Characterization of Sputtered Titanium Carbide Film as Diffusion Barrier for Copper Metallization

Shui Jinn Wang, Hao Yi Tsai, and S. C. Sun

In this study, the physical and electrical properties as well as thermal stability of sputter-deposited titanium carbide (TiCx) films as diffusion barriers for Cu metallization were investigated for the first time. With thermal annealing in N2 ambient for 30 min, the unpatterned Cu (2000 Å)/TiCx (500 Å)/n-Si structure was found to be metallurgically stable up to a temperature between 600 and 650°C without formation of a Cu2Si phase, while the reverse leakage current of the patterned Cu (2000 Å)/TiCx (500 Å)/p+n-Si diode structures showed that the TiCx barrier layer was capable of withstanding annealing temperatures up to 500°C. The failure of the TiCx layer after high temperature annealing is attributed to the diffusion of Cu along localized defects or grain boundaries of the TiCx barrier layer into Si substrate, which caused the high junction leakage currents for the patterned structure and formation of Cu2Si for the unpatterned structure.

Experimental

n-Type (100) oriented Si substrates with a resistivity of 1-10 Ω cm were employed in the experiments. The wafers were cleaned with a standard RCA clean process prior to loading them into the deposition chamber. TiCx films of about 500 Å thickness were deposited by dc magnetron sputtering a Ti/C (50:50 atom %) target with 99.5% purity in Ar atmosphere. The deposition was carried out at room temperature without intentionally heating or biasing the substrates as the system was evacuated to 9 × 10⁻⁷ Torr. Prior to deposition, the TiCx target was cleaned by a 10 min presputtering while the shutter was closed. The deposition pressure was maintained at 7.6 × 10⁻³ Torr and the applied dc power was kept at 200 W. The deposition rate of the TiCx film was measured to be around 0.33 Å/s. X-ray photoelectron spectroscopy (XPS) using Mg Kα radiation was performed to characterize the chemical composition of the as-deposited TiCx film. Additionally, both XRD and transmission electron microscopy (TEM) techniques were used to study the phase and microstructure of the TiCx film. SEM was used to inspect the thickness and surface morphology of the barrier films. A four-point probe was used to measure the resistivity of the as-deposited TiCx film.

In order to study the thermal stability of TiCx barrier films between Cu and Si, unpatterned Cu (2000 Å)/TiCx (500 Å)/n-Si and patterned Cu (2000 Å)/TiCx (500 Å) p+n-Si diode structures were prepared. The 2000 Å Cu film was deposited followed by the TiCx barrier layer without breaking the vacuum system. The p+n diode used in this study was formed by BF2 implantation at an energy of 60 keV and a dose of 3.5 × 10¹⁵ cm⁻² followed by a thermal annealing in N2 ambient at 900°C for 30 min. The diode area and junction depth were measured to be 5.8 × 10⁻² cm² and 0.3 μm, respectively.

As the Cu/TiCx/Si and Cu/TiCx/p+n-Si diode structures were successfully prepared, they were subsequently annealed in N2 ambient at temperatures ranging from 400-850°C for 30 min. After that, the annealed samples were allowed to cool in N2 ambient before removing from the furnace. Thermal stability of the TiCx film between Cu and Si was investigated by several analytical tools including XRD, SEM, and AES analyses. Furthermore, to clarify the barrier properties of the TiCx film in a more sensitive way, the leakage currents of the Cu/TiCx/p+n-Si diodes were measured by HP 4145B.

Results and Discussion

The chemical states of the TiCx films were examined first by XPS. The XPS spectra were systematically recorded for both the TiCx films exposed to air and the Ar⁺-cleaned surface (4 keV Ar⁺). Figure 1a shows the XPS survey spectrum of the TiCx film after an Ar⁺ cleaning for 5 min. In the figure, Ti 2p, C 1s, and O 1s peaks were identified clearly. The concentration of Ti, C, and O in
the TiC film measured by XPS analysis was around 44.4, 41.1, and 14.5 atom %, respectively. Figures 1b-d present the narrow scan XPS spectra as a function of the Ar⁺ etching time for Ti 2p, C 1s, and O 1s, respectively. As shown in Fig. 1b, the Ti 2p spectrum after 5 and 10 min of surface etching is composed of Ti 2p 3/2 and Ti 2p 1/2 doublets with a binding energy at 455 and 460.8 eV, respectively. It is rather difficult to identify whether these peaks reflect the formation of Ti-C or Ti-O bonds because the binding energies of Ti-C and Ti-O are nearly identical in these compounds.15,16 As shown in Fig. 1c, the C 1s spectrum after 5 and 10 min Ar⁺ etching exhibits a large carbidic peak at 282 eV that corresponds to the chemical bonding between Ti and C. Additionally, a broader peak appears at 284.5 eV, which indicates that the graphitic carbon exists in the deposited

![Figure 1](image1.png)  
**Figure 1.** Characterization of the as-deposited TiCₐ (500 Å)/Si structure. (a) XPS survey spectra after 5 min Ar⁺ surface cleaning, (b) Ti 2p XPS spectra vs. Ar⁺ etching time, (c) C 1s XPS spectra vs. Ar⁺ etching time, and (d) O 1s XPS spectra vs. Ar⁺ etching time.

![Figure 2](image2.png)  
**Figure 2.** XRD pattern of the TiCₐ (500 Å)/Si structure annealed at 600-850°C for 30 min in N₂ ambient. The as-deposited sample is shown for comparison.

![Figure 3](image3.png)  
**Figure 3.** TEM image of bright field plan view and SAD pattern of the as-deposited TiCₐ/Si structure.
film. The graphitic C 1s component is thought to be from the TiC target itself. The chemical states of deposited TiC$_x$ films are in good agreement with the report by Rist et al.\textsuperscript{17} For the O 1s spectra as shown in Fig. 1d, the air-exposed sample exhibited a strong and broad peak centered at around 530.6 eV which is assigned to be metal oxide. After 5 min Ar\textsuperscript{+} surface etching, a relatively weak peak compared to the air-exposed one was observed. For the case with 10 min Ar\textsuperscript{+} etching, the peak remains at the same position but with a smaller full width at half maximum (fwhm).

In order to determine the crystalline structure of the prepared TiC$_x$ films and identify possible interfacial reactions between TiC$_x$ film and the underlying Si substrate, glancing angle XRD analysis was performed; the results are shown in Fig. 2. Note that the angle of incidence was kept at 0.5°. It is found that reflection lines corresponding to \textit{TiC(111)}, \textit{TiC(200)}, and \textit{TiC(220)} were observed on the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Sheet resistance of the Cu (2000 Å)/TiC$_x$ (500 Å)/Si structure after thermal annealing at temperatures ranging from 500 to 700°C for 30 min in N\textsubscript{2} ambient.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{AES depth profiles of the Cu (2000 Å)/TiC$_x$ (500 Å)/Si structure. (a) As-deposited and annealed at (b) 600, (c) 650, and (d) 700°C for 30 min in N\textsubscript{2} ambient.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6}
\caption{XRD patterns of the annealed Cu (2000 Å)/TiC$_x$ (500 Å)/Si samples after thermal annealing at temperatures ranging from 600 to 800°C for 30 min in N\textsubscript{2} ambient. The as-deposited sample is shown for comparison.}
\end{figure}
as-deposited sample. However, after annealing at 600°C, several peaks corresponding to TiO$_2$ were observed on the XRD pattern. Since the chemical affinity of Ti and O are very high, TiC$_x$ film is liable to react with oxygen. In our work, the origin of oxygen was thought mainly coming from the air exposure of the annealed TiC$_x$ film before material analysis. Similar results have also been reported by Eizenberg et al.\textsuperscript{18} In their work, though the as-deposited film was nearly oxygen-free, they showed that a significant amount of oxygen (about 20 atom %) has been incorporated inside the film after exposures to air. In view of the results obtained from XRD analysis, noteworthy is that the TiSi$_x$ phase was not observed after a 700°C annealing, which suggests that the TiC$_x$ film is thermally stable under a 700°C annealing for 30 min.

To further clarify the microstructures of the as-deposited TiC$_x$ film, TEM was used to examine the TiC$_x$/Si structure. Both the bright field plan view image and the selected area diffraction (SAD) pattern of the as-deposited TiC$_x$ film are shown in Fig. 3. It shows that the TiC$_x$ film is mainly composed of nanocrystals with size of a few nanometers. Interplanar spacings derived from the SAD pattern agree with those of TiC.

The sheet resistance of the Cu (2000 Å)/TiC$_x$ (500 Å)/n-Si structure annealed at various temperatures was measured by a four-point probe and the result is shown in Fig. 4. As shown in the figure, it is observed that the sheet resistance of Cu/TiC$_x$/Si structure remains almost unchanged at a value of around 140 mΩ/□ after annealing at temperatures ≤600°C as compared to the as-deposited one. However, for annealing temperatures ≥650°C, the sheet resistance sharply increases, indicating a considerable amount of Cu has already diffused through the TiC$_x$ barrier layer and reacted with the underlying Si substrate. The resulting Cu$_x$Si compounds thus strongly deteriorated the conductivity of the contact system. Further evidence was given by XRD results, as shown in Fig. 5, in which Cu$_x$Si phase does appear in 650°C annealed samples.

Figure 5 outlines the possible formation of new phases on the annealed Cu/TiC$_x$/Si structures. It reveals that the structure keeps intact without forming any new phases up to 600°C annealing. However, as the annealing temperature was increased to 650°C, an obvious peak corresponding to Cu$_x$Si phase (at $2\theta = 65.6°$)\textsuperscript{19} was observed. The appearance of Cu$_x$Si indicates that Cu has reacted with the underlying silicon, and the TiC$_x$ barrier has lost its barrier function. Further increasing the annealing temperature up to 700°C, results in one additional reflection line, corresponding to Cu$_x$Si peaks, found centered at $2\theta = 45.2°$. The intensity of Cu peak is seen decreasing with increasing annealing temperature and finally disappears after an 800°C annealing. Noted that no detectable CuTi$_x$ or TiSi$_x$ compounds appeared on the XRD patterns of all annealed samples.

Figure 6 shows the AES depth profiles of the as-deposited and 600, 650, and 700°C annealed Cu/TiC$_x$/Si structures. Samples annealed at temperatures below 600°C show almost the same depth profile as that of the as-deposited ones, and are not shown here. For the sample after 600°C annealing (Fig. 6b), it is seen that only a very limited amount of Cu atoms diffused into the TiC$_x$ layer but did not reach the Si surface. Moreover, as compared to the as-deposited case (Fig. 6a), the out-diffusion of Ti atoms into the Cu layer and Si atoms into the TiC$_x$ layer was also observed. It indicates that the CuTi$_x$ and TiSi$_x$ compounds might have occurred after 600°C annealing although the formation of the CuTi$_x$ and TiSi$_x$ compounds were not detected by XRD analysis. As the annealing layer was increased to 650°C, the AES result kept almost the same depth profile as that observed on the 600°C annealed sample (Fig. 6c). Further increasing the annealing temperature to 700°C, as shown in Fig. 6d, a large amount of Cu atoms have diffused into Si substrate and the whole top 2000 Å thick Cu layer was consumed, it clearly reveals that the contact system was totally collapsed.

The surface morphology of the unpatterned Cu/TiC$_x$/Si samples before and after high temperature annealing (600-700°C) was investigated by SEM; the result is shown in Fig. 7. It is found that the Cu surface of the 600°C annealed sample (Fig. 7b) became relatively rough as compared to the as-deposited one (Fig. 7a). However, after removing the Cu overlayer by diluted HNO$_3$ solution, no damage or etch pits were observed (Fig. 7e) on the surface of the barrier layer, indicating such rough surface might be due to the grain growth of...
the Cu overlayer. Similar phenomenon was also reported by Suh et al.\textsuperscript{20} With increasing annealing temperature up to 650 and 700°C, as shown in Fig. 7c and d, respectively, bright protrusions were observed on the samples, which might be assigned to be Cu\textsubscript{3}Si precipitates according to XRD analysis mentioned previously. This suggests that a strong reaction between Cu and Si might have commenced and the barrier film was no longer retaining its integrity. As the Cu overlayer was removed, bright reaction products were found on the barrier layer surface (Fig. 7f), indicating the failure of the 650°C annealed Cu/TiC\textsubscript{x} /Si structure. In conjunction with sheet resistance measurement, XRD, and AES analyses discussed above, the Cu/TiC\textsubscript{x} /Si contact system was thought to be totally failed after the 650°C annealing.

To further characterize the thermal stability of the TiC\textsubscript{x} barrier layer between Cu and Si, junction leakage currents of the as-deposited and annealed Cu (2000 Å)/TiC\textsubscript{x} (500 Å)/p"n-Si diodes were made. The junction leakage current measurement would provide a better sensitivity in evaluating the thermal stability of the barrier system as compared to analytical analyses based on XRD, SEM, and AES, etc.\textsuperscript{21} Figure 8 depicts the histogram of the measured leakage currents, in which 36 diodes were measured under a reverse bias voltage of 5 V. Our results show that the leakage current density retains less than 10\textsuperscript{−7} A/cm\textsuperscript{2} before and after a 500°C annealing. However, after a 530°C annealing, the diode leakage current densities were seen distributing in a relatively wide range within 10\textsuperscript{−3} to 10\textsuperscript{−4} A/cm\textsuperscript{2}; more specifically, about 80% of diodes were with a leakage current density falling in the range of 10\textsuperscript{−3} to 10\textsuperscript{−4} A/cm\textsuperscript{2} (Fig. 8c). With increasing the annealing temperature up to 550°C, all the leakage current densities were seen above 10\textsuperscript{−3} A/cm\textsuperscript{2}, suggesting a severe electrical degradation of the Cu/TiC\textsubscript{x}/p"n-Si diodes occurred after such thermal annealing.

In view of the experimental results obtained by four-point probe, XRD, and SEM analyses, under thermal annealing in N\textsubscript{2} ambient for 30 min, the 500 Å thick TiC\textsubscript{x} layer in the unpatterned Cu/TiC\textsubscript{x}/Si structure was found to be metallurgically stable at a temperature between 600 and 650°C, which is at least 100°C higher than that of pure Ti barrier metal between Cu and Si.\textsuperscript{22} The incorporation of carbon into Ti, as expected, is indeed beneficial in improving the thermal stability of the Ti barrier metal in Cu metallization. Nevertheless, based on leakage current measurement on patterned Cu/TiC\textsubscript{x}/p"n-Si structure, the failure temperature of the 500 Å thick TiC\textsubscript{x} layer was estimated to be around 500°C.

Here the mechanism concerning the failure of the TiC\textsubscript{x} film in both the unpatterned and patterned contact structures was discussed. As was evident by the sharp increase in leakage current of the Cu/TiC\textsubscript{x}/p"n-Si structure and based on the fact that no evidence of the presence of CuTi, and TiSi\textsubscript{x} reaction compounds could be found for the sample annealed under temperatures less than 530°C, the failure of the TiC\textsubscript{x} barrier layer in the patterned Cu/TiC\textsubscript{x}/p"n-Si structure was mainly attributed to Cu diffusion through grain boundaries and localized defects of the TiC\textsubscript{x} barrier layer into the Si substrate. Though there is only a tiny amount of Cu atom migrated into the Si substrate, the Cu atoms indeed exerted a vital influence on the diode leakage current by serving as effective recombination centers inside the p"n junction. The situation became much worst while the annealing temperature was increased up to 550°C. At that temperature, an increased amount of Cu atoms, which was still not detectable by analytical material analysis using XRD and AES have diffused into the p"n junction, as a result, all tested diodes were failed in the leakage current measurement. Note that the sheet resistance of the annealed Cu/TiC\textsubscript{x}/Si contact systems remained almost unchanged when the annealing temperatures were not higher than 600°C. The sharp increase in sheet resistance of the contact system subjected to thermal annealing with temperatures higher than 650°C was due to the formation of Cu\textsubscript{3}Si. The same situation was also observed from the SEM image of the 650°C annealed sample in which the surface of the barrier layer has been damaged. Especially

Figure 8. Histogram of the reverse leakage current density of the Cu (2000 Å)/TiC\textsubscript{x} (500 Å)/p"n diodes structure. (a) As-deposited and after annealing at (b) 500, (c) 530, and (d) 550°C for 30 min in N\textsubscript{2} ambient. Diode area is 5.8 × 10\textsuperscript{−5} cm\textsuperscript{2}. All reverse leakage currents were measured at −5 V and 36 randomly chosen diodes were measured.
noteworthy regarding the out-diffusion of Si into the TiC$_x$ barrier layer of the 600°C annealed sample analyzed by AES, is that it is suspected that the interfacial reaction between the TiC$_x$ barrier layer and the Si substrate at higher annealing temperatures (e.g., >650°C) might further speed up the collapse of the unpatterned Cu/TiC$_x$/Si contact structure.

**Conclusion**

We investigated sputter-deposited TiC$_x$ film as a potential diffusion barrier for Cu metallization. The incorporation of C atoms into Ti barrier layer was shown to be beneficial in improving the thermal stability of the Cu/barrier/Si contact system. The unpatterned Cu/TiC$_x$/Si system was found metallurgically stable up to a 600°C annealing in N$_2$ for 30 min without formation of Cu$_3$Si phase, while the more sensitive reverse-bias leakage current measurement of the Cu/TiC$_x$/p$^-$n-Si diode structures showed that the TiC$_x$ barrier layer was capable of withstanding thermal annealing up to 500°C for 30 min without degradation of the diode's electrical characteristics. Material analysis by XRD, SEM, AES, and sheet resistance measurement reveal that the failure of TiC$_x$ film is mainly due to the presence of Cu atoms inside the p$^-$n junction. Though the Cu atoms are tiny in amount, they exerted a vital influence on the p$^-$n diode leakage current by serving as an effective recombination center therein.

**Acknowledgments**

This work was supported in part by the National Science Council (NSC) of Taiwan, R.O.C., under contract no. NSC 88-2215-E-006-014.

The National Cheng Kung University assisted in meeting the publications costs of this article.

**References**