NdYAG surface modification of ZnO for solar cells

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Abstract. Zinc oxide films are used as a photovoltaic transparent electrodes for current collection. They are a good substitute for expensive transparent electrodes on the basis of Indium tin oxide. The ZnO films fabricated with a certain morphology of the structure are able to act as a light diffuser.

1. Introduction
Large size (~1.4 m\textsuperscript{2}) silicon-based thin-film solar module (SM) consists of elements connected between each other in a way to get the maximum efficient solar energy conversion in the output. In solar modules production the technological process of separating elements is realized using laser scribing. The research includes analysis of possibility to decrease the «dead zone» and to increase the parameters of electrical energy output.

2. Experiment
The glass film with deposited thereon zinc oxide was used as an experimental sample. Processing of the sample was performed by laser radiation with a wavelength of 355 nm, the laser pulse energy ranged from 14 mJ to 21 mJ (± 0.05 mJ). There were seven groups for different cuts of focus distance that vary in increments in 0.1 mm. Each group included five consecutive scribes obtained with the power of laser pulses of 14 mJ, 16 mJ, 18 mJ, 20 mJ, 21 mJ, respectively. Pulse repetition rate was 60 kHz and a pulse duration was 30 ns. There was detected scribe, which has the following characteristics: a minimum width on the surface of 27 ± 0.5 µm scribe, scribe at the bottom (on the side of the glass substrate), the width is 25 ± 0.5 µm; width of cut on the surface and at the bottom is constant in different coordinates of the cutting length; minimum number of chips and no shunt elements.
The intensity of the laser pulse has a shape close to a Gaussian distribution with a maximum at the center of focus of the beam. Data matrix was obtained during the experiment. Scribe control was performed using optical microscopy. Photographing of groups of scribes was conducted in different coordinates of the sample. There was detected scribe, which has the following characteristics: a minimum width on the surface of 27 ± 0.5 µm, scribe at the bottom (on the side of the glass substrate), the width is 25 ± 0.5 µm; width of cut on the surface and at the bottom is constant in different coordinates of the cutting length; minimum number of chips and no shunt elements. This scribe was obtained by defocusing value (the distance from the focus to the treated surface) of the laser beam by 1.5 mm and a laser pulse energy of 20 mJ. When passing by through the glass beam was focused to the treated layer ZnO.

### Table 1. ZnO main characteristics.

|      | Bandgap (eV) | Conductivity (S cm\(^{-1}\)) | Electron concentration (cm\(^{-3}\)) | Mobility (cm\(^{2}\)V\(^{-1}\)c\(^{-1}\)) |
|------|--------------|-------------------------------|-------------------------------------|----------------------------------|
| ZnO  | 3.35         | 8000                          | > 1021                              | 20                               |

### 3. Results

During the experiments it was found that at low energies of the laser pulse (less than 3 mJ) it is impossible to obtain uninterrupted scribe, as a result there are shunts because is not enough energy to remove material by laser ablation. The value of the width of the resulting "track" is an important factor. Increasing the width of cut reduces the active area of the solar module, as a consequence, the decrease of the photocurrent values of the solar module.

The power of the laser radiation used in the processing has a direct influence on the cutting depth (scribe). Scribe depth determined by the equation:

\[
h \approx Pt / (\pi r_0^2 L_u)
\]

where \(P\) - power of laser beam, \(t\) - duration of the laser pulse, \(r_0\) - the radius of the laser spot on the surface to be treated, \(L_u\) - hide heat of vaporization.
Laser spot size will also affect the width of the scribe. The dependence of the width of the scribe on the laser spot size is described by equation:

\[ l \approx 2 \left( r_0 + \frac{Ptg\gamma}{\pi n_0 L_o} \right) \]  

(2).

If using equation (1) we determine \( r_0 \) and put the value obtained in the equation 2, we obtain the following relation:

\[ l \approx 2 \left( \frac{P_{rf}}{h \pi L_o} + \frac{P_{tg\gamma}}{\pi r_0 L_o} \right) \]  

(3),

where \( l \) - scribe width - half angle of the focused beam impinges on the sample, \( h \) - thickness of ZnO layer in place of the laser beam.

The best results for laser treatment have been achieved by annealing the films of zinc oxide ZnO with a laser beam at power density ranging 0.163 ÷ 0.260 W / cm². Laser radiation with the power density less than 0.163 W / cm² causes almost no change, and when the power density was over 0.260 W / cm², sections with significant areas of melting and cracking of the film were obtained. Moreover it should be noted here that due to the energy distribution in the laser beam Gaussian surface annealed films unevenly and a large enough portion of the film was hardly processed.

Study of the samples micro relief was conducted using atomic force microscope Ntegra Therma (NT-MDT), the results are shown in Figure 1, 2. It is revealed that with an increase in power incident on the sample the surface roughness increases and this leads to an increase in Haze-factor.

![Image of atomic force microscope images](image)

**Figure 2.** The image surfaces of the samples number 11 (left) and 12 (right) obtained by an atomic force microscope.

The films were treated by radiation with a wavelength of 355 nm. The structure of the films was examined by Raman spectroscopy (Fig. 3). To study the vibrational properties of ZnO crystal lattice the Raman spectroscopy was used. Raman spectra were recorded in the reverse scatter geometry at room temperature with a spectrometer LabRam HR800, combined with a confocal microscope (manufactured by Jobin-Yvon Horiba). As the excitation source was used second harmonic of Nd: YAG-laser (wavelength 532 nm). The laser beam is focused to a spot with a diameter of ~ 1-2 μm on the sample surface.

In the hexagonal symmetrical structures C46v, such as ZnO, there are six branches of optical phonons at \( \Gamma \) (the center of the Brillouin zone) \( \Gamma = A1 + E1 + 2B1 + 2E2 \) [12-15]. Phonon modes of symmetry A1 and E1 are polar at the point \( \Gamma \) and split into longitudinal and transverse optical vibrations (LO and TO, respectively). Non-polar phonon modes symmetry E2 shares two frequencies: E2(high) related to
the vibrations of the atoms of oxygen and E2(low) related to the vibrations of the atoms of zinc. [16] Mode B1 is «silent mode» and does not appear in the optical spectra of [16,17].

Figure 3. The Raman spectra of the film ZnO: 1 - before modification; 2 - after modification.

4. Conclusion

Processing with of optimum focus settings allows to obtain correct geometrical form of cuts, the width of which is almost independent on the ZnO film thickness unevenness (in the case cutting width variations differ in less than 0.5 microns), with a minimum number of chips and absence of the shunt elements. Implementation of the results achieved in the TFSM production technology will increase the output current about 2-5 % by reducing the area of laser micromachining (compared with typical TFSM produced by this technology).

Summing up the results of the analysis, it can be concluded that the polycrystalline ZnO structure is destroyed by modifying laser radiation, while in the center of the spot amorphous zinc oxide is formed. The results can be used to create thin-film solar modules of a large size.

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