Article

Enhanced Thermal Stability of Sputtered TiN Thin Films for Their Applications as Diffusion Barriers against Copper Interconnect

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Abstract: In this work, the deposition of titanium nitride (TiN) thin film using direct current (DC) sputtering technique and its application as diffusion barriers against copper interconnect was presented. The deposited film was analyzed by using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and X-ray photoelectron spectroscopy (XPS) techniques. XRD patterns showed the face-centered cubic (FCC) structure for the TiN/SiO_2/Si film, having (111) and (200) peaks and TiN (111), Cu(111), and Cu(200) peaks for Cu/TiN/SiO_2/Si film. FESEM images revealed that the grains were homogeneously dispersed on the surface of the TiN film, having a finite size. XPS study showed that Ti2p doublet with peaks centered at 455.1 eV and 461.0 eV for TiN film was observed. Furthermore, the stoichiometry of the deposited TiN film was found to be 0.98. The sheet resistance of the TiN film was analyzed by using a four-point probe method, and the resistivity was calculated to be 11 μΩ cm. For the utilization, TiN film were tested for diffusion barrier performance against Cu interconnect. The results exhibited that TiN film has excellent performance in diffusion barrier for copper metallization up to a temperature of 700 °C. However, at a higher annealing temperature of 800 °C, the formation of Cu_3Si and $TiSi_2$ compounds were evident. Thus, stoichiometric TiN film with high thermal stability and low resistivity produced in this study could be applied for the fabrication of microelectronic devices.

Keywords: thin films; diffusion barriers; TiN; Sputtering; XRD

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1. Introduction

While metallization is a strong technique for manufacturing integrated circuits built on silicon substrates, interconnect materials, such as copper, are favorable for ultra-large scale integration (ULSI) circuits, owing to higher resistance to electro-migration than aluminum and its alloys and low electrical resistivity [1]. However, the electrical performance of ULSIs is severely damaged or degraded by the copper and silicon contact because copper diffuses into the silicon or SiO_2, even at low temperatures [2]. Therefore, a barrier between the copper and the silicon is of high importance to separate the two layers. Besides, the required barriers should not only have the property of resisting copper penetration, but they should also be highly adhesive [3]. So far, refractory metal nitrides are being used as promising diffusion inhibitors, owing to their high thermal stability, conductivity, and melting point.

Different refractory metal nitrides, such as Ti-N [4–6], W-N [7], Zr-N [8], Ta-N [9–11], and TiZr-N [12–15] have been used for their applications as diffusion barriers in copper metallization. Nanocrystalline TiN, however, has gained substantial attention due to its

hard metallurgical coatings [16]. Additionally, it has the property of showing different colors on different types of surfaces. Furthermore, the deposition of TiN on any type of surface is relatively easy, as compared to other nitrides, providing a chemically stable coating. Stoichiometric crystalline TiN films with a NaCl-type face-centered cubic structure are found to be good conductors of electricity, as they show golden color and are found to be ideal candidates as diffusion barriers [17]. Furthermore, the stoichiometric TiN films resulted in low resistivity. Therefore, TiN films deposited with different deposition processes and at different deposition conditions possess diverse microstructural properties [1,2]. Therefore, in order to achieve better performance of TiN thin films, deposition process and deposition parameters need to be optimized. Much research has been performed so far to understand the effect of deposition conditions on the properties and structure of TiN films [2,3]. Additionally, several deposition methods have been employed so far for the deposition of nanocrystalline TiN films [6–10]. Direct-current (DC) sputtering, however, is considered to be most promising deposition technique for obtaining stoichiometric TiN films among the various physical vapor deposition (PVD) techniques. The sputter method has the advantage of low gaseous contamination, compositional homogeneity, and good adhesion between the substrate and deposited films. Additionally, films of different morphological and crystal structures can be produced [11]. A study [11] shows that thinner diffusion barriers employed in metallization, showing stability at high temperatures, are the future research direction. The effect of thickness and resistivity of diffusion barriers on copper interconnect resistivity is given by the relation [18].

$$\rho(Cu) = \frac{1.7\ \mu\Omega\ \text{cm}}{\left[\left(1-\frac{B}{M2}\right)\left(1-2\frac{B}{M1}\right)+\left(\frac{1.7}{\rho b}\right)\left(\frac{B}{M1}\right)\left(2+\frac{M1}{M2}-2\ \frac{B}{M2}\right)\right]} \tag{1}$$

where, height and width of metal interconnects are given by $M1$ and $M2$, and B and ρb are the thickness and resistivity of diffusion barriers, respectively. Apart from thickness effect, copper interconnect resistivity is also affected by the resistivity of diffusion barriers based on Equation (1). Therefore, low resistive diffusion barrier yields a low resistive copper interconnect. Therefore, in order to have an effective application of TiN for diffusion barrier in microelectronic devices, we need to focus on the thermal stability of the low resistive TiN films. Thus, TiN films with low resistivity, good stoichiometry (golden color film), and high thermal stability are highly desired.

The aim of this work was to produce a high temperature stable stoichiometric TiN film with low resistivity using DC sputtering technique. The diffusion barrier performance of the TiN film for copper interconnect has been investigated at high temperature of ~700 °C for its successful utilization in microelectronic devices. This study will provide a clear direction towards the fabrication of microelectronic devices with high thermal stability and high performance.

2. Results and Discussion

The XRD pattern of as-deposited TiN film is shown in Figure 1a, where single phase and face centered cubic (FCC) symmetry, with (111) and (200) crystal planes, having a (111) plane, as preferred its orientation, can be observed. The calculated d-spacing values are in good agreement with the standard JCPDS (65-5759) for TiN structure. Scherrer's formula [2] was used to calculate the grain size (D) of the film, and the grain size was found to be ~42 nm.

Figure 1b shows the XRD patterns acquired from the Cu/TiN/SiO_2/Si film. In Figure 1b, the diffraction peaks of as-deposited film of Cu/TiN/SiO_2/Si and annealed at 700 °C and 800 °C can be clearly seen. It could be observed, from Figure 1b, that, for as-deposited Cu/TiN/SiO_2/Si film, the peaks correspond to TiN (111), Cu (111), and Cu (200) are detected. On annealing at a temperature of 700 °C, the intensity of Cu (111) and Cu (200) peak increases. However, on further annealing the film at 800 °C, there is a sharp decrease in intensity of Cu (111) peak, and subsequently diffraction peaks of $TiSi_2$

and Cu_3Si peak appear, which indicate intermixing of Cu and Si through the TiN film. Therefore, it can be concluded that, above 700 °C, the barrier fails. Additionally, the Cu peak in the XRD pattern (Figure 1b) disappears, which is an indication of Cu diffusion through the barrier film. The Cu becomes diffused into the Si to form Cu_3Si.

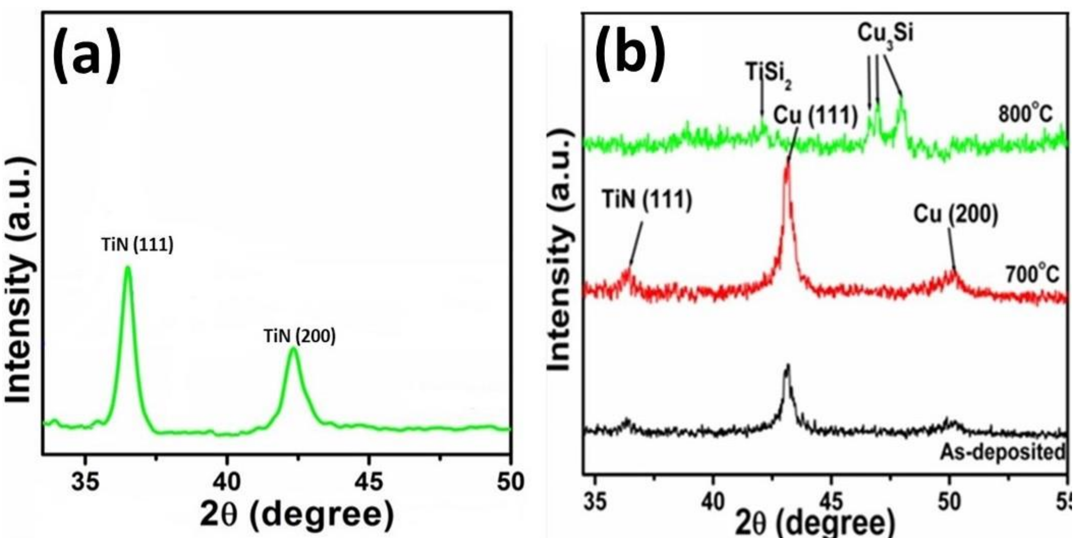

Figure 1. XRD patterns of (**a**) TiN film deposited on Si/SiO_2 substrates at 3 sccm nitrogen flow, (**b**) Cu/TiN films deposited on Si/SiO_2 substrates for as-deposited, annealed at 700 °C, and 800 °C.

XPS survey spectra for TiN film (not shown here) indicate that the film is not only composed of Ti and N, but also a small amount of Oxygen (O) and Carbon (C). However, the presence of O and C in the measurement could be attributed to the existence of ambient atmosphere in the analysis chamber during the XPS analysis [19]. XPS core level spectra in the Ti2p and N1s regions for the sputtered TiN film are shown in Figure 2. The presence of the binding energy doublet peaks for TiN at 455.1 eV and 461.0 eV [20] can be observed from Figure 2a. Deconvoluted Ti2p and N1s spectra for deposited TiN film are shown in Figure 3.

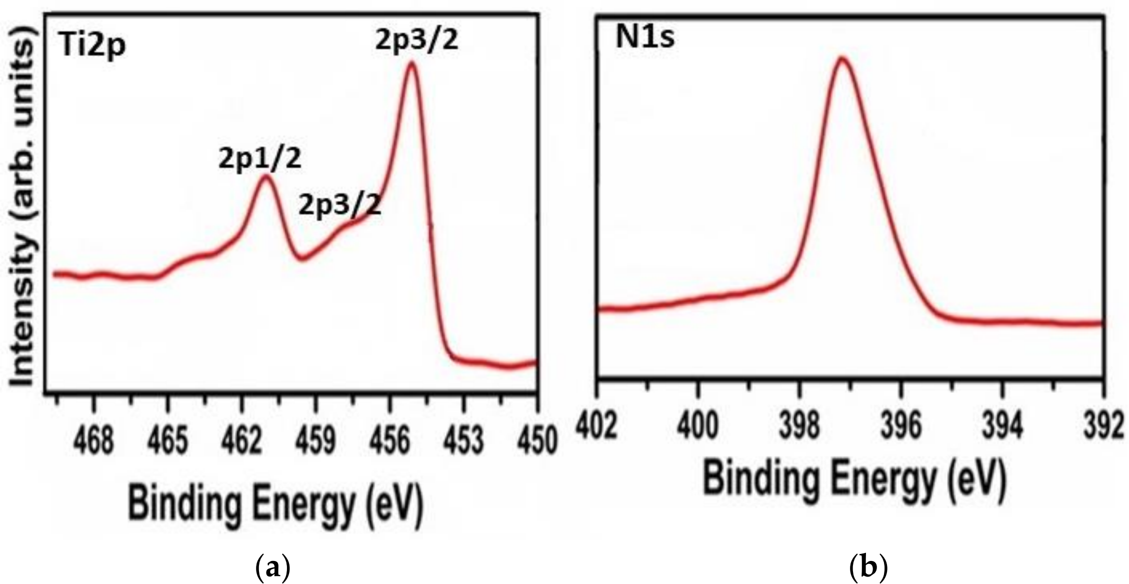

Figure 2. XPS spectra of (**a**) Ti2p, and (**b**) N1s for the deposited TiN film at 3sccm nitrogen gas flow.

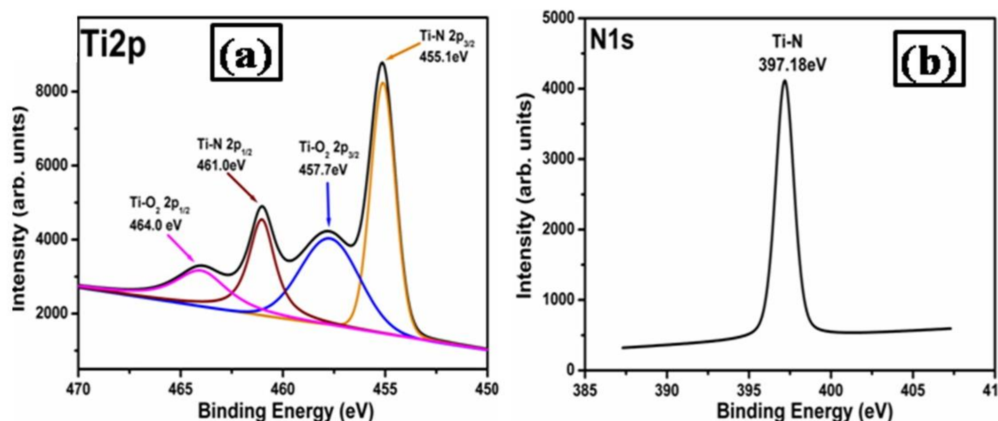

Figure 3. Deconvoluted XPS spectra of (**a**) Ti2p and (**b**) N1s for TiN film deposited at 3 sccm nitrogen tflow.

It can be seen, in Figure 3a, that the $Ti2p_{3/2}$ peaks can be fitted with two mixed Gaussian–Lorentzian curves, with binding energy of the first peak centered at 455.1 eV for TiN [20] and the second peak corresponds to TiO_2 and is observed at 457.8 eV [20]. However, it was noted that $Ti2p_{1/2}$ has only one peak at 461.0 eV for TiN [20]. The N1s fitting shows only one peak, as shown in Figure 3b, with a peak centered at 397.1 eV [20]. The N1s photoelectron peak position of TiN film is found to vary from 396.3 eV to 397.7 eV, as mentioned in the earlier reports [21]. However, reportedly, the N1s spectrum of pure nitride has full width at half maxima (FWHM) of about 1.6–1.9 eV and is of simple Gaussian shape [22]. The presence of oxygen in the film may be due to the use of commercial nitrogen gas, which can have some amount of oxygen impurities [23]. The stoichiometry of the TiN film was found to be ~0.98, as obtained from XPS analysis. It has been reported earlier that [17] the nitrogen vacancy is the most significant defect in sub-stoichiometric compositions, and for over-stoichiometric case, excess nitrogen acted as an interstitial defect. In the present work, only nearly stoichiometric nitride film was grown and investigated to avoid any interference from the composition variations of nitride film.

Figure 4 shows the FESEM image, EDX spectrum, and cross-sectional FESEM image for the as-deposited TiN film. It can be seen from the FESEM image (Figure 4a) that the grains of finite size are uniformly distributed on the surface of the film. The grain size is found to be ~40 nm, as shown in Figure 4a. EDX analysis gives the percentage composition so as to obtain the stoichiometric of TiN film. The stoichiometry of the TiN film was found to be 0.98. The stoichiometry obtained by EDX (Figure 4b) is found to be comparable with the XPS result.

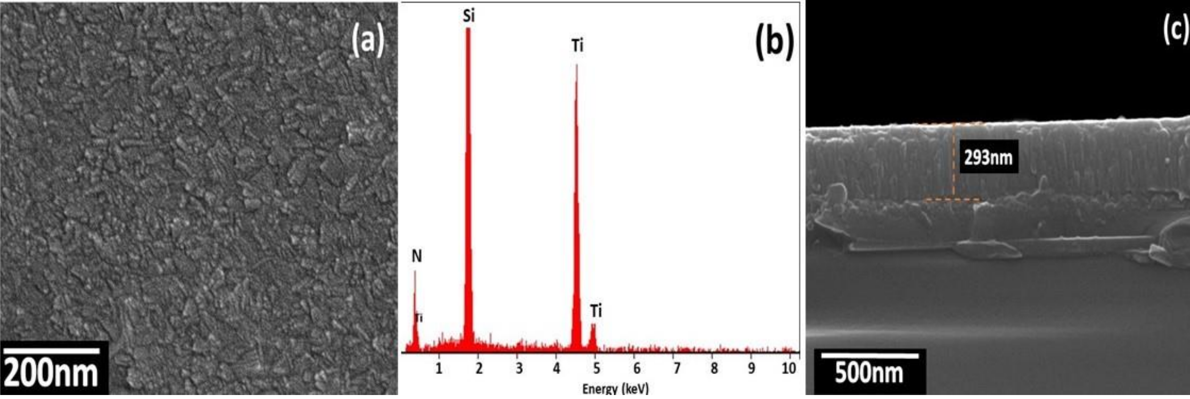

Figure 4. (**a**) FESEM and the corresponding (**b**) EDX and (**c**) cross-sectional FESEM images of the TiN film at 3 sccm nitrogen gas flow rate.

The cross-sectional image of the TiN film can be seen in Figure 4c. As can be seen from Figure 4c, that film is dense, with columnar structures, which is often the uniqueness of the DC sputtered films. The thickness of the film was found to be ~290 nm.

Figure 5 shows the FESEM images of the Cu surface for as-deposited and annealed Cu/TiN/SiO_2/Si films. As can be seen from FESEM image in Figure 5a, the surface of as-deposited Cu film remained smooth, and there were no visible defects, which can also be confirmed from EDX spectrum (Figure 5b). However, at 800 °C (see Figure 5c), Cu almost disappeared from the surface, and large conglomerations are formed, having many defects and voids. From the EDX spectrum (see Figure 5d), it can be seen that these conglomerations mostly comprise Cu and Si, which confirms that the conglomerations are mainly Cu_3Si. The results obtained by EDX analysis are in good agreement with the results attained by XRD.

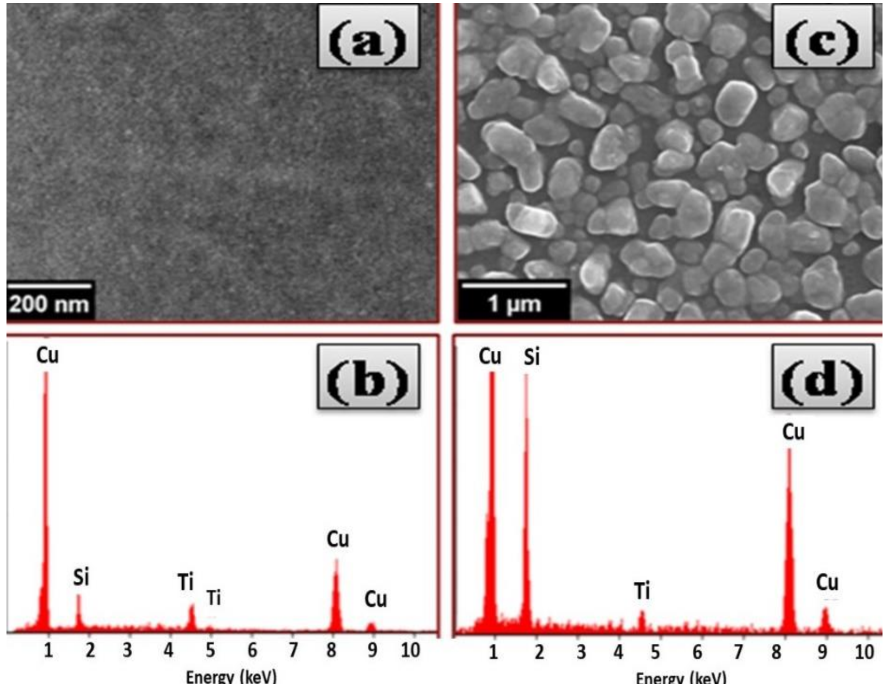

Figure 5. (**a**) FESEM and corresponding (**b**) EDX spectrum of as deposited Cu/TiN/SiO_2/Si system. (**c**) FESEM and the corresponding (**d**) EDX spectrum of Cu/TiN/SiO_2/Si system annealed at 800 °C.

The electrical resistivity of the obtained TiN film was found to be 11 µΩ cm. Variation in the resistivity of the film can be observed due to many parameters, such as thickness, structure, texture, stoichiometry (N/Ti), and impurity concentrations in various layers [24]. The resistivity of CVD-deposited TiN film has been reported to be of the order of 100 µΩ cm or higher [25], while a resistivity of 36 µΩ cm has been reported for the reactive sputtered TiN films with a substrate bias of −100 V [3]. A 220 µΩ cm resistivity for reactively sputtered films at 400 °C and a substrate bias of −40 V has also been reported earlier [17,26,27]. A resistivity of 11 µΩ cm with a nitrogen flow of 3 sccm is obtained in this study, which was found to be lower than the resistivities obtained in other studies [17,26,27]. As reported earlier, a resistivity lower than 300 µΩ cm for TiN film is required in order to have its diffusion barrier applications for ULSI generation, which clearly is an indication that TiN film deposited here can be an ideal candidate for its successful usage as a diffusion barrier in future applications [4].

Cu sheet resistance as a function of the annealing temperature was used to observe the ability of diffusion barrier against copper diffusion. Figure 6 presents the variation percentage of sheet resistance as a function of annealing temperature for the Cu/TiN/SiO_2/Si film and is compared with the Cu/SiO_2/Si, as calculated using Equation (2). The resistivity of the as-deposited Cu film was found to be ~2.3 µΩ cm, which is slightly higher, as compared

to the bulk value (bulk value: 1.7 μΩ cm). For both the films, the average value of sheet resistance initially decreases after annealing with respect to that of as-deposited films. This could be due to the grain growth and defect annihilation of the Cu films during annealing. The sheet resistance of $Cu/SiO_2/Si$ film is found to increase drastically at a temperature above 200 °C, concluding that the film without a TiN barrier cannot withstand at high annealing temperature. However, the sheet resistance for $Cu/TiN/SiO_2/Si$ barrier film starts to increase abruptly at an annealing temperature above 700 °C. Additionally, the color of Cu changes from reddish–yellow (the color of Cu) to gray. This increase in the resistivity is associated with the fact that thermally activated Cu atoms begin to diffuse into the Si substrate through the TiN barrier. Therefore, with increasing annealing temperature, Cu atoms create larger amounts of defects, i.e., the formation of Cu_3Si and the sheet resistance of Cu films tends to increase drastically, resulting in the increase in electrical resistance. The outcome reveals that TiN barrier film is stable up to an annealing temperature of 700 °C for 60 min. However, drastic increases in the sheet resistance were observed after annealing above 700 °C for the $Cu/TiN/SiO_2/Si$ film. Thus, TiN can be used as a diffusion barrier for Cu metallization and can meet the future research direction of diffusion barriers. These results of sheet resistance are also in good agreement with the results obtained by XRD analysis. The disappearance of Cu in the XRD pattern (Figure 1b) is a clear indication of a large amount of Cu diffusing through the barrier film into Si substrate where it reacts with Si to form Cu_3Si on annealing at high temperature, which is also further confirmed by FESEM images. Therefore, the development of high resistivity Cu_3Si corresponds to the drastic increase in sheet resistance of Cu film. The failure mechanism of the $Cu/TiN/SiO_2/Si$ system has been studied previously by I. Chen and J.L. Wang [28]. The suggested mechanism is that Cu breaks Si-Si bonds as it reaches the $TiN/SiO_2/Si$ interface and Si point defects generated there, which resulted in the formation of Cu_3Si and $TiSi_2$. Therefore, it is highly anticipated that, as copper promotes the formation of silicides, Cu may act as a catalyst for the silicidation of TiN in this study. In addition, the concentration of these point defects is greatly increased during thermal annealing and supports the reaction of Si with TiN, and then the formation of Cu_3Si and $TiSi_2$. Therefore, the failure of a multilayered system can be determined when the high resistivity of the film is obtained.

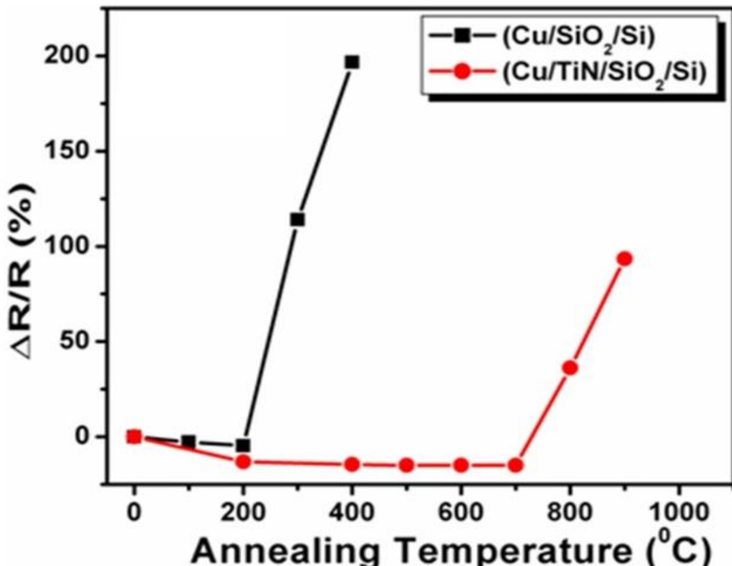

Figure 6. Plot of sheet resistance (%) vs. annealing temperature for Cu and Cu/TiN films deposited on Si/SiO_2 substrates.

A compilation of diffusion studies reported earlier has been shown in Figure 7. The results of this work have been compared with these previous reports. L. Slot et al. [29] performed in situ measurement of sheet resistance, backscattering, and XRD analysis to

monitor the reaction between Cu and Si and to obtain the results of overall compositions. It was observed that Cu_3Si phase with various concentration of Si ranging from 17–20 at.% was formed at temperature of about 200 °C on crystalline Si. Shin et al. [30] reported the deposition of TiN barrier film using flow modulation chemical vapor deposition (FMCVD) technique with titanium tetrachloride and ammonia. Diffusion barrier results showed that, at 400 °C, Cu became diffused through the TiN layer, resulting in copper silicides. In order to improve the diffusion barrier property, Shin et al. introduced a monolayer of Al atoms between the two TiN films. Their results showed that, for TiN films with a Al interlayer, there is enhancement in the diffusion barrier, and the diffusion of Cu through the barrier occurred at a temperature of 500 °C, which is higher than that of their TiN film without a Al interlayer. In general, at a temperature as low as 200 °C, the formation of Cu-Si compounds occurs, which resulted in the increase in sheet resistance of Cu film in the Cu/barrier/Si samples. In another work, Chaipyang et al. and Kim et al. [31,32] showed that the sheet resistance of Cu/TiN/Si film remains stable after annealing up to a temperature of 600 °C. However, the sheet resistance was found to increase drastically after annealing above 600 °C due to the formation of Cu_3Si. Therefore, it can be seen clearly that the thermal stability of TiN film obtained in this work is higher (~700 °C) than the other reported works, and the TiN film produced in this work is stoichiometric and has lower resistivity.

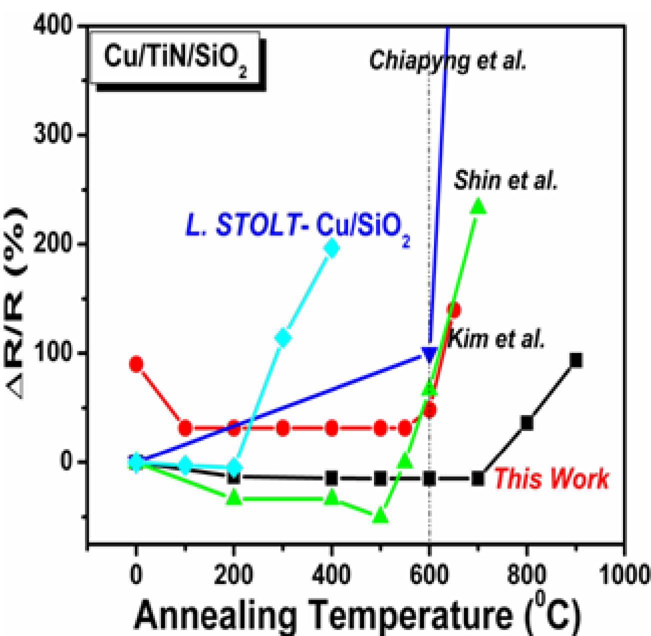

Figure 7. Plot of sheet resistance (%) vs. annealing temperature for TiN films deposited on Si/SiO_2 substrates and its comparison with earlier reports [29–31].

3. Experimental Details

In order to have a successful deposition of TiN film, a DC magnetron sputtering technique with a commercial titanium (Ti) target (purity 99.99%, 100 mm and 5 mm diameter and thickness, respectively) was used. Prior to the deposition, Si/SiO_2 (100) substrate was oxidized for 1 h in a furnace at 1000 °C, and it was further cleaned with acetone and methanol in ultrasonic baths. The substrate was clamped on the substrate holder at a distance of 12 cm from the target. The chamber was maintained at 1×10^{-6} torr vacuum condition. Once the desired vacuum was achieved, the chamber was then filled with argon and nitrogen gas, as per the required working gas flow. The target was pre-sputtered for 5 min in argon gas before introducing nitrogen gas into the chamber. The argon and nitrogen gas flow rates were fixed at 10 sccm and 3 sccm, respectively, during

the deposition process. The substrate temperature of 200 °C and DC power of ~350 W were maintained throughout the deposition process.

The thermal stability of the TiN film for diffusion barrier was studied against Cu/Si metallization. DC sputtering technique described above with a commercial copper (Cu) (purity 99.99%, 100 mm and 5 mm diameter and thickness, respectively) was used for the deposition of Cu film. The Cu film was deposited on a TiN/SiO_2/Si substrate, and the substrate was fixed to a substrate holder at a distance of ~12 cm from the target. The chamber was maintained at 1×10^{-6} torr vacuum condition. The DC power was fixed at ~350 W, and argon gas flow rate was maintained at 10 sccm throughout the deposition process. The target was pre-sputtered for 5 min in argon gas before the deposition. The deposition of the film was performed for 8 min, and, to avoid any type of diffusion within the layers, the substrate was kept at room temperature. After deposition of Cu film of ~350 nm, the heat treatment of Cu/TiN/SiO_2/Si sample at 200–1000 °C for 60 min was performed in vacuum with pressure maintained at 6.7×10^5 torr during each annealing condition.

Cu sheet resistance as a function of the annealing temperature was used to observe the ability of the diffusion barrier against Cu diffusion. The variation percentage of sheet resistance ($\Delta R_s/R_s\%$) is defined in Equation (2):

$$\frac{\Delta R_s}{R_s}\% = \frac{R_{s,after-anneal} - R_{s,as-deposited}}{R_{s,as-deposited}} \times 100\% \quad (2)$$

The crystallographic structure and texture of the TiN/SiO_2/Si and Cu/TiN/SiO_2/Si films were studied within the scan range of 35 to 50° using X-ray powder diffractometer (XRD) (X'pert MPD 3040) with 40 kV and 30 mA operating parameters, using CuKα (1.541 Å) radiation. The chemical and phase composition of TiN film was studied using X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 XPS) with a VG-Scientific Sigma Probe spectrometer, having a monochromated Al-Kα source with hemispherical analyzer. The sample was etched using a 3 keV argon ion beam prior to the analysis until the 1 s peak of oxygen reached a minimum stable value. The morphological study and the thickness of the deposited TiN/SiO_2/Si and Cu/TiN/SiO_2/Si films were performed using field-emission scanning electron microscopy (FESEM) (TESCAN; MIRA II LMH microscope) attached with Energy Dispersive X-ray (EDX) analysis. The resistivity study for the deposited films were performed using four-point probe (Keithley-2002) method operated at room temperature.

4. Conclusions

In summary, TiN film has been successfully deposited on SiO_2/Si substrate using DC sputtering technique at 3 sccm nitrogen gas flow rate, and its barrier performances and failure mechanisms were studied. The structural, morphological, and electrical properties of the as-deposited TiN/SiO_2/Si and Cu/TiN/SiO_2/Si films were analyzed. The XRD patterns revealed the presence of face centered cubic (FCC) phase for TiN/SiO_2/Si, having (111) preferred orientation and a grain size of ~42 nm, was obtained. The existence of different phases on the film surface was observed from the XPS analysis. Doublet peaks of Ti2p, corresponding to TiN and TiO_2, were observed in the spectra of TiN film with stoichiometry of 0.98 for TiN. The FESEM images show a uniform distribution of finite-sized grain on the surface of film with a columnar structure. The electrical resistivity of ~11 μΩ cm was achieved. In particular, high crystallinity, high stoichiometry, and lower resistivity TiN film have been obtained. The diffusion barrier property shows that TiN film can be used successfully as diffusion barrier for metallization in Cu up to a temperature of 700 °C, and, upon further increase in temperature to 800 °C, the diffusion of Cu through the barrier occurred. The failure of diffusion barrier at higher annealing temperature is due to the formation of various copper silicide phases. The present study shows that the structural stability of TiN film at high temperatures possesses key parameters that improve the barrier properties.

Author Contributions: Conceptualization, A.A. (Abdullah Aljaafari) and F.A.; methodology, F.A. and A.A. (Abdullah Aljaafari); validation, S.K. and N.M.S.; formal analysis, S.K. and A.A. (Abdullah Alsulami); investigation, F.A., S.K. and N.M.S.; resources, A.A. (Abdullah Aljaafari); data curation, A.A. (Abdullah Alsulami); N.M.S.; writing—original draft preparation, A.A. (Abdullah Aljaafari) and F.A.; writing—review and editing, S.K., N.M.S. and A.A. (Abdullah Alsulami); visualization, S.K.; supervision, A.A. (Abdullah Aljaafari).; project administration, A.A. (Abdullah Aljaafari); funding acquisition, A.A. (Abdullah Aljaafari). All authors have read and agreed to the published version of the manuscript.

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