CHAPTER 4 RESULTS AND DISCUSSIONS

The experimental results in previous chapter will be discussed here. The discussion outlines the processes of this research work from analyzed the characteristics of $AlTi_3N$ thin films, crystal structure, crystallinity then, surface morphology, thickness and finally microstructure of $AlTi_3N$ films were discussed.

4.1 Characteristic of Aluminium Titanium Nitride Thin Films

The result of characteristics of the as-deposited $AlTi_3N$ thin films on glass slides at different deposition time by observation are shown in Table 4.1. In case of deposition time for 15 min, the film exhibited the light brown color with uniform pattern and appeared to be transparent because of insufficiency of sputter atom to form $AlTi_3N$ thin films. At 30 min, the film was more opaque with remain semitransparent whereas not the film are not uniform with brown mixed dark brown color on the right side of the glass slide. At 45 min, the opaque of the film was increase for both sides on substrate and show more dark brown color on the left side but the right side perform violet black color with uniform. The film deposited at 60 min appeared to be more opaque, violet black color along the surface with uniform characteristic on right side but the semi color of dark brown and violet black was appeared on the left side as illustrated in Figure 4.1.

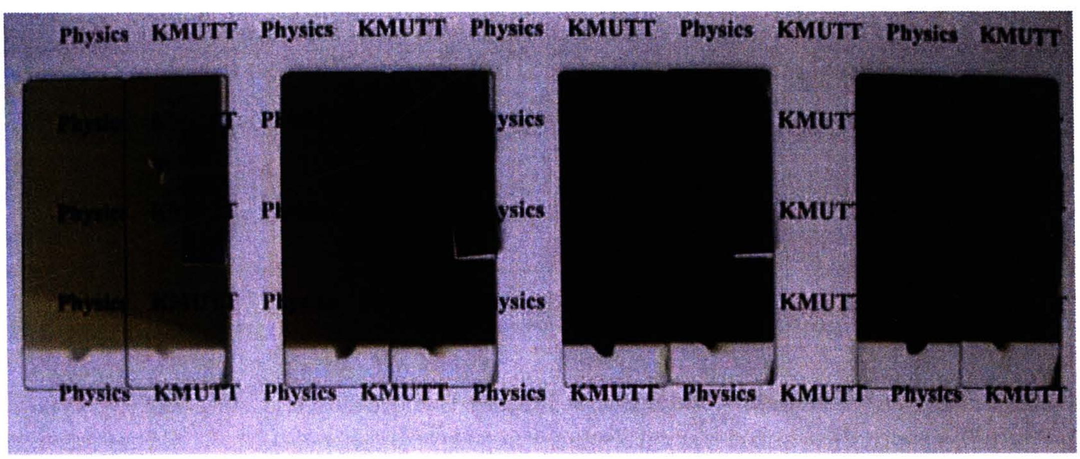


Figure 4.1 The color of $AlTi_3N$ thin film deposited with I_{Ti} 0.6 A and I_{Al} 0.6 A for different deposition times for 15 min (left) to 60 min (right)

Table 4.1 Optical properties of $AlTi_3N$ thin films deposited with different deposition time with I_{Ti} 0.6 A and I_{Al} 0.6 A

Deposition time (min)	Optical properties of $AlTi_3N$ thin films
15	Semi transparent with light brown color
30	Semi transparent with mixed of light and dark brown color
45	More opaque, dark brown mixed with a violet black color
60	Almost opaque, all violet black color with dark brown

The characteristic of $AlTi_3N$ thin films deposited on glass slides at different deposition time can be investigated by optical properties are summarized in Table 4.2. The result form observation of the film deposited for 15 min exhibited the brown color and appeared to be semitransparent due to insufficiency of sputter atom to form $AlTi_3N$ thin films. At 30 min, the film was more opaque with remain semitransparent with dark brown color. At 45 min, the film was almost opaque and show violet black mixed with a uniform pattern. Furthermore, the film deposited at 60 min appeared to be completely opaque with uniform characteristic of violet black color which indicated that also show the color of the $AlTi_3N$ thin film as illustrated in Figure 4.2.

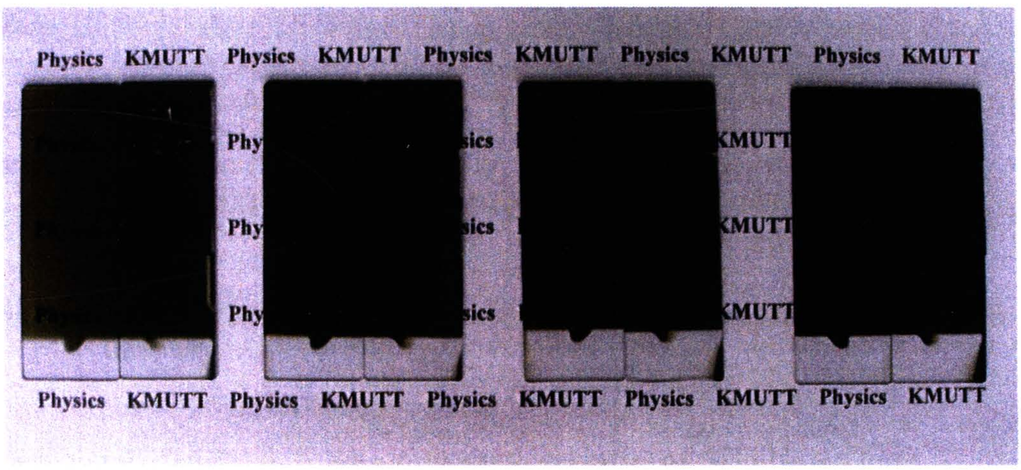


Figure 4.2 The color of $AlTi_3N$ thin film deposited with I_{Ti} 0.7 A and I_{Al} 0.6 A for different deposition times for 15 min (left) to 60 min (right)

Table 4.2 Optical properties of $AlTi_3N$ thin films deposited with different deposition time with I_{Ti} 0.7 A and I_{Al} 0.6 A

Deposition time (min)	Optical properties of $AlTi_3N$ thin films
15	Semi transparent with brown color
30	Semi transparent, dark brown color with more opaque
45	Almost opaque, with violet black color
60	opaque, all violet black color

The optical properties of $AlTi_3N$ thin films deposited on glass slides at different deposition time are presented in Table 4.3. Remark for the case of deposition time for 15 min, the film exhibited the brown color mixed and appeared to be semitransparent due to insufficiency of sputter atom to form $AlTi_3N$ thin films. At 30 min, the film was more opaque with remain semitransparent with brown mixed with black color. At 45 min, the film was almost opaque and show black mixed with a little of brown color. The film deposited at 60 min appeared to be completely opaque, violet black color along the surface with uniform characteristic which perform the color of the $AlTi_3N$ thin film as illustrated in Figure 4.2.

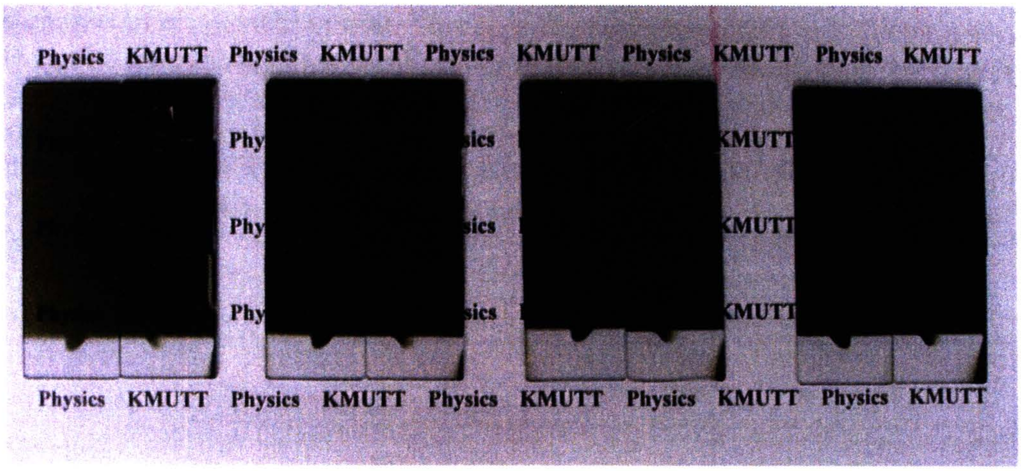


Figure 4.3 The color of $AlTi_3N$ thin film deposited with I_{Ti} 0.8 A and I_{Al} 0.6 A for different deposition times for 15 min (left) to 60 min (right)

Table 4.3 Optical properties of $AlTi_3N$ thin films deposited with different deposition time with I_{Ti} 0.8 A and I_{Al} 0.6 A

Deposition time (min)	Optical properties of $AlTi_3N$ thin films
15	Semi transparent with brown color
30	Semi transparent, brown mixed with black color
45	Almost opaque, black mixed with a little of brown color
60	Opaque, all violet black color

The results revealed that the film the color and uniform pattern were developed by increasing titanium sputtering currents and deposition times. The color of the as deposited films were changed from brown color with semitransparent to more opaque with violet black when increase deposition time until 60 min for all titanium sputtering current values. Moreover, the similar trend was observed by comparing the films deposited at various titanium sputtering currents with fixed deposition time. It can be conclude that the films deposited for 60 min for all coating exhibited most opaque with color according to standard $AlTi_3N$ thin films of violet black color [39]. The reason was due to sufficiency of sputter atom from sputtering target to form high amount of deposited atom agglomerated on substrates for long deposition time and high titanium sputtering current resulting the $AlTi_3N$ thin films.

The characteristic of $AlTi_3N$ thin films deposited on glass slides at different deposition time can be investigated by optical properties are summarized in Table 4.4. The result form observation of the film deposited for all deposition time exhibited the violet black color and appeared to be opaque with uniform characteristic due to sufficiency of sputter atom to form $AlTi_3N$ thin films which indicated that also show the color of the $AlTi_3N$ thin film as illustrated in Figure 4.4

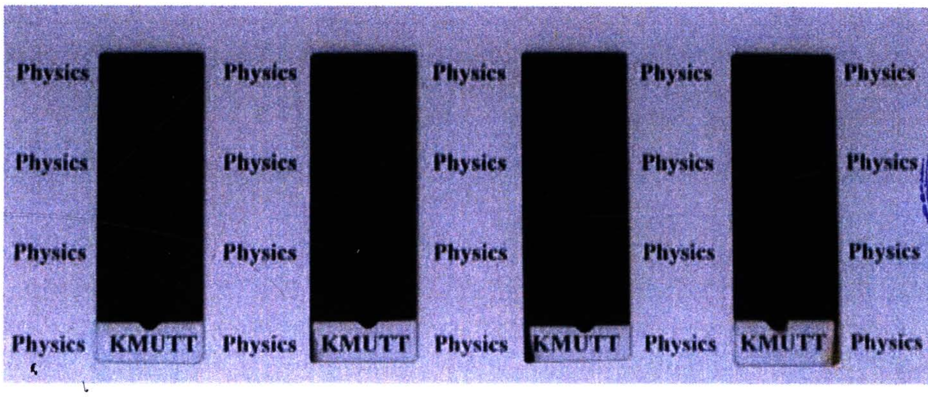


Figure 4.4 The color of $AlTi_3N$ thin film deposited with I_{Ti} 1.0 A and I_{Al} 0.6 A for different deposition times for 15 min (left) to 60 min (right)

Table 4.4 Optical properties of $AlTi_3N$ thin films deposited with different deposition time with I_{Ti} 1.0 A and I_{Al} 0.6 A

Deposition time (min)	Optical properties of $AlTi_3N$ thin films
15	Opaque, all violet black color
30	Opaque, all violet black color
45	Opaque, all violet black color
60	Opaque, all violet black color

The results revealed that the film with violet black color and uniform pattern were observed for all titanium deposition times. The color of the as deposited films were not changed and remain violet black color when increase deposition time until 60 min for all titanium sputtering. It can be conclude that the films for all coating exhibited opaque with color according to standard $AlTi_3N$ thin films of violet black color [39]. The reason was due to sufficiency of sputter atom from sputtering target to form high amount of deposited atom agglomerated on substrates for long deposition time resulting the $AlTi_3N$ thin films.

The characteristic of $AlTi_3N$ thin films deposited on glass slides at different deposition time can be investigated by optical properties are summarized in Table 4.4. The result form observation of the film deposited for all deposition time exhibited the violet black color and appeared to be opaque with uniform characteristic due to sufficiency of sputter atom to form $AlTi_3N$ thin films which indicated that also show the color of the $AlTi_3N$ thin film as illustrated in Figure 4.4.

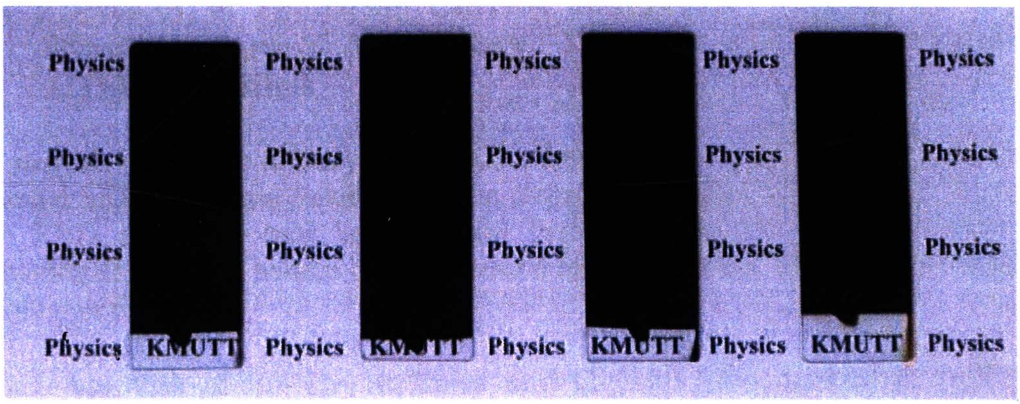


Figure 4.5 The color of $AlTi_3N$ thin film deposited with I_{Ti} 1.2 A and I_{Al} 0.6 A for different deposition times for 15 min (left) to 60 min (right)

Table 4.5 Optical properties of $AlTi_3N$ thin films deposited with different deposition time with I_{Ti} 1.2 A and I_{Al} 0.6 A

Deposition time (min)	Optical properties of $AlTi_3N$ thin films
15	Opaque, all violet black color
30	Opaque, all violet black color
45	Opaque, all violet black color
60	Opaque, all violet black color

The results revealed that the film the color and uniform pattern were developed by increasing titanium sputtering currents and deposition times. The color of the as deposited films were changed from brown color with semitransparent to more opaque with violet black when increase deposition time until 60 min for all titanium sputtering current values. Moreover, the similar trend was observed by comparing the films deposited at various titanium sputtering currents with fixed deposition time. It can be conclude that the films deposited for 60 min for all coating exhibited most opaque with color according to standard $AlTi_3N$ thin films of violet black color [39]. The reason was due to sufficiency of sputter atom from sputtering target to form high amount of deposited atom agglomerated on substrates for long deposition time and high titanium sputtering current resulting the $AlTi_3N$ thin films.

4.2 Characterization of Aluminium Titanium Nitride Thin Films

All the appropriate parameters are applied for preparation of $AlTi_3N$ thin films. The characteristic of the film such as; phase, crystal size and crystallinity structure of $AlTi_3N$ thin films, morphology, thickness, and microstructure, prepared at different Ti and Al sputtering currents and deposition times will be discussed as following:

4.2.1 Effects of Ti Sputtering Current and Deposition Time on Crystal Structure, Surface Morphology, Thickness and Microstructure of $AlTi_3N$ Thin Films

The analysis of the crystallinity, crystal size, crystal structure of $AlTi_3N$ thin films was separated into three parts according to the techniques applied in the study. The results from XRD technique will be discussed first and then followed by crystal size calculation from XRD pattern using Sherrer's formula, finally TEM analysis results of $AlTi_3N$ thin films.

4.2.1.1 Analysis of the Crystallinity and Crystal Structure of $AlTi_3N$ Thin Films by XRD

The crystal structures of deposited films were investigated by XRD measurements. Figure 4.6-4.10 show XRD patterns of the films deposited at a constant aluminium current of 0.6 A with different titanium current of 0.6, 0.7, 0.8, 1.0, 1.2 A, and different times of 15, 30, 45 and 60 min. The angles (2θ) of 36.96°, 42.96°, 56.50° and 62.26° corresponding to (112), (004), silicon (100) and (153) planes are clearly observed for all deposited films. The line positions in the XRD patterns are formed to be consistent with the orthorhombic $AlTi_3N$ structures are in agreement with the standard JCPDS card of $AlTi_3N$ (file no. 51-0724). It was implied that the film have aluminum content than 50.%. The XRD results show that all films exhibited similar crystal structures development over the deposition time. The x-ray intensity of films increased with deposition times indicated that the higher crystallinity with longer deposition time; energy accumulation of atoms on film which resulting in the increases of adatom mobility during film formation and leading to higher crystallinity of the films through longer deposition time.

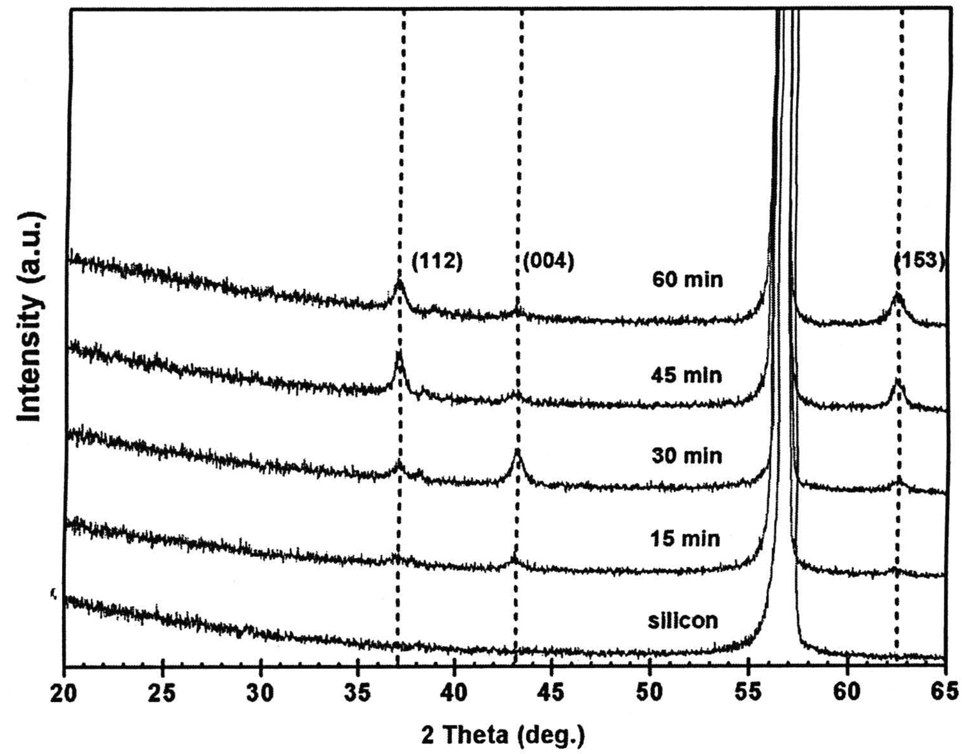


Figure 4.6 The XRD patterns of $AlTi_3N$ thin film deposited with I_{Ti} 0.6 A and I_{Al} 0.6 A for different deposition times

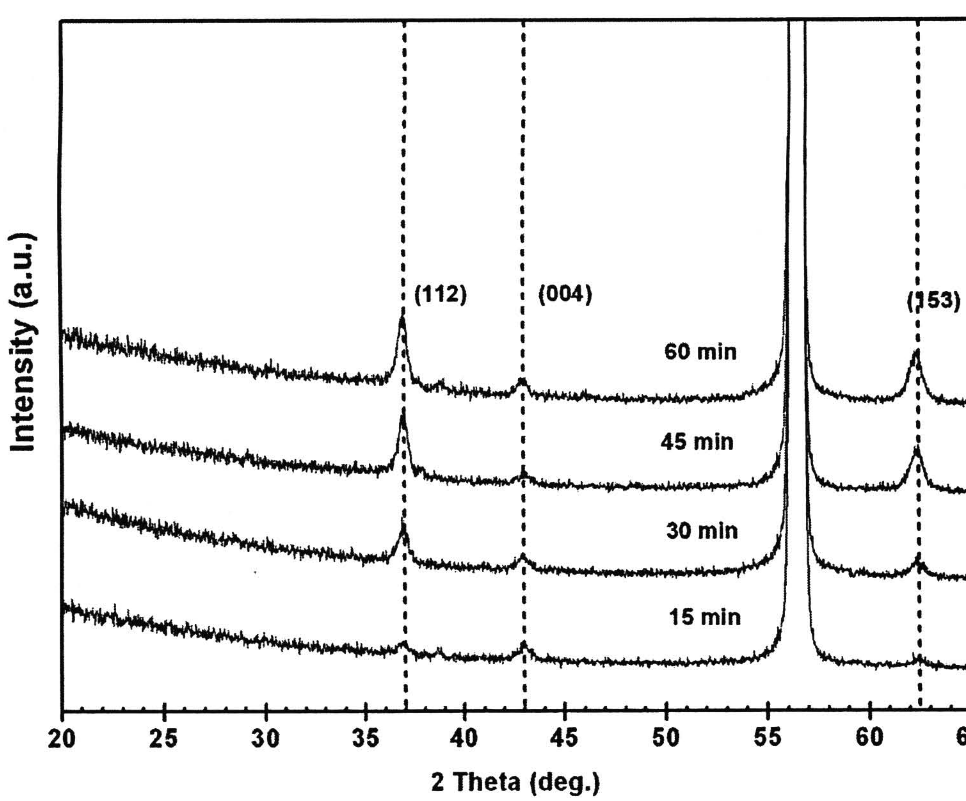


Figure 4.7 The XRD patterns of $AlTi_3N$ thin film deposited with I_{Ti} 0.7 A and I_{Al} 0.7 A for different deposition times

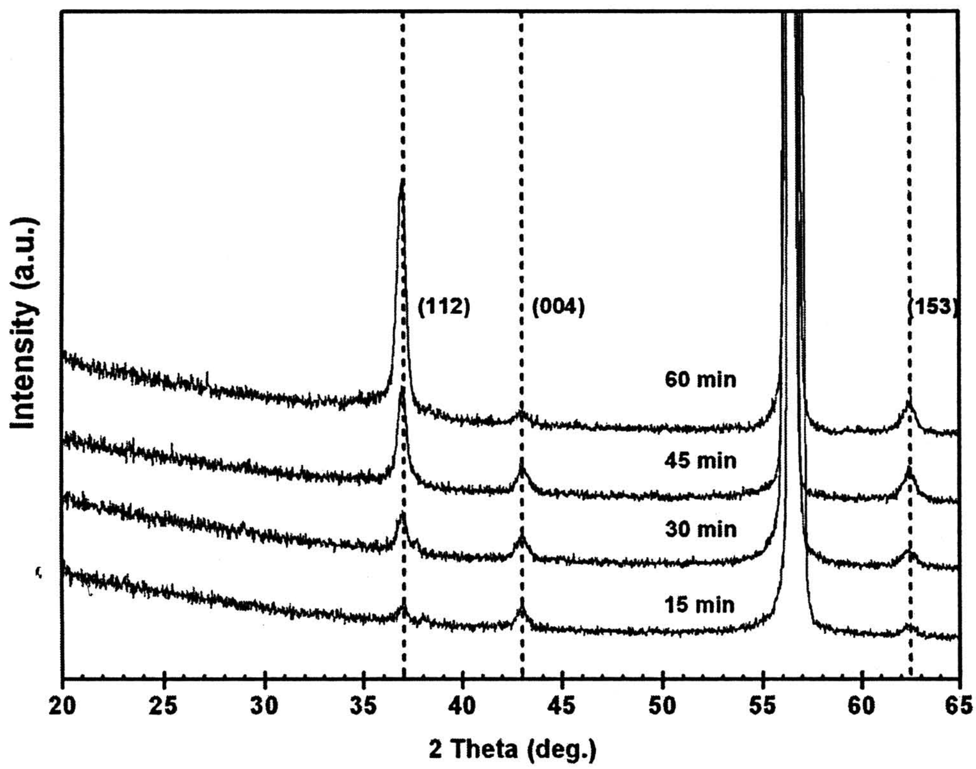


Figure 4.8 The XRD pattern of $AlTi_3N$ thin film deposited with I_{Ti} 0.8 mA and I_{Al} 0.6 A for different deposition times

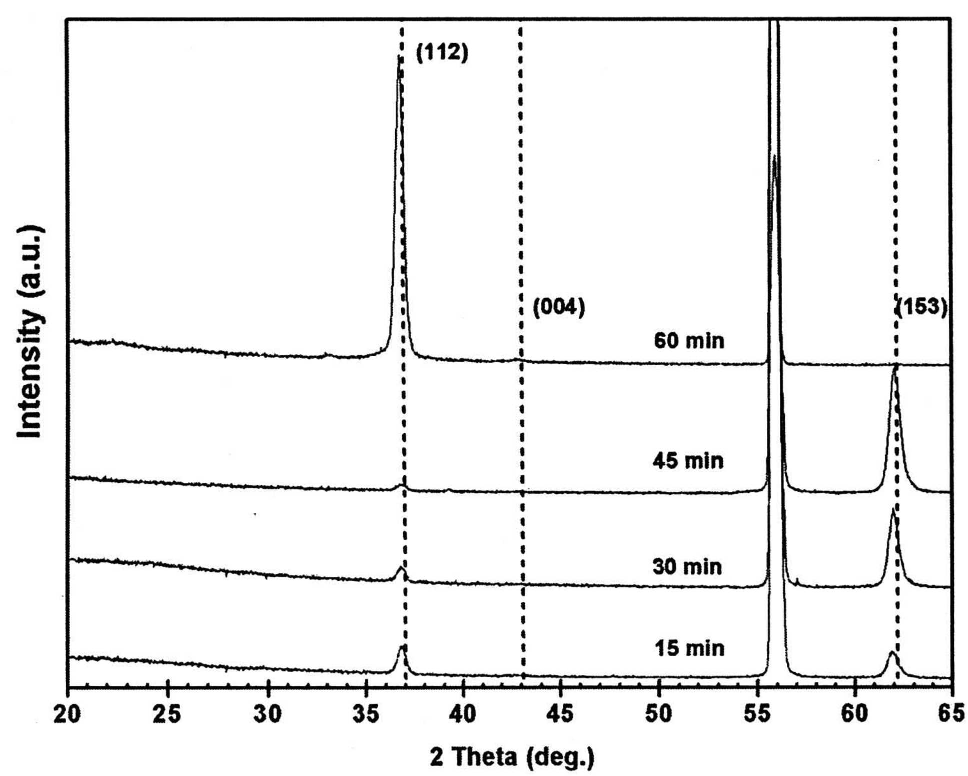


Figure 4.9 The XRD pattern of $AlTi_3N$ thin film deposited with I_{Ti} 1.0 A and I_{Al} 0.6 A for different deposition times

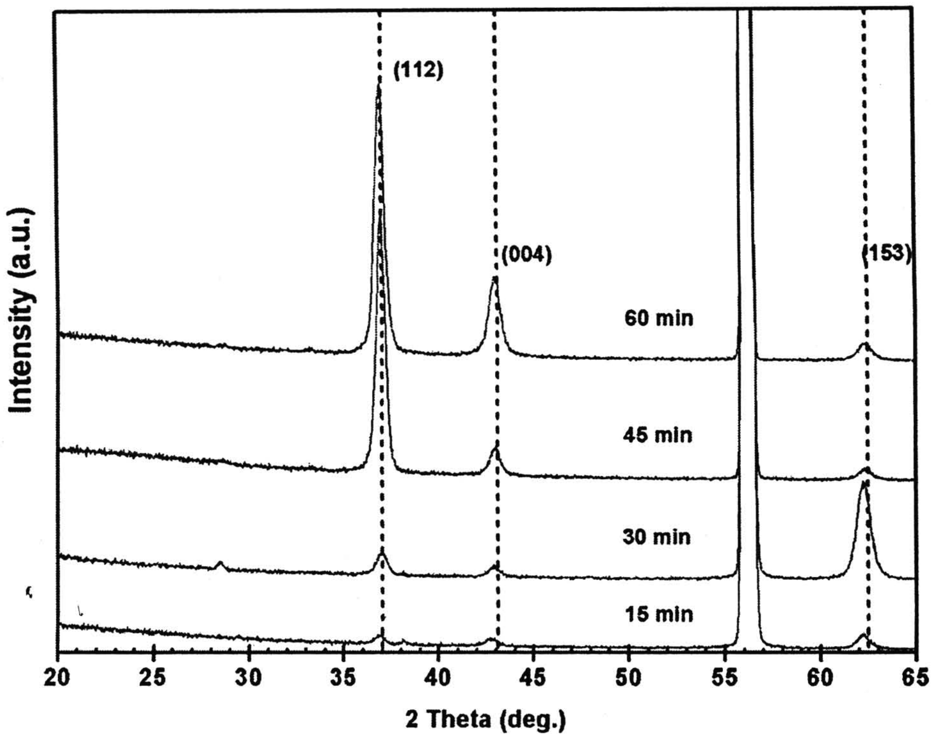


Figure 4.10 The XRD pattern of $AlTi_3N$ thin film deposited with I_{Ti} 1.2 A and I_{Al} 0.6 A for different deposition times

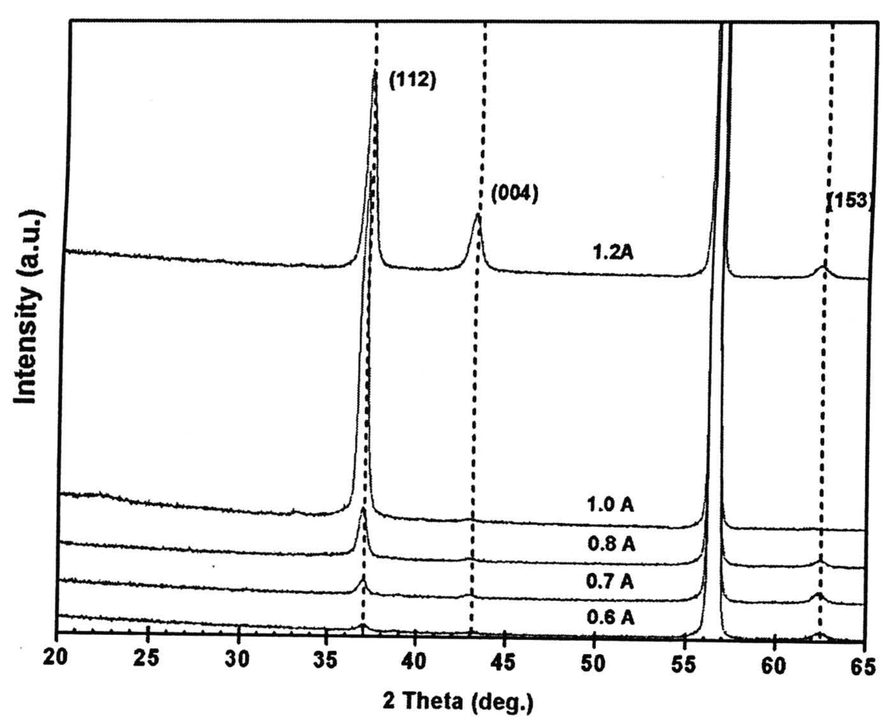


Figure 4.11 The XRD pattern of $AlTi_3N$ thin film deposited at different sputtering current for 60 min

It can be conclude that the result from XRD measurement for the film deposited at various deposition time of each Ti sputtering current revealed the XRD intensity increased as longer deposition time with exhibited highest intensity of (112) plane for 60 min. Therefore, the $AlTi_3N$ thin films deposited at 60 min show the highest crystallinity for all coatings. In case study how the Ti sputtering current related to the crystal structure, Figure 4-11 show XRD patterns of the films deposited at a constant deposition time for 60 min with different titanium current of 0.6, 0.7 , 0.8 , 1.0 and 1.2 A, respectively. The XRD peaks attributed to (112), (004) and (153) planes are clearly observed for all deposited films. The X-ray intensity of (112) plane increases significantly with sputtering current up to 1.0 A. When the sputtering current further increase to 1.2 A, the XRD results show that all films exhibited similar crystal structures but the intensity at (112) plane decrease while the (004) plane was clearly observed. The x-ray intensity of films increased with sputtering current indicated that the higher crystallinity with longer sputtering current; energy accumulation of atoms on film which resulting in the increases of adatom mobility during film formation and leading to highest crystallinity when sputtering reach to 1.0 A. The further increase sputtering attributed to exceed the atom mobility which destroy the crystal structure resulting the decrease of (112) plane and finally effect to more generate the low stable (004) plane.

4.2.1.2 Crystal Size Calculation of $AlTi_3N$ Thin Films by XRD

The crystal size was determined from Scherrer equation. The full width at half maximum of the x-ray diffraction peaks of (112), (004) and (153) planes, respectively, were employed into the equation to calculate the crystal size. As shown in table 4.6, the crystal size was calculated and varied from 22.9 to 53.4 nm which depended on the deposition parameters as titanium sputtering current and deposition time, indicating that $AlTi_3N$ thin films deposited by reactive co-unbalanced magnetron sputtering exhibit a nanocrystalline structure. In addition, the results revealed that the crystal sizes are in good agreement with the crystallinity development for each sputtering current of titanium target due to the increase of deposition time from 15 to 60 min will enhance heat accumulation and also multiply the adatom mobility inside thin films structure, thus rearrangement of random orientation in the crystal structure to more order orientation which turn to reduce void or pore formation located in the structure of thin film, therefore created the higher crystallinity of the structure resulting the changing of crystal size through longer deposition time for each sputtering current that summarized in Table 4.6.

Table 4.6 Variations of the crystal size of $AlTi_3N$ thin films with four different deposition times and three different titanium sputtering currents of 0.6, 0.7, 0.8, 1.0 and 1.2 A

Deposition time (min)	Crystal size (nm)				
	0.6 A	0.7 A	0.8 A	1.0 A	1.2 A
15	31.0	30.0	53.4	34.2	39.9
30	28.5	40.8	31.0	36.4	27.5
45	33.5	27.9	35.6	40.8	33.5
60	27.9	32.2	33.5	34.9	28.9

4.2.1.3 Analysis of the Crystallinity and Structure of $AlTi_3N$ Thin Films by TEM

The crytallinity and structure of AlT_3N thin films in nano-scale may be difficult to characterize when employing XRD inspection because the thickness of the films is too thin for inspection. Transmission Electron Microscopy (TEM) technique is considered as a better alternative tool for crytallinity and structure of $AlTi_3N$ thin films. For TEM analysis, the films were deposited on TEM grids substrate. Figure 4.12 (a)-(b) show High-Resolution Transmission Electron Microscopy (HRTEM) images and the corresponding Selected-Area Electron Diffraction (SAED) patterns of $AlTi_3N$ thin films deposited with a Ti sputtering current of 0.6 A and for different deposition times of 15, 30, 45 and 60 min, respectively. However, the HRTEM images and SAED patterns obtained with Ti sputtering currents of 0.7 and 0.8 A were very similar to that from $AlTi_3N$ thin film deposited with a sputtering current of 0.6 A as previously presented in Figure 4.8.

Figure 4.12 (a), showing the HRTEM images of $AlTi_3N$ thin films deposited at a Ti sputtering current of 0.6 A, crystalline growth can be identified from the random orientation of several lattice planes. The four measured d-spacings are indexed in the Figures i.e. 0.24, 0.22, 0.23 and 0.25 nm, respectively. The corresponding SAED patterns; Figure 4.15 (b), are used for phase determination. The electron diffraction patterns display rings, indicating a polycrystalline structure. In the diffraction rings, the d-values is corresponding to the (112), (004), (200), (153) and (243) planes of the crystalline orthorhombic $AlTi_3N$ in the Joint Committee on Powder Diffraction Standard-International Center for Diffraction Data (JCPDF-ICDD) card no. 51-0724.

The diffraction rings were clearly observed at short deposition time for 15 min implied that the crystal rather not good structure as shown in Figure 4.12 (b). As the longer deposition time reach to 60 min, it was found that the diffraction rings pattern become disappear and obviously seen diffraction with spot pattern. Moreover, the SAED patterns of the films deposited for 60 min exhibited diffraction of spotty characteristic across the measurement area which related to the pattern from theory. These result from above can summary that the $AlTi_3N$ thin films were higher crystallinty as a function of deposition time which correlative the XRD measurement. The results from TEM measurement were not only can evidently conclude with a good agreement to the standard data of $AlTi_3N$, but also able to confirm the crystal structure from the XRD results.

The HRTEM image which illustrate the crystal structure and crystallinity of the $AlTi_3N$ thin films deposited at different deposition time of 15, 30, 45 and 60 min with applied current to Ti sputtering target for 0.7 A are shown in Figure 4.13 (a). The crystal planes and lattice orientation given from TEM measurement can be explored the crystal structure development and crystal growth. The d-spacings between lattice planes of four different deposition times were measured and identified from the Figures are 0.25, 0.25, 0.26 and 0.25 nm, respectively which corresponding SAED patterns; Figure 4.13 (b), are used for phase determination. The electron diffraction patterns display rings, indicating a polycrystalline structure. In the diffraction rings, the d-values is corresponding to the (112), (004), (153) and (242) planes of the crystalline orthorhombic $AlTi_3N$ in the Joint Committee on Powder Diffraction Standard-International Center for Diffraction Data (JCPDF-ICDD) card no. 51-0724.

The result from electron diffraction of the film deposited for 15 min revealed clearly the diffraction rings pattern of $AlTi_3N$ structure as shown in Figure 4.13 (b). The diffraction ring patterns were start more discontinuous line characteristic with dot patterns were take place along when increase deposition time to 30 and 45 min. As the longer deposition time reach to 60 min, it was found that the diffraction rings pattern become completely disappear and obviously seen diffraction with spot pattern. Moreover, the SAED patterns of the films deposited for 60 min exhibited diffraction of spotty characteristic across the measurement area which related to the pattern from theory. It can summarized that the low crystallinity observed from short deposition time because of appear the diffraction ring patterns, however, the films exhibited high crystallinity as increase deposition time to 60 min.

Fig. 4.14 (a) show the typical plan-view HRTEM images and SAED pattern obtain from this area of the films deposited at different deposition time of 15, 30, 45 and 60 min with applied current to Ti sputtering target for 0.8 A. The crystal planes and lattice orientation given from TEM measurement can be explore the crystal structure development and crystal growth. The d-spacings between lattice planes of four different deposition times were measured and identified from the Figures are 0.25, 0.22, 0.22 and 0.24 nm, respectively which corresponding SAED patterns; Figure 4.14 (b), are used for phase characterization. The electron diffraction patterns display rings, indicating a polycrystalline structure. In the diffraction rings, the d-values is corresponding to the (112), (004), (153), (135) and (204) planes of the crystalline orthorhombic $AlTi_3N$ in the Joint Committee on Powder Diffraction Standard-International Center for Diffraction Data (JCPDF-ICDD) card no. 51-0724.

The diffraction pattern of the film deposited for 15 min revealed the diffraction rings which are not complete continuous line of circumference with compose of dot pattern along these line as demonstrated in Figure 4.14 (b). The diffraction ring patterns were began disappear whereas dot patterns were clearly investigated with increasing the deposition times to 30 and 45 min. At 60 min, the diffraction rings pattern become completely disappear and obviously seen diffraction with spot pattern. Moreover, the SAED patterns of the films deposited for 60 min exhibited diffraction of spotty characteristic across the measurement area which related to the pattern from theory. It can summarized that the low crystallinity observed from short deposition time because of appear the diffraction ring patterns, however, the films exhibited high crystallinity as increase deposition time to 60 min.

The structure of $AlTi_3N$ films deposited at different Ti sputtering current for 60 min were also investigated by TEM. Figure 4.15 (a) shows a typical plane view of HRTEM image of a film deposited for 60 minutes. According to the HRTEM image, the lattice fringes are clearly distinguish and the measured distance of the fringe was 0.24 nm which is in a good agreement with the standard JCPDS:51-0724 of (112) and (023) planes with d value of 0.24 and 0.25 nm for $AlTi_3N$ orthorhombic phase. For Ti sputtering current of 0.6, 0.7 and 0.8 A, the related SAED pattern of the $AlTi_3N$ thin films is shown in Figure 4.9 (b). The (112), (004) and (153) diffraction rings of the orthorhombic structure correspond to the nanocrystalline $AlTi_3N$ structure from standard data (JCPDS:51-0724). The highest crystallinity of $AlTi_3N$ thin films are confirmed by the more spotty pattern appearing in the electron diffraction pattern as shown in Figure 4.9 (b) when increase sputtering current. The reason is a high sputtering current value tends to increase adatom mobility resulting enhance formation energy of $AlTi_3N$ structure.

These result from above can conclude that the $AlTi_3N$ thin films were higher crystallinty as a function of titanium sputtering current and deposition times which correlative the XRD measurement. The results from TEM measurement were not only can evidently conclude with a good agreement to the standard data of $AlTi_3N$, but also able to confirm the crystal structure from the XRD results.

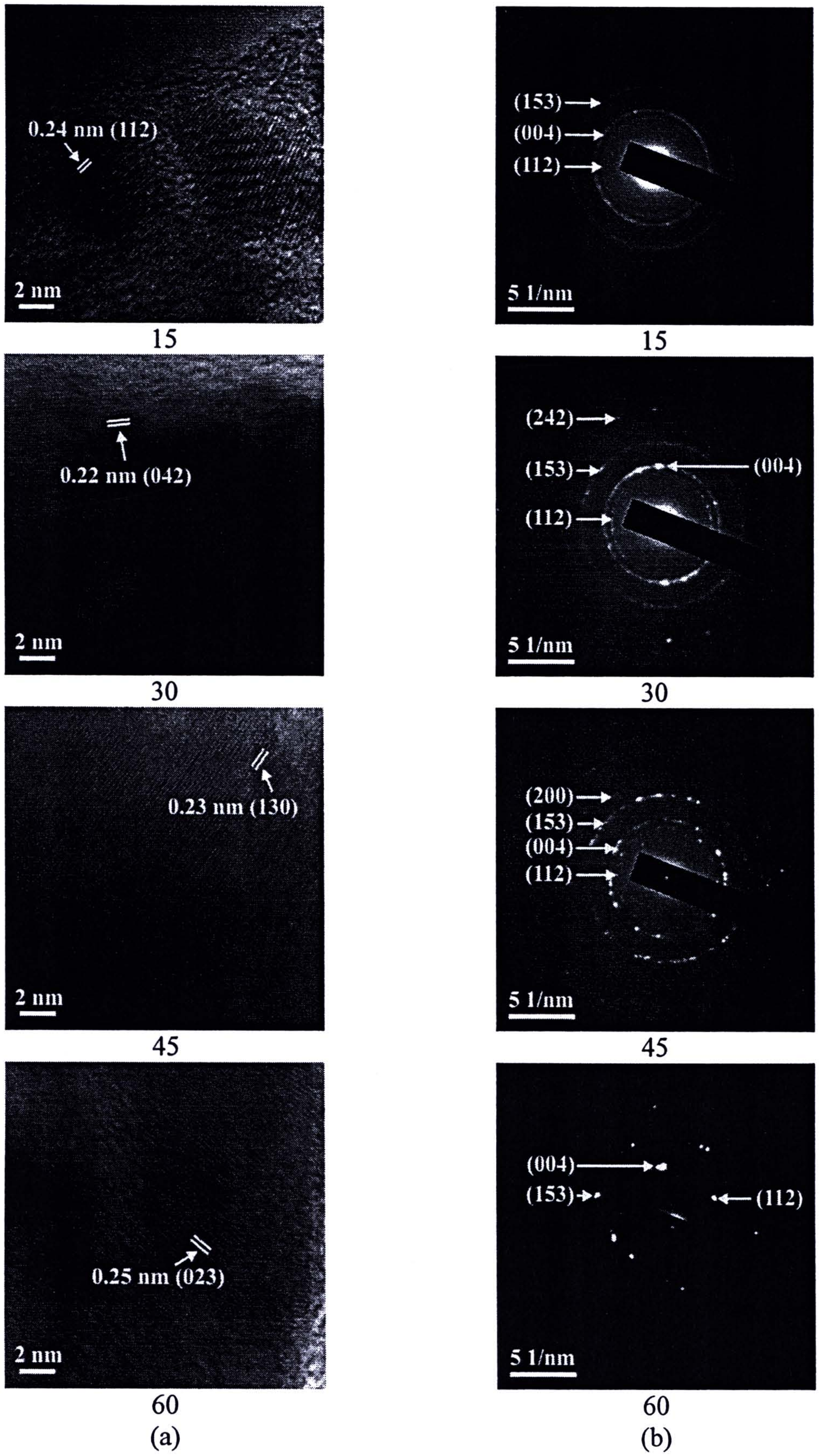


Figure 4.12 (a) HRTEM images and (b) SAED images of $AlTi_3N$ thin films deposited with a constant Ti sputtering current of 0.6 A and for four different deposition times of 15, 30, 45 and 60 min

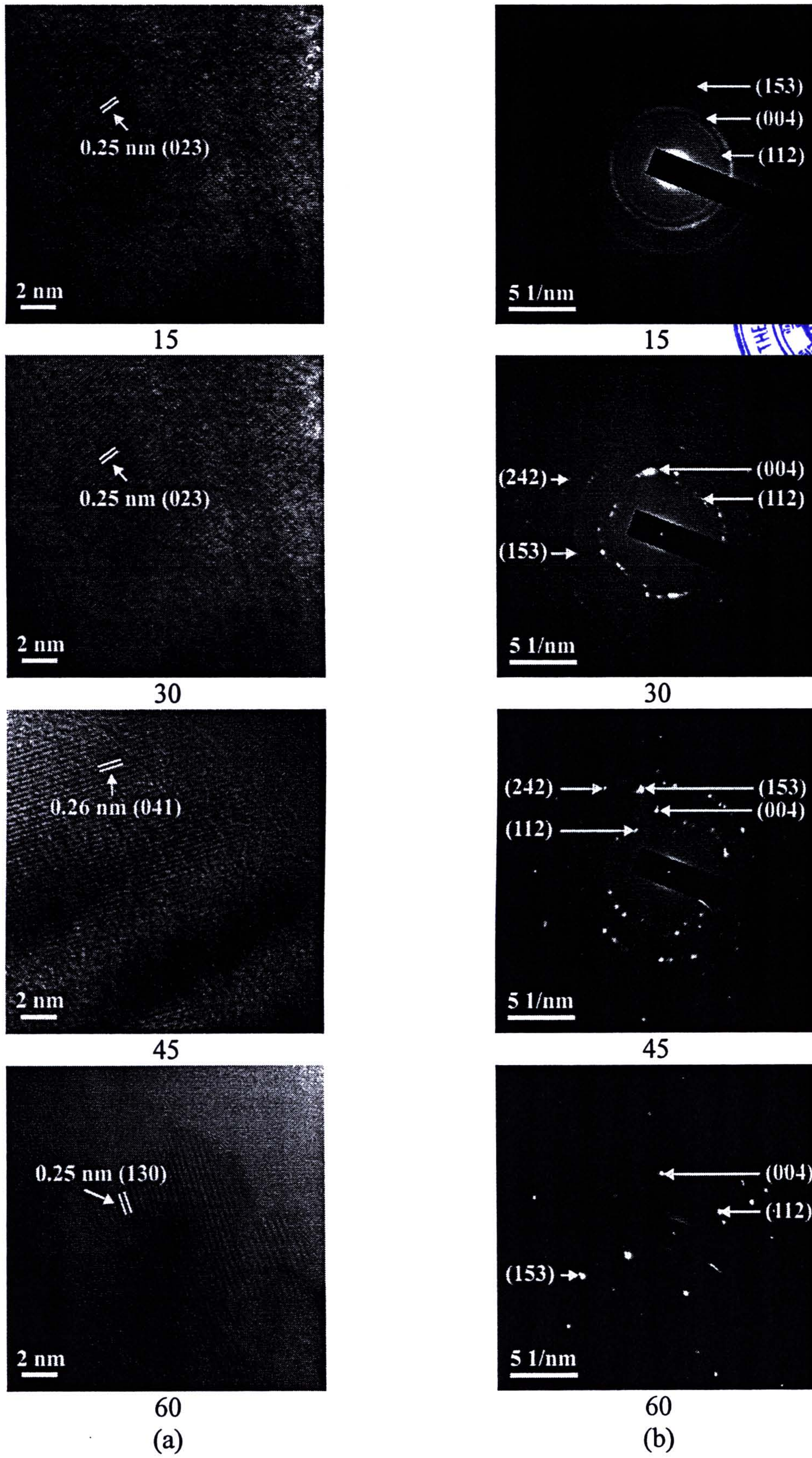


Figure 4.13 (a) HRTEM images and (b) SAED images of $AlTi_3N$ thin films deposited with a constant Ti sputtering current of 0.7 A and for four different deposition times of 15, 30, 45 and 60 min

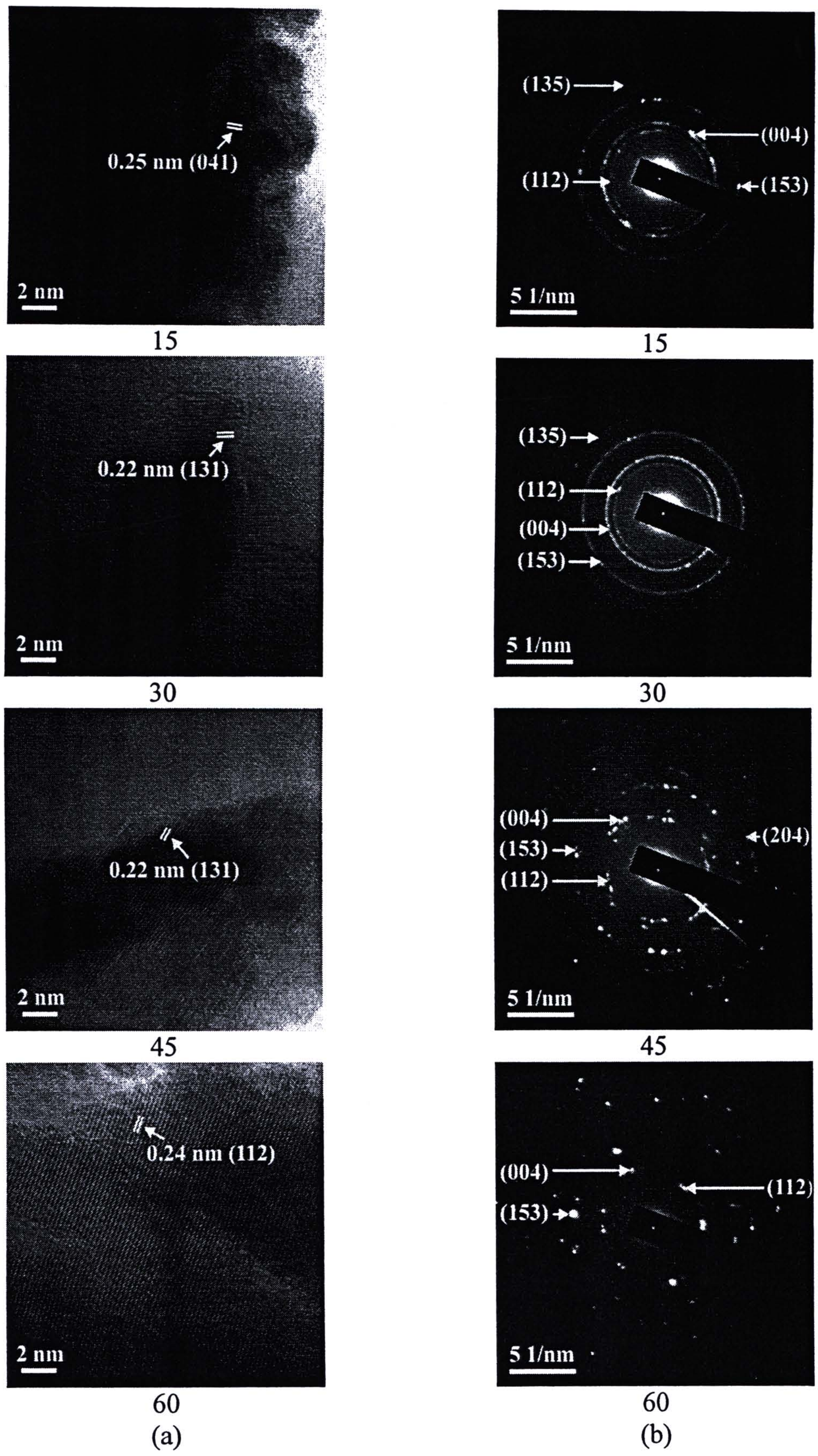


Figure 4.14 (a) HRTEM images and (b) SAED images of $AlTi_3N$ thin films deposited with a constant Ti sputtering current of 0.8 A and for four different deposition times of 15, 30, 45 and 60 min

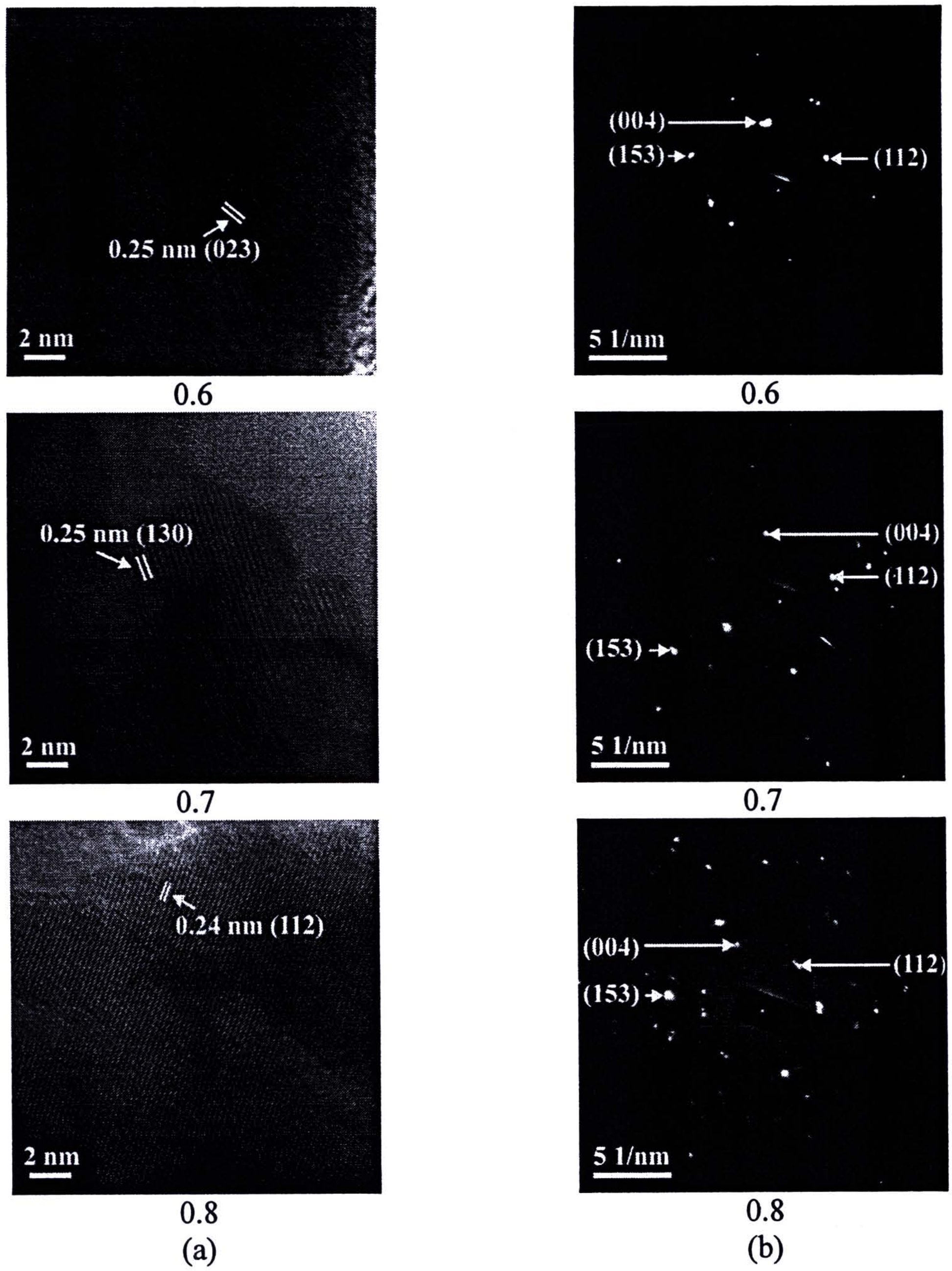


Figure 4.15 (a) HRTEM images and (b) SAED images of $AlTi_3N$ thin films deposited with a constant deposition time of 60 min and for three different Ti sputtering current of 0.6, 0.7 and 0.8 A

4.2.1.4 Analysis of the Surface Morphology of $AlTi_3N$ Thin Films by AFM

Surface Morphology of $AlTi_3N$ Thin Films Deposited at I_{Ti} = 0.6 A

Surface morphology of the $AlTi_3N$ thin films deposited on glass slide substrates were investigated by AFM technique. The surface morphology as studied by AFM consisted of surface roughness (R_{rms}) and thickness of films. Generally, R_{rms} parameter is the average height or depth of discrete profiles deviation. Figures 4.16 (a)-(d) show two- and three-dimensional images by atomic force microscopy (AFM) obtained from four sample surfaces deposited at a Ti sputtering current of 0.6 A with different deposition times of 15, 30, 45 and 60 min, respectively. The columnar grains were observed on the sensing film surface for all samples with the grain sizes were found to be 13.7 (for deposition time of 15 and 30 min) 13.2 and 15.0 nm, respectively. The surface roughness of three samples surface are also shown in Figure 4.16 (a)-(d) and found to be 1.8, 2.0, 5.9 and 9.0 nm, respectively. The results on the surface roughness and columnar grains are concluded in Table 4.7. The results indicate that the surface roughness and grain size are increased with the increasing of deposition time.

The grain size of $AlTi_3N$ thin films as estimated from the 2D-AFM images in Figure 4.16 (a)-(d), however, was found to increase almost linearly with the increasing of the deposition times from 15 min to 45 min. The rapidly increase were found as the deposition time up to 60 min. The increase of deposition time led to the increase of substrate temperature and the increase of surface roughness as high crystallization was developed.

Table 4.7 Variation of surface roughness and grain sizes of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.6 A for four deposition times

Deposition time(min)	RMS roughness (nm)	Grain size (nm)
15	1.8	13.7
30	2.0	13.7
45	5.9	14.7
60	9.0	19.6

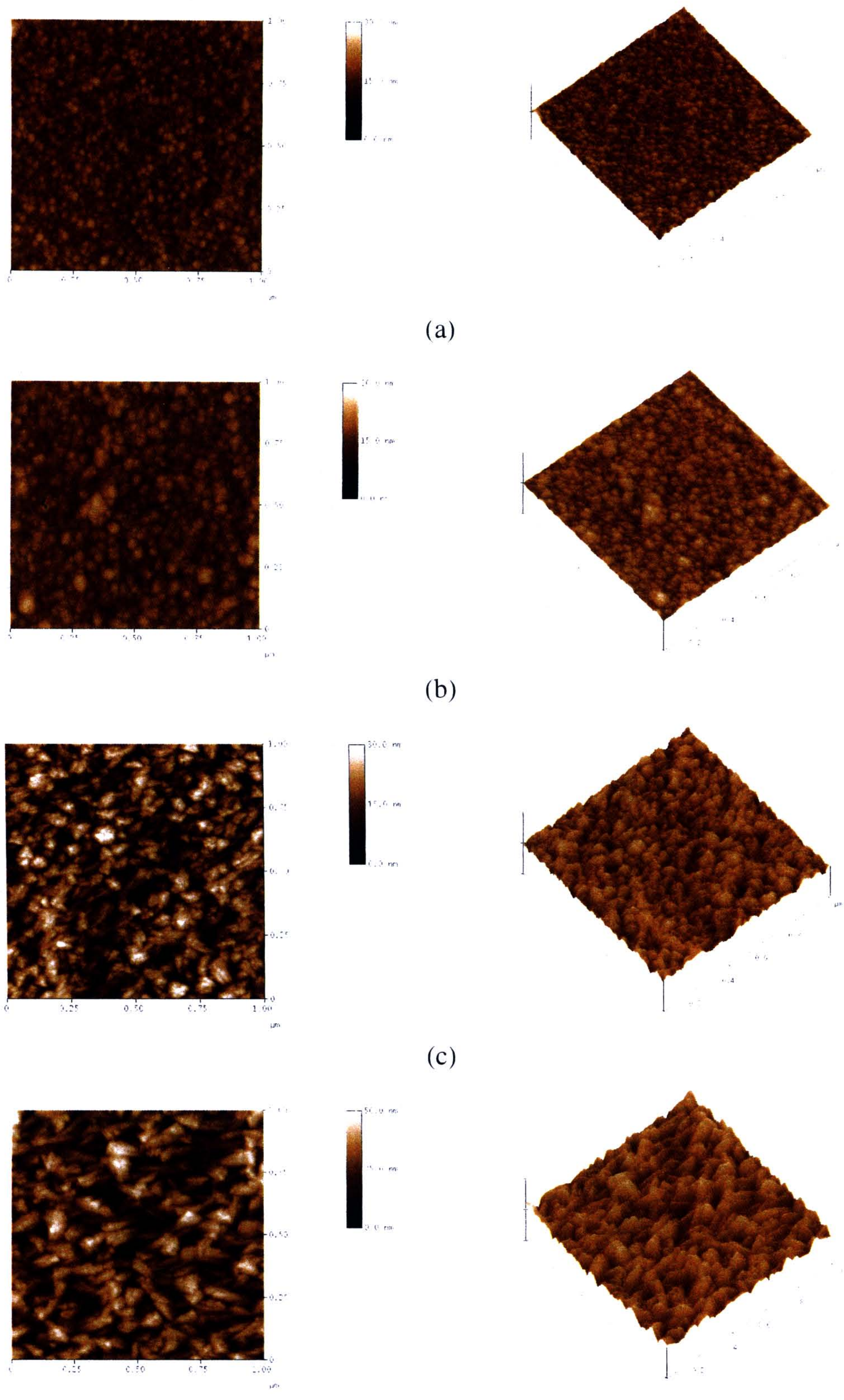


Figure 4.16 The AFM images of $AlTi_3N$ thin films (2D images, left, and 3D images, right) deposited at various deposition time : (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min for sputtering current of I_{Ti} = 0.6 A and I_{Al} = 0.6 A

The thickness of $AlTi_3N$ thin films can be measured from section analysis of 2D-AFM images. Figure 4.17 shows a typical film thickness analysis of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.6 A for deposition times of 15, 30, 45 and 60 min. Four values of the film thickness were measured by scanning the tip of AFM at three different areas from left to right of each different color line as shown in Figure 4.17 and the thicknesses of $AlTi_3N$ thin films for deposition times of 15, 30, 45 and 60 min were determined and the results are shown in Table 4.8. It was found that the average film thickness was varying from a minimum value of 141.7 nm to the maximum value of 581.9 nm. The surface morphology evolution was related to the enhancement of atom energy from the increasing of titanium current that resulting not only the larger grain size and less dense grain, but also affecting thickness of the films as the increasing of titanium current will generates more Ti particles off the target and are readily to form the structure.

Table 4.8 The thickness of $AlTi_3N$ thin films deposited at Ti sputtering current of 0.6 A and for deposition times of 15, 30, 45 and 60 min

Deposition time(min)	Film thickness(nm)
15	141.7
30	265.6
45	416.2
60	581.9

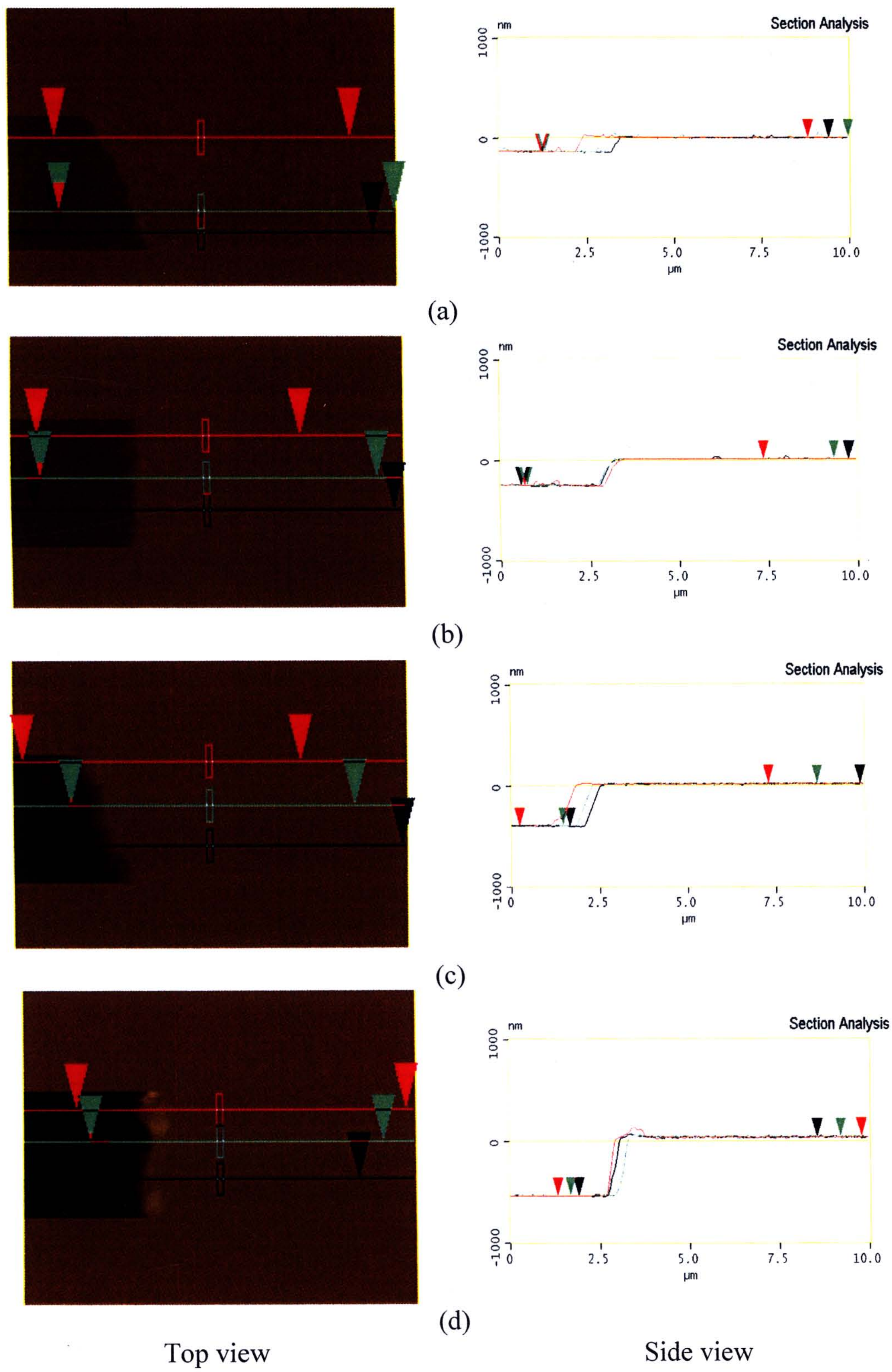


Figure 4.17 Section analysis of $AlTi_3N$ thin films deposited at a constant Ti sputtering current of 0.6 A and for four different deposition times of: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

Surface Morphology of $AlTi_3N$ Thin Films Deposited at I_{Ti} = 0.7 A

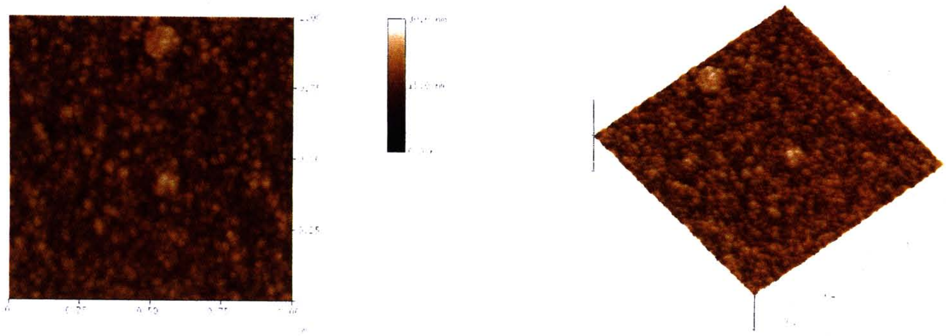
Scan measurements of the AFM analysis across the grain structure of four sample surfaces deposited at a sputtering current of 0.7 A with different deposition times of 15, 30, 45 and 60 min, respectively are illustrated in Figure 4.18 (a) – (d). The result indicate that the columnar diameter of the thin films also increased substantially from 21.6 nm to 90.2 nm as the deposition time increased from 0 to 60 min. Refinement of grain structure was most effective by varying the deposition time through longer deposition time from 0 to 60 min. The AFM area analysis also showed significant surface morphological changes on the thin film with increasing deposition time. It was found that as the deposition time increased from 15 to 30 min, the rms roughness decreased are similar value of 2.0 nm to 2.7 nm, the rms roughness significant decreased to 7.0 for 45 min and increase to 11.0 nm at 60 min was observed in Table 4.9.

The grain size of $AlTi_3N$ thin films as estimated from scan measurement of the 2D-AFM images in Figure 4.18 (a)-(d). It was found to constant increase the grain size with the increasing of the deposition times from 15 min to 60 min. The similar results can observed for the rms roughness for all thin films. The increase of deposition time leads to increase of substrate temperature resulting to the adatom mobility enhancement therefore crystallization and surface evolution were developed.

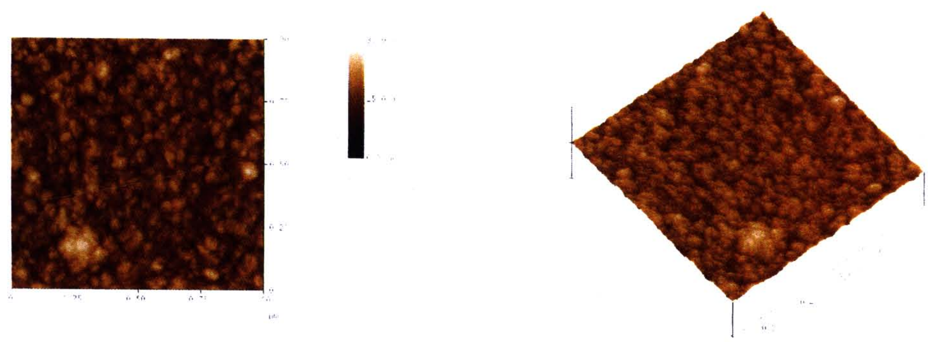
Table 4.9 Variation of surface roughness and grain sizes of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.7 A for four deposition times

Deposition time(min)	RMS roughness (nm)	Grain size (nm)
15	2.0	21.6
30	2.7	64.7
45	7.0	73.5
60	11.0	90.2

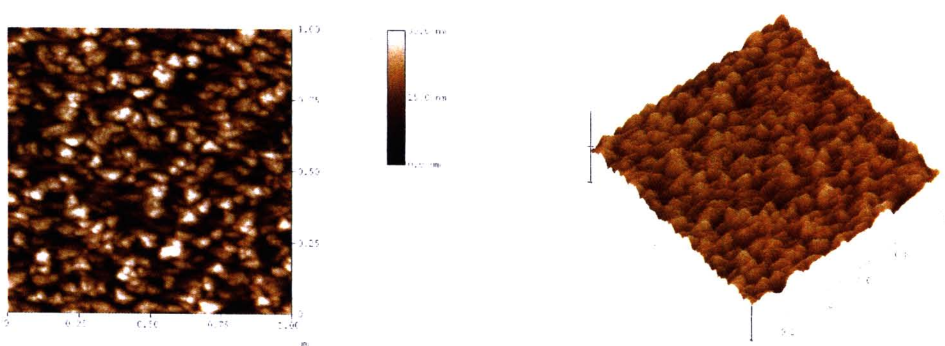
The thickness of $AlTi_3N$ thin films can be measured from section analysis of 2D-AFM images. Figure 4.19 shows a typical film thickness analysis of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.7 A for deposition times of 15, 30, 45 and 60 min. Four values of the film thickness were measured by scanning the tip of AFM at three different areas from left to right of each different color line as shown in Figure 4.19 and the thicknesses of $AlTi_3N$ thin films for deposition times of 15, 30, 45 and 60 min were determined and the results are shown in Table 4.10. It was found that the average film thickness was varying from a minimum value of 183.8 nm to the maximum value of 823.5 nm.



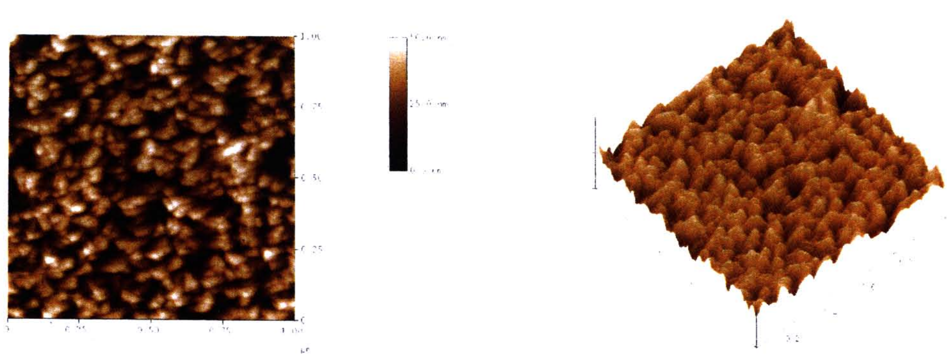
(a)



(b)

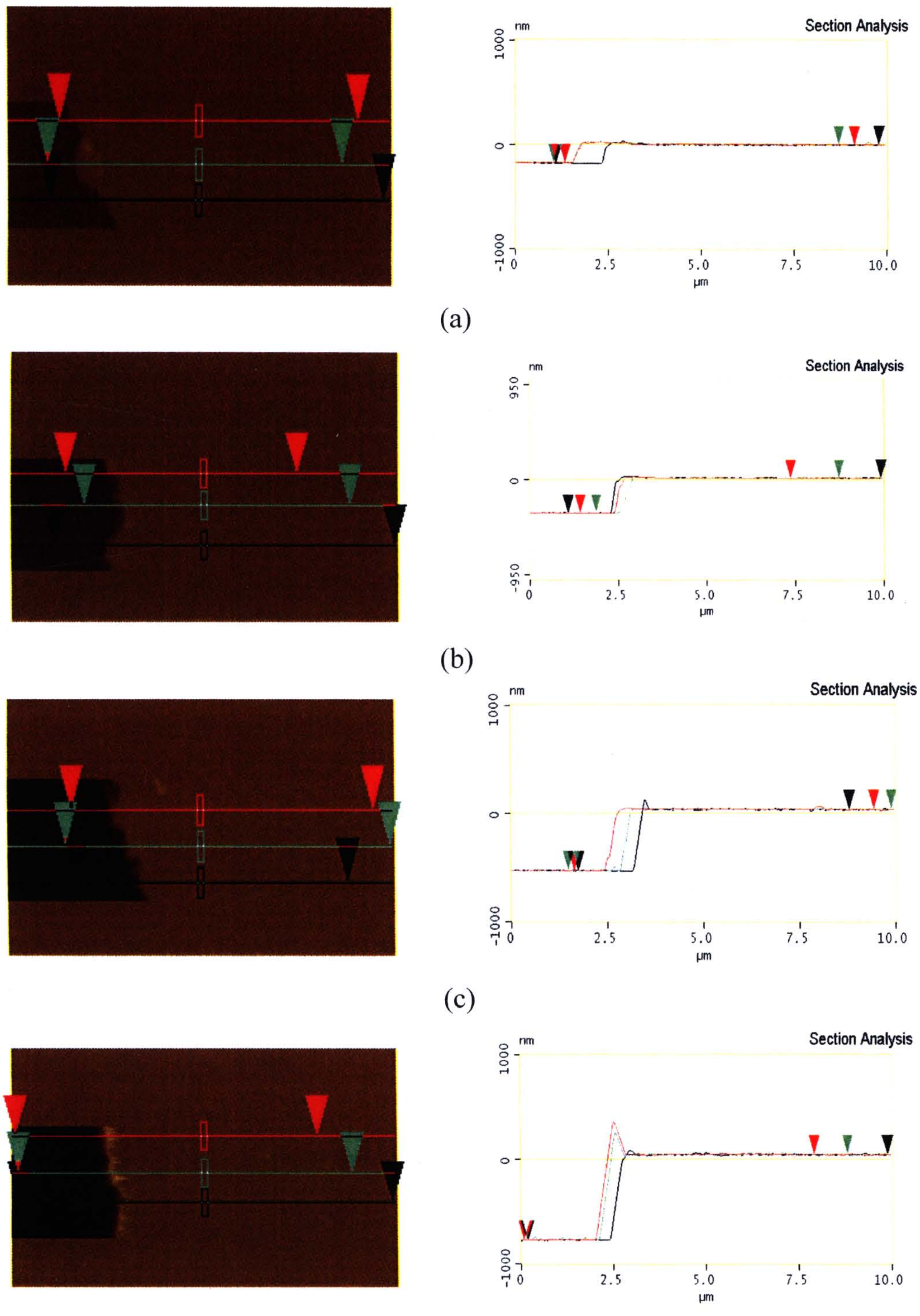


(c)



(d)

Figure 4.18 The AFM images of $AlTi_3N$ thin films (2D images, left, and 3D images, right) deposited at various deposition time : (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min for sputtering current of I_{Ti} = 0.7 A and I_{Al} = 0.6 A.



(a)

(b)

(c)

(d)

Top view

Side view

Figure 4.19 Section analysis of $AlTi_3N$ thin films deposited at a constant Ti sputtering current of 0.7 A and for four different deposition times of: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

Table 4.10 The thickness of $AlTi_3N$ thin films deposited at Ti sputtering current of 0.7 A and for deposition times of 15, 30, 45 and 60 min

Deposition time(min)	Film thickness(nm)
15	183.8
30	353.3
45	568.3
60	823.5

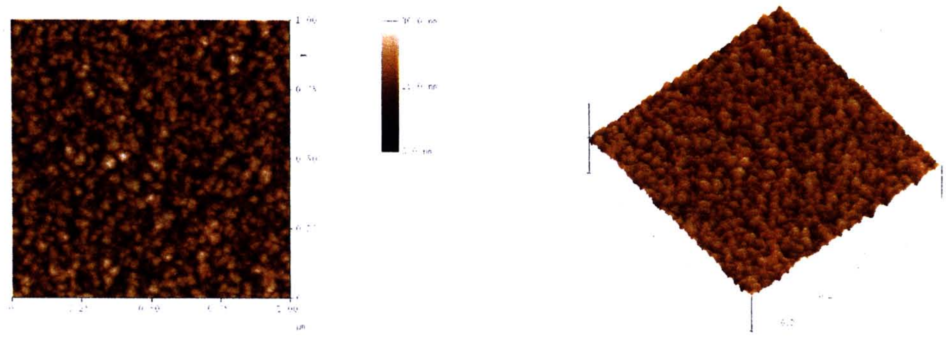
Surface Morphology of $AlTi_3N$ Thin Films Deposited at I_{Ti} = 0.8 A

For Figure. 4.20, surface morphologies of the as-deposited $AlTi_3N$ thin films for four values of deposition time for 15, 30, 45 and 60 min are displayed. The surface morphology at deposition time of 15 min as-deposited thin films (Figure. 4.20 (a)) is mainly composed of individual small grain which has same size. Some of grains deposited at 30 min were bigger, as shown in Figure 4.20 (b). At total pressure 45 (Fig.4.20 (c)) exhibited a much large grain size spread across its surface. As further increase deposition time to 60 min, the surface exhibited large triangle shape grain with separate each other. When the deposition time increase, the surface morphology will change compare with short deposition time, grain size become bigger with in the range of 49.8 to 125.1 nm and roughness increased from 3.3 nm to 14.0 nm with increase of deposition time. The results on the surface roughness and columnar grains are concluded in Table 4.11.

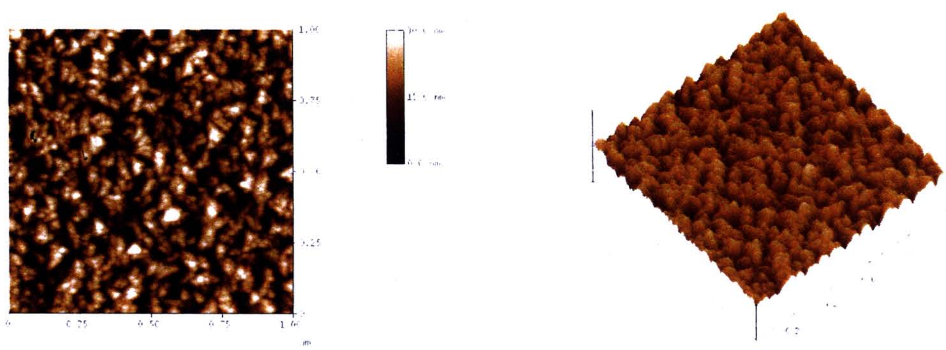
The grain size of $AlTi_3N$ thin films as estimated from the 2D-AFM images in Figure 4.20 (a)-(d), however, was found to increase almost linearly with the increasing of the deposition times from 15 min to 60 min. The increase of deposition time led to the increase of substrate temperature and the increase of surface roughness as high crystallization was developed.

Table 4.11 Variation of surface roughness and grain sizes of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.8 A for four deposition times

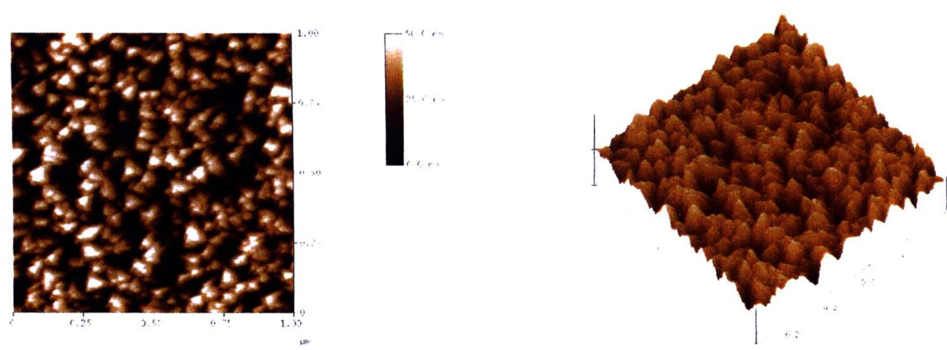
Deposition time(min)	RMS roughness (nm)	Grain size (nm)
15	3.3	49.8
30	6.1	75.2
45	11.0	81.1
60	14.0	125.1



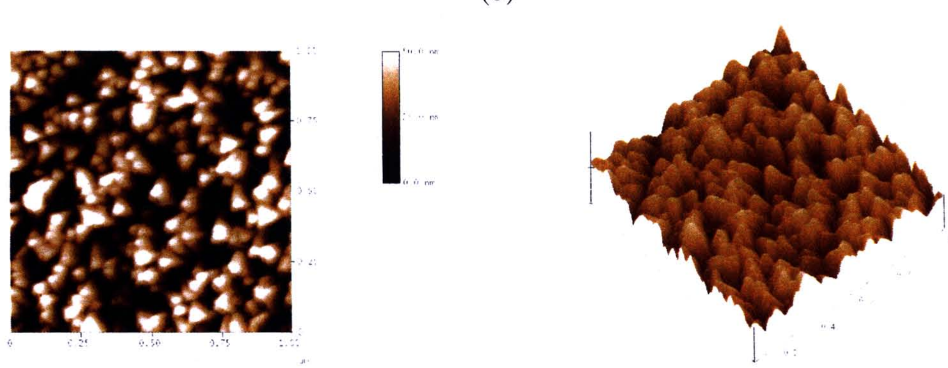
(a)



(b)



(c)



(d)

Figure 4.20 The AFM images of $AlTi_3N$ thin films (2D images, left, and 3D images, right) deposited at various deposition time : (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min for sputtering current of I_{Ti} = 0.8 A and I_{Al} = 0.6 A.

The thickness of $AlTi_3N$ thin films can be measured from section analysis of 2D-AFM images. Figure 4.21 shows a typical film thickness analysis of $AlTi_3N$ thin films deposited with Ti sputtering current of 0.8 A for deposition times of 15, 30, 45 and 60 min. Four values of the film thickness were measured by scanning the tip of AFM at three different areas from left to right of each different color line as shown in Figure 4.21 and the thicknesses of $AlTi_3N$ thin films for deposition times of 15, 30, 45 and 60 min were determined and the results are shown in Table 4.12. It was found that the average film thickness was varying from a minimum value of 255.2 nm to the maximum value of 1184.7 nm.

Table 4.12 The thickness of $AlTi_3N$ thin films deposited at Ti sputtering current of 0.8 A and for deposition times of 15, 30, 45 and 60 min

Deposition time(min)	Film thickness(nm)
15	255.2
30	469.0
45	906.2
60	1184.7

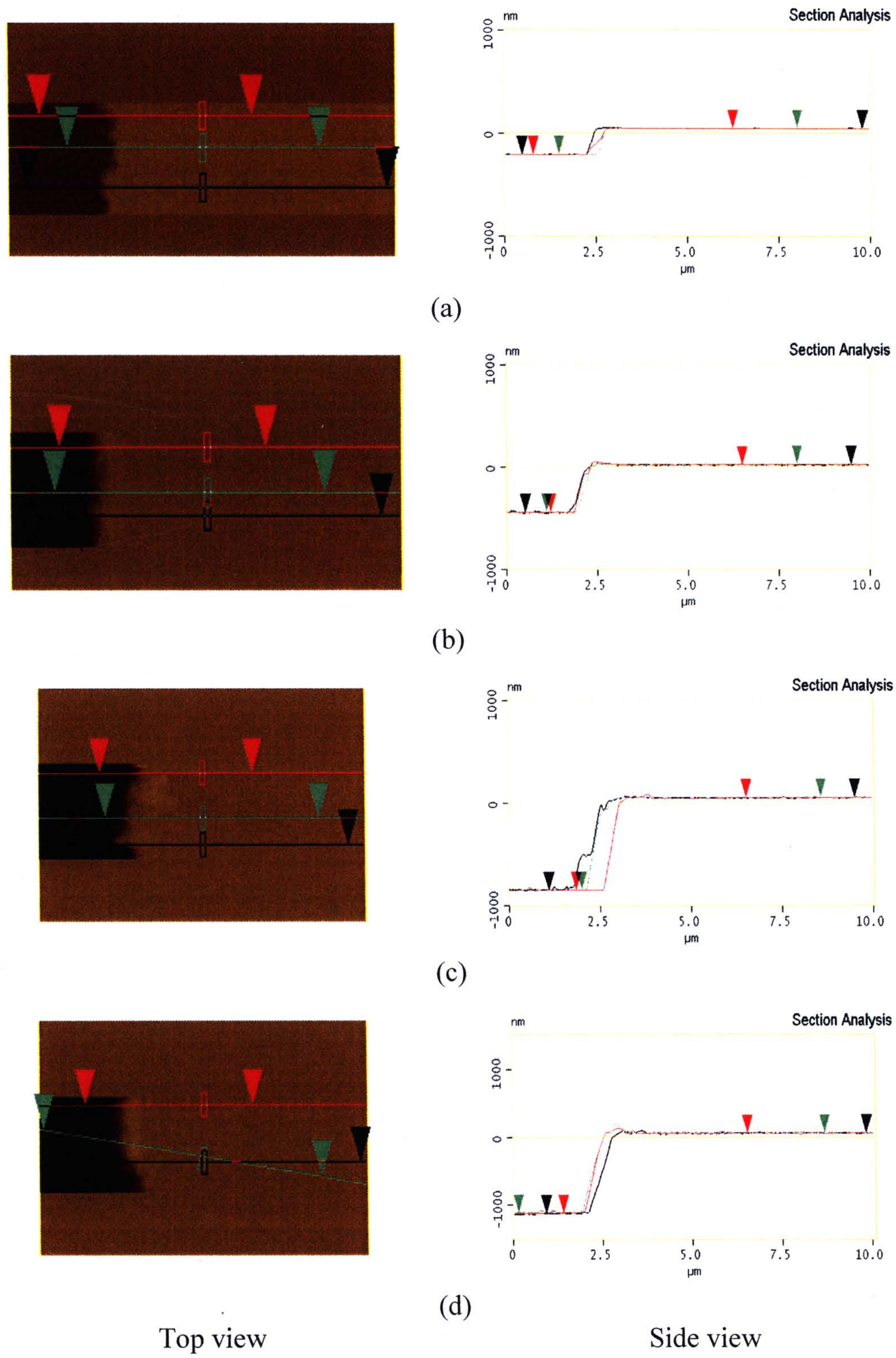


Figure 4.21 Section analysis of $AlTi_3N$ thin films deposited at a constant Ti sputtering current of 0.8 A and for four different deposition times of: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

Surface Morphology of $AlTi_3N$ Thin Films Deposited at I_{Ti} = 1.0 A

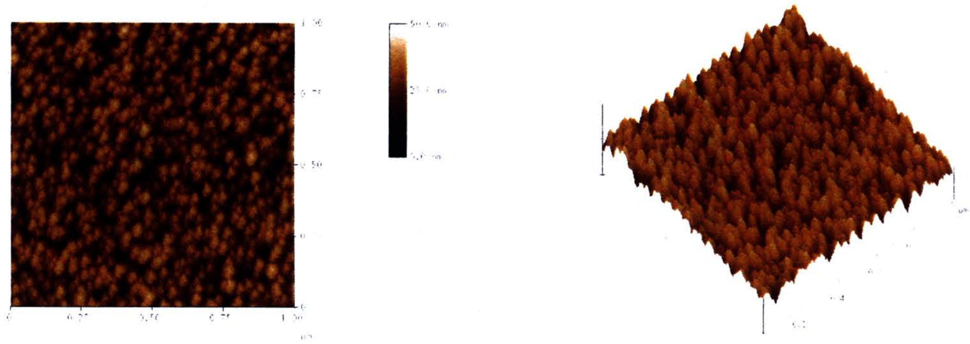
The AFM micrographs which illustrate the surface morphology and surface evolution of the $AlTi_3N$ thin films deposited at different deposition time of 15, 30, 45 and 60 min with applied current to Ti sputtering target for 1.2 A are shown in Figure 4.22. The AFM region scan analyses were performed on the four samples on glass slide substrates resulted in the two and three dimension picture. The investigation of topographical changes on thin film surface was found that the nanocrystalline $AlTi_3N$ grain were formed nodules-shape particles which can be clearly identified as shown in Figure 4.22 (a). The grain gradually diffused and linked together with obviously generate triangle shape which can be seen the individual grain as increase deposition time to 45 min, Figure 4.22 (a) – (c). When deposition time increase to 60 min, the grain become small but containing the same shape as shown in Figure 4.22 (d). The results indicated that as the deposition time increased from 0 to 60 min, the rms roughness of the thin films increase from 4.8 nm to 9.8 nm for 45 min and then decrease to 8.4 nm at 60 min. On the other hand, the development in grain size perform different trend with increasing from 3.8 nm to the highest value of 121.5 at a deposition time of 45 min as summarize in Table 4.13.

The grain size of $AlTi_3N$ thin films as estimated from the 2D images by AFM measurement in Figure 4.22 (a)-(d), however, was found not to increase as a function of the deposition times from 15 min to 60 min. The exceed increase of deposition time to 60 min led to the increase of substrate temperature, adatom mobility the decrease of surface roughness as high crystallization was developed resulted grain re-arrangement.

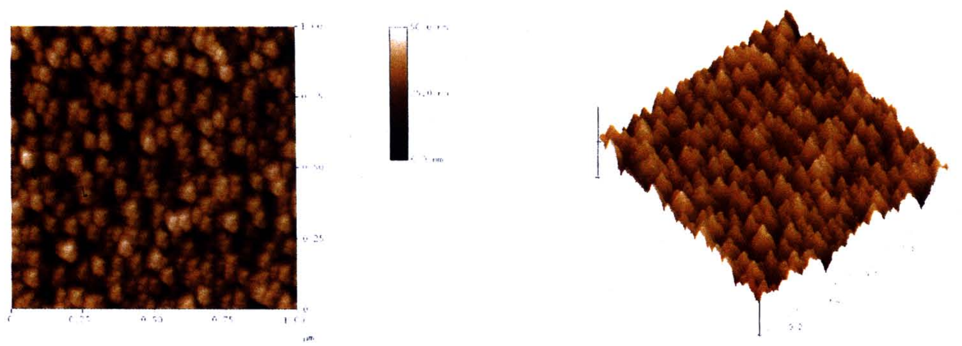
Table 4.13 Variation of surface roughness and grain sizes of $AlTi_3N$ thin films deposited with Ti sputtering current of 1.0 A for four deposition times

Deposition time(min)	RMS roughness (nm)	Grain size (nm)
15	4.8	14.7
30	6.1	25.5
45	9.8	121.5
60	8.4	15.7

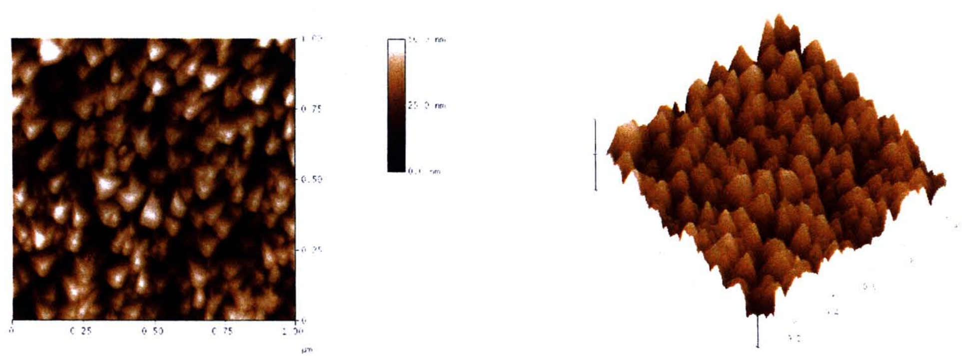
The thickness of $AlTi_3N$ thin films can be measured from section analysis of 2D-AFM images. Figure 4.23 shows a typical film thickness analysis of $AlTi_3N$ thin films deposited with Ti sputtering current of 1.0 A for deposition times of 15, 30, 45 and 60 min. Four values of the film thickness were measured by scanning the tip of AFM at three different areas from left to right of each different color line as shown in Figure 4.23 and the thicknesses of $AlTi_3N$ thin films for deposition times of 15, 30, 45 and 60 min were determined and the results are shown in Table 4.14. It was found that the average film thickness was varying from a minimum value of 416.4 nm to the maximum value of 1598.7 nm.



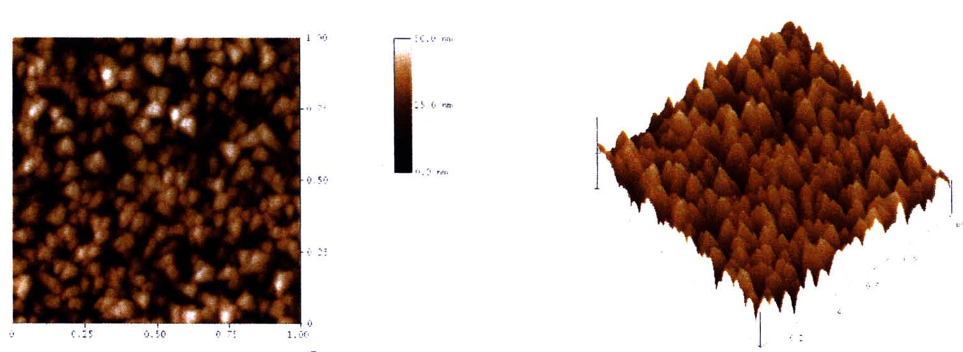
(a)



(b)



(c)



(d)

Figure 4.22 The AFM images of $AlTi_3N$ thin films (2D images, left, and 3D images, right) deposited at various deposition time : (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min for sputtering current of I_{Ti} = 1.0 A and I_{Al} = 0.6 A.

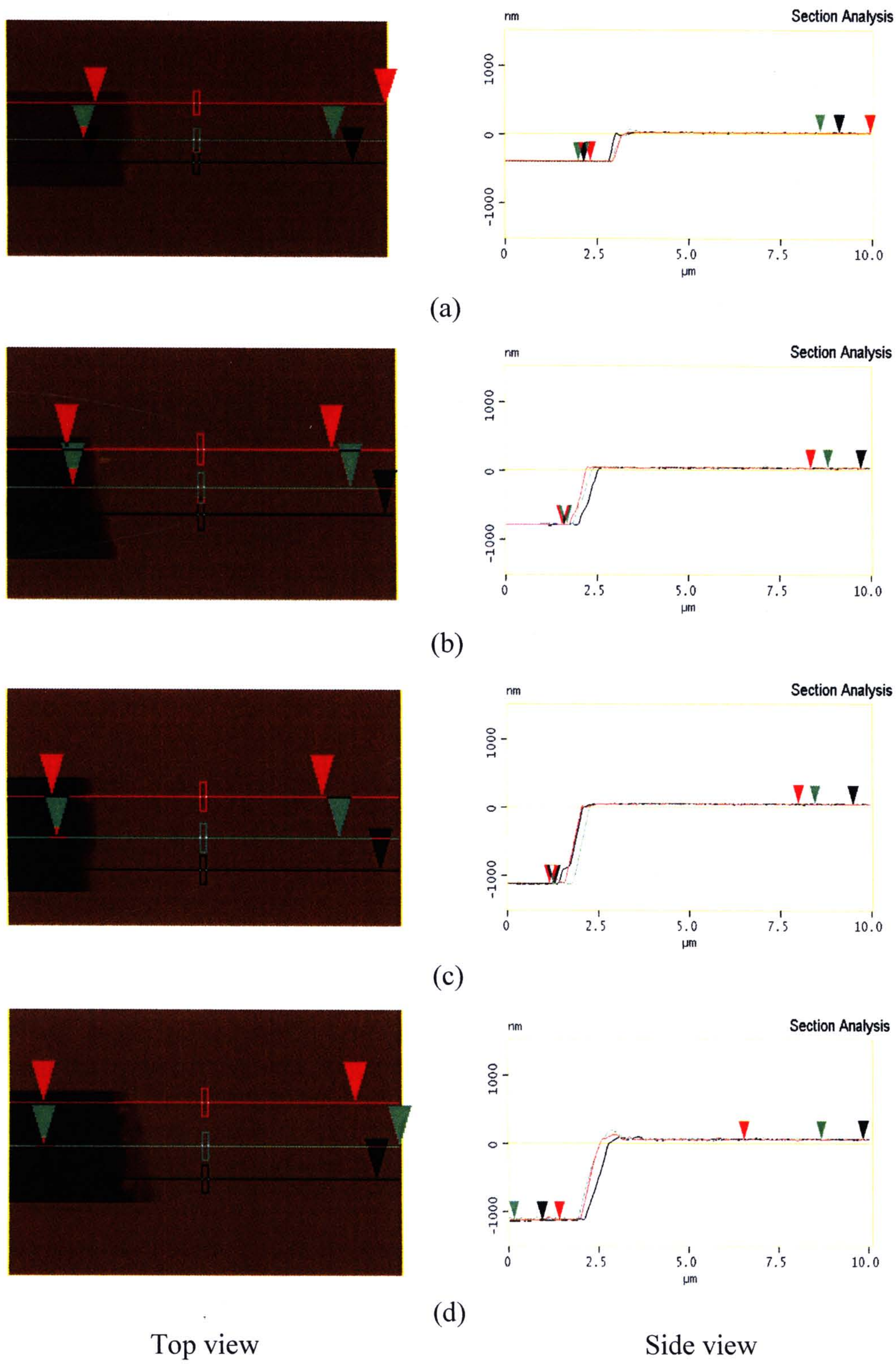


Figure 4.23 Section analysis of $AlTi_3N$ thin films deposited at a constant Ti sputtering current of 1.0 A and for four different deposition times of: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

Table 4.14 The thickness of $AlTi_3N$ thin films deposited at Ti sputtering current of 1.0 A and for deposition times of 15, 30, 45 and 60 min

Deposition time(min)	Film thickness(nm)
15	416.4
30	817.8
45	1168.0
60	1598.7

Surface Morphology of $AlTi_3N$ Thin Films Deposited at I_{Ti} = 1.2 A

The surface morphologies and roughness of the $AlTi_3N$ thin films examine on various sample as recorded by the AFM tapping mode. The measurement will scan on different four samples which deposited by varying deposition time for 15, 30, 45 and 60 min, respectively, with constant Ti sputtering current of 1.2 A were summarized in Figure 4.24 (a) – (d). The result indicated that the grain shape evolution of the thin films also same trend as I_{ti} =1.0 A with in the range of 36.3 – 48.0 nm as the deposition time increased from 0 to 60 min. Refinement of grain structure was most effective by varying the deposition time through longer deposition time from 0 to 60 min. The AFM area analysis also showed surface morphological changes from the small island shape with clearly distinguish to grain agglomeration across the surface with deposition increase from 15 to 45 min. At 60 min, the surface morphology found to be smoother than deposition time for 45 min. From AFM surface analysis, It was found that as the deposition time increased from 15 to 45 min, the rms roughness increased are from 4.0 nm to 7.6 nm, the rms roughness value slightly reduced to 6.4 for 60 min was observed in Table 4.15.

The grain size of $AlTi_3N$ thin films as estimated from scan measurement of the 2D-AFM images in Figure 4.24 (a)-(d). It was found to constant increase and decreased the grain size with the increasing of the deposition times from 15 min to 60 min. The exceed increase of deposition time to 60 min led to the increase of substrate temperature, adatom mobility the decrease of surface roughness as high crystallization was developed resulted grain re-arrangement.

Table 4.15 Variation of surface roughness and grain sizes of $AlTi_3N$ thin films deposited with Ti sputtering current of 1.2 A for four deposition times

Deposition time(min)	RMS roughness (nm)	Grain size (nm)
15	4.0	36.3
30	5.9	47.1
45	7.6	48.0
60	6.4	26.5

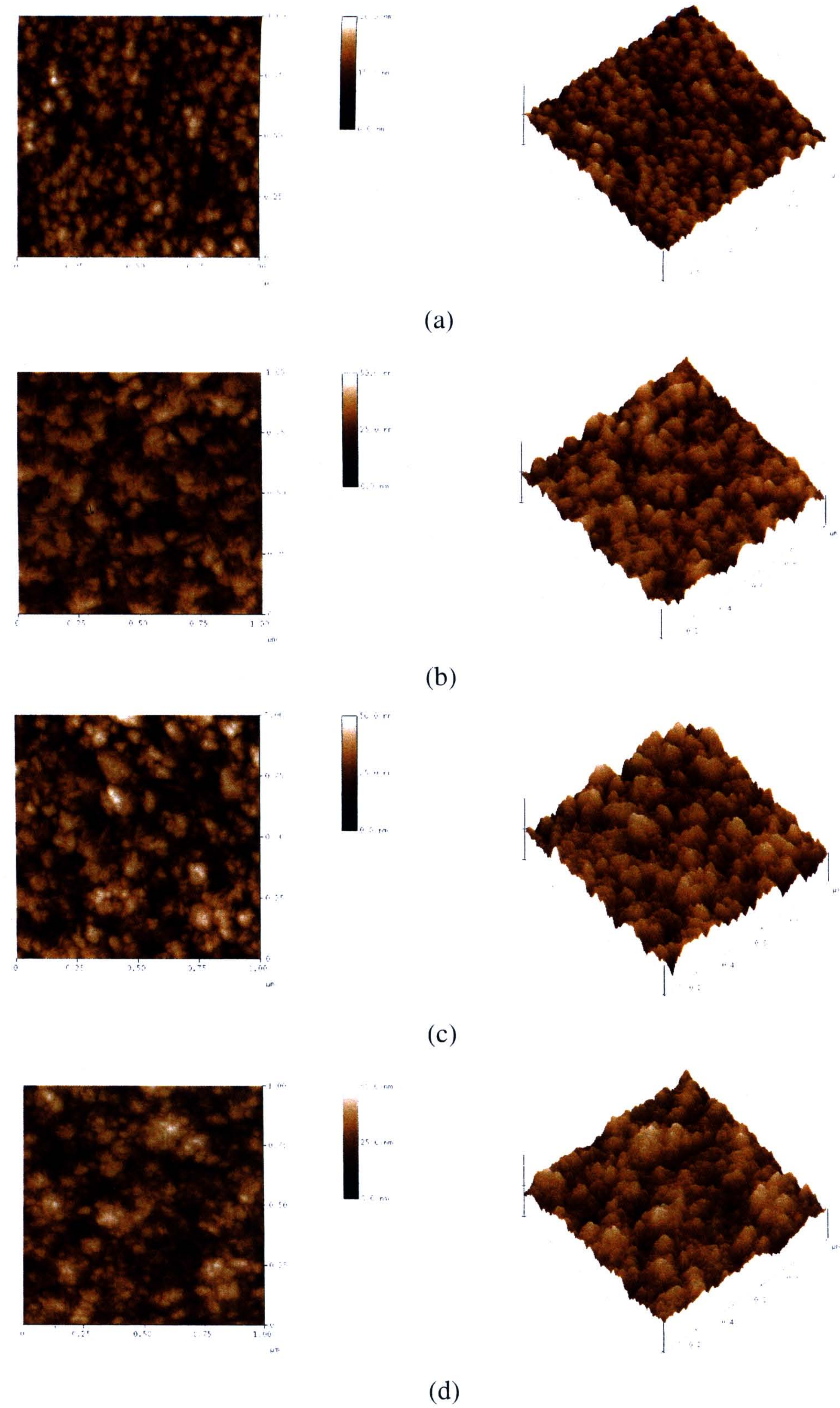


Figure 4.24 The AFM images of $AlTi_3N$ thin films (2D images, left, and 3D images, right) deposited at various deposition time : (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min for sputtering current of I_{Ti} = 1.2 A and I_{Al} = 0.6 A.

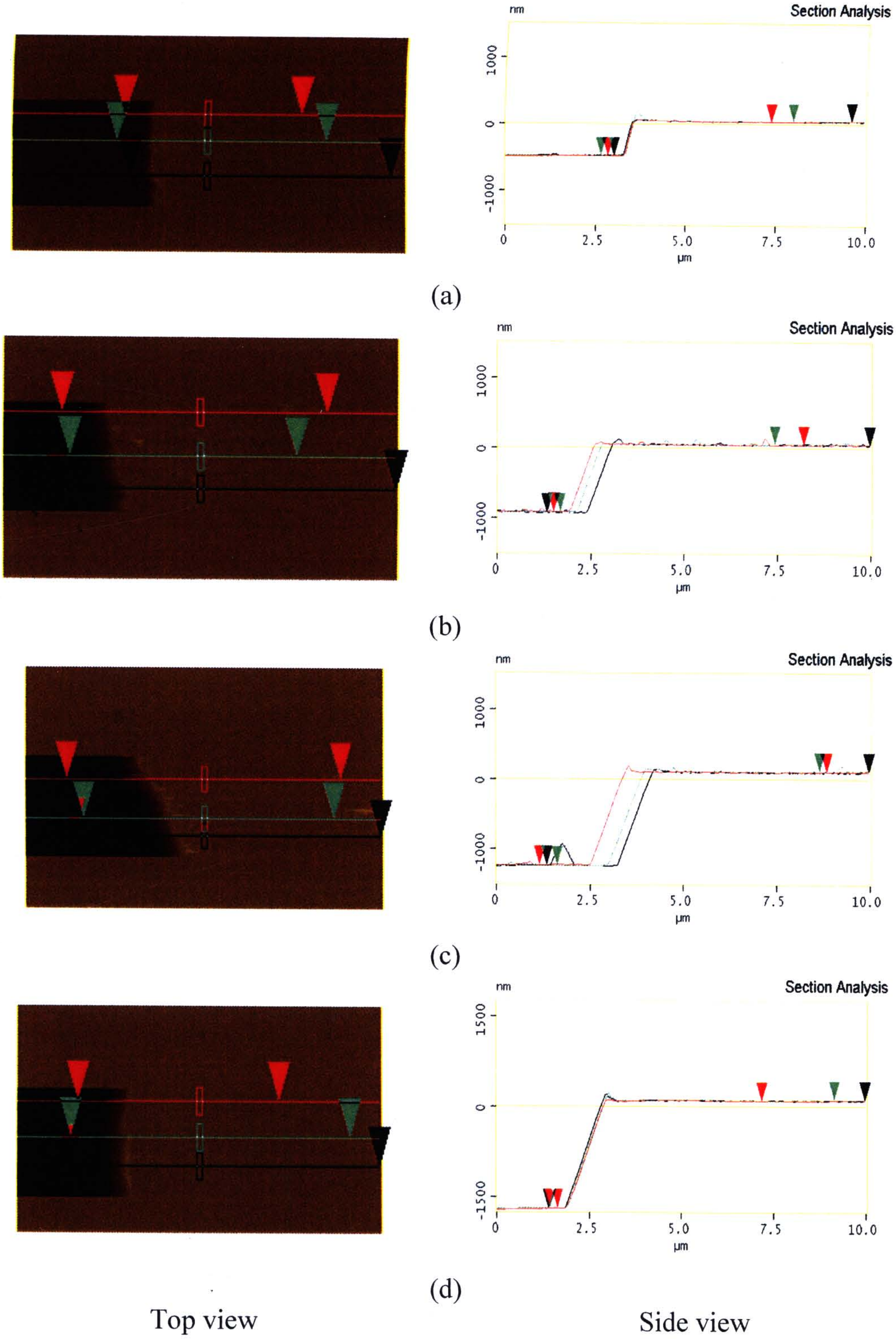


Figure 4.25 Section analysis of $AlTi_3N$ thin films deposited at a constant Ti sputtering current of 1.2 A and for four different deposition times of: (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min

The thickness of $AlTi_3N$ thin films can be measured from section analysis of 2D-AFM images. Figure 4.25 shows a typical film thickness analysis of $AlTi_3N$ thin films deposited with Ti sputtering current of 1.2 A for deposition times of 15, 30, 45 and 60 min. Four values of the film thickness were measured by scanning the tip of AFM at three different areas from left to right of each different color line as shown in Figure 4.25 and the thicknesses of $AlTi_3N$ thin films for deposition times of 15, 30, 45 and 60 min were determined and the results are shown in Table 4.16. It was found that the average film thickness was varying from a minimum value of 514.9 nm to the maximum value of 1802.0 nm.

Table 4.16 The thickness of $AlTi_3N$ thin films deposited at Ti sputtering current of 1.2 A and for deposition times of 15, 30, 45 and 60 min

Deposition time(min)	Film thickness(nm)
15	514.9
30	970.9
45	1339.7
60	1802.0

The overall results of surface morphology of $AlTi_3N$ thin films investigated by AFM technique are concluded in Table 4.17-4.18. This table shows variations of surface roughness and the grain size of $AlTi_3N$ thin films for four different deposition times and sputtering currents. The surface roughness of $AlTi_3N$ thin films deposited at the same sputtering current (0.6-0.8 A) was increase over for deposition times except 1.0 A and 1.2 A, while higher current tend to increase the surface roughness for each deposition time but the exceed of current will reduced the surface roughness. In the case of grain size, it can be concluded that for each sputtering current, grain size increases with deposition time and for the same deposition time, the grain size increases and decreases with sputtering currents.

The explanation on the evolution of the surface roughness over longer deposition time is the increment of substrate temperature such that atoms and molecules move actively and re-arrange themselves more orderly i.e. increment and decrement of surface roughness as the result. The effect of sputtering current on surface roughness is that higher current increase the coating rate i.e. particles have less time to arrange orderly in spite of the increasing of substrate temperature.

Table 4.17 Variation of surface roughness of $AlTi_3N$ thin films deposited for five different deposition times and with sputtering currents of 0.6, 0.7, 0.8, 1.0 and 1.2 A

Deposition time (min)	RMS roughness (nm)				
	0.6 A	0.7 A	0.8 A	1.0 A	1.2 A
15	1.8	2.0	4.1	5.9	4.0
30	2.0	2.7	7.6	7.6	5.9
45	5.9	7.0	13.7	11.2	7.6
60	9.0	11.0	17.4	10.4	6.4

Table 4.18 Variation of grain sizes of $AlTi_3N$ thin films deposited for five deposition times and with sputtering currents of 0.6, 0.7 , 0.8 , 1.0 and 1.2 A from AFM technique

Deposition time (min)	Grain size (nm)				
	0.6 A	0.7 A	0.8 A	1.0 A	1.2 A
15	13.7	21.6	49.8	14.7	36.3
30	13.7	64.7	75.2	25.5	47.1
45	14.7	73.5	81.1	121.5	48.0
60	19.6	90.2	125.1	15.7	26.5

Increasing of deposition times and currents lead to an increment of substrate temperature and having the effect on grain size of the film directly; orderly arranging of molecules i.e. compact and having more density, that is larger gain size.

The investigation of thickness of $AlTi_3N$ thin films deposited on glass slides by AFM can be concluded as shown in Table 4.19. The effect of increment of deposition times on the films thickness can be easily understood i.e. longer depositing yields the thicker film. Similarly, the increment of sputtering currents indicates the higher coat rates i.e. getting thicker films deposited as the results.

Table 4.19 The thickness of $AlTi_3N$ thin films deposited at three sputtering currents of 0.6, 0.7, 0.8, 1.0 and 1.2 A for deposition times of 15, 30, 45 and 60 min

Deposition time (min)	Film thickness (nm)				
	0.6 A	0.7 A	0.8 A	1.0 A	1.2 A
15	141.7	183.8	255.2	416.40	514.9
30	265.6	353.3	469.0	817.8	970.9
45	416.2	568.3	906.2	1168.0	1339.7
60	581.9	823.5	1184.7	1598.7	1802.0

4.2.1.5 Analysis of the Microstructure and Thickness of $AlTi_3N$ Thin Films by FE-SEM

The cross-sectional observations from Figure 4.26 indicate that the films have columnar structure. However, the columnar structure exhibited some changes when varied the deposition time while the deposition current were fixed at titanium current of 0.8 A and aluminium current of 0.6 A. The surface morphology of the sample deposited for 15 min as shown in Figure 4.26 (a) apparently reveals columnar grains with dense structure. The films are also exhibits good columnar pattern and individual of each grain can be observed for 30 min, as shown in Figure 4.26 (b). The films prepared at the higher deposition times of 45 and 60 min (Figure 4.26 (c) –(d)) show individual grain clearly with columnar characteristic and having more open boundaries such as pores or void through the surface between columns than for denser films prepared for shorter deposition times (15 and 30 min). In addition, it is noticed that the films growth continuously along the deposition time as indicated by thickness measurement from cross-section analysis of SEM images. When the applied current on titanium target is further increased, the denser packing of the grain column was the result of incoming atom on surface with features similar to the zone 2 microstructure according to the Thornton's model.

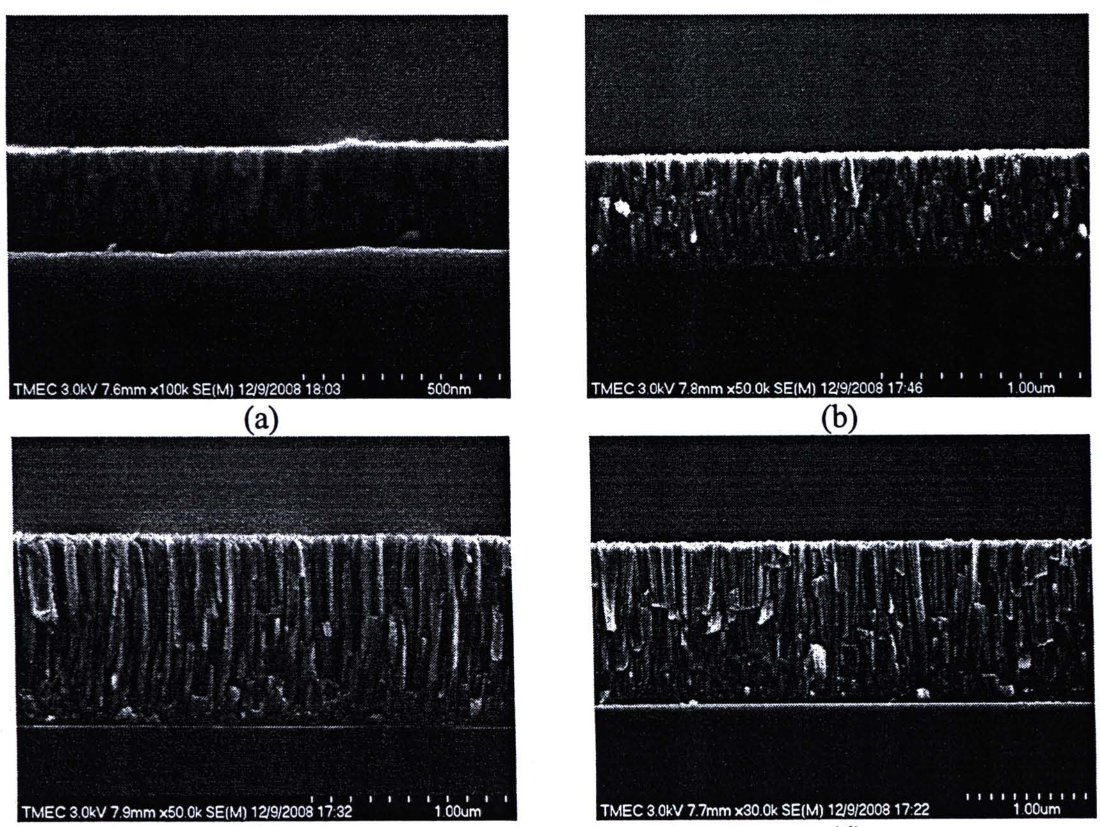


Figure. 4.26 The cross-section morphology of $AlTi_3N$ thin films from different deposition times (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min at Ti sputtering current of 0.8 A.

For comparing the thickness results of $AlTi_3N$ thin films analyzed by the AFM, the film thickness is analyzed by SEM. The film thickness is evaluated from FE-SEM cross-section images of the $AlTi_3N$ thin films. Typical FE-SEM cross-section images of the $AlTi_3N$ thin films deposited with Ti current of 0.8 A for four different deposition time of 15, 30, 45 and 60 min and the thickness of the $AlTi_3N$ thin films are given in Table 4.19.

Table 4.20 The thickness of $AlTi_3N$ thin films measured by FE-SEM and AFM. The films were deposited with four different deposition time of 15, 30, 45 and 60 min for a Ti sputtering current of 0.8 A

Deposition time (min)	Thickness from AFM (nm)	Thickness from FE-SEM (nm)
15	255.2	256.0
30	469.0	552.0
45	906.0	944.0
60	1184.8	1369.0

From the results in Table 4.20, it can be remarks that the thickness of $AlTi_3N$ thin films as determined by AFM and FE-SEM corresponding to each other and also in a related with the AFM results.

4.4.2 Effects of Al Sputtering Current on Crystallinity and Structure of $AlTi_3N$ Thin Films

The analysis of the crystal structure of $AlTi_3N$ thin films from XRD technique will be discussed.

4.4.2.1 Analysis of the Crystallinity and Structure of AlTi3N Thin Films by XRD

The crystal structure of $AlTi_3N$ thin films deposited on silicon wafers were investigated by XRD measurements. Figure 4.27 shows typical XRD patterns of thin films deposited for 60 minutes with Al sputtering currents of 0.2, 0.4 and 0.6 A. The observed peaks in Figure 4.27 reveal that all deposited $AlTi_3N$ thin films exhibited the polycrystalline of $AlTi_3N$ structure which correspond to JCPDS data no. 51-0724. As observed in the X-ray spectra in Figure 4.27, the crystal plane were obviously change from (004) plane to (112) plane. The result indicates that the crystallinity of the films increased with the increase of Al sputtering current due to the high energy of sputter atom bombard to substrate resulting adatom mobility and self-heating which the crystal plane become more stable phase. The X-ray spectra of (112) plane is also confirm this evident because of the plane is stable characteristics. Moreover, the results indicate that the crystal structure are not change by deposit at various Ti,Al sputtering current for all coatings.

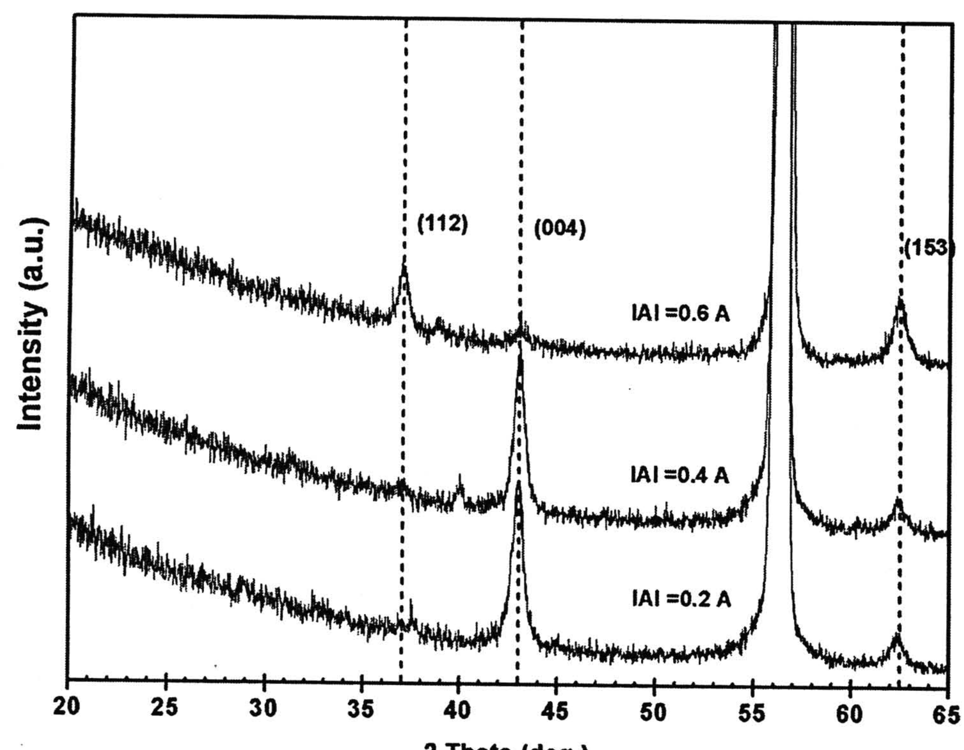


Figure 4.27 The XRD pattern of $AlTi_3N$ thin film deposited at different Al sputtering current from 0.2 to 0.6 A for 60 min