Optical and electrical properties of SnO₂ thin films after ultra-short pulsed laser annealing

D. Scorticati^{1a}, A. Illiberi^c, G.R.B.E. Römer^a, T. Bor^a, W. Ogieglo^a, M. Klein Gunnewiek^a, A. Lenferink^a, C. Otto^a, J.Z.P. Skolski^{a,b}, F. Grob^c, D.F. de Lange^d, A.J. Huis in 't Veld^{a,c},

^aUniversity of Twente, Faculty of Engineering Technology, Enschede, The Netherlands;

^bMaterials innovation institute (M2i), Enschede, The Netherlands;

^cTNO Technical sciences, 5600 HE Eindhoven, The Netherlands;

^dUniversidad Autónoma de San Luis Potosí, Facultad de Ingeniería, México.

ABSTRACT

Ultra-short pulsed laser sources, with pulse durations in the *ps* and *fs* regime, are commonly exploited for cold ablation. However, operating ultra-short pulsed laser sources at fluence levels well below the ablation threshold allows for fast and selective thermal processing. The latter is especially advantageous for the processing of thin films. A precise control of the heat affected zone, as small as tens of nanometers, depending on the material and laser conditions, can be achieved. It enables the treatment of the upper section of thin films with negligible effects on the bulk of the film and no thermal damage of sensitive substrates below. By applying picosecond laser pulses, the optical and electrical properties of 900 nm thick SnO₂ films, grown by an industrial CVD process on borofloat[®]-glass, were modified. The treated films showed a higher transmittance of light in the visible and near infra-red range, as well as a slightly increased electrical sheet resistance. Changes in optical properties are attributed to thermal annealing, as well as to the occurrence of Laser-Induced Periodic Surface Structures (LIPSSs) superimposed on the surface of the SnO₂ film. The small increase of electrical resistance is attributed to the generation of laser induced defects introduced during the fast heating-quenching cycle of the film. These results can be used to further improve the performance of SnO₂-based electrodes for solar cells and/or electronic devices.

Keywords: Ultra Short Laser Pulses, laser surface modification, SnO₂, thin film, LIPSS, optical transmittance

1. INTRODUCTION

Tin-dioxide (SnO₂), also known as stannic oxide, is a widely used and studied ceramic material [1]. Stoichiometric SnO₂ is an insulator, while shallow doping (i.e. with F or Sb) or small shifts from its perfect stoichiometry (i.e. SnO_{2-x}, with $x < 1$) associated with oxygen vacancies, lead to n-type semi-conductive behavior of the material. For this reason, optimized SnO₂ is grouped with a category of materials that combines high electrical conductivity with optical transparency. Such materials are usually referred to as Transparent Conductive Oxides (TCOs). They constitute an important component for opto-electronic devices [2].

Due to their low fabrication cost, SnO₂ thin films find application in different areas, including: glass coatings for thermal insulation, oxidation catalysts, gas sensor materials, flat panel displays, touch panels, flexible electronics, dye-sensitized solar cells (DSSC), thin film a-Si solar cells, light-emitting diodes (LEDs), etc. [2].

Strong interest for TCO materials led recent research to investigate the effects of post-deposition annealing by nanosecond (ns) pulsed lasers on the optical and electrical properties of different TCOs [3-10]. The use of rapid thermal laser annealing, as an alternative process to conventional furnace annealing, is a cost effective solution. It also reduces thermal damage on thermally sensitive low cost substrates (i.e. with low melting points) [3].

A next step in this research is the investigation of (thermal) effects of ultra-short pulsed lasers on the optical and electrical properties of TCOs. Compared to ns-pulses, ultra-short laser pulses in the pico- and femtosecond regime, can induce the same high surface temperatures of the film, but at a significantly lower energy input. This is advantageous for thin film processing where a precise control of the heat affected zone is necessary.

The present research aims to investigate the effects of picosecond laser irradiation on the optical and electrical properties of industrially optimized thin SnO₂ films.

¹ *D.Scorticati@utwente.nl; phone +31 53 489-3532; http://www.utwente.nl/ctw/wa/people/d._scorticati/

2. EXPERIMENTAL SETUP

2.1 Laser setup

An Yb:YAG (TruMicro 5050 of Trumpf) laser source was used. This laser source is characterized by a fixed pulse duration of 6.7 ps, 50 W maximum power output (P_{out}) at a central wavelength of 1030 nm (IR) and maximum pulse repetition frequency (f_p) of 400 kHz. The laser radiation was linearly polarized. The power density profile shows a nearly Gaussian distribution, $M^2 < 1.3$. The source is equipped with a pulse-picker, allowing the user to change the repetition frequency without affecting the energy per pulse. A Third Harmonic Generation (THG) unit was employed to convert the central wavelength to 343 nm (UV).

The diameter d of the focused laser beam on the surface was determined using the D^2 method [4] and was found to be 17 μm . Given the spot diameter d , the peak laser fluence F_0 -here defined as: $F_0 = (8E_0)/(\pi d^2)$, where E_0 is the pulse energy- was then calculated for single pulses. We also define the term overlap (OL) as the spatial overlap ratio of the laser spots of successive pulses as $OL = 1 - v/(d \cdot f_p)$, where v (m/s) denotes the velocity of the laser spot relative to the substrate, and f_p (Hz) the repetition frequency of the laser source. Note that, for increasing velocity, OL goes to zero, or will even become negative, indicating no spatial overlap between subsequent laser pulses on the surface.

A galvano-scanner (IntelliScan14 of Scanlab) was used to scan the focal spot at defined velocities (v) over the surface of the samples. A telecentric F-theta lens (Ronar of Linos) with 100 mm focal length was used to focus the laser beam. A polarizer ($\lambda/2$ plate) was used to rotate the linear polarization direction of the laser in order to study the effect of the polarization direction on the laser-induced surface modifications.

2.2 Analysis tools

Morphological inspection of surfaces was performed by High-Resolution Scanning Electron Microscopy (HRSEM, Merlin of Zeiss, equipped with X-Max detector of Oxford Instruments), as well as Atomic Force Microscopy (AFM, VEECO Dimension 3100 Atomic Force Microscope). Spectroscopic techniques were employed to determine the thickness (spectroscopic ellipsometry, using a variable angle rotating compensator spectroscopic ellipsometer M2000X from J.A. Woollam Co., with Xe arc discharge lamp as light source and light spot size ~ 2 mm) of the SnO_2 layers and their composition (Raman spectroscopy, home built apparatus described elsewhere [18]) before and after laser processing.

The optical properties (transmittance, reflectance and haze in transmittance) of the samples were measured in the near-ultraviolet, visible and near-infrared, by a UV-3600 Shimadzu spectrophotometer equipped with an integrating sphere.

The electrical properties were determined by using a Jandel universal 4-point probe and, finally, X-Ray Diffraction (XRD) (X'Pert, Panalytical equipped with a Co-K α source), was used to determine changes of the grain size and lattice structure after laser processing.

2.3 Samples

SnO_2 coatings of 900 nm thickness deposited by chemical vapor deposition (CVD) on 1 mm thick borofloat[®]-glass were used. The latter combination of thin SnO_2 layers on glass is meant for the production of a-Si thin film solar cells. Deposition of the samples was performed at TNO in the Netherlands using an industrial process [21].

3. RESULTS & DISCUSSION

3.1 Experimental procedure

The experimental procedure consisted of three steps. During the first step, “laser lines” were created by scanning the focal spot over the sample. Lines with varying pulse-to-pulse overlap (OL), number of overscans (OS) and fluence levels were produced. During these experiments the repetition frequency f_p was fixed at 100 kHz. After initial SEM analysis, to find laser conditions for damage-free (crack-free and no ablation) layers, we iterated this step by choosing finer variation of the processing parameters (OL, OS and fluence). The third and final step of the experimental procedure consisted of choosing one set of processing parameters from the second step to create areas composed of several parallel overlapping laser lines. Here the pitch (distance) between parallel lines was varied in order to obtain samples free of thermal damage.

Finally, three samples were selected for further analysis, namely:

- As-deposited (no laser treatment),
- Low fluence regime ($F_0 = 0.17 \text{ J/cm}^2$, 1 OS, OL=98.7%, pitch = 3 μm),
- High fluence regime ($F_0 = 0.26 \text{ J/cm}^2$, 1 OS, OL=98.7%, pitch = 3 μm).

These two laser processed samples were chosen based on their initial enhanced transparency by a first naked eye inspection.

3.2 Surface morphology, optical properties & electrical properties

3.2.1 Surface morphology

The surface morphology of the as-deposited sample is characterized by relatively big and sharp crystals, as is depicted in Fig. 1(a) and Fig 2(a). These crystals show low electric resistance and scatter light in the NIR-VIS-UV range. The latter enhances the so-called light trapping mechanism, as is required in thin film solar cells in order to enhance the short circuit current (I_{ss}). A similar morphology was observed in the sample processed at low laser fluence (Fig. 1 (b)). Here, only small dissimilarities were observed between the as-deposited material and the laser treated sample. Only small “cuts” on the edges of the crystals, as shown in Fig 1(d), were observed. In the case of the sample treated at high(er) laser fluence, a remarkable difference was observed. Here, small oriented nano-ripples were induced by the laser-material interaction (Fig. 1 (c) and (e)). These wavy structures, with amplitudes and periodicity Λ in the nanometer regime, are usually referred to as Laser Induced Periodic Surface Structures (LIPSSs) [11]. In particular, the LIPSSs observed in the sample are ascribed to a particular type, usually referred to as High Spatial Frequency LIPSSs (HSFLs) [16]. HSFLs are ripples with a spatial periodicity Λ significantly smaller than the wavelength of the laser radiation λ . Their periodicity can be as small as $\Lambda = 0.08 \lambda$ [17]. HSFLs have been reported to be orthogonal [16] or parallel [17] to the laser beam polarization. Similar to our laser conditions, HSFLs have been observed mostly for laser pulse durations in the femtosecond and picosecond regime. Moreover, they are reported by researchers upon irradiation with hundreds to thousands of laser pulses per spot and at fluence levels typically below the single-pulse ablation threshold [13].

To ascertain that the observed nano-ripples are indeed LIPSSs, an experiment was carried out where the polarization of the laser radiation was varied. That is because it is known [12] that the orientation of LIPSS depends on the polarization direction of the laser radiation. Using a $\lambda/2$ -plate the polarization was rotated. As is shown in Fig. 3, the orientation of the ripples follows the angle of the polarizer. This implies that the observed nano-ripples are indeed LIPSSs.

Further inspection of the surface morphologies was carried out by AFM measurements (see Fig. 2), revealing an increased roughness for the high fluence sample ($R_a = 42 \text{ nm}$), when compared to the other two samples ($R_a = 37 \text{ nm}$). To characterize the frequencies and periodicities of the surface morphology, a fast Fourier transform (FFT) of the HRSEM measurements was calculated (see Fig. 4) from the data (shown in Fig. 1 (a) and (b)). Fig. 4 shows that the nano-ripples are superimposed on the as-deposited surface morphology of the film, creating a “double-scale” roughness.

Figure 1. HRSEM pictures of the three samples: (a) as deposited (bar = 1 μm), (b) laser processed at low fluence (bar = 1 μm), (c) laser processed at high fluence (bar = 1 μm). Laser processing conditions as listed in section 3.1. (d) Detail of the small “cuts” visible at the edges of the crystals in the samples treated at low fluence (bar = 100 nm). (e) Enlarged view of the observed nanostructures (ripples) on the surface of the high fluence sample (bar = 200 nm).

Figure 2. AFM height measurements of the three samples: (a) as deposited, (b) low fluence, (c) high fluence. The gray scale (fixed from 0 to 500 nm) shows the height of the different morphologies. The dimension of the analyzed area was $3 \times 3 \mu\text{m}^2$. R_a values measured for (a) and (b) are 37 nm and for (c) 42 nm.

Figure 3. SEM images of nano-ripples, obtained at three different polarization directions of the laser radiation. The dashed arrow shows the scanning direction of the laser spot. The fixed solid black arrow shows the initial orientation of the LIPSSs. From left to right, the position of the polarizer was rotated from initial position (0°) to 36° and 72° respectively. As the polarization is rotated, the orientation of the ripples follows the polarization direction (white solid arrow).

Figure 4. Fast Fourier Transforms (FFT) of the as-deposited surface morphology (left) and of the high fluence sample (right), plotted in the K -space (normalized frequency domain). The ‘ring’ in the as-deposited material shows spatial isotropy of the analyzed structures. In the right picture, the ring can still be observed, but its oriented and elongated lobes reveal an orientation of the LIPSS, which are characterized by high spatial frequencies. It is known that the orientation of LIPSS depends on the polarization direction of the laser radiation. It can be concluded from these images that the LIPSSs are superimposed on the original morphology of the material.

3.2.2 Optical properties

When compared to the as-deposited samples, both laser treated samples displayed an enhanced transparency in the wavelength range relevant to photovoltaic cells (i.e. NIR-VIS-UV), see Fig. 6. These samples also showed a decreased reflectance, see Fig. 7.

Calculated linear absorption coefficients α from transmittance ($T = e^{-\alpha t}$, where t is the thickness of the layer), depicted in Fig. 8, show the effect of the laser treatment on the bulk optical properties of the layer. As expected after thermal annealing [3], SnO_2 becomes more transparent for wavelengths below 1100 nm. This points out that increased transmittance is not only the result of a reduced reflectance (due to morphological changes of the surface), but also the result of decreased absorptivity of the SnO_2 layer. Probably, also part of the decreased reflectance is due to changed bulk properties (i.e. reduced refractive index). Further analysis is ongoing, to confirm the latter.

Figure 5. Left: Measured transmittance (T), reflectance (R) and calculated absorption (A), with $A+T+R=1$, of the glass substrate. Negligible absorption is displayed for wavelengths over 380 nm. For this reason, the transmittance (Fig. 6) and haze (Fig. 9) of the samples are only shown for wavelengths over 380 nm.

Figure 6. (a): Transmittance of the three samples as function of the wavelength. Low transmittance in the long wavelength region over 1500 nm is expected due to strong absorption near the plasma frequency ω_p of SnO_2 . An increase of the transmittance of the high fluence sample indicates a slightly reduced carrier density due to the laser treatment. (b) Relative increase of transmittance of the low fluence and high fluence samples compared to the as-deposited material.

Figure 7. (a) Measured reflectance of the three samples as function of the wavelength. (b) Relative decrease of reflectance of the low fluence and high fluence samples compared to the as-deposited material.

Figure 8. Absorption coefficients α , calculated from transmittance T data in fig. 6 - i.e. $T = e^{-\alpha t}$, where t is the thickness of the layer). Absorption of the glass substrate was taken into account.

Of interest is the increased haze observed in the high fluence sample, while only small differences can be observed between the as-deposited film and the low fluence samples (see Fig. 9 (a)). The role of the morphology and the increased roughness R_a on the increase of haze are demonstrated by the increase of the absolute scattering level, as shown in Fig. 9 (b). The absolute scattering level of transmitted light from a textured interface is described by the haze parameter for transmittance, $H_T(\lambda)$, which is the ratio between the total and the diffused transmittance (haze).

Figure 9. (a) Measured haze for the three different samples. (b) Ratio between the haze in transmittance and the transmitted light at an angle of 90° $H_T(\lambda)$. This ratio higher at each wavelength in the case of the high fluence sample, compared to the as-deposited sample. This demonstrates the beneficial effect of LIPSSs on the haze.

A higher optical transmittance could be attributed to a thinning of the laser treated SnO_2 layer due to laser ablation. Spectroscopic ellipsometry (SE) was applied to measure the thickness of the samples, see Fig. 10. SE measurements showed negligible thinning of the SnO_2 layers. Hence, the increased transmittance of the laser treated samples is not simply due to thinning of the layers. Moreover, it can be concluded from this measurement that no significant reduction of the thickness between the three samples was induced by ablation. For the samples treated at high fluence, SE analysis also predicted an increased width of the transition from air towards full density bulk SnO_2 of about 30 nm. The latter matches with the cumulative height distributions from AFM data (see Fig. 11). Here, the slopes of the two curves of the samples differ and show a longer transition in the textured sample, in agreement with the SE prediction. This figure proves that the nano-ripples, superimposed on the original morphology, increase the transition region between air and SnO_2 , thus creating a smoother change from one refractive index to the other and thereby decreasing the reflectance.

Figure 10. Measured and fitted Psi and Delta parameters from SE. Data were fitted using the Cauchy relationship from 600 to 950 nm range, where the material was supposed to be highly transparent (setting the extinction coefficient $k = 0$). A good fit ($MSE < 20$) was provided for both the as deposited and the high fluence samples.

Figure 11. Cumulative height distributions from AFM data for as-deposited material and high fluence sample, showing the integrated solid/void ratio along a plane, parallel to the surface, starting from the outside and proceeding deep into the bulk material.

3.2.3 Electrical properties

Measurements of the electrical sheet resistances did not show differences (within the experimental error) between the as-deposited film and the film processed at low fluence, see table 1. Variations in the resistance between the as-deposited film and the film treated at low fluence is within the experimental error (possibly arising from thickness variations of the SnO_2 layers during deposition), while for the high fluence sample R_s is slightly higher than as-deposited. A slightly higher value was found for sheet resistance of the high fluence sample. The latter confirms the observed higher optical transmittance in the long wavelength range (see Fig. 6 (a)).

Table 1. Average values of the sheet resistance, measured by the 4 point probe technique, at several locations of the samples.

Sample	Sheet resistance R_s [$\Omega/\square$]
As-deposited	13.5 ± 2
Low fluence	14.5 ± 2
High fluence	16.1 ± 2

3.3 Bulk material properties: phase composition and grain structure

3.3.1 Phase composition

As the changes in absorptivity showed that the bulk properties of the film were modified by the laser treatment (see Fig. 8), Raman spectroscopy was employed to investigate the composition of the bulk material before and after the laser treatment. Fig. 12 reveals that only peaks (namely at 244, 293, 475, 500, 618, 630, 687 cm^{-1}) corresponding to SnO_2 in its rutile phase [14,19] were present in all samples. This implies that only small stoichiometry changes (SnO_{2-x} , with $x < 1$) are present and therefore it can be concluded from these measurements that only small stoichiometric shifts from SnO_2 are possible. And that neither SnO nor Sn_3O_4 phases are present in the thin film, neither before, nor after laser irradiation.

Figure 12. Raman spectra of the three samples as well as of the bare glass (substrate) used. The observed peaks correspond to the SnO_2 spectrum.

3.3.2 Micro structure

From exploratory XRD measurements (see Fig. 13), the average grain sizes of the crystallites were determined from the widths and shapes of the reflections. Here, employing the $\{110\}$ and $\{220\}$ SnO_2 reflections, the contribution to the broadening from small diffracting crystallites was determined from the respective integral breadths. The contribution to the broadening from the instrument itself was removed. On average, the crystallite size is in the range of 70 – 150 nm for the as-prepared sample and approximately 100 nm for the other samples, showing no significant differences between the as deposited material and the laser treated samples. However, the structural broadening of the second order, $\{220\}$ SnO_2 reflection is larger than that of the first order $\{110\}$ reflection for all samples. The latter indicates the presence of additional micro-strain sources. The contribution of these micro-strain sources increases with the amount of fluence. Another indication for the presence of micro-strain sources is the highly anisotropic character of the line broadening as a function of the reflection $\{hkl\}$, which is not expected if all structural broadening is due to the finite size of the diffracting crystallites only. Further study is currently carried out in this direction. It is not unlikely that the observed micro-strain sources also influence the electrical properties of the samples.

Figure 13. XRD measurements of the three different samples using Co radiation. Small differences can be observed between the as-deposited and the low fluence samples, where the relative numbers of counts for different peaks start to differ. More evident are the differences between the as-deposited and the high fluence samples. Analysis of the peaks revealed a broadening in the high fluence sample, indicating a lower crystalline quality (i.e. smaller size of the grains, more crystallographic defects) with respect to the as-deposited material.

3.4 Overall efficiency of the treated SnO₂

A way to characterize the overall performance of the SnO₂ layers is via the so called figure of merit (ϕ), combining the total contribution of the increased optical transmittance and the increased sheet resistance. A common formula for the figure of merit is present in literature for TCO layers. This figure is meant for the production of photovoltaic devices [20] and reads:

$$\phi = T^{10}/R_{sh} \quad [1]$$

where T is the average transmittance in the wavelength range from 400 to 1100 nm.

An increase of the ϕ in the laser treated layers is clearly shown from calculated data (see table 2).

Table 2. Figure of merit ϕ of the three different samples and their ratio to the ϕ of the as-deposited film.

	As-deposited film	Low fluence sample	High fluence sample
$\phi \times 10^3 [\Omega^{-1}]$	2.55	3.05	4.07
$\phi/\phi_{\text{as deposited}}$	1	1.20	1.59
Improvement [%]		20	59

4. CONCLUSIONS

Thin SnO_2 films on Borofloat[®]-glass were irradiated by 6.7 ps UV laser pulses using two different laser conditions: (i) $F_0 = 0.17 \text{ J/cm}^2$, 1 overscan, overlap=98.7%, line-to-line pitch = 3 μm , $f_p = 100 \text{ kHz}$, and (ii) $F_0 = 0.26 \text{ J/cm}^2$, 1 overscan, overlap = 98.7%, pitch = 3 μm , $f_p = 100 \text{ kHz}$. Nano-ripples were found on samples irradiated at the higher fluence level. It was shown that these nano-structures are Laser Induced Periodic Surface Structures (LIPSSs). An increased optical transparency was found in the wavelength range from 380 to 1100 nm -i.e. the working range of photovoltaic cells. Increased optical transmission was found not due to a thinning of the layers after the laser treatment, but due to morphological changes on the surface, as well as the effect of the annealing on the bulk properties of the treated SnO_2 . Both combined result in a decrease of the reflectivity, and also in a lower absorption within the annealed layer.

It was shown that the changed morphology also resulted in an increase of the absolute scattering level, which is strongly dependent on the small-scale LIPSSs roughness superimposed on roughness of the as-deposited layer. This latter result can be used to further optimize the SnO_2 layer.

Measurement of the sheet resistance of the films revealed a light detrimental effect of the picosecond laser radiation on the sheet resistance of the SnO_2 layer; a detailed explanation of these effects on the electrical properties needs further study.

The overall contribution of the changes in optical and electrical properties was evaluated by using a figure of merit usually applied for TCO layers for solar cells application, showing a 20 to 59% improvement in the laser treated samples compared to the as-deposited sample.

ACKNOWLEDGEMENTS

This work was done within the Advanced Dutch Energy Materials Innovation Lab (ADEM) program, funded by the Dutch Ministry of Economic Affairs, Agriculture and Innovation. The authors want also to acknowledge Dr. P. Schön for his expertise and comments on AFM measurements.

REFERENCES

- [1] M. Batzill et al., The surface and materials science of tin oxide, *Prog. In Surf. Science* 79, 47-154 (2005).
- [2] R. Gordon, Criteria for choosing transparent conductors, *MRS Bulletin*, **25**(8), 52-57 (2000).
- [3] S. F. Tseng et al., Mechanical and optoelectric properties of post-annealed fluorine-doped tin oxide films by ultraviolet laser irradiation, *Appl. Surf. Science* 257, 7204-7209 (2011).
- [4] W. Chung, et al., Room temperature indium tin oxide by XeCl excimer laser annealing for flexible display, *Thin Solid Films* 460, 291-294 (2004).
- [5] J.J. Kim et al., Characteristics of laser-annealed ZnO thin film transistors, *Thin Solid Films* 518, 3022-3025 (2010).
- [6] G. Legeay et al., Excimer laser beam/ITO interaction: from laser processing to surface reaction, *Phys. Stat. Sol.*, 5, 3248-3254 (2008).
- [7] C.W. Cheng et al., Patterning crystalline indium tin oxide by high repetition rate femtosecond laser-induced crystallization, *Thin Solid Films*, 518, 7138-7142 (2010).
- [8] M.F. Chen et al., Effects of laser-induced recovery process on conductive property of SnO₂:F thin film, *Mater. Sci. Eng. B* 176, 127-131 (2011).
- [9] B.D. Ahn et al., Effect of excimer laser annealing on the performance of amorphous indium gallium zinc oxide thin-film transistors, *Electrochem. Solid-State Lett.* 12, H430-H432 (2009).
- [10] J. Chae et al., High-resolution, resistless patterning of indium-tin oxide thin films using excimer laser projection annealing process, *Mater. Lett.* 64, 948-950 (2010).
- [11] W. M. Birnbaum, Semiconductor surface damage produced by ruby lasers, *J. Appl. Phys.* **36**(11), 3688-3689 (1965).
- [12] M. Huang, Origin of laser-induced near-subwavelength ripples: interference between surface plasmons and incident laser, *ACS Nano*, **3**(12), 4062-4070 (2009).
- [13] D. Dufft et al., Femtosecond laser-induced periodic surface structures revisited: A comparative study on ZnO, *J. of Appl. Phys.* 105, 034908/1-9 (2009).
- [14] R. S. Katiyar et al., Dynamics of the rutile structure III. Lattice dynamics, infrared and Raman spectra of SnO₂, *J. Phys. C: Solid St. Phys.*, 4., 2421-2431 (1971).
- [15] V.I. Kaydanov et al., Studies of Band Structure and Free-Carrier Scattering in Transparent Conducting Oxides Based on Combined Measurements of Electron Transport Phenomena, NREL/CP-520-29064 (2000).
- [16] A. Borowiec et al., Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses, *Appl. Phys. Lett.*, **82**(35), 4462-4465 (2003).
- [17] J. Bonse et al., Sub-100-nm laser-induced periodic surface structures upon irradiation of titanium by Ti:sapphire femtosecond laser pulses in air, *J. Appl. Phys. A*, 110(3), 547-551 (2012).
- [18] V. V. Pully et al., Hybrid Rayleigh, Raman and two-photon excited fluorescence spectral confocal microscopy of living cells, *J. of Raman Spectroscopy*, **41**(6), 599-608 (2010).
- [19] M. Ristić et al., Dependence of nanocrystalline SnO₂ particle size on synthesis route, *J. of Non-Crystalline Solids*, 303, 270-280 (2002).
- [20] G. Haacke, New figure of merit for transparent conductors, *J. Appl. Phys.* 47, 4086-4089 (1976).
- [21] A. de Graaf et al., Development of atmospheric pressure CVD processes for high quality transparent conductive oxides, *Energy Procedia* 2, 41-48 (2010).