



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : H01L 21/443	A1	(11) International Publication Number: WO 91/17566 (43) International Publication Date: 14 November 1991 (14.11.91)
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(21) International Application Number: PCT/US91/03049

(22) International Filing Date: 3 May 1991 (03.05.91)

(30) Priority data:
519,538 4 May 1990 (04.05.90) US

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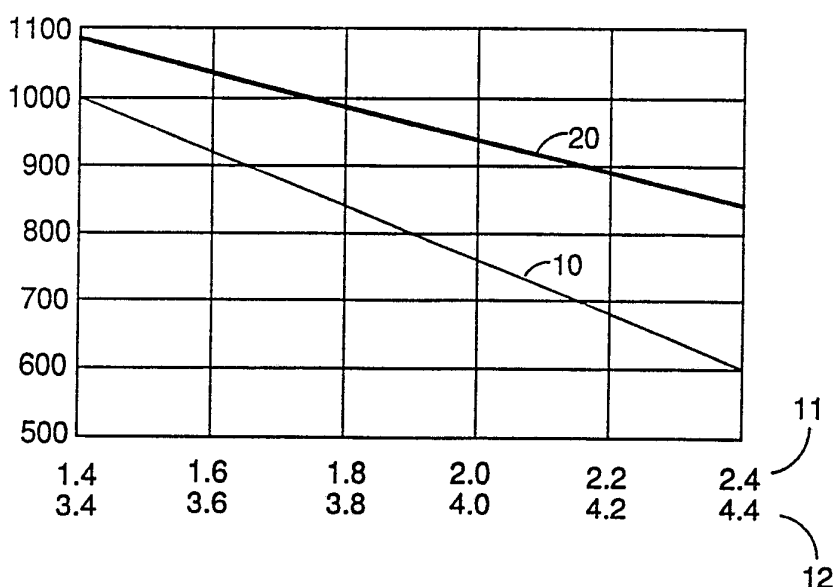
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(81) Designated States: DE, JP, KR, NL.

Published
With international search report.

(54) Title: TUNGSTEN DISILICIDE CVD



(57) Abstract

Tungsten disilicide (WSi_x) films are deposited onto doped or undoped polysilicon by reducing WF_6 with a mixture of dichlorosilane (SiH_2Cl_2) and disilane (Si_2H_6). The addition of disilane provides a mechanism for increasing the resistivity (silicon to tungsten ratio) of the film (fig. 1) without adversely affecting the uniformity (fig. 2) or deposition rate of the film (fig. 3). A high silicon to tungsten ratio prevents degradation of the silicide film and the underlying polysilicon film during subsequent growth of an oxide (SiO_2) dielectric. The excess silicon in the film also provides desirable etching and annealing characteristics.

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TUNGSTEN DISILICIDE CVDTechnical Field

The invention relates to the manufacture of semiconductor wafers using chemical vapor deposition (CVD) of tungsten silicide and, in particular, to a process for depositing tungsten silicide by the reduction of tungsten hexafluoride (WF_6) by silane gases.

10 Background Art

Because of their stability at high temperature, refractory metal silicides, such as tungsten silicide, have received increasing use in the manufacture of semiconductor integrated circuits, e.g. as Schottky barriers, ohmic contacts, or gate metallizations. For the latter application, a low resistivity tungsten silicide layer is formed on a polysilicon layer. Due to the ever decreasing geometry of devices in an integrated circuit, uniformity of the deposition is of great concern. Similarly, deposition rate is of concern since it determines production rates.

Low pressure CVD of tungsten silicide using a mixture of WF_6 and monosilane (SiH_4) is described in Solid State Technology April, 1983, pages 183-185. Monosilane has a greater tendency to nucleate particles in the gas phase than do the chlorosilanes. The accumulation of silicon within the deposition chamber will eventually fragment, generating particles which can contaminate a wafer. Thus, the use of chlorosilanes, such as dichlorosilane (DCS) ($SiCl_2H_2$) will lead to a cleaner deposition chamber.

Other compounds dissociate less readily, such as silicon tetrachloride ($SiCl_4$), but this causes difficulty in starting the deposition cycle. Intermediate compounds, such as dichlorosilane (SiH_2Cl_2), have intermediate characteristics. The use of dichlorosilane

instead of silane is described in U.S. Patent 4,692,343; in J. Vac. Sci. Technol. B 6 (6), Nov-Dec 1988, pages 1707-1713; in Surface and Interface Analysis, Vol 14 (1989), pages 13-17; and in J. Electrochem. Soc., Vol 136, No. 4, April 1989, pages 1177-1180.

Alternatively, as described in J. Electrochem. Soc., Vol. 134, No. 5, May 1987, pages 1220-1224, it is known to use disilane (Si_2H_6) instead of silane for reducing the WF_6 . In this article, results from silane and disilane are compared.

In all of these processes, one is confronted with the conflicting requirements of high deposition rate and uniformity of deposition. Improving one while keeping the other constant is desirable; improving both is very difficult.

Further complicating the process, it is difficult to increase the silicon to tungsten ratio without degrading both deposition rate and uniformity. A high silicon to tungsten ratio, i.e. greater than 2.6:1, prevents degradation of the silicide film in subsequent steps and poor adhesion to the underlying polysilicon film. A silicon to tungsten ratio greater than 2.6:1 is desirable to suppress oxidation of the tungsten in the silicide film and to control consumption of the underlying polysilicon film during formation of the SiO_2 dielectric. The excess silicon in the silicide film also reduces film stress and provides for more desirable etching characteristics. In the prior art, the ratio could be increased only by decreasing the partial pressure of the WF_6 (or increasing the partial pressure of $\text{SiH}_4/\text{SiH}_2\text{Cl}_2/\text{Si}_2\text{H}_6$). This leads to lower deposition rates and worse uniformity.

One technique for modifying the silicon to tungsten ratio is to deposit a thin layer of silicon prior to depositing the silicide, as described in U.S. Patent 4,737,474. While this provides greater adhesion, it

does not modify the silicon content of the bulk of the silicide layer.

In view of the foregoing, it is therefore an object of the present invention to provide an improved process for depositing silicide by the chemical reduction of WF_6 .

Another object of the present invention is to provide a process for controlling the silicon to tungsten ratio independently of deposition rate and uniformity.

A further object of the present invention is to provide a silicon to tungsten ratio of 2.6:1 or greater.

Disclosure of Invention

The foregoing objects are achieved in the present invention wherein the silicon to tungsten ratio in a tungsten silicide film can be significantly increased by adding less than ten percent disilane (Si_2H_6) to the gas mixture of WF_6 and SiH_2Cl_2 ; i.e. disilane is added to the mixture rather than replacing another gas, as in the prior art. As more fully described herein, it has been discovered that this addition provides significantly improved and unexpected results.

Brief Description of Drawings

A more complete understanding of the present invention can be obtained by considering the following detailed description in conjunction with the accompanying drawings, in which:

FIG. 1 illustrates the present invention in terms of the effect of the flow of WF_6 on film resistivity.

FIG. 2 illustrates the present invention in terms of the effect of the flow of WF_6 on film uniformity.

FIG. 3 illustrates the present invention in terms of the effect of the flow of WF_6 on film deposition rate.

Best Mode for Carrying Out the Invention

In FIGS. 1-3, the abscissa represents the rate of

flow of WF_6 in SCCM. Value labels 11 and 12 indicate the WF_6 flow without and with disilane, respectively. The ordinate in FIG. 1 represents resistivity. Line 10 indicates the result of using a combination of SiH_2Cl_2 and WF_6 only. Line 20 indicates the result of adding disilane to the mixture. Clearly, adding disilane reduces the effect of increasing the flow of WF_6 .

In FIG. 2, the ordinate represents uniformity, expressed as a percent. Line 13 shows the typical relationship obtained in the prior art without the addition of disilane. Line 23 shows the effect of adding disilane. Unexpectedly and unpredictably, the slope of the line is reversed from that of line 13.

In accordance with the present invention, one can increase the resistivity by adding disilane without affecting deposition rate or uniformity. Further, as indicated by FIGS. 1 and 2, one now has the choice of reducing WF_6 to further increase resistivity. By adding disilane, one not only obtains an increase in resistivity, but uniformity improves also.

The increase in resistivity (Si:W ratio) is not without limit. For reasons unrelated to the present invention, one wants a resistivity before annealing of $800-1200\mu\Omega\text{-cm}$. Thus, the combination of flow, pressure, temperature, etc. is chosen so that the resistivity stays within these limits. As discussed in the Background Art, it was difficult to achieve a resistivity much above $850\mu\Omega\text{-cm}$. with good uniformity and high deposition rate using processes of the prior art. With the present invention, that difficulty is removed. This does not mean that the resistivity should increase as much as possible. It means that the wafer manufacturer has a much easier time defining a process since a former compromise need no longer be made.

In FIG. 3, line 15 indicates a typical result without the use of disilane. Line 25 indicates the

result of adding disilane to the mixture of WF_6 and SiH_2Cl_2 . As seen from the respective slopes of the lines, adding disilane in accordance with the present invention reduces the effect of increasing WF_6 flow.

5 The following example is a preferred embodiment of the deposition process in accordance with the present invention. This and the other examples were performed in a reactor similar to that described in the above-identified patents and in J. Vac. Sci. Technol. B 6 (6),
10 Nov-Dec 1988, pages 1707-1713.

EXAMPLE 1

	Wafer temperature	560	°C
	SiH_2Cl_2 par. press.	82	mtorr
	WF_6 par. press.	4	mtorr
15	Si_2H_6 par. press.	4	mtorr
	Pressure	90	mtorr
	Deposition rate	1300	Å/min.
	Resistivity	900	$\mu\Omega$ -cm.
	Si:W ratio	2.7	
20	Uniformity	3	%

Films produced as above were annealed at a temperature of 1050°C for 180 seconds. The resistivity dropped to 60 $\mu\Omega$ -cm. Films which were oxidized showed very uniform SiO_2 growth without oxidation of tungsten.

25 As another example of the present invention, the following produced satisfactory results.

EXAMPLE 2

	Wafer temperature	500	°C
	SiH_2Cl_2 par. press.	84	mtorr
30	WF_6 par. press.	4	mtorr
	Si_2H_6 par. press.	2	mtorr
	Pressure	90	mtorr
	Deposition rate	1080	Å/min.
	Resistivity	923	$\mu\Omega$ -cm.
35	Si:W ratio	2.8	
	Uniformity	3.4	%

In the following examples, the partial pressure of Si_2H_6 is varied. For all these examples, the wafer temperature is 560°C and the pressure is 90 mtorr.

5	<u>EXAMPLE</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
	SiH_2Cl_2 par. press.	87.3	86.6	85.2	82.5 mtorr
	WF_6 par. press.	1.9	1.9	1.8	1.8 mtorr
	Si_2H_6 par. press.	.8	1.5	3.0	5.7 mtorr
	Deposition rate	1334	1309	1190	1141 Å/min.
10	Resistivity	769	823	943	1255 $\mu\Omega\text{-cm.}$
	Si:W ratio	2.6	2.6	2.8	3.2
	Uniformity	3.35	3.71	7.39	6.80 %

In general, adding less than ten percent disilane produces acceptable results. While the deposition rate decreases, the decrease is much less pronounced than would be obtained from decreasing the relative amount of WF_6 to obtain the same increase in resistivity (and silicon to tungsten ratio).

In the following examples, processes with and without Si_2H_6 are compared. This is a portion of the data used to generate FIGS. 1-3, described above. For these two examples, the wafer temperature is 560°C and the pressure is 90 mtorr.

25	<u>EXAMPLE</u>	<u>7</u>	<u>8</u>	
	SiH_2Cl_2 par. press.	88.6	84.4	mtorr
	WF_6 par. press.	1.4	2.8	mtorr
	Si_2H_6 par. press.	0	2.8	mtorr
	Deposition rate	1300	1300	Å/min.
30	Resistivity	800	900	$\mu\Omega\text{-cm.}$
	Si:W ratio	2.6	2.8	
	Uniformity	3	3	%

Note that the deposition rate and uniformity are unchanged, yet the resistivity (and silicon to tungsten ratio) increase with the addition of disilane. This was

not expected.

There is thus provided by the present invention an improved process for depositing tungsten silicide having a silicon to tungsten ratio of 2.6:1 or greater, wherein
5 said ratio is controllable relatively independently of deposition rate and uniformity.

Having thus described the invention, it will be apparent to those of skill in the art that various modifications can be made within the scope of the
10 present invention. For example, wafer temperature can vary from 450°C to 650°C, the higher temperatures increasing deposition rate. Suitable pressures are from 30 to 300 mtorr. The partial pressure of dichlorosilane can vary from 27 to 285 mtorr, with corresponding
15 adjustments in the partial pressures of WF_6 and disilane. The amount of disilane added can comprise up to ten percent of the gas mixture. Thus, as previously indicated, one now has the ability to modify other parameters over a wider range without sacrificing
20 resistivity.

Claims:

1. A method for depositing a tungsten disilicide layer on a wafer heated to a temperature above 450°C in a chamber through which a gas mixture of WF_6 and SiH_2Cl_2 flows;
5 characterized by the step of:
adding less than ten percent disilane to said gas mixture.
- 10 2. A process for depositing a tungsten silicide layer on a semiconductor wafer in a reaction chamber, including the step of supplying a gas mixture of dichlorosilane and tungsten hexafluoride to said reaction chamber;
15 characterized by the steps of:
a. adding disilane to said gas mixture of dichlorosilane and tungsten hexafluoride, wherein said disilane comprises less than ten percent of said gas mixture;
20 b. maintaining the pressure in said chamber between 30 and 300 mtorr; and
c. heating the wafer to a temperature of from 450°C to 650°C to deposit said tungsten silicide layer.
25
3. The process as set forth in claim 2, wherein the partial pressure of dichlorosilane is from 27 to 285 mtorr.
- 30 4. The process as set forth in claim 2, wherein said wafer is heated to a temperature of approximately 560°C, the partial pressure of dichlorosilane is approximately 82 mtorr, the partial pressure of tungsten hexafluoride is approximately 4 mtorr, and
35 the partial pressure of disilane is approximately 4 mtorr.

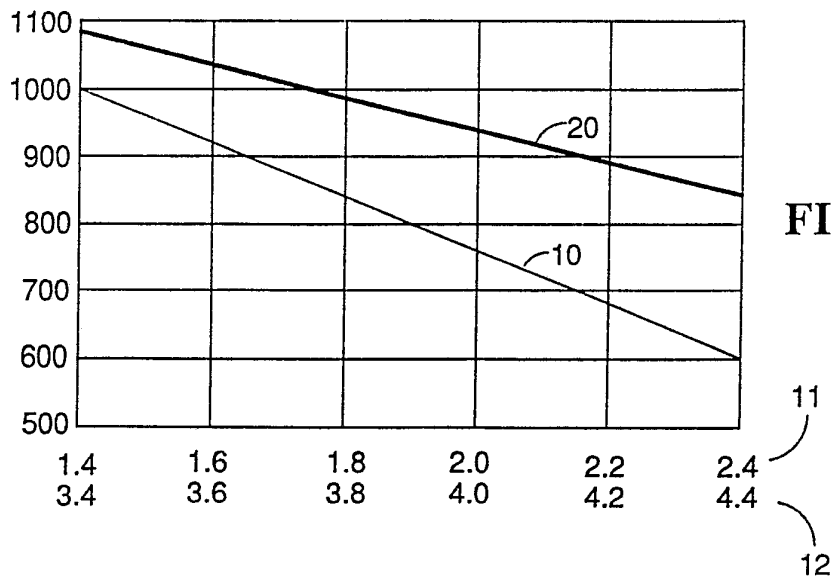


FIG. 1

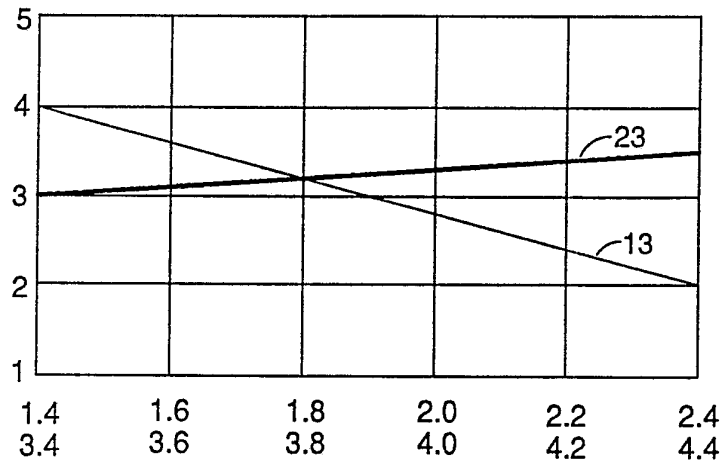


FIG. 2

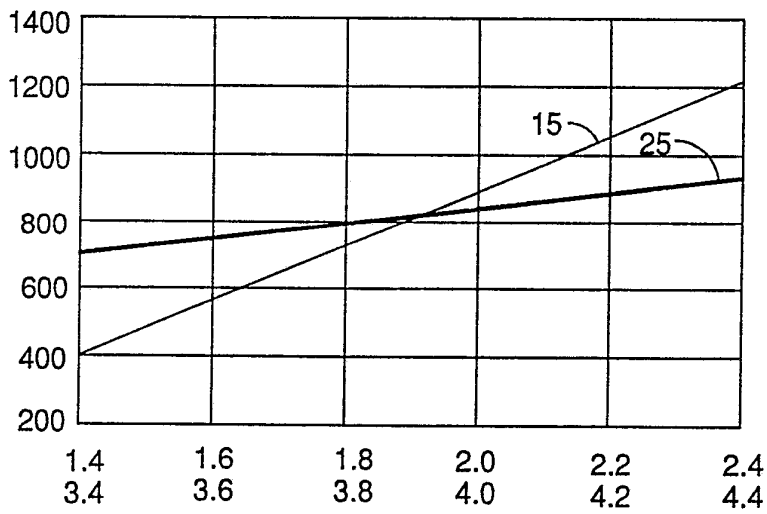
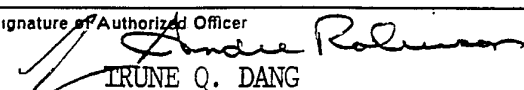


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/03049

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): H01L 21/443 US CL.: 437/200		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
US	437/192,196,200; 148/Dig. 147	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,501,769 (HIEBER et al.) 26 February 1985	
A	US, A, 4,692,343 (PRICE et al.) 08 September 1987	
A	US, A, 4,737,474 (PRICE et al.) 12 April 1988	
A	US, A, 4,902,645 (OHBA) 20 February 1990	
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IV. CERTIFICATION		
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ISA/US		 TRUNE Q. DANG