The properties of ZnO films obtained by high-frequency magnetron deposition with subsequent vacuum annealing and plasma treatment

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Abstract. The method of high-frequency magnetron sputtering allows to obtain thin films of zinc oxide with nanostructured surface morphology and, consequently, with unique optical characteristics. Such coating can provide an increase in the number of particles penetrating the photovoltaic structure and the length of their optical path. Vacuum-plasma processing of ZnO films allows to change the morphology of their surface, and annealing largely influences the optical transmission.

1. Introduction
Zinc oxide films are attractive for use in photovoltaics (and in solar converters in particular) as transparent electrodes for current collection [1], as a heterocontact in oxide heterostructures [2–4] and other oxide photovoltaic media [5] as well as in sensorics, for example, as an active layer in sensors on surface acoustic waves [6–9], etc. One of the problems of oxide film structures is their instability under various external influences [2, 10]. Zinc oxide can possess an electronic type of conductivity due to a high concentration of intrinsic defects such as interstitial zinc or oxygen vacancies. These defects are responsible for an increase in n-type conductivity and a decrease in crystallinity [11]. If a certain morphology of the structure can be created in ZnO films, then they can perform the functions of the diffusive light diffuser in the solar energy converter. When passing through a layer of such material, the ray of solar radiation changes its trajectory, i.e. the radiation scattering occurs that leads to an increase in the optical path of the particle in the photoactive structure. Due to this, a more effective conversion of solar energy into electrical energy is carried out, and the short-circuit current is increased. The annealing of the material leads to the formation of a more uniform structure, the reduction of hardness, the removal of stresses, the equalization of chemical inhomogeneity and the improvement of optical characteristics [12, 13]. On the other hand, the annealing temperature mainly affects the orientation in the plane. Processing in plasma allows changing the physical properties of the material, hardness and morphology of the surface [14].

2. Preparation of zinc oxide films by high-frequency magnetron sputtering
As targets for the deposition of zinc oxide films, ZnO powders that were uniformly distributed over the entire surface of the magnetrons (figure 1(a)) were used. A complex of experiments showed that
the studied oxide is characterized by low sputtering rates. Dependences of the growth rate between zinc oxide and the power of the high-frequency discharge are shown in figure 1(b). It should be noted that further increase in the power of the HF discharge to increase the growth rates of the films is undesirable, because this will lead to overheating of the magnetrons and their possible failure. The gas mixture of the process contained 76 % Ar and 24 % O₂. The operating pressure of the gas mixture was 10⁻² Torr. The substrate temperature (self-heating) was 260–270 °C.

Figure 1. The internal equipment of the vacuum chamber (a), the dependence of the growth rate of zinc oxide on the power of the HF discharge (b).

3. Investigation of the optical properties of zinc oxide

The transmittance and reflection spectra of the films of zinc oxide (ZnO) were studied, which are intended for use as transparent electrodes in thin-film solar cells; parameters of the samples are given in table 1. The data of films thickness were obtained by an interference method, the surface resistance was measured by a four-probe method.

Table 1. Characteristics of ZnO film samples.

| Sample № | Thickness, nm | Surface resistance, Ohm/kV |
|----------|---------------|---------------------------|
| ZnO 4    | 192           | –                         |
| ZnO 3    | 510           | 155                       |
| ZnO 2    | 982           | 43                        |
| ZnO 1    | 1609          | 18                        |

The spectra were measured on a Cary-5000 double-beam spectrophotometer in the wavelength range of 400–1000 nm. The integrating sphere was additionally installed in the instrument, because a significant light scattering, which is necessary to increase the proportion of absorbed radiation in subsequent semiconductor layers, is observed in the studied zinc oxide. The sphere allows to measure both the radiation flux passing through the sample or reflected from it (flux into the hemisphere) and diffusely scattered radiation flux (flux into the hemisphere excluding flux along the normal to the sample), which makes it possible to determine the coefficients of total (TT) and diffuse (TD) transmission and reflection. Figures 2, 3 show the spectra of the total transmission and reflection of the studied samples. According to the results of the transmission measurement, the spectral dependences of the HF (haze factor) parameter were calculated for each film. It determines the fraction of diffusely scattered radiation in the transmitted flux (figure 4).

According to the graphs in figures 3, 4, a high haze factor (a significant proportion of the diffuse-scattered radiation) and a relatively small losses because of optical absorption (10–15 %) are achieved only for a 1.6 μm film (sample ZnO 1), which should probably be considered optimal. For films of
smaller thicknesses, the loss of absorption decreases slightly (figure 2), but the haze factor falls sharply (figure 4), and the surface resistance increases (table 1).

Figure 2. Spectra of total transmission for ZnO obtained by the method of magnetron sputtering (1 – sample ZnO 1; 2 – ZnO 2; 3 – ZnO 3; 4 – ZnO 4).

Figure 3. Spectra of total reflection for ZnO obtained by the method of magnetron sputtering (1 – sample ZnO 1; 2 – ZnO 2; 3 – ZnO 3; 4 – ZnO 4).

Figure 4. Effects of light scattering of ZnO films (1 – ZnO 1; 2 – ZnO 2; 3 – ZnO 3; 4 – ZnO 4).

4. Effect of annealing in vacuum and processing in plasma on the properties of ZnO films

Further, the samples were annealed in vacuum at different temperatures and different annealing times. The results of the total transmission measurement are shown in figure 5. According to the graphs, the annealing time and temperature affect the transmission considerably at the annealing temperature of 300 °C, but there is no such strong effect at the annealing temperature of 250 °C.

Plasma treatment of ZnO that is aimed at the surface modification of films was performed in magnetron sputtering systems at ambient temperature and at a typical pressure of about 60 Torr. For processing, the samples were placed as a target directly above the magnet with the sputtered target. This position of the samples provides a strong magnetic field near the processed sample, which increases the
efficiency of ionization of argon atoms (Ar) by electron pulses and, consequently, increases the plasma density and the Ar ion flux to the treated surface.

![Figure 5. Change in the total transmission at a wavelength of 1600 nm with a variation of temperature (250 °C and 300 °C) and the annealing time.]

As a result, the processing time can be expected to decrease without increasing the power of the HF signal. The processing time was 5 min at a power density of 1.3 W/cm². We have shown that plasma treatment of boron-doped ZnO layers allows to transform the V-shape surface into a U-type morphology. Plasma treatment leads to a decrease in the turbidity values in the entire range from 400 to 900 nm for all samples. The turbidity value for the sample treated for 5 min has a value of 22 % at 600 nm, and an increase in the treatment time leads to a decrease in the turbidity values. The light-scattering factor also decreases, as can be seen in figure 6.

![Figure 6. Light scattering effects of ZnO film: 1 – before plasma treatment; 2 – after 5 min of plasma treatment; 3 – after 10 min.]

To verify the electronic properties of the films, we performed measurements of the electrical conductivity of the samples, carrier concentration and mobility. The results show that there is no significant change in the values of mobility and carrier concentration for samples with a short treatment period (5 min), while a longer exposure to radio-frequency magnetron plasma leads to a deterioration in the electronic properties. This result can be explained either by the formation of defects in the bombardment with massive Ar ions or by overheating of films deposited on glass substrates with a low thermal conductivity during prolonged treatment with intense plasma and low pressure. It can be expected that under these conditions the structural properties of the films can also deteriorate. As we have shown, processing for five minutes is sufficient to transform the surface morphology from V-type to U-type without decreasing the electronic properties of the films.

5. Conclusion
In the framework of this paper, we obtained samples of zinc oxide films with a nanostructured surface on substrates made from special photovoltaic glass with increased light transmission (reduced iron oxide content). The optimal film thickness was 1.6 μm, since in this case relatively small losses for
optical absorption (10–15 %) and optimal values of the light scattering factor are obtained. It was also found that the effect of annealing in vacuum at 300 °C significantly influences the value of optical transmission, namely, it increases it, which indicates an improvement in the structural parameters of the film. By vacuum-plasma treatment it is possible to change the structure of the surface from the V-shape to the U-type morphology, which is more advantageous for use in photovoltaics. Also, the optimal plasma processing time is 5 min, since this is sufficient to reduce the turbidity values without disturbing the electronic properties of the material.

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