Effect of thin Mo$_2$C layer on thermal stability of Si/SiO$_2$/Ti/Cu system

C C TRIPATHI*, MUKESH KUMAR and DINESH KUMAR

Electronic Science Department, Kurukshetra University, Kurukshetra 136 119, India

Abstract. The effect of introducing a thin Mo$_2$C (30 nm) layer between Ti and Cu on the thermal stability of Si/SiO$_2$/Ti/Cu system was studied using four-point probe (FPP), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX) and X-ray diffraction (XRD) techniques. The measured value of the sheet resistance in the bi-layered diffusion barrier structure does not show any change up to an annealing temperature of 750°C. The sheet resistance when measured after annealing at 800°C marginally increases but less than twice its value at room temperature. The XRD analysis indicated no copper diffusion and the formation of Cu$_3$Si phase up to 800°C. The bi-layered barrier structure annealed at elevated temperature shows copper-depleted and agglomerated regions. The sheet resistance measurement, study of surface morphology and the XRD analysis confirm that the insertion of thin Mo$_2$C layer increases the thermal stability of the system from 400°C to 750°C. The increased thermal stability of the system is ascribed to longer diffusion path length in the bi-layered system probably because of grain boundaries mismatch at Ti–Mo$_2$C interface.

Keywords. Bi-layer; diffusion barrier; titanium; molybdenum carbide; thermal stability.

1. Introduction

New materials and process technology (Kumar *et al* 2002; Yen *et al* 2007) are being developed meticulously to produce high-density and high-performance integrated circuits (ICs). Copper, due to its low electrical resistivity and resistance to electromigration (Rosenberg *et al* 2000) has replaced aluminum to be the metal of choice for metallization in the future generation of integrated circuits. However, the successful use of copper for interconnections in power devices will largely depend upon the integrity of a suitable diffusion barrier metal between copper and silicon/silicon dioxide (Li 1992). The adhesion at the copper–dielectric interface should also be sufficiently good and the interface must act as a diffusion barrier to the transport of copper atoms from the metal lines into sensitive regions of the devices. Titanium and its nitride are found to offer good adhesion and diffusion barrier properties for conventional aluminum interconnects (Sekiguchi *et al* 1994). Ti/TiN barrier-based copper interconnects fail at low temperature (400–500°C) due to metallurgical reaction at copper–titanium interface and the formation of intermetalics (Karlsson 1989; Pfeifer *et al* 1989). Copper also diffuses through grain boundary in titanium-based copper interconnect system, resulting in the formation of high-resistance Cu$_3$Si phase. The use of an intermediate layer between copper and titanium may

lead to a more thermally stable system, as the atoms may have to diffuse through a longer path as compared to single layer due to grain boundaries mismatch (Majumder and Takoudis 2008). Further, a suitable intermediate barrier layer between titanium and copper may also limit the reaction of titanium with copper. Molybdenum and its carbide can be a potential intermediate layer due to its high melting point, high coefficient of thermal expansion, low bulk resistivity (Mo 5·7 μΩ-cm) and limited solubility with copper (Shuangxi *et al* 2005). Furthermore, the low resistivity of the Mo$_2$C film and its good thermal stability in Si/Mo$_2$C/Cu system (Tripathi *et al* 2009) make it an attractive alternative to be probed as a barrier in conjunction with titanium for copper metallization on silicon dioxide. In this paper, the effect of insertion of a thin molybdenum carbide layer between copper and titanium on the thermal stability of Si/SiO$_2$/Ti/Cu system is reported.

2. Experimental

The silicon wafers (6 in. diameter) with resistivity of 3–5 Ω-cm were used for the deposition of SiO$_2$ films. Prior to the film deposition, the substrates were cleaned using standard RCA procedure and finally dipped in 5% HF solution to remove the native oxide. A thin SiO$_2$ layer (50 nm) was deposited using plasma-enhanced chemical vapour deposition (PECVD) at 375°C. Thereafter, 60 nm thick titanium layer was deposited using DC sputtering (Novellus 3290) at a substrate temperature of 250°C. As-

prepared substrates were cut into $2'' \times 2''$ pieces and the Si/SiO$_2$(50 nm)/Ti(60 nm)/Cu(80 nm) structures with and without molybdenum carbide were prepared.

The saddle field fast atom beam (FAB) is defined to consist of energetic neutral atoms ranging in energy from a few electron volts to several thousand electron volts (Shimokwa 1992). In the FAB plasma source, there are two positive parallel anode rods symmetrically arranged around the main axis of a rectangular cathode cylinder oscillator (Mcllraith 1972). By the application of high voltage to the rod anodes, electrons oscillate at high frequency backward and forward through a saddle point of the electrostatic field between the anodes. With this arrangement, the electrons can follow a long oscillatory path and a large number of ions are produced when the electrons collide with gas molecules, i.e. a high intensity cold cathode discharge is produced at low pressure. The arrangement of the electrostatic field close to the out put grid allows the recombination of the secondary electrons and ion with little loss of energy. This results in a beam of virtually 100% atoms of the supply gas Ar in the present case. The atoms produced from the source escape through the aperture, in cathode wall in the form of highly energetic atom beam. A very low processing temperature (near room temperature) in the range of 20–100°C can be maintained when operating the saddle field source equipment. The FAB sputtering is the most suitable technique for thin film formation of one or more than one metal, which may be magnetic, non-magnetic or an insulator.

The Mo$_2$C layer in the Si/SiO$_2$(50 nm)/Ti(60 nm)/Mo$_2$C(30 nm)/Cu(80 nm) structure was deposited using composite target of molybdenum and graphite by FAB sputtering technique at room temperature. A molybdenum sheet (99·99% pure) and an electronic grade graphite sheet embedded together were taken as the composite target for the deposition of molybdenum carbide films. The composite target had 83% Mo and 13% C surface coverage. The source to target distance was kept as 65 mm. The uniformity of the film was achieved by rotating the substrate with a DC motor. The deposition of 30 nm molybdenum carbide film was carried out at room temperature with estimated deposition rate of 1·2 Å/min. The detailed experimental set-up was reported earlier (Tripathi *et al* 2009).

During the deposition, the gas flow needle valve was set to keep plasma current at 14·8 mA. The supply voltage and the chamber pressure were maintained at 1·35 keV and $1·4 \times 10^{-3}$ torr, respectively. Finally, copper films in the Si/SiO$_2$(50 nm)/Ti(60 nm)/Mo$_2$C(30 nm)/Cu(80 nm) system were deposited using physical vapour deposition technique at room temperature. The as-prepared samples of Si/SiO$_2$ (50 nm)/Ti(60 nm)/Cu(80 nm) and Si/SiO$_2$ (50 nm)/Ti(60 nm)/Mo$_2$C(30 nm)/Cu(80 nm) structures were annealed in vacuum (4×10^{-4} torr) at different temperatures between 400 and 800°C for 30 min.

The *ex situ* four-point probe (FPP) set-up was employed to measure electrical resistivity of as-prepared and annealed samples. The surface morphology and film composition were examined using field-enhanced scanning electron microscopy (FESEM) (Quanta 200 FEG make FEI Netherlands with EDAX-ZAF algorithm). The structural phase formation analysis was carried out using X-ray diffraction (XRD) technique with CuKα ($\lambda = 1·5408$ Å) line, on D-8 advance model (Bruker AXS analytical instruments).

3. Results and discussion

The sheet resistance of the layered metallization structure as a function of temperature is displayed in figure 1. The sheet resistance of the Si/SiO$_2$/Ti/Cu structure shows its lowest value at 400°C and then increases up to 500°C, followed by a dip at 600°C. Further, its value increases sharply above 600°C. The increase in the sheet resistance of the titanium barrier structure above 400°C is attributed to the formation of intermetallic compounds like Cu$_2$Ti, Cu$_3$Ti$_2$ and Cu$_4$Ti, as a result of copper–titanium reactions. The inset in figure 1 is an enlarged view of sheet resistance of bi-layered diffusion barrier structure. The value of the sheet resistance in Si/SiO$_2$/Ti/Mo$_2$C/Cu structure remains stable up to 750°C. At 800°C, the sheet resistance is less than twice its value at room temperature. The slight increase in sheet resistance at elevated temperature is ascribed to depletion of copper film as a result of annealing.

In order to identify the structure and the phase formation at elevated temperature, XRD patterns of the samples annealed at various temperatures were recorded between $2\theta = 15–75°$. For comparison, the XRD spectra of the bi-layered barrier structure were plotted in the same graph as shown in figure 2. The XRD spectra of the *p*-Si/SiO$_2$/Ti/Cu structure before and after annealing at
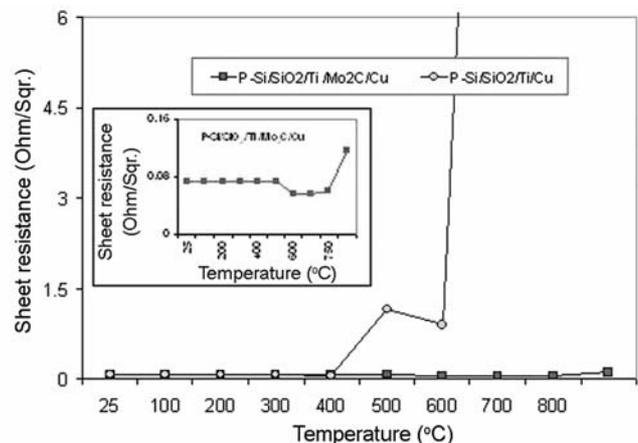
Figure 1. Sheet resistance vs temperature graph of Si/SiO$_2$/ Ti/Mo$_2$C/Cu and Si/SiO$_2$/Ti/Cu structures.

600ºC are shown in figures 2(a) and 2(b), respectively. The XRD peaks at $2\theta = 37$, 38.25 and $64.9°$ were indexed as titanium (111), titanium (002) and titanium (220) reflections, respectively. The reflections due to Cu (111) and Cu (200) were observed in XRD spectra of all the samples. The XRD pattern of titanium barrier structure annealed at 500°C (not shown) reveals the formation of Cu_3Ti and Cu_4Ti phases, as seen in XRD pattern at 600°C (figure 2b). The increase in the intensity of the Ti (111) reflection of the Si/SiO₂/Ti/Cu structure annealed at 600°C confirms the grain growth as a result of annealing. The increased grain size in the annealed titanium layer enables grain boundary diffusion of copper atoms and the formation of the high-resistance Cu_3Ti phase as evidenced by the appearance of the reflections at $2\theta = 39.15°$ and $45.25°$ and also due to Cu_4Ti phase at $2\theta = 44.70°$.

The increased sheet resistance observed in the Ti-based Si/SiO₂/Ti/Cu barrier structure measured after annealing at and above 400°C is ascribed to the formation of high-resistance Cu–Ti intermetallics. It was also confirmed by XRD measurements and is in accordance with the literature (Hong *et al* 2004). The sharp decrease in the sheet resistance between 500 and 600°C may be due to titanium-free copper layer, which is a result of complete consumption of titanium in the formation of intermetallic compounds, and interface titanium oxide layer. The effect of increased titanium thickness in the Si/SiO₂/Ti/Cu structure has been reported to decrease the thermal stability (Hong *et al* 2004). Therefore, instead of using a thicker titanium barrier layer in the structure, a bi-layered barrier may prohibit titanium copper intermetallics formation and may result in increased thermal stability of the system.

Nevertheless, good wetting property of titanium and its process compatibility with SiO₂ suggest the investigation of other barrier metals along with titanium for copper metallization. Because of the immiscibility of the metal carbides, particularly of molybdenum with copper, an introduction of Ti/Mo₂C bi-layer barrier in the structure may result in better thermal stability. In order to verify this, a 30 nm Mo₂C layer was introduced in the structure prior to copper metallization.

The as-deposited molybdenum carbide (Mo₂C) films were characterized as nanocrystalline (Tripathi *et al* 2009). The film composition measured by RBS confirms the formation of Mo₂C in accordance with the phase diagram (Hugosson *et al* 2001; Tripathi *et al* 2009). The resistivity of the as-deposited films was of the order of 62 μΩ-cm. The diffusion barrier properties of Mo₂C films for copper metallization on silicon were reported earlier (Tripathi *et al* 2009). The XRD spectra of the *p*-Si/SiO₂/Ti/Mo₂C/Cu structure annealed at 750°C is shown in figure 2(c). The XRD reflections due to titanium (111) and (002) along with the reflections due to Cu (111) and Cu (200) and nanocrystallized molybdenum carbide can be seen in the figure. There is no change in the XRD pattern of bi-layered barrier structure annealed up to 700°C (not shown). As expected from Mo₂C–Cu phase diagram (Subramanian *et al* 1990), no reflections due to the Mo₂C–Cu phases were observed in the XRD spectra at 750°C or 800°C (figures 2c and d). The disappearance of XRD reflection at $2\theta = 64.9°$ corresponding to Ti (002) in figure 2(d) of the bi-layer barrier structure may be due to the reaction between oxygen and titanium at the dielectric interface as no titanium–molybdenum intermetallic reflections were observed. A slight increase in the sheet resistance between 750 and 800°C in the bi-layer barrier structure is due to the depletion of copper layer as confirmed in SEM measurements. The absence of high resistance the Cu_3Si phase in the XRD spectra of annealed bi-layer barrier structure at 800°C and no appreciable change in copper Cu(111) and Cu(200) reflections confirms the integrity of structure at an elevated temperature.

In order to understand the increase in the sheet resistance of the samples at elevated temperatures and to see the change in the surface morphology, the SEM images were recorded. The *in situ* elemental mapping using energy dispersive spectrophotometric (EDS) spectroscopy was carried out to probe the film composition. The whitish regions in the SEM micrograph of the Si/SiO₂/Ti/Cu samples annealed at 600°C (figure 3) were identified as the Cu_3Si phase. The dark region near the whitish grain was characterized as the copper-denuded zone. Further annealing of samples increases the copper-denuded zone due to agglomeration of surface copper films. The SEM images (figure 4) of the bi-layered barrier Si/SiO₂/Ti/Mo₂C/Cu structure at 750°C shows no major degradation of the surface morphology except few pinholes and tiny whitish contaminations. The surface morphology of the bi-layer barrier Si/SiO₂/Ti/Mo₂C/Cu structure annealed at 800°C shows slight degradation (figure 5) of surface due
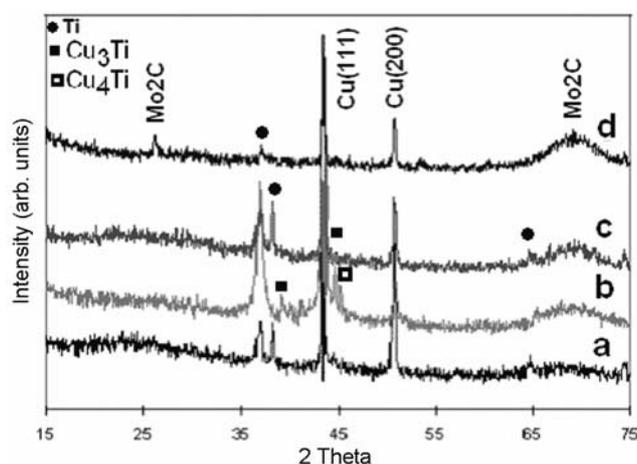

Figure 2. Comparative XRD patterns: (a) *p*-Si/SiO₂/Ti/Cu (*RT*), (b) *p*-Si/SiO₂/Ti/Cu (600°C), (c) *p*-Si/SiO₂/Ti/Mo₂C/Cu (750°C) and (d) *p*-Si/SiO₂/Ti/Mo₂C/Cu (800°C).

to the agglomeration of surface copper layer and on-set of formation of the high-resistance Cu_3Si phase, although not seen in the XRD spectra. The presence of the Cu_3Si in the elemental mapping of the film surface and slight increase in the sheet resistance above 750°C of the bi-layered barrier system indicate that SiO_2 has reacted to form the Cu_3Si phase.

The detailed analysis of diffusion mechanism and the formation of the Cu_3Si phase in the bi-layered barrier system necessitates the study of diffusion profile using more reliable techniques such as SIMS, RBS, AES, etc. However, the present study using FPP, XRD, SEM and EDS confirms that the use of Mo_2C between copper and titanium in the $Si/SiO_2/Ti/Cu$ system prevents the formation of copper–molybdenum compound (Subramanian *et al* 1990) as expected (due to immiscibility of copper and molybdenum below 1083°C). Further, no observation of copper–titanium intermetallics and/or the titanium silicides up to 750°C confirms our observation.

A single 60 nm thick titanium layer in the $Si/SiO_2/Ti/Cu$ system in the present investigation has been found to be thermally stable up to 400°C as reported in the literature (Hong *et al* 2004). Similar systems such as the $Si/SiO_2/Ta/Cu$ and the $Si/SiO_2/TaN/Cu$ when tested under the MOS device structure were found to fail at 600°C temperature (Loh *et al* 2004). The physical vapour-deposited titanium oxy-nitride barrier films in the $Si/SiO_2/Ti(O)N/Cu$ systems have been reported to result in barrier integrity up to 650°C (Maung *et al* 2002). The slight increase in the sheet resistance of the bi-layered barrier structure at 800°C in the present case is due to the depletion of copper from the top surface. However, no appreciable change in the observed sheet resistance of the bi-layered diffusion barrier structure up to 800°C along with the analysis of the XRD and the SEM data confirms that a 30 nm Mo_2C layer between titanium and copper prohibits copper diffusion in the silicon dioxide or silicon up to 750°C. Relatively longer diffusion path encountered by copper or silicon atoms in bi-layer Ti/Mo_2C barrier structure probably because of the grain boundary mismatch at the interface is believed to be the reason for the increased thermal stability in the present case.
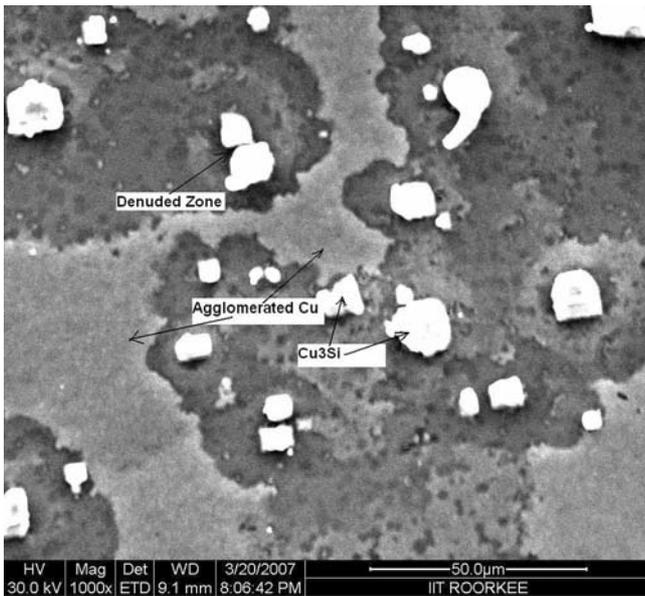
Figure 3. SEM image of $Si/SiO_2/Ti/Cu$ structure annealed at 600°C.
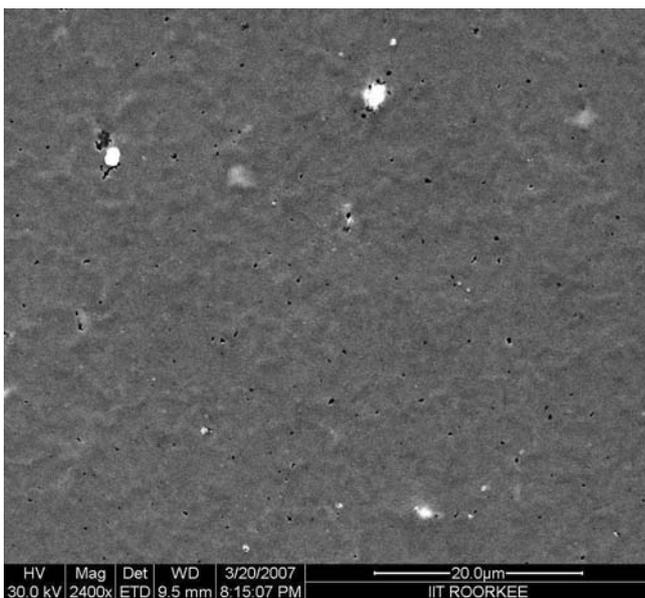
Figure 4. SEM image of $Si/SiO_2/Ti/Mo_2C/Cu$ structure annealed at 750°C.
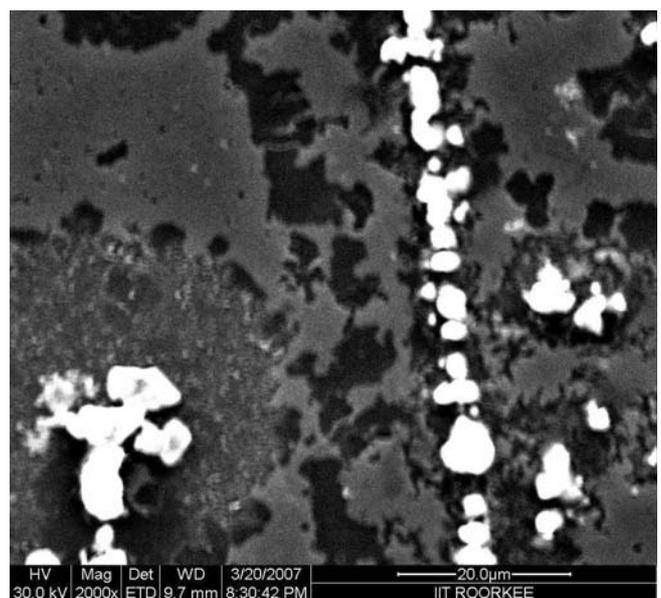
Figure 5. SEM image of $Si/SiO_2/Ti/Mo_2C/Cu$ structure annealed at 800°C.

4. Conclusions

We report the effect of introduction of a 30 nm Mo_2C layer in between copper and titanium in the $Si/SiO_2/Ti/Cu$ structure with the objective of increasing the thermal stability of the system. The Mo_2C/Ti bi-layered barrier has been found to prohibit copper diffusion up to 750°C as evidenced by no change in sheet resistance, XRD spectra and SEM micrographs. Good adhesion property of titanium with SiO_2 and the immiscibility of molybdenum and its carbides with copper increase the thermal stability of the system and prevent high-resistance phase formation. The observed high thermal stability of the bi-layer Mo_2C/Ti barrier for copper metallization may be ascribed to grain boundary mismatch at the titanium and the molybdenum carbide interface.

Acknowledgements

References

Hong S J *et al* 2004 *Semicond. Sci. Technol.* **19** 1315

Hugosson H W, Jonsson U, Johnsson B and Eriksson O 2001 *Chem. Phys. Lett.* **333** 444

Kaloyeros A E and Eisenbraun E 2000 *Annu. Rev. Mater. Sci.* **30** 363

Karlsson 1989 *J. Inst. Met.* **79** 391

Kumar M, Rajkumar D and George P J 2002 *Bull. Mater. Sci.* **25** 6

Li J, Strane J W, Russell S W, Hong S Q, Marris J W, Theron T K and Pretorius C C 1992 *J. Appl. Phys.* **72** 2810

Loh S W, Zhang D H, Li C Y, Liu R and Wu A S 2004 *Thin Solid Films* **462–463** 240

Majumder P and Takoudis C 2008 *Nanotechnology* **19** 205

Maung L K, Park H S, Seng H, Osipowics L T Y K, Lee S and Li 2002 *Mater. Sci. Eng.* **B90** 25

Mcllraith A H 1972 *J. Vac. Sci. Technol.* **9** 209

Rosenberg R, Edelstein D C, Hu C K and Rodbell K P 2000 *Annu. Rev. Mater. Sci.* **30** 220

Sekiguchi, Sawada M K and Fukumoto M 1994 *J. Vac. Sci. Technol.* **B12** 2992

Shimokwa F 1992 *J. Vac. Sci. Technol. Vac. Surf. Films* **10** 1352

Shuangxi S, Mao, L, Dali Y, Huiqin L and Ming Li 2005 *Thin Solid Films* **476** 142

Subramanian P R and Laughlin D E 1990 in *Binary alloy phase diagrams* (ed.) T B Massalski (Materials Park, OH: ASM International Materials) 2nd ed., pp. 1435–1438

Tripathi C C, Kumar M and Kumar D 2009 *J. Appl. Surf. Sci.* **255** 3518

Tripathi C C, Kumar M, Kumar D, Avasthi D K and Nair K G M 2010 *Mater. Sci. Technol.* **26** 318

Yen Y-W, Kuo Y-L, Chen J-Y, Chiapyng L and Chung-Yu L 2007 *Thin Solid Films* **515** 7209