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 film 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 5x10⁻¹ 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°C. 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. Grain size was obtained using X-ray broadening and scherrer formula. Resistivity 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°C 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°C.

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 conversion5. 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 decorcorative purposes.

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

For TiN Films the most commonly observed growth orientation is (111) (100) 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 Å.

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 Å. Because of the vacancy defect structure that is stable over a broad composition range the lattice parameter decreased for both over stoichiometric and understoichometric 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/mm² and electrical rectivity from 18 to 10° 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..Parameters such as deposition rate745Å, scanning...
Microelectroni

mbar

400, 600, 650, 700, 750, 800 and 900. TiN films were annealed for the different temperatures viz.

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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.

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°C in the vacuum at 3x10^-5

mbar, to study the deposited TiN film capability for

microelectronic applications.

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 resistivity)

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

given for 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 report. Stoichio-

metric 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. The TSD was kept quite large

(11 cm) 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. Total nitrogen and argon pressure was

kept at 5x10^-3 mbar.

Stresses are low at 5x10^-3 mbar Ar pressure 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. Presently it was

observed that the films, deposited at lower than 5x10^-3 mbar

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TiN films were annealed for the different temperatures viz -

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microelectronic applications.

Four probe method is used to obtain the resistivity at different temperature Philips Analytical X-Ray
diffractometre (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.

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)](Image)

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

Philips Analytical X-Ray diffractometre (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
1 and 2. The scanning magnetron sputtered TiN films

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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 et al. The preferential orientations is controlled by certain growth conditions such as bias voltage of the substrate and the arrival ratio of the number of sputtered titanium and nitrogen atoms .Xiao et al have observed that the films deposited by R.F. magnetron sputtering at the deposition rate 480A/min show preferred orientation of (200).Where as those deposited by the arc plating at the deposition rate 3000A/min 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 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

\[
T = E(a-a_0)/2\nu a_0
\]

Where E is the young's modulus (590 KN/mm² ) : \(\nu\) the Poisson ratio (0.3) and \(a_0\) the lattice constant (4.240Å) 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 Å for the films prepared at room temperature without any bias voltage the lattice constant reduces to 4.248297Å 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.

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

\[
t = 0.9 \lambda / 2v \cos \theta
\]

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

**Grain Size and Stress**

![Graph showing stress and grain size](image)

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

**Dependence of resistivity on annealing temperature**

![Graph showing resistivity variation](image)

**Figure 4:** Resistivity variation of the amorphous TiN films with annealing temperature (Films deposited at 180ma ion current)
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°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 µΩcm (at 750°C). Also for the samples deposited with bias voltage -40 V resistivity of the crystalline samples decreases from 320 µΩcm to 132 µΩcm (at 750°C) for temperatures around 800°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°C may be due to higher grain size.

SEM results

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°C in the present study. Poitovin et al.28 have observed many failures in the TiN structure, after annealing at 1000°C they observed some big holes (around 10 micro m. in diameter) and many little holes (around 1 micro 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 Å which increases and attains shape of 374.7 Å around -35 volt which decreases further and grain size is 200 Å 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 -52 volt 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°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 (at 800°C). The stress was found to decrease from 2.4 G.P.a. at 0 volt substrate bias to 1.3 G.P.a. at -80 volt substrate bias.
132 micro ohm cm (at 750ºC), for temperature around 800ºC 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 900ºC, in the present study.

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431