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Characterisation of laser-treated Ag, Al, and Al/Ag metal thin films deposited by DC sputtering

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Abstract Structural, optical and electrical properties of Nd:YAG pulsed laser treated silver (Ag), Aluminium (Al) and Al/Ag bi-layer metal thin films deposited by direct current (DC) sputtering technique is investigated. Laser-metal interaction treatment as an alternative to temperature annealing was used to treat the surface of the metal thin films. Measurements from X-ray diffraction indicated an enhanced grain growth and crystallisation for the laser treated thin films with strong and dominant Ag diffraction peaks at (111) and (200) crystal planes from Ag and Al/Ag films. The surface roughness of Ag and Al thin films increased when expose to 120 mJ laser energy as measured by an atomic force microscopy (AFM). However, smooth surface and reduction in surface roughness were observed when under-layer Al film was deposited below the Ag thin films (Al/Ag bi-layer). The bi-layer Al/Ag film shows a reduced reflectance in most of the visible range as determined by UV-vis spectrophotometer. Surface to volume atomic ratio of the laser treated films increased with a decrease in resistivity as examined by four-point probes. All the Nd:YAG laser treated metal films show a significant decrease in resistivity, sheet resistance and optical reflectance indicating possible application as intermediate layer in transparent conductive oxide (TCO/Metal/TCO) electrode for solar cell devices.

Key words: silver; aluminium; DC sputtering;Nd:YAG laser; reflectance; solar cell

1. INTRODUCTION

Photonics and optoelectronics devices employed broader advantages of metal thin films nowadays to enhance performance and stability. The performance of these devices can be improved through the use of good transparent and conductive metal thin films [1, 2]. Numerous scientific and modern technology applications applied metal thin films as a transparent electrode in solar cell front windows [3], highly conductive and reflective layer in satellite applications [4], and as an intermediate layer between transparent conductive oxide (TCO) in LED devices [5]. Moreover, quite a lot of thin metal films have been used; from Ag-to-Ti in terms of resistivity in recent optoelectronics devices, but each metal exhibits its properties due to a wide range of optical absorption, refractive index and near-total reflectivity in the visible spectrum [6–8]. Semimetal Al thin films have found major application in the field of optoelectronics and microelectronics while noble metal Ag thin films are widely used in thin coated optical waveguides due to their low electrical resistivity and high reflectance [6,7,9]. Al-Ag alloys are commonly used in electrical conductors and superconductors because of the appreciable conductivity that are obtained at given temperature [10].

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Thin film technology is required for the production of films of uniform thickness, adhesiveness, structural homogeneity and high purity on a large-scale material [4]. The method used in the deposition of metal thin films are voluminous and hence plays an enormous role in obtaining the desired films of different structural and optoelectronic properties. Some of these methods are; direct current (DC) or radio frequency (RF) magnetron sputtering [11,12], spray pyrolysis [13], thermal evaporation [14], or electron beam deposition [15]. Excellent thin films over a wide range area deposited by magnetron sputtering have been reported [10,14,16]. This is because sputtering parameters can be well controlled to produce the desired good quality thin films [7,14]. The deposited metal thin films can be continuous, discontinue, uniform or of island structure [16]. But mostly, metal thin films quality are enhanced by the thermal annealing process. Thermal or temperature annealing is widely conducted to improve the structural and optoelectrical properties of metal or metal oxide thin films. Alternatively, laser-metal interactions or annealing have been used as a substituted treatment to temperature annealing, and it has been found to have actively improved the metal films properties [1,12,18,19]. This treatment can provide a large amount of energy accurately into selective regions of a given material [20]. The laser energy of irradiated metal thin films are absorbed in the near surface of the material, thereby modifying the surface chemical reaction, morphology and crystalline structure without affecting the bulk properties [20,21]. Moreover, the exposed laser-irradiated metal thin films surface shows some decrease in electrical resistivity characteristics which at the same time increases the conductivity of the material [12,18,19].

The low adhesion effect of Ag films, when deposited on an oxide substrate, enables easy movement of its atoms which causes agglomeration. Alloying Ag thin film with Al film (Al/Ag bi-layer) allows one to put an end to Ag films agglomeration [9]. The existence of impurity scattering effect in the alloyed thin films also increases the resistivity value. A laser treatment process can overcome this effect due to transient and non-equilibrium kinetic nature of the incident laser[22]. In this work, Nd:YAG pulsed laser treatments effects on Ag, Al and Al/Ag bi-layer thin films properties including structural, electrical and optical properties are presented.120 mJ of laser energy is chosen to provide a quick heat (radiation) absorption at a particular surface point in the thin film without affecting the other surface area.

2. EXPERIMENTAL DETAILS

Ag (99.999 % purity) and Al (99.999 % purity) targets were used in the deposition of Ag, Al and Al/Ag thin films using DC sputtering system on silicon (Si) and glass substrates. Before deposition, Si substrates were first cleaned by heating in acetone solution at 55º C and then rinsed in IPA solution and later deionised water (DI). Similarly, glass cleaner decon90 solution and DI water were used to clean glass substrates. Both the Si and glass substrates were dried in N_2 gas atmosphere and then loaded into the DC sputtering chamber. Table 1, displays the sputtering parameters of the single and bi-layer thin films. The deposited thin films surface were then exposed to 120 mJ nanosecond Nd:YAG pulsed laser radiation (Litron Nano Series) with 1064 nm fundamental wavelength and 4 ns pulse duration treatments. Metals at this wavelength are not reflective, thereby making the Nd:YAG laser type suitable for metal surface treatment. This type of laser has the advantage of compactness, providing a precise treatment to desirable surface regions of the material.

Morphological, optical and electrical characterisations were carried out for all the prepared metal samples. The thickness of the samples was measured by ellipsometry system. Atomic force microscopy (AFM) was used to scan the surface morphology and roughness at 1μm × 1μm area. The electrical characteristics were examined by four-point probe system while UV-Vis spectrophotometer was considered for optical reflectance and absorption spectra.

TABLE 1. Details of the sputtering parameters, thickness and laser energy used.

Sputtering Parameters	Al Films	Ag Films	Al/Ag Films
Vacuum pressure	6.9×10^{-6} Torr	6.6×10^{-6} Torr	6.35×10^{-6} Torr

DC Power	100 W	100 W	100 W
Working Pressure	5.00 mTorr	4.97 mTorr	5.02 mTorr
Target to substrate distance	13 cm	13 cm	13 cm
Pre-Sputtering	15 minutes	15 minutes	15 minutes
Deposition Time	50 seconds	300 seconds	340 seconds
Thickness	20 nm	50 nm	70 nm
Laser Energy	120 mJ	120 mJ	120 mJ

3. RESULTS AND DISCUSSION

Pulsed laser annealing can be localised at a near surface of material thin films using high energy pulses as shown schematically in Figure1. This can be achieved without distorting the other active part of the material. There are possibilities of unlocking other unique surface properties by this type of annealing treatment[22].

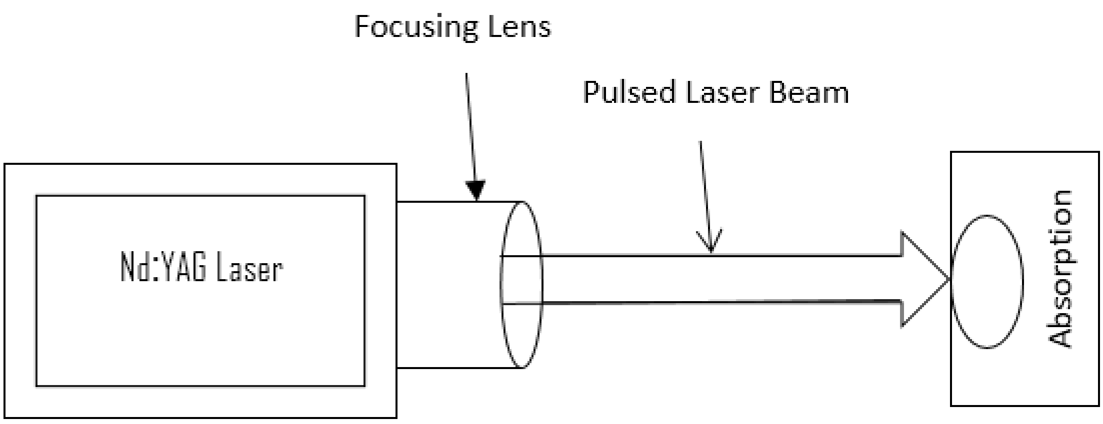


Figure 1. Near-surface pulsed laser localised annealing of a conductive material

Figure 2 shows the three XRD pattern of laser treated (trd) and untreated metal thin films. Both the single layer Ag and Al/Ag multilayer films indicate quality crystalline diffraction peak with cubic Ag phase and Si substrate reflection dominating the diffraction peaks. The two most intense Ag peak reflections at (111) and (200) in Figure 2a and 2b can be clearly identified. It can be concluded that the preferential crystallographic orientation of Ag grain is along [111] direction since the crystal plane (111) has the strongest reflection peak intensity. This type of orientation is mostly seen in polycrystalline thin films[23][24]. The diffraction peak intensity of (111) and (200) planes increased with laser energy treatment. Therefore, the treatment of metal films surface with laser energy radiation also improved adatoms surface energy of the films and hence enhanced crystallisation. Liu et al. also reported relative phenomena [25].

Similarly, from the treated Al/Ag (Al/Ag_{trd}) sample, weak Al diffraction peak (220) reflection is observed. In essence, one can say that the sputtered Ag films surface interactions with the laser energy radiation enables the surface adatoms to gain higher kinetic energy which enhances grain growth and crystallisation [25]. No diffraction peak of Al reflection has been observed in both the treated (trd) and untreated Al samples indicating the amorphousness nature of the films as shown in Figure 2c

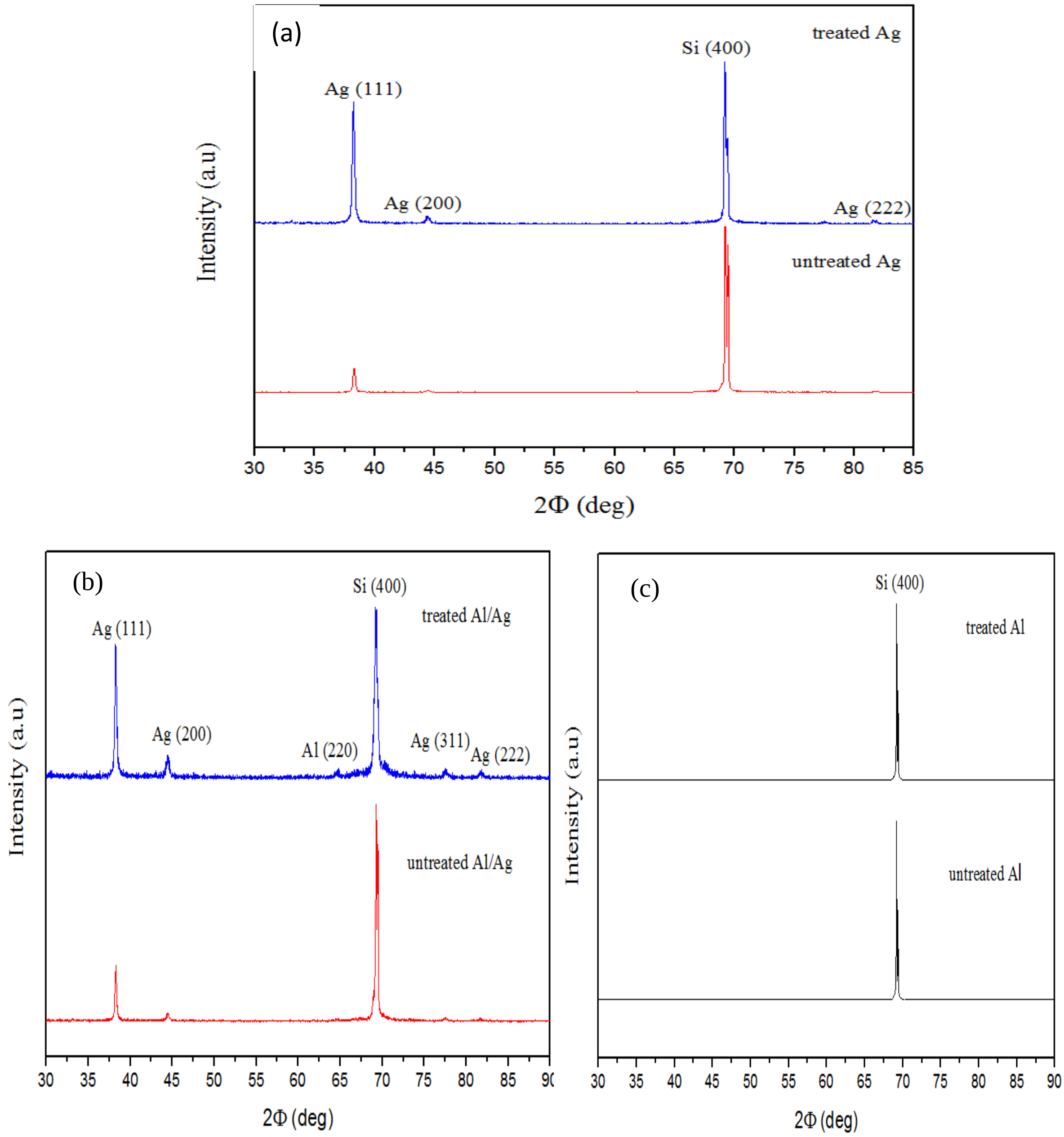


Figure 2. XRD spectra of (a) Ag, (b) Al/Ag and (c) Al metals thin films

Changes in the surface morphology of metals thin films have been characterized by AFM technique. Three-dimensional (3D) 1µm × 1µm scan area of Ag, Al and Al/Ag thin films AFM images are shown in Figure 3. From Table 2, it can be seen that the nano-size of root mean square RMS roughness R_q and average roughness R_a of the laser treated films of all the metals were found to be larger compared to as-deposited (untreated) films, which also tallied with the work of Sivaramakrishnan et al. [26]. Likewise, the grain boundary and barrier height (Figure 3) decreased due to the increased in grain sizes as a result of laser energy absorption. This in effect, paves the way for enhancing carrier mobility and consequently improved the electrical conductivity[1]. Moreover, Ag film surface roughness reduces, and the surface becomes smooth when under-layer Al film was deposited below Ag film (Al/Ag bi-layer). This process suppresses the agglomeration of Ag particles as obtained in the deposited single Ag films due to low adhesion effects which make the movement of Ag atoms easier[9].

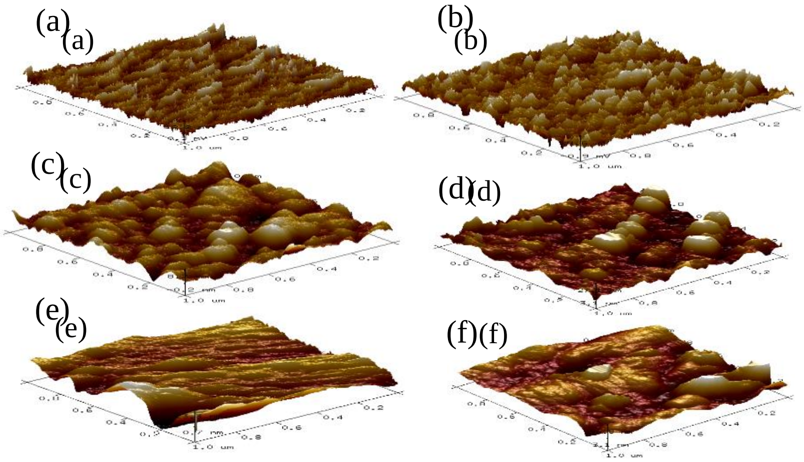
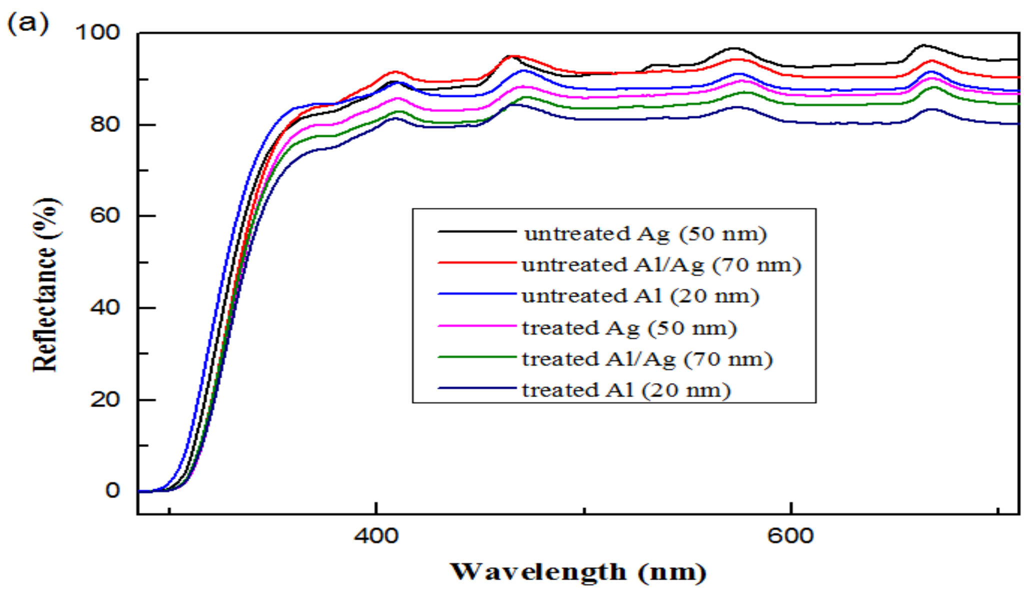


Figure 3. AFM three dimensional (3D) images of (a) Untreated Ag (b) Treated Ag (c) Untreated Al/Ag (d) Treated Al/Ag (e) Untreated Al (f) Treated Al.

Low reflectivity and energy absorption are required for metals films to be used as an intermediate layer in the TCO electrode. Thin films of Ag, Al and bi-layer Al/Ag metals optical reflectance and absorbance spectra are shown in Figure 4. From Figure 4(a), it can be seen that the untreated Ag (50 nm) film has the highest reflectance peak of 96.8 % in the upper wavelength of the visible range while in the lower wavelength range, the untreated Al/Ag (70 nm) film with 95.1 % reflectance is the highest. This is attributed to the reduced surface roughness and subsequent smoothness in the film as obtained in Al/Ag bi-layer thin film. Alloying Ag thin films with Al film will have no significant effect on reflectance in visible range since the absorption edge of this material is in the ultraviolet region due to glass substrate absorption abilities[9,14,27]. Also, high optical reflectance was observed in Al (20 nm) film nearly equal to Ag film at 400 nm wavelength but far less than the latter at most of the visible region. In Figure 4b, laser treated Ag film exhibited a higher percentage of absorbance in visible spectrum due to the vast increased in RMS roughness R_q and average roughness R_a. Absorbance drops substantially at 300 nm in the ultraviolet region before rising to the higher percentage at the extreme ultraviolet region of the spectrum. Moreover, the high energy absorption abilities displayed by all the laser treated films were as a result of a decrease in reflectance and increased surface roughness. In all the treated metal films, a manifestation of high absorbance was observed with the absorption spectra shifting toward lower wavelengths.



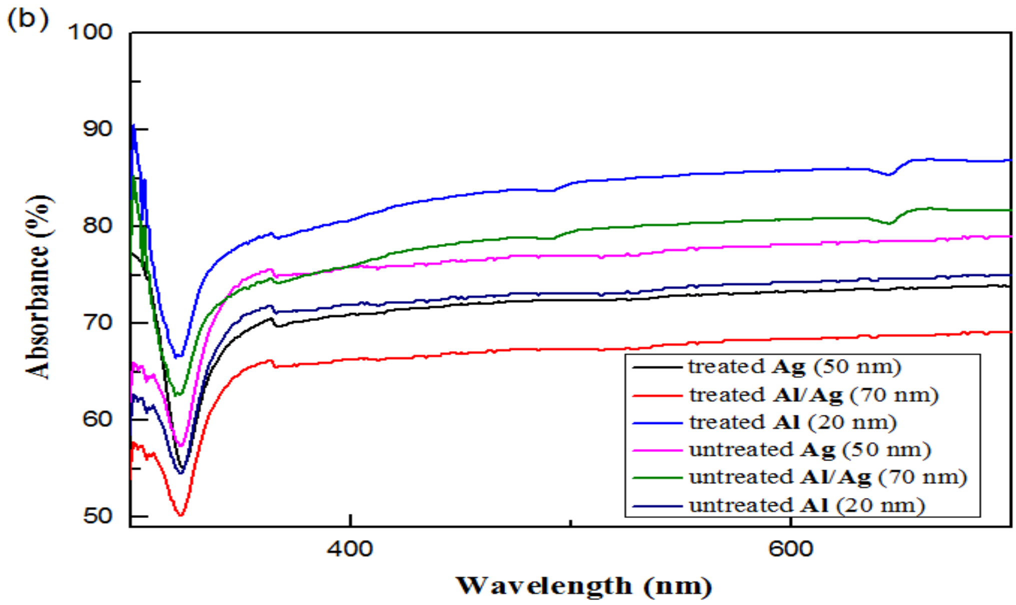


Figure 4. Percentage measurements of Al, Ag and Al/Ag thin films for (a) reflectance (b) absorbance.

Table 2: electrical and morphological parameters of the as-deposited and treated (trd) metals thin films.

Metals	$\rho(\mu\Omega cm)$	$R_{sh}(\Omega/sq)$	$\sigma(\Omega^{-1}cm^{-1})$	$R_q(nm)$	$R_a(nm)$
Al	63.4	2.53	15772.87	1.74	1.40
Al_{trd}	15.1	2.02	66225.17	5.10	3.21
Ag	3.35	0.134	298507.10	3.17	2.52
Ag_{trd}	0.72	0.144	138888.89	7.84	6.25
Al/Ag	7.49	0.60	133511.35	2.38	1.93
Al/Ag_{trd}	1.56	0.122	641025.64	11.8	9.56

Electrical characteristics of a material is determined by resistivity (ρ) and sheet resistance (R_{sh}). Table 2, highlighted the electrical conductivity of the treated and untreated metal thin films. Considerable decrease in resistivity was observed in all the three metal films when treated with 120 mJ laser energy radiation. The reduction in resistivity from the treated Ag film indicates a significant drop in agglomeration of Ag particles that tends to suppress its free energy. Hence, the increased in surface to volume atomic ratio and also formation of continues film [26,28]. Furthermore, the surface electrical conductivity of Al/Ag bi-layer film increases as compared to the single Ag film due to impurity scattering effect [9].

4. CONCLUSION

Metals thin films of Al, Ag and bi-layer Al/Ag deposited by DC sputtering technique have been investigated. 120mJ pulse Nd:YAG laser energy radiation is used as an alternative annealing process.

Grain growth and crystallisation were enhanced as a result of metal-laser energy interactions. Strong diffraction peaks (111) and (200) for Ag phase and Al (220) reflections were observed in laser treated Ag and Al/Ag samples. Moreover, the Al/Ag bi-layer thin film shows a reduced root mean square RMS and average roughness value with more flat and smoother surface compared to single Ag film. The shift in absorption spectra toward lower wavelengths clearly demonstrated high absorbance of energy by the metal films. The high absorption of the untreated metals thin films contributed to their low reflectance compared to the laser treated films. The laser treated samples revealed a significant drop in both electrical resistivity and sheet resistance which directly improved the conductivity.This treatment method reduces the possible agglomeration of Ag particles, thereby increases the surface to volume atomic ratio of the film.

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6. REFERENCE

[1] R. A. Ahmad, A. H. Ali, A. K. Isiyaku, and B. Z. Bhari, "Improved Resistivity and Surface Morphology of Laser Treated Cr / Pd Metal Contact Sputter Deposited on Si," *J. Sci. Technol.*, vol. 9, no. 3, pp. 101–105, 2017.

[2] M. Swain, D. Bhattacharya, K. G. Bhushan, and S. Basu, "Deposition of a Nickel Film by DC Magnetron Sputtering and its Characterization," in *AIP Conf. Proc.*, vol. 184, pp. 182–184, 2012.

[3] M. S. R. Khan and A. Reza, "Optical and electrical properties of optimized thin gold films as top layer of MIS solar cells," *Appl. Phys. A Solids Surfaces*, vol. 54, no. 2, pp. 204–207, 1992.

[4] F. Target, S. Ido, T. Suzuki, and M. Kashiwagi, "Aluminum films deposition by magnetron sputtering systems : Influence of target state and pulsing unit," in *Journal of Physics: Conference Series*, vol. 741, p. 12193,2016.

[5] M. M. D. Kumar, S. Mi Baek, and J. Kim, "The influence of Ni layer and thickness of AZO layers on the optoelectronic properties of AZO/Ni/AZO tri-layer deposited at room temperature," *Mater. Lett.*, vol. 137, pp. 132–135, 2014.

[6] P. J. D. Whiteside, J. A. Chininis, and H. K. Hunt, "Techniques and Challenges for Characterizing Metal Thin Films with Applications in Photonics," *Coatings*, vol. 6, no. 35, pp. 1–26, 2016.

[7] C. Guillén and J. Herrero, "TCO/metal/TCO structures for energy and flexible electronics," *Thin Solid Films*, vol. 520, pp. 1–17, 2011.

[8] E. Akbarnejad, E. A. Soleimani, and Z. Ghorannevis, "Chromium thin film deposition on ITO substrate by RF sputtering," *J. Theor. Appl. Phys.*, vol. 8, no. 3, p. 129, 2014.

[9] E. Kudo *et al.*, "Optical properties of highly stable silver thin films using different surface metal layers," *Thin Solid Films*, vol. 660, pp. 730–732, 2018.

[10] P. Afzali, M. Yousefpour, and E. Borhani, "Effect of Deformation-Induced Defects on the Microstructure and Pitting Corrosion Behavior of Al-Ag Alloy," vol. 31, no. 12, pp. 2092–2101, 2018.

[11] M. Inoue, K. Hashizume, H. Tsuchikawa, M. Inoue, K. Hashizume, and H. Tsuchikawa, "The properties of aluminum thin films sputter deposited at elevated temperatures The properties of aluminum thin films sputter deposited at elevated temperatures," *J. Vac. Sci. Technol. A*, vol. 1636, no. 1988, pp. 1–5, 2014.

[12] A. K. Isiyaku, A. H. Ali, and N. Fauziyyah Ramly, "Characterization of Cr / Ag metal thin films interaction with infra-red laser," *Mater. Today Proc.*, vol. 7, no. March, pp. 692–696, 2019.

[13] D. Perednis and L. J. Gauckler, "Thin film deposition using spray pyrolysis," *J. Electroceramics*, vol. 14, no. 2, pp. 103–111, 2005.
[14] A. Axelevitch, B. Gorenstein, and G. Golan, "Investigation of Optical Transmission in Thin Metal Films," in *Physics Procedia*, vol. 32, pp. 1–13, 2012.
[15] V. P. Siller, K. Andrews, and A. B. Kaye, "The effects of substrate plasma etching on the performance of thin metal films," *Thin Solid Films*, vol. 626, pp. 200–208, 2017.
[16] A. Axelevitch and B. Apter, "In-situ investigation of optical transmittance in metal thin films," *Thin Solid Films*, vol. 591, no. Part B, pp. 261–266, 2015.
[17] O. Tuna, Y. Selamet, G. Aygun, and L. Ozyuzer, "High quality ITO thin films grown by dc and RF sputtering without oxygen," *J. Phys. D. Appl. Phys.*, vol. 43, no. 5, p. 55402, 2010.
[18] B. Z. Bhari, A. H. Ali, A. K. Isiyaku, and R. A. Ahmad, "Comparative Study of Infrared Nd : YAG Pulsed Laser Radiation on Pt Thin Film," *J. Sci. Technol.*, vol. 9, no. 3, pp. 83–86, 2017.
[19] S. Eckhardt, M. Siebold, and A. F. Lasagni, "Laser microstructured metal thin films as promising alternative for indium based transparent electrodes," *Opt. Express*, vol. 24, no. 6, p. A553, 2016.
[20] M. S. Brown and C. B. Arnold, "Fundamentals of Laser-Material Interaction and Application to Multiscale Surface Modification," in *Laser Precision Microfabrication*, vol. 135, Springer-Verlag, pp. 91–120, 2010.
[21] I. The, Z. Hwang, V. Deijck, and M.- Blankenburg, "Interaction of a Laser Beam with Metals . Part I : Quantitative Studies of Plasma Emission *," *Appl. Spectrosc.*, vol. 45, no. 3, pp. 435–441, 1991.
[22] S. M. Michael Scarpulla, "Laser annealing in thin-film chalcogenide photovoltaics," *SPIE Newsroom*, no. 22, pp. 1–3, 2016.
[23] P. Ukahapunyakul *et al.*, "Texture orientation of silver thin films grown via gas-timing radio frequency magnetron sputtering and their SERS activity," *RSC Adv.*, vol. 6, no. 9, pp. 7661–7667, 2016.
[24] a. Rizzo, M. a. Tagliente, M. Alvisi, and S. Scaglione, "Structural and optical properties of silver thin films deposited by RF magnetron sputtering," *Thin Solid Films*, vol. 396, no. 1–2, pp. 29–35, 2001.
[25] W.-S. Liu *et al.*, "Indium tin oxide with titanium doping for transparent conductive film application on CIGS solar cells," *Appl. Surf. Sci.*, vol. 354, pp. 31–35, 2015.
[26] K. Sivaramakrishnan, A. T. Ngo, S. Iyer, and T. L. Alford, "Effect of thermal processing on silver thin films of varying thickness deposited on zinc oxide and indium tin oxide," *J. Appl. Phys.*, vol. 105, no. 6, 2009.
[27] K. S. Shamala, L. C. S. Murthy, and K. N. Rao, "Studies on optical and dielectric properties of Al2O3thin films prepared by electron beam evaporation and spray pyrolysis method," *Mater. Sci. Eng. B*, vol. 106, no. 3, pp. 269–274, 2004.
[28] A. K. Isiyaku, S.B. Ghoshal, "Photoluminescence spectral features of silicon nanowires," *J. Teknol.*, vol. 2, no. 78, pp. 153–158, 2016.