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Resistivity XRD, SEM, EDAX of CU/TiN /Si Structure Using Scanning Magnetron Sputtered TiN as Diffusion Barrier

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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 with low resistivity[1], parameters. Such as deposition rate, scanning speed, target substrate distance (T.S.D.) and ion current ma, Nitrogen partial pressure, were optimized. Total nitrogen and argon pressure was kept at $5x10^{-3}$ m bar. TiN films were sputter deposited on to Si with different substrate bias. Cu film is sputter deposited on to as deposited TiN films since it is found as best substitute for diffusion barrier. Thickness of the TiN film is determined keeping in consideration diffusion length[2] of Cu in TiN at different temperature. Stylus Dektak is used to obtain desired thickness of TiN and copper films. Cu /TiN /Si Structure thus formed were annealed at different temperature to study microelectronic application for diffusion barrier. Resistivity fig1of the Cu/TiN /Si structure were obtained using four probe method, low resistivity Cu/TiN/Si structure were preferred. Inter diffusion of silicon and or top metal through the TiN film was investigated. XRD fig 2 SEM fig 3, 4, 5 EDAX fig6 of Cu/TiN /Si is obtained to determine its feasibility for microelectronic application.***

1. Introduction

TiN is used as a diffusion barrier in advanced integrated circuit devices due to its chemical stability and low resistivity. Ideal diffusion barrier for a contact metallization is defined as a chemically and mechanically stable and electrically conductive layer that inhibits inter diffusion between its bordering media TiN has been reported as diffusion barrier material for silicon devices which acts as an impermeable barrier to silicon atoms [1].

The diffusion length of Cu in TiN at temperature between 600 and 700 ^{0}C has been reported about 400 A^0 the diffusion length [2]of Cu in TiN at 800^{0}C was observed 800$A^{0.}$

There has been considerable interest in TiN as diffusion barrier in multilevel metallization schemes for integrated circuits[3, 4-7] in Al/TiN /Ti/Si system it has been shown that TiN films as thin as 1000A^0 thick can prevent the silicon aluminum inter diffusion at 600^0 c for 30 min, as observed by RBS. But it was found that that the electrical devices fabricated using these metallization schemes failed during a much lower thermal annealing cycle[5, 8-11]

Suni et al[12] found that there were two failure mechanism for the breakdown of TiN diffusion barriers. First fracture of barrier layer caused by very large compressive stress in the film due to negative bias applied to the substrate; second inter diffusion of the contact metal and silicon through defects such as pinholes and voids. In TiN /Ti/ Thick SiO_2 [13]structure peeling was found creating problem.

With the continuing progress of integrated circuits technology the requirements to increase the device density necessitates the improvements of multilevel metallization. Copper (Cu) has been extensively studied as a potential substitute for Al and Al alloys in multilevel metallization of semiconductor devices and integrated circuits[14-15]. Cu metallization for multilevel inter connects has advantages such as high melting point[15-16], high electro migration resistance[17], low bulk resistivity, low reaction tendency with commonly used diffusion barrier materials[14, 16-18].

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 target (274mm × 174mm) is mounted on the cathode plate which is scanning magnetron with optimized speed 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. A high voltage type, with15 Kv and 10A rating was used. TiN films were deposited on to Si in reactive environment nitrogen argon is taken as sputtering gas. Parameters such as deposition rate745A^0, scanning speed14cm/sec, target substrate distance(T.S.D.) 11cm and ion current 200ma, Nitrogen partial pressure at $3x10^{-5}$m bar, total nitrogen and argon pressure at $5x10^{-3}$ m bar were optimized

Stylus dektak is used to determine the thickness of thin film. 800 A^0 thick TiN film is sputter deposited on to Si then 600 A^0 thick film is sputter deposited on to as deposited TiN film. CU/TiN /Si structure thus formed were annealed for 1 h at 650, 750 800 and 900 ^{0}c in the vacuum at $3x10^{-5}$ m bar.

Four probe methods are used to determine the resistivity at different temperature. Philips Analytical X-Ray diffrectometre (pw 3710) using Xpert software was used to study X.R.D of the prepared samples at different temperature. Jeol scanning Microscope (JSM-840) was used to study SEM photograph of the prepared samples at different temperature. Chemical analysis is done by X-ray analysis EDAX method of the surface layer.

Preparation of the TiN films: In the present study TiN film have been deposited on to silicon substrate to study their feasibility for microelectronic 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 resistibility) 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 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[19-22]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[22 -23]. 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[24-26].Total nitrogen and argon pressure was kept at $5x10^{-3}$ mbar.

Stresses are low at $5x10^{-3}$ mbar Ar pressure[27] 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[27]. 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[28]. Films were deposited at different substrate biasing voltages viz...o, -20, -10, -60-80, -100, and -120 v.

Resistivity of Cu/TiN/ Si Structure: FIG 1
Annealing of Cu/TiN/ Si structure did not change color of the copper films up to 750 ^{0}c.However color of the film annealed at 800 and 900 ^{0} c was found changed. Showing formation of new materials, the variation of the resistivity of the copper films with annealing temperature is shown in fig 1as observed from fig 1 the resistivity did not significantly change up to 750^{0}c. However a small decrease in resistivity with increasing annealing temperature was observed, which can be attributed to the change in grain size and reducing defects.. But this decrease in resistivity of cu is not as high as Deenamma et al observed [29]. Since in the present study Cu was deposited on the as deposited TiN films, the grain size of underlying TiN layer may also be increasing causing the stress in copper films. The fact that the copper resistivity did not change significantly for the samples annealed up to 750^{0}c indicating that there is no inter diffusion of Cu and /or Si through TiN films up to 750 ^{0}c. But at 800 ^{0}c resistivity was found increasing indicating the starting of diffusion beyond 800^{0}c, resistivity was found anomalously increasing showing significantly rise in diffusion.

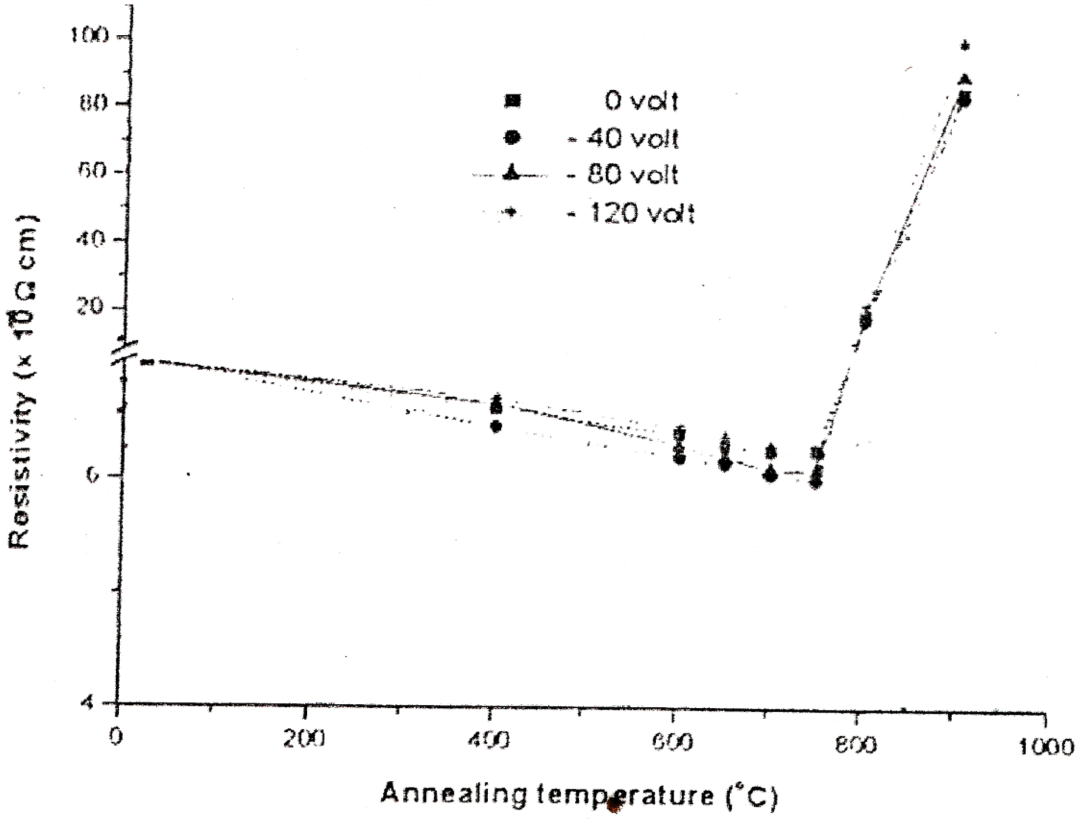


Figure 1: Variation of resistivity of Cu/TiN/Si structure with annealing temperature

XRD OF CU /TIN/SI Structure: Fig 2

Fig 2 shows that X.R.D. patterns of the CU/TiN /Si samples annealed at different temperatures. The increase in the intensity of the copper lines with increasing annealing temperature is due to the larger grain size and better orientation resulting from annealing. Also there are no extra peaks corresponding to any compound of Si, Ti and Cu up to 750 ^{0}c. These results confirms the absence of any inter diffusion of Cu and Ti through TiN film. For the samples annealed at 800 and 900 ^{0}c, some extra peaks of Cu and Si through TiN barrier are observed. The resistivity fig1 are supported by X-RAY diffraction results.

The resistivity and XRD results suggest that up to 750^0 c the scanning magnetron TiN film is a good diffusion barrier for silicon devices.

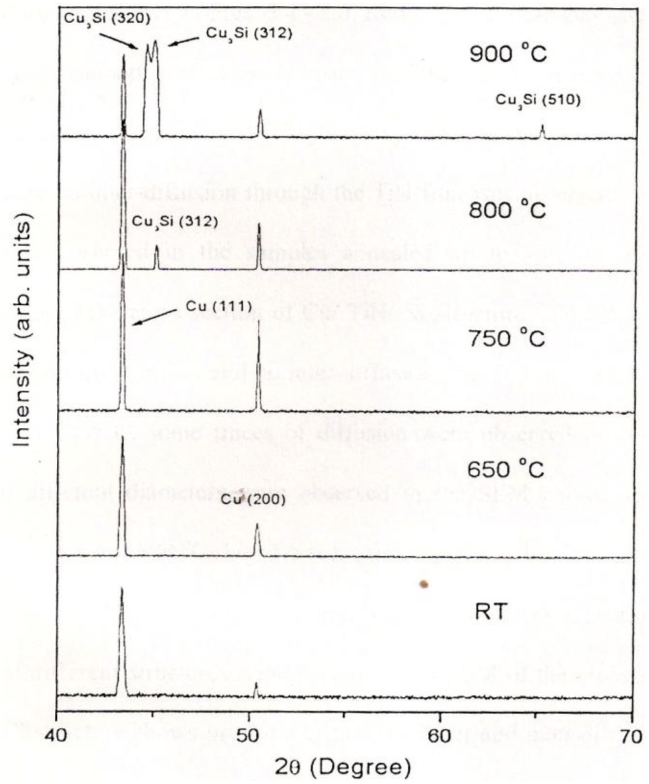
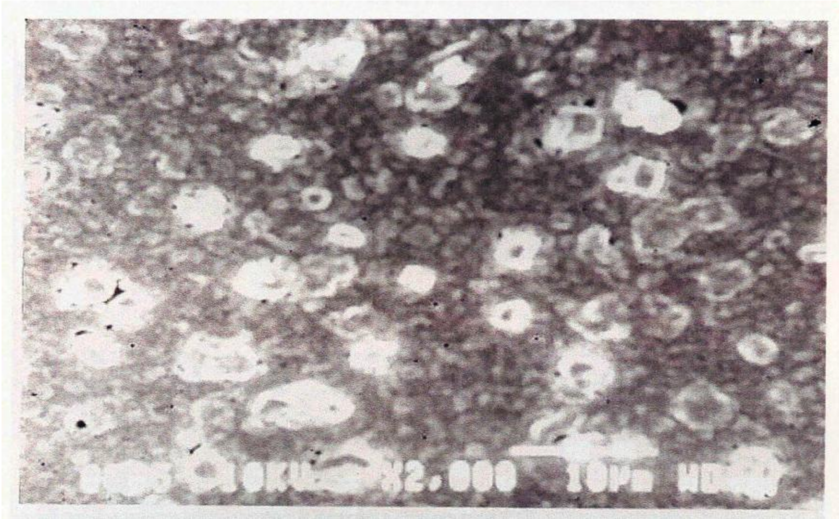


Figure 2: XRD results of Cu/TiN /Si Structure

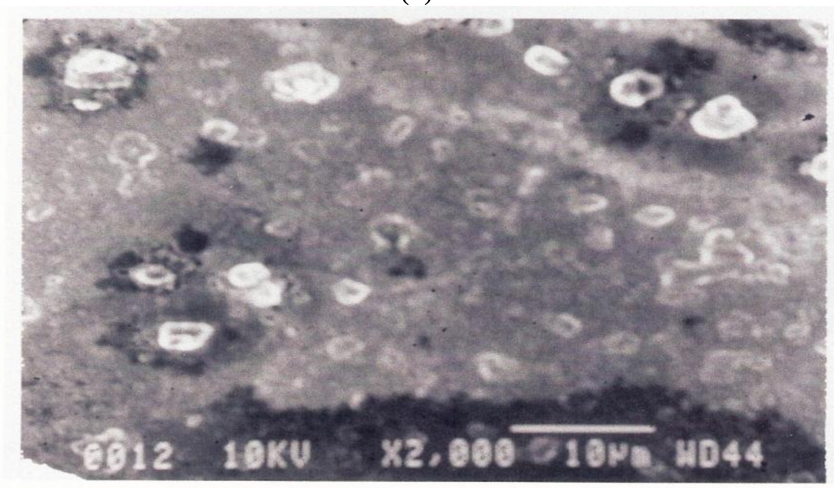
SEM results: Fig 3, 4, 5

The inter - diffusion of the border media across the TiN film was studied by SEM. The SEM photographs of Cu/TiN/Si structure, annealed at different temperatures, are shown in fig3 - 5. Room temperature deposited samples show flat and smooth surface, and clusters of Cu grains were seen due to grain growth in the samples annealed at higher temperatures. Up to 750^{0}C.annealing temperature no inter-diffusion through the TiN film was observed. fig.3. No holes were observed in the samples annealed up to 750^{0}C. Also. SEM photographs of the cross section of Cu/TiN/Si structure, annealed at 650^{0}C, show three different layers and no inter-diffusion, fig. 4 (a). In the samples, annealed at 800^{0}C, some traces of diffusion were observed on the surface. Holes of different diameters were observed in the SEM photographs of the samples annealed at 800^{0}C, fig. 5 (a). And, significantly high diffusion was observed in the SEM results of the samples annealed at 900^{0}C, surfaces show islands of different structures, fig. 5. (b). Also SEM of the cross section of Cu/TiN/Si structure shows breaking of the TiN layer and inter-diffusion of Cu and Si, in the samples annealed at 900^{0}C, fig.4 (b)

(i)

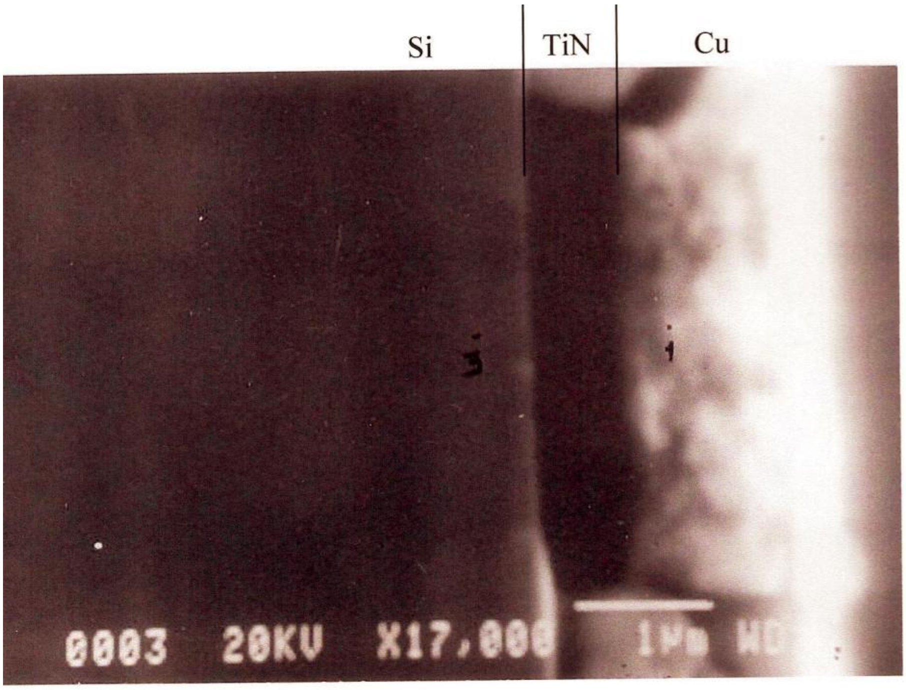


(ii)

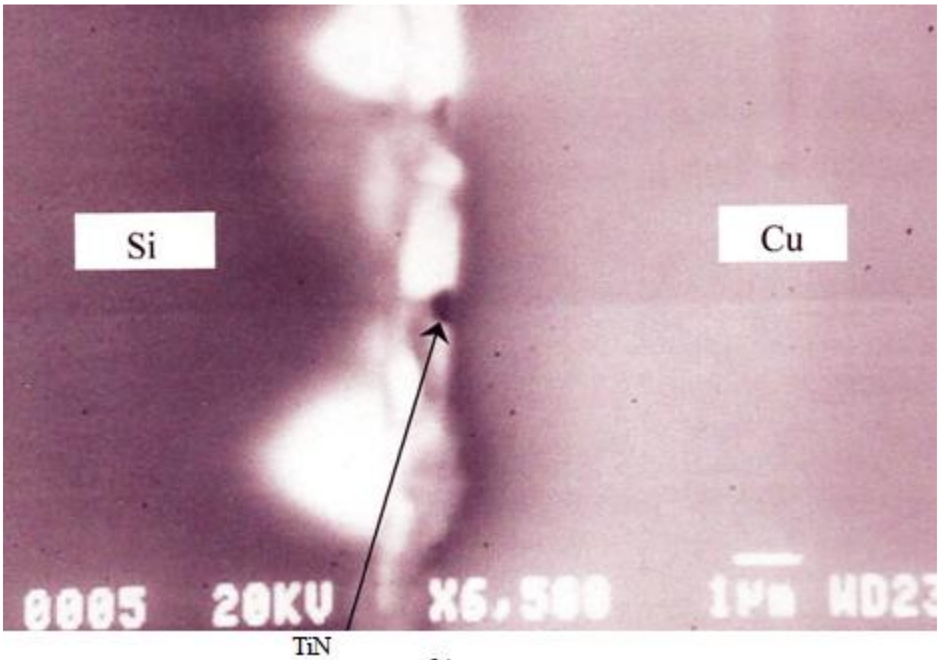


(iii)

Figure 3: Surface SEM photographs of Cu / TiN / Si, samples annealed at (i) RT, (ii) 650 ^{0}C, and (iii) 750^{0}C

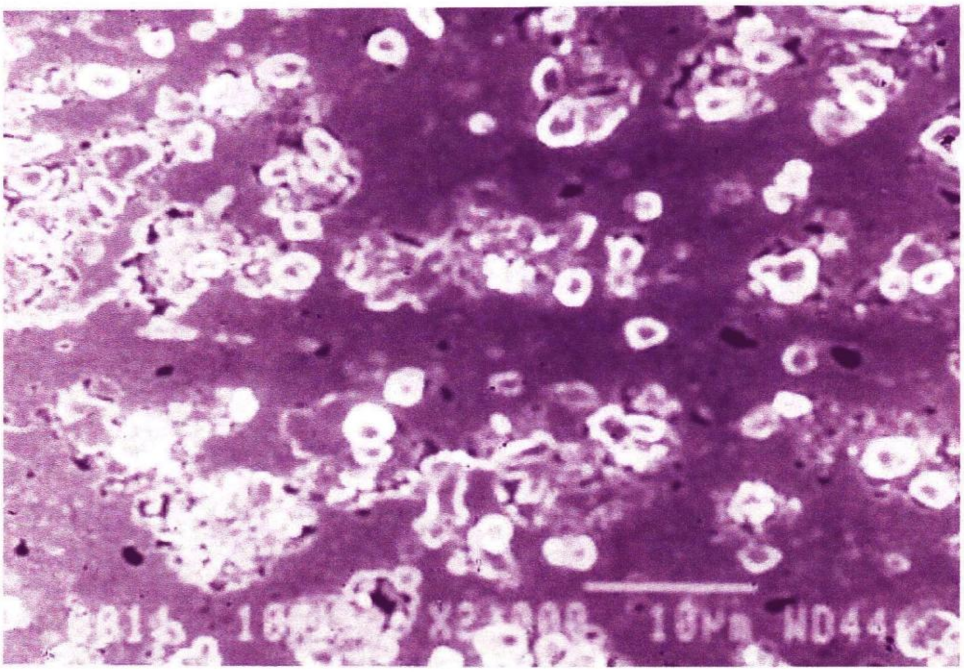


(a)

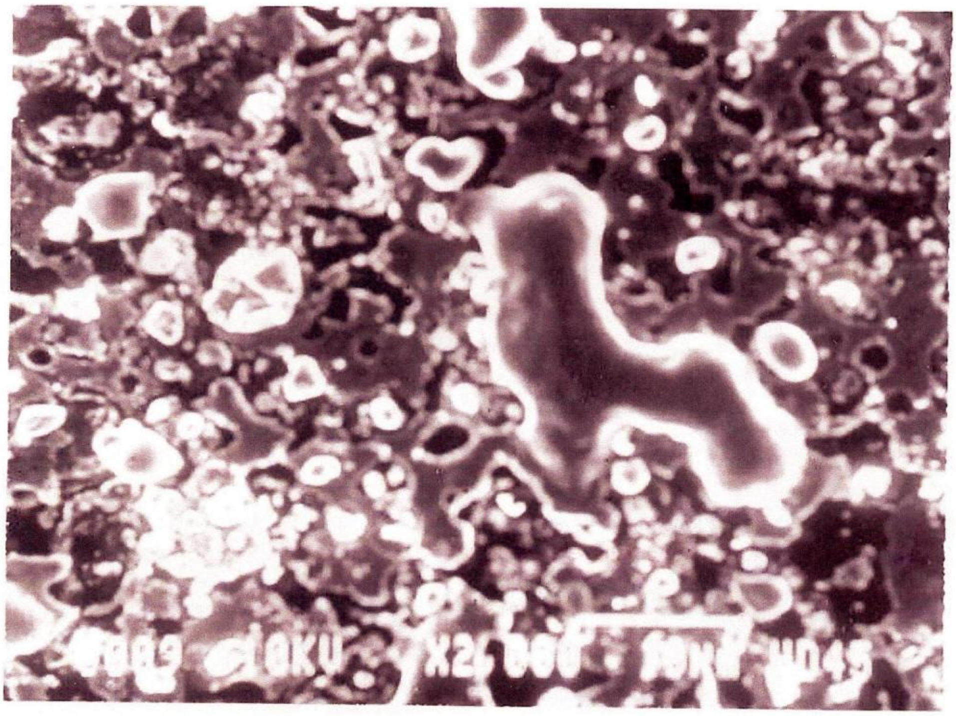


(b)

Figure 4: Cross Sectional SEM photographs of Cu/TiN/Si, samples annealed at (a) 650^{0}C, and (b) 900^{0}C



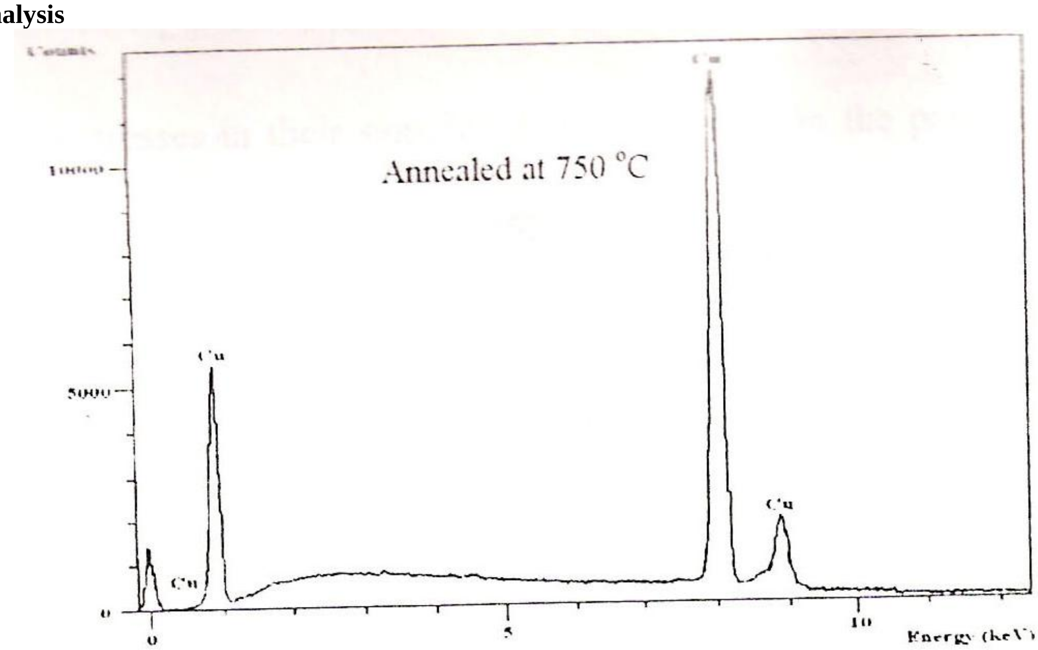
(a)



(b)

Figure 5: Surface SEM photographs of Cu/TiN/Si, samples annealed at (a) 800^0C, and (b) 900^0C

Chemical Analysis



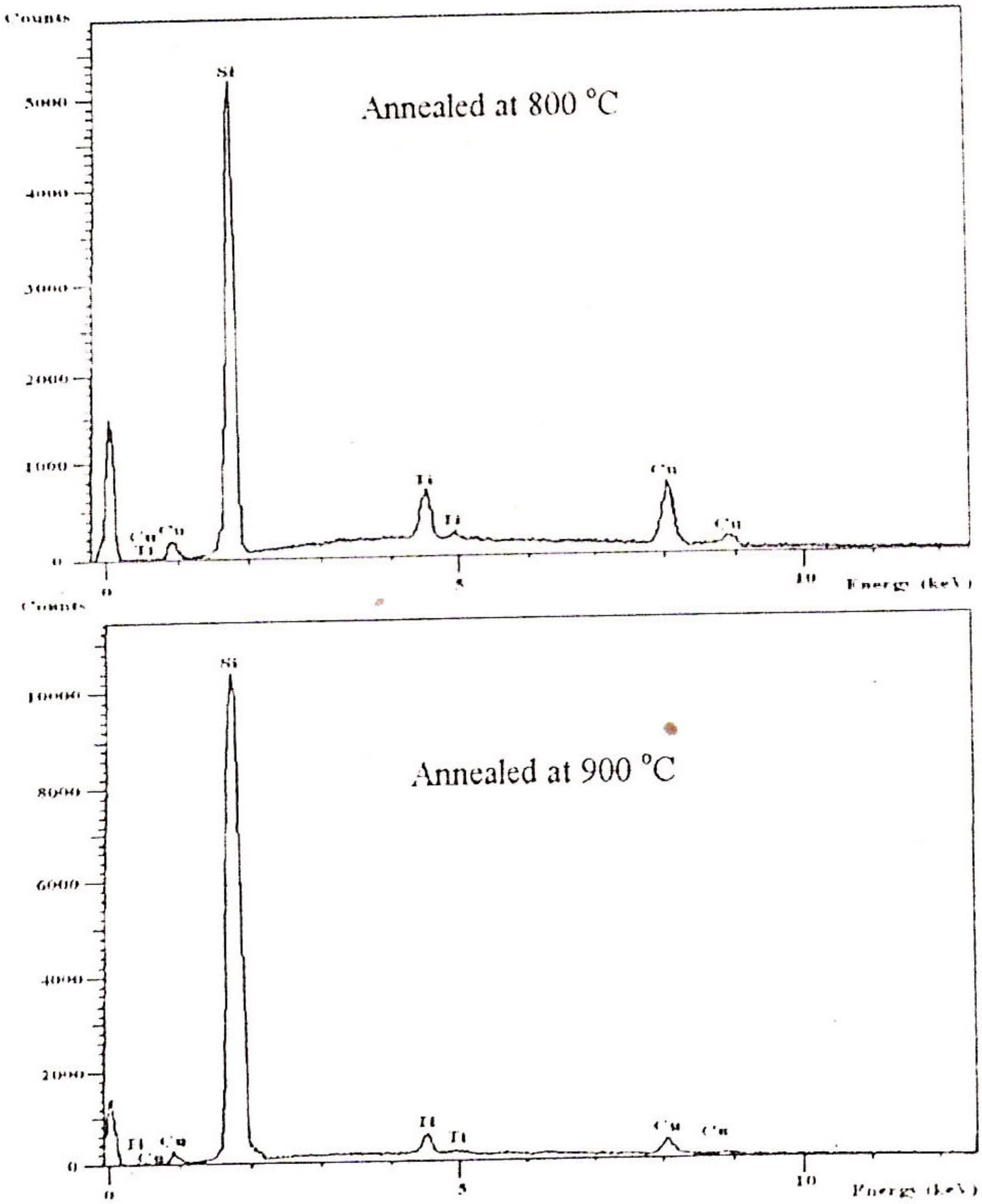


Figure 6: EDAX results of the Cu/TiN /Si Structure annealed at different temperature

Chemical analysis by energy dispersive X -ray analysis EDAX methods of the surface layer of the annealed samples was carried out using jeol scanning microscope (J.S.M.840) to observe any change in surface chemistry due to annealing. The observe results are given in fig 6.

Sample annealed up to 750 ^{0}c show only copper peaks indicating no inter diffusion of copper and silicon through the TiN barrier. Chemical analysis of the holes observed in the SEM of the sample annealed at 800 ^{0}c give the Si and Ti peaks with Cu peaks.

Indicating the inter diffusion of Cu and Si through TiN layer. Chemical analysis of the islands observed in the SEM results of the samples annealed at 900 ^{0}c show Si, Cu and Ti peaks indicating high inter diffusion of Cu and /or Si through the barrier.

Resistivity XRD, SEM and EDAX results are consistent with each other for the scanning magnetron sputtered TiN samples investigated as diffusion barrier for silicon devices. The diffusion length [2]of Cu in TiN at temperature 600 and 700 ^{0} c has been reported about 400 A ^{o}. The thickness of the TiN films used in the present study was 800 A ^{0} which becomes comparable to the diffusion length of cu in TiN at 800 ^{0} C. Deenamma et al have reported diffusion through TiN films at 750 ^{0}c which may be due to smaller thickness and high stresses in their samples. Films deposited in the present study show lower stresses than those reported [29]earlier.

3. Results

(1) In fig 1

At 750^{0}c with substrate bias -40 volt, resistivity was found to decrease which is abut6X 10^{-4} Ω cm which occurs due to increase in grain size and reducing defects. But at 800^{0}c resistivity was found increasing indicating the starting of diffusion.

(2) In fig 2

XRD reveals that there was no extra peaks corresponding to any compound of Si, Ti and Cu up 750^0c. For the samples annealed at 800^0c and 900^0c, some extra peaks of Cu and Si compounds were observed indicating inter diffusion of Cu and / or Si through the TiN barrier. The resistivity measurements are supported by X ray diffraction results.

(3) In fig 3, 4, 5,

Up to 750^0 c annealing temperature no inter diffusion through the TiN films was observed, no holes were observed in the samples annealed up to 750^0c. Also SEM photographs of the cross section of Cu/TiN /Si structure annealed at 650^0c show three different layers and no inter diffusion.

(4) In fig 6

Up to 750^0c there was no indication of inter diffusion only copper peaks are observable. EDAX of the TiN films used in the present study was 800^0c give the Si and Ti peaks with copper peaks indicating the inter diffusion of Cu and Si through TiN layer.

The thickness of the film used in present study was 800 A^0 which becomes comparable to the diffusion length of Cu in TiN at 800^0c. The diffusion length of Cu in TiN at temperature 600 and 700 ^{0} c has been reported[2] about 400 A $^{o.}$ All the results and discussion reveals that TiN film act as good diffusion barrier up to temperature 750^0c.

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