SYNTHESIS OF TANTALUM NITRIDE DIFFUSION BARRIERS FOR Cu METAL BY PLASMA IMMERSION ION IMPLANTATION

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ABSTRACT

A Tantalum nitride diffusion barrier layer for copper metal was synthesized by Plasma Immersion Ion Implantation technique (PIII). Effect of nitrogen dose in Ta layer was investigated in improving its diffusion barrier properties. Silicon wafers coated with Ta were implanted with nitrogen at two different doses viz. $10^{15}$ions/cm$^2$ and $10^{17}$ions/cm$^2$ corresponding to low and high dose regime. High dose of implanted nitrogen ions in the film render it to become Ta(N). Thereafter a copper (Cu) layer was deposited on the samples to produce Cu/Ta(N)/Si structure. To evaluate the barrier properties of Ta(N) these samples were annealed up to 700°C for 30 minutes. Sheet resistance, X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) measurements were carried out to investigate the effect of annealing. Low dose implanted Ta layer does not show any change in its diffusion barrier properties, while high dose implanted layer stops the diffusion of Cu metal through it at annealing temperature of 700°C.
INTRODUCTION

Aluminium has long been the conductor of choice for interconnections in IC’s, but this metal is found to be inadequate for ULSI (ultra-large-scale integration) and GSI (giga-scale integration) era. The use of this metal in two-dimensional networks has been considered to be inadequate because of unacceptably high values of the interconnection RC delay [1, 2]. Copper with its inherent properties of low resistance and high resistance to electromigration naturally became the metal of interest with the potential to meet up the challenge [3, 4]. Due to its low conductivity the ohmic losses of conductors are reduced. This is also beneficial in photovoltaic applications in addition to the analog, digital microcircuits and microprocessors [5]. Higher resistance to electromigration makes it possible to apply higher currents in Cu-metallized microcircuits and to use narrower and thinner conductors and interconnections.

When used in integrated circuits copper poses some problems that need to be addressed before implementing copper in IC’s. One of the disadvantage of Cu as interconnection material is due to its rapid diffusion into silicon, silicon dioxides and other dielectrics, causing line-to-line leakage, and its reaction with silicon at processing temperatures 200° C causing device failure [6-8]. Therefore there is a need to develop a new and advanced diffusion barrier to eliminate this threat. The diffusion barrier layers required must be effective against copper diffusion and it must be conformal and continuous and be as thin as possible. Ideally, the diffusion barrier is electronically transparent and atomically opaque. Electronically transparent means the voltage drop across the barrier layer should be negligibly small [9, 10]. This condition is met by many substances, and includes heavily doped semiconductors, amorphous metallic alloys, and conducting oxides. Understanding the mechanism of diffusion through the solid films is essential for the designing of effective thin film diffusion barriers. There are many possible diffusion mechanisms in solids. At high temperatures, diffusion mechanisms through the bulk of the material dominate. At low temperature, diffusion along extended defects and grain boundaries of the material is faster than through the bulk. The temperature of transition from bulk to defect mechanisms depends on the density of these extended defects, and lies typically near half of the absolute melting point for crystalline materials. The obvious choice of a diffusion barrier will be thin films that have less number of grain boundary and defects. Improving deposition conditions can reduce number of defects. Grain boundary diffusion can be reduced by segregation of some impurities like nitrogen, carbon etc. at the grain boundaries.
Nitridation of refractory metals have found to improve their diffusion barrier properties. In recent past, the nitridation of diffusion barrier layers by reactive sputtering and also by sputtering from a composite target have been carried out. Researchers have developed various diffusion barriers to prevent Cu from diffusing into the Si, such as W, Ti, Ta, Ni, Cr, V, Nb, TaN, TiN, TiW, W-Si, W-Si-N, Ta-Si-N, and WN etc [11-15]. In the present research work, the nitride layer for diffusion barrier application was formed by ion implantation process. Conventional ion implantation process is not suitable for implanting thin metal layers, so Plasma immersion Ion Implantation (PIII) technique was used to carry out the nitridation of thin metal diffusion barrier layers. PIII is a simple process of ion implantation in which no beam extraction, acceleration or rastering mechanism is employed [16].

The PIII technique was initially developed for treatment of large area samples, but now it is also being developed for semiconductor applications [17-18]. The main interests are in ultra shallow junction doping [19], thin film transistor hydrogenation, silicon on insulator [20], near surface modification of different layers etc [21]. In this technique wafers for implantation are placed on a conducting chuck in a vacuum chamber and plasma of ions to be implanted is generated by employing various techniques. Then negative voltage pulses of required magnitude are applied to the wafer immersed in plasma. Electron being lightest particle in plasma will be repelled away from the substrate within a short period of applied pulse, leaving behind a sheath of uncompensated positive ions near the surface of substrate. Positive ions will accelerate through the sheath towards the wafer and get implanted in all the exposed surfaces. Thus unlike conventional ion implantation in PIII no ion extraction and acceleration take place and whole wafer gets implanted at one time. Thus PIII not only overcome the limitations of conventional line of sight process, but also offer other advantages like shallow implantation with high dose, low cost, less sample heating, ease in design, and can handles large area samples. As this method does not incorporate any beam filtering mechanism, species of all ionic states along with contamination will also be implanted. As well all the ions implanted are not of single energy, rather there exist a spread in energy of implanted ions as a consequence of pulse dynamics.
EXPERIMENTAL DETAILS

Cu/Si, Cu/Ta/Si and Cu/Ta(N)/Si structures were prepared for this study. The substrates used were n-type silicon with <100> orientation having resistivity of 1-10 Ωcm. Deposition of ~100nm thickness of Ta metal film was carried out by RF sputtering technique. These samples were implanted with nitrogen ions by plasma immersion ion implantation, which results in the formation of Ta(N)/Si structure.

Nitrogen implantation was carried in a PIII system. For implantation purpose, samples were placed on a metallic chuck and were connected with a -20 KV pulse voltage. Chamber was evacuated to a base pressure of 10⁻⁶ Torr. Nitrogen was then introduced in the chamber and a working pressure of 10⁻³ Torr was maintained by controlling the gas flow. In the present studies, RF power of 100 W was used to generate plasma needed for carrying out implantation. Pulse voltage and ion current were measured using an oscilloscope. Implanted dose was estimated using the average ion current according to the formula given below:

\[
Dose\ per\ pulse = \int_{t=0}^{t=\text{pw}} \frac{I \cdot dt}{q \cdot \gamma \cdot A}
\]

Here 'I' is implant current, 'pw' is pulse duration, 'q' is ion charge, 'A' is the open area of the chuck, 'γ' is the coefficient of secondary electrons emission and 't' is the implant time per pulse.

Final dose can be calculated by considering total implant time 'T' (T = f \cdot t), Where 'f' is the pulse frequency,

Hence final dose per unit area is given by

\[
Total\ Dose = \int_{t=0}^{t=\text{pw}} \frac{I \cdot dt \cdot T}{q \cdot \gamma \cdot A}
\]

Dose calculated may not be exact due to uncertainty in the value of 'γ' and measured ion current. Here 'γ' = 2.5, a typical value for voltages greater than 10 kV was used. But exact value of 'γ' depends upon many factors like target material, ion mass, pulse voltage etc.
The samples were implanted at two doses; 10^{15} ions/cm^2 (low dose) and 10^{17} ions/cm^2 (high dose). For low dose, frequency and pulse width was maintained at 50 Hz and 10 \mu s respectively. For high dose, frequency and pulse width was selected at 1 kHz and 50 \mu s respectively. Total implantation time was maintained at 10 minutes for both, i.e., low and high dose samples. After implantation, Copper layer of 200nm thickness was deposited on Ta/Si, Ta(N)/Si and Si samples by DC sputtering system. Measurement of thickness was performed by Dektek 3030 Profilometer. Annealing of samples was carried out in N_2 ambient. For this purpose first of all, the annealing chamber was evacuated using rotary pump and then flushed with N_2 gas for few minutes. Then the flow of nitrogen was controlled using needle valve. Pressure inside the chamber during annealing was 0.4 Torr. Annealing at different temperatures was carried out for 30 minutes. To avoid the oxidation of the top Cu layer, samples were allowed to cool down inside the chamber itself before unloading.

The characterization of these samples at room temperature were carried out by SEM, X-ray diffraction and four probe sheet resistance measurement techniques. SEM micrographs were obtained using JEM-1200 EX (JEOL) electron microscope at an accelerating voltage of 20KV. For X-ray diffraction Philips Model PW 1729 X-ray Diffractometer was used. The target consists of copper metal whereas nickel metal was used as a \beta-filter. The accelerating voltage was kept at 35 KV. The tube current was kept at 10 mA. The Goniometer range used was 25° to 60° values. X-ray diffraction pattern (2θ vs. intensity) results were obtained and plotted using X-Y recorder. JCDPS data files were used to identify the various peaks obtained in XRD spectrum.

RESULTS

A four-probe system was employed to measure the relative change in sheet resistance of Si/TaN/Cu samples following annealing at various temperatures. Such measurements allows the integrity of top layer as well as the efficiency of Ta(N) diffusion barriers to be determined. Fig. 1 shows the sheet resistance variation of Cu/Si, Cu/Ta/Si, Cu/Ta(10^{15} ions/cm^2 N_2)/Si and Cu/Ta(10^{17} ions/cm^2 N_2)/Si structures versus annealing temperature. Sheet resistance of Cu/Si structure increases after annealing at 200°C for 30 minutes. Annealing at 300°C causes it to increase rapidly and becomes about 400% of its original value. This increase in sheet resistance may be due to some reactions at the Cu-Si
interface. Annealing at up to 500°C of Cu/Ta/Si structure doesn’t lead the sheet resistance to increase. However for samples annealed at 600°C, a slight increase in sheet resistance is observed. But after annealing at 700°C, abrupt change in sheet resistance is observed which indicate some type of interaction between constituents, so it shows that Ta layer no longer acts as the diffusion barrier at 700°C. It is also observed that a dose of 10^{15} ions/cm^2 in Ta is not sufficient to cause any change in the sheet resistance curve to that of un-implanted sample. However, implantation with a dose (10^{17} ions/cm^2) of nitrogen in Ta layer has resulted significant change in the sheet resistance curve. In this case, sheet resistance is found to remain constant even after annealing the sample at a temperature of 700°C. It seems that interaction in the form of any chemical reaction or inter-diffusion has not taken place in the structure even after annealing at 700°C.

FIG. 2 shows the diffraction pattern of as-deposited Cu/Si structure in which (111) and (200) peaks of copper are observed. As a result of annealing the Cu/Si structure at a temperature of 200°C for 30 minutes, reactions between Cu and Si seem to occur, as it is evident from the XRD spectra. Cu_2Si (320) is the only copper silicides phase detected. This phase was not present in as-deposited structure. Formation of high resistivity Cu_3Si phase may be responsible for increase in sheet resistance at 200°C as already indicated in Fig. 1.

FIG. 3 illustrates the XRD pattern of Cu/Ta/Si structures annealed at various temperatures. Un-annealed sample shows the peaks of Cu (111), Cu (200) and Ta (410). The sample annealed at 500°C does not experience any intermixing and all peaks are intact. Peak of TaSi_2 (112) is observed after annealing the sample at 700°C. Cu_3Si (320) and Cu_4Si (310) peaks were also obtained. Intensity of copper peaks has decreased which indicates that some copper has depleted from the top surface of the structure. It shows that at 700°C copper has penetrated the Ta layer and reached to silicon to form copper silicide. Formation of copper silicides explains the increase in sheet resistivity at 700°C that was heated at 700°C for 30 minutes. SEM morphology of the un-annealed Cu/Ta/Si is shown in Fig. 4, which indicates that a uniform layer of copper exist on the surface. Surface morphology of the sample annealed at 700°C indicates that some local defect sites have formed on the surface (Fig. 5). These local defect sites may be due to penetration of copper from these sites, which left behind a region where underlying Ta metal is exposed.
Fig. 6 illustrates the typical set of XRD patterns for the nitrogen implanted and un-implanted Ta layer on Si. It is evident from this figure that implantation of $10^{15}$ ions/cm$^2$ nitrogen does not cause any nitridation of the Ta film as no tantalum nitride phase is observed, while $10^{17}$ ions/cm$^2$ dose of nitrogen results in the formation of Ta$_2$N phase as shown in figure. Fig. 7 shows XRD patterns of Cu/Ta($10^{15}$N)/Si samples. The XRD data of sample annealed at 700°C indicates a similar type of chemical interaction as obtained in case of un-implanted Ta barrier layer (Fig. 3). Formation of tantalum silicide and copper silicide is detected in this sample after annealing at 700°C. So, we can say that there is no change in the diffusion barrier properties of Ta layer after its implantation with $10^{15}$ ion/cm$^2$ dose of nitrogen.

XRD of as-deposited and annealed Cu/Ta($10^{17}$N)/Si structure is shown in Fig. 8. Un-annealed sample shows the peaks of Cu (111), Cu (200), Ta (410) along with two peaks of Ta$_2$N. Sample annealed at 500°C shows that no interaction among the metal layers has taken place and all the peaks are intact. After annealing at 700°C, peaks of TaSi$_2$ are obtained. No peak of copper silicide was observed in this sample. Intensity of copper peaks was also found to be unchanged which indicates that there is no loss of Cu from the top layer of the structure. SEM micrograph of Cu/Ta($10^{17}$N)/Si structure in Fig. 9 also indicates that the surface still contains a continuous layer and no local defect sites, which were present in case of un-implanted samples, are observed. It shows that even at 700°C the structure is stable and hence diffusion barrier properties of Ta has been improved by implantation of $10^{17}$ ions/cm$^2$ dose of nitrogen in it by Plasma Immersion Ion Implantation.

DISCUSSION

The failure of diffusion barrier can occur due (a) Reaction of Cu with barrier metal (b) Due to diffusion of Cu atoms through barrier layer without reacting. Elemental Ta barrier failure cannot be explained as its reaction with Cu metal, because no phase of Cu-Ta was detected in XRD studies. This is in agreement with the Cu-metal binary phase diagrams. Li et al. [22] have reported that reactions of Cu metal binary systems proceed in various manners with variation of the binary phase diagrams. Ta forms virtually no solid solutions with Cu. Only explanation for failure of Ta
barrier can be the penetration of Cu through this barrier without reacting with it. The exact mechanism of Cu penetration is not easy to describe. The nature of penetration through the Ta layer could be either due to lattice diffusion, defect mediated diffusion (including grain boundary diffusion), or a combination of both [9]. However with high melting point materials such as Ta, one would not expect lattice diffusion of Cu through the barrier. So, only possibility, which exist for Cu diffusion through Ta, is through grain boundaries until it reaches to the Ta-Si and a Cu$_3$Si nucleation site is encountered.

No phases of tantalum nitride were found in the samples implanted at $10^{15}$ ions/cm$^2$ dose of nitrogen, whereas at $10^{17}$ ions/cm$^2$ dose of nitrogen, formation of nitride (Ta$_2$N) phase is observed. This is in consistent with the work carried out by other workers, which shows that low dose of nitrogen does not result in formation of any new nitride phase [23,24]. In this case nitrogen is 10 atomic % to that of tantalum. The addition of $10^{15}$ atoms/cm$^2$ of nitrogen has no effect in stopping copper motion. However, if enough nitrogen is incorporated ($10^{17}$ ions/cm$^2$) to form the nitride phase (Ta$_2$N), Cu-Si interaction can be prevented at higher temperatures. The Ta-N equilibrium phase diagram shows that at room temperature, the solubility of nitrogen is just over 2 atomic % in bcc Ta [25]. Solubility rises with temperature; but 5 at. % N would not be dissolved into the Ta until 800°C is reached. So the excess nitrogen in case of $10^{17}$ions/cm$^2$ seems to get segregated at grain boundaries and may be responsible for stopping the penetration of Cu through the Ta metal film.

CONCLUSION

The results presented here shows that a Ta layer, acts as a diffusion barrier layer between copper and silicon up to a annealing temperature of 500°C for 30 minutes. Dominant mechanism for failure of diffusion properties is supposed to be the presence of grain boundaries in the layer. Implantation of Ta layer with $10^{17}$ions/cm$^2$ dose of nitrogen by plasma immersion ion implantation technique improves its diffusion barrier properties at least up to 700°C temperature. So we conclude that Plasma Immersion Ion Implantation technique can be used as a tool to enhance diffusion barrier properties of Ta layer. Further studies in term of depth profiling using RBS, XPS and SIMS can be undertaken to understand the diffusion mechanism of copper through nitrogen implanted barrier layers.
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References

Figure Captions

Fig. 1 Sheet resistance variation of Cu/Si, Cu/Ta/Si, Cu/Ta(10^{15} ions/cm^2 N_2)/Si and Cu/Ta(10^{17} ions/cm^2 N_2)/Si structures versus annealing temperature.

Fig. 2 X-ray diffraction pattern for as-deposited and annealed Cu/Si samples.

Fig. 3 X-ray diffraction pattern for Cu/Ta/Si samples annealed at different temperatures.

Fig. 4 SEM morphology of as-deposited Cu/Ta/Si sample.

Fig. 5 SEM morphology of Cu/Ta/Si sample annealed at 700°C.

Fig. 6 X-ray diffraction pattern of Ta/Si samples implanted with two different doses of nitrogen.

Fig. 7 X-ray diffraction pattern of as-deposited and annealed Cu/Ta(10^{15} ions/cm^2 N^+)/Si samples.

Fig. 8 X-ray diffraction pattern of as-deposited and annealed Cu/Ta(10^{17} ions/cm^2 N^+)/Si samples.

Fig. 9 SEM morphology of Cu/Ta(10^{17} ions/cm^2 N^+)/Si sample annealed at 700°C for 30 minutes.
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