were attained among films deposited at different Ar pressures.

2. The target voltage, V_{dc}, decreased from 555 to 455V with increasing Ar pressure from 4 to 20 mtorr. The composition of as-deposited WSi_x films increased from $x = 2.46$ to 2.61 with increasing Ar pressure from 4 to 20 mtorr.

3. When annealing was performed at temperatures below 900°C, Ar concentration was unchanged from the As-deposited films. With annealing at 1000°C, however, the Ar concentration decreased to 2×10^{20} cm^{-3}. As a result, the same film properties were achieved in all these films.

It can be concluded that film properties are not affected by Ar impurities and the inclusion of Ar is not a serious problem if annealing was performed at the conventionally used annealing temperature of 1000°C.

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Tungsten Silicide Films Deposited by SiH_2Cl_2-WF_6 Chemical Reaction

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ABSTRACT

This paper studies tungsten silicide films deposited by the SiH_2Cl_2 (DCS)-WF_6 chemical reaction. The deposition rate was held at around 1500 Å/min at temperatures above 500°C. However, the deposition rate decreased rapidly below 500°C because the surface reaction is dominant. The Si/W ratio (Si composition) of WSi_x film decreased from 2.38 to 2.15 at the WF_6 flow rate changed from 4 to 6 sccm in deposition at 580°C. Resistivity decreased from 740 to 530 μΩ-cm with these compositional changes. The resistivity increased with the increase of deposition temperature. Since tetragonal WSi_2 grains are grown in as-deposited film, lower resistivity films can be achieved.

Low-resistivity films with excellent thermal stability and conformality can be achieved in chemical vapor deposition (CVD) tungsten silicides. Such films have been extensively used in polycide gates and interconnections of very large scale integrated circuits (1). Deposition from the reaction between monosilane (SiH_4, denoted hereafter as MS) and tungsten hexafluoride (WF_6) has been reported by many authors (1, 2). However, the high fluorine concentration of MS WSi_x film leads to flatband voltage shifts and a reduction of gate capacitance in CVD WSi_x polycide gates (3). Film peeling during the oxidation process and microcracking at the inside corner of the step are also serious problems.

Recently, high temperature CVD WSi_x employing dichlorosilane (SiH_2Cl_2 abbreviated as DCS hereafter) and WF_6 was reported (4, 5). Films made using these reactants have lower fluorine and hydrogen contents. The major advantages of the process are a reduction of microcracking at the inside corner of the step and improvement of adhesion performance. Therefore, DCS WSi_x films are a promising material for polycide gate and interconnection applications.

DCS-WF_6 chemical reactions are inherently cleaner than MS reactions; thus resulting in less opportunity for gas phase reactions and less deposition of by-products in the process chamber. Therefore, deposition of high quality film with less particulate, better conformality, and better adhesion is expected. However, few papers prior to this work have reported DCS WSi_x film deposition (4, 5). Details of the film properties have not been presented.

Experimental Procedures

WSi_x films were deposited by chemical reaction of DCS and WF_6 by employing a cold wall, single wafer type low pressure CVD reactor (5). Before thermal CVD WSi_x film deposition, a 150Å thick amorphous Si (a-Si) film was deposited on (100) p Si at 0.2 torr by plasma CVD to eliminate the effect of Si substrate surface. Next, thermal CVD WSi_x film was deposited successively in the same reactor at temperatures ranging from 470° to 600°C. The composition was measured by 1.5 MeV He^+ Rutherford backscattering spectrometry (RBS).

Experimental Results

WSi_x films were deposited by the DCS-WF_6 chemical reaction at temperatures ranging from 470° to 600°C, where the flow rates of DCS and WF_6 were held at 80 and 2.5

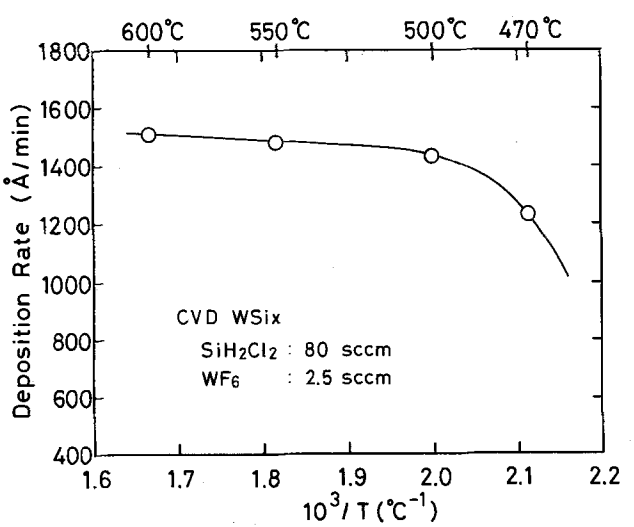

Fig. 1. Deposition rate of DCS CVD WSi_x as a function of deposition temperature. Flow rate of SiH_2Cl_2 (DCS) and WF_6 was 80 and 2.5 sccm.

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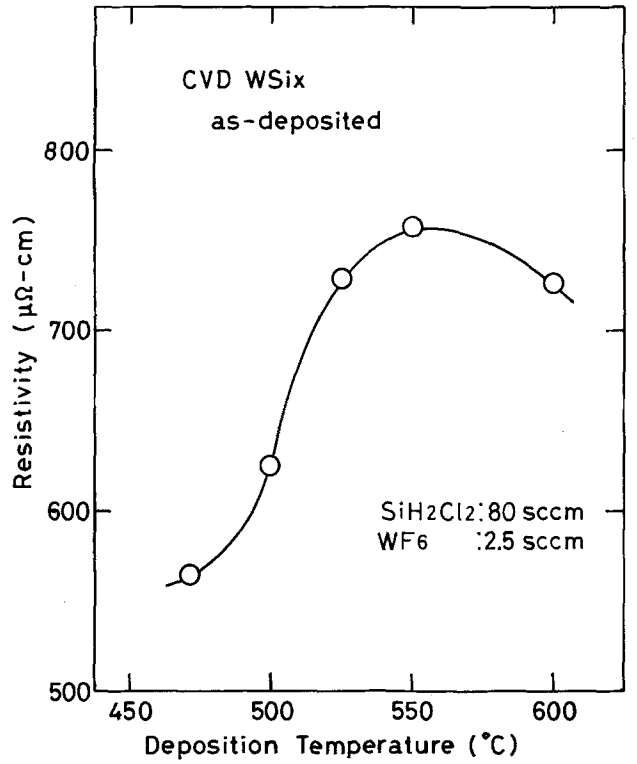

Fig. 2. Variation of resistivity of as-deposited DCS CVD WSi_x film with deposition temperature. The deposition was performed with SiH_2Cl_2 (DCS) and WF_6 flow rates of 80 and 2.5 sccm, respectively.

sccm, respectively. The deposition rate is shown as a function of reciprocal deposition temperature in Fig. 1. The

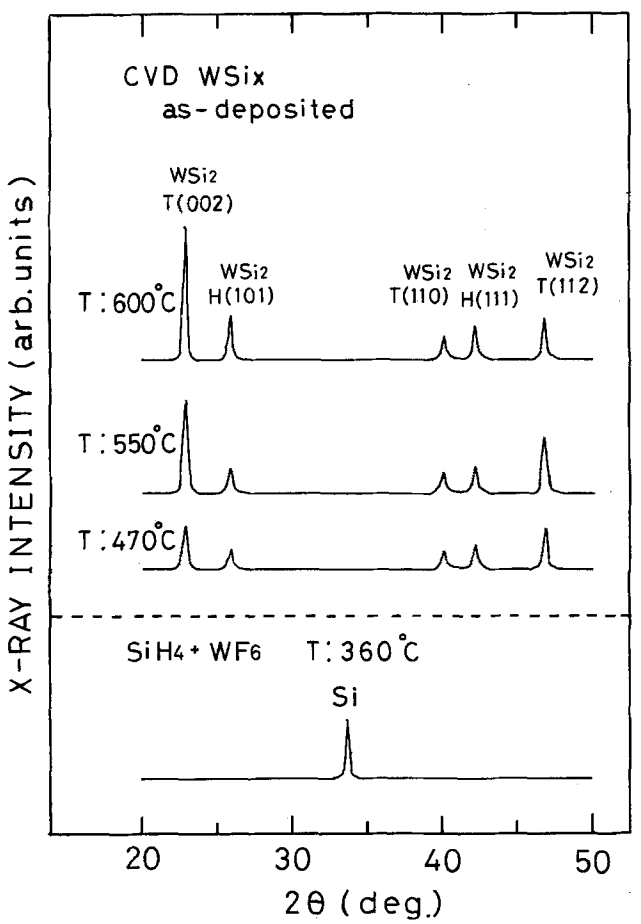

Fig. 3. X-ray diffraction spectra of DCS CVD WSi_x deposited at temperatures of 470°, 550°, and 600°C. The deposition was performed with SiH_2Cl_2 (DCS) and WF_6 flow rates of 80 and 2.5 sccm, respectively.

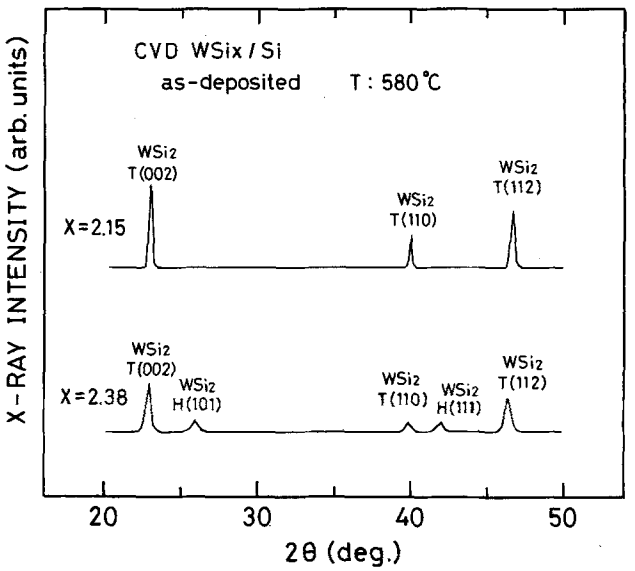

Fig. 4. X-ray diffraction spectra of as-deposited DCS CVD WSi_x with compositions of 2.5 and 2.38, where the deposition was performed on a Si substrate at 580°C. The DCS flow rate was held at 200 sccm.

thickness of films deposited on a-Si was determined from the RBS spectrum of W in WSi_x film and by weight changes.

The deposition rate was held around 1500 Å/min at temperatures above 500°C. This rate is much greater than the MS CVD WSi_x rate of 350-500 Å/min. The temperature variation of deposition rate of DCS above 500°C shows that mass transfer of DCS or WF_6 gases is the dominant deposition process. Since homogeneous nucleation occurs in the mass-transfer deposition process, a clean deposition process cannot be achieved. Therefore, the deposition chamber needs to be cleaned to achieve high quality film deposition.

However, the deposition rate decreased below 500°C in DCS-WF_6 process. The surface reaction is dominant in these temperatures; therefore, better conformality deposition can be expected.

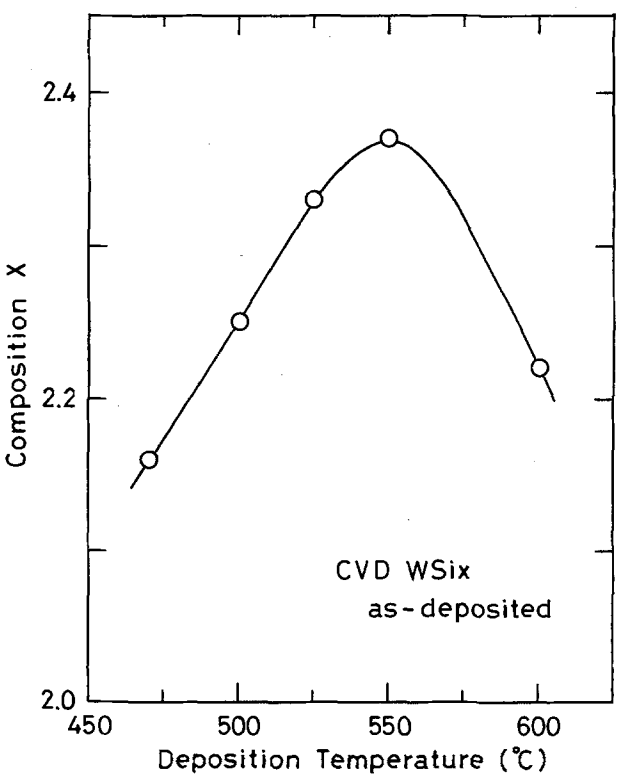

Fig. 5. Variation of composition, X, of DCS CVD WSi_x with deposition temperature. Flow rate of SiH_2Cl_2 (DCS) and WF_6 was 80 and 2.5 sccm.

The resistivity of as-deposited films is shown as a function of deposition temperature in Fig. 2. DCS and WF_6 flow rates were held at 80 and 2.5 sccm, respectively. As seen in this figure, the resistivity increased with increasing temperature. However, it decreased at 600°C. This reduction is due to the precipitation of excess Si from Si-rich WSi_x. These resistivity variations are mainly due to the composition and grain size variation of WSi_x films, as will be shown in Fig. 4.

X-ray diffraction spectra of these films were measured in order to study the grain growth during deposition. Typical spectra for 2000Å thick DCS WSi_x films deposited at different temperatures are shown in Fig. 3. Spectrum of MS film with an x of 2.6 deposited at 360°C is also shown. Since amorphous films are always deposited in MS-WF_6 CVD system, no WSi_2 peaks appeared in Si-rich MS $WSi_{2.6}$ film.

In DCS film deposited at 470°C, however, small hexagonal and tetragonal WSi_2 peaks were observed. The intensity of tetragonal (002) WSi_2 peaks increased with the increase in deposition temperature. Specifically larger sized grains were formed at 600°C. However, the intensity of the (112) and (110) peaks were invariant with temperature. the hexagonal (101) WSi_2 peak also increased with increasing temperature.

The spectra of films with a Si composition of 2.15 and 2.38 deposited at 580°C are shown in Fig. 4. Tetragonal (002), (110), and (112) WSi_2 peaks appeared in near stoichiometry films (x = 2.15). However, the intensity of the tetragonal peaks decreased in Si-rich WSi_x (x = 2.38) films. This measurement also indicates that the grain size of the tetragonal WSi_2 increased from 250 to 300Å when the composition varied from 2.38 and 2.15. Small (101) and (111) peaks of hexagonal WSi_2 appeared in Si-rich film.

The WSi_x film composition (Si/W ratio) is a very important parameter affecting film properties (6). Film adhesion can be markedly improved by employing Si-rich films, for instance, with compositions of x = 2.5-2.6. Compositional changes of Si-rich MS WSi_x films occurring during annealing were reported by many papers (1, 7). The Si composition was determined from RBS measurements of the Si and W yield ratios (8).

The average composition of these films deposited on an a-Si buffer layer is shown as a function of deposition temperature in Fig. 5. The composition increased from 2.16 to 2.37 with temperature increasing from 470° to 550°C. The increase of Si composition with temperature is mainly due to the increase of the amount of DCS reduced by WF_6. However, the Si content decreased rapidly at 600°C because excess silicon precipitated from Si-rich WSi_x occurred during the deposition. The decrease in Si did not evidently appear in films deposited on silicon dioxide (7). As shown in the x-ray diffraction spectra in Fig. 3, tetragonal WSi_2 grains were grown at 600°C with grain sizes of 220Å at 470°-500°C to 270-310Å at 600°C, together with the precipitation of excess Si.

The average composition at the uniform region of the films deposited at 580°C with different WF_6/DCS flow rate ratios is shown in Fig. 6. A value of x = 2.38 was obtained at a flow rate of 0.02. The Si content decreased rapidly with increasing WF_6/DCS ratio. However, the decrease slowed above a flow ratio of 0.025 and reached 2.15 at 0.03.

In-depth composition profiles of WSi_x deposited at 525°C on a-Si and Si substrates are shown in Fig. 7, where the deposition was performed under the conditions indicated. DCS and WF_6 flow rates were 80 and 2.5 sccm. The average value of x in the uniform region for each film was 2.33 and 2.23 on a-Si and Si substrates, respectively. These profiles show that a more uniform profile was attained in films formed on a-Si buffer layer. However, the value of x decreased markedly at the interface in the deposition on the Si substrate. These results show that film properties are largely affected by the substrate surface as reported elsewhere (7). Uniform composition films can be deposited when an a-Si buffer layer is employed (9).

When such W-rich regions are formed at the interface, film peeling easily occurs in the annealing process. Peeling is a serious problem in CVD WSi_x polycide gate technology. Sheet resistance deviation within a wafer is much greater in DCS films than that of MS films. This deviation is due to variation of the composition with depth at the interface. Details of the origin of this effect will be reported soon (9).

The resistivity of films deposited at 580°C is shown as a function of composition in Fig. 8. Resistivity of MS WSi_x film is shown by a closed circle. Resistivity of DCS film decreased from 740 to 530 μΩ-cm with varying composition from 2.38 to 2.15. Lower resistivity films could be obtained with lowering the composition due to the grain growth of tetragonal WSi_2 as mentioned above. However, Si-rich films, for instance, with x = 2.5-2.6, are needed in practice in WSi_x polycide gate processes in order to eliminate film peeling during annealing.

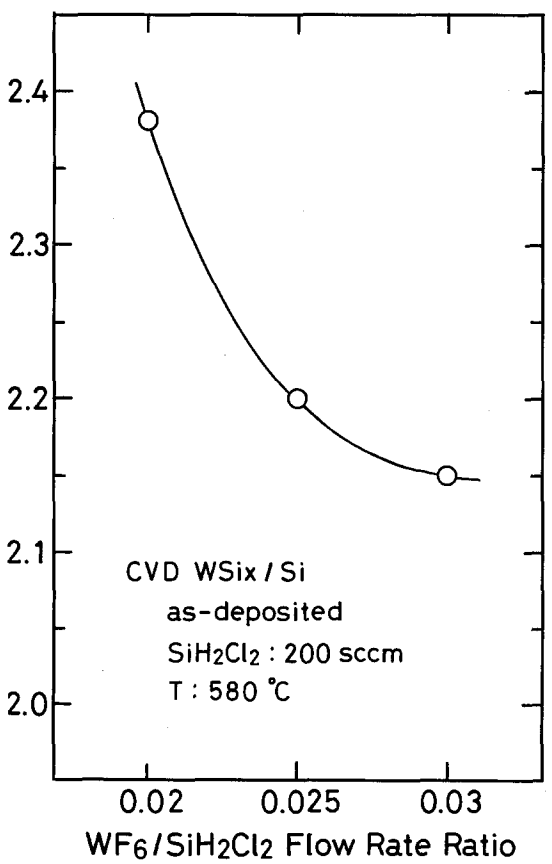

Fig. 6. Variation of composition, X, of DCS CVD WSi_x with gas feed rate ratio, WF_6/SiH_2Cl_2, where the films were deposited on Si substrate at 580°C and the SiH_2Cl_2 (DCS) flow rate was held at 200 sccm.

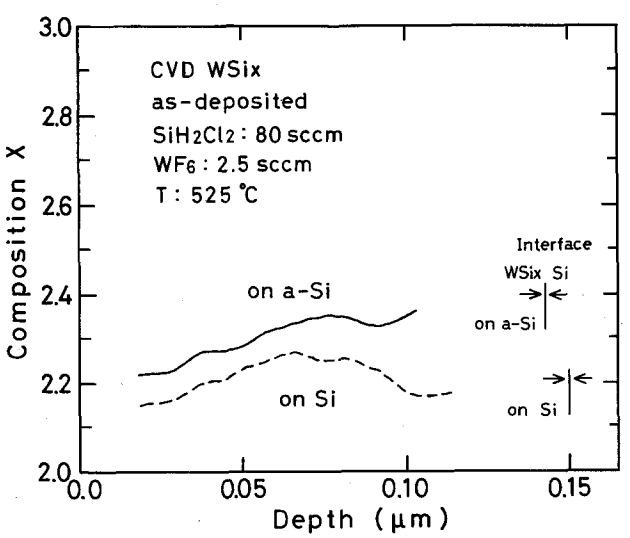

Fig. 7. In-depth composition profiles of DCS WSi_x deposited at 525°C on a-Si and Si substrates with DCS and WF_6 flow rates of 80 and 2.5 sccm.

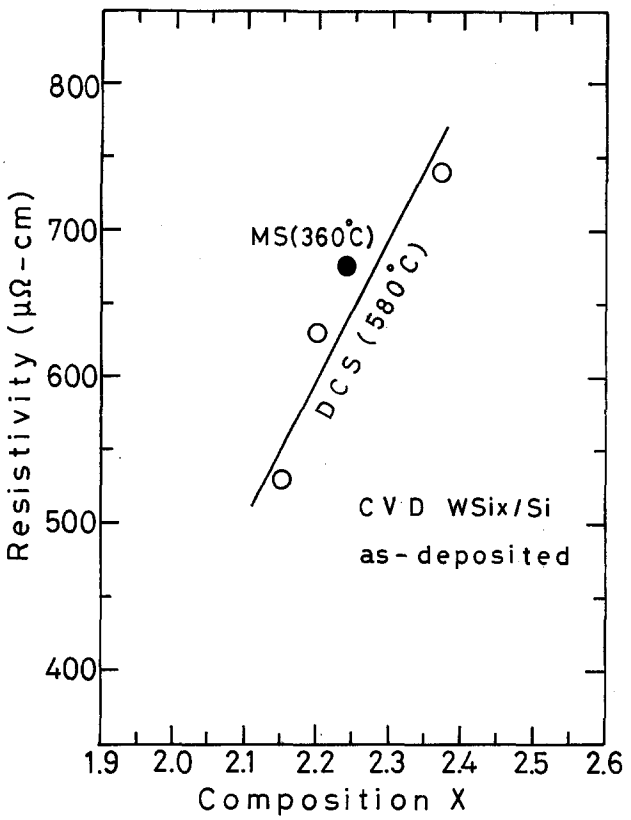

Fig. 8. Resistivity of as-deposited CVD WSi_x as a function of Si composition, x. Deposition temperature was 580°C.

Conclusions

The deposition rate of DCS WSi_x film was around 1500 Å/min, more than three times greater than that attained in MS WSi_x deposition. The deposition rate was held nearly constant at temperatures above 500°C. However, it decreased rapidly below 500°C, because surface reaction was the dominant process.

Film composition increased with increasing deposition temperature. However, it decreased at 600°C. This reduction may be due to the precipitations of excess Si occurring during the deposition at the interface. The Si composition changed from 2.38 to 2.15 with a WF_6/DCS flow rate ratio variation from 0.02 to 0.03.

X-ray diffraction spectra showed that WSi_2 grains are grown during the deposition, although the WSi_2 peaks did not appear in MS films. The intensity of tetragonal WSi_2 peaks increased with increasing deposition temperature. Grain size increased from 250 to 300Å with composition varying from 2.38 to 2.15. Hexagonal WSi_2 peaks appeared in Si-rich film. However, these peaks disappeared in the near stoichiometry film.

The resistivity of as-deposited films decreased with decreasing Si composition. When compared with MS WSi_x films, the resistivity decreased more rapidly at the low Si composition region because WSi_2 grain growth was more evident at lower Si composition.

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