Evaluation of Adherence of CVD Tungsten Silicide Film to Polycrystalline Silicon*

By Seiichi Iwata**, Naoki Yamamoto**, Nobuo Hara***
and Akira Ookawa****

It is not easy to evaluate thin film/substrate adherence and characterize the thin film/substrate interface when adherence is strong. For this purpose, a new method (scratch-ESCA test), which is a combination of the scratch test, the peeling (by an adhesive tape) test, and the ESCA (Electron Spectroscopy for Chemical Analysis) measurement, has been developed and applied to the study of CVD (Chemically vapor deposited) WSi_x (tungsten silicide)/poly (polycrystalline) Si adherence. Besides the conventional adherence evaluation by the scratch test, it is found possible to evaluate the adherence by the ESCA measurement of the amount of WSi_x films peeled off from poly Si with an adhesive tape after the scratch test and also to carry out the characterization of the WSi_x /poly Si interface.

The results of the adherence evaluation described above are found to be related with the tendency of WSi_x films to delaminate or peel off during the semiconductor device manufacturing processes. The interface characterization by ESCA shows that the WSi_x adherence is affected by the presence of such elements as F, O, C and N at this interface.

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I. Introduction

With the increase in the integration density of MOS (Metal-Oxide-Semiconductor) IC's (Integrated Circuits), the metallization materials to be used in these VLSI's (Very-large-scale Integration) should have a lower resistivity⁽¹⁾ because the gate electrodes and interconnects become narrower and longer, resulting in higher electrical resistance.

Poly Si (polycrystalline silicon) with a resistivity of about $10^{-5} \text{ S}^{-1} \cdot \text{m}$ has been the main material used for gate electrodes and interconnects up to 64 kb (kilobit) DRAM's (Dynamic Random Access Memories). However, for higher-density DRAM's, a two-layer structure composed of refractory metal silicide with resistivity $\leq 1 \times 10^{-6} \text{ S}^{-1} \cdot \text{m}$ and poly Si has gradual-

ly begun to take the place of poly Si. This two-layer structure is called a "polycide".

CVD (Chemical-vapor-deposited) tungsten silicide (this will be written as WSi_x because it contains excess Si in WSi_2) has drawn attention as a candidate material for DRAM's of Mb (Megabit) class or higher because of its low resistivity ($\sim 5 \times 10^{-7} \text{ S}^{-1} \cdot \text{m}$) and good step coverage, which become more necessary with increasing integration density.

Although CVD WSi_x looked very promising at the beginning, it was soon found that there were problems associated with WSi_x /poly Si adhesion. This is probably the most important problem to be solved for making the use of WSi_x possible. This is due to the fact that, as the integration density increases, the gate electrodes and interconnects become narrower, the number of steps increases, the pitch between the steps becomes narrower, and the steps becomes sharper, all of which call for higher adherence of WSi_x .

The adherence of as-deposited WSi_x to poly Si was good, and neither delamination nor peeling was observed by the tests using an adherence tester or various adhesive tapes.

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** Central Research Laboratory, Hitachi, Ltd., Kokubunji 185, Japan.

*** Takasaki Works, Hitachi, Ltd., Takasaki, Japan.

**** Musashi Works, Hitachi, Ltd., Kodaira 187, Japan.

However, the WSi_x films delaminated at steps after annealing at around 1200 K which is needed for the device fabrication. With the involvement of many processes besides annealing, the problem has become more difficult to solve. There were too many factors which cause the delamination and there are no tests available for the assessment of the adherence of well-adhering films like WSi_x .

Finding a suitable adherence test alone is not sufficient, since one also wants to know the cause of the delamination or peeling. In many cases, the cause can be clarified if the characterization of the interface is possible. The aim of this study is therefore two-fold: Namely,

- (1) to find an adherence test whose result can be correlated with the delamination in the fabrication process, and
- (2) to find a method of interface characterization to know the causes of this delamination.

The adherence test was sought for from several existing tests for various applications. The requirement for the selection was that the results of this test could be correlated with the appearance of this delamination in the actual fabrication process. It was also desirable to carry out the test right after the WSi_x deposition and predict the delamination. For the interface characterization it was considered important that chemical state as well as elemental analysis was possible.

II. Experimental

The following factors were therefore taken into consideration for the selection of the most suitable method for testing this adherence.

- (1) Is there any delamination at the WSi_x /poly Si interface?
- (2) Can the results of the test be correlated with the WSi_x /poly Si delamination during device fabrication?
- (3) Can the same specimen be used for the interface characterization, which facilitates the correspondence between the results of the adherence test and the interface characterization?

1. Various tests for adherence evaluations

The following five methods were tried.

- (1) Adhesive tape test:
This is the so-called "tape test", in which the WSi_x film was peeled off from the substrate with an adhesive tape.
- (2) Test using adhesives:
Various kinds of paper and metal films which were bonded onto the WSi_x films with various adhesives were peeled off from the substrates.
- (3) Adherence tester:
A commercially available Sebastian Adherence Tester was used. A stud with a contact head (2.8 mm diameter) coated with a thermosetting adhesive was bonded to the WSi_x surface. The adherence was tested by pulling this stud until delamination failure occurred (a tensile test).
- (4) Thermal shock test:

The specimen was first heated to about 450 K and then immersed in a liquid nitrogen bath. This was repeated several times to see if any delamination occurred.

- (5) Hardness test:

The WSi_x surface was indented by using a Knoop Hardness Tester to see if any delamination occurred around the indentation.

- (6) Scratch test:

A diamond stylus with a tip radius of 75 μm was moved across the WSi_x surface at the applied load of 0–6 N and the velocity of about 1 mm/s to find the lowest load (critical load L_c) at which delamination was observed. A Taber Scratch-Shear Tester was used for this purpose.

2. WSi_x film formation

CVD equipment (Genus 8402) was used to deposit 300 nm-thick WSi_x films with the values of x ranging from 2.6 to 3. The deposition was carried out under the total pressure of 50 Pa, the flow rates of SiH_4 and WF_6 being 1.667×10^{-5} and $(1.5 \sim 3.3) \times 10^{-7}$ m^3/s , respectively. The substrate temperature was 633–673 K.

3. Interface analysis

ESCA was used for this purpose, because

chemical state as well as elemental analysis was considered important. The measurements were carried out in a vacuum of 0.1 mPa using $\text{MgK}\alpha$ X-radiation. Peak positions could be determined within the accuracy of ± 0.1 eV and the resolution was 1.4 eV (full width at half maximum of $\text{Au } 4f_{7/2}$). The measured values of electron kinetic energy were calibrated by setting the kinetic energy of $\text{Au } 4f_{7/2}$ electrons to be 1166.7 eV and the difference in the kinetic energy of $\text{Si}2p$ and $\text{O}1s$ electrons from SiO_2 to be 429.5 eV.

III. Results and Discussion

Various factors influencing the $\text{WSi}_x/\text{poly Si}$ adherence were clarified after selecting the most suitable method for evaluating this adherence and characterizing the $\text{WSi}_x/\text{interface}$.

1. Selection of the adherence test

The delamination occurs at the steps (about $0.5 \mu\text{m}$ high) on the substrate at a fairly later stage of the VLSI fabrication process. It is desirable that one can predict this failure right after the WSi_x deposition.

Various adherence tests are compared in Table 1. Only the scratch test could satisfy the required criteria. The concentration (x in WSi_x) dependence of the critical load L_c , determined from the scratch test is shown in Fig. 1. The same diagram shows that no delamination in the fabrication process occurred for L_c near 5N, but delamination occurred for L_c around 3N. Accordingly, this critical load L_c is

Fig. 1 Composition dependence of critical load, L_c , as obtained from scratch test (●: good adherence, ○: delamination in the fabrication process).

Fig. 2 WSi_x surface after scratch test.

Table 1 Comparison of various adherence tests.

Testing method	Delamination occurs?	Corresponds to actual failure?
Adhesive tape ¹⁾	No	No
Adhesive ²⁾	No	No
Adherence tester ³⁾	No	No
Thermal shock ⁴⁾	No	No
Hardness tester ⁵⁾	Yes	Sometimes
Scratch tester ⁶⁾	Yes	Yes

1), 2): several kinds commercially available, 3) Sebastian Adherence Tester, 4) Specimen at 450 K dropped into liquid nitrogen several times, 5) Knoop Hardness Tester, 6) Taber Scratch-Shear Tester.

designated as “adherence” in this paper. The scanning electron micrograph of the delaminated WSi_x surface after the scratch test is shown in Fig. 2.

One of the problems in the scratch test is the reproducibility of the results. In a short period during which one obtains a set of data in a series of experiments, it is usually possible to obtain the values of L_c within the accuracy of $\pm 0.1\text{N}$. However, the values are different in

some cases from those remeasured several months later. This is due mostly to the change in the surface condition of the diamond tip. One factor is the sticking of particles on the tip surface or the wear of the diamond tip and another is the direction in which the tip is attached to the Adherence Tester. The reproducibility was checked by using a standard specimen. If the value of L_c was different from the previous value, the tip surface was cleaned, the direction of the tip was altered, or the tip was replaced, so that the same value of L_c could be obtained.

2. Interface characterization

Interface characterization, in general, is not easy⁽¹⁾⁽²⁾⁽⁵⁾⁽⁶⁾ because it is difficult to expose the interface without changing the chemical state or composition. We therefore have not used argon ion etching for this purpose. We have succeeded in characterizing such interfaces as Mo/SiO₂, W/SiO₂ and Mo/Si by using chemical etching followed by the ESCA measurement⁽¹⁾⁽²⁾⁽⁷⁾.

However, this method cannot be used unless a suitable etching solution is found. In this case, the etching should be stopped at the interface and should not change the chemical state of the substrate surface. A mechanical peeling method can sometimes be also used⁽⁷⁾. In the case of WSi_x/poly Si adherence, both of these methods could not be used because a suitable etching solution was not available and the adherence was too strong to be peeled.

In this study, the WSi_x/poly Si interface characterization was attempted by noting the following points after the scratch test:

(1) Some WSi_x/poly Si delamination is realized though locally (see Fig. 2).

(2) Small pieces of the delaminated (some not yet delaminated) WSi_x films can be collected by an adhesive tape if this peeling is carried out after the scratch test.

The tape with the fragments of WSi_x films delaminated from the substrates was examined by ESCA. This procedure is shown in Fig. 3. One scratch across the specimen did not yield the amount of WSi_x films necessary for the ESCA measurement, and many scratches (about two scratches per mm) were made. The

Fig. 3 Sampling method for investigation of adhesion interface by ESCA after scratch test and peeling by adhesive tape (scratch-ESCA test).

Fig. 4 Si 2p spectra from WSi_x at WSi_x/poly Si interface (scratch-ESCA test).

metal tape (3M copper adhesive tape) was used in order to keep electric charging during ESCA measurements to a minimum.

Figure 4 shows the result obtained by using this method. Here, it can be seen that Si in WSi_x is less oxidized for the better adhering WSi_x film. C, O, F and N were also found besides W and Si. Of these elements, C, O and a small amount of Si are present in the adhesive tape. Therefore, W, F, N, and most of Si are from the WSi_x film. No differences in F or N were observed for the specimens in Fig. 4.

On the other hand, it was not usually easy to

Table 2 Example of scratch-ESCA test result (see Fig. 3).

Composition, x^1	W4f _{7/2} intensity ²⁾		Critical load, L_c/N
	Load 4N	Load 6N	
3.0	0	0.03	4.5~5.0
2.6	0.10	0.25	2.5~3.0

1) x in WSi_x , 2) normalized intensity (intensity ratio of W4f_{7/2} to Cls electrons).

examine the poly Si side of the interface because complete delamination was very rare. Micro-electron-beam Auger electron spectroscopy was used to examine the small delaminated area of the poly Si. It was only found that the poly Si was oxidized in the two specimens in Fig. 4.

Another measure of adherence besides the critical load L_c was found from the above experiments. Namely, there was the correspondence between L_c and the peak intensity of W4f_{7/2} electrons from the adhesive tape, the intensity being normalized with respect to the Cls intensity. Table 2 shows the comparison of the two specimens in Fig. 4. There is a correlation between L_c and the normalized intensity $[W]/[C]$ for the two loads shown in the Table. For comparing many specimens, it is better to use a load above L_c since no delamination occurs below L_c . Figure 5 shows the relation between L_c and $[W]/[C]$ for several specimens. A load of 6N ($L_c \leq 5N$) was used in the scratch test and the adhesive tapes were examined by

Fig. 5 Dependence of critical load, L_c , on W4f_{7/2} intensity from adhesive tape with peeled-off WSi_x (scratch-ESCA test, load 6N).

ESCA. $[W]/[C]$ is considered to be a measure of the amount (area) of WSi_x delaminated from poly Si. Thus, a good correlation is to be expected; namely, the higher the adherence, the less $[W]/[C]$.

3. Various factors affecting WSi_x /poly Si adherence

Various factors contributing to the WSi_x /poly Si adherence were investigated by using the method described above (which was named the "scratch-ESCA test"). Such elements as O, C, F, N were found to influence the adherence by comparing the results of the interface characterization and the critical load L_c .

(1) Oxidation of WSi_x /poly Si interface

(a) WSi_x oxidation

Figure 6 shows the ESCA spectra of the various elements found on the adhesive tape used for peeling after the scratch test. Besides W, Si, O, C, and F, a small amount of N was detected although the spectrum is not shown in the figure. Of these elements, W, F, N and a

Fig. 6 ESCA spectra of elements found on adhesive tape used for peeling after scratch test (A very small amount of N was also detected, but it is not shown here.).

greater part of Si are from WSi_x because the tape contains C, O and a small amount of Si.

If one looks at the chemical state of W and Si, it is seen that W is scarcely oxidized whereas Si is oxidized to some degree as shown in Fig. 6. This results from the stability of SiO_2 in comparison with that of W oxides⁽⁸⁾. The degree of oxidation of Si, however, was not always the same. As shown already in Fig. 4, the adherence was greater for the WSi_x with the Si less oxidized. The reasons for this will be discussed in section (c).

(b) Poly Si oxidation (before WSi_x deposition)

The oxidation of the interface on the poly Si side should also be investigated although it is not usually possible to examine the poly Si surface as mentioned before. To look into the effects of the poly Si oxidation, the poly Si surfaces were examined before WSi_x deposition and the results of the scratch test was compared with the oxidation observed on the poly Si surface before the deposition.

Table 3 shows the correlation between the critical load L_c and the poly Si oxide thickness. Here, too, the adherence is greater for the poly Si with thinner oxide films. These differences in the oxide thickness come from the variation in the surface treatment using hydrofluoric acid (HF).

(c) Discussion

In the examples shown in the previous sections, the WSi_x /poly Si adherence was found to be influenced by the oxidation of both the substrate (poly Si) and the WSi_x deposited on the poly Si. The reason for this is not clear, but it is considered to be as follows.

If there are no impurities, the bond at the in-

terface is either W-Si or Si-Si, which should be strong⁽⁹⁾. However, in effect, the Si in WSi_x or poly Si at the interface is oxidized. Therefore, for the W in WSi_x , the adherence should be smaller if the poly Si is oxidized because the free energy of reaction[†] of W and SiO_2 is positive^{††}₍₈₎. For the Si, if it is oxidized, the adherence is also expected to be smaller because the oxidized state (SiO_2) is very stable (less active)⁽⁸⁾⁽⁹⁾.

(2) C on poly Si surface

Table 4 shows the effect of carbon (C) contamination of the poly Si surface on the critical load L_c . The critical load is greater for the sample with less C. The C is considered to be due to the hydrocarbon adsorbed on the poly Si surface.

Table 5 shows the effects of the surface treatment after the removal of a photoresist film on the poly Si. The effects of both Si oxidation and C contamination seem to be present. In this case, the C contamination comes from the photoresist film which could not be completely removed.

(3) F at WSi_x /poly Si interface

Figure 7 shows the relation between the normalized Fls intensity $[F]/[W]$ and the critical load L_c . This correlation was obtained when the Si oxidation and C contamination were brought down to a permissible level by controlling the surface treatment and deposition conditions. This result shows that the deposition condition is not yet well controlled because this F comes from WF_6 gas used for the deposition of WSi_x ⁽¹⁰⁾. Another source of F is the HF solution used for the pre-deposition surface treatment. However, the amount of F from this source is about one order of magnitude smaller.

The chemical shift of this F was examined

Table 3 Dependence of L_c on oxide thickness¹⁾ on poly Si.

Oxide thickness ²⁾ /nm	Critical load, L_c /N
1.3	1.0
1.0	1.7
0.85	4.4
0.70	5.4

1) amounts of C, F, and N were about the same ($\pm 10\%$) for these specimens, 2) estimated from peak intensity ratios of oxidized to unoxidized Si(2p) electrons.

[†] $\text{W} + \text{SiO}_2 = \text{WO}_2 + \text{Si}$ (free energy also positive for WO_3 formation).

^{††} A qualitative correlation between the adherence (not the adhesive strength, but the occurrence or non-occurrence of delamination) and the free energy of reaction is generally observed. For example, Ti or Al (the free energy negative) adheres to SiO_2 better than Au or Cu (the free energy positive).

Table 4 Effect of C(on poly Si) on critical load, L_c . (scratch-ESCA test)

Sample	poly Si		WSi _x		Critical load, L_c/N
	[C]/[Si] ¹⁾	[W]/[Si] ¹⁾	[F]/[W] ¹⁾	[Si-O]/[Si] ¹⁾	
1	1.1	0	0.024	0.45	0.5
2	0.43	0	0.024	0.42	1.0

1) [C], [F], [W], [Si-O] and [Si] are ESCA peak intensities of Cls, Fls, W4f_{7/2}, Si2p (oxidized) and Si2p (unoxidized) electrons. These peak intensities could be obtained on both poly Si and WSi_x surfaces because of low adherence (oxide thickness on poly Si 1.3 nm).

Table 5 Effects of poly Si surface treatment on critical load, L_c .

Surface treatment ¹⁾	Oxide thickness/mm	[C]/[Si]	Critical load, L_c/N
HF	0.90	0.60	2.0
NH ₄ OH/ H ₂ O ₂ ²⁾ -HF	0.85	0.40	4.5
HF (no photoresist)	0.80	0.45	4.9

1) given after removing the photoresist (organic material) film on poly Si. 2) 1~1.5 nm oxide film is formed by this treatment. This oxide film is then removed by HF (hydrofluoric acid) along with any photoresist film remaining on poly Si surface.

Fig. 7 Dependence of critical load, L_c , on Fls intensity (scratch-ESCA test).

for that on the WSi_x surface. However, there were too much scatter in the data (kinetic energy of 562.6–563.6 eV) to reach any conclusion. The attempt was therefore made to examine this F on the poly Si side. For this purpose, the adherence was intentionally lowered (see Table 3) by using an oxidized poly Si substrate to enable the WSi_x film to be completely removed with an adhesive tape after the

scratch test. The poly Si surface to which WSi_x adhered was thus successfully examined. The position of the Fls peak was fairly constant in this case (562.6 ± 0.1 eV). This position was furthermore found to be the same as that in the case of HF-treated SiO₂, which indicates that this Fls position is due to the Si-F bonds formed in the reaction,

The reason for the lowering of the adherence is not apparent, but it is considered that the formation of strong Si-F bonds⁽⁹⁾ makes the poly Si surface less active (or more stable) so that the adherence is reduced. The same tendency (adherence lowering by F) is also observed in the case of the W deposition (also by CVD) on SiO₂⁽¹¹⁾⁽¹²⁾.

The F at the WSi_x/poly Si interface can easily be supplied by the reaction such as:

However, HF in the gaseous state does not appreciably etch SiO₂, but the presence of H₂O greatly facilitates the reaction of HF and SiO₂⁽¹¹⁾. It is considered that more F remains on the poly Si (the surface being oxidized Si) if there is H₂O present in the CVD atmosphere. This is supported by the experimental results that the amount of F at the WSi_x/poly Si interface increases if H₂O is deliberately added to the gas components or if the inside of the CVD chamber is exposed to air for a long time. Further studies are being carried out and will be reported elsewhere.

Finally, in a special case, N was a contributing factor in the WSi_x/poly Si adherence. When the deposition temperature was raised to 723 K, the critical local L_c decreased from 5N

(633 K) to 1N. N was detected at the interface, and there was a shift to the lower kinetic energy of W4f electrons, indicating the possibility of W nitridation. This N comes from the carrier gas used in the CVD.

4. Application

As mentioned in the Introduction, the delamination of thin films is one of the most common problems in the LSI fabrication. However, it is also one of the most difficult problems to solve. Trial-and-error methods are often used, and real solutions cannot be obtained in many cases.

An example of the application of the scratch-ESCA test will be shown in the following. In this example, the cause for the variation of the WSi_x/poly Si adherence was investigated during a period extending to about eight months. The following results were obtained as shown in Fig. 6.

(1) The critical load L_c becomes lower when the delamination failures occur.

(2) The amount of F at the WSi_x/poly Si interface is increased when these failures occur.

By utilizing the scratch-ESCA test, it was possible to pinpoint the actual cause (reduced pumping capacity of the rotary pump for the CVD equipment and the H₂O adsorption inside the chamber) and the problem was solved.

IV. Conclusion

When the thin film/substrate adherence is strong, it is difficult to evaluate this adherence and also to characterize this interface. In this study, the conventional scratch test, the peeling test and the interface characterization by ESCA were combined (scratch-ESCA test) to make the above evaluations possible.

This method was applied to the study of the adherence of CVD WSi_x films to poly Si and it was shown that this test could be used right after the WSi_x deposition to predict delamination failures occurring later in the LSI fabrication process. Furthermore, the interface characterization showed that the elements such as O, F, C and N influenced the adherence. These results were used to determine the depo-

Table 6 Example of scratch-ESCA test for controlling CVD process.

Time	[F]/[W] ¹⁾	Critical load, L_c/N
Feb.-Jul. (No delamination)	0.020~0.040	4.5~5.0
Aug. (Delamination)	0.040~0.20	0.01~3.0
Sept. (No delamination)	0.020~0.030	4.0~5.5

1) ESCA peak intensity ratio of Fls to W4f_{7/2} electrons from WSi_x in contact with poly Si.

sition chamber maintenance conditions for guaranteeing sufficient adherence of the WSi_x films. This method can also be used to characterize strongly-adhering interfaces in general.

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