# Study of Phase Evolution in Sputtered Al/Ru Bi-layers Nanocrystalline Thin Films

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Physical vapor deposited Al/Ru bi-layers on silicon substrates have been annealed to study reactions development. Temperature induced changes after increasing time from 10 to 2880 min in vacuum annealing at 500 $^o$C were studied. Grazing incidence X-ray Diffraction indicates $RuAl_2$ phase formation in all samples. Electron diffraction pattern of a thin foil extracted from annealed bi-layers shows spots for $RuAl_2$ and $Al_6Ru$ phases. Focused ion beam cross sections, shows non-uniform 500 nm thickness reaction layer at the Al/Ru interface. Decreasing thickness at a fixed ratio of Ru/Al = 1.224 reduces the time required to start reaction at the same temperature. Formed intermetallic phase layer acts as a diffusion barrier that controls further atomic diffusion from both Al and Ru sides into the formed reaction layer.

## 1. Introduction:

Ru/Al system contains intermetallic compounds as RuAl, which has attractive properties, like structural, high temperature oxidation resistance, good mechanical properties and aqueous corrosion resistance in some very aggressive environments [1]. Also, $Al_6Ru$ has quasicrystalline [2] and $RuAl_2$ has semiconducting behaviors [3]. This motivates the research in intermetallic thin films because of the high surface to thickness ratio that insures large-scale usage of their properties. The known Al/Ru binary phase diagram exhibits bulk materials equilibrium state of reactions that is different from nanocrystalline non-equilibrium state, such as thin film alloys and coatings. There is no publication reported in the Al/Ru system about first interfacial phase formed between thin film layers, thermodynamic data and the temperature at which the reaction starts. Previous work made on platinum-group alumenides like Al/Fe, Al/Ni thin films, indicates $FeAl_3$ formation at 625 $^o$C at the interfacial contact [4] in Al/Fe multilayers contrary to Bene`s rule [5, 6], which predicts that first

phase nucleating in such structures is that neighbor to the low temperature eutectic in the binary phase diagram, i.e., to the Al side. The $Al_3Ni$ intermetallic phase formation in Al/Ni multilayers at $160^oC$ confirms Bene's rule. Thermodynamic considerations on the basis of the free energy differences $\Delta G$ [7, 8] favor always the formation of AlNi in Al/Ni system and not $Al_3Ni$. The phases $FeAl_3$, $Fe_2Al_5$ and $FeAl_2$ ($\Delta H = -27.9$ kJ mol$^{-1}$), ($\Delta H = -27.0$ kJ mol$^{-1}$), and ($\Delta H = -26.1$ kJ mol$^{-1}$) respectively, having quite similar values of the heat of formation to that of the body centered phase (B2), ($\Delta H = -25.1$ kJ mol$^{-1}$) [9], which forms first, while thermodynamic considerations favor $FeAl_3$ phase formation. Therefore the thermodynamic driving forces derived from equilibrium diagrams are not suitable to explain the observed phase evolution in nanocrystalline systems like Al/Ni and Al/Fe. In this work the interfacial reaction exists in the nanocrystalline Ru/Al thin films prepared by DC magnetron sputtering technique was studied.

## 2. Experimental:

DC magnetron sputtering system used to sputter the Al/Ru bi-layer thin films with the detailed preparation parameters shown in Table (1). Different individual layer thicknesses at constant ratio of d(Al)/d(Ru) $\approx$ 1.224 equals the atomic densities ratio between Al and Ru to reach 1:1 atomic percent of Al to Ru in the reaction zone. Ru/Al bi-layers were sputtered on single crystal Si substrates on (004) plane orientation at temperature of 74 $^oC$ during sputtering, and constant Ar flow and ion beam energies shown in Table (1). The Al layer was first sputtered on the Si substrate to insure good adhesion to the substrate and helping Ru add atoms diffusion inside Al layer. The chosen methods to investigate Al/Ru bi-layers were able to show interfacial reaction zone development and phase analysis. Therefore, we have used focused ion beam (FIB) tool to cut away (mill) material from a defined area with dimensions typically in square microns [10]. Firstly, we have deposited platinum material onto the surface to protect surface damage, while cutting using concentrated ions and electrons beams. Secondly, Milling is achieved by accelerating concentrated gallium ions to a specific site, which etches off any exposed material, leaving a very clean hole or surface. By introducing inert gases, the FIB can selectively etch one material much faster than surrounding materials, or deposit a metal or oxide.

Phase analysis were made using X-ray diffraction in the grazing incidence (GIXRD) mode at $1^o$, which depends on reduced penetration depth resulted from small angle incidence of the x-ray beam. While diffraction can happen at the near surface layer or at the interfacial zone, that intermetallic phase formation can be detected by using grazing incidence technique [11]. Electron diffraction and transmission electron microscope (TEM) give us phase

analysis of the resulted intermetallic phases at different points in the reaction zone. Annealing treatments were made at constant temperature of 500 °C for different annealing times, where lower annealing temperatures have no effect on the reaction and higher temperatures cause thermal stresses on samples surfaces, which causes thin film cracking and sample damage.

Table (1): DC sputtered parameters of the bi-layer thin films at constant thickness ratio ≈ 1.224, pressure = 3 x $10^{-3}$ m. bar, Ar. flow = 80 Sccm and energy = 100 Watt.

| Sample | Metal | Sputtering rate (nm/min) | Sputtering time (sec) | Sputtering temp. (°C) | Thickness (nm) |
|---|---|---|---|---|---|
| Thick bi-layers S2 | Al | 12 | 5702 | 74 | 1150 |
| | Ru | 15.7 | 3600 | | 940 |
| Thin bi-layers S3 | Al | 12 | 1425 | 45 | 287 |
| | Ru | 15.7 | 900 | | 235 |

## 3. Results and Discussion:

### 3.1. Phase Analysis (XRD):

X-ray diffraction (GIXRD) experiments for Al/Ru bi-layers sputtered on single crystal Si substrates at 1° grazing incidence angle shows no phase change until annealing temperature of less than 500 °C for 45 min. At 500 °C for 45 min, $RuAl_2$ can be identified with the GIXRD patterns [12]. Annealed bi-layers at
500 °C of (S3) thin film bi-layers shows a small increase in intensities of (111), (202) and (004) planes of orthorhombic unit cell for increasing times from 18 to 2880 minutes in $6x10^{-5}$ mbar vacuum atmosphere. As shown in Fig. (1) the small intensity increase can be due to small amount of phase formation mainly at the interface, because of fast grain boundary diffusion, and short penetration depth of X-rays. Therefore, grazing incidence X-ray diffraction is not the best method to analyze the phases in between the bi-layers. The GIXRD was used with transmission electron microscope (TEM) to analyze a foil from this reaction zone.

### 3.2. Transmission Electron Microscope (TEM):

A foil of approximately 100 nm thick was extracted from (S2) sample after annealing at 500 °C for 45 minutes using focused ion beam technique (FIB) for TEM analysis [10]. The foil dark field image of the reaction zone shows non-uniform reaction zone formation of about 500 nm thickness, due to high surface roughness of the aluminum layer. Reaction layer morphology as shown in Fig. 2(c) had an equiaxed and regular shape grain structures in the

reaction zone in one region and lamellar grain growth adjacent to the Ru layer. This regular shape grains belongs to the $Al_6Ru$ intermetallic phase that has an orthorhombic structure in annealed Al rich alloys at high temperatures [13]. The other grains belong to the $RuAl_2$ intermetallic phase formed near the Ru layer interface because it may be the first formed phase. Also, electron diffraction pattern results of the inter-planer spacing matching indicating $Al_6Ru$ [14] and $RuAl_2$ intermetallic phases with other unmatched d-spacing values, due to unstable phases.
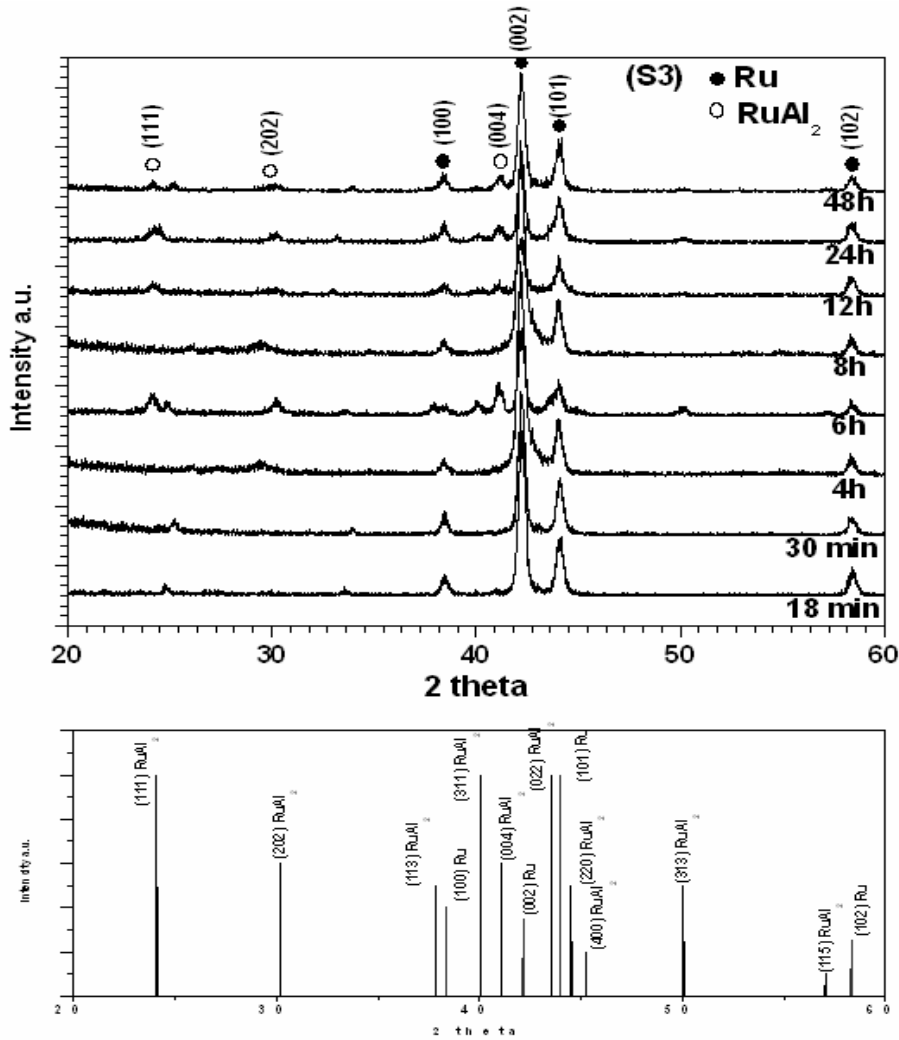


**Fig. (1):** Grazing incidence X-ray diffraction patterns for annealed S3 sample at 500 $^{o}$C at increasing time in hours.
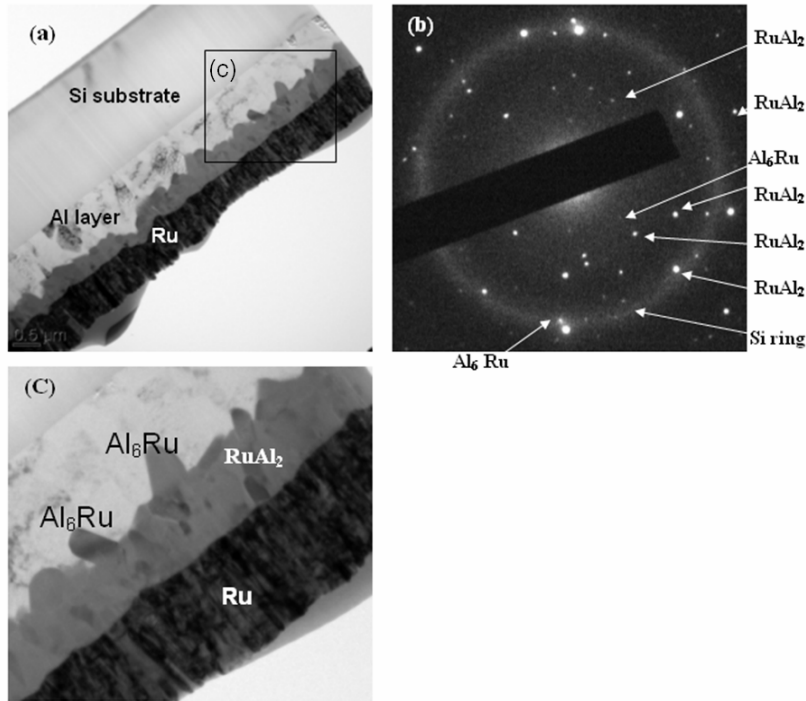
**Fig. (2).** TEM foil dark field image of thick bi-layer S2 sample:
      (a) Dark field image of TEM foil extracted with FIB technique.
      (b) Electron diffraction pattern obtained through a spot in the reaction zone.
      (c) Shows a mgnefied part (black square) from Fig. (2a).

### 3.3. Focused Ion Beam (FIB) and Reaction zone kinetics:

      Annealing of bi-layers (S2 samples) as listed in Table (2) at temperatures of 180 $^o$C and 300 $^o$C for 45 minutes showed no reaction at the interface between Al and Ru bi-layers as shown in Fig. (3a, b). While increasing annealing temperature to 500 $^o$C for the same time (45 min) resulted in a non-uniform reaction zone of approximately 500 nm thickness because of the non-uniform surface topography of sputtered Al and Ru bi-layers and the texture formed in certain planes during reaction zone growth is shown in Fig. 3(c). Decreasing bi-layers total thickness at the same thickness ratio to the thin bi-layers (S3 samples) as listed in Table (1), resulted in a reaction zone at same annealing temperature of 500 $^o$C after shorter time of 10 minutes as shown in Fig. 3(d). Therefore, to reveal the reaction zone growth mechanism at constant temperature of 500 $^o$C, the effect of bi-layers total thickness and increasing annealing time were studied by making further FIB cross sections in the annealed thin Al/Ru bi-layers (sample S3) for times in the range from 10 minutes to 2880 minutes as shown in Fig. (3).
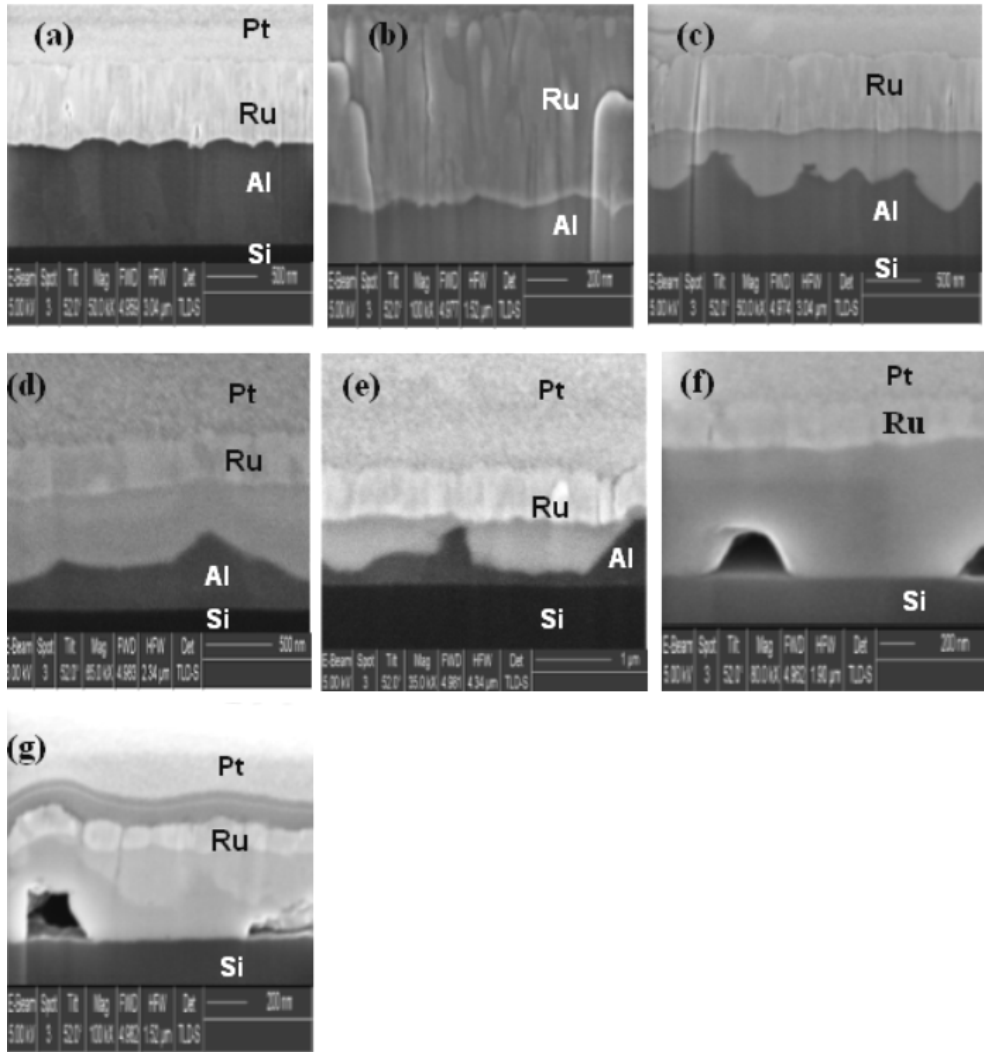
Fig. (3). FIB cuts in annealed bi-layers S2 and S3 samples.
(a) S2 sample at 180$^o$C for 45 min.
(b) S2 sample at 300$^o$C for 45 min.
(c) S2 sample at 500$^o$C for 45 min.
(d) S3 sample at 500$^o$C for 10 min.
(e) S3 sample at 500$^o$C for 18 min.
(f) S3 sample at 500$^o$C for 30 min
(g) S3 sample at 500$^o$C for 2880 min.

Table (2): Data of sputtered samples of different thicknesses, with different heat treatment conditions and pressure = $6 \times 10^{-6}$ m.bar. (X-ray diffraction phase analysis from ICDD – CARD No. 19-0045).

| Sample | Anneal. Time (min) | Elements | Metal Thickness (nm) | Anneal. Temp. ($^{o}$C) | Reaction development |
|---|---|---|---|---|---|
| Thick bi-layers S2 | 45 | Al | 1150 | 180 | No. reaction |
|  |  | Ru | 940 |  |  |
|  | 45 | Al | 1150 | 300 | No. reaction |
|  |  | Ru | 940 |  |  |
|  | 45 | Al | 1150 | 500 | $RuAl_2$ |
|  |  | Ru | 940 |  |  |
| Thin bi-layer S3 | 10 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 18 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 30 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 120 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 240 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 360 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 480 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |
|  | 2880 | Al | 287 | 500 | $RuAl_2$ |
|  |  | Ru | 235 |  |  |

The average of different measured thicknesses along reaction zone FIB cross sections were taken as a measure of the reaction zone thickness at every annealed S3 sample because of non-uniform reaction zone thickness. All measurements were carried out using dual beam workstation (Strata 235, EFI) software in nanometer range. The observation had shown that, the reaction zone thickness increases with increasing annealing time from 10 to approx 120 min at constant temperature of 500 $^{o}$C as shown in Fig. (4). The measured Al layer thickness decreases sharply and after 30 min nearly totally consumed and very little Ru contribution to the reaction zone. The Ru layer shows no further decrease in thickness with increasing annealing time and the reaction zone thickness increases no more. it may be a stable bi-layer of Ru plus a reaction

zone after 120 min at 500 $^{o}$C has formed and showing nearly horizontal region with time increase. Observed voids formation on the reaction zone Si substrate interfacial contact are due to unit cell volume variation of intermetallic phases formation observed as in Fig. (3g).
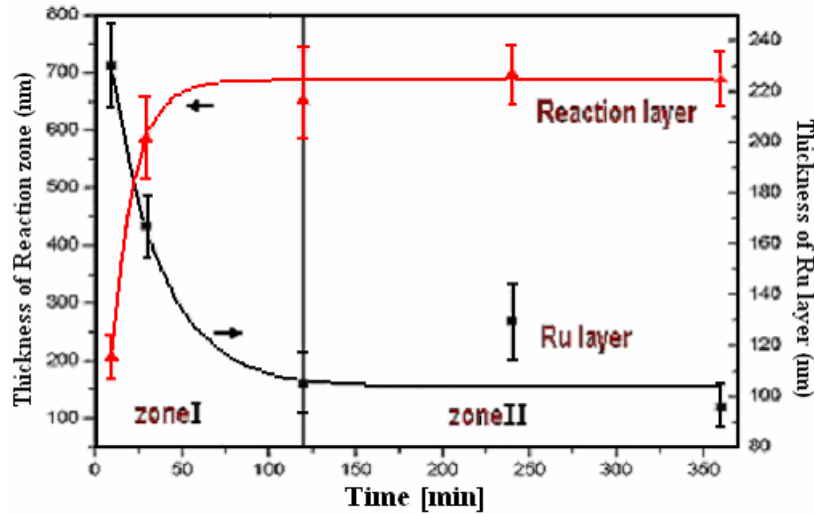


**Fig. (4).** Reaction zone kinetics.

The relation between annealing time versus the reaction zone and Ru layer thickness is shown in Fig. (4), which can be divided into two zones (I, II) corresponding to annealing time from (10 to 360 min). Zone I can be characterized by the following two processes I(1) and I(2). In process I(1) Aluminum layer thickness is nearly consumed after 30 min of annealing and the diffusion process is still in progress as shown FIB cross section of Fig.3(e). During process I(2) Unstable intermetallic phases can be formed which are characterized by TEM and XRD. In zone II other processes takes place II(1) and II(2). In II(1) which the diffusion stops and no more Al material exists in the thin films for further reaction to happen with increasing time. Also, the Ru layer contributes no more in the diffusion reaction and the reaction zone growth stops. In II(2) Stable intermetalic phases have been formed.

### 3.4. Effect of layer thickness on the reaction layer kinetics:

Al and Ru individual layer thicknesses play an important role in the phase evolution in the interfacial region. Individual layer thickness determines how long time required for a diffusion-controlled reaction to cover a defined zone length, and the temperature required to start the reaction. The annealing time has been found to be directly proportional to the Ru/Al layer thickness at constant temperature. The reaction temperature was 500$^{o}$C for 45 min in the Ru/Al bi-layers of 1150 nm Al, 940 nm Ru thick nesses (thick bi-layers) and

$500^{o}C$ for 10 min in bi-layers of 287.5 nm Al and 235 nm Ru (thin bi-layers) thin films. Measured reaction zone thickness % of the total thickness of the two layers Al and Ru decreases from 39.2 % to 27.8 % when the total thickness of both layers increase from thin to thick bi-layers at constant Ru/Al thickness ratio. The reaction zone thickness is decreased when the total thickness layer is larger at constant temperature. This due to dependent on the melting point depression of thinner thicknesses at the early stages of nucleation grain sizes. In other words, the smaller a nanostructure grains is the lower melting temperature [15].

The results can be discussed on the basis of the differences between bulk polycrystalline and thin film materials cases, since the resultant phases after annealing are different. In bulk Al/Ru system the equilibrium solubility of Ru and Al was determined using alloys, which had been annealed for 50 hours at $650^{o}C$ and quenched in water. Also, the equilibrium solubility of Ru in Al did not exceed 0.1 wt % Ru and in alloys cooled from $1400^{o}C$ at $10^{6}$ Deg/sec, the variation in the lattice parameters as a function of composition indicates that the solubility in the solid solution increases linearly up to 11.1 wt% Ru [16, 17]. While in Ru/Al thin films the reaction can happen at lower temperature $500^{o}C$ at a rate of heating and cooling of $2^{o}C$/min for short annealing times (10 min) as shown in the focused ion beam cross sections in Fig. 3(c).

From the last reaction zone kinetics depicted in Fig. (4), we can see that the reaction zone grows more on the account of Al layers than on the Ru layer as shown in Fig. 3(f). This was due to higher solubility of aluminum in Ru, meanwhile the Ru has a maximum solubility of 14 wt% in Al under non-equilibrium thermodynamic conditions [16], which are generally applied in nanocrystalline thin films. The diffusion controlled reaction layer forms a diffusion barrier, which controls further diffusion from both Al and Ru sides. Therefore, the Al atoms seem to be the main moving atoms inside the reaction zone. Meanwhile, the Ru atoms contributing less in the diffusion process until annealing time ends. This can be concluded from the thickness comparison of both layers after long time annealing shown in Fig. 3(f). The matched planes were belonging to $RuAl_2$ and $Al_6Ru$. The non-uniform reaction zone thickness formation has different reasons. Firstly may be due to non-uniform surface topography of sputtered aluminum layers or high surface roughness, due to insufficient pressure during sputtering. Secondly, the non-uniform thickness formation could be due to induced grain boundary diffusion along certain crystallographic planes because of textured growth of both Al and Ru layers after sputtering, which is a normal feature in thin film growth [18] as can be seen from reaction layer morphology in Fig. (2a).

## 4. Conclusion:

DC magnetron sputtering technique is cabable to produce Al/Ru bi-layers of different thicknesses at nearly room temperature. Annealing at 500°C for short time (10 min) is enough to produce intermetallic compounds between Al and Ru bi-layers thin films. Increasing annealing times from 10 minutes to 2880 minutes increases the reaction zone thicknesses on the account of the Al layer more than the Ru layer. Reaction layer contains mainly $RuAl_2$ and $Al_6Ru$ intermetallic compounds, those are important intermetallics in industry. Reactions of Al/Ru nanocrystalline thin films of small thicknesses are different from bulk materials, because reactions starts at lower temperatures for short times of annealing which consumes energy and costs less than in the bulk case. Al/Ru thin film thickness increase at constant thickness ratio has a pronounced effect on the formed intermetallic compound layer thickness at the contact interface. The diffusion at the contact interface had stopped after certain time of annealing, because of the $RuAl_2$ and $Al_6Ru$ intermetallic phases formation, which controls further diffusion from both sides into the reaction layer.

## Acknowledgments:

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