Applied Surface Science 256 (2010) 7446–7450

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of mesh patterning with UV pulsed-laser on optical and electrical properties of ZnO/Ag–Ti thin films

K.S. Kao [a], D.L. Cheng [a,*], S.H. Chang [a], P.T. Hsieh [b], H.S. Chin [c], H.K. Lin [d]

[a] Department of Computer and Communication, SHU-TE University, 59, Hengshan Rd., Yanchao, Kaohsiung County, Taiwan
[b] Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan, Taiwan
[c] Opto-Electronics System Section Metal Industries Research and Development Center, Kaohsiung, Taiwan
[d] Laser Application Technology Center/Industrial Technology Research Institute South, Liujia Shiang, Taiwan

ARTICLE INFO

Article history:
Received 11 February 2010
Received in revised form 4 May 2010
Accepted 25 May 2010
Available online 2 June 2010

Keywords:
Transparent conducting oxide
ZnO
Ag–Ti
Laser patterning

ABSTRACT

In this study, the ZnO/Ag–Ti structure for transparence conducting oxide (TCO) is investigated by optimizing the thickness of the Ag–Ti alloy and ZnO layers. The Ag–Ti thin film is deposited by DC magnetron sputtering and its thicknesses is well controlled. The ZnO thin film is prepared by sol–gel method using zinc acetate as cation source, 2-methoxiethanol as solvent and monoethanolamine as solution stabilizer. The ZnO film deposition is performed by spin-coating technique and dried at 150 °C on Corning 1737 glass. Due to the conductivity of ZnO/Ag–Ti is dominated by Ag–Ti, the sheet resistance of ZnO/Ag–Ti decrease dramatically as the thickness of Ag–Ti layer increases. However, the transmittances of ZnO/Ag–Ti become unacceptable for TCO application after the thickness of Ag–Ti layer beyond 6 nm. The as-deposited ZnO/Ag–Ti structure has the optical transmittance of 83% @ 500 nm and the low resistivity of 1.2×10^{-5} Ω-cm. Furthermore, for improving the optical and electrical properties of ZnO/Ag–Ti, the thermal treatment using laser is adopted. Experimental results indicate that the transmittance of ZnO/Ag–Ti is improved from 83% to 89% @ 500 nm with resistivity of 1.02×10^{-5} Ω-cm after laser drilling. The optical spectrum, the resistance, and the morphology of the ZnO/Ag–Ti will be reported in the study.

1. Introduction

Transparent conducting oxide (TCO) has been widely used in solar cells, optoelectronics, touch panel, liquid crystal display and various types of flat panel displays [1,2]. Indium tin oxide (ITO) is widely used for transparent conducting oxide (TCO) because of its good transparence and conducting, however, indium resources are supposed to be exhausted in the next few decades [3]. Nowadays, zinc oxide (ZnO) has attracted much attention as transparent conductive films. For practical applications, undoped ZnO films are inferior to indium or tin-based oxide films [4]. ZnO with impurity doped and metal-based ZnO multilayer structures are reported as good transparent conducting electrodes in the replacement of ITO [5–8]. For increasing the mobility with moderate doping in ZnO will get better conductivity and without compromising the transparency [9]. It is worthy to mention that ZnO with heavy doping, the transparency degrades due to the increased free carrier absorption and carrier mobility decreased results from the impurities scattering [10].

The multilayer TCO structure is another usual method for the improvement of the conductivity. The properties of multilayer structure are strongly dependent on the metal layer [11]. Silver is a popular metal used in various multilayer structures because it possesses the lowest resistivity of 1.6×10^{-6} Ω-cm among all metals. The ultra-thin film of activated metal likes silver is extremely easy to be oxidized and therefore decline its conductivity and transparency. Chen et al. proposed the Ag–Ti alloy film for stabilize the surface morphology of ultra-thin silver films [12]. The composition of ZnO and Ag–Ti multilayer structure is therefore focused in this study. In addition, the optical properties of ZnO are varied with specific thermal treatment [13–15]. The advantages of laser treatment include wavelength selection for specify material, high precision working area, local district temperature coverage and thus a variety of substrates can be used. The advantages of laser treatment include wavelength selection for specify material, high precision working area, local district temperature coverage and thus a variety of substrates can be used. Therefore, the thermal process with laser annealing affects the optical and electrical properties of ZnO/Ag–Ti structure is investigated. The optical spectrum, the resistance, and

* Corresponding author. Tel.: +886 7 6158000x4811; fax: +886 7 6158000x4899.
E-mail addresses: dlcheng@stu.edu.tw, dlcheng@mail.stu.edu (D.L. Cheng).

0169-4332/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.05.088

Table 1
Deposition parameters of Ag–Ti thin films.

Deposition system	DC sputter
Target	Ag–Ti
Substrate-to-target distance (mm)	80
Base pressure (Torr)	5×10^{-6}
DC power (W)	10
Deposition pressure (mTorr)	6
Substrate temperature (°C)	R.T.
Ar flow rate (sccm)	7

the morphology of the ZnO/Ag–Ti structure are presented in this study.

2. Experimental procedure

The ZnO/Ag–Ti thin films are prepared on glass (corning 1737F) by two-step coating. At first, the Ag–Ti thin film is deposited by sputtering and following the ZnO thin film is prepared with sol–gel method and spin coating. The Ag–Ti alloy is used as metal target and then the film is deposited with a DC sputter. The base pressure of system was evacuated to 5×10^{-6} Torr using the diffusion pump. The working pressure and gas flow of argon (Ar) were kept at 6 mTorr and 7 sccm. The distance between the target and substrate was fixed at 80 mm. The DC power was hold as low as 10 W to sustain the plasmas for the purposes of high accuracy of Ag–Ti film thickness. The detail sputtering parameters for Ag–Ti thin films are shown in Table 1.

Fig. 1 shows the flow chart of the preparation of the ZnO solution and the heat-treated condition of the ZnO film. Zinc acetate dihydrate (ZnAc), 2-methoxyethanol and monoethanolamine (MEA) is used as a starting material, solvent and stabilizer, respectively. ZiAc was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio MEA:ZnAc is 1:1. The solution was stirred at 120 °C for 1 h, and then refluxed at 80 °C for 1 h to yield a clear and homogeneous solution. The solution is uniform spread on substrate using spin coater and then dried at 150 °C for 1 h to evaporate the solvent and remove organic residuals. For the spin coating process under fixed rotation speed, the film thickness is proportional to its stick coefficient. The film thickness will increased as the concentration of the solution raised. The thickness of ZnO films were controlled using various mol concentration of solutions. For the purpose of laser patterning, a Q-switched 355 nm

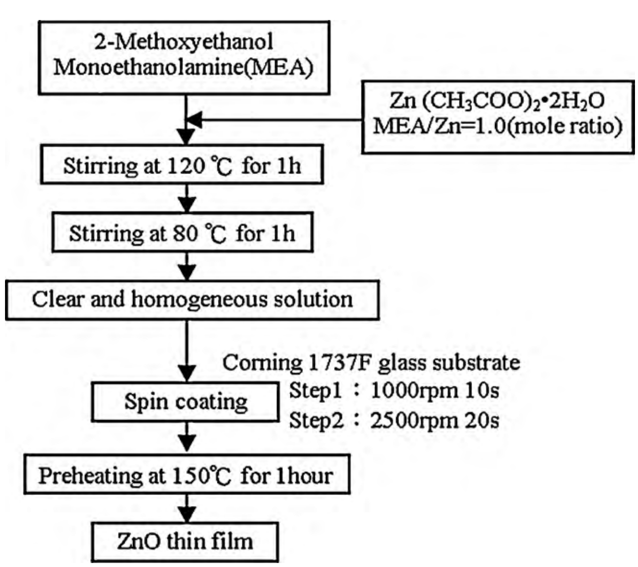

Fig. 1. The flow chart of ZnO film preparation.

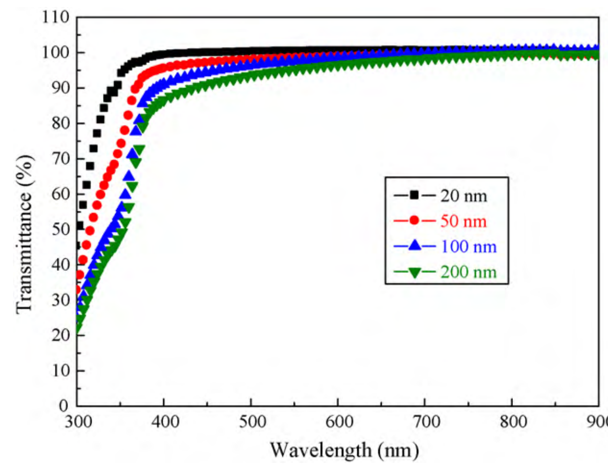

Fig. 2. Transmittance of ZnO thin films with various thicknesses.

laser (DPSS Lasres Inc.) is adopted which has a pulse duration of 30 ns and a stability of less than 5%, a scanner (Scanlab) with an the focus of a 53 mm focal length lens and XYZ stage. The power density of laser for TCO patterning by DPSS laser system was carried out from 9.9 MW/cm^2 to 45.3 MW/cm^2.

Sheet resistance of ZnO/Ag–Ti was measured using 4-point probe method. The optical transmittance was measured using a UV–vis–NIR spectrophotometer (V-570, JASCO) in the wavelength range from 300 nm to 900 nm. Surface images were observed by optical microscope and cross-section images were observed using field emission scanning electron microscope (FE-SEM).

3. Results and discussion

Because of the optical property of ZnO thin film is great influenced by its thickness. Various concentrations of 0.2–0.8 M of ZnO gel were prepared in order to fabricate distinct thicknesses of ZnO thin films. The thickness of ZnO thin film is increased from 20 nm to 200 nm with the concentration of ZnO gel increased from 0.2 M to 0.8 M. There are three phenomena occurred when the light pass through a media: reflection, refraction and absorption. The absorption means the intensity attenuation of light when it propagated in a media. For the formula of intensity attenuation of the light propagation:

$$\frac{I(x)}{I(0)} = \exp(-\alpha x), \quad (1)$$

where the α is the attenuation coefficient and x is the propagation distance.

The transmittances of ZnO thin films with various thicknesses are shown in Fig. 2. It is apparently that the transmittance reached to 98% for the wavelength of 500 nm for ZnO film thickness thinner then 50 nm. The transmittance decreased as the ZnO thickness increased [16,17]. In order to obtain optimal transmittance of ZnO/Ag–Ti thin film, ZnO thin film with the thickness of 20 nm is determined.

The Ag–Ti thin film was deposited on the glass by DC sputtering with the deposition rate of 1 Å/s. The thickness of the Ag–Ti layer was varied from 3 nm to 11 nm by modulating the sputtering time. Fig. 3 illustrates the transmittance and resistivity of Ag–Ti thin film with various thicknesses of Ag–Ti layers. The transmittance is measured at the specific wavelength of 500 nm. The transmittance for the Ag–Ti thin film of 3 nm is 68% and then increased with the increasing thickness and reached to 80% for the thickness of 6 nm. After the thickness was exceeded 6 nm, the transmittance decreased. The transmittance fell to 59% with Ag–Ti thickness of

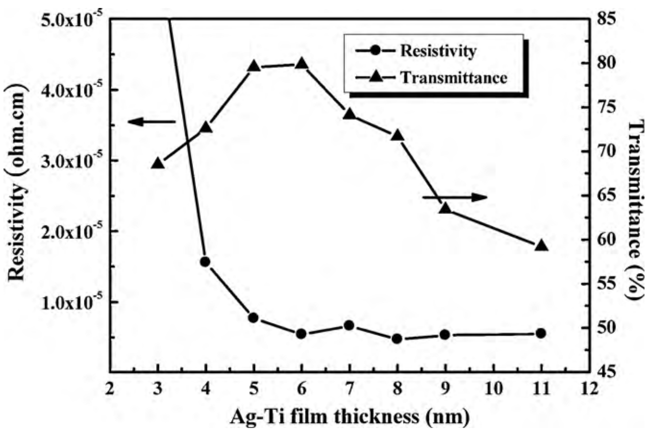

Fig. 3. Dependence of sheet resistances and transmittances of various Ag–Ti film thicknesses (Transmittance is measured at wavelength of 500 nm).

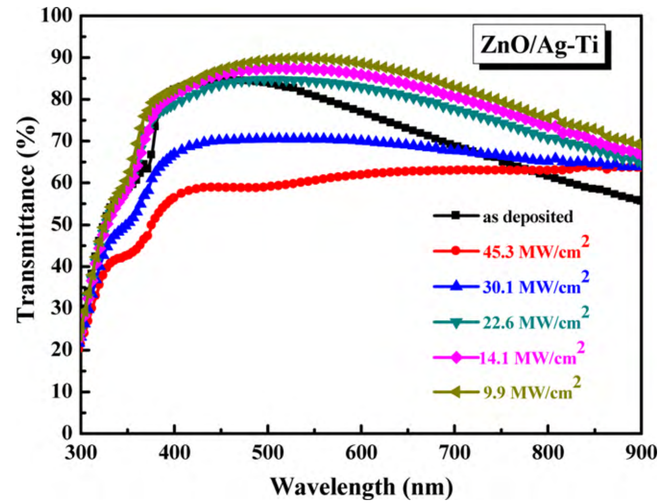

Fig. 5. Transmittance of ZnO/Ag–Ti thin films with various laser power densities.

11 nm. It is obviously that a critical thickness of the Ag–Ti layer was required for obtaining a superior transmittance. Besides, the resistivity of the Ag–Ti film deposited for 3 nm is 2.5×10^{-4} Ω-cm. The resistivity of Ag–Ti layer decreased from 2.5×10^{-4} Ω-cm to 5.5×10^{-6} Ω-cm with the thickness increased from 3 nm to 11 nm. As the thickness increased to 4 nm, the resistivity abrupt decreased to 1.6×10^{-5} Ω-cm. The phenomenon is attributed to a transition from a formation of distinct islands of tiny Ag–Ti to a continuous layer with adequate thickness. According to Fahland [18], only a continuous metal layer exhibits good electrical conductivity. The 4 nm of Ag–Ti film is the critical thickness for conducting since its resistivity dropped abruptly. As the Ag–Ti layer is thicker than the critical thickness, the transmittance decreased and the reflectance increased because the function of the Ag–Ti layer turns to a mirror [19]. The absorption and reflection of light is owing to the inter-reaction between the electromagnetic wave and sufficient free electron. Under the consideration of acceptable transmittance and resistivity, the Ag–Ti layer of 6 nm is selected. Not until the ZnO thin film thickness of 20 nm and the Ag–Ti thin film thickness of 6 nm were determined, the ZnO/Ag–Ti multilayer thin film was accomplished.

For improving the properties of ZnO/Ag–Ti thin film in TCO application, the UV laser with wavelength of 355 nm is adopted. Various laser conditions are generated and treated on the ZnO/Ag–Ti thin film and its optical and electrical properties are studied. Due to the focusing beam of laser, the beam profiles are varied with defocusing length. The laser power density is corresponding to the specific effective working area of laser beam. Fig. 4 shows the surface of the ZnO/Ag–Ti films treated with various laser power density investigated using optical microscope. As it shown clearly that the treated areas are identified as laser's focus and the areas vanished as the power density decreased. There is no obviously trace until the power density of 9.9 MW/cm^2. The transmittance spectra of ZnO/Ag–Ti treated with various power densities are shown in Fig. 5. The transmittance increased from 83.5% to 89.5% (@ wavelength 500 nm) as the power density increased to 9.9 MW/cm^2. However, the ZnO/Ag–Ti films treated with energy exceeding 22.6 MW/cm^2 will cause damage to the structure and result in irretrievable transmittance destroying.

Fig. 6 shows the surface and cross-section images of the ZnO/Ag–Ti thin films. It is observed that hollows are appeared for the sample treated with the laser power density of 35.7 MW/cm^2. The visible non-destructive and smooth surface is obtained under the laser power density of 20.4 MW/cm^2. Moreover, the transmittance spectra are taken as illustration for optical properties evaluation. The spectra shown in Fig. 7 executed in the UV–VIS–NIR wavelength range (300–900 nm). Two representative values of laser power densities of 20.4 MW/cm^2 and 35.7 MW/cm^2 are

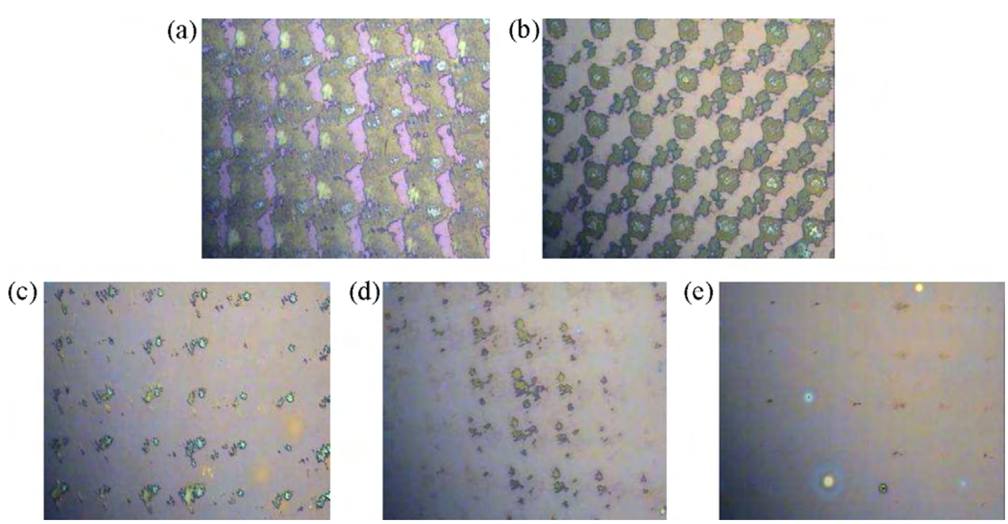

Fig. 4. The photograph of the surface of the ZnO/Ag–Ti films treated with various laser power densities of (a) 45.3 MW/cm^2, (b) 30.1 MW/cm^2, (c) 22.6 MW/cm^2, (d) 14.1 MW/cm^2 and (e) 9.9 MW/cm^2.

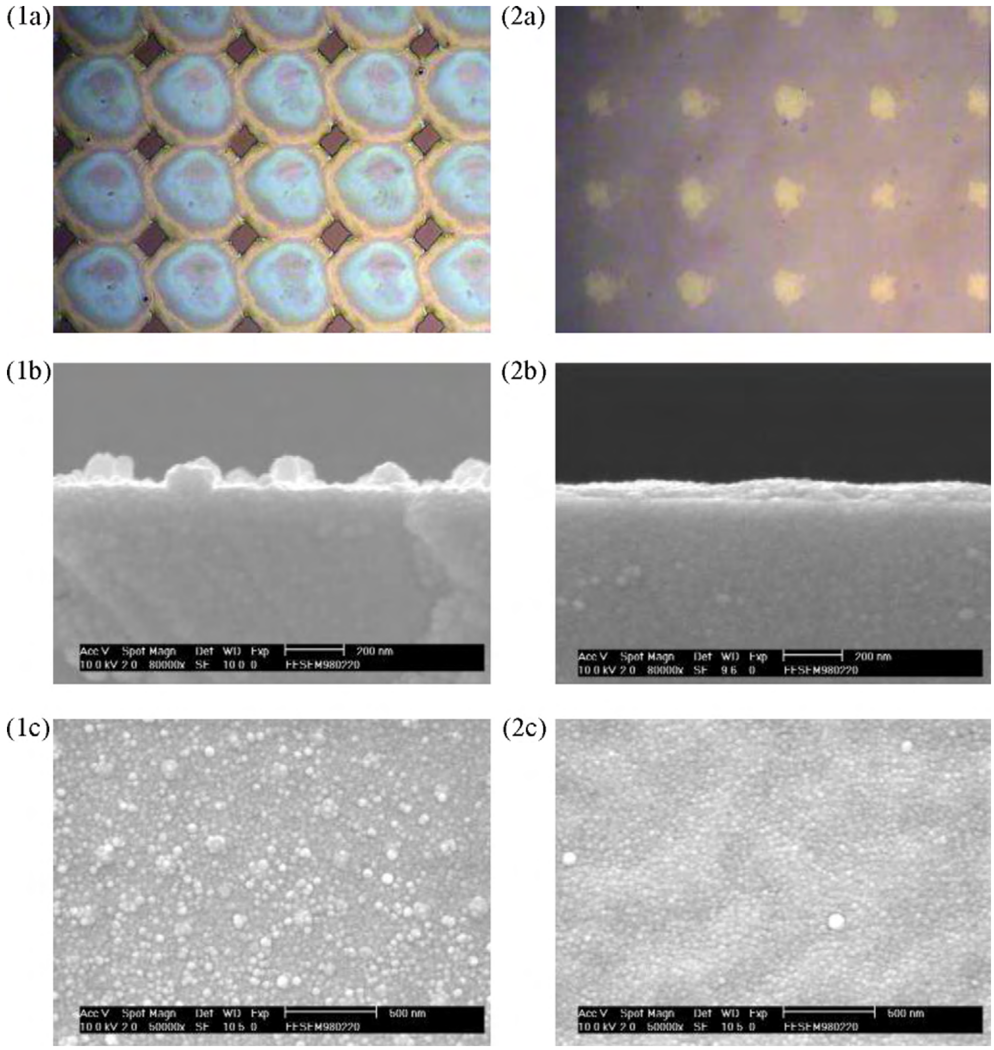

Fig. 6. The photographs of the ZnO/Ag–Ti films treated with laser power densities of (1) 35.7 MW/cm^2 and (2) 20.4 MW/cm^2.

adopted for reference. As it shown clearly in Fig. 7, the overall transmittance of ZnO/Ag–Ti thin film treated with power density of 35.7 MW/cm^2 is worse then the as-deposited. On the contrary, transmittance of sample treated with power density of 20.4 MW/cm^2 better then the as-deposited one proves that the recrystalline and uniform of ZnO/Ag–Ti is facilitated by suitable laser annealing. The sheet resistance of the sample treated with power density of 22 MW/cm^2 maintained the same as the as-deposited.

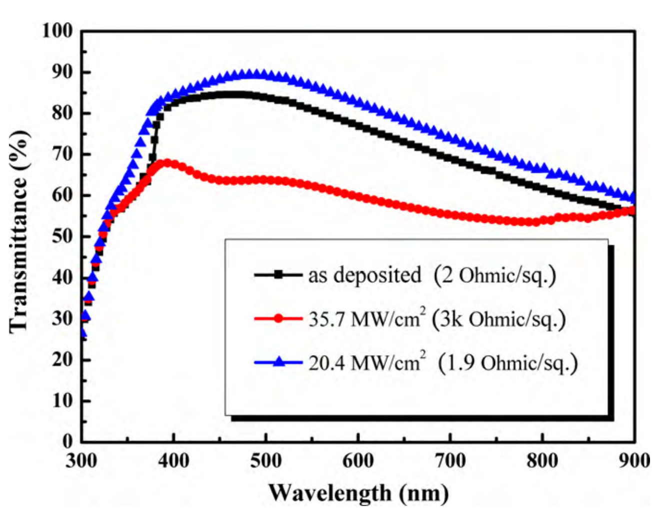

Fig. 7. Transmittance of ZnO/Ag–Ti thin films treated with laser power densities of 35.7 MW/cm^2 and 20.4 MW/cm^2.

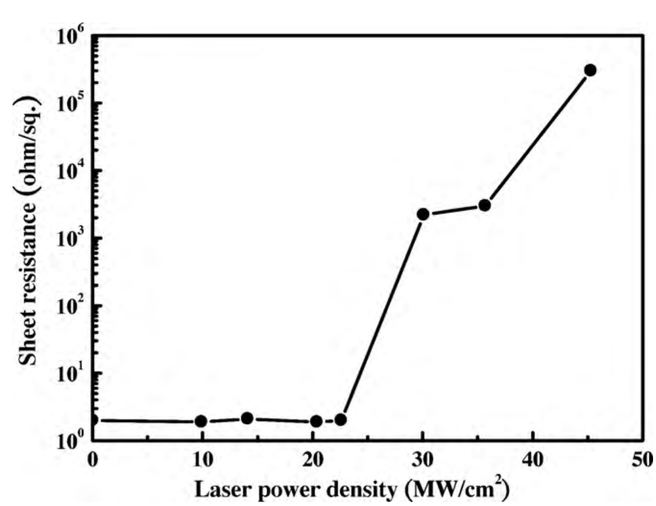

Fig. 8. The electrical properties of the ZnO/Ag–Ti films treated with various laser power densities.

The change of electrical properties of the films before and after the laser treatment has illustrated in Fig. 8. The unacceptable sheet resistance of the sample treated with power density of 30 MW/cm^2 shows the continuous of Ag–Ti was ruin by laser.

4. Conclusion

The essential optical and electrical properties of ZnO/Ag–Ti structure are dominant by Ag–Ti film. The acceptable transmittance of 79% at 500 nm and conductivity of 5.4×10^{-6} Ω-cm are corresponding to the 6 nm Ag–Ti film. For the prevention of light reflection and oxidization of Ag–Ti, an upper layer of ZnO is introduced as protection. The transmittance of 83.5% at 500 nm of ZnO/Ag–Ti structure is obtained as expected; however, the resistivity of the sample is harm. For pursuing better TCO performance, the laser treatment has put into practice. The outstanding transmittance of 89.5% at 500 nm and conductivity of 1.02×10^{-5} Ω-cm of the ZnO/Ag–Ti structure is fabricated. A TCO thin film construct with ZnO and Ag–Ti shows good transmittance and conductivity is achieved.

Acknowledgements

This study was supported by the Metal Industries Research and Development Center (MIRDC) and the National Science Council, Taiwan, R.O.C. under contract no. NSC 96-2221-E-366-006.

References

[1] M.K. Puchert, A. Hartmann, R.N. Lamb, J.W. Matin, J. Mater. Res. 11 (1996) 2463.
[2] H.S. Ullal, K. Zwaibel, B. Von Roedern, Proceedings of the 29th IEEE Photovolatic Specialists Conference, 2002, p. 472.
[3] S. Kobayakawa, Y. Tanaka, A. Ide-Ektessabi, Nucl. Instrum. Methods Phys. Res. B 249 (2006) 536.
[4] S.S. Lin, J.L. Huang, D.F. Lii, Surf. Coat. Technol. 190 (2005) 372.
[5] M. Bender, W. Seelig, C. Daube, H. Frankenberger, B. Ocker, J. Stollenwerk, Thin Solid Films 326 (1998) 67.
[6] Y. Igasaki, H. Saito, Thin Solid Films 199 (1991) 223.
[7] T. Komaru, S. Shimizu, M. Kanbe, Y. Maeda, T. Kamiya, C.M. Fortmann, I. Shimizu, Jpn. J. Appl. Phys. 38 (1999) 5796.
[8] T.Y. Ma, D.K. Shim, Thin Solid Films 410 (2002) 8.
[9] E.J.J. Martin, M. Yan, M. Lane, J. Ireland, C.R. Kannewurf, R.P.H. Chang, Thin Solid Films 461 (2004) 309.
[10] X. Wu, T.J. Coutts, W.P. Mulligan, J. Vac. Sci. Technol. A 15 (1997) 1057.
[11] E. Bertran, C. Corbella, M. Vives, A. Pinyol, C. Person, I. Porqueras, Solid State Ionics 165 (2003) 139.
[12] S.W. Chen, C.H. Koo, Mater. Lett. 61 (2007) 4097.
[13] R.J. Winfield, L.H.K. Koh, S. O'Brien, G.M. Crean, Appl. Surf. Sci. 254 (2007) 855–858.
[14] T. Sameshima, S. Usui, M. Sekiya, IEEE Electron Dev. Lett. EDL-7 (1986) 276.
[15] T. Nagase, T. Ooie, J. Sakakibara, Thin Solid Films 357 (1997) 151.
[16] D.R. Sahu, J.L. Huang, Thin Solid Films 515 (2006) 876–879.
[17] C. Guilleĭn, J. Herrero, Vacuum 84 (2010) 924–929.
[18] M. Fahland, P. Karlsson, C. Charton, Thin Solid Films 392 (2001) 334.
[19] X. Liu, X. Cai, J. Qiao, J. Mao, N. Jiang, Thin Solid Films 441 (2003) 200.