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Controlling the optical performance of transparent conducting oxides using direct laser interference patterning

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ABSTRACT

In this study, a laser based process called Direct Laser Interference Patterning (DLIP) was used to fabricate micro-textured boron doped zinc oxide (ZnO:B) thin films to be used as electrodes in thin-film silicon solar cells. First, the ablation thresholds of the ZnO:B film were determined using a nanosecond pulsed laser at wavelengths of 266 and 355 nm (100 mJ/cm^2 and 89 mJ/cm^2, respectively). After that, DLIP experiments were performed at 355 nm wavelength. Line-like periodic surface structures with spatial periods ranging from 0.8 to 5.0 μm were fabricated using two interfering laser beams. It was found that the structuring process of the transparent conducting oxide (TCO) is mainly based on a photo-thermal mechanism. The surface of the ZnO:B film was molten and evaporated at the interference maxima positions and the depth and width of the generated microfeatures depend on the laser parameters as well as the spatial period of the interference pattern. The optical properties of the structured TCOs were investigated as a function of the utilized laser processing parameters. Both diffuse and total transmission and the intensity of the diffraction orders were determined. These data were used to calculate the increase of the optical path of the transmitted light.

1. Introduction

Thin-film solar cells are an efficient and attractive alternative to crystalline silicon (c-Si) wafer-based cells. In general, conventional silicon based solar cells are expensive due to the high energy demand for producing crystalline silicon. On the other hand, they can reach efficiencies up to 25% [1,2]. Thin-film silicon solar cells can be produced by evaporating thin layers of Si on glass-, steel- or plastic substrates [3,4]. Furthermore, they are not limited by the size of the wafers [5]. A low-cost production, an upscaling to a large scale manufacturing and savings of raw materials are their main advantages [3,6,7]. However, thin amorphous-silicon solar panels have shown efficiencies of approximately 10–11%, what is much lower than c-Si modules [8].

One reason for this difference is the smaller thickness of the active material in the thin-film cells. The active material is typically thinner than the absorption length of the light, so that only a part of the incoming light is absorbed [3]. Therefore, less electron-hole pairs can be generated [9]. In addition, under diffuse illumination thin-film solar cells lose less efficiency compared to crystalline cells [10]. Another advantage of semitransparent solar cells is that they can be used for building-integrated photovoltaics as semi-transparent designs [3,11].

In order to improve the efficiency of thin-film solar cells, different concepts have been developed in the past. One approach is to use materials with different band gaps in tandem or multi-junction cells, permitting to obtain efficiencies over 12–13% [12]. A typical configuration of tandem cells is presented in Fig. 1. Hydrogenated amorphous Silicon (a-Si:H) is used as top cell material where light with high photon energy in the wavelength region between 400 and 800 nm is absorbed [13]. The transmitted infrared light is led to the bottom cell with μc-Si:H (microcrystalline) as absorber [13]. Typical thicknesses of these layers are 380 nm for a-Si:H and 1850 nm for μc-Si:H. The transparent conducting oxide (TCO) layer and the back contact act as electrodes to conduct the photocurrent (Fig. 1a).

Another approach to improve the efficiency is to increase the optical path length of the light. This can be done by increasing the surface roughness of the TCO and thus enhancing the contribution of the scattered light (diffuse transmission).

A technology permitting the fabrication of rough boron-doped zinc oxide films is Low Pressure Chemical Vapor Deposition (LPCVD). The rough surface is directly produced during the deposition process at temperatures above 145 °C. This surface shows a typical pyramidal morphology [14,15]. The geometrical characteristics of the pyramids, such as height and width, can be adjusted by changing either the deposition

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temperature or the target film thickness, By using proper conditions, the diffuse transmission can be increased up to ~60% [16].

Another possibility to increase the diffuse transmission is by fabricating diffractive structures (Fig. 1b) [17–20]. In this case, the incoming light is diffracted at certain angles, resulting in a longer optical path length through the active material layer. Due to this effect, the thickness of the active layer can be reduced, which consequently leads to less charge carrier recombination and higher efficiencies [21,22]. Furthermore, the light induced degradation of the amorphous silicon layer decreases significantly [13].

Several technologies can be used to fabricate periodic surface structures. The most common techniques are based on photolithographic processes, where a photoresist coating is illuminated with UV-light and afterwards developed and etched to transfer the pattern to the substrate [23]. Another photolithographic method that has been utilized to produce periodic patterns is Laser Interference Lithography (LIL). The interference patterns are obtained by splitting a laser beam into two or more coherent sub-beams which are overlapped on the resist [24]. Also in this case, several process steps are necessary to obtain the final structure on the desired material, because the structure cannot be produced directly on the surface. In addition, the necessary chemicals to etch the material are considered to be hazardous waste. Further patterning methods are direct laser ablation (or direct laser writing) or jet printing [25,26]. These methods are generally limited to feature sizes over 10 μm.

A promising method for the fabrication of periodic structures is Direct Laser Interference Patterning (DLIP) [27–30]. In contrast to LIL, in DLIP a high power pulsed laser beam is utilized to directly ablate the material at the interference maxima positions. The geometry of the interference pattern can be adjusted by varying the number of overlapped laser beams (e.g. line- and dot-like patterns using two and three laser beams, respectively). The spatial period is controlled by the angle between the individual beams [31–33]. Furthermore, this technique allows periodic patterns with feature sizes that are smaller than the used laser wavelength. This makes DLIP suitable to fabricate high efficient diffraction gratings.

In this study, two-beam Direct Laser Interference Patterning was utilized to produce diffractive patterns on low pressure chemical vapor deposited zinc oxides. The ablation threshold of the films was determined for the wavelengths of 266 and 355 nm to evaluate the quality and behavior of the laser process. Subsequently, line-like structures with spatial periods between 0.8 and 5.0 μm were fabricated. The structured TCO substrates were topographically characterized by using confocal and atomic force microscopy. The optical transmission of the laser-treated films was measured using UV-VIS spectroscopy. The increase of the optical path length of the produced DLIP structured TCO was calculated considering the diffraction efficiency of the different diffraction orders.

2. Materials and methods

2.1. Materials

Boron-doped zinc oxide (ZnO:B) films were deposited on soda-lime glass substrates using low pressure chemical vapor deposition (LPCVD) by Bosch Solar Energy AG. The film thickness was 1.5 μm. The produced films had a polycrystalline morphology, formed with large columnar monocrystalline grains, leading to surface pyramidal shape features [34]. This surface structure causes light to scatter, so that the material shows a translucent characteristic (e.g. like in frosted glass). These TCOs are mainly used for thin film silicon solar cells [35–37].

2.2. Ablation threshold experiments

The ablation threshold laser experiments were conducted by using a Nd:YAG laser (Quanta Ray Pro 290–10, Spectra-Physics) with a pulse duration of 8 ns at 266 and 355 nm wavelength. The threshold experiment was essential for a quantitative understanding of the laser interaction with the material. The laser beam was formed to a Gaussian profile by passing through a lens with a 500 mm focal length and a pin hole (100 μm). After the pin hole, the beam was focused to the TCO substrates using a second lens with 200 mm focal length. By assuming the spatial fluence profile of an ideal Gaussian beam, it was possible to calculate the ablation thresholds [38].

The laser pulse energy (E) was gradually varied and the diameters (D) of the ablated areas were measured via light microscopy. By applying a linear regression analysis, the radius of the Gaussian laser beam (ω_0) could be determined. The threshold energy (E_{th}) and the ablation threshold (F_{th}) were calculated using Eqs. (1) and (2) [38–40].

$$D^2 = 2\omega_0^2 \cdot \ln\left(\frac{E}{E_{th}}\right) \tag{1}$$

$$F_{th} = \frac{E_{th}}{\pi \cdot \omega_0^2} \tag{2}$$

2.3. Direct Laser Interference Patterning

To obtain the interference patterns, the primary laser beam was split into two coherent beams of the same intensity, which were later overlapped on the substrate's surface using mirrors. Additional information about the experimental setup can be found elsewhere [27–30].

The spatial period (Λ) of the interference pattern is defined by the laser wavelength (λ) and the angle of incidence (α) of the laser beams as indicated in Eq. (3)

$$\Lambda = \frac{\lambda}{2\sin\alpha} \tag{3}$$

To fabricate the periodic structures, the overlapped laser beams were formed to a rectangular beam shape by using a rectangular ceramic mask (5×7 mm^2). An XYZ-motion system allowed the processing of large areas by moving the samples. The total processed area was 50×50 mm^2.

The influence of the laser fluence and the number of laser pulses were investigated. The number of laser pulses was varied between 1 and 6 pulses, and the laser fluence between 50 and 400 mJ/cm^2. Patterns with spatial periods between 0.8 and 5.0 μm were produced.

2.4. Surface characterization

The morphology of the irradiated films was determined by scanning electron microscopy (SEM) at an operating voltage of 5 kV (Philips XL30 ESEM-FEG). The SEM images were used to determine the ratio of the molten surface, by measuring the width of molten region at the maxima positions. The structure depth was measured by atomic force microscopy (AFM) (JEOL, JSPM-5200) and a confocal microscope (Leica DCM 3D system).

2.5. Characterization of optical properties

The diffusive and total transmission of the laser-treated and non-treated ZnO:B films were determined by using UV–Vis spectroscopy (Perkin Elmer Lambda 950) in the range of 250 to 2000 nm. Total transmission is the sum of direct and diffuse transmission measured for normally incident light. The diffraction efficiency of the surface pattern as a measure for the quality of the diffraction was determined by measuring the intensity of the diffraction orders. This was realized by irradiating the treated TCO substrates with a 633 nm non-polarized He-Ne laser (Uniphase, model 1135). The power of the diffracted beams (±1 and ±2 orders) was measured by using a power meter (Molect, Powermax