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Preparation of WSi_2 by rapid thermal annealing of CVD thin films of tungsten

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Tungsten silicide (WSi_i) films were prepared by rapid thermal annealing (RTA) of W films obtained by chemical vapor deposition (CVD) from carbonyl precursor—$W(CO)_6$. The RTA process proceeds at 800–1400°C *in different gas environments—argon, nitrogen, vacuum, etc. Investigations of the crystal phase structure were performed by Reflection High Energy Electron Diffraction (RHEED) method. Difference in the phase composition was observed for ''thin'' and ''thick'' WSi_2. Close to the surface of W films, a pure metal rich phase is formed, and at the interface W/Si, a phase rich of Si is found. Diffusion was considered to be the controlling process in the kinetics formation of WSi_2. The influence of the gas environment on WSi_2 was also studied. The comparison made shows that nitrogen favours WSi_2 formation. Some of the samples have shown a certain degree of texturing.* © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

A system formed by two materials separated by a sharp interface is not thermodynamically stable. Upon heating, it will evolve toward a more stable state in which each element will tend to its minimum activity. Because of the practical interest of silicides for microelectronic industry, the solid state reaction between a thin metal film and a silicon wafer which is the simplest method to get silicides has been intensively studied.[1,2] The metal–Si thin film reaction has been thoroughly investigated and a conclusion made about differences between film and bulk reactions: there are peculiarities in thin film solid state reactions appearance of phases, absence of certain ones, very rapid kinetics of phase formation, etc. The basic mechanism—reactive diffusion and the influence of technological conditions on metal–Si thin film reaction—are precisely considered in Refs 3–5.

In our previous work[6] studying CVD-W films obtained by low temperature (300–400°C) CVD process involving $W(CO)_6$ as a precursor after annealing at higher temperatures (740–800°C) for 10 min to decrease carbon and oxygen impurities in as-deposited W films, we have seen a diffusion-based silicide phase as a result of annealing. The result was used as a starting point for W silicides formation by solid state reaction in the two layered system W/Si choosing CVD-W film thickness properly. In a more recent work,[7] we reported on WSi_2 formation by rapid thermal annealing of CVD W films in vacuum. A conclusion was made that it was possible to obtain WSi_2 by RTA at 800°C if the metal film was 20 nm thick. For thickness about 100 nm, a metal phase as well as the silicide one, was detected at this temperature. Temperatures higher than 800°C and RTA time durations at least 30 s lead to WSi_2 phase formation in the ''thick'' films.

Here new results are presented for WSi_2 film formation by solid state reaction at the W/Si interface. The influence of gas media is investigated by applying RTA in different gas environment, such as Ar, N_2, N_2 and H_2 mixture, etc.

Experimental

Tungsten films with thicknesses of 20, 80 and 100 nm were deposited on Si(100) by pyrolitical decomposition of $W(CO)_6$, according to the following reaction:

$$W(CO)_6 \xrightarrow{400^\circ C} W + 6CO\uparrow$$

The hexacarbonyl vapors carried by an argon flow of 0.68 l min^{-1} enter the CVD reactor. Separately, another Ar flow of 0.8 l min^{-1} joins the carrier flow before entering the reaction chamber. The process goes on at atmospheric pressure. The substrates are heated indirectly by a graphite susceptor coated by a SiC protective layer. A high frequency generator allows temperature regulation by anode voltage or by disconnection of one of the

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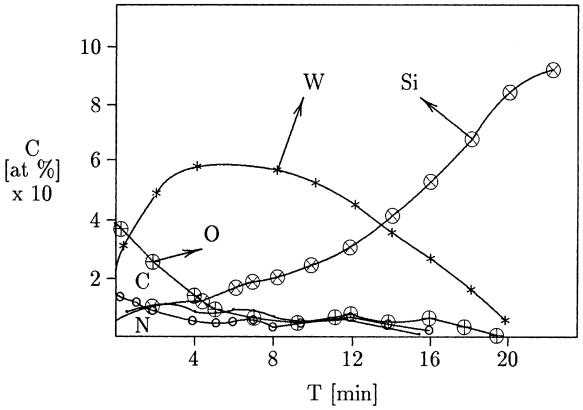

Figure 1. Auger Electron Spectrometry analysis of CVD-W film deposited by pyrolitical decomposition of $W(CO)_6$ at 400°C and additionally annealed at 740°C. Film thickness is 600 nm.

Table 1. RTA technological parameters for formation of WSi_x crystal phase by solid state reaction between W and Si in CVD-W/Si system. Formation of WSi_2 by solid state reaction between W and Si in CVD-W/Si system

W-film thickness t (nm)	Temperature (°C)	Time (s)	Gas
20	800±5	15±0.1	N_2
	800±5	30±0.1	N_2
	800±5	180±0.1	N_2
	800±5	180±0.1	10^{-5} torr
80	800±5	15±0.1	N_2
	800±5	30±0.1	N_2
	800±5	30±0.1	N_2+H_2
	800±5	30±0.1	Ar
	800±5	30±01	10^{-5} torr

three feed phases. The temperature regulator with Pt/Pt. Rh thermocouple controls the temperature of the graphite susceptor with an accuracy of ±10°C. The sublimator immersed in a silicon oil bath is kept at temperature of 100°C assuring enough vapor pressure. Argon of an initial purity of 99.95% is further purified by removal of oxygen and moisture with zeolite and palladium catalyst:

$$H_2+O_2 \xrightarrow{\text{Pd (catal.)}} 2H_2O$$

The film sheet resistance is measured by VEECO FPP-100 device, thickness by Talystep profilometer. Annealings are made by using two systems: a vacuum-RTA system, and an ONIKS-5 equipment. The vacuum system heating is resistive, in the ONIKS equipment is KG-220-1000-3 type halogen lamps. The RTA temperature in the two systems is changed in the range 600–1400°C. Time duration controlling accuracy in the two RTA systems is ±0.1 s.

Results and discussion

A CVD tungsten film with thickness of 600 nm was deposited by pyrolitical decomposition of $W(CO)_6$ at 400°C on Si(100) wafers. The as-deposited film contains considerable amount of carbon and oxygen (about 20–30%). For decreasing impurities, concentration annealing at 740°C was usually applied for about 10 min.[7] A typical Auger analysis of such a film is presented in Fig. 1. Diffusion of Si and W was detected, but no silicide formation was found. An additional adjusting of W film thickness was made and two sets of samples (thin ones—CVD-W films with thickness $t = 20$ nm, called "thin") and thick ones ($t = 80$ nm, called "thick") were submitted to rapid thermal annealing at 800°C (and 1000, 1200 and 1400°C) in nitrogen and other gases environment (in ONIKS equipment) for different time durations in the range 15–180 s. As-prepared samples were investigated by Reflection High Energy Electron Diffraction (RHEED) and the RHEED patterns were analyzed. In Table 1, RTA technological conditions are shown. The RTA temperature of 800°C is the interesting one, as the most acceptable for microelectronic technology. Some results at higher temperatures are shown for comparison and for tracing the tendency. Such results might be interesting, since serious IC damages based on diffusion could not be expected for short time diffusion.

The obtained RHEED diffraction patterns of RTA annealed at 800°C for 15 s "thick" CVD-W film in nitrogen and in vacuum show that nitrogen (Fig. 2(b)) improves microstructure and favors silicide formation. In the film, RHEED of which is presented in Fig. 2(a), W phase dominates while the other film contains a mixture of $WSi_{0.7}$ and WSi_2. The initial thickness of W film is important and should also be optimized. Results from Reflection High Energy Electron Diffraction are presented in Table 2. The expected data for WSi_2 d-spacings[8]: 0.3927, 0.2962, 0.2262, 0.196, 0.16, 0.14 nm (3.927, 2.962, 2.262, 2.026, 1.96, 1.6, 1.4 Å) are not exactly found in the observed results—Fig. 3.

One common feature of the reflections observed experimentally is the reflection at $d = 0.333$ nm, which is characteristic for $WSi_{0.7}$, for which the expected d-spacings data are: 0.338, 0.323, 0.302, 0.295, 0.257, 0.247 nm (3.38, 3.23, 3.02, 2.95, 2.57, 2.47 Å). The

a b

Figure 2. RHEED diffraction patterns of RTA annealed "thick" W film deposited on Si(100)—(a) annealing in vacuum; (b) annealing in nitrogen.

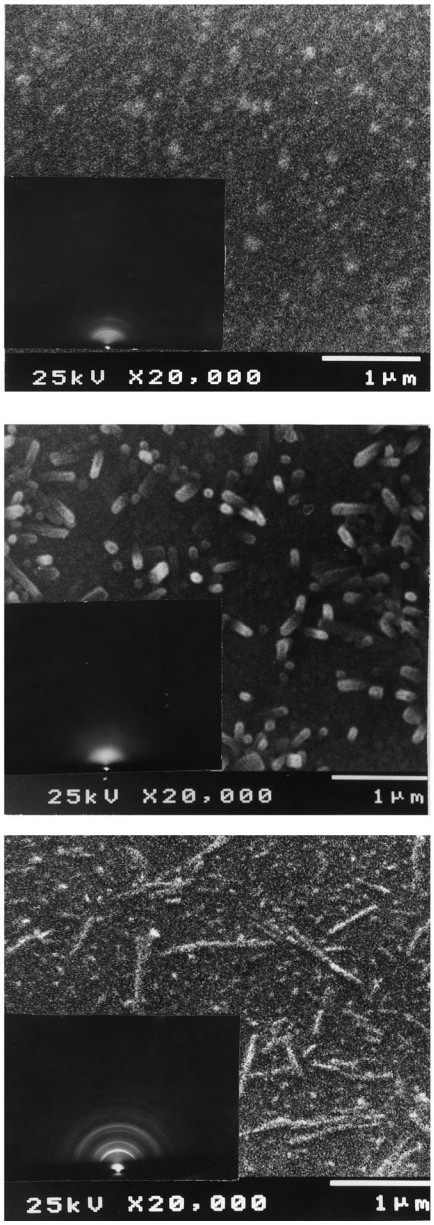

Figure 3. RHEED diffraction patterns and SEM micrographs of W silicides films formed by rapid thermal annealing of CVD-W film deposited on Si(100) : (a) at 800°C for 15 s ; (b) at 1000°C for 15 s ; (c) at 1400°C for 15 s.

triplet at $d = 0.338$, 0.323 and 0.302 nm has probably resulted in the reflection at $d = 0.333$ nm. The reflection for WSi_2 at $d = 0.3927$ nm is found as reflection at $d = 0.388$ nm for a ''thin'' film of 20 nm thickness, heated at 1000°C for 15 s and as reflection at $d = 0.4$ nm for a ''thick'' film of 80 nm thickness and heated for 15 s at the same temp. The very weak reflection at $d = 0.295$ nm existing in the expected data for $WSi_{0.7}$ and in WSi_2 as 0.2962 is not found in the observed data. The medium strong reflection at $d = 0.226$ nm is not observed in samples annealed at 800°C but it is observed in the sample annealed at 1000°C. WSi_2 at $d = 0.202$ nm (medium strong) is observed in a 20 nm ''thin'' film heated at 800°C for 15 s. The reflection at $d = 0.196$ nm is found as reflection at 0.184 nm in all samples heated at 800°C. The reflection at 0.16 nm is observed in all samples heated at 800°C. The very strong reflection at $d = 0.14$ nm is also observed in these samples. As a result, a conclusion could be reached that when RTA at 800°C is applied, WSi_2 is not the only crystal phase formed. A mixture of tungsten silicides (WSi_2 and $WSi_{0.7}$) grows when the RTA temp. does not exceed 800°C. Results from a previous study show that WSi_2 could be formed at RTA of 800°C if the thickness of the CVD-W film deposited on Si is small (20 nm) and the rapid thermal annealing process duration is 3 min.[7] For comparison, these results are shown in the same Table 2. Results for WSi_2 formation in ''thick'' (80 nm or 100 nm) films annealed at 800°C show that when RTA heating goes in vacuum, even after 3 min metal W phase dominates. On the contrary, if RTA heating proceeds in N_2 environment, a mixture of W silicides phases at time duration of 15 s is formed. In conclusion,

Table 2. RHEED structural characterization of RTA annealed CVD-W "thin" and "thick" films deposited on Si(100) substrates

RTA temperature (°C)	RTA annealing time (s)	Gas	"Thick" W Films (80 and 100 nm)	"Thin" W films (20 nm)
800	15	N_2	$WSi_2+WSi_{0.7}$	$WSi_2+WSi_{0.7}$
	30	N_2	$WSi_2+WSi_{0.7}$	$WSi_2+WSi_{0.7}$
	30	N_2+H_2	W_3Si	$WSi_2+WSi_{0.7}$
	30	Ar	W phase dominates	$WSi_2+WSi_{0.7}$
	180	N_2	W phase dominates	WSi_2
	180	Vacuum	W phase dominates	WSi_2
1000	15	N_2	WSi_2	WSi_2
	15	Vacuum	WSi_2	WSi_2
	30	N_2	WSi_2	WSi_2
	30	Vacuum	WSi_2	WSi_2
	180	Vacuum	WSi_2	WSi_2
1400	15	Vacuum	Well expressed WSi_2	WSi_2
	180	Vacuum	Well expressed WSi_2	WSi_2

nitrogen (as well as nitrogen mixed with hydrogen) favors formation of W silicide phases. Simultaneous growth of two (or more) phases in our experiments has also been observed by other authors.[3] The lowest resistivities measured for as-formed W silicide films are 2.2 mohm.cm for the "thick" films, formed at 800°C and 0.5 mohm.cm for "thick" films formed at 1400°C. The highest value measured for "thin" W silicide is about 4 mohm.cm.

Conclusion

By rapid thermal annealing of CVD W on Si (100) at 800–1400°C and different time durations, tungsten silicide films were formed by solid state reaction between W and Si. RTA at temperatures of 800°C silicide mixture of WSi_2 and $WSi_{0.7}$ formation is favored by N_2 and N_2+H_2 gas atmosphere. These films have a resistivity of 2.2 mohm.cm. WSi_2 films are formed at higher RTA temperatures (1000°C or 1400°C) for a short time duration of 15 s.

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