Manuscript submitted July 21, 1986; revised manuscript received Dec. 12, 1986.

AT&T Bell Laboratories assisted in meeting the publication costs of this article.

REFERENCES

- 1. G. K. Celler, L. E. Trimble, and L. O. Wilson, Mater. Res.
- Soc. Symp. Proc., **35**, 635 (1985). G. K. Celler, McD. Robinson, L. E. Trimble, and D. J. Lischner, Appl. Phys. Lett., 43, 868 (1984).
- 3. G. K. Celler, McD. Robinson, and D. J. Lischner, ibid., 42, 99 (1983).
- D. G. Schimmel, *This Journal*, **126**, 479 (1979).
 D. L. Lischner and G. K. Celler, in "Laser-Solid Interactions and Transient Thermal Processing of Materials," J. Narayan, W. L. Brown, and R. A. Lemons, Editors, North-Holland Publishing Co., New York (1983). 6. L. O. Wilson and G. K. Celler, *This Journal*, **132**, 2748
- (1985).
- E. Yablonovitch, J. Opt. Soc. Am., 72, 899 (1982).
 c.f. G. J. Fowles, "Introduction to Modern Optics," 2nd ed., Holt, Rinehart and Winston, Inc., New York (1975).

Properties of Chemical Vapor Deposited Tungsten Silicide Films Using Reaction of WF₆ and Si₂H₆

Yoshimi Shioya, Kaoru Ikegami, Ikuro Kobayashi, and Mamoru Maeda

Fujitsu Limited, Process Development Department, 1015 Kamikodanaka, Nakahara-ku, Kawasaki 211, Japan

ABSTRACT

Tungsten silicide films were formed by the chemical vapor deposition method using the reaction WF_6 and Si_2H_6 . The deposition rate, resistivity, composition, stress, crystal structure, and content of impurities were studied and compared with tungsten silicide films deposited by reaction of WF_6 and SiH_4 . The tungsten silicide films made using Si_2H_6 have a higher deposition rate and higher Si concentration than those made by using SiH_4 at the same substrate temperature. For these reasons, the tungsten silicide films made by using Si_2H_6 were found to have a resistivity that is a little higher and, after annealing, a stress that is smaller than that made by SiH_4 . Also, the resistance of tungsten silicide to peeling is larger than that of the film made by using SiH₄. The crystal structure of the WSi_x films made by Si₂H₆ is almost the same as that made by SiH₄; however, a tetragonal W_5 Si₃ structure easily forms even in Si-rich films of WSi_{2.6}. Content of fluorine in films made by SiH₄ is smaller than that in films made by SiH₄.

Recently, doped poly-Si has been mainly used for interconnection materials for very large scale integrated circuits. However, resistivity of interconnection becomes higher and propagation delay of signals becomes larger as devices reach higher densities and as line widths become smaller. Consequently, refractory metal silicides replacing doped poly-Si are being studied and becoming widely used.

WSi₂, MoSi₂, TiSi₂, and TaSi₂ are in this class of refractory metal silicides. There are several methods for forming these refractory metal silicides, e.g., sputtering, mixing by ion implantation, and chemical vapor deposition (CVD). Of these methods, CVD is mainly used for deposition of tungsten silicide $(WSi_r)(1)$.

CVD-WSi_x films are becoming widely used because of fewer impurities (2), easier fine-patterning, and having better step coverage than the sputtering method. However, in our study, it was found that there is a lot of fluorine and hydrogen induced with reaction gases of SiH₄ and WF₆ and these concentration values are in the order of 10²¹ and 10²⁰ cm⁻³, respectively (3). Therefore, for using CVD-WSi_x as the gate material of a metal oxide semiconductor (MOS) transistor, it is better to stack CVD- WSi_x on polysilicon to prevent gate SiO_2 from "fluorine" diffusing.

There is another method to form $CVD-WSi_x$; this method uses the reaction of WF_6 and Si_2H_6 (Si_2H_6 decomposed at a lower temperature than SiH₄), as well as the reaction of WF_6 and SiH_4 . In the method of forming WSi_x with the reaction of WF₆ and Si₂H₆, it is possible to make films rich in Si, which are stable at high temperature annealing and capable of low temperature deposition. There is also the possibility of decreasing the content of fluorine and hydrogen in the film. If these possibilities could be actualized, then, if the films were used as an electrode on gate SiO₂ for MOS transistors, the breakdown voltage of gate SiO₂ would increase, and peeling of films after annealing would decrease. These films could then be useful in the progress of integrated circuits process technology. In this study, we deposited WSi_x films by using the reaction of WF_6 and Si_2H_6 in cold wall type CVD equipment and then compared the deposition rate, the resistivity, the stress, the crystal structure, and the contents of fluorine and hydrogen with the values of the films formed by using the reaction of WF₆ and SiH₄.

Experimental

CVD-WSi_r films were deposited by the reaction of WF₆ and Si_2H_6 in cold wall type equipment; this equipment has a shower-type gas nozzle cooled with water. The substrate temperature was changed from 225° to 425°C. The pressure was 40 Pa. WF_6 , Si_2H_6 , and He were induced in the chamber through mass flow controllers. The flow rate of WF₆ was fixed at 2 cm³/min, and the flow rate of Si₂H₆ was changed from 40 to 120 cm³/min. The flow rate of He was 400 cm³/min.

He gas was added to the reaction gases. WSi_x films were deposited at about 2000Å on the 1000Å oxidized (100) plane of a 4 in. wafer. These films were annealed in N₂ gas at several temperatures under 1000°C for 30 min to prevent contamination of oxygen.

The thickness of the films was measured by Talystep after etching by HNO₃ and NH₄F (ratio of 50:2). The resistivity was measured by the four-point probe method. The composition was measured by Rutherford backscattering spectroscopy (RBS), the stress by the Newton ring method, the crystal structure by an x-ray diffractometer, and the impurities by secondary ion mass spectroscopy (SIMS).

Results and Discussion

Deposition rate.—The deposition rates of WSi_r films using reaction of WF_6 and Si_2H_6 and of WF_6 and SiH_4 are indicated as a function of the substrate temperature in Fig. 1. The flow rate of Si₂H₆ and SiH₄ were 120 cm³/min, and the flow rate of WF_6 was 2 cm³/min.

In this substrate temperature range, the deposition rates of WSi_x films using Si₂H₆ were 900-1250 Å/min; this



Fig. 1. The deposition rate of WSi_x films deposited by the reaction of Si₂H₆ + WF₆ and SiH₄ + WF₆ as a function of the substrate temperature. The flow rate of WF₆ is fixed at 2 cm³/min, and the flow rate of Si₂H₆ and SiH₄ is 120 cm³/min.

value is about 60-180 Å/min larger than that of WSi_x films using SiH₄. This is because Si₂H₆ is more easily decomposed and reacts with WF₆ at a lower temperature than SiH₄. The deposition rates of WSi_x films using both Si₂H₆ and SiH₄ were decreased as the substrate temperature was raised because the ratio of the deposition rate on the shower and the wall became larger. From these differences of deposition rate, it is supposed that the compositions of WSi_x films using Si₂H₆ would be richer in Si than that of WSi_x films using SiH₄.



SUBSTRATE TEMPERATURE (°C)

Fig. 2. The resistivity of WSi_x films deposited by the reaction of Si₂H₆ + WF₆ and SiH₄ + WF₆ in the deposited state and after annealing at 1000°C for 30 min in N₂ as a function of the substrate temperature. The flow rate of WF₆ is fixed at 2 cm³/min, and the flow rate of SiH₆ and SiH₄ is 120 cm³/min.



Fig. 3. Change in resistivity of WSi_x films using Si₂H₆ as a function of the substrate temperature. The substrate temperature is 225°, 325°, and 425°C. The flow rate of WF₆ is 2 cm³/min. The flow rate of Si₂H₆ is 120 cm³/min.

Resistivity.—The resistivities of WSi_x films at the asdeposited state and after annealing at 1000°C for 30 min in N₂ are indicated as a function of substrate temperature in Fig. 2. These resistivities become larger as the substrate temperature rises, and the resistivities of WSi_r films using Si_2H_6 are about 1.5-1.8 times larger than that of WSi_x films using SiH₄ at the same substrate temperature. The resistivity of the WSi_x film that was deposited at 275°C using Si₂H₆ after annealing at 1000°C has minimum value of about 1 imes 10⁻⁴ Ω -cm. The resistivity of WSi_x films using Si_2H_6 is larger than that of WSi_x films using SiH₄ at a substrate temperature about 325°C. The annealing temperature dependence of resistivities is indicated in Fig. 3. These values have a maximum at about 600°C, and therefore fit the same tendency as WSi_r films using SiH₄ (see Fig. 4).

The deposition rate and the resistivity of WSi_x films as a function of the flow rate of Si_2H_6 and SiH_4 are indicated in Fig. 5 and 6, respectively. The deposition rate of WSi_x films using Si_2H_6 is more sensitive to the flow rate of reaction gas than that of WSi_x films using SiH_4 . This is be-



Fig. 4. Change in resistivity of WSi_x films using SiH₄ as a function of the substrate temperature. The substrate temperature is 325°, 350°, and 425°C. The flow rate of WF₆ is 2 cm³/min. The flow rate of SiH₄ is 120 cm³/min.

Downloaded on 2015-03-07 to IP 169.230.243.252 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Fig. 5. The deposition rate of WSi_x films using Si₂H₆ and SiH₄ as a function of the flow rate of Si₂H₆ and SiH₄. The flow rate of WF₆ is 2 cm³/min. The substrate temperature is 325°C.

cause the decomposition of Si_2H_6 begins at a lower temperature than that of SiH_4 , and the deposition rate of WSi_x films using Si_2H_4 is regulated by the flow rate of Si_2H_6 . The resistivity of WSi_x films using Si_2H_6 is also more sensitive to the flow rate of reaction gas than that of WSi_x films using SiH_4 .

The resistivity of WSi_x films using Si_2H_6 after annealing at 1000°C is larger for Si_2H_6 flow rate of above 100 cm³/ min and lower for Si_2H_6 flow rate of under 100 cm³/min than that of WSi_x films using SiH_4 . The reason for the above results is assumed to be as follows: WSi_x films using Si_2H_6 are rich in Si for the small flow rate of Si_2H_6 . However, WSi_x films using SiH_4 reach the stoichiometry value of WSi_2 for the small flow rate of SiH_4 , and, after annealing at 1000°C, a crystal structure of nontetragonal WSi_2 (e.g., tetragonal W_5Si_3) begins to appear. In results, the resistivity of WSi_x films using SiH_4 for a flow rate of under 100 cm³/min.

Composition.—The compositions of WSi_x films using Si_2H_6 and SiH_4 as a function of the substrate temperature are indicated in Fig. 7. The flow rates of WF₆, Si_2H_6 , and SiH_4 are 2, 120, and 120 cm³/min, respectively. The Si/W



FLOW RATE OF Si2H6, SiH4 (cc/min)

Fig. 6. Change in resistivity of WSi_x films using Si₂H₆ and SiH₄ as a function of the flow rate of Si₂H₆ and SiH₄. The flow rate of WF₆ is 2 cm³/min. The substrate temperature is 325°C.



Fig. 7. Si/W ratio of WSi_x films using Si₂H₆ and SiH₄ as a function of substrate temperature. The flow rate of WF₆ is 2 cm³/min. The flow rate of Si₂H₆ and SiH₄ is 120 cm³/min.

ratio of WSi_x films using Si₂H₆ increases from 1.8 to 2.9 as the substrate temperature rises from 225° to 425°C. On the other hand, the Si/W ratio of WSi_x films using SiH₄ increases slightly from 2.2 to 2.4 as the substrate temperature rises from 325 to 425°C. The reason for the lack of data under 300°C is that the film easily peeled off. The cause of substrate temperature dependence on the change of the Si/W ratio is the difference in decomposition between Si₂H₆ and SiH₄. Another reason that the Si/W ratio of WSi_x films using SiH₄ did not change so much is assumed to be as follows: SiH₄ was not decom-



Fig. 8. Stress in WSi_x films using Si₂H₆ and SiH₄ as a function of annealing temperature. Annealing was done for 30 min in N₂. The flow rate of WF₆ is 2 cm³/min. The flow rate of Si₂H₆ and SiH₄ is 120 cm³/min.

Downloaded on 2015-03-07 to IP 169.230.243.252 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Fig. 9. Stress in WSi_x films using Si_2H_6 as a function of substrate temperature. The flow rate of WF₆ is 2 cm³/min. The flow rate of Si_2H_6 is 120 cm³/min.

posed so much because of the cooling effect of gas supplying shower even if the substrate temperature rose. This figure shows that Si_2H_6 can deposit WSi_r films, which are richer in Si than SiH_4 , and the Si/W ratio is easily affected by the substrate temperature.

Stress.—The stress of WSi_x films using Si₂H₆ and SiH₄ after annealing is indicated in Fig. 8. The tensile stress of $WSi_{2.2}$ films using Si_2H_6 or SiH_4 is to the order of 10^{10} dyn/cm² and reaches a maximum at about 500°C. The deposition temperatures of WSi_x films using Si_2H_6 and SiH₄ are 275° and 325°C, respectively. The thickness of WSi_x films using Si_2H_6 and SiH_4 is 1610-1895Å and 1335-2100Å, respectively. This figure shows that the stress of WSi_x films using Si_2H_6 is lower than that of WSi_x films using SiH₄ after above 400°C annealing at the same Si/W ratio of 2.2. This figure also shows the stress of WSi_x films using Si_2H_6 that were deposited at 325°C. The film thickness is 1400-1900Å. At the same substrate temperature, the stress of WSi_x films using Si_2H_6 was found to be lower than that of WSi_x films using SiH₄. The cause of the difference in the stress between WSi_x films using Si_2H_6 and WSi_x films using SiH₄ was considered to be the differences in crystal structure and impurity content. Also, the substrate temperature dependence on stress is indicated in Fig. 9. The stress decreases suddenly to the order of dyn/cm² at a substrate temperature of above 325°C (Si/W ratio is larger than 2.6).

Crystal structure.—The crystal structure of WSi_x films using Si₂H₆ were studied by x-ray diffraction analysis. The annealing temperature dependence of x-ray diffraction intensity from various crystal planes of WSi_{2.6} film is indicated in Fig. 10. The crystallization begins at 400°C; the hexagonal structures of WSi₂ mainly begin to appear under 550°C (5). Above 600°C, tetragonal WSi₂ structure becomes dominant. This behavior of crystal structure on annealing temperature is same as that in WSi_x films using WF₆ and SiH₄. However, the difference between WSi_x films using Si_2H_6 and SiH_4 is that x-ray diffraction from the tetragonal $W_5Si_3(002)$ plant appeared only in WSi_x films using Si₂H₆ at 800° and 1000°C. The tetragonal W₅Si₃ structure also appeared in WSi_{1.8} film. It is assumed that this structure is the cause of the stress being smaller in WSi_x films using S₂H₆ than in WSi_x films using SiH₄ at 800° and 1000°C. A comparison of x-ray diffraction intensities for various compositions of WSi_x films formed by Si₂H₆ and WF₆ after annealing at 1000°C is given in Table I. This table shows that, in WSi_{1.8} film, the x-ray diffraction intensities become smaller in the order of tetragonal $W_5Si_3(002) > tetragonal WSi_2(101) > tetragonal WSi_2(002)$ > tetragonal WSi₂(110). . . .



Fig. 10. Change in x-ray intensity from various planes of WSi_{2.6} film as a function of annealing temperature. WSi_{2.6} film was deposited at 325°C. The film thickness is 1305-1585Å.

In WSi_{2.6} film, however, x-ray diffraction intensities become smaller in the order of tetragonal WSi₂(101) > tetragonal WSi₂(100) > tetragonal WSi₂(103) > tetragonal WSi₂(002) > tetragonal W₅Si₃(002)... And, in the WSi_{2.9} film, they become smaller in the order of tetragonal WSi₂(101) > tetragonal WSi₂(002) > tetragonal WSi₂(103) > tetragonal WSi₂(103) > tetragonal WSi₂(110) > tetragonal WSi₂(112)...

In short, tetragonal W_3Si_3 structure appears easily as the ratio of tungsten in the WSi_x film becomes larger; however, tetragonal W_5Si_3 structures can only appear above 800°C. Also in Si-rich films of $WSi_{2.6}$, tetragonal W_5Si_3 structures were found to appear above 800°C.

In Si-rich films of $WSi_{2.9}$, only tetragonal WSi_2 appears, and the diffraction intensity from $WSi_2(101)$ plane becomes largest. The crystal structure of $WSi_{2.9}$ film is almost the same as that of the $WSi_{2.2}$ to $WSi_{2.6}$ films using SiH_4 .

Impurities in the films.—Fluorine and hydrogen were introduced into WSi_x films at deposition from reaction gases. Their content was analyzed by SIMS to investigate the difference between WSi_x films using Si_2H_6 and SiH_4 . The content of fluorine and hydrogen indicates the value at the half-depth point of the film. The changes in these values after annealing were investigated. The annealing time is 30 min. The results are shown in Fig. 11 and 12. The content of impurities for WSi_x films using SiH_4 were indicated within a range because of the quantity of data. From these figures, the content of fluorine in WSi_x films using Si_2H_6 is less than that in deposited WSi_x films using SiH_4 .

After annealing at 800° -1000°C, the content of fluorine in WSi_x films using Si₂H₆ increases and almost equals the value of the lower content limit in WSi_x films using SiH₄.

Table I. Comparison of x-ray diffraction intensity for three different WSi_x, films after annealing at 1000°C for 30 min in N₂ gas

WSi _x	X-ray diffraction intensity (arbitrary units)						
	WSi ₂ T(002)	WSi ₂ T(101)	W ₅ Si ₃ T(002)	WSi ₂ T(110)	WSi ₂ T(103)	WSi ₂ T(112)	WSi ₂ T(200)
WSi _{2 2} WSi _{2 6}	197 328	$\begin{array}{c} 231 \\ 476 \end{array}$	402 279	183 432	153 380	57 114	28 48
WSi .	572	690	0	393	441	177	66

Downloaded on 2015-03-07 to IP 169.230.243.252 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Fig. 11. Concentration of fluorine in WSi_x films using Si₂H₆ and SiH₄ as a function of annealing temperature. The substrate temperature is 325°C. These data come from the half-depth point of the WSix film.

The increase of content was induced by fluorine diffusion from the boundary side of WSi_x and substrate SiO_2 . After annealing at 1000°-1100°C, the fluorine content again becomes lower than that in WSi_x films using SiH₄.

This means the lowering of fluorine diffusion from the boundary side. These data are explained by the fact that WSi_x films using Si_2H_6 become richer in Si than those using SiH₄ at the same substrate temperature. The content of hydrogen in WSi_x films using Si_2H_6 is 1×10^{20} cm⁻³ at deposited state and the same for WSi_x film using SiH_4 .

Summary

The properties of WSi_r films deposited by reaction of WF_6 and Si_2H_6 were investigated and compared with WSi_x films using WF_6 and SiH_4 . The following facts were clarified. WSi_x films using Si₂H₆ become richer in Si than those using SiH₄ at the same substrate temperature. The deposition rate in 900-1250 Å/min, about 60-180 Å/min larger than that of WSi_x films using SiH₄ at a substrate temperature of 225°-425°C. The resistivity is 1.5-1.8 times as large as that in WSi_x films using SiH₄ in the deposited state and becomes about $1 \times 10^{-4} \Omega$ -cm after annealing at 1000°C for 30 min in N₂. The Si/W ratio becomes larger as the substrate temperature rises and its value becomes 2.9 at 425°C

The dependence of the substrate temperature on the Si/W ratio is larger than that in WSi_x films using SiH₄. The stress is to the order of 1010 dyn/cm2 at the deposited state and reaches a maximum after annealing at about 500°C; this is the same for WSi_x films using SiH₄. After annealing above 800°C, the stress is smaller than that in



Fig. 12. Concentration of hydrogen in WSi_x films using Si₂H₆ and SiH4 as a function of annealing temperature. The substrate temperature is 325°C. These data come from the half-depth point of the WSi_x film

WSi_x films using SiH₄ at the same composition. The crystal structure is amorphous in the deposited state, crystallization begins from 400°C. Mainly hexagonal WSi₂ is crystallized under 600°C, and, above 600°C, mainly tetragonal WSi₂ is crystallized. However, tetragonal W₅Si₃ structure appears even richer in an Si film of WSi2.6 after annealing at above 800°C. The content of fluorine is smaller than that in WSi_x film using SiH_4 . The content of hydrogen is as large as that in WSi, films using SiH₄.

Acknowledgment

The authors would like to express their gratitude to T. Itoh for his assistance in this study.

Manuscript submitted Feb. 21, 1986; revised manuscript received Sept. 15, 1986.

Fujitsu Limited assisted in meeting the publication costs of this article.

REFERENCES

- 1. D. L. Brors, J. A. Fair, K. A. Monnig, and K. C. Saraswat, Solid State Technol., 26, 183 (1983).
- 2. K. C. Saraswat, D. L. Brors, J. A. Fair, K. A. Monnig, and R. Beyers, IEEE Trans. Electron Devices, ED-30, 1497 (1983)
- Y. Shioya, T. Itoh, I. Kobayashi, and M. Maeda, *This Journal*, To be published.
 C. M. Drum and M. J. Rand, J. Appl. Phys., 39, 4458 (1999)
- (1968).
- 5. M. Y. Tsai, F. M. d'Heurle, C. S. Petersson, and R. W. Jhonson, ibid., 52, 5350 (1981).