenyl phthalide molecules [18,19,28]. The calculated energies of the orbitals were corrected by 1.2 eV, i.e. by the energy of medium polarization in condensed state for the case of semiconductor organic films [29]. Taking into account this literature data, the TSTCS maxima P_1-P_5 in phenolphthalein films located in the energy range from 5 to 8 eV above E_F (Fig. 4), can be connected with boundaries of bands of π^*-electron states.

The formation of a potential barrier in the process of phenolphthalein coating depositing on the ZnO layer surface was studied by recording energy position of the first TCS-maximum. Thus, using the results of TCS-tool calibration on known surfaces the changes in E_{vac} can be determined for the surface under study in relation to E_F. It is known, that work function of the atomically clean Au surface is 5.2 eV, while for HOPG surface it is about 4.6 eV [24]. $E_{vac}-E_F$ error is 0.1 eV due to the dispersion of electron energies in the testing beam. Work functions of the ZnO surface formed by ALD were 4.2±0.1 eV. This value is approximately 0.5 eV less than the work function of ZnO surface (0 0 0-1), as it was found by us in [14]. This difference is attributable to the different structure of surfaces, as well as the difference in the content of oxygen atoms in the near-surface region. A number of papers reported that different crystalline orientation of metal oxide surface, as well as surface degeneration, including full oxidation, results in the changes of surface bend of bands and equalization of energy levels at the interface with the organic film [10,15,30]. Thus, the predominance of Zn atoms was found on the ZnO surface (0 0 0-1) [14], while for the surface of ZnO layer formed by the ALD method it was found in this study that O atoms prevail. An insignificant decrease in work function by 0.1 eV was found as a result of phenolphthalein films deposition. Thus, work functions for phenolphthalein films were 4.1 ± 0.1 eV. These values are 0.1−0.2 eV less than the work functions for diphenyl phthalide films determined by us earlier [14]. Thus, the introduction of hydroxyl functional groups into diphenyl phthalide molecules(Fig. 1) resulted in a work function decrease by 0.1−0.2 eV.

4. Conclusion

Films of phenolphthalein molecules were formed by the method of thermal vacuum deposition on the surface of ZnO prepared by means of the ALD technique. XPS-diagnostics of atomic composition of ZnO samples formed by the ALD method has shown the predominance of O atoms by 5−10% as compared with the content of Zn atoms. XRD-diffraction pattern of the formed ZnO layers has demonstrated reflections typical for ZnO of the Wurtzite type. TCS method was used to determine the change in the structure of maxima of unoccupied electronic states in the energy range from 5 to 20 eV above E_F in the process of forming the organic coating of phenolphthalein with a thickness of up to 8 nm. Maxima of TSTCS-films of phenolphthalein located in the energy range from 5 to 8 eV above E_F are attributable to boundaries of bands of π^*-electron states. Work functions of the ZnO surface formed by ALD were 4.2 ± 0.1 eV. Phenolphthalein films deposition resulted in a decrease of the surface work function by 0.1 eV.

Funding

The TCS-studying of phenolphthalein films was supported by grant of the Russian Science Foundation No. 19-13-00021, https://rscf.ru/project/19-13-00021/. The studying of ZnO layers was supported by grant of the Russian Foundation of Basic Research (20-03-00026). The XPS-measurements were supported by the St. Petersburg State

University (project № 93021679) using the equipment of the St. Petersburg University Research Park Physical Methods of Surface Research, Innovation Technology of Composite Nanomaterials, X-ray Diffraction Methods of Research.

Conflict of interest

The authors declare that they have no conflict of interest.

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