

# Journal of Nanophotonics

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**Abstract.** Al-doped ZnO (AZO) films were deposited on glass and polycarbonate (PC) at room temperature by using pulsed Nd:YAG laser at 355 nm. AZO thin films were obtained for both substrates at laser fluences from 2 to 5 J/cm<sup>2</sup> in O<sub>2</sub> partial pressure of 2.1 Pa. The effects of laser fluence on the structural, electrical, and optical properties of the films were investigated. The films with lowest resistivity and highest transmittance have been obtained at 2 J/cm<sup>2</sup>. The resistivities were  $2.29 \times 10^{-3} \Omega \text{ cm}$  for AZO on glass and  $1.49 \times 10^{-3} \Omega \text{ cm}$  for AZO on PC. With increasing laser fluence, the deposited films have lower crystallinity, higher resistivity, and smaller optical bandgap. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JNP.8.084091](https://doi.org/10.1117/1.JNP.8.084091)]

**Keywords:** zinc oxide; Al-doped zinc oxide; pulsed laser deposition; laser ablation; transparent conducting oxide; polycarbonate; flexible electronics.

Paper 14045SS received Apr. 1, 2014; revised manuscript received Aug. 29, 2014; accepted for publication Sep. 19, 2014; published online Oct. 10, 2014.

## 1 Introduction

Al-doped ZnO (AZO) films are promising transparent conducting oxides (TCOs) that can be used in optoelectronics devices. Among the various deposition methods, pulsed laser deposition (PLD) offers the capability to produce vapor/species with a wide range velocity and energy for films growth. This is achieved by using lasers with different photon energy and fluence for ablation. Subsequently, the generated plasma plume can be regulated by controlling the background gas or applying external magnetic field. Finally, materials growth by the impinging species progresses with or without additional thermal energy. In addition, heating of substrate during PLD enables crystalline ZnO nanostructures or nanorod formation from 550°C to 700°C.<sup>1,2</sup> AZO nanostructure films were reported to achieve resistivity in the order of  $10^{-4} \Omega \text{ cm}$  at about 300°C to 400°C.<sup>3,4</sup> However, low substrate temperature is desired to enable the growth of TCO on polymer substrates for flexible electronics. At the temperature range <300°C, crystallinity of the films decreases, although often accompanied by an increase in optical transparency.<sup>5</sup> Thus, optimization in deposition conditions at a low substrate temperature will be needed to preserve the resistivity and optical transparency of AZO films. First, the type of dopant and its concentration play a major role; a resistivity of  $10^{-4} \Omega \text{ cm}$  has been reported with Al- or Ga-doped ZnO films when deposited at 230°C.<sup>6</sup> The same range of resistivity has been achieved by carefully optimizing the background pressure at 200°C,<sup>7</sup> at 300°C,<sup>8</sup> or by use of an oxygen radical in place of oxygen gas for deposition at room temperature.<sup>9</sup> In addition, regulating the content of the laser produced plasma plume externally has enabled the growth of the lowest resistivity AZO film ( $8.54 \times 10^{-5} \Omega \text{ cm}$ ).<sup>10</sup> External magnetic field was applied to the plume during deposition. On the other hand, several attempts have been reported in order to

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accommodate polymer substrates. One of the best results for the growth of AZO on polyethylene terephthalate (PET) and polyethersulfon (PES) polymer substrate was obtained by using PLD with added beam-rastering function, where the resistivities in the range of  $10^{-4}$   $\Omega$  cm are achieved.<sup>11</sup> Recently, AZO films with resistivity  $\sim 10^{-3}$   $\Omega$  cm have also been achieved by pulsed excimer laser deposition on PET substrates at room temperature at laser fluence range of 1.5 to 3.2 J/cm<sup>2</sup>.<sup>12</sup> As laser fluence increased, the roughness increased and the optical bandgap decreased. To date, most of the depositions were performed with 193 and 248 nm lasers; there were only a few reports on Nd:YAG laser deposition of AZO. AZO thin films on polycarbonate (PC) were grown by using Nd:YAG laser (1064 nm) at room temperature and 100°C.<sup>13</sup> In total, 75% transmittance was obtained for the films, but the resistivity was not measured. In another report, 355-nm laser was used for deposition of AZO on a glass substrate at 25°C and 200°C, but the films have higher resistivity than those deposited at shorter wavelength, attributed to lower absorption at 355 nm.<sup>14</sup> However, no in-depth studies have been reported.

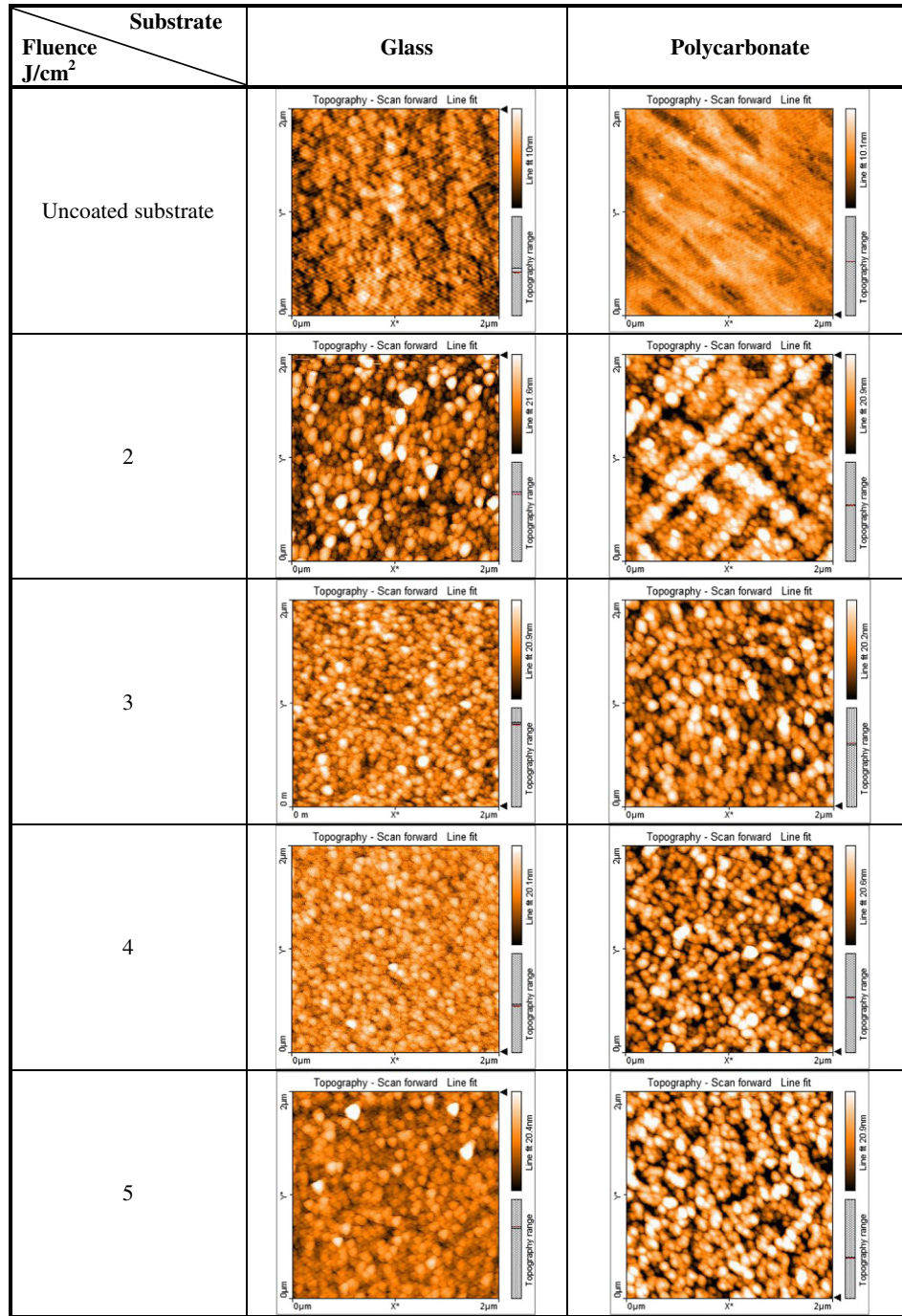
In addition to substrate temperature, polymeric substrate subjected to growth conditions is more susceptible to damage by the impinging species as compared with glass substrate. For example, femtosecond laser has been reported to produce highly energetic species that can disrupt the film property.<sup>15</sup> Thus, room temperature deposition together with low to moderate energetic plasma condition would be ideal for deposition on polymer substrates. In this work, a 355-nm laser, which is expected to produce less energetic plasma, was used for deposition of AZO thin films onto glass and PC substrates. A fluence range (1 to 5 J/cm<sup>2</sup>) was investigated to complement the reported work. In addition, the beam-rastering method was used for deposition. The structural, optical, and electrical properties of AZO films were analyzed and discussed with respect to the deposition conditions.

## 2 Experiment

A Nd:YAG laser (third harmonic, 355 nm, 3.49 eV, 4.7 ns; EKSPLA, NL301), 10-Hz repetitive rate was used for the ablation of the AZO target (Kurt J. Lesker, Pittsburgh, 99.99% purity, 98% ZnO + 2wt. % Al<sub>2</sub>O<sub>3</sub>) in a stainless steel vacuum chamber. Corning glass slides (Corning #26003, Ted Pella Inc., California) and PC (Goodfellow Ls401316, Huntingdon, England) substrates with the dimension of 1.5 × 1.5 cm<sup>2</sup> were ultrasonically cleaned and placed at 5-cm distance from the target. The deposition chamber was first evacuated to  $5 \times 10^{-4}$  Pa, and O<sub>2</sub> gas was subsequently introduced into the chamber to obtain the partial pressure of 2.1 Pa for thin film deposition. The laser beam was focused to a size of  $\sim 0.007$  cm<sup>2</sup>, and this resulted in laser fluences from 1 to 5 J/cm<sup>2</sup>. The laser beam was steered by a motorized mirror to raster an area of 0.6 × 1.0 cm<sup>2</sup> on the target during ablation, while the target and substrates were fixed in position. The films were deposited for 54,000 pulses at room temperature. No postgrowth annealing was performed. The thickness of the films was measured by using a stylus profilometer, whereas the structural, optical, and electrical properties of the films were characterized by using x-ray diffraction (XRD) with CuK <sub>$\alpha$</sub>  line at 1.5418 Å (Bruker, Massachusetts, D5000), UV-vis-NIR spectrophotometer (AvaLight-DHc and Oceanoptics S2000), four-point probe (Keithley 236 and probe station, Ohio), atomic force microscopy (Nanosurf, Liestal, Switzerland), and scanning electron microscope (Hitachi, Tokyo, Japan).

## 3 Results and Discussions

AZO thin films of  $\sim 130$  to 180 nm were deposited onto glass and PC substrates at laser fluences of 2 to 5 J/cm<sup>2</sup>. At 1 J/cm<sup>2</sup>, the thickness of the deposited film was only 40 nm, which suggests that the laser fluence was close to the ablation threshold of 355 nm of AZO. As such, only samples deposited at 2 to 5 J/cm<sup>2</sup> will be discussed in details in this paper. Figure 1 shows the atomic force microscope (AFM) images of the substrates and AZO films on glass and PC. The root-mean-squared roughnesses ( $R_{\text{rms}}$ ) of the substrates were typically  $< 2$  nm. The lateral grain size in AZO films was  $\sim 100$  nm for the both substrates.  $R_{\text{rms}}$  for AZO films is tabulated in Table 1. The values are slightly higher for PC substrate as compared with glass substrate.



**Fig. 1** Atomic force microscope (AFM) images for Al-doped ZnO (AZO) thin films deposited on glass and polycarbonate (PC) at different laser fluence.

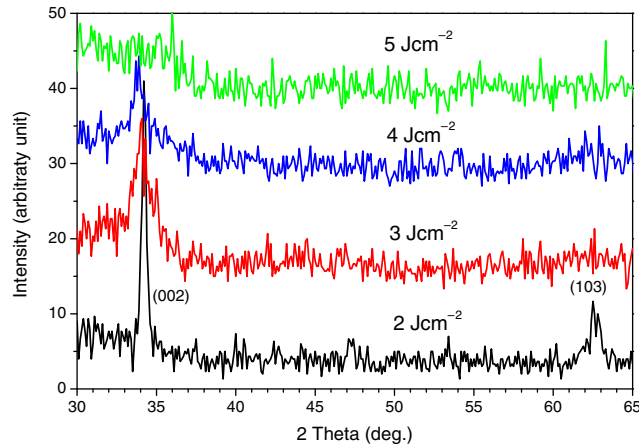
Figure 2 shows the XRD pattern of the AZO films deposited at 2 to 5 J/cm<sup>2</sup>. A sharp and most intense (002) and a small (103) reflection were observed for AZO deposited at 2 J/cm<sup>2</sup>. The sharp (002) reflection broadened with increasing laser fluence and diminished from AZO deposited at 5 J/cm<sup>2</sup>. The crystallinity of the films was highest for the sample deposited with 2 J/cm<sup>2</sup>, although the film is the thinnest. A slight shift was also observed when laser fluence increases. The broadening of the peak at higher fluence can be caused by smaller crystallite size and/or higher strain in the films.

Figure 3 shows the optical transmittance spectra for AZO thin films on the glass and PC substrates at various laser fluences. The average transmittance of the films from 400 to

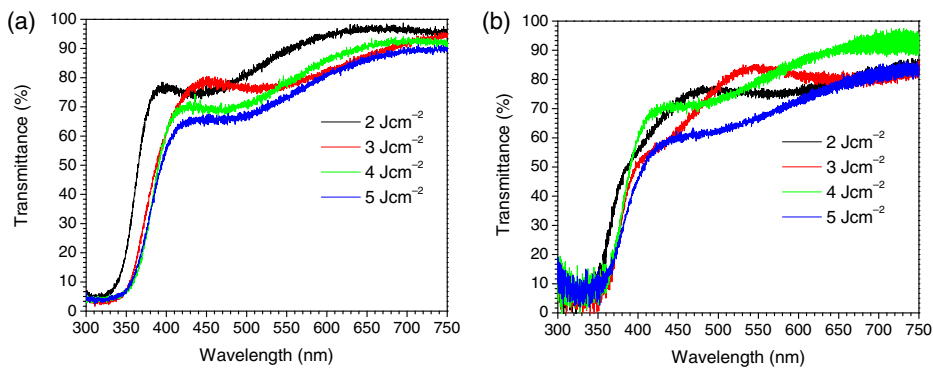
**Table 1** The morphology, optical, and electrical properties of Al-doped ZnO (AZO) films deposited on glass and polycarbonate (PC) at 2 to 5 J/cm<sup>2</sup>.

Fluence (J/cm <sup>2</sup> )	Thickness (nm)	$R_{rms}^a$ (nm)		Lateral grain size (nm)		Transmission @600 nm		Optical bandgap (eV)		Four-point probe resistivity ( $\Omega$ cm)	
		Glass	PC	Glass	PC	Glass	PC	Glass	PC	Glass	PC
2	130	5.55	6.01	105	105	90	75	3.48	3.45	2.29 $\times 10^{-3}$	1.49 $\times 10^{-3}$
3	150	3.83	4.83	103	105	80	80	3.35	3.3	4.36 $\times 10^{-3}$	3.50 $\times 10^{-2}$
4	170	2.95	5.62	88	103	82	82	3.3	3.28	2.16	15.4
5	180	3.00	6.24	90	94	78	70	3.28	3.23	8.54	38.4

<sup>a</sup>From AFM.



**Fig. 2** X-ray diffraction (XRD) pattern obtained from AZO films deposited at 2 to 5 J/cm<sup>2</sup>.

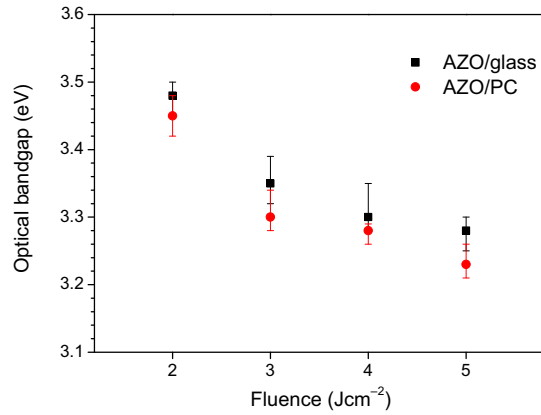


**Fig. 3** Transmittance of AZO on (a) glass and (b) PC at different laser fluence.

750 nm was about 80% on the glass substrate as compared with 75% on PC. The optical bandgap,  $E_g$ , is deduced from a Tauc plot of  $(\alpha h\nu)^2$  versus  $h\nu$  based on Eq. (1)

$$\alpha h\nu = A(h\nu - E_g)^m, \tag{1}$$

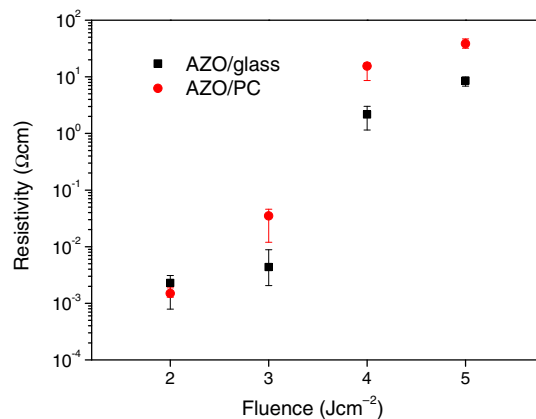
where  $A$  is the constant and  $m$  is the one-half for direct transition.  $E_g$  for an AZO deposited at a different laser fluence on glass and the PC is shown in Fig. 4 and Table 1. There is a consistent decrease of  $E_g$  when the laser fluence increased for AZO deposited on both substrates.



**Fig. 4** Optical band gap of AZO on PC and glass at different laser fluence.

The resistivity for the AZO films on glass and PC is shown in Fig. 5. The resistivities for AZO on glass and the PC increased up to four orders of magnitude with laser fluence. At high fluence, the resistivities of AZO on PC were higher than AZO on glass substrates. The best resistivity was obtained at 2 J/cm<sup>2</sup> for both glass and PC, where the values were  $2.29 \times 10^{-3} \Omega \text{ cm}$  for AZO on glass and  $1.49 \times 10^{-3} \Omega \text{ cm}$  for AZO on PC.

Laser parameters such as pulse length and wavelength influence the ablation process, and subsequently the plume contents. Excimer lasers were normally used in deposition of ZnO, with shorter wavelength/higher photon energy<sup>3,4,9-12</sup> that is able to produce highly energetic species than our current setup with a 355-nm laser. However, numerical results show that bombardment of ions with energy  $\gg 10 \text{ eV}$  is capable to disturbed or displaced atoms in the growing films, which can potentially lead to crystallographic defects to the films.<sup>15</sup> The lower photon energy and fluence in the current setup would minimize such an effect. In addition, rastering laser beams instead of the common rotating target approach would reduce continuous direct bombardment of ions onto the same spot. In a rastering laser beam, the laser beam and the created plasma plume scan across the target; therefore, the most intense part of the plasma plume arrived on a different part of the substrate. Whereas for a rotating target, only the target moves, the plasma plume will arrive onto the same position on the substrate. The method was reported to improve the morphology for the growth of AZO on polymer substrate, where the substrate is more susceptible to damage.<sup>11</sup> On the other hand, we observed a rather low growth rate of the films as compared with deposition by excimer laser, which may be because of extensive optical excitation by a 355-nm laser. It is noted that 355-nm laser excitation can induce room temperature photoluminescence and even lasing action from a ZnO thin films or nanostructures.<sup>16-18</sup> A 8-mm-thick bulk ZnO target optically pumped by a pulsed 355-nm laser lased above 1500 kW/cm<sup>2</sup>.<sup>18</sup> The incident laser energy of the current setup may contribute to optical excitation, which affects the deposition



**Fig. 5** Resistivity of AZO films on PC and glass at different laser fluence.

**Table 2** Comparison of results from current work with reported values.

Reference	20	4	11	12	13	14	This work
Laser wavelength (nm)	248	248	248	248	1064	355	355
Laser fluence (J/cm <sup>2</sup> )	1.5	2	200 mJ raster	1.5	2.1	2	2
Target	AZO (98% ZnO + 2 wt. % Al <sub>2</sub> O <sub>3</sub> )	AZO (97% ZnO + 3 wt. % Al <sub>2</sub> O <sub>3</sub> )	AZO (98% ZnO + 2 wt. % Al <sub>2</sub> O <sub>3</sub> )	AZO (98% ZnO + 2 wt. % Al <sub>2</sub> O <sub>3</sub> )	(Zn: Al 2 wt. %)	AZO (98% ZnO + 2 wt. % Al <sub>2</sub> O <sub>3</sub> )	AZO (98% ZnO + 2 wt. % Al <sub>2</sub> O <sub>3</sub> )
Target-substrate distance (cm)	4	6	10	4	2.3	6	5
Substrate temperatures (°C)	250	RT	RT	RT	RT/100	RT/200	RT
O <sub>2</sub> pressure (Pa)	50	27	0.5	5	3, 5, 7	2	2.1
Substrate	Glass	Quartz	PET and PES	PET	PC	Glass	Glass
Film thickness (nm)	200 to 250	300	205 to 240	372	300	200 to 450	130
Resistivity (Ω.cm)	3.12 × 10 <sup>-4</sup>	6 × 10 <sup>-1</sup>	2.349 × 10 <sup>-4</sup>	1.3 × 10 <sup>-3</sup>	—	0.028–0.0028	2.29 × 10 <sup>-3</sup>
Transmittance at 600 nm (%)	75	90	85–90	85	85	90	80
Optical bandgap (eV)	3.43	3.48	3.60	3.61	—	—	3.48
							3.45

efficiency. The low growth rate of  $\sim 0.03$  nm/s is comparable with the reported value by a 355-nm deposition of ZnO.<sup>19</sup>

The deposited AZO films present satisfactory transmittance in the visible. The reduction of  $E_g$  for AZO films deposited on glass and PC when fluence increased has also been observed in 248-nm deposition.<sup>12</sup> The relation of the change in  $E_g$  with carrier concentration is given by

$$\Delta E_g = \frac{h^2}{8m^*} \left(\frac{3}{\pi}\right)^{2/3} n_e^{2/3}, \quad (2)$$

where  $m^*$  is the effective mass for electrons and  $n_e$  is the carrier concentration. Based on Eq. (2), the carrier concentration decreases when the change in  $E_g$  with reference to an undoped ZnO film reduced. In our results,  $E_g$  reduced with increasing laser fluence, and conductivity decreased with increasing fluence. The results suggest that the carrier concentration of the deposited AZO films, whether on glass or on PC, reduced when laser fluence increased, leading to low  $E_g$  and low conductivity. In addition, based on the XRD results, crystallinity decreased as a laser fluence was increased. The results obtained here are compared with those deposited at similar conditions in Table 2. The best resistivities obtained here were one order of magnitude lower than those deposited by 248 nm with rastering a beam on PES and PET substrates,<sup>11</sup> but close to those obtained on PET.<sup>12</sup> It is also noted that the properties of AZO deposited by 355-nm laser are highly dependent on laser fluence, unlike in the case of 248-nm laser, where resistivities of  $10^{-3}$   $\Omega$ cm can be obtained in a large fluence range of 1.5 to 3.2 J/cm<sup>2</sup>.

## 4 Conclusion

In this work, AZO thin films were deposited on glass and PC substrates at room temperature by using a 355-nm laser. The best films were obtained at 2 J/cm<sup>2</sup>, where the resistivities were  $2.29 \times 10^{-3}$   $\Omega$ cm for AZO on glass and  $1.49 \times 10^{-3}$   $\Omega$ cm for AZO on PC. The properties of AZO films on glass and PC were within the same range. At high fluence, AZO films with lower optical bandgap and higher resistivity were obtained ascribed to lower crystallinity and carrier density. The results also show a narrower fluence window for deposition of AZO films with resistivity of  $10^{-3}$   $\Omega$ cm as compared with deposition by excimer lasers.

## Acknowledgments

We acknowledge the support from Telekom Malaysia (RDTC/130823) and the University of Malaya (BK019-2014).

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