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PROPERTIES OF Mo COMPOUNDS AS A DIFFUSION BARRIER BETWEEN Cu AND Si PREPARED BY CO-SPUTTERING

**Yong-Hyuk Lee, Jun-Yong Park, Jeong-Woon Bae,
and Geun-Young Yeom**

*Department of Materials Engineering, SungKyunKwan University,
Suwon, Kyunggi-do, 440-746, Korea*

Abstract

In this study, the diffusion barrier properties of 1000Å thick molybdenum compounds (Mox=1-5 Si) were investigated using sheet resistance measurements, X-ray diffractometry(XRD), and Rutherford backscattering spectrometry(RBS). Each barrier material was deposited by the dc and rf magnetron co-sputtering of Mo and Si, respectively, and annealed at 500-700℃ for 30 min in vacuum. Each barrier material was failed at low temperatures due to Cu diffusion through grain boundaries and defects of barrier thin films or through the reaction of Cu with Si within Mo-barrier thin films. It was found that Mo rich thin films were less effective than Si rich films to Cu penetration activating Cu reaction with the substrate at a temperature higher than 500℃.

1. 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 annealing[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 metallization 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 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)-6)].

In this study, the effects of Mo compounds such as Mo_xSi (x=1-5) on the diffusion barrier properties between Cu and Si were investigated. Mo compounds are not widely studied for 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)].

2. EXPERIMENT

To deposit 1000Å of Mo_xSi (x=1-5), dc and rf magnetron co-sputter deposition was used with Mo and Si sputter targets respectively in Ar environments on (100) silicon wafers after the pretreatment in a 10 : 1 HF solution. Different compositions of Mo_xSi (x=1-5) thin films were deposited by changing the dc/magnetron power and deposition time to keep constant thickness (1000Å) under a rotational substrate. In case of Cu (3000Å)/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 within 10^{-6} Torr. The deposition pressure was kept at 5mTorr with a throttle valve in Ar and Ar flow rate was kept at 10sccm. After the deposition, the samples were annealed in a vacuum from 500 to 700℃ for 30min to observe the effects of composition of Mo(x=1-5)Si on the characteristics the diffusion barrier materials.

Sheet resistance 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 diffractometry (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.

3. RESULTS AND DISCUSSION

3. 1 Mo_xSi thin film/Si

Physical and electrical properties of deposited Mo_xSi (x=1-5) thin films were studied before investigating properties as a diffusion barrier between silicon substrate and copper. Deposited Mo_xSi thin films were annealed from 500℃ to 700℃ in a vacuum for 30minutes and electrical properties of deposited and annealed Mo_xSi thin films were measured using a 4 point probe. The resistivities measured for those deposited and annealed Mo_xSi thin films are shown in Fig. 1. The deposited Mo_xSi showed high resistivity and, as the annealing temperature was increased, the resistivity was decreased. Among the deposited Mo_xSi thin films, MoSi showed the highest resistivity and, as Mo percent in Mo_xSi increased, that is, as the thin film became more Mo rich, the resistivity of the film was decreased. Similar results could be obtained for the annealed Mo_xSi thin films even though the resistivities were generally lower than deposited Mo_xSi thin films. Decrease of resistivity for Mo rich thin film is from the decrease of highly resistive silicon component in the film. However, the decrease of resistivity with increasing annealing temperature for all of MoxSi thin films is probably due to the increase

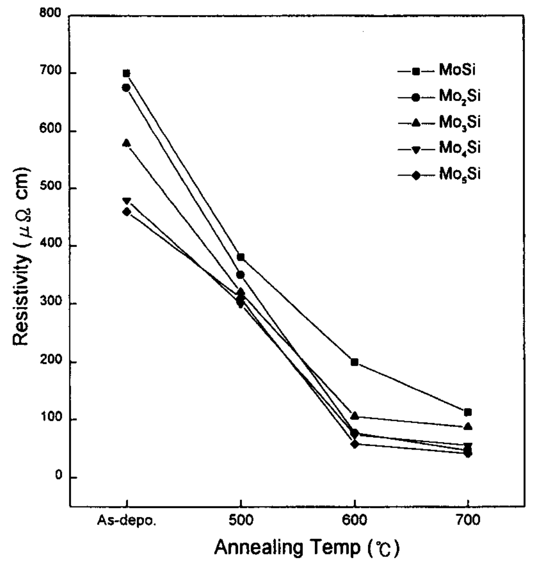


Fig. 1 Resistivity as a function of annealing temperature for Mo$_x$Si(x=1-5)

of crystallization of the films.

To study the effect of annealing on the change of the crystal structure of deposited MoxSi thin films, XRD data of deposited and annealed Mo$_3$Siwere taken and are shown in Fig. 2(a). The deposited Mo$_3$Siwas also annealed from 500℃ to 700℃ in the vacuum for 30 minutes. As shown in the figure, the deposited thin film showed the amorphous structure and, as the annealing temperature was increased, the degree of crystallization of the thin film was increased. The result was consistent with the electrical data shown in Fig. 1. Therefore, the decrease of resistivity of the films with increasing annealing temperature in Fig. 1 was originated from the increased crystallinty of the films. Crystal structures of Mo$_x$Si thin films annealed at 600℃ were also investigated using XRD and are shown in Fig. 2(b). Deposited Mo$_x$Si thin films with different composition showed different degree of crystallization and formed different stable compounds after the annealing at 600℃. Between Mo and Si, known thermodynamically stable compounds are Mo$_5$Si, Mo$_3$Si, Mo$_5$Si$_3$, MoSi$_2$, etc. and these stable compounds were formed after the annealing depending on the specific composition of the deposited Mo$_x$Si thin film. These compounds were formed

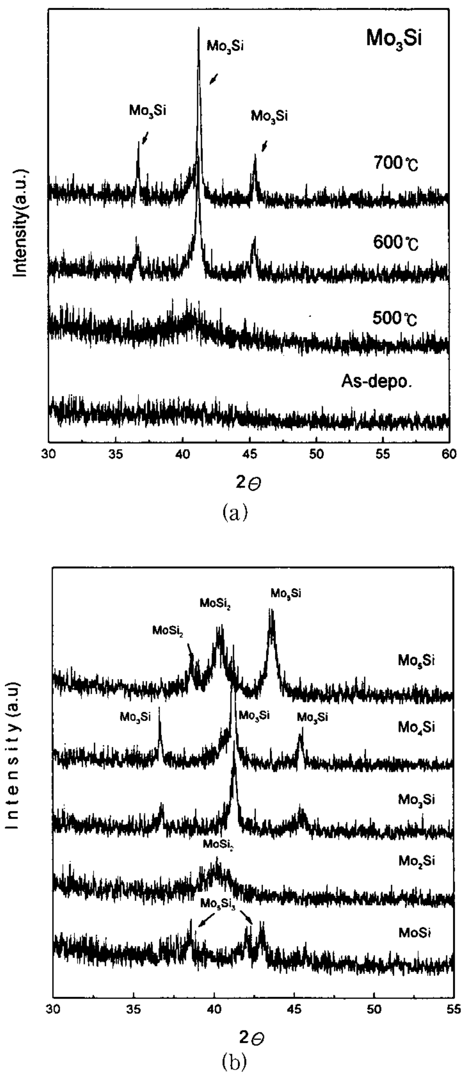


Fig. 2 XRD spectra as a function of annealing temperature for Mo$_3$Si(a) and Mo component ratio Mo$_x$Si(x=1-5) after 600℃ annealing (b).

more for the Mo$_x$Si thin film containing more Mo percent in the film. Therefore, more degree of crystallization was obtained for the Mo richer Mo$_x$Si thin film at the same annealing temperature.

3. 2 Cu/Mo$_x$Si thin fim/Si

To study the effects of above mentioned Mo$_x$Si thin films on the properties as diffusion barrier materials between Cu and silicon substrate, 3000Å Cu was deposited on the 1000Å Mo$_x$Si thin films consecutively after the deposition of Mo$_x$Si thin film on the silicon substrate. After the deposition of Cu layer, these samples were annealed from 500℃ to 700℃ in the vacuum for 30 minutes and, electrical and physical properties of these samples were investigated using 4-point probe, XRD, and RBS.

Fig. 3 shows sheet resistances of the Cu/Mo$_x$Si/Si samples as-deposited and annealed from 500℃ to 700℃. The deposited Cu/Mo$_x$Si/Si samples showed the sheet resistances of about 1.7Ω/□ and the annealing of the samples at 500℃ decreased the sheet resistances to about 0.8Ω/□. Further increase of annealing temperature, however, increased the sheet resistances drastically as shown in the figure. The drastic increase of sheet resistance shown after the annealing above 600℃ is related to the interdiffusion between Cu and silicon through the grain boundaries of Mo$_x$Si crystallized at the temperature, therefore, the formation of Cu silicides having higher resistivity. The effects of crystallization of Mo$_x$Si thin film on the effectiveness as a diffusion barrier could be confirmed by depositing Cu on the annealed Mo$_x$Si thin films, therefore, already crystallized Mo$_x$Si thin films (not shown). These diffusion barriers failed at much lower temperatures than those with deposited (that is, amorphous) Mo$_x$Si thin films shown in Fig. 3.

The decrease of sheet resistance after the annealing at 500℃ in Fig. 3 appears to be related to the crystal growth of deposited Cu and the removal of internal defects in Cu. No failure of the Mo$_x$Si diffusion barriers was observed after the annealing at 500℃ for 30 minutes. This result agrees with the XRD data of 500℃ annealed Mo3Si in Fig. 2 (a), where most of Mo3Si annealed at 500℃ appeared to remain amorphous. In case of the annealing at 600℃, the widest range of sheet resistances for different Cu/Mo$_x$Si/Si were obtained suggesting different degree of failure for different Mo$_x$Si diffusion barriers. Data were scattered, however, in general, the use of Mo richer thin film showed higher sheet resistance of Cu/Mo$_x$Si/Si after the annealing at 600℃, therefore, indicating higher degree of failure. Higher degree of failure of Mo richer thin film as

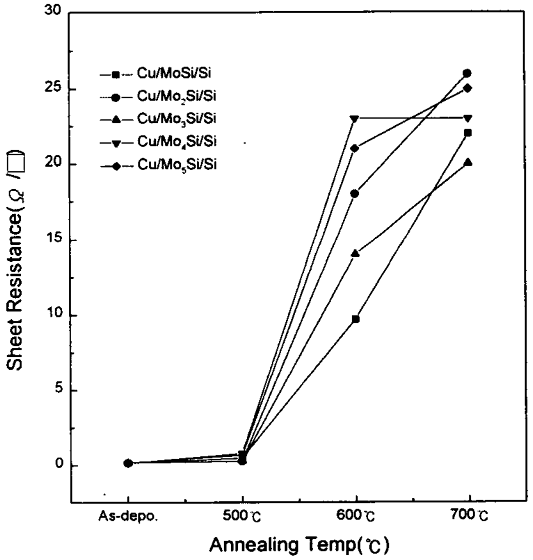


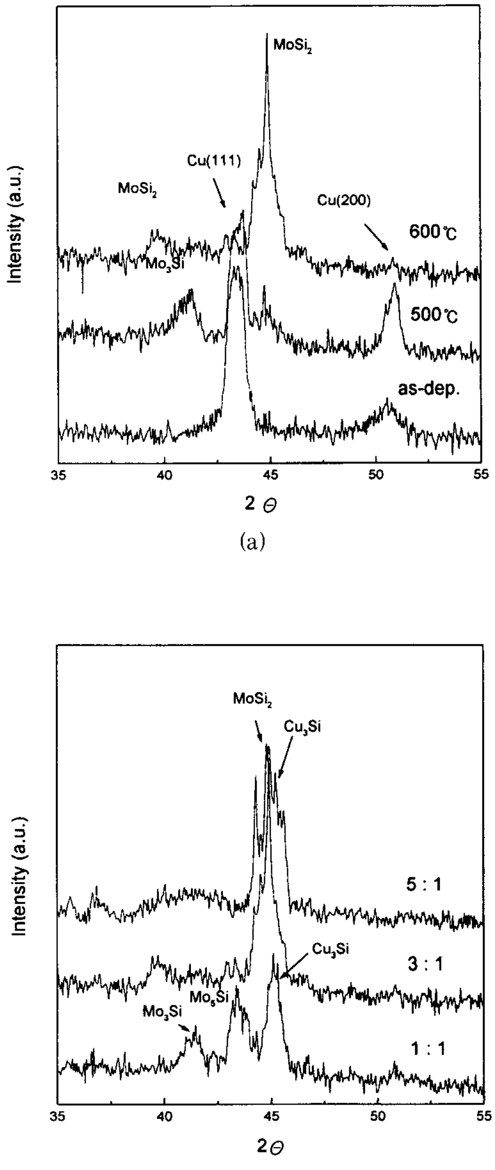
Fig. 3 Sheet resistance of Cu/Mo$_x$Si(x=1-5)/Si samples as a function of annealing temperature

the diffusion barrier appears to be also related to the higher degree of crystallization shown in Fig. 2 (b) for Mo richer Mo_xSi thin film after the annealing at 600℃.

Fig. 4 shows XRD data of (a) $Cu/Mo_3Si/Si$ measured as deposited and after annealings at 500℃ and 600℃ for 30 minutes and (b) $Cu/Mo_xSi/Si$ ($x = 1, 3, 5$) measured after the annealing at 600℃ for 30 minutes. In Fig. 4 (a), deposited $Cu/Mo_3Si/Si$ showed only Cu related XRD peaks indicating (111) preferred orientation, however, for the sample annealed at 500℃, recrystallized Cu peaks are shown, therefore, suggesting as one of the reasons for the decrease of sheet resistance after the annealing at 500℃ in Fig. 3. Almost no Cu silicide appears to form after the annealing at 500℃, however, the annealing at 600℃ showed a peak related to Cu3Si formed by the reaction between Cu and silicon, and peaks related to Mo silicides by the crystallization of Mo3Si diffusion barrier. In Fig. 4 (b), Mo richer Mo_xSi appears to form more Cu silicides and the result also agrees with the sheet resistance data in Fig. 3.

Deposited and annealed $Cu/Mo_xSi/Si$ samples were also examined uisng RBS and the results are shown in Fig. 5 (a) for $Cu/Mo_3Si/Si$ deposited and annealed at 500℃ and 600℃ for 30 minutes, and (b) for $Cu/Mo_xSi/Si$ ($x=1, 3, 5$) annealed at 600℃ for 30minutes. As shown in Fig. 5 (a), almost no Cu diffusion through Mo3Si was observed after the annealing at 500 ℃, however, after the annealing at 600℃, Cu diffused into the silicon substrate, therefore, formed a thick Cu silicide.

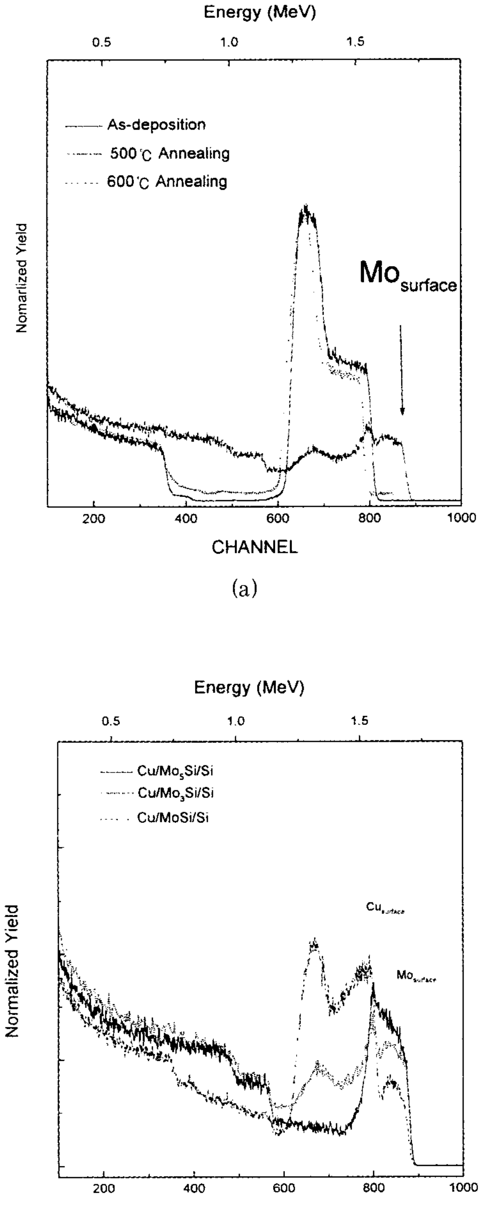
The increase of Mo in Mo_xSi also increased the diffusion of Cu into silicon through Mo_xSi, therefore, more Mo was found on the sample surface as shown in Fig. 5 (b).



(a)

(b)

Fig. 4 XRD spectra as a function of annealing temperature for $Cu/Mo_3Si/Si$ (a) and Mo component ratio $Cu/Mo_xSi(x=1\text{-}5)/Si$ after 600℃ annealing (b).



(a)

(b)

Fig. 5 RBS as a function of annealing temperature for Cu/Mo_3Si/Si (a) and Mo component ratio Cu/Mo_xSi(x=1-5)/Si after 600℃ annealing (b)

Therefore, the measured RBS data agreed well with XRD data in Fig. 4.

4. CONCLUSION

Characteristics of Mo_xSi thin films as a diffusion barrier between Cu and silicon substrate were studied as a function of annealing temperature for different Mo/Si compositions (x=1-5) using a 4-point probe, XRD, and RBS. Deposited Mo_xSi thin films showed the amorphous structure and the annealing upto 500℃ for 30minutes did not change the structure, however, the annealing equal to and above 600℃ crystallized the Mo_xSi thin films by forming thermodynamically stable Mo compounds such as Mo_3Si, Mo_5Si_3, and $MoSi_2$. The crystallization of Mo_xSi during the annealing was responsible for the failure of Cu/Mo_xSi/Si, therefore, accelerating Cu diffusion through the grain boundaries of Mo_xSi crystallized during the annealing process. If different compositions of Mo_xSi thin films are compared, Mo richer Mo_xSi thin film showed the lower resistivity, however, exhibited worse properties as a diffusion barrier between Cu and silicon, therefore, failed at the lower annealing temperature by the increased crystallization of Mo richer Mo_xSi thin films.

5. ACKNOWLEDGEMENTS

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