CHAPTER-5

Investigation on the effect of Process Parameter on physical properties of RF sputtered Mo-Ni thin films as a back contact thin-film solar cell

Chapter 5

5.1. Introduction

Molybdenum (Mo) has been widely employed as back contact material, notably in thin-film solar cells [120, 125, 285, 286], because of its outstanding properties, such as strong thermal stability, better adhesion, better electrical conductivity [121, 287], and good reflectivity [288]. Moreover, Molybdenum thin film layers also serve as diffusion barriers in very large-scale integrated circuits, manufacturing hard-wear resistant materials, and semiconductor devices [289-292]. Process parameters like RF power, base pressure, deposition time, and temperature of substrate affect the properties of Mo thin films. Films deposited at low pressure and high power form compressive films that are very conductive but have poor adherence to the substrate, whereas films deposited at high base pressure generate improved resistive films with better adherence grown on the substrate [293-298]. It is very difficult to obtain both excellent conductivity and better adhesion to the soda-lime substrates with a single Molybdenum layer [299]. Introducing a bilayer Molybdenum thin film with a small amount of Ni sputtered at various RF power has been employed to achieve good adhesion and optimize the physical, electrical and optical properties [300-303]. Bilayer thin films of various materials have been reported in previous literature [304, 305].

In this chapter, the effects of RF Power and deposition time in vacuum conditions on the structural, surface morphology and electrical properties of RF sputtered Mo-Ni thin films. Sputtering is the most frequent method for depositing the Mo bilayer because it has higher efficiency and gives better adhesion [108, 125, 306-309]. A sputtering Mo-Ni back contact can improve the conversion efficiency of the solar cell [310, 311]. In a thin-film solar cell, a Molybdenum layer with high reflectivity, low resistance, and good adhesion are desirable. For instance, reflectivity is influenced by applying gas pressure [120] and increases by RF Power [125]. Moreover, the increment in power gives good adhesion and decreases resistivity [285].

Additionally, the ways of producing more adhesive and thinner film by optimizing Mo-bilayer thin film having low resistivity and high reflectance has been investigated. Moreover, on comparison, the influence of RF Power and deposition time, ranging from low to high, for the better adhesion of the Mo-single layer. Molybdenum bilayer films were grown by RF magnetron sputtering technique in two phases and examined the effects of RF power and deposition time on the structural, electrical, and morphological aspects of the films, which were deposited on soda-lime glass. As a result, we were able to obtain a very thin Mo bilayer with extremely low resistivity and high reflectivity, as well as better adhesion, crystallinity, and surface morphology.

5.2. Materials and Methods

5.2.1. Fabrication of film

In present chapter, a series of Molybdenum bilayer thin films have been synthesized via RF magnetron sputtering (Kurt J. Lesker Co) under controlled growth conditions on soda-lime glass substrate by varying two parameters like RF power and deposition time. A Mo-Ni (diameter, 63.5 mm; purity, 98% Mo, 2% Ni) target was used as a sputtering source. To remove surface contamination, the soda-lime glass substrates were ultrasonically cleaned with acetone and methanol for 15 minutes each, then dried with a nitrogen gas flow.

An indigenously designed and locally constructed RF magnetron sputtering system was used to produce Mo-Ni thin films on soda-lime glass substrates. The schematic diagram of the RF magnetron sputtering system is shown in Figure 5.1. This sputtering system can hold up to four targets at once, making it perfect for generating thin-film solar cells while maintaining a high vacuum. The substrates can be rotated to place them under the next target, and various layers can be deposited one by one under a high vacuum.

It contains a cylindrical chamber with a Turbo molecular pump (TMP), which is followed by a mechanical pump that produces a base pressure $8x10^{-6}$ Torr. The separation between the substrate and the target was maintained at 5 cm. A stepper motor was used to keep the substrates rotating throughout the sputtering process to provide a uniform film. Using rotary and turbo pumps, the chamber was initially evacuated to a high vacuum of 8×10^{-6} Torr, with the working pressure set at $2x10^{-2}$ Torr. RF sputtering was used in this study, with two different parameters of deposition time and RF power being changed. Before the Mo-Ni depositions, the RF power was increased from 100 to 200 W, and the target was pre-sputtered for 15 minutes to eliminate impurities and any contamination. Two effective sputtering parameters were chosen as mentioned previously: RF power (100, 150, and 200 W) and deposition time (15, 30, and 45 min). The resulting Mo-Ni thin film was studied by varying using a range of relevant techniques for their morphological, electrical, and optical properties then, the RF power of 200 W was chosen as an optimal power to explore the effect of deposition time on thin-film physical properties.

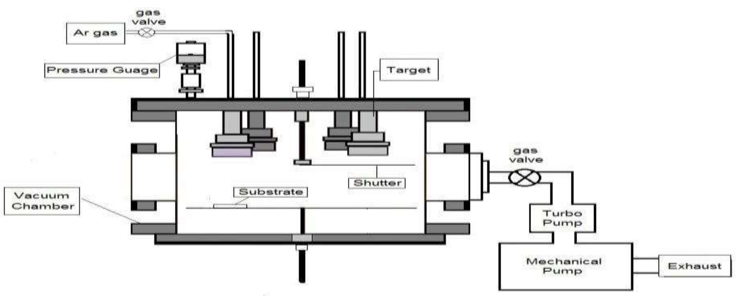

Figure 5.1. Schematic of RF magnetron sputtering

5.2.2. Characterization of Film

Several techniques were used to characterize the sample, including XRD, FESEM, AFM, electrical analysis, and reflectance spectra. The morphology of the as-prepared Mo-Ni thin film was studied using a field emission scanning electron microscope (Hitachi S4160). The structural investigation of prepared thin films was performed using an XRD (Stoe, X'pert PRO) using Cuk$_\alpha$ irradiation. A dual-beam UV-Vis spectrophotometer (Cary 500 UV/VIS/NIR spectrophotometer) was also used to evaluate reflectance characteristics and transparency in the 200-800 nm spectral regions for optical analysis. The electrical resistivity's of all samples were measured using four-point probe techniques (MELLER) at room temperature. AFM was used to determine the roughness of the surface (Park scientific instruments atou probe cp). The thickness of the films was measured with profilometer by Dektak3. The scotch tape method was also used to analyze thin film adhesion to the substrates [299]. Except Mo thin film deposited at 250W, all other samples passed the test and showed appropriate adhesion to the substrate.

5.3 Results and Discussion

5.3.1 Influence of the RF power

5.3.1.1 Structural studies

The phase identification, crystallinity, and the size of crystallites within a layer of Mo and Mo-Ni thin films sputtered at varying RF powers of 100 W, 150 W, and 200 W were determined using X-ray diffraction techniques. Figure 5.2 shows XRD spectra which demonstrate that all the films have the most intense peak at $2\ \theta = 40.5$ corresponding to (110) preferred orientation represents the crystalline formation [297]. Structural parameters calculated by using the shifting of (110) peak are summarized in table 1. The intense and sharp peaks of sputtered Mo-Ni thin films represent crystallinity. On the other hand, Mo-Ni thin film with increasing RF power shows extra peaks at the orientations of (111), (200), (311), and (110) planes indicating Mo-Ni thin-film crystallizes in body-centered cubic (BCC) structure. As a result, raising the RF power of an RF-sputtered Mo-Ni thin-film lowers the (110) peak intensity while increasing the crystallinity of the (200) orientation, which is conceivable due to the higher kinetic energy.

Debye- Scherrer's equation was used to estimate the crystallite size [312].

$$D = \frac{k\,\lambda}{\beta(hkl)\cos\theta}$$

where D is the crystallite size and β is the full-width half-maximum (FWHM), while θ is the Bragg angle and λ the wavelength of the X-ray of Cuk_{α} and k is a constant known as shape factor whose value is approximately 0.9 [313].

Micro strain is caused by imperfections in the crystalline lattice, such as vacancies, dislocations, and stacking faults [314]. the micro strain that results, which can be estimated using the equation below [144]

$$\mathcal{E} = \beta\ (hkl)/4\ \tan\theta$$

Where ε is the strain and β is the FWHM while θ is Bragg's angle.

RF Power (W)	Thickness (nm)	RMS (nm)	Ra (nm)	**ρ(Ω·m)**	h k l	2θ (Deg.)	β(hkl)	Crystal size (nm)	Micro strain × 10^{-3}
100	300	3.78	2.95	32.4	110	39.73	0.0061	24	4.23
150	550	5.64	4.35	25.1	110	40.23	0.0173	9	11.6
200	850	6.53	5.05	12.2	110	40.55	0.0164	9	11.1

Table 5.1: Summary of the XRD measurements and the result for thickness, roughness, and electrical resistivity test for various RF powers

As a result, it can be concluded that thermal annealing in the vacuum of RF-sputtered Mo thin films improves the crystallinity of the (2 1 1) orientation, which is presumably owing to the increased thermal energy given during the heat treatment.

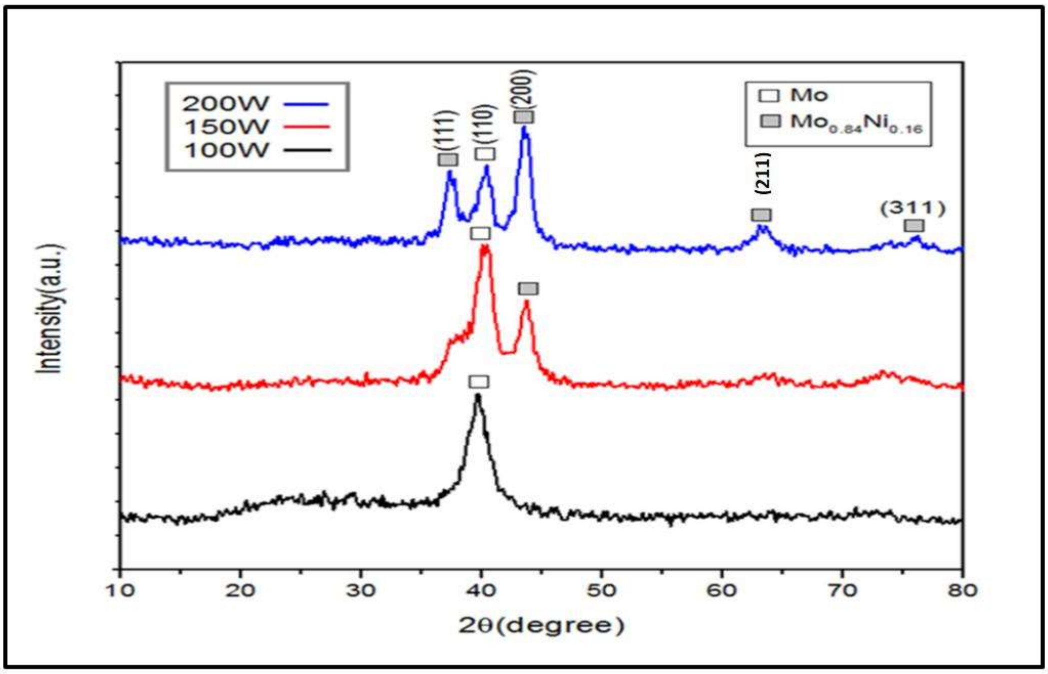

Figure 5.2. XRD spectra for the samples deposited at various RF powers of a) 100 W, b) 150 W and c) 200 W.

5.3.1.2 Surface morphology

Figure 5.3 shows the 2D and 3D AFM images of Mo-Ni thin films deposited at various RF powers of 100 W, 150 W, and 200 W. The AFM images demonstrated that the surface consists of small, close-packed, and uniform structures. The Mo film deposited at RF power of 100 W shows the needle-like structure of various sizes. When the RF power increased to 150 W the height of the needle-like grains increased from 0.018 µm to 0.042 µm. At 200 RF power appears elongated, highly interconnected, and clustered structures, which indicates on increasing RF power there is growth on the surface morphology of Mo-Ni thin films hence densification larger particle on the surface. The roughness, grain size of sputtered Mo-Ni thin films was observed to vary with RF power as indicated in Table 5.1. At lower RF power the kinetic energy of sputtered particles is lower than the higher RF power resulting in more random orientation and different grain sizes which lead to the roughness of the surface.

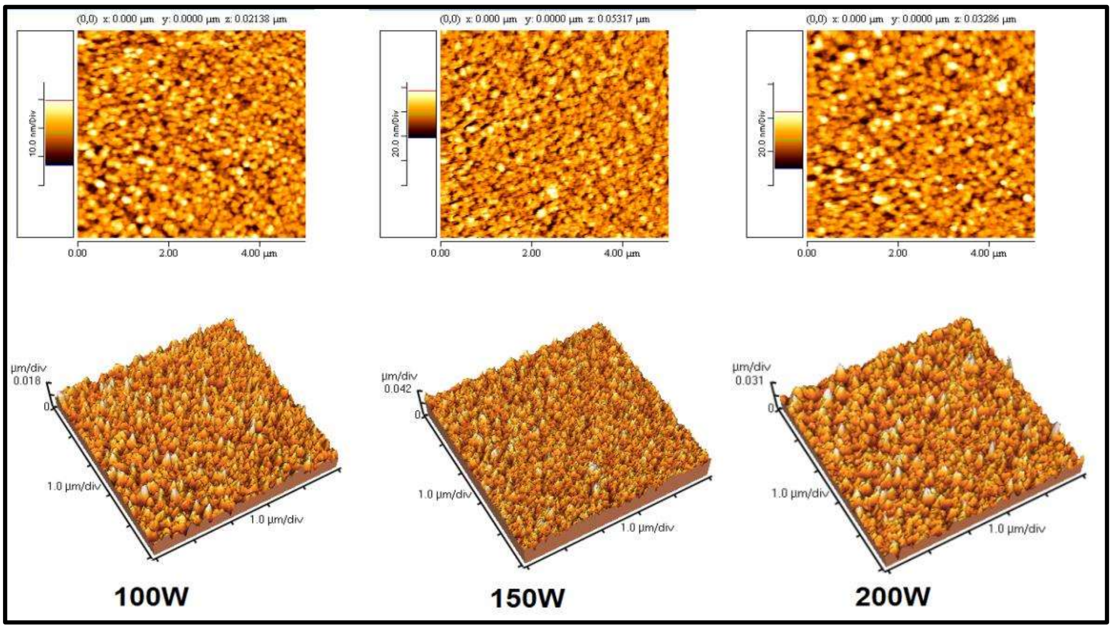

Figure 5.3. AFM images (3D and 2D) of Mo-Ni thin films deposited at various RF powers of 100, 150, and 200 W.

The kinetic energy of the Mo particles increases as the power increases, and bombardment of high kinetic energy particles can cause higher surface roughness. Furthermore, when the kinetic energy of Mo particles increases, so does the vibration of Mo particles on the surface, which might result in increased surface roughness. To illustrate the surface morphology and surface roughness of Mo-Ni films were observed using field emission Scanning Electron Microscopy (FESEM), Atomic Force Microscopy (AFM). Figure 5.4 represents the FESEM image of Mo-Ni thin films deposited at various RF powers of 100, 150, and 200 W. As seen in the figure, the average film thickness of Mo-Ni thin films increases with increasing RF power shows uniform denser microstructure [315]. These changes in particle size at different RF power show the effect of RF power on the growth mechanism of the thin film. At lower deposition power, the deposition rate decreases which results in a fewer number of foreign particles arrived at the surface of the substrate. The FESEM image of Mo-Ni thin film at 100 RF power represents uniformly stacked grains in the dimension of 10-100 nm. When the RF power increased to 150 and 200 W because of the condensation of the close grains to each other the grain sizes increased and grain boundaries were not easily observed.

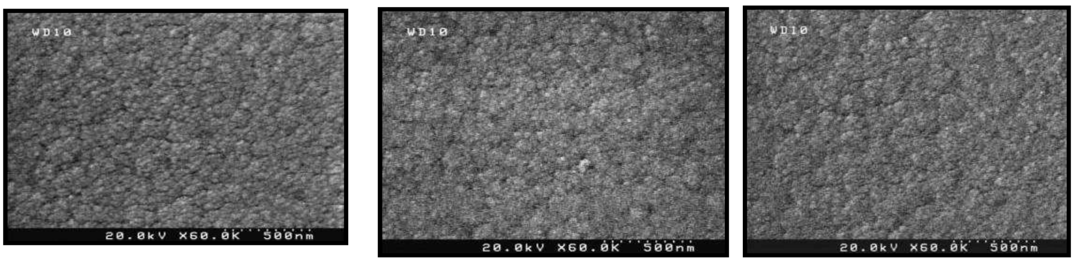

Figure 5.4. FESEM images of Mo-Ni thin films deposited at different RF power: a) 100 W, b) 150 W and c) 200 W.

5.3.1.3 Electrical properties

For electrical analysis, the electrical resistivity of Mo-Ni thin films prepared at different RF sputtering of 50W, 100W, and 150W powers were performed using four-point probe conductivity measurement. Parts of the results are listed in Table 5.1. This implies that by increasing the RF power the resistivity decreases drastically [316, 317]. The electrical resistivity of thin-film grown at 100 W and 200 W varies from 32.4 to 12.2 (Ω·m), respectively. Decreasing the resistivity can be due to the increasing the thickness of the films by applying higher RF powers, which leads to higher amounts of the sputtered atoms.

5.3.1.4 Optical properties

To investigate the optical properties of Mo-Ni thin films, UV-Visible-NIR spectroscopy has been used. Figure 5.5 represents the optical reflectance spectra of the deposited Mo-Ni films at different RF powers. The wavelength increased alongside the reflectance, showing that the elevated RF power results in a fluctuation of the reflectance spectra. In addition, the surface roughness of the deposited film significantly increased with the thriving of pores and structures of grain boundaries. Finally, the ability of light scattering was reduced to improve optical absorption for the incident light while decreasing the reflectance of the films. For RF power of 200 W, optimal reflectance can be obtained at 30%. On the other hand, increasing the power enabled obtaining sufficient energy for Mo-Ni thin film deposition during crystal growth. In this instance, the structures of the deposited thin film grow more compact while the surface roughness declines. Accordingly, reducing optical scattering and the enhancement of optical absorption of the film is a significant improvement [318].

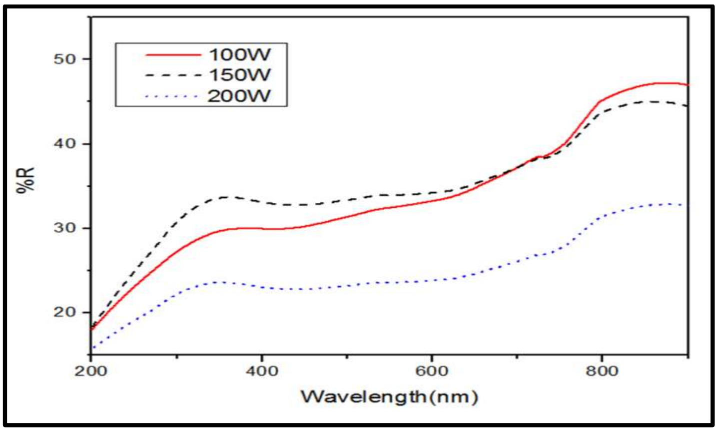

Figure 5.5. Reflectance spectra of Mo-Ni thin films deposited at different RF power.

5.3.2 Influence of the deposition time

5.3.2.1 Structural studies

To determine the structure and crystallinity of the prepared Mo-Ni thin films, X-ray diffraction analysis was employed. Figure 5.6 shows the XRD spectra of various Mo-Ni thin films deposited at different deposition times of 15, 30, and 45 min at the same RF power 200 W. it is observed that all of the spectra contain strong diffraction peaks corresponding to (200) reflection at $2\theta = 42.99°$. The peak indicates a strong preferential a-axis orientation of the Mo-Ni structure and is located close to the standard Ni crystal. The intensity of the (200) peak increases with increasing deposition time and some peaks like (311) emerged at 45 min deposition time. In other words, as the deposition rate increases, the Mo-Ni thin film develops a more noticeable crystalline structure. Greater crystallinity occurs as the amount of solute reaching the substrate's surface grows with deposition time, increasing the electrostatic interaction between solute atoms, thereby promoting the formation of crystalline structures. Figure 5.6 represents that deposition at higher power leads to more crystalline structure and higher intensity for the crystallite plane of (111), (200), and (311). The Different parameters of XRD like crystal size and micro strain have been tabulated in Table 5.2. Thus it has been observed that by increasing the deposition time which leads to higher crystallinity of the Mo-Ni films, resistivity also decreases which can be explained by the higher ordering of the film structure by a higher degree of crystallinity.

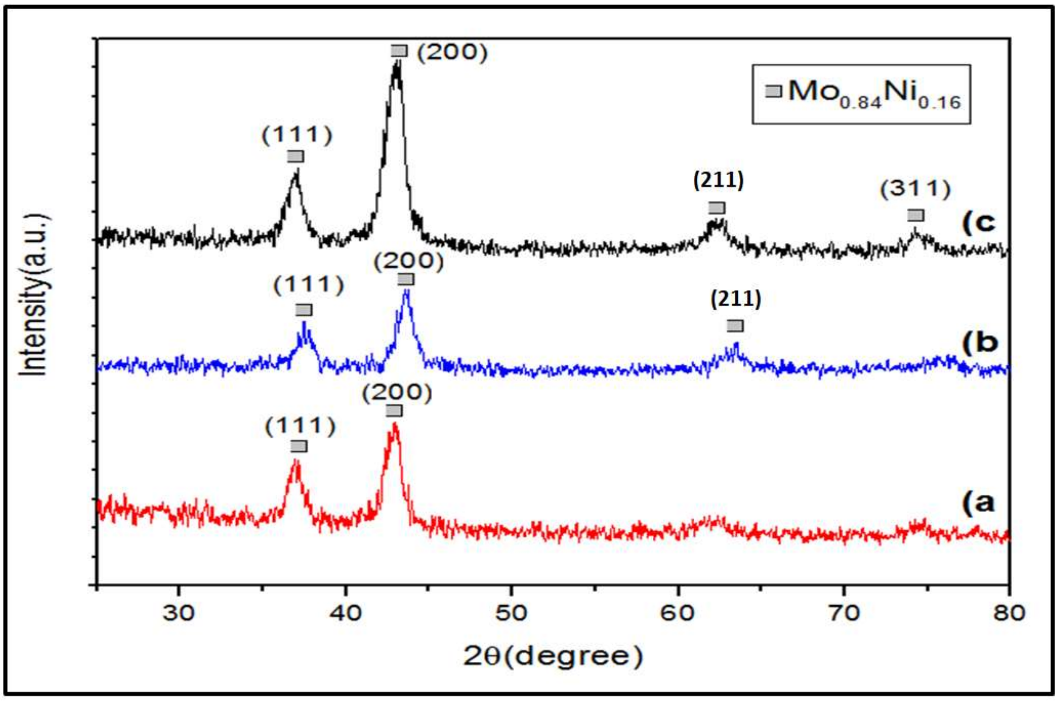

Figure 5.6.XRD pattern for Mo-Ni thin films deposited at various deposition times: a) 15min, b) 30min, and c) 45min.

5.3.2.2 Surface Morphology

The surface morphology of Mo-Ni thin films at various deposition times was characterized by AFM analysis. The AFM images exhibit that the films are uniform and homogenous. The Mo-Ni film deposited at 15min deposition time shows the needle-like structure of various sizes. When the deposition time increases to 30 min the grains become larger. With a further increase in deposition time to 45min, the films with rare small grains are observed. The average RMS roughness escalated from 6 nm to 13 nm as the deposition time increased from 15 min to 45 min. The AFM parameters are listed in table 5.2. As the Deposition time increases both of the surface roughness (RMS and R_a) are increased at the constant RF power.

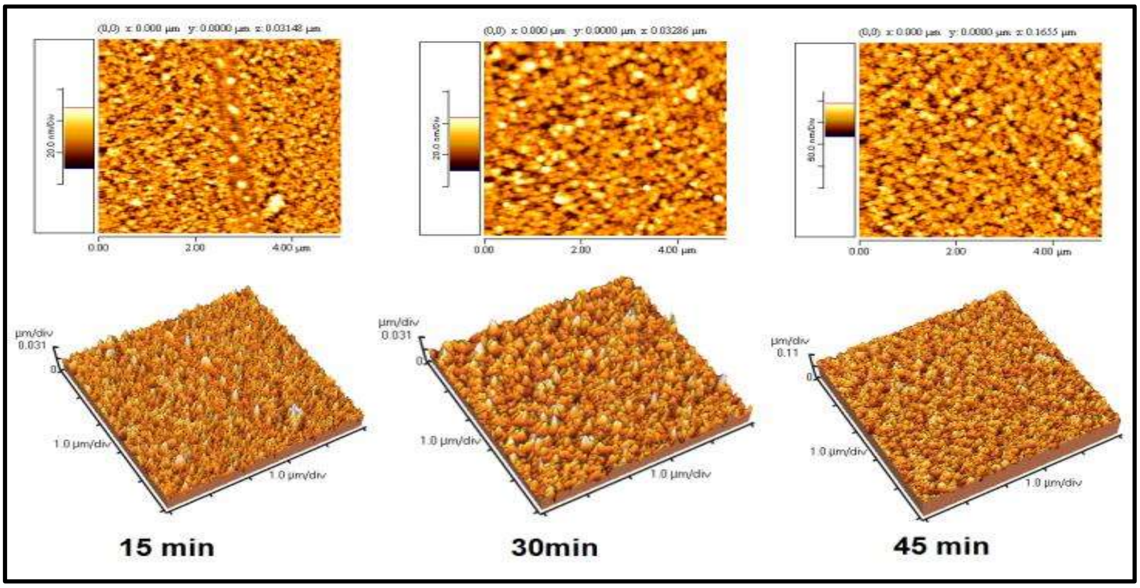

Figure 5.7. AFM images of Mo-Ni thin films deposited at different deposition times and constant RF power.

FE-SEM images of the Mo-Ni thin films deposited under different deposition times of 15, 30, and 45 min are illustrated in Figure 5.8. All FESEM images the formation of continuous, smooth, and dense films without defects such as voids, cracks, and protrusion. The micrograph of the film deposited for 15 min shows the cauliflower-like grains of various sizes in the dimensions of 10-100nm. When the deposition time is increased to 30min, the grain sizes are increased significantly and the surface becomes rough and less dense [319]. As the deposition time further increased to 45 min, similar surface morphology is obtained compared with the former one regarding roughness and compactness.

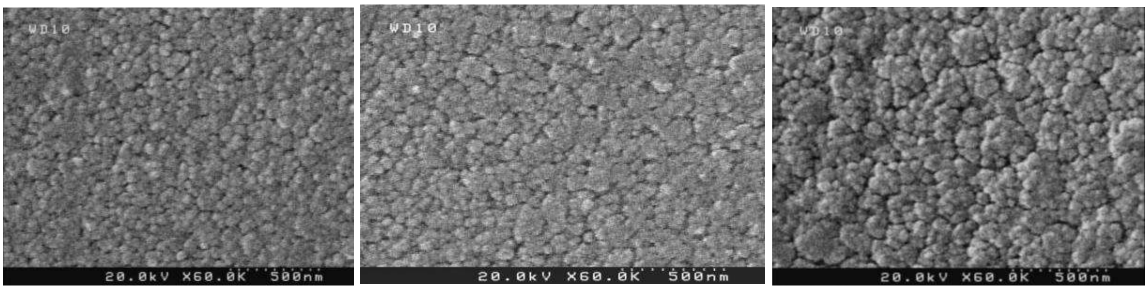

Figure 5.8. FESEM images of Mo-Ni films deposited at various deposition times: a) 15 min, b) 30 min and c) 45 min.

5.3.2.3 Electrical properties

Table 5.2 For various deposition times, a summary of the XRD data and the results for thickness, roughness, and electrical resistivity tests.

Deposition time (min)	Thickness (nm)	ρ (Ω·m)	RMS (nm)	Ra(nm)	h k l	2θ (Deg.)	β (hkl)	Crystal size (nm)	Micro strain $\times 10^{-3}$
15	850	24.1	6.43	5.04	200	42.99	0.0201	7	12.7
30	1500	12.2	6.53	5.07	200	43.55	0.0167	9	10.4
45	2800	4.60	13.21	10.3	200	43.67	0.0134	11	8.3

The variation of electrical resistivity of as-prepared Mo-Ni thin films could be mainly attributed to the difference in microstructural evolution. All the samples were measured electrically using the four-point probe and the measured values of resistivity are given in Table 5.2, which implies that by increasing the RF power the resistivity decreases drastically. As the deposition time increases from 15min to 45 min, the electrical resistivity, showing approximately an order in reduction, varied from 24.1 to 4.60 (Ω·m), respectively, at the RF power 200 W. Observation suggest that that increasing the deposition period, which results in higher crystallinity of the Mo-Ni films, resistivity also decreases which can be explained by the higher ordering of the film structure by a higher degree of crystallinity.

5.3.2.4 Optical properties

Figure 5.9 shows the optical reflectance of Mo-Ni thin-film sputters deposited at various deposition periods. The reflectance of thin films was observed to increase with increasing the thickness of thin films. As stated in previous studies, the decrease in reflectance can be due to an increase in surface roughness and crystallite size, both of which cause increased light scattering and hence lower reflectance [295]. In the case study of the sample deposited for 45 min, reflectance in all wavelengths was less than 20% because much of the light was transmitted by the film and absorbed by the substrate. This low reflectance was also due to

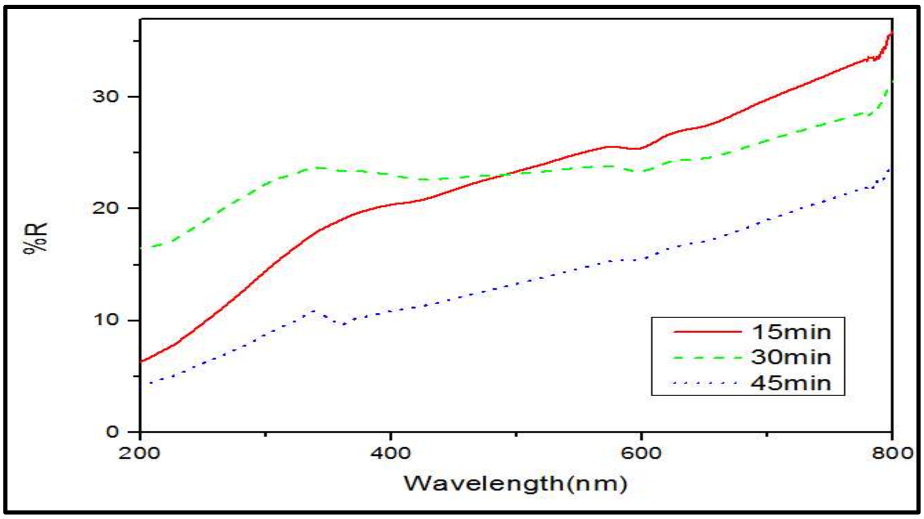

Figure 5.9. Reflectance of the Mo-Ni thin films deposited at different deposition times: a) 15min, b) 30min and c) 45min.

the nonlinearity and non-smoothness of the surface. The surface roughness of the deposited film effectively increased with the formation of pores and structures of grain boundaries.

5.4. Conclusion

Microstructural properties such as crystal structure, grain size, surface morphology, micro strain, electrical and optical analysis have been investigated for RF-sputtered Mo-Ni thin films, which were deposited under different RF power of 100 W, 150 W, and 200 W and deposition time of 15min, 30min and 45min. The result showed that applying higher RF power can lead to increasing the thickness of the films, which has a significant influence on the resistivity of the thin films. When the sputtering RF power was increased from 100 W to 200 W, the crystallinity and resistivity improved significantly. Furthermore, the working RF power had a strong impact on the surface morphology and adhesion of the Mo-Ni thin films to the soda-lime substrate, in addition to crystallinity and resistivity. At different RF power, the XRD result represents that the crystallites in the films are mostly focused in the (110) direction. In the visible spectrum, the bilayer Mo-Ni thin film was found to have an optimum reflectivity of 30% and resistivity of approximately 12.2 ($\Omega \cdot m$) at RF power 200 W. Furthermore, this chapter shows that as the deposition period increases, the resistivity of the Mo films falls, which is accompanied by an increase in grain size. When sputtered at 200 W RF power and a longer deposition period, the thin film's electrical, optical, and morphological properties were found to be the best. In conclusion, it is observed that by introducing the Ni atoms to the Mo structure physical properties improved significantly, therefore Mo-Ni compound can be good candidate for the back contact layer in CIGS solar cells application.