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Model for prediction of coating composition deposited by sputtering using composite target in a reactive gas environment

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Abstract : Reactive sputtering is a widely used deposition technique for compound coatings. Ternary compound or multi component compound coatings are finding increasing applications due to their exotic properties. The properties of the coatings depend strongly on the composition of the films. A mathematical model has been developed to predict the composition of the metallic constituents of the coatings deposited by reactive sputtering using two metals composite target in the presence of a reactive gas (nitrogen) atmosphere. The model is worked out utilizing first order approximation and taking into consideration that there is no re-sputtering effect at the substrate. The model developed can also calculate the percentage of covered areas of the target surfaces (target poisoning) with reactive gas partial pressure. The model has been tested experimentally for titanium aluminum composite target in a nitrogen gas environment.

Keywords : Sputtering; Coating; Model; Composition; Target; Ti-Al.

INTRODUCTION

Reactive sputtering is a widely used deposition technique for compound coatings. Hard nitride coatings have been successfully applied for many applications including cutting tools since 1980s[1,2]. Ternary compound or multi component compound coatings are finding increasing applications due to their exotic properties. Synthesis of the nano-composites and ternary compounds such as Ti-VB-VN, Ti-VSi-VN, Ti-Al-N, Ti-Nb-N, Ti-Cr-N has been tried for various applications and it has been found that the properties of these composites depend strongly on the composition of the film and film structure[3,4,5,6,7,8]. Thus, controlling the film composition and structure is important. Therefore, the prediction of composition and in turn the physical properties of the films are an important contribution since it will allow the synthesis of specific, tailor-made surface coatings. Reactive magnetron sputtering is widely used for deposition of compound and composite coatings under reactive gas such as nitrogen[9,10,11]. With this technique it is possible to fabricate thin films with different compositions. The Important process parameters involved in a reactive sputtering process include the gas pressure, bias, the ion current density and the voltage applied to the target[12,13]. The control of the reactive gas is especially critical for the optimization of film properties.

Theoretical models have been previously simulated by several researchers[14,15,16,17,18] for reactive sputtering with different combinations of processing parameters for investigating new compounds. These models deal mostly with binary compounds. Berg et al.[16,18] presented a reactive sputtering model for binary compound and correlated deposition rate and film composition with flow rate by considering the gettering effects and pump exhaustion.

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In this paper a mathematical model has been simulated for ternary compounds starting with the Berg's basic model to predict the composition of the metallic constituents of the coating, deposited by reactive magnetron sputtering utilizing two metals composite target, with varying partial pressure of nitrogen. The model developed can also calculate the percentage of covered areas of both the target surfaces (target poisoning) with nitrogen partial pressure.

SPUTTERING

Sputtering (Fig. 1) is a complex process involving many components like target surface, substrate surface, various ions, neutrals, molecular species, cluster particles and the chamber wall. Then there are parameters like incidence angle, target-substrate distance and presence of reactive gas (N_2 here) molecules everywhere in the chamber.

Assumptions

Various assumptions made are :

- Nitride formation in the space between target and substrate is neglected, which is true for low pressures of nitrogen.
- Sputtering of higher order particles (clusters) are neglected.
- Because of the low energy of Ar ions, sputtering occurs only from the topmost atomic layer.
- Non thermalised - direct particle emission is assumed.
- Ion current density is uniformly distributed over the plasma zone of the target surfaces.
- Deposition of metal atoms with nitrogen takes place at substrate.
- There is no resputtering effect at the substrate.

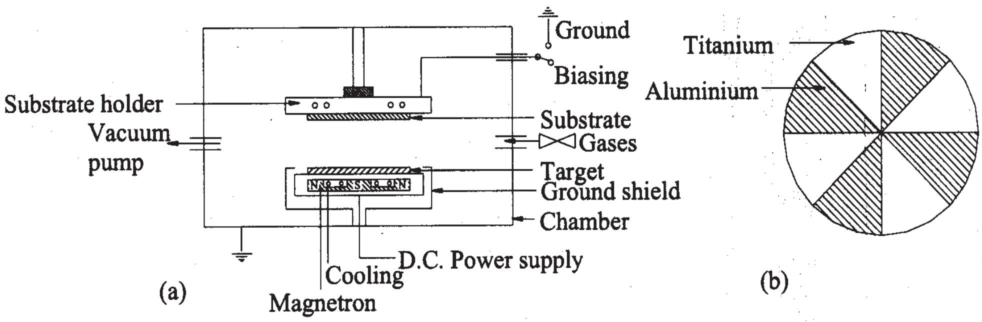

Fig. 1 : (a) sputtering system, (b) composite target

THEORETICAL MODEL

The model has been worked out utilizing first order approximation and taking into consideration that there is no re-sputtering effect at the substrate. The model developed can also calculate the percentage of covered areas of the target surfaces (target poisoning) with nitrogen pressure.

Proposition

- 2 targets A & B of equal surface areas.
- Sputtering gas = Ar & Reactive gas = N_2
- Species at the target surface :

  Towards target : Ar^+, N_2^+, N_2

  From target : M_A, M_B, MN_A, MN_B, N
- Species at the substrate surface : Ar^+, N_2^+, N_2 , M_A , M_B , M_AN , M_BN , N
- Neglecting higher order particles.
- Resulting major particles are, therefore,

  : Ar^+, N_2^+ towards target

  : M_A , M_B from target to substrate
- At substrate the presence of Ar^+, N_2^+ play the role of biasing/resputtering, which is ignored here.
- $I_{Ar+} >> I_{N2+}$ The energy of N_2 molecule further reduces to half when it breaks down to N atom (N_2=N+N). Sputtering with N_2+ is, thus, ignored.

First order approximation

- Sputtering due to Ar^+ at the target surface (N_2 is present).
- Deposition of metal atoms with nitrogen at the substrate.

Processes at the target surface

Nitrogen adsorption at the target surface

At any point of time (Fig. 2) :

Let θN^A = Surface area of target A covered with N

Let θN^B = Surface area of target B covered with N

The surface areas of metals A and B not covered with N are, therefore, :

- Metal A = 0.5 - θN^A
- Metal B = 0.5 - θN^B

At any point of time the flux adsorption can be given by :

On metal A, $Fad^A = FN_2\ 2\ \alpha^A\ (0.5 - \theta N^A)$ ... (1a)

On metal B, $Fad^B = FN_2\ 2\ \alpha^B\ (0.5 -V\ \theta N^B)$ ... (1b)

Where α = sticking coefficient and factor 2 is due to diatomicity of N_2 gas.

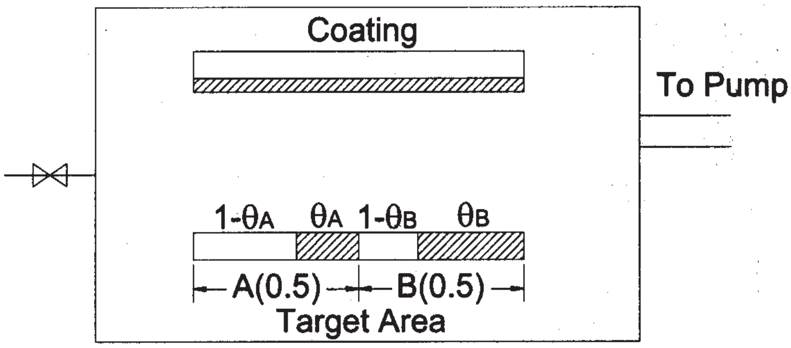

Fig. 2 : Sputter model -V target surface areas

From kinetic theory of gases the N_2 flux[16,19] is

$FN_2 = PN_2 / \sqrt{(2\pi\ kTM)} = k^1\ P^{N2}$ ... (2)

Where k = Boltzman constant, T = Temperature, M = wt of N_2 molecule

Nitrogen desorption from the target surface

From A, $F^{desA} = S^{MNA}\ J^T\ \theta^{NA}$ ... (3a)

From B, $F^{desB} = S^{MNB}\ J^T\ \theta^{NB}$ ... (3b)

Where J^T = Target current density, and S^{MN} = Sputtering yield of compound

Metals sputtering flux from targets

From A, $F^{MA} = S^{MA}\ J^T\ (0.5\ \sqrt{\theta^{NA}})$ ... (4a)

From B, $F^{MB} = S^{MB}\ J^T\ (0.5 - \theta^{NB})$ ... (4b)

Nitride coverage areas at targets

At steady state 1(a) = 3(a) and 1(b) = 3(b)

From 1(a) = 3(a), we get

$F^{N2}\ 2\ \alpha^A\ (0.5 - \theta^{NA}) = S^{MNA}\ J^T\ \theta^{NA}$

$\theta^{NA} = 1/\ [2 + S^{MNA}\ J^T/(\alpha^A\ F^{N2})]$ ... (5a)

Similarly from 1(b) = 3 (b), we get

$\theta^{NB} = 1/\ [2 + \{S^{MNB}\ J^T/(\alpha^B\ F^{N2})\}]$ ... (5b)

Replacing F_{N2} form equation (2) in equation (5)

$\theta^{NA} = 1/\ [2 + \{S^{MNA}\ J^T/(\alpha^A\ k^1 P^{N2})\}]$ ... (6a)

$\theta^{NB} = 1/\ [2 + \{S^{MNB}\ J^T/(\alpha^B\ k^1 P^{N2})\}]$ ... (6b)

This gives the coverage of nitride formation on the target surface with respect to P_{N2}. Therefore, the nitride coverage area (%) on the target surface can be graphed with respect to P_{N2} and theoretically predicted.

Metallic fluxes from targets

Putting the values from equation (6) in equation (4)

$$F^{MA} = S^{MA} J^{T} \{0.5\text{-}1/ [2+(S^{MNA}J^{T})/(\alpha^{A} k^{1}P^{N2})]\} \quad \text{... (7a)}$$

$$F^{MB} = S^{MB} J^{T} \{0.5\text{-}1/ [2+(S^{MNB}J^{T})/(\alpha^{B} k^{1}P^{N2})]\} \quad \text{... (7b)}$$

Equation (7) represent the metallic fluxes leaving from the targets A & B

Prediction of metallic constituents of coating

Deposition rate $D \propto x F$

Where F = sputtered flux, & A = system factor, which depends on angular distribution of emitted particles, and target-substrate distance.

Assuming each metal atom impinging on the substrate surface is retained (α =1), then

$$D = A x F \quad \text{... (8)}$$

Here, $D^{A} = A x F^{A}$ & $D^{B} = A x F_{B}$

$$D_{A}/D_{B} = F_{A}/F_{B} = X_{A} / X_{B} = X_{A} /(1\text{-}X_{A}) \quad \text{... (9)}$$

For metallic portion $X_{A} + X_{B} = 1$

From equations (7) and (9), the values of X_{A} and X_{B} with respect to P_{N2} can be estimated.

Metallic and nitride fluxes from targets

Equation (7) accounts for only metallic fluxes. When compound fluxes sputtered from the targets are also taken into consideration, total flux becomes -

$$F^{TA} = F^{MA} + F^{MNA} \quad \text{... (10a)}$$

$$F^{TB} = F^{MB} + F^{MNB} \quad \text{... (10b)}$$

$$F^{TA}=S^{MA} J^{T}(0.5\text{-}\theta^{NA}) + S^{MNA}J^{T}\theta^{NA} \quad \text{... (11a)}$$

& $$F^{TB} = S^{MB}J^{T}(0.5\text{-}\theta^{NB}) + S^{MNB}J^{T}\theta^{NB} \quad \text{... (11b)}$$

Replacing θ_{N}^{A} and θ_{N}^{B} from equation (6), we get total flux

$$F^{TA}=J^{T}\{S^{MA}(0.5\text{-}1/[2+(S^{MNA}J^{T})/(\alpha^{A}k^{1}P^{N2})]) + S^{MNA}1/[2+(S^{MNA}J^{T})/(\alpha^{A} k^{1}P^{N2})]\} \quad \text{... (12a)}$$

$$F_{T}^{B}=J_{T}\{S_{M}^{B}(0.5\text{-}1/[2+(S_{MN}^{B}J_{T})/(\alpha_{B}k_{1}P_{N2})]) + S_{MN}^{B}1/[2+(S_{MN}^{B}J_{T})/(\alpha_{B} k_{1}P_{N2})]\} \quad \text{... (12b)}$$

Total Metallic constituents of coating

Fraction of constituents

$$A = F^{TA}/(F^{TA} + F^{TB}) \quad ...(13a)$$

$$B = F^{TB}/(F^{TA} + F^{TB}) \quad ...(13b)$$

Equations (12) & (13) give the composition prediction of metallic constituents of sputtered coatings with respect to partial pressure of nitrogen. The graphs can be plotted for θ_N^A, θ_N^B and composition Vs P_{N2} and the values can be predicted theoretically at different values of P_{N2}.

TESTING THE PROPOSITION / MODEL

Experiments

The experimental system consisted of a magnetron sputtering system (Fig.1). Coatings were deposited on to the stainless steel substrates. For testing the simulated model titanium aluminium nitride (Ti-Al)N coatings have been deposited at various

parameters and coating composition analyzed by energy dispersive X-ray (EDX) analysis techniques. Ti/Al mosaic (composite) targets (Fig.1b) was used to deposit Ti-Al-N films on stainless steel substrates by reactive d.c. magnetron sputtering in a custom built unit shown in Fig.1a. The coating system consists of a vacuum chamber supported by a diffusion pump backed by a rotary pump which can give a base pressure of better than $1x10^{-5}$ mbar. Magnetron is attached beneath the water-cooled copper cathode on which a 160mm target can be screwed. Chamber is grounded. An adjustable height substrate holder is situated about 60mm away in front of the target on which a variety of plane substrates can be mounted. The substrates were ultrasonically pre-cleaned sequentially using an aqueous alkaline bath, ethanol and acetone before being placed in the vacuum chamber. Gases after passing through moisture and oxygen traps and flow meters were introduced in to the chamber via needle valves. Substrate holder is insulated from the chamber and can be kept floating with or without biased power supply. Total pressure of the deposition chamber was kept at approximately $5\text{-}10^{-3}$ mbar (3.8 mtorr). Target current was kept at 0.6 ampere. Nitrogen gas to total (nitrogen + argon) gas flow ratio was varied from 0-40%. The power to the target was supplied by a stabilized d.c. power supply (0-1000V, 6 Amperes maximum). No external heating or biasing was applied to the substrate.

Calculations

$$K^1 = 1/\sqrt{(2\pi kTM)}$$

$$K^1 = 1/\sqrt{(2x3.14x1.38x10^{-23}x300x28x1.66x10^{-27})}$$

$$= 2.876 \times 10^{22} \text{ sec / (kg.m)}$$

Current density calculation

Target current density $J^T = I/(A.q)$

Where I = Target current (Amp), q = electronic charge

A = Effective sputter area (Fig. 3) = $\pi \cdot (R_1^2 - R_2^2)$

$$J^T = 1.0 \text{ Amp}/ (94.25 \times 10^{-4} \text{ m}^2 \times 1.6 \times 10^{-19} \text{ Amp.sec})$$

$$= 6.63125 \times 10^{20} \text{ /m}^2\text{.sec} = 6.63125 \times 10^{16} \text{ /cm}^2\text{.sec}$$

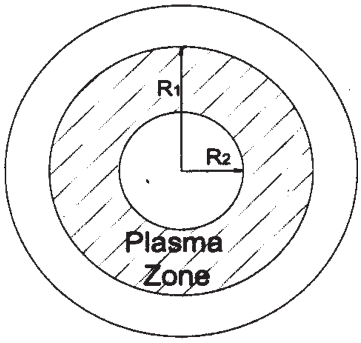

Fig. 3 : Plasma zone on target surface

Nitride coverage areas (θ^{N}) at target : θ^{NTi} & θ^{NAl}

$$\theta^{NTi} = 1 / [2 + (S^{TiN}.J^{T})/(\alpha^{Ti}.k^{1}.p^{N2})]$$

and $\theta^{NAl} = 1 / [2 + (S^{AlN}.J^{T})/(\alpha^{Al}.k^{1}.p^{N2})]$

Sputter yields were found out experimentally using empirical formula[20] for 500ev Ar ions as - $S^{Ti} = 0.51$, $S^{Al} = 1.05$, $S^{TiN} = 0.10$ & $S^{AlN} = 0.154$

Which matched with the values available in the literature[21,22,23,24].

And the assumed unity values for sticking coefficients[16,25] as

$$\alpha^{TiN} = 1 \ \& \ \alpha^{AlN} = 1$$

The nitride coverage areas at different flow ratios of nitrogen or partial pressures of nitrogen have been calculated and shown in the Table 1. The estimated sputtered fluxes from metallic portions of the targets, and therefore the resulting composition have been shown in the Table 2 and the estimated total sputtered fluxes (from metallic as well as nitrided portions of the targets) and the resulting composition of the coatings have been shown in the Table 3.

Table 1 : Nitride coverage portions on targets (α^{TiN}=1; α^{AlN}=1)

N_2 /Ar Flow %	P^{N2} 10^{-4} mbar	θ^{NTi}	θ^{NAl}
2.5	1.219	0.4568	0.4364
5	2.381	0.4769	0.4653
10	4.545	0.4876	0.4812
15	6.522	0.4913	0.4867
20	8.333	0.4932	0.4896
25	10.00	0.4943	0.4913
30	11.538	0.4950	0.4924
35	12.963	0.4956	0.4932
40	14.286	0.4960	0.4938

Table 2 : Sputtered flux from only metallic portions (α_{Ti}^{N}=1, α_{Al}^{N}=1)

N_2 /Ar Flow %	P^{N2} 10^{-4} mbar	F^{MTi} $10^{18}/m^2$.Sec	F^{MAl} $10^{18}/m^2$.Sec	Comp Ti at%	Comp Al at%
2.5	1.219	14.61	44.26	24.82	75.18
5	2.381	7.81	24.16	24.43	75.57
10	4.545	4.18	13.09	24.22	75.78
15	6.522	2.94	9.23	24.15	75.85
20	8.333	2.31	7.26	24.11	75.89
25	10.00	1.93	6.07	24.09	75.91
30	11.538	1.67	5.27	24.07	75.93
35	12.963	1.49	4.70	24.06	75.94
40	14.286	1.35	4.70	24.05	75.95

Table 3 : Sputtered total flux and composition (α_{Ti}^{N}=1, α_{Al}^{N}=1)

N_2 Flow %	P^{N2} 10^{-4} mbar	Ti Flux-F^{TiT} $10^{18}/m^2$.Sec	Al Flux-F^{AlT} $10^{18}/m^2$.Sec	Comp. Ti at%	Comp. Al at%
2.5	1.219	44.90	88.83	33.57	66.43
5	2.381	39.43	71.67	35.49	64.51
10	4.545	36.52	62.23	36.98	63.02
15	6.522	35.52	58.93	37.60	62.40
20	8.333	35.01	57.26	37.94	62.06
25	10.00	34.71	56.24	38.16	61.84
30	11.538	34.50	55.56	38.31	61.69
35	12.963	34.35	55.07	38.41	61.59
40	14.286	34.24	54.71	38.49	61.51

Fig. 4 shows the nitride coverage areas of titanium and aluminium metals with increasing partial pressure of nitrogen. Both metals show the similar trend of increasing poisoning area of

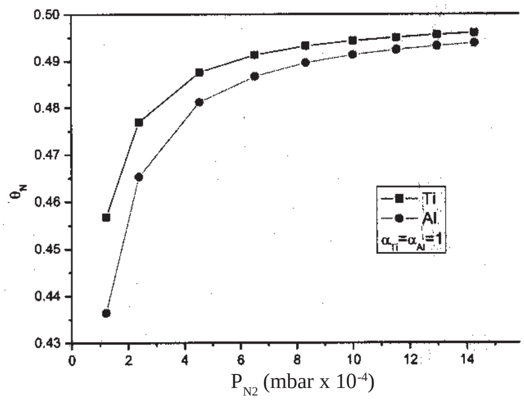

Fig. 4 : Nitride coverage areas for Ti and Al targets (α_{Ti}^{N}=1, α_{Al}^{N}=1)

target surface with the increase in nitrogen partial pressure. Fig. 5 graphs the composition of titanium and aluminium in the coating vis-a-vis partial pressure of nitrogen considering sputtering taking place only from metallic portions of the targets. While Fig. 6 depicts the composition of Ti and Al in the coatings versus partial pressure of nitrogen considering sputtering taking place from metallic and nitrided both portions of the targets.

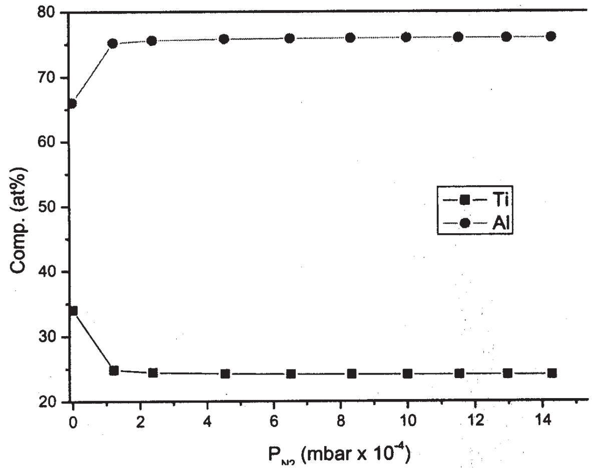

Fig. 5 : Composition prediction considering fluxes from metallic portions of targets only (α_{Ti}^{N}=1, α_{Al}^{N}=1)

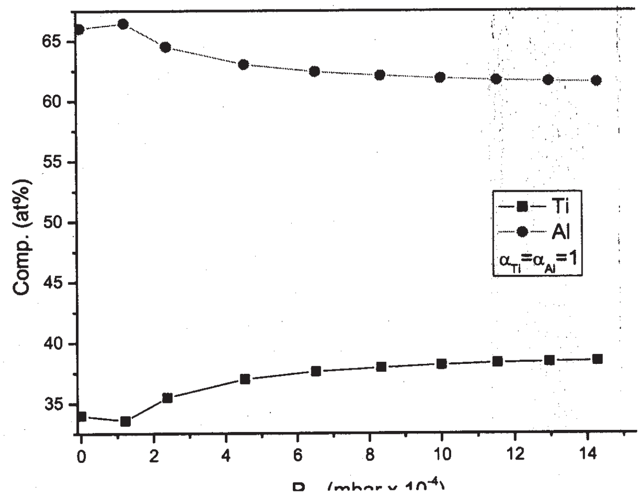

Fig. 6 : Composition prediction considering total flux (α_{Ti}^{N}=1, α_{Al}^{N}=1)

DISCUSSION

In the calculations above, the nitrogen sticking coefficients for titanium and aluminium both have been assumed to be unity (as referred in the previous literature). According to thermodynamic data, the values of ΔG_f^o for TiN and AlN are -.308.3 and -.287.0 KJ/mol, respectively. Nitrogen must therefore firstly react with titanium before aluminium. This difference in reactivity could probably affect the nucleation during the deposition of TiAlN, their composition and subsequently influence the microstructure and property. Therefore, it is unlikely that the nitride coverage areas for titanium and aluminium will follow the pattern as depicted in Fig.4. Similarly it is unlikely to follow the prediction of coating composition as stipulated in the Table 3 (Fig. 6) based on the sticking coefficient values assumed to be unity (in the literature) for both of the metals simultaneously. Titanium exhibits higher reactivity and therefore higher sticking coefficient (α_{Ti}) to nitrogen than aluminum due to their different standard free energy of formation. Therefore, the model is further extended by assuming α_{Ti} as 1 and different smaller values for α_{Al} as 0.5 and 0.1 too. The nitride coverage areas and composition prediction have been qualitatively modeled below for the above α_{Al} values too. Theoretical value for equal areas of titanium and aluminium targets without nitrogen gas is predicted to give 34 at% Ti and 66 at% Al.

Nitride coverage areas on titanium target will remain same. However, nitride coverage areas on aluminium target for different values of α_{Al} will differ. Data for nitride coverage areas, total sputtered flux and resulting composition for titanium and aluminium emanating from metallic and nitrided both portions of the targets have been shown in Table 4 and the coating composition has been graphed in Fig.7 with increasing partial pressure of nitrogen for sticking coefficient

Table 4 : Nitride coverage, total fluxes and composition (α_{Ti}^{N}=1; α_{Al}^{N}=0.5)

N_2 Flow %	P_{N2} 10^{-4}mbar	θ_N^{Ti} α_{Ti}^N=1	$\theta_{\tilde{N}}^{Al}$ α_{Ai}^N=0.5	F_{Ti}^T 10^{18}/m^2.Sec	F_{Ai}^T 10^{18}/m^2.Sec	Comp. Ti at%	Comp. Al at%
2.5	1.219	0.4568	0.3872	44.90	118.07	27.55	72.45
5	2.381	0.4769	0.4351	39.43	89.61	30.56	69.44
10	4.545	0.4876	0.4637	36.52	72.59	33.47	66.53
15	6.522	0.4913	0.4742	35.52	66.40	34.85	65.15
20	8.333	0.4932	0.4795	35.01	63.20	35.65	64.35
25	10.00	0.4943	0.4828	34.71	61.25	36.17	63.83
30	11.538	0.4950	0.4851	34.50	59.93	36.53	63.47
35	12.963	0.4956	0.4866	34.35	58.98	36.81	63.19
40	14.286	0.4960	0.4878	34.24	58.26	37.02	62.98

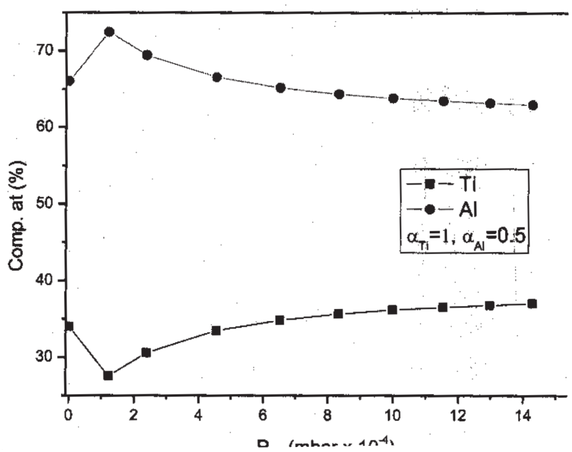

Fig. 7 : Composition prediction considering total flux (α_{Ti}^{N}=1, α_{Al}^{N}=0.5)

values of α_{Ti}^{N}=1 and α_{Al}^{N}=0.5. Similarly - nitride coverage values, total sputtered flux and resulting composition for sticking coefficient values of α_{Ti}^{N}=1 and α_{Al}^{N}=0.1 have been shown in Tables 5; and composition graph in Fig. 8. Fig.9 shows the nitride coverage areas for aluminium target with partial pressure of nitrogen at sticking coefficient values of α_{Al}^{N}=1, 0.5, and 0.1.

Table 5 : Nitride coverage, total fluxes and composition (α_{Ti}^{N}=1; α_{Al}^{N}=0.1)

N_2 Flow %	P_{N2} 10^{-4}mbar	θ_N^{Ti} α_{Ti}^{N}=1	$\theta_{\tilde{N}}^{Al}$ α_{Ai}^{N}=0.1	F_{Ti}^{T} $10^{18}/m^2$.Sec	F_{Ai}^{T} $10^{18}/m^2$.Sec	Comp. Ti at%	Comp. Al at%
2.5	1.219	0.4568	0.2035	44.90	227.20	16.50	83.50
5	2.381	0.4769	0.2864	39.43	177.96	18.14	81.86
10	4.545	0.4876	0.3595	36.52	134.51	21.35	78.65
15	6.522	0.4913	0.3930	35.52	114.63	23.65	76.35
20	8.333	0.4932	0.4122	35.01	103.24	25.32	74.68
25	10.00	0.4943	0.4246	34.71	95.85	26.58	73.42
30	11.538	0.4950	0.4333	34.50	90.68	27.56	72.44
35	12.963	0.4956	0.4397	34.35	86.85	28.34	71.66
40	14.286	0.4960	0.4447	34.24	83.90	28.98	71.02

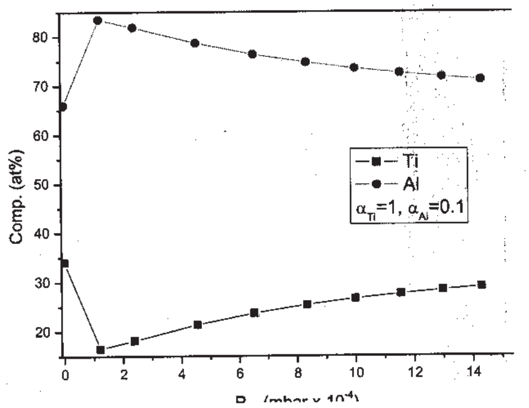

Fig. 8 : Composition prediction considering total flux (α_{Ti}^{N}=1; α_{Al}^{N}=0.1)

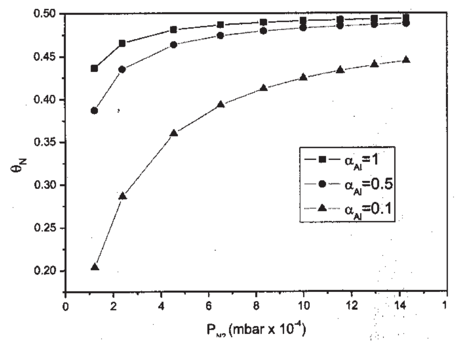

Fig. 9 : Nitride coverage areas for Al at different lower values of α

EXPERIMENTAL CURVE

The experimental values obtained for titanium and aluminium analysis of coatings deposited at various flow ratios of nitrogen by energy dispersive X-ray (EDX) technique have been graphed in Fig. 10. Fig. 11 compares the experimentally obtained values with theoretically estimated values for titanium composition at different sticking coefficient values. The values nearly correspond to the theoretical values having sticking coefficient values as $\alpha_{Ti}^{N}=1$ and $\alpha_{Al}^{N}=0.5$. Therefore, it is unrealistic to assume the sticking coefficient value as unity as has been assumed often in the literature previously. The theoretical model simulated is, thus, able to predict the composition of the metallic constituents of the coatings obtained at various partial pressure of a reactive gas (here nitrogen) utilizing composite target during sputtering. However, more realistic values of sticking coefficient must be taken in to account rather than assuming them to be unity for the metal systems being used in the composite target.

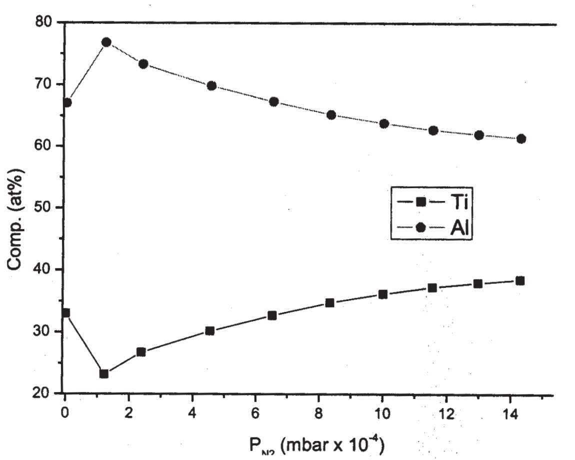

Fig. 10 : Experimental curves for Ti and Al composition

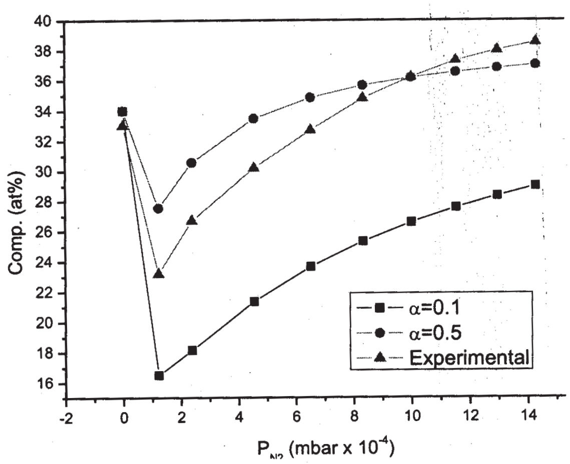

Fig.11 : Theoretical (α_{Al}=0.5 & 0.1) and experimental values of Ti composition in the coatings Vs P_{N2}

CONCLUSION

A theoretical model has been simulated to predict the composition of the metallic constituents of the coatings deposited by sputtering using two metals composite target in the presence of a reactive gas (nitrogen) atmosphere. The model has been worked out utilizing first order approximation and taking into consideration that there is no re-sputtering effect at the substrate. By this model it is possible to predict the metallic constituents of the coatings deposited by using two metals composite target with the partial pressure of reactive gas. The model developed can also calculate the percentage of covered areas of the target surfaces (target poisoning) with nitrogen partial pressure. The model has been tested experimentally for titanium aluminum system under nitrogen gas environment. The sticking coefficient for nitrogen on titanium target has been presumed to be unity (α_{Ti}^{N}=1) while for aluminium besides taking α_{Al}^{N}=1, different lower values of α_{Al}^{N} = 0.5, and 0.1 have also been considered for sticking coefficient of nitrogen on aluminium target. The composition prediction of the metallic constituents of the coatings follow the approximate pattern with the sticking coefficient values of α_{Ti}^{N} = 1 and α_{Al}^{N}=0.5.

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