The effect of oxygen impurity on growth of molybdenum disilicide and its distribution during rapid thermal annealing of co-sputtered MoSi$_x$ thin films*

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Abstract

Thin films of MoSi$_x$ (with and without oxygen) were deposited by co-sputtering of molybdenum and silicon targets. As-deposited films were annealed in argon environment in the temperature range 700–1150 °C for 15–120 s. Rapid thermal annealing of oxygen-contaminated films at low temperature (700–800 °C) in an argon environment results in evolution of a mixture of MoSi$_x$, Mo$_2$Si$_y$, polycrystalline silicon and amorphous phases. Subsequent annealing at higher temperature (above 800 °C) results in further growth of Mo$_2$Si$_y$, Mo$_3$Si, and polycrystalline silicon. At 1150 °C, a 15–120 s annealing time produces successive growth of tetragonal MoSi$_2$ phase at the expense of Mo$_2$Si$_y$ and silicon. Auger electron spectroscopy depth profiles of annealed films indicate the accumulation of oxygen impurity at the MoSi$_x$–Si (crystalline) interface, which is initially distributed uniformly throughout the MoSi$_x$ matrix. However, oxygen-free MoSi$_x$ films do exhibit the growth of MoSi$_2$ (both tetragonal and hexagonal) during rapid thermal annealing up to 1050 °C. At higher temperature (1150 °C) a single-phase MoSi$_2$ (tetragonal) is observed. The surface morphology of oxygen-free annealed films reveals a uniform distribution of silicide grains as compared with oxygen-containing films. The sheet resistance of the finally annealed films (1150 °C and 120 s) was found to be 9.5 Ω/□ for oxygen-contaminated films and 7.6 Ω/□ for oxygen-free films.

1. Introduction

The quest for smaller dimensions and a higher level of integration in semiconductor devices has posed several unprecedented complexities in the design and fabrication of very-large-scale integrated circuits (VLSIC). The search to replace aluminum and polysilicon at gate level, interconnection and metallization has finally resulted in the development of metallization schemes based on refractory metals and refractory metal silicides. Successful incorporation of refractory metal and refractory metal silicides has allowed the speed, density and reliability of these devices to be enhanced [1, 2]. Silicides are normally used as interconnection, shallow contact and gate metallization materials in VLSIC. The most desirable features of silicides for incorporation in VLSIC are processing compatibility in metal–oxide–semiconductor (MOS) device processing, low resistivity for interconnections, contacts and gate metallization, high thermal stability, good chemical resistivity and fine line patternability. However, the reproducibility and integrity of the silicides are highly desirable for reliability and high yield of MOS devices. In the past, codeposition of silicides has been found to be attractive for the proposed applications as it offers improved and reproducible properties of silicides. At present, codeposition of silicides followed by rapid thermal annealing (RTA) has further improved the quality and integrity of the silicides [3, 4]. These processing steps have overcome most of the problems associated with the conventional silicide formation process of metal/silicon or (metal–silicon)/silicon or (metal–silicon)/silicon dioxide followed by furnace annealing.

Because silicides are scientific and technologically strategic materials, it is desirable to understand their growth process, metallurgical interaction, structural transformation and electrical characteristics. In addition, it is desirable to understand the effect of impurities such as oxygen, carbon and nitrogen on the above properties. The role of impurities such as oxygen (which is a movable impurity) has been found to be catastrophic on the growth and surface morphology of silicides and directly affects the above properties [5]. The effect of oxygen impurity is well understood in planar metal/silicon systems for most of the refractory
metal/transition metal silicides [5-7]. This has been explained on the basis of thermodynamic considerations (e.g., free energy of formation of oxides). However, the effect of oxygen on structural transformation, surface morphology and its distribution during RTA has not been studied in most of the codeposited silicides. Similar to metal/silicon planar systems, in codeposited multilayer metal–silicon systems, oxygen is expected to play a decisive role in determining the first phase nucleation, metallurgical interaction, surface morphology, and electrical properties depending on the concentration of impurity. However, the extent and the nature of influence is not very clear in the RTA process, as there might be some differences in growth kinetics—nucleation of silicides because of the very short time and dynamic nature of annealing.

In this paper, we present the effect of oxygen on structural transformation, surface morphology and electrical properties and its distribution during RTA of co-sputtered MoSi$_2$ thin films, as well as a comparison with oxygen-free films.

2. Experimental details

Thin films of MoSi$_2$ were deposited by co-sputtering of high purity molybdenum (99.999%) and silicon (99.999%) targets on (i) 5–7 $\Omega$ cm resistivity, phosphorus-doped n-type Si(100), (ii) polycrystalline silicon (polysilicon)/Si(100) (polysilicon deposited by low pressure chemical vapor deposition) and (iii) thermally grown SiO$_2$/Si(100) substrates. The silicon and polysilicon substrates were cleaned ultrasonically in electronic grade trichloroethylene and acetone, and dipped in buffered hydrofluoric acid (1% HF) for 2 min. Finally, they were rinsed ultrasonically in deionized water and dried with dry nitrogen before loading into the chamber. SiO$_2$/Si(100) substrates were cleaned by dipping in buffered hydrofluoric acid (1% HF) for 2 min and rinsing in deionized water. The chamber was pumped to $8 \times 10^{-4}$ mbar by an oil diffusion pump. This level of vacuum allowed us to introduce the desired concentration of oxygen contamination in the films. Before sputtering, the chamber was bled with argon gas for 20 min. A pre-sputtering was performed for 15 min to clean the targets. During sputtering, the partial pressure of argon gas was maintained at $2 \times 10^{-2}$ mbar. The distance between the substrate and the target was kept at about 5 cm. During deposition, the substrates were rotated with a speed of 20 rev min$^{-1}$. The thickness of each layer of molybdenum and silicon is expected to be 3–5 Å and 8–12 Å respectively. These thicknesses have been estimated from the deposition rate and the time that the substrate stayed below the target during deposition in one rotation. A schematic diagram of the sputtering system is shown in Fig. 1. The total thickness of as-deposited films, as measured with a Talystep instrument (Taylor-Hobson, UK), was found to be 1000 Å. Another set of samples was prepared using similar deposition conditions except that the ultimate

![Diagram](image-url)

Fig. 1. A schematic diagram of a dual magnetron sputter deposition system.
vacuum was $1 \times 10^{-6}$ mbar. Such a low pressure during compositional analysis revealed an oxygen contamination of 1–2 at.% or less, which is within the detection limit of the Auger electron spectroscopy (AES) system. The as-deposited samples were annealed in an argon environment by an RTA system (AG Associates, model-210 T) in the temperature range 700–1150 °C for 15–120 s. The compositional analysis of these films was performed with a scanning Auger microprobe (model PHI-590). AES depth profile measurements were taken at an accelerating electron beam voltage of 3 kV, a beam current of 10 μA and a modulation voltage of 3 V. The samples were sputtered using Ar$^+$ ions of energy 1 kV rastered over an area of 1 mm × 1 mm. The argon ion gun was calibrated against a standard sample of Ta$_2$O$_5$ of known thickness. Therefore, the sputtered thicknesses of our samples in the present paper are with respect to Ta$_2$O$_5$. The sputter rate for MoSi$_2$ was found to be about 110 Å min$^{-1}$ with respect to Ta$_2$O$_5$. Before the actual data were recorded, the films were sputter cleaned for 1–2 min to avoid contributions from any contamination adsorbed on the surface during exposure to the environment. The crystallographic structure during subsequent annealing
was determined by glancing angle X-ray diffraction (XRD) using Rigaku's rotating anode X-ray diffractometer (model: Geigerflex, D-Max RU-200 B) with a Cu Kα (λ = 1.54 Å) source. During XRD, the sample was fixed at glancing angle α = 5°, while 2θ was scanned between 20° and 90°. In order to find the preferred orientation during the growth of MoSi₂, the sample was rotated along the axis perpendicular to its surface. XRD measurements were taken at a scanning rate of 10° min⁻¹ at accelerating voltage of 40 kV and a current of 120 mA. The sheet resistance of as-deposited and annealed films was measured using a linear four-probe method.

3. Results and discussion

3.1. Structural and compositional analysis

Figure 2 shows the XRD spectra of as-deposited and annealed MoSi₂, films with oxygen contamination. The XRD spectrum of the as-deposited film reveals the presence of an amorphous phase, indicating the existence of very fine grains (Fig. 2(a)). Compositional analysis of as-deposited samples as observed by AES depth profile measurements results in a composition close to 33:67 Mo:Si. The distribution of molybdenum and silicon during deposition is found to be quite uniform (Fig. 3(a)). Annealing of oxygen-contaminated
films at 700 and 800 °C by rapid thermal processing in an argon atmosphere for 30–60 s results in the evolution of a mixture of silicon-rich phase $\text{MoSi}_2$ (both hexagonal and tetragonal) and metal-rich phase $\text{Mo}_3\text{Si}_2$ (Figs. 2(b) and 2(e)). In addition to these phases, the growth of polycrystalline silicon is also observed. XRD spectra of oxygen-contaminated films annealed at 950 °C for 30–120 s show the continuous growth of $\text{Mo}_3\text{Si}_2$, $\text{MoSi}_2$, and polysilicon. However, at 1050 °C enhanced growth of $\text{MoSi}_2$ and silicon phases is observed (Fig. 4). The growth of $\text{MoSi}_2$ occurs at the expense of metal-rich phase $\text{Mo}_3\text{Si}_2$ and silicon, while the growth of silicon is due to recrystallization of polycrystalline silicon grains. An AES depth profile of the samples annealed at 1050 °C is shown in Fig. 3(b). The AES depth profile indicates the movement of oxygen during annealing towards the $\text{MoSi}_2$–Si(100) interface. Figure 5 shows the XRD spectra of $\text{MoSi}_2$ films annealed at 1150 °C for 15–120 s. The spectra show successive growth of the $\text{MoSi}_2$ phase. After 15 s of annealing, the peaks corresponding to the dominant phase $\text{MoSi}_2$ (tetragonal phase) are observed. The growth occurs at the expense of metal-rich $\text{Mo}_3\text{Si}_2$ and silicon. The spectra at successive annealing times show the diminishing intensity of $\text{Mo}_3\text{Si}_2$ and silicon. After 120 s of annealing time, only single-phase $\text{MoSi}_2$ (tetragonal) is observed. Further
growth of MoSi$_2$ at longer annealing times occurs as a result of interaction of Mo$_2$Si$_3$ and polycrystalline silicon. An AES depth profile of the sample annealed at 1150 °C for 120 s shows the accumulation of oxygen at the interface (Fig. 3(c)). Similar results of the same composition were observed on SiO$_2$ and polysilicon substrates.

To compare the growth behavior of oxygen-contaminated films with that of oxygen-free films, similar annealing experiments were performed for oxygen-free films in an argon environment. Figure 6 shows the XRD spectra of the as-deposited and annealed samples. As-deposited samples are amorphous. The corresponding compositional analysis is given in Fig. 7(a). Annealing of these films at low temperature (800 °C or less) results in a mixture of MoSi$_2$ (both hexagonal and tetragonal) and amorphous phases. The MoSi$_2$ (hexagonal) phase is a low temperature phase and is transformed to the tetragonal phase at high temperature. The growth of MoSi$_2$ (both hexagonal and tetragonal) is continued up to 1050 °C. Figure 8 shows the XRD spectra of MoSi$_2$ films at 950 °C. However, at 1150 °C a single-phase MoSi$_2$ (tetragonal) is observed (Fig. 9). Figure 7(b) shows the AES depth profile of MoSi$_2$ films annealed at 1050 °C for 60 s. In these investigations, similar results were obtained on SiO$_2$ and polysilicon substrates. However, a variation in the XRD peak intensities was observed, indicating preferential growth for certain planes during annealing.

It has been reported that small amounts of impurities such as oxygen play a very important role in determining the phase formation—nucleation of silicides in a metal/
Fig. 8. XRD spectra of oxygen-free MoSi₂ films annealed at 950 °C for 15, 30, 60, 90 and 120 s.

silicon binary system. In Mo/Si or W/Si bilayer structures, the impurity, which is present either at the interface or within the metal film deposited on silicon, moves towards the interface during annealing [8, 9]. The movement of oxygen starts thickening the silicon oxide layer at the interface, which inhibits the diffusion of silicon required for the formation of silicide. However, the thickness of the interfacial layer is crucial and may cause the growth of a mixture of metal-rich phases together with the silicon-rich phase MoSi₂ (M = Mo or W). These investigations have been reported by several workers [8–10]. Thus, for example, in Mo/Si system, the growth of Mo₂Si₂ and Mo₅Si phases is expected to occur together with that of MoSi₂ and will depend on the thickness of the interfacial oxide layer. Thermodynamic and kinetic data on the MoO₃ and SiO₂ systems also suggest that the reaction between molybdenum and SiO₂ is not favorable because of the large difference in free energy of formation. Heats of formation for MoO₃ and SiO₂ are 40.3 kcal (g atom)⁻¹ and 80.2 kcal (g atom)⁻¹ respectively. In the present co-sputtered MoSiₓ films, there are alternating thin layers of molybdenum and silicon. These thin layers are expected to be discontinuous. The oxygen impurity in these films is expected to be bonded to silicon forming SiOₓ, instead of to molybdenum, which is explicit from thermodynamic data. During annealing, this SiOₓ layer acts as a diffusion barrier for the reaction between molybdenum and silicon. Bonding of oxygen with silicon slows down the reaction between molybdenum and silicon thin layers. This has also been observed in TaSi₃ formation by RTA of an evaporated multilayer structure of tantalum and silicon [11, 12]. The layer thickness of tantalum was varied from 100 Å to 150 Å, while the silicon layer thickness was varied according to the desired composition of tantalum and silicon. In oxygen-contaminated multilayer stacks, oxygen was found to be bonded with tantalum in as-deposited films as observed by XPS investigations. On annealing, tantalum oxide (substoichiometric) reacts with silicon to form SiOₓ (X ≤ 2) and slows the reaction.
of tantalum and silicon layers as observed by AES depth profile analysis. In our films, oxygen contamination is 6–7 at.% and is distributed uniformly. At low temperature, the growth of Mo$_2$Si$_3$, Mo$_5$Si$_3$ and silicon occurs as a result of slow reaction between molybdenum and silicon due to the presence of oxygen. Polysilicon grains (as a result of recrystallization) are distributed in Mo$_2$Si$_3$ and Mo$_5$Si$_3$ matrix. A schematic diagram of the possible reaction process is given in Fig. 10. At high temperature (1150 °C), the oxide layer is broken—dissociated and helps in further reaction of Mo$_2$Si$_3$ and silicon to form Mo$_5$Si$_3$. In addition, there could be a possibility of silicon diffusion from the bulk silicon as a result of higher annealing temperature and time. The reaction could be presented as follows:

$$\text{Mo} + \text{Si} \xrightarrow{\text{low temperature}} \text{Mo}_2\text{Si}_3 + \text{Mo}_5\text{Si}_3$$

and

$$\text{Mo}_2\text{Si}_3 + \text{Si} \xrightarrow{\text{high temperature}} \text{Mo}_5\text{Si}_3$$

The oxygen, which is debonded during the reaction, moves towards the interface and is accumulated. However, a trace amount of oxygen is distributed in Mo$_5$Si$_3$ matrix.

3.2. Surface morphology

Surface morphology of as-deposited films with and without oxygen contamination do not show any features. Figure 11 shows the surface morphology of oxygen-contaminated films annealed at 1150 °C (Fig. 11(a)) and oxygen-free films annealed at 1150 °C (Fig. 11(b)). Oxygen-free films do exhibit a more uniform distribution of grains than oxygen-contaminated films. Oxygen-contaminated films reveal the effect of impurities resulting in a non-uniform reaction and surface morphology. It
has been observed that codeposition of co-sputtered oxygen-free MoSi$_x$ ($x > 2$) and other refractory metal silicides results in a more uniform and significantly improved surface morphology [13, 14].

3.3. Electrical properties

As-deposited oxygen-contaminated and oxygen-free films appeared to be shiny. The sheet resistance of as-deposited and annealed films is shown in Fig. 12. The high sheet resistance of these films is attributed to high silicon content, impurities and defects. At 800 °C, a sharp drop in sheet resistance is attributed to slow crystallization-growth and, hence, increased grain size. On further increasing the annealing temperature, the sheet resistance drops monotonically and reaches a minimum value of 11.2 $\Omega/\square$ and 10.7 $\Omega/\square$ respectively for oxygen-contaminated and oxygen-free films. The sheet resistance 11.2 $\Omega/\square$ corresponds to a mixture of Mo$_3$Si$_2$, MoSi$_2$ and Si, while 10.7 $\Omega/\square$ corresponds to single-phase MoSi$_2$. The final values of the sheet resistance for the two sets, i.e. oxygen-contaminated and oxygen-free compositions, are 9.5 $\Omega/\square$ and 7.6 $\Omega/\square$ respectively at 1150 °C and after a 120 s annealing time.

4. Conclusions

(a) The effect of oxygen impurity in co-sputtered MoSi$_x$ thin films has been investigated during RTA in...
an argon environment. Low temperature annealing (800 °C or less) results in the formation of a mixture of (i) silicon-rich MoSi$_2$, (ii) molybdenum-rich Mo$_2$Si$_3$, (iii) polycrystalline silicon and (iv) amorphous phases. At high temperature (1150 °C), single-phase MoSi$_2$ is obtained at the expense of silicon and molybdenum-rich phase. The growth of a mixture of phases is assigned to the oxygen impurity, possibly bonded to silicon to form SiO$_2$, which acts as a temporary barrier for the reaction of molybdenum and silicon layers. During the reaction, dissociated oxygen moves towards the interface and is accumulated there. However, oxygen-free films do display the growth of MoSi$_2$ at all reaction temperatures.

(b) The surface morphology of oxygen-contaminated films was found to be non-uniform as compared with that of oxygen-free films as a result of non-uniform reaction due to presence of oxygen.

(c) The sheet resistance of oxygen-contaminated films was observed to be 9.5 $\Omega/\square$, while that of oxygen-free films was 7.6 $\Omega/\square$.

References