Journal of Korean Institute of surface Engineering
Vol. 29, No. 6, Dec., 1996

MO-COMPOUNDS AS A DIFFUSION BARRIER BETWEEN Cu AND Si

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ABSTRACT

In this study, the diffusion barrier properties of 1000Å thick molybdenum compounds (Mo, Mo-N, $MoSi_2$, Mo-Si-N) were investigated using sheet resistance measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), and Rutherford backscattering spectrometry (RBS). Each barrier material was deposited by the dc magnetron sputtering, and annealed at 300-800℃ for 30min in vacuum. Mo and $MoSi_2$ barrier were failed at low temperature due to Cu diffusion through grain boundaries and defects of Mo thin film and the reaction of Cu with Si within $MoSi_2$, respectively. A failure temperature could be raised to 650℃-30min in the Mo barrier system and to 700℃-30min in the Mo-silicide system by replacing Mo and $MoSi_2$ with Mo-N and Mo-Si-N, respectively. The crystallization temperature in the Mo-silicide film was raised by the addition of N_2. It is considered that not only the N_2 stuffing effect but also the variation of crystallization temperature affects the reaction of Cu with Si within Mo-silicide. It was found that Mo-Si-N is more effective barrier than Mo, $MoSi_2$, or Mo-N to copper penetration preventing Cu reaction with the substrate for 30min at a temperature higher than 650℃.

INTRODUCTION

In semiconductor processing, Al-Cu alloy instead of pure aluminum is currently used for the metallization material to prevent electromigration phenomena together with diffusion barrier materials such as Ti, TiN, TiW, etc. between Al and silicon to prevent junction spiking phenomena resulting from the interdiffusion of aluminum and silicon during the post-metal annealings.[1][2] However, the decrease of the device size of integrated circuits requires more conformal deposition method of metals (such as chemical vapor deposition), lower resistivity, higher melting point, higher electromigration resistive materials, etc., and currently, Cu is known as the best material for the metalliza-

tion of the next generation semiconductor integrated circuits. Problems remained to Cu for the metallization are easy etchability and reliability due to the high diffusivity of Cu in Si which includes poisoning of Si due to the formation of deep trap level of Cu in Si, the formation of highly resistive Cu_3Si compound, etc.[3] Some of the reliability problems can be solved by using more strict diffusion barrier material between Cu and silicon, and the nitrides of transition metals or their silicides have been studied by many researchers to prevent the interdiffusion between Cu and Si more effectively at high metal annealing temperatures.[4][5][6]

In this study, the effects of Mo compounds such as Mo, Mo-N, and Mo-Si-N on the diffusion barrier properties between Cu and Si were investigated. Mo compounds are not widely studied for the diffusion barrier materials compared to other transition materials such as Ta and W even though Mo has less lattice mismatch with silicon and lower resistivity compared to other materials.[7]

EXPERIMENTAL PROCEDURE

To deposit 1000Å of Mo-(N) and Mo-Si-(N), reactive dc magnetron sputter deposition was used with Mo and $MoSi_2$ sputter targets respectively in $Ar/(N_2)$ environments on (100) silicon wafers after the pretreatment with 10:1 HF. In case of Cu (5000Å)/Mo compound(1000Å)/Si structure, Cu was deposited using dc magnetron sputtering consecutively after the deposition of Mo compound on the silicon without breaking the vacuum. All of the depositions were conducted after the base pressure was reached below 1×10^{-6} Torr. The deposition pressure was kept at 5mTorr with a throttle valve and N_2 was added to Ar from 0 to 20% while Ar flow rate was kept at 10sccm. After the deposition, the samples were annealed in a vacuum furnace (lower than 10^{-5} Torr) from 300 to 800℃ for 30min to observe the characteristics for the diffusion barrier materials.

Sheet resistances of the deposited and annealed thin films were measured using a 4-point probe and the change of the thin film structure during the annealing was analyzed using X-ray diffractometer(XRD). Rutherford backscattering spectrometry(RBS) was used to analyze the composition of the diffusion barrier materials and the degree of interdiffusion between Cu and silicon substrate after the annealing. Also, the diffusion of silicon to Cu surface after the annealings was monitored using X-ray photoelectron spectroscopy(XPS). Defects formed on the silicon surface due to the interdiffusion between Cu and silicon was observed using Scanning electron microscopy (SEM) after removing Cu and diffusion barrier materials followed by etching silicon surface using Secco etchant.[8] Cu was removed by HNO_3+H_2O, Mo-N using $H_2SO_4+HNO_3+H_2O$, and Mo-Si-N using $HF+HNO_3$, respectively.

RESULTS AND DISCUSSION

Mo-(N)/Si and Mo-Si-(N)/Si

Sheet resistances of Mo-(N) and Mo-Si-(N) deposited on 1~10Ω-cm (100) silicon were measured after the annealing at various temperatures and are shown in Figure 1. As shown in the figure, the increase of nitrogen in Mo increased the sheet resistance and the

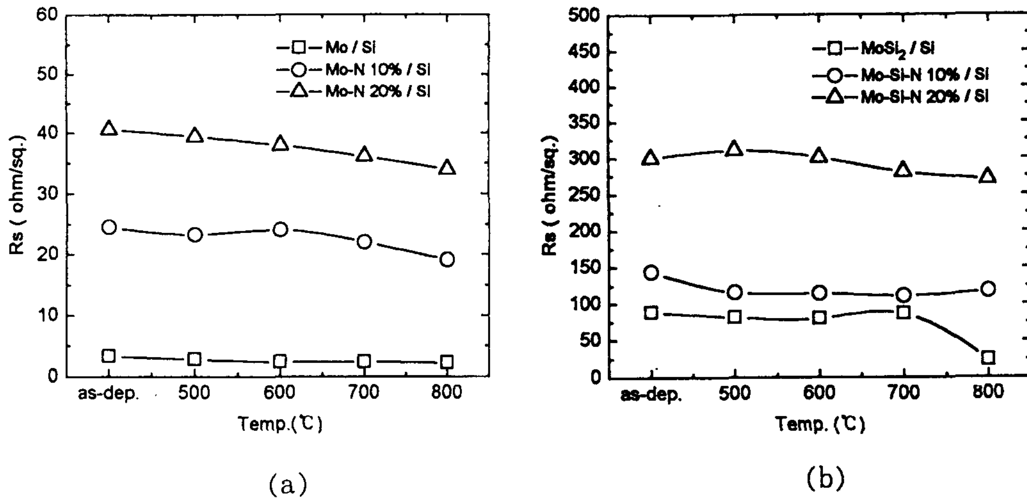

Fig. 1 Sheet resistance as a function of annealing temperature for (a) Mo-(N)/Si and (b) Mo-Si-(N)/Si

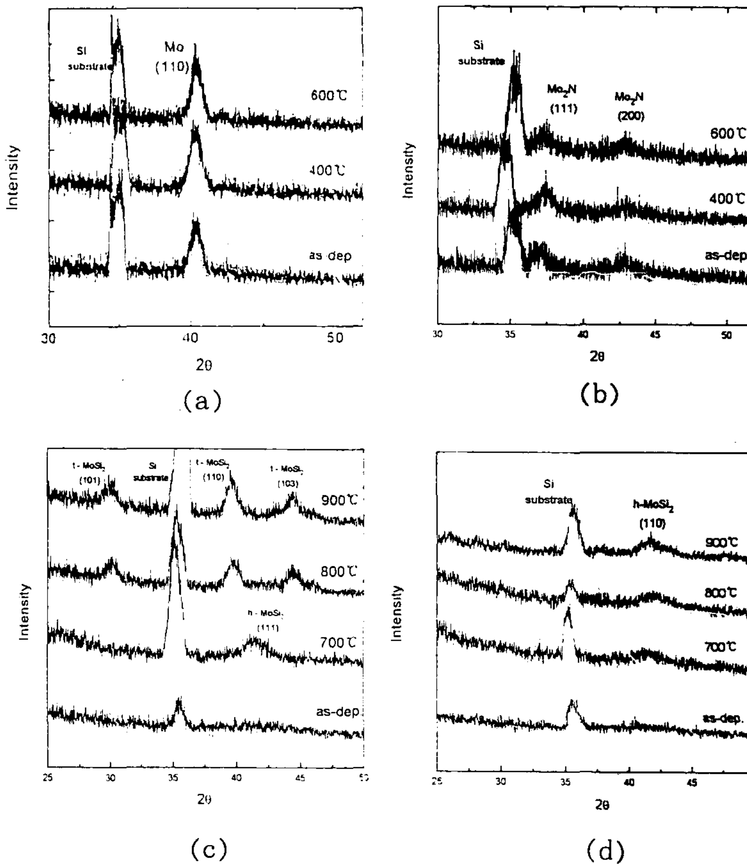

Fig. 2 XRD data as a function of annealing temperature for (a) Mo/Si, (b) Mo-N(10%)/Si, (c) $MoSi_2$/Si, and, (b) Mo-Si-N(20)%/Si

increase of the annealing temperature slowly reduced the sheet resistance. In case of Mo-Si-N, the sheet resistance also increased with the increase of nitrogen percent and the increase of the annealing temperature also slowly reduced the sheet resistance in general. However, for $MoSi_2$, drastic decrease of sheet resistance was observed after the annealing at 800℃.

Figure 2 shows the XRD data of Mo-(N) and Mo-Si-(N) measured as a function of annealing temperature. Deposited Mo showed a (110) Mo peak and deposited Mo-N(10% nitrogen) showed (111) Mo_2N and (200) Mo_2N peaks.

The annealing of Mo and Mo-N(10% nitrogen) did not change the peak intensities significantly. On the other hand, the deposited *or 600℃ annealed (not shown)* $MoSi_2$ *and* Mo-Si-N showed amorphous structures and the increase of annealing temperature above 700℃ showed increased transformation from amorphous to crystal structure. In case of $MoSi_2$, tetragonal $MoSi_2$ showed up after the annealing above 800℃. Sheet resistances measured in Figure 1 appear to be related with the change of crystal structure shown in Figure 2. No significant change of sheet resistances for Mo-(N) in Figure 1 (a) may be due to no significant structural change as shown in Figure 2 (a) and (b) and the drastic change in sheet resistance in MoSi2 above 800℃ in Figure 1 (b) appears to be related with the increase of crystallity and phase change to tetragonal $MoSi_2$ of Figure 2 (c) which has low resistivity.

In case of Mo-Si-N, very slow progress of crystallization with the increase of annealing temperature up to 900℃ and the formation of more resistive hexagonal $MoSi_2$ appears to show no drastic decrease of sheet resistance as shown in Figure 1(b).

Cu/Mo-(N)/Si and Cu/Mi-Si-(N)/Si

Figure 3 shows the sheet resistances of Cu/Mo-(N)/Si and Cu/Mo-Si-(N)/Si measured as a function of annealing temperature. Depending on the diffusion barrier materials, the sheet resistance of the Cu/Mo-(N)/Si and Cu/Mo-Si-(N)/Si increased sharply at different annealing temperatures. The increase of the sheet resistance was related to the diffusion of Si into Cu and to the formation of copper silicides. The increase of sheet resistance was also accompanied by the color change of Cu. The reddish yellow color of pure Cu changed to silver gray as the sheet resistance increased which indicates the formation of Cu silicides. In case of Mo-(N), the Mo-N(10% nitrogen) showed the highest temperature of 650℃ where the sheet resistance increase sharply, however, in case of Mo-Si-N, the temperature increased with the increase of nitrogen in Mo-Si-N for the *investigated experimental conditions.*

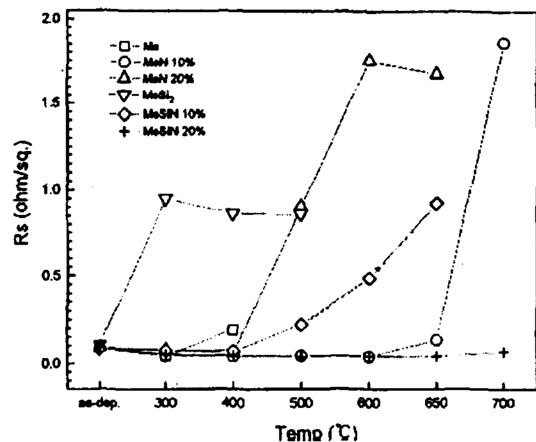

Fig. 3 Sheet resistance of Cu/Diffusion Barrier/Si samples as a function of annealing temperature

The failure of Cu/Mo-(N)/Si or Cu/Mo-Si-(N)/Si systems by the diffusion between Cu and Si after the annealings can be also monitored by observing the silicon surface. If Cu diffuses through the diffusion barriers, Cu reacts with silicon forming copper silicides, and it can be easily observed after the etching of the reacted silicon surface with Secco etchant. The shape of the etch pits were inverted pyramid where square edges were in ⟨110⟩ directions and faces were in {111} planes. Figure 4 shows the silicon surfaces of a Cu/Mo-Si-N/Si system after selectively removing the metal layers followed by etching

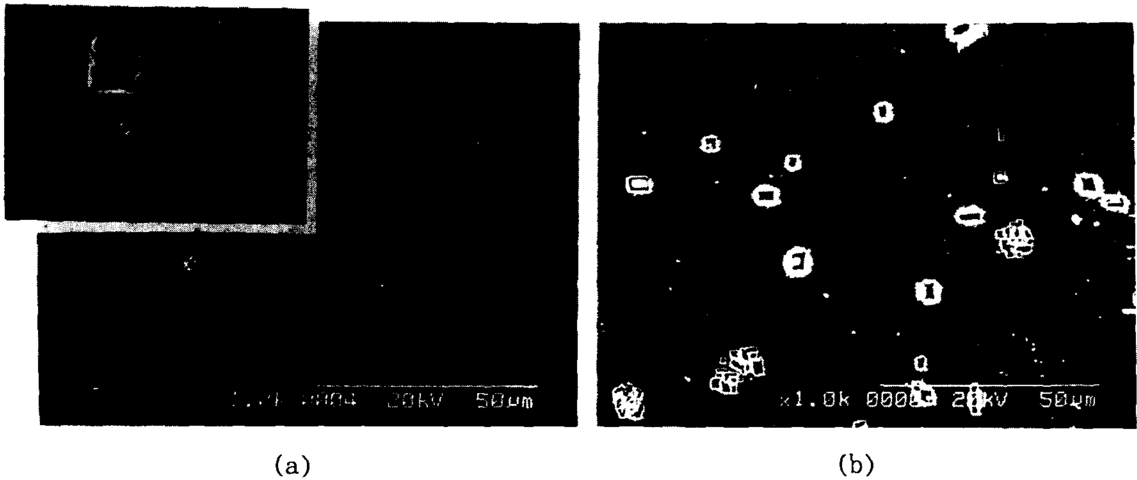

Fig. 4 SEM micrographs of silicon surface after Secco etching for (a) Cu/Mo-Si-N(20%)/Si after 700℃ annealing and (b) Cu/Mo-Si-N(20%)/Si after 800℃ annealino

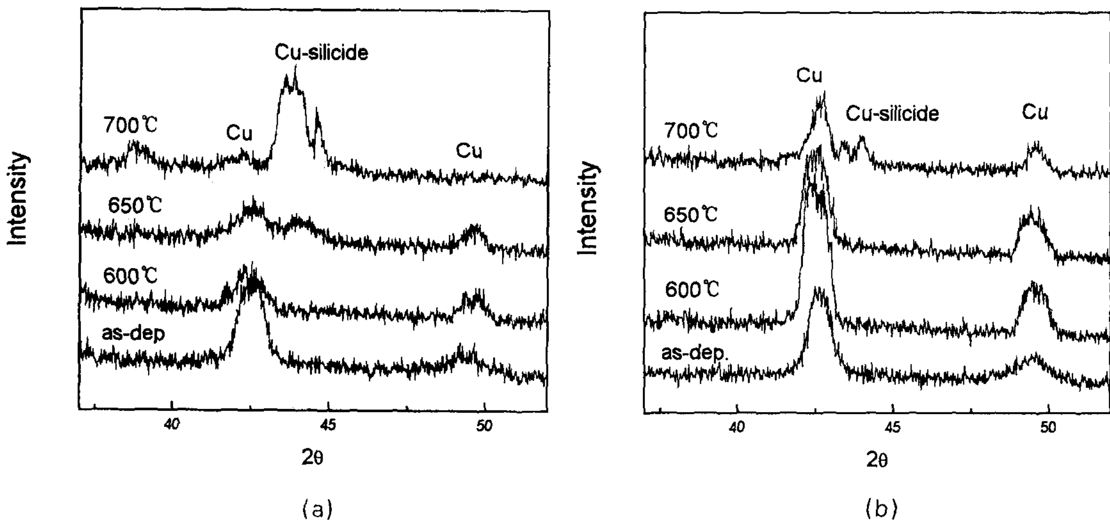

Fig. 5 Fig. 5 XRD data as a function of annealing temperature for (a) Cu/Mo-N(10%)/Si and (b) Cu/Mo-Si-N(20%)/Si

of silicon surface using Secco etchant. As shown in the figure, the silicon surface from the Cu/Mo-Si-N(20% nitrogen)system showed a few etch pit of a micron size after the annealing at 700℃ for 30min indicating the partial failure of the diffusion barrier. No etch pit was observed on the silicon surface for the deposited and 650℃ annealed Cu/Mo-Si-N(20% nitrogen)/Si system and the increase of annealing temperature to 800℃ increased the number of etch pits. In case of Cu/Mo-N(10% nitrogen)/Si system, etch pits were observed from 650℃ (not shown), which is consistent with the results in Figure 3.

Deposited and annealed Cu/Mo-N(10%nitrogen)/Si and Cu/Mo-Si-N(20% nitrogen)/Si were examined using XRD and are shown in Figure 5. As shown in the figure, a peak related to Cu silicide resulting from the diffusion between Cu and silicon could be also observed from the annealing above 700℃ for the Cu/Mo-Si-N(20% nitrogen)/Si system, and above 650℃ for the Cu/Mo-N(10% nitrogen)/Si system.

Composition of the deposited diffusion barrier materials and the degree of interdiffusion after the annealings were investigated using RBS. RBS data revealed that the deposited Mo-Si-N(20% nitrogen) has the actual atomic ratio of 1 : 2 : 2 and the deposited Mo-N(10% nitrogen) has 2 : 1.

In case of sputter deposited $MoSi_2$ using a $MoSi_2$ target in argon, the ratio was silicon rich as 1 : 2.3 and RBS data showed the active interdiffusion between silicon in $MoSi_2$ and Cu (not shown), therefore, the low failure temperature shown in Figure 3 for $MoSi_2$ appears to be related with the reaction of Cu with silicon from $MoSi_2$ rather than that from silicon substrate. Figure 6 shows RBS data of the deposited and annealed Mo-N(10% nitrogen)/Si and Mo-Si-N(20% nitrogen)/Si after the removing the Cu layer using $HNO_3 + H_2O$. The tails near the channel number of 800 appear to be related to the Cu diffused into diffusion barrier/Si and, as shown in Figure 6 (b) for Mo-Si-N(20%nitrogen), as the annealing temperature is increased from 700℃, the tail height and length were increased indicating more and deeper diffusion

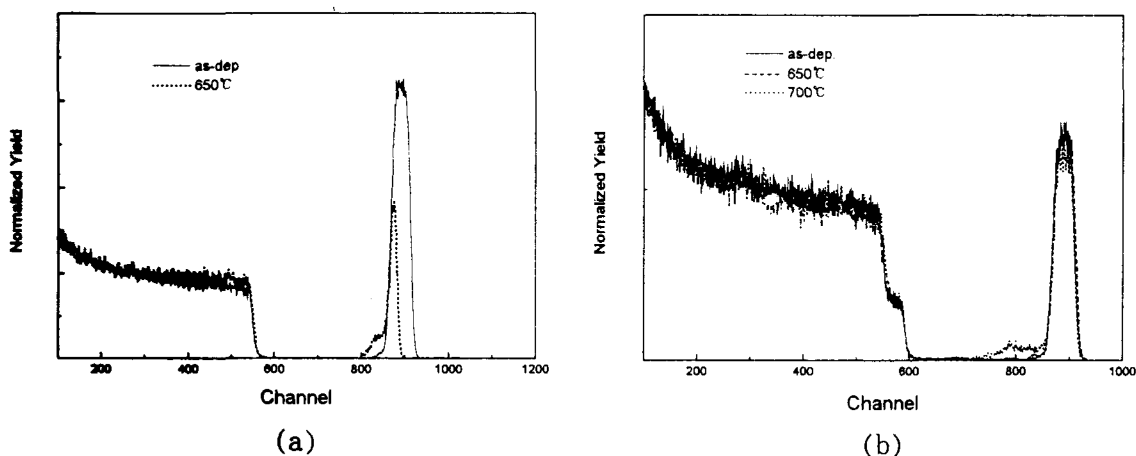

Fig. 6 Rutherford backscattering spectra of (a) Cu/Mo-N(10%)/Si and (b) Cu/Mo-Si-N(20%)/Si (after Cu Stching)

of Cu into silicon substrate through the diffusion barrier materials. Similar phenomena was observed for Mo-N(10% nitrogen) at the lower temperature of 650℃ compared to that for Mo-Si-N system as shown in Figure 6 (a). The loss of the thickness of Mo-N in Figure 6 (a) after the annealing is probably due to the etching of some of the reacted Mo-N during the Cu etching.

Figure 7 shows the XPS narrow scan data of silicon measured on Cu surfaces of the Cu/Mo-N(10% nitrogen)/Si and Cu/Mo-Si-N(20% nitrogen)/Si after removing 1000Å of Cu to investigate the diffusion of silicon to Cu through the diffusion layers. Silicon peak was observed from 700℃ for Cu/Mo-Si-N(20% nitrogen)/Si and higher silicon peak was observed at 650℃ for Cu/Mo-N(10% nitrogen)/Si. In case of Cu/$MoSi_2$/Si, the silicon peak was observed even at 300℃ (not shown).

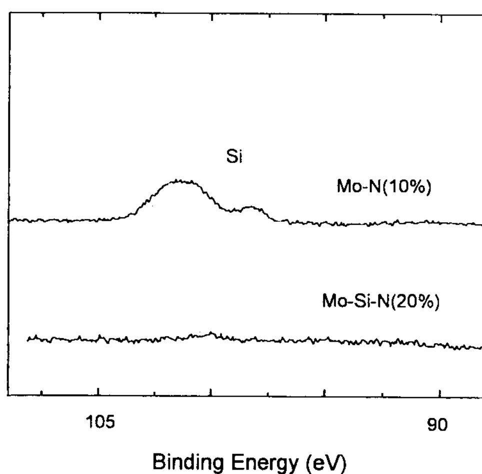

Fig. 7 XPS narrow scan data of silicon peak on Cu after 650℃ annealing for (a) Cu/Mo-N(10%)/Si and for (b) Cu/Mo-Si-N(20%)/Si

CONCLUSIONS

Characteristics of Mo-(N) and Mo-Si-(N) as the diffusion barrier materials between Cu and silicon substrate were investigated as a function of annealing temperature using XRD, sheet resistance, RBS, SEM, and XPS.

The deposited Mo-N showed Mo_2N structure and did not change its crystal structure as the annealing temperature increased to 600℃. However, the deposited Mo-Si-N showed amorphous structure and crystallized to hexagonal $MoSi_2$ as the annealing temperature increased above 700℃. In case of $MoSi_2$, phase transformation from amorphous state or hexagonal $MoSi_2$ to tetragonal $MoSi_2$ having lower resistivity was observed after the annealing above 800℃. XRD, SEM, RBS, and XPS data showed that, in case of Cu/Mo-(N)/Si, Mo-N formed by dc magnetron sputtering of the Mo target in 10% nitrogen added argon showed the best diffusion barrier properties among the investigated Mo-(N) diffusion barriers and its failure temperature was 650℃. In case of Cu/Mo-Si-(N)/Si, Mo-Si-N formed by the $MoSi_2$ target in 20% nitrogen (highest limit in our experimental condition) added argon showed the best diffusion barrier properties for all of the investigated diffusion barrier materials and its failure temperature was 700℃. The failure temperature appears to be determined by nitrogen stuffing for Mo-N and by both crystallization of amorphous state and nitrogen stuffing for Mo-Si-N.

ACKNOWLEDGMENTS

This work was supported by KOREA SCIENCE & ENGINEERING FOUNDATION.

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