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Preparation Optimization of $CoSi_x$ Anti-Oxidation Barrier Layer for ULSI-Cu Metallization*

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Abstract: In order to get Co(W,P) film with better anti-oxidation performance, a silicidation process design of cobalt layer using SiH_4 or Si_2H_6 is proposed. Throughout the silicidation process there is competition between Si diffusion in the Co and Cu out-diffusion through the Co. It is necessary to quantify the diffusion rates in order to realize a better silicidation effect. The diffusivities of Cu and Si in Co are examined via X-ray photoelectron spectroscopy depth profile to get some useful data for obtaining the best process sequence. On the basis of analysis of the diffusion process, the optimized region can be plotted and the anti-oxidation performance of CoSi film as verified by experiments of chemical vapor deposition of the silicidation reaction in the optimized region is improved significantly over the non-optimized process.

Key words: CoSi barrier film; hydrogen annealing; silicidation; diffusion; process optimization; anti-oxidation performance
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1 Introduction

In the development of ultra-large scale integrated circuits, improvements in speed and functionality are driven by the decreasing of the resistance-capacitance (RC) delay time of interconnect schemes.[1] In order to decrease the RC delay time, aluminum metallization is replaced by copper (Cu) metallization due to its lower resistivity. But Cu is easily oxidized and diffused. Silicon nitride (SiN_x) is most commonly used as anti-oxidation dielectric layers at present, but while it has good anti-oxidation performance, its high dielectric constant makes a long delay time and thus decreases the working speed. One approach to overcome this disadvantage is to replace SiN_x layer with a conductive barrier layer, such as cobalt-tungsten-phosphorous (Co(W,P)) or other cobalt- or nickel- alloys.[2~5] Since silicide materials often have a high anti-oxidation property by forming silicon oxide layer during oxidation and CoSi has high chemical stability,[6,7] silicidation of the layer might improve the anti-oxidation performance of a cobalt-based alloy layer.

One-step silicidation can be realized without requiring any etch-back or chemical-mechanical polishing processes if selective silicidation of a Co-based alloy layer can be achieved and shown in Ref.[8]. CoSi materials have been studied by different authors as reviewed in different papers,[8~10] and a low temperature preparation process is recommended for applying this material in ULSI-Cu metallization. In our previous work,[11] the reaction of Co with 5% (vol.) SiH_4/H_2 and with 1.2% (vol.) Si_2H_6/H_2 at 400Pa at lower temperatures (200~300℃) has been examined to realize the selective silicidation of Co without Si deposition on SiO_2 surfaces. Although the anti-oxidation performance of CoSi film after silicidation has been improved to some degree, the problem remains that Cu diffuses out to the surface during the silicidation process and the increasing amount of Cu in the surface leads to the

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breakdown of anti-oxidation performance of CoSi film. In order to avoid the diffusion of Cu and get better anti-oxidation, the competition between Si diffusion into Co and Cu out-diffusion through Co should be paid attention and the diffusion rate of Cu and Si in Co should be quantified. High temperature and long annealing time are necessary for obtaining a better silicidation layer, but these perhaps aggravate the diffusion of Cu out to the surface. Cu diffusion may come from the long hydrogen annealing of 20min. Therefore the whole process must be optimized to keep the balance of preparing Co-Si films and avoiding Cu diffusion. In this work our purpose is to investigate and find the optimized condition for getting better combined effect of good hydrogen annealing reduction effect, no Cu diffusion, and a better silicide Co layer. For this purpose some relevant experiments on hydrogen annealing and Cu diffusion in Co and Si diffusion in Co have been done by using rapid thermal annealing (RTA) and relative XPS surface and depth analysis results. The optimized process and obtained optimized region can supply some useful information for the preparation of Co-Si anti-oxidation barrier films.

2 Experiments

Magnetron sputtered Co(40nm)/TiN (100nm)/Si substrate samples were used to do the hydrogen annealing experiments from 200 to 320℃ for different times in the RTA reactor. The elemental composition of the surfaces were examined using ex-situ X-ray photoelectron spectroscopy (XPS, ULVAC PHI 1600), and the ratio of metallic Co and whole (Co + CoO) was calculated from the XPS surface analysis results. Sputtered Co(40nm)/Cu(40nm)/TiN(100nm)/Si and Si (40nm)/Cu(40nm)/TiN(100nm)/Si substrate were used, respectively, to measure Cu and Si diffusion in the Co during hydrogen annealing from 250 to 320℃ for 5min. Diffusion depths were calculated from XPS depth analysis results. Sputtered Co(40nm)/ Cu(40nm)/TiN(100nm)/Si substrate samples were used to realize Co silicidation experiments in a cold-wall thermal CVD reactor with 1.2% (vol.) Si_2H_6/H_2 premixed gases. The base pressure of all the experiments was 1×10^{-5} Pa, and the whole working pressure of all the experiments was 400Pa.

3 Results and discussion

3.1 Design of whole process

The whole preparation process can be designed as shown in Fig. 1. The oxide Co of the surface can be reduced through step 1 of hydrogen annealing, and silicidation reaction can be realized by step 2. The question that must be resolved is in which region can steps 1 and 2 supply better anti-oxidation and no Cu diffusion of the silicide sample.

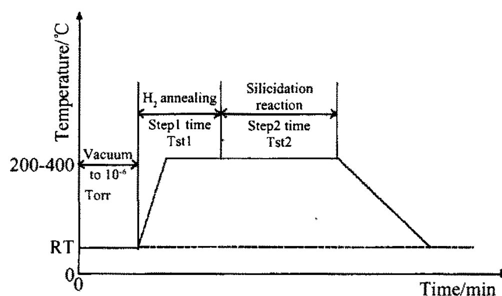

Fig. 1 Sequence of the whole process

In order to find the optimum region of the whole preparation process, some relevant experiments on hydrogen annealing and Cu diffusion in Co and Si diffusion in Co were done and researched by using RTA and the relative XPS surface and depth analysis results. From the results, a better hydrogen annealing reduction effect region can be obtained, diffusion coefficients of Cu in Co and Si in Co can be calculated, and atomic concentration distributions of Cu and Si can be simulated using the error function of concentration distribution. The Co-Si layer regions with no Cu diffusion that satisfy better anti-oxidation performance can also be proposed from summarizing the above three effects. Then using a few points of the optimized area CVD experiments of the silicidation reaction, RTA experiments can be done and the anti-oxidation performance of the obtained Co-Si film in the optimized region can be examined.

3.2 Hydrogen annealing

As hydrogen annealing helps to produce more metallic Co, which allows us to get more CoSi,

some experiments were done to research the relationship between hydrogen annealing reduction, temperature, and time. For example, the variation of the Co2p peak via XPS analysis after hydrogen annealing at 200℃ for different times from 30s to 30min is shown in Fig. 2, in which peaks 1 and 3 at the binding energies of 778 and 794eV are metallic cobalt, peaks 2, 4, and 5 at the binding energies of 781, 797, and 803eV are Co-oxidized peaks respectively, and peak 2′ is the shake-up satellite of peak 2, which indicates that a shift of the Co 2p peak from the substrate with no annealing to different annealing times corresponding to the oxidized Co peak to metallic cobalt.

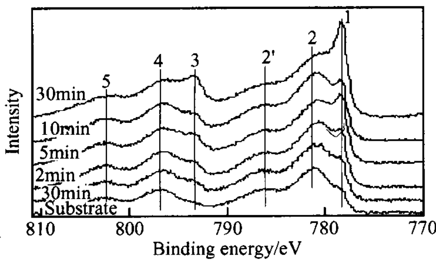

Fig. 2 Co2p peak of XPS analysis after hydrogen annealing at 200℃

Similar results were also obtained for other annealing temperatures and times. This suggests that the Co2p peak shifts to the metallic peak gradually with increasing annealing temperature and time. According to thermodynamic calculations, metallic Co can be more easily produced at a higher temperature of 320℃ with a Gibbs energy variation of − 22.22kJ than at a lower temperature of 200℃ with a Gibbs energy variation of − 19.53kJ during the reaction in which the CoO is hydrogen reduced. The reduction effect is summarized and shown in Fig. 3 from the XPS analysis. Figure 3 shows that the metallic Co content of the substrate surface increases with increasing hydrogen annealing temperature and time, and it tends to saturate as increasing time up to a certain value at a certain temperature. The reason that the Co saturates around 25% may be the re-oxidation of Co on the surface when the substrates were taken out of the reactor. From this figure, a better reduction effect region is summarized and given in Table 1.

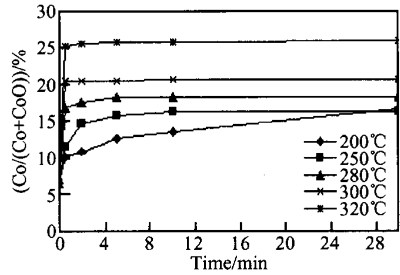

Fig. 3 Dependence of the ratio of Co/(Co + CoO) on temperature and time

Table 1 Better reduction effect region at hydrogen annealing conditions

Temperature/℃	Time/min
200	⩾30
250	⩾10
280	⩾5
300	⩾0. 5
320	⩾0. 5

3.3 Cu diffusion

Atomic concentration percentages of Cu and Co from XPS depth analysis with hydrogen annealing for 5min at 320℃ and no annealing treatment are shown in Fig. 4. Atomic concentration percentages of Cu and Co for the other conditions are not shown here. Considering the limitation of XPS depth resolution and the need for calculating diffusion coefficients of Cu and Co, we adopt the depth difference ($\Delta_{\text{no annealing}}$) between 16% Cu (or 84% Co) and 16% Co (or 84% Cu) of no hydrogen annealing as our calculation standard. Then the diffusion depths of Cu and Co at different

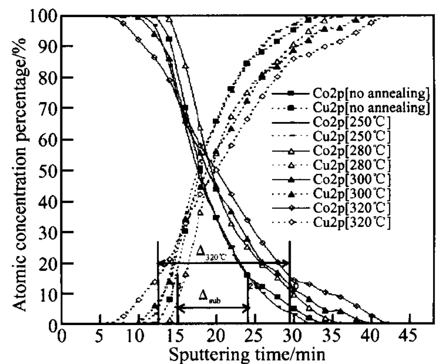

Fig. 4 Atomic concentration percentage of Cu and Co from XPS depth analysis after hydrogen annealing at different conditions

dealing conditions can be calculated using the difference between the different scope at the situation of 16% Cu or 16% Co between different temperatures and no annealing. For example the diffusion depth of Cu at 320℃ can be expressed as a product using the sputtering rate of Cu multiplied by $\Delta_{320℃} - \Delta_{no\ annealing}$. The diffusion depths of Cu in Co and Co in Cu at different temperatures for 5min were calculated and are given in Table 2. The diffusion coefficients of Cu and Co were calculated using the Boltzmann-Matano formula ($x^2 = 4Dt$)[12] and also are given in Table 2.

Table 2 Diffusion depths and diffusion coefficients of Cu in Co and Co in Cu at different conditions

Temperature /℃	Diffusion depth of Cu into Co /nm	Diffusion coefficient of Cu/(cm²/s)	Diffusion depth of Co into Cu /nm	Diffusion coefficient of Co/(cm²/s)
25	0	–	0	–
250	2.88	1.38×10^{-16}	3.12	1.62×10^{-16}
280	4.51	3.39×10^{-16}	4.89	3.99×10^{-16}
300	7.64	9.73×10^{-16}	8.28	1.14×10^{-15}
320	11.14	2.07×10^{-15}	12.08	2.43×10^{-15}

The relationships between the diffusion coefficients of Cu and Co and temperature are given by the following equations:

$$D(\text{Cu in Co}) = 1.55\times10^{-6}\times\exp(-12164/T),\quad \Delta E = 1.05\text{eV} \tag{1}$$

$$D(\text{Co in Cu}) = 1.84\times10^{-6}\times\exp(-12171/T),\quad \Delta E = 1.05\text{eV} \tag{2}$$

The error function formula[13] for the diffusion coefficients and diffusion depths are

$$\frac{c - c_s}{c_0 - c_s} = \text{erfc}(x/2\sqrt{Dt}) \tag{3}$$

where $t = 0, C_0 = C(x,0); t > 0, C_s = C(0,t)$.

$$\text{erfc}(z) \equiv \frac{2}{\sqrt{\pi}}\int_z^{\infty} e^{-u^2}\,du \tag{4}$$

The dependence of atomic concentration distribution of Cu diffusion on diffusion depth can be simulated. The region of no Cu diffusion out to 40nm Co surface is summarized in Table 3 from the simulated results. The next factor that should be considered is the diffusion of Si in Co, which influences the formation of Co-Si layer depth during the silicidation reaction process.

Table 3 Region of no Cu diffusion out 40nm Co layer at different annealing conditions

Temperature/℃	Time/min
250	≤20
280	≤15
300	≤10
320	≤5

3.4 Silicon diffusion

Atomic concentration percentages of Si and Co from XPS depth analysis with hydrogen annealing for 5min at 320℃ and no annealing treatment are shown in Fig. 5. Atomic concentration percentages of Cu and Co under other conditions are not shown here. Using the same method as the above, the diffusion depths of Si and Co under different dealing conditions can be calculated from the difference between the scope for the situation of 16% Si (84 % Co) and 16% Co (84% Si) between different temperatures and no annealing. The diffusion depths of Si in Co and Co in Si at different temperatures for 5min have been calculated and are shown in Table 4.

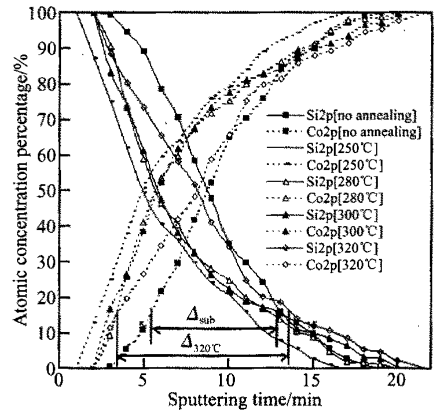

Fig.5 Atomic concentration percentage of Si and Co from XPS depth analysis after hydrogen annealing at different conditions

Table 4 Diffusion depths and diffusion coefficients of Si in Co and Co in Si at different conditions

Temperature /℃	Diffusion depth of Si into Co /nm	Diffusion coefficient of Si /(cm²/s)	Diffusion depth of Co into Si /nm	Diffusion coefficient of Co/(cm²/s)
No annealing	0	–	0	–
250	3.29	1.80×10^{-16}	1.73	4.99×10^{-17}
280	4.39	3.21×10^{-16}	2.31	8.89×10^{-17}
300	8.19	1.12×10^{-15}	4.31	3.10×10^{-16}
320	10.92	1.99×10^{-15}	5.75	5.51×10^{-16}

The diffusion coefficients of Si in Co and Co in Si have also been calculated using the Boltzmann-Matano formula and are also given in

Table 4. The relationship between the diffusion coefficients of Si and Co and temperature can be given as the following formulas:

$$D(\text{Si in Co}) = 2.45\times10^{-7}\times\exp(-11090/T),\quad \Delta E = 0.96\text{eV} \tag{5}$$

$$D(\text{Co in Si}) = 6.92\times10^{-8}\times\exp(-11102/T),\quad \Delta E = 0.96\text{eV} \tag{6}$$

Also using the error function formula for diffusion coefficients and diffusion depth, the dependence of atomic concentration distribution of Si diffusion on diffusion depth can be simulated. Because a Co-Si layer depth greater than five nanometers was shown to have a better anti-oxidation property in our previous work,[11] the region of making CoSi layer above 5nm has been summarized in Table 5 from the simulated results. This region can supply better Co silicidation layers that have better anti-oxidation properties.

Table 5 Region of Si diffusion bigger than 5nm in Co layer at different annealing conditions

Temperature/℃	Time/min
250	⩾2.0
280	⩾1.0
300	⩾0.5
320	⩾0.17

3.5 Optimization and verification

The optimized region was obtained and is plotted in Fig. 6 as the gray area through summarizing better hydrogen annealing reduction effect region, Cu diffusion low than 40nm region and Si diffusion above 5nm region. Points in region A and B of Fig. 6 are the experiment points for the whole process before and after optimization respectively. In order to verify that the optimization

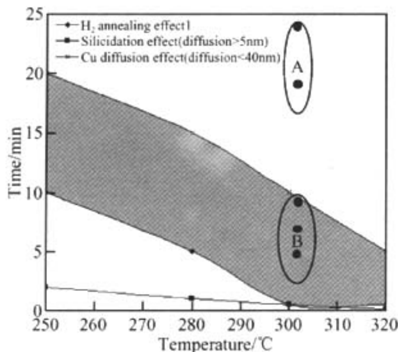

Fig. 6 Optimized region of considering hydrogen annealing, Cu diffusion and Si diffusion

region is the ideal region which can get better anti-oxidation performance, some silicidation experiments, such as annealing the substrate at 300℃ in hydrogen for 3min and 27s or 5min, and silicidation for 30s or 5min, were done, and the relative RTA analysis and sheet resistivity results were examined. Figure 7 shows a comparison of the results before (area A) and after (area B) optimizing the whole process. The results show that the anti-oxidation performance of CoSi film after optimization has been greatly improved. The whole optimization process can give useful information for supplying a better Co-Si anti-oxidation film.

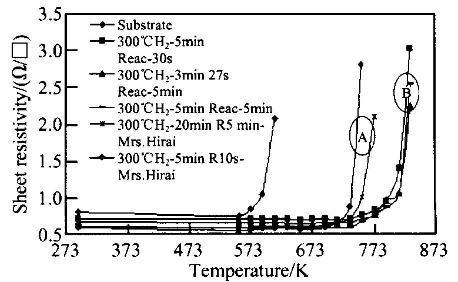

Fig. 7 Comparison of before and after optimization the whole process

4 Conclusion

In order to optimize the silicidation process, some experiments have been done to research the reduction effect of hydrogen annealing on Cu diffusion in Co and Si diffusion in Co. Diffusion coefficients of Cu in Co, Co in Cu, Si in Co and Co in Si have been calculated from the RTA experiments and XPS depth analysis results. Atomic percentage distributions of Cu in Co and Si in Co have been simulated using the error function for diffusion coefficients. The competition between Si diffusion in Co and Cu out-diffusion through Co has been quantified in order to realize a better silicidation effect. Better hydrogen annealing reduction region, no Cu diffusion out to 40nm Co region, and Si diffusion above the 5nm region have been obtained from the relative analysis results. The whole process-optimized region has been obtained and plotted by combining the above three optimized effect regions. On the basis of the optimized region, verification experiments have been done and the anti-oxidation performances of Co-

Si film after optimization has been significantly improved over that before optimization. This whole optimization process can give useful information for supplying better Co-Si anti-oxidation performance film in ULSI-Cu metallization.

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超大规模集成电路 $CoSi_x$ 抗氧化阻挡层的制备优化*

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摘要：为了制备性能良好的Co(W,P)抗氧化层薄膜材料，提出用 SiH_4 或 Si_2H_6 对Co层进行硅化的方案.在整个硅化过程中存在着Si在Co中的扩散和Cu在Co中的扩散，为了实现较好的硅化效果有必要对扩散速率进行定量化.利用X射线光电子能谱(XPS)对Cu在Co中的扩散和Si在Co中的扩散进行深度剖面分析得到了有用的数据，在讨论了扩散过程的基础上，绘制了条件优化区域.实验结果表明：硅化反应的化学气相沉积(CVD)所得到的CoSi薄膜的抗氧化性能明显地比过程优化前得到了提高.

关键词：CoSi阻挡层薄膜；氢气退火；硅化；扩散；过程优化；抗氧化性能

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