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Mo-Silicides Bias-Sputtering and Its Application to Thermally-Stable, Via-Hole-Filled Contact Formation

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Thermally-stable via-hole-filled MoSix/Si contacts have been developed by two-step bias sputtering with a $MoSi_4$ target, which produced the best result among $MoSi_4$, $MoSi_{2.7}$ and $MoSi_2$ targets. The Si/Mo composition ratio decreased with increasing substrate bias voltage. No peeling occurred in the low-stress-MoSix/Si contacts fabricated using the $MoSi_4$ target. Contact resistivities for MoSix/n^+-Si and /p^+-Si were $1{\sim}2\times10^{-5}\Omega\cdot cm^2$, after 900°C annealing for 60 minutes. It was found that the stoichiometric or Si-rich silicide films are desirable as a contact material.

1. Introduction

The advance in VLSI technology and the advent of three dimensional LSIs have created a need for thermally-stable planarized interconnections. Such interconnections are required to be stable at up to 900°C~1000°C process temperature for PSG or BPSG flow, ion-implanted dopant activation and SOI recrystallization. It was reported that $10^{-5}{\sim}10^{-6}\Omega\cdot cm^2$ contact resistivity (ρ_c) was obtained after high temperature annealing in W/TiN/TiSix/Si contact structures[1),2)]. However, silicidation reaction between W and Si was not completely suppressed, although the TiN barrier layer was used in such structures[2)]. On the other hand, in a refractory-metal-silicide/Si contact structure, a higher thermal stability can be expected, even without a barrier layer, because little or no silicidation reaction can take place in this structure.

Bias sputtering has a unique feature, wherein both interconnect film deposition and via-hole filling are achieved on a substrate simultaneously[3),4)]. The authors demonstrated such a feature for Mo deposition[3)]. High reliability and simple contact formation process were expected in achieving a via-hole-filled contact fabricated by bias sputtering. However, there have been few reports published regarding metal-silicide deposition by bias sputtering. This paper reports Mo-silicides bias sputtering and its application to thermally-stable, via-hole-filled contact formation.

2. Experiment

MoSix films were deposited by a planar RF magnetron bias sputtering system with a hot-pressed Mo-silicide target. Mo-silicide target compositions were $MoSi_4$, $MoSi_{2.7}$ and $MoSi_2$. The substrate temperature before the sputtering was 200°C. The substrate heater was turned off during the sputtering.

The composition for MoSix films was measured by XMA. The stress in films was measured by Newton's rings method. The cross section of via-holes with deposited

MoSix was observed by SEM. The contact resistance was measured using the four-probe technique. The atomic concentration depth profile was measured by SIMS.

3. Results

3.1 MoSix film composition and stress

Figure 1 shows that the Si/Mo composition ratio decreases with increasing substrate bias voltage (V_{sub}). This means that the Si re-sputtering rate on the substrate is higher than the Mo re-sputtering rate. Figure 2 shows the film stress dependence on V_{sub}. Compressive stress in a film deposited with the $MoSi_4$ target decreased with increasing $|V_{sub}|$, while the stress with the $MoSi_{2.7}$ or the $MoSi_2$ target increased to high values with increasing $|V_{sub}|$.

3.2 Via-hole-filling with Mo-silicide

Figure 3 shows a cross sectional SEM micrograph of a via-hole filled with MoSix by the two-step bias sputtering technique, in which, after a thin film deposition at a low V_{sub} value, the via-hole was filled at a high V_{sub} value. This technique was used to protect a Si substrate from resputtering at the high V_{sub} value. The via-hole was filled without sputter-induced trenches in the Si substrate and the MoSix surface was planarized.

3.3 Dopant diffusivity in MoSix films

Since the dopant out-diffusion from Si to MoSix is one of the reasons ρ_c increase was induced by high temperature annealing, it is important to investigate dopant diffusivity at high temperature in MoSix films. Figure 4 shows As depth profiles in MoSix. As was doped by ion-implantation under 180keV, $2\times10^{-16}cm^{-2}$ condition. From these profiles, As diffusivities at 900°C for the $MoSi_{0.4}/MoSi_{1.5}$ film, deposited from an $MoSi_2$ target, and the $MoSi_{1.5}/MoSi_{2.8}$ film, deposited from an $MoSi_{2.7}$ target, were estimated to be $10^{-14}\sim10^{-15}cm^2/sec$ and over $10^{-10}\sim10^{-11}cm^2/sec$, respectively. B diffusivity dependence on the film composition was similar to As diffusivity dependence.

3.4 MoSix/Si contact resistivity

MoSix/Si contacts were fabricated with $MoSi_4$, $MoSi_{2.7}$ and $MoSi_2$ targets by the two-step bias sputtering technique. Mo silicide was deposited to a 0.1µm thickness at −100V V_{sub} in the first step and to a 0.4µm thickness at −500V V_{sub} in the second step. Table 1 shows the contact resistivity (ρ_c) for such contacts. The lowest ρ_c values for the MoSix/n^+-Si contact and /p^+-Si contact, fabricated with an $MoSi_4$ target, were $1\sim2\times10^{-5}\Omega\cdot cm^2$ after annealing at 900°C for 60 minutes. On the other hand, the ρ_c values for the $MoSi_{2.7}$ and the $MoSi_2$ targets became extremely high after annealing at 900°C.

4. Discussion

It is important to know As concentration distribution in the MoSix/Si structure, because high As concentration in Si near the MoSix/Si interface is needed to maintain low contact resistivity. Figure 7 shows depth profiles for As, Mo and Si concentrations obtained from SIMS, before and after annealing, for the $MoSi_{1.5}$(0.4µm) /$MoSi_{2.9}$(0.1µm)/n^+-Si sample (sample (a)) and the $MoSi_{1.6}$(0.4µm)/$MoSi_{4.4}$(0.1µm)/n^+-Si sample (sample (b)). In sample (a) after annealing, the MoSix/Si interface moves into the Si substrate and As diffuses from the Si substrate to the MoSix film. The MoSix/Si interface movement is due to silicidation reaction between MoSix(x<2) and Si. Low dopant diffusivity in Mo-rich silicide was lost because this reaction made a stoichiometric silicide film of the Mo-rich silicide film. This leads to a low As concentration near the new MoSix/Si interface after annealing, as shown in Figure 5. On the other hand, in sample (b) after annealing, As diffuses from the Si substrate to the MoSix film. However, the MoSix/Si interface does not move. The moderate decrease in the As concentration near the MoSix/Si interface after annealing results from simple-thermal dopant out-diffusion. The relation between the MoSix/Si interface movement and the composition for MoSix films in the MoSix/p^+-Si structure is similar to that in the MoSix/n^+-Si structure. The silicidation reaction in Mo-rich silicide/Si contact might cause p-n junction degradation or even spiking. However, such critical failure is not expected in stoichiometric or Si-rich silicide/Si contact. Therefore, stoichiometoric or Si-rich silicide films are desirable as a contact material.

Mo-silicide films peeling was observed in contacts fabricated using $MoSi_{2.7}$ and $MoSi_2$ targets, but no peeling occurred for the $MoSi_4$ target. Such differences are attributed to the differences in the stress values for MoSix films, as shown in Fig. 2. To avoid the MoSix films peeling, a $MoSi_4$ target is desirable in contacts fabrication.

5. Conclusion

MoSix film deposition and thermally-stable MoSix/Si contacts fabrication by bias sputtering have been investigated. It was found that the Si/Mo composition ratio for the MoSix films decreased with increasing $|V_{sub}|$ and that the MoSix film stress depended on the target composition and V_{sub}. Via-hole filling with Mo-silicide was accomplished by two-step bias sputtering. Thermal stability, up to 900°C, was realized in such via-hole-filled-MoSix/Si contacts fabricated by two-step bias sputter-deposition, using an $MoSi_4$ target.

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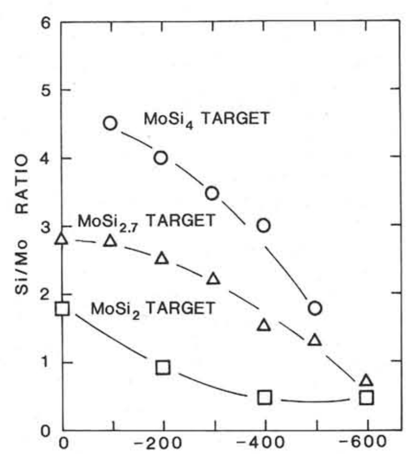


Fig.1 Si/Mo ratio for films as a function of substrate bias voltage.

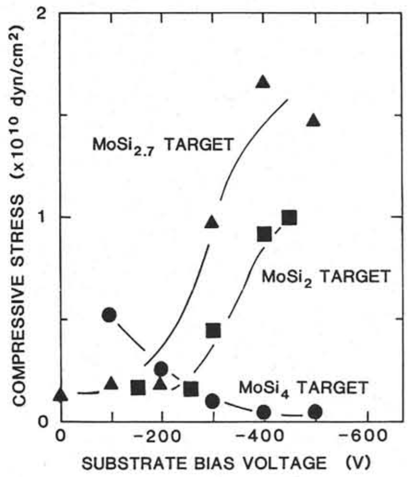


Fig.2 Film stress as a function of substrate bias voltage.

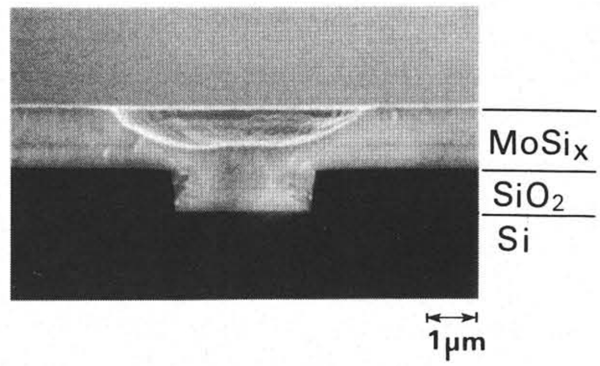


Fig.3 Cross sectional SEM micrograph of a via-hole filled with Mo-silicide by two-step bias sputtering. 1st step: 0.4μm deposition at −100V V_{sub}. 2nd step: 0.85μm deposition at −600V V_{sub}.

SAMPLE STRUCTURE			ρ_c ($\Omega\cdot cm^2$)	ρ_c ($\Omega\cdot cm^2$)
SUBSTRATE	TARGET	DEPOSITED FILM 1st/2nd	AS DEPOSITED	ANNEALED 900C,60min
n^+-Si	$MoSi_4$	$MoSi_{4.4}$ $MoSi_{1.6}$	4×10^{-6}	2×10^{-5}
	$MoSi_{2.7}$	$MoSi_{2.8}$ $MoSi_{1.5}$	8×10^{-7}	8×10^{-3}
	$MoSi_2$	$MoSi_{1.5}$ $MoSi_{0.4}$	1×10^{-6}	1×10^{-3}
p^+-Si	$MoSi_4$	$MoSi_{4.4}$ $MoSi_{1.6}$	2×10^{-6}	1×10^{-5}
	$MoSi_{2.7}$	$MoSi_{2.8}$ $MoSi_{1.5}$	2×10^{-6}	2×10^{-1}
	$MoSi_2$	$MoSi_{1.5}$ $MoSi_{0.4}$	6×10^{-5}	1×10^{-3}

Table 1 Contact resistivity for MoSix/Si contacts before and after annealing. MoSix films were deposited with $MoSi_4$, $MoSi_{2.7}$ and $MoSi_2$ target by two-step bias sputtering.

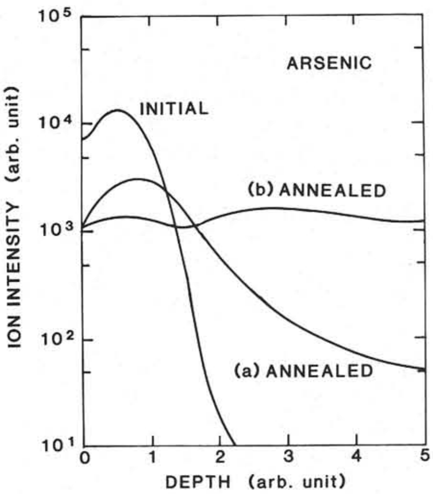
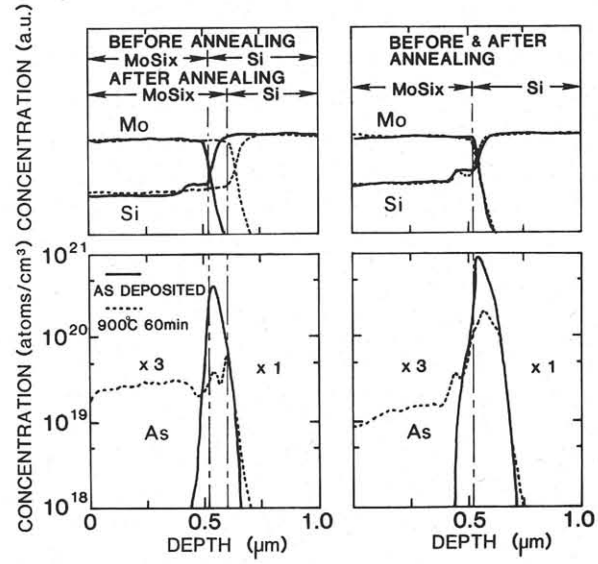


Fig.4 Arsenic depth profiles in Mo-silicide film, before and after annealing. (a) Depth profile in $MoSi_{0.4}/MoSi_{1.5}$ after annealing at 900°C for 30 minutes. (b) Depth profile in $MoSi_{1.5}/MoSi_{2.8}$ after annealing at 900°C for 60 minutes.



(a) (b)

Fig.5 As, Mo and Si depth profiles in MoSix/n^+-Si structure, measured by SIMS, before and after 900°C annealing for 60 minutes.
(a) $MoSi_{1.5}/MoSi_{2.8}/n^+$-Si
(b) $MoSi_{1.6}/MoSi_{4.4}/n^+$-Si