Scanning Magnetron Sputtered TiN Films Characterisation and Properties

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Abstract: ***Scanning magnetron target(274mmx174mm) is used to deposit TiN film on to Si (<100> p type 10 ohm cm resistivity) substrate for microelectronic application, to deposit best quality TiN films parameters such as deposition rate , scanning speed ,target substrate distance (TSD), ion currents are optimized, nitrogen partial pressure. Total nitrogen and argon pressure was kept at $5x10^{-3}$ m bar. TiN film is sputter deposited at different substrate bias viz 0,-40, -60,-80, -100,-120, volt and annealed at different temperature viz 400,600,750,800 and 950^0c. XRD of the films deposited at 180ma and200ma ion current is carried out to determine crystal structure. Stress in the TiN Film is calculated using XRD results of the deposited TiN film.Grian size was obtained using X-ray broadening and scherrer formula. Resistivitiy of the TiN film deposited at different substrate bias viz 0,-40,-60,-80,-100,-120 volt and annealed at different temperature viz400, 600,650,750,800 and 950^0c is obtained using four probe method .SEM analysis is done to study the surface morphology of TiN films deposited at room temperature and annealed at900^0c.***

1. Introduction

TiN films has attracted high attention as a gate metallization for self aligned metal semiconductor FETs ,as a thermally stable schottkey barrier contact and as diffusion barrier to protect the shallow silicon junction in the formation of metallic contacts on silicon , or as a glue layer because it is hard and chemically stable [1-4] low resistivity films is preferred for above application. Also TiN has been studied for selective transparent films and for high temperature photo thermal conversion[5]. It has been observed that structure and properties depends upon the growth condition variation in growth condition significantly alter structure and properties of TiN films. Optically stoichiometric TiN is similar to gold in the visible region and therefore it is also used for decorecorative purposes.

The grain size in TiN Films as determined from X ray broadening is generally below 1000 A^0 if the films are grown below approximately 500^0c. For the magnetron sputtered films without any substrate bias the grain size was found to increase from 350 A^0 at 200 ^{0}c to 700 A^o at 650^0c.

For TiN Films the most commonly observed growth orientation is (111) (100) and (110) however (200) and (220) orientation are also reported in the literature.

Morphology also changes with stoichiometry of the films loosely bonded powdery films can even be deposited if the flow of nitrogen is too high for understoichiometric TiN films extremely dense film are commonly observed. Parameters such as growth rate substrate roughness and substrate motion have been shown to effect the morphology of the TiN film, TiN films normally grow with (111) ,(100) and (110) preferred orientation and have a lattice parameter slightly deviating from the bulk value of 4.24 A^0.

Even though the TiN is stable over broad composition range its structure and properties depends critically on the actual composition .Stoichiometric TiN has the Nacl structure with a lattice parameter of 4.240 A^0. Because of the vacancy defect structure that is stable over a broad composition range the lattice parameter decreased for both over stoichiometric and understoichiometric films.

One of the most successful application areas of TiN is hard coatings over very high speed tools. Coatings with thickness of about 2-10 micro meter are generally found to increase tool life by many hundred percent.

Variation in growth condition significantly alter structure and properties of TiN films hardness was observed ranging from 340 to above 3000kgf/mm^2 and electrical receptivity from 18 to 10^4 micro ohm cm for single phase TiN films.

Sputtered films normally show compressive stresses incorporation of sputtered gases and ion bombardment during growth was found responsible for compressive stresses.

The coating microstructure, microchemistry and relationship among structure properties and processing have to be extensively investigated.

The resistivity, composition color defects, surface roughness, grain size and grain boundaries of TiN all depends strongly on the formation conditions.

2. Experimental Procedure

The present system is a sophistication of a D.C. sputtering unit having a combination of 300 lit /sec diffusion pump with a 200lit /min rotary vacuum pump the system gives an ultimate vacuum of $5x10^{-6}$ milli bar. The pressure monitoring is done by using pirani and penning gauge combination. The vacuum chamber is a 300mm diameter S.S cylinder opened at both ends. The scanning magnetron target (274mmx174mm) is mounted on the cathode plate and deposition is carried out in sputter down mode. The substrate holder with silicon substrate(<100> p type 10 ohm cm receptivity) fixed to the base plate Iolar- 2 grade argon (99.999%) has been used as sputtering gas, flow of which is controlled by combination of two needle valve in series. TiN films were deposited in reactive environment of nitrogen..Parametres such as deposition rate745A^0, scanning speed14cm/sec ,Target substrate distance(T.S.D.) 11cm and ion current180ma, 200ma, Nitrogen partial pressure was kept at $3x10^{-5}$m bar, total nitrogen and argon pressure was kept at $5x10^{-3}$ m bar are optimized A variable power supply of high voltage type, with15 Kv and 10A rating was used .Cu film was sputter deposited in Ar atmosphere alone.

Four probe method is used to obtain the resistivity at different temperature Philips Analytical X-Ray diffrectometre (pw 3710) using Xpert software was used to obtain X.R.D of the prepared samples. Jeol scanning Microscope (JSM-840) was used to obtain SEM photograph of the prepared samples.

Preparation of the TiN film

In the present study TiN film have been deposited on to silicon substrate to study their feasibility for micro electronic application, using Scanning magnetron, titanium target and Ar as sputtering gas N_2 as reactive gas TiN films were deposited onto silicon (<100>,p-type,1-10 ohm resistitivity) substrate under varying N_2/Ar pressures ,varying currents, varying target substrate distances (T.S.D.) varying bias conditions and varying annealing temperatures N_2 Pressure for given sputtering ion current of 180 to 200 MA at 11 cm T.S.D.was determined empirically by visualizing the golden color of the deposited films. The gold like appearance of the film was presumed to be TiN according to other reports[6-9] Stoichiometric TiN film is obtained only within a narrow range of N_2 partial pressure, N deficient films are obtained below the optimal N_2 partial pressure and N rich films at excess N_2 partial pressure[9 -10]. The TSD was kept quite large (11cm) to achieve homogeneous composition of the deposited films by scanning magnetron sputtering while the ultimate pressure was achieved $5X10^{-6}$ mbar good golden color TiN films were obtained at nitrogen pressure$3x10^{-5}$mbar for sputtering ion currents 180 and 200 ma . The effect of ultimate vacuum on mechanical properties of sputtered coatings is significant. In the coatings deposited by sputtering techniques the contamination of the deposition atmosphere can influence the properties owing to different phenomena which can arise during substrate cleaning and for coating growth[11-13].Total nitrogen and argon pressure was kept at $5x10^{-3}$ mbar.

Stresses are low at $5x10^{-3}$ mbar Ar pressure[14] below this Ar pressure compressive stresses increase with decreasing pressure almost linearly and at higher pressure this turns to be tensile stress around $6x10^{-3}$ mbar.As Ar pressure is increased further the internal stress seems to decrease only slightly becoming essentially Zero[14]. Presently it was observed that the films, deposited at lower than $5x10^{-3}$ mbar Ar pressure, Peel out after few hours which indicated high stresses in the films deposited at lower pressures. The crystal structure of TiN film is also affected by total gas pressure[15]. Films were deposited at different substrate biasing voltages viz...o,-20,-10,-60-80,-100,and -120 v. Thus as deposited TiN films were annealed for the different temperatures viz -400,600,650,700,750,800 and 900^0c in the vacuum at $3x10^{-5}$ mbar, to study the deposited TiN film capability for microelectronic applications.

R. D. Study of the Deposited TiN Films: **Fig 1, 2**

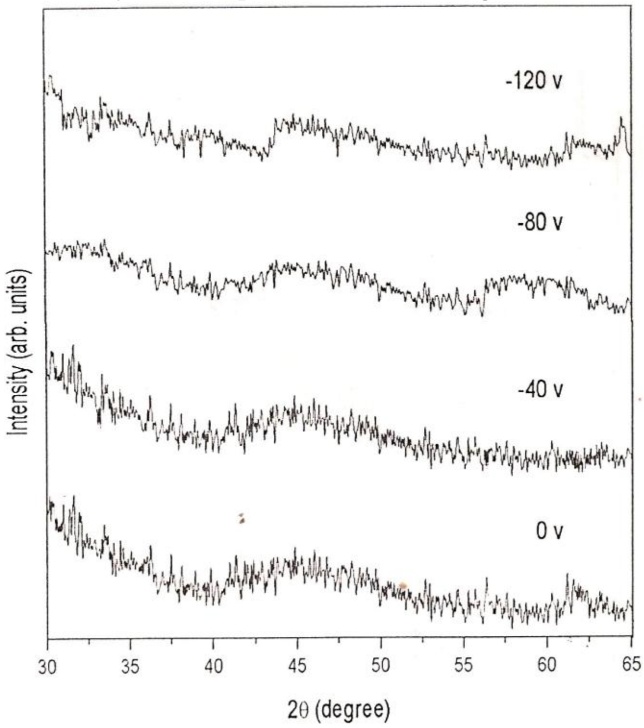


Figure 1: XRD patterns for TiN films deposited at different substrate biasing (ion current was kept 180 ma)

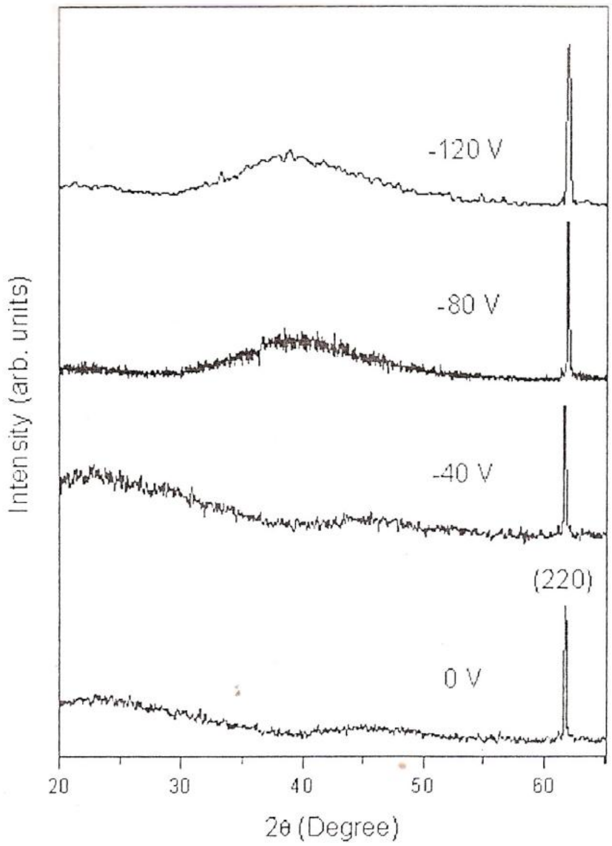


Figure 2: XRD pattern for TiN films deposited at different substrate biasing (ion current was kept 200ma)

Philips Analytical X-Ray diffrectometre (pw 3710) using Xpert software was used to study X.R.D of the prepared samples. The observed XRD patterns of the golden TiN films deposited at different substrate bias are given in fig 1and 2 .The scanning magnetron sputtered TiN films deposited at 180 ma ion current shows amorphous structure fig .1 and films deposited at 200ma ion current show crystalline structure with a single (220) face orientation fig 2, which indicates the strong dependence of the film structure on the ion current.

X-ray diffraction patterns of the TiN films deposited by Arc ion plating show strong dependence on bias voltage .At zero volt biasing a strong (220) peak , at -80 and -100 V strong (111) peaks and at -30v random orientation of film have been observed by Matsue[16] et al. The preferential orientations is controlled by certain growth conditions ,such as bias voltage of the substrate[17]and the arrival ratio[18-19] of the number of sputtered titanium and nitrogen atoms .Xiao[20] et al have observed that the films deposited by R.F. magnetron sputtering at the deposition rate 480A^0 /Min show preferred orientation of (200).Where as those deposited by the arc plating at the deposition rate 3000A^0 indicated strong (111) preferred orientation , this indicates the film orientation depends on the deposition rate.

TiN films grows along the (100) plane in R.F.sputtering because the atoms on the substrate has more time to migrate due to low deposition rates. Assuming the total strain energy of the TiN film pellag[21] et al have proposed a model of correlation between surface energy(Shkl) and strain energy(Uhkl) of TiN film, to explain the mechanism resulting in preffered orientation .They showed that both surface energy and strain energy have directional properties and correlation of surface energy and strain energy are described as Whkl =Shkl +Uhkl were Whkl represents the total free energy of the system , which should minimal in thermodynamic equilibrium . A preferred (100) orientation can be considered as one for which the surface energy is dominant over the strain energy on the contrary (111) orientation should be preferred when the strain energy is large and dominant. The X.R.D. pattern patterns of the present crystalline films show (220) orientation indicating the equal dominance of surface and strain energies for the scanning magnetron sputtering deposited TiN films

Grain Size and Stress

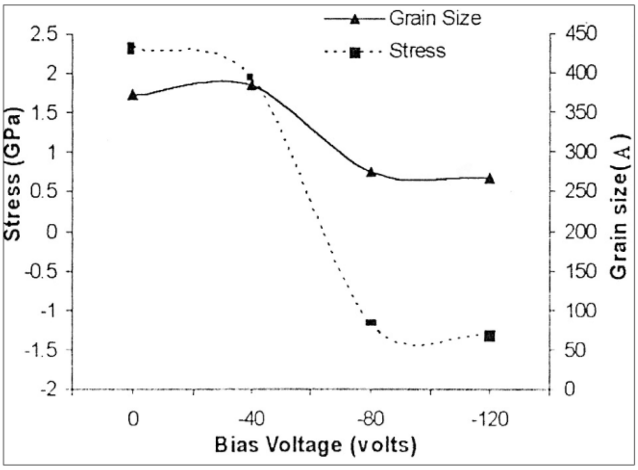


Figure 3: Variation of stress and grain size of the crystalline TiN films with substrate bias voltage

The stress in the film and grain size is calculated from the XRD data. For polycrystalline film with isotropic biaxial stress, the stress T is given by [22]

$T=E(a-a_0)/ 2va_0$

Where E is the young's modulus (590 KN/mm^{-2}) ; v the Poisson ratio (o.3) and a_0 the lattice constant (4.240A^0) of the face centered cubic TiN a is the measured lattice constant. From the X.R.D. patterns, Fig 2 the lattice constant is obtained 4.249967 A^0 for the films prepared at room temperature without any bias voltage the lattice constant reduces to 4.248297A^0 for the film prepared at room temperature with -40 bias voltage .The change in the lattice constant can be attributed to the stress in thin films. Stress in the film can be due to the presence of oxygen and also in the low pressure sputtering regime, ion bombardment during film growth results in compressive stress due to atomic peening mechanism. Calculated from these fig 3, shows the variation of the stress with substrate biasing voltage. The films deposited at room temperature and with biasing voltage up to -40 volt show compressive stress. Films deposited at higher substrate biasing show transformation to tensile mode intrinsic stress and resistivity of TiN films depends on various deposition parameters and on substrate position. They appeared mainly to be controlled by the effect of oblique incidence of sputtered particles and by the bombardment of energetic species on growing films[23].

Also the nitrogen partial pressure and the argon partial pressure were found influencing the internal stress crystallographic structure and resistivity. The internal stress of the deposited TiN Films changes as a function of both argon and nitrogen partial pressure and films deposited at low argon pressure tends to have high compressive stress. The internal stress is also related to preferred orientation of the film. The internal stress of the TiN films depends on its microstructure. Films deposited with (111) preferred orientation have smaller internal stress then that for the films with (100) preferential orientation[24,25]. The grain size (t)of the deposited crystalline TiN films was determined from the X ray line broadening Using the scherrer:s formula[26] t = 0.9 λ/ Bcos Ø

Where λ is the wave length of x ray used, B the full width at half maximum corresponding to 2 ə. The grain size was observed changing from 371.7 A^0 to 385 A^0 as the substrate biasing voltage changes from zero to -40 volt grain size decreases with further increase in the negative biasing voltage.

Dependence of resistivitty on annealing temperature

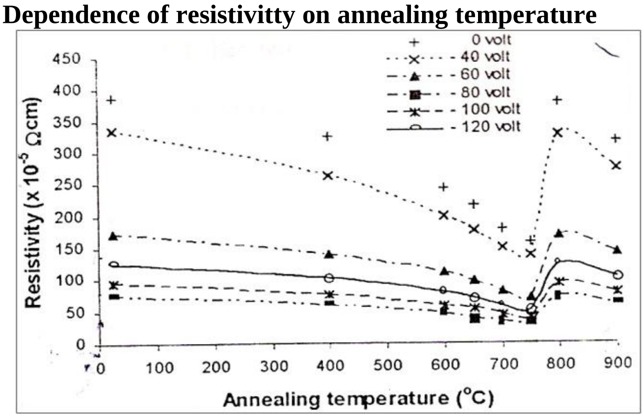


Figure 4: Resistivity variation of the amorphous TiN films with annealing temperature (Films deposited at 180ma ion current)

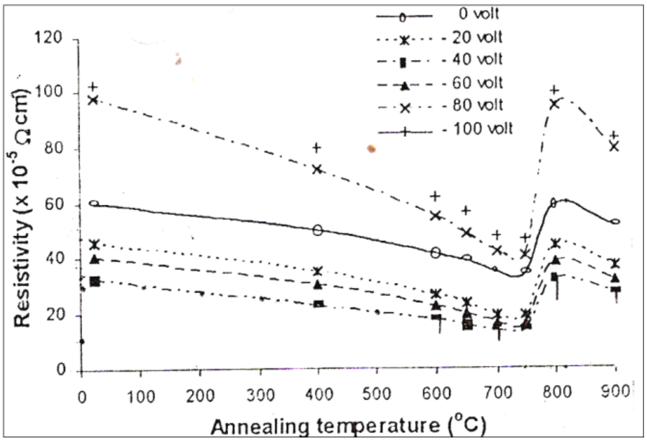
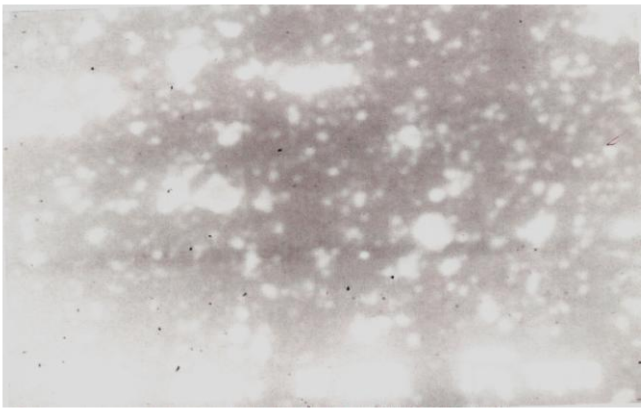


Figure 5: Resistivity variation of the crystalline TiN Films with annealing temperature (films deposited at 200ma ion current)

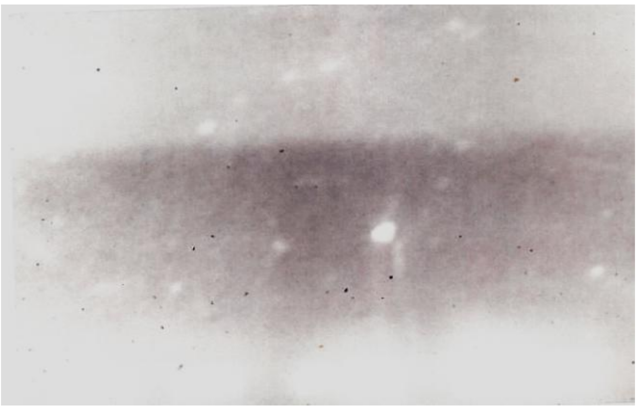


(b)

Figure 6: Surface SEM photographs of TiN films, annealed at (a) RT, and (b) 900^{0}C

Variation of the observed resistivity of the scanning magnetron sputtering deposited TiN films with annealing temperature has been shown in figs. 4 and 5. It has been observed that resistivity decreases with increasing annealing temperature, showing a minimum at 750^{0}c , for all the samples . For the amorphous TiN film, deposited with bias voltage -80 volt resistivity was observed decreasing from 737 μΩcm (room temperature value) to 304 μΩ-cm (at 750^{0}c) . Also for the samples deposited with bias voltage -40 v resistivity of the crystalline samples decreases from 320 μΩcm to 132μΩcm(at 750 ^{0} c)for temperatures around 800^{0}c the resistivity increases to a maximum value and then decreases at higher temperature , for all the prepared TiN thin films samples. The decrease of resistivity with increasing annealing temperature may be due formation of oxide layer (due to oxygen migration across the film) and decrease of the resistivity above 800^{0}c may be due to higher grain size[27].

SEM results



(a)

Jeol scanning Microscope (JSM-840) was used for SEM study of the prepared samples .SEM results of the surface morphology of the crystalline TiN films deposited with -40V substrate bias and annealed at different temperatures are shown in Fig.6(a) (b) Surfaces of the films were observed smooth. flat and compact and there was no sign of holes or degradation of TiN Surface up to 900^{0}c in the present study,. Poitovin et al[28] have observed many failures in the TiN structure, after annealing at 1000^{0}c they observed some big holes (around 10 micro m. in diameter) and many little holes (around 1micro m. in diameter)

3. Results

TiN films were deposited under varying currents varying target substrate distance (TSD) varying bias conditions and varying annealing temperatures. Good golden color film were obtained at nitrogen partial pressure of 3x10^{-5} mbar ion currents were 180 and 200 ma. Total argon and nitrogen pressure was kept at 5x10^{-3}m bar.

XRD study of the deposited TiN films reveals that TiN films deposited at 180 ma ion current have amorphous film structure and film deposited at 200 ma ion current exhibits crystalline structure . At 200 ma ion current film is crystalline having (220) face orientation, which indicates strong dependence of the film structure on the ion current.

The grain size with zero volt substrate bias is observed 371.7 A^0 which increases and attains shape of 374.7 A^0 around -35 volt which decreases further and grain size is 200 A^0 at -80 volt substrate bias.

Stress was found 2.4 G..p.a. at 0 volt substrate bias which decreases sharply after -35 volt and attains minimum at -52volt which is 1.3 G.P.a

From the observation it is clear that stress decreases with grain size sharply.

It has been observed that resistivity decreases with increasing annealing temperature showing a minimum at 750^{0}c for all samples. For the samples deposited with bias voltage -40 volt resistivity of the crystalline samples decreases from 320 micro ohm (at room temperature) to

132 micro ohm cm (at 750^{0}c) , for temperature around 800 ^{0}c the resistivity increases to a maximum value and then decreases at higher temperatures. SEM analysis reveals that crystalline film surface were smooth flat and compact and there were no sign of degradation up to 900^{0}c, in the present study.

4. Acknowledgment

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References

[1] J.B. price O. Borland and S. Sel berd thin solid films 236 (1993)311
[2] E.O. Travis and R.W. Fiorddice thin soid films 236(1993)
[3] J.M.E. Harper S.E. Hornstrom ,O.Thomes,A. Charai j.vac. Sci Technol A7 (1989) 875
[4] R.M.Charatan , M.E Gross D.j. Eaglesham J.Applied Physics 76 (1994) 4377
[5] Valkomnen . T. Karlsson and B.O. Johansson in thin film technologies proc. sov. photo opti instrument Eng 401 (1983)
[6] J. Perry J.Vac .SCi Technol, A6 (1988)2140
[7] B Karlson R.P. shimshock B.O.Seraphin and J.c. Heygarth sol. Energy mater 7(1983) 401
[8] Kikuo tomiagu S inoue ,R.P.Howson K. Kusaka and T. Hanabusa Thin Solid Films 281-282 (1996) 182
[9] I.petrov , A . Mayers .J. E. Geen thin solid films 97 (1982) 79
[10] A.Pan and J.E. Green Thin solid films 97(1982)79
[11] Berg , S.W. Kim V. Grajewaskie S.W. Kim and Fromm mat sci A139(1991)345
[12] S.Berg , N. Eguchi V. Grajewaskie S.W. Kim and Surf Coat Technol 49 (1991) 336
[13] A. Cavaleiro , M .T. Vieira F Ramos and J.P. Dias Thin Solid Films 290-291 (1996) 238
[14] S . Inoue T. ohaba , H. Takata K. Koterazau 343 -344
[15] Y.Ando I.Sakamoto . I. Suzukie and S. Marumo Thin Solid films 343-344
[16] T Matsue ,T. Hanabusa , Y. Miki , K.Kusaka and E.Maitani Thin solid films343-344(1999) 257
[17] U.C. OH and J.H.Je J.Appl. Physics 74 (1993) 1692
[18] M. Satou , K.Fujji , M. Kiuchi and F. Fujimoto Nuc. Instrument . Metods B 39(1989) 166
[19] K.Min , S.Hofman and R . Shimizu Thin Solid films 295 (1997)1
[20] S. Xio C.P.Lungn O Takai Thin Solid Films 334 9(1998) 173
[21] J.Pelleg L.Z. Zevin and S. Lungo Thin solid films 197 (1991) 80
[22] M . Ohring The material science of Thin films Academic press Newyork 1992
[23] A.Neidhardi U.Reienhold E.Schroeter and W wattke Thin Solid film 173 (1989) 109
[24] S. Inoue T.Ohaba ,H Takata And K Koterazawa Thin solid films 343-344
[25] K. Deenamma Vargheese , G. Mohan Rao T.V. Balasubramanium and sanjeev kumar Mat. Sci. Engineer B83 (2001)242
[26] B.D.Cullaty elements of X Ray diffraction Addition Wesley Wokingham U.K.1967
[27] A.F.Mayadas and M. shatzkes phys . Rev . B1 (1970) 1382
[28] J.M. poitevin , D. M aheo G. Lemperiere. Thin Solid Film,s 176 (1989) 7

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