Oxidation of Si-rich chemical-vapor-deposited films of tungsten silicide

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We have studied dry oxidation characteristics of Si-rich WSi_x thin films prepared by LPCVD directly on SiO_2, with $x = 2.7$ for as-deposited films. It has been reported previously that thin (less than 100 nm) CVD tungsten silicide adheres well to SiO_2. Using Auger depth profiling and Rutherford backscattering spectroscopies, we find that silicon in excess of stoichiometric WSi_2 diffuses through the silicide toward the surface to form a SiO_2 passivating overlayer. The extracted activation energy for this oxidation process is $E_a = 1.2$ eV, consistent with oxygen diffusion in SiO_2. A similar value of E_a is found for WSi_x deposited on polysilicon. During the anneal, the stoichiometry x of WSi_x decreases monotonically with the annealing temperature, reaching $x = 2$ after 30 min at 900°C or 20 min at 950°C. Longer times or higher temperatures result in silicon depletion, with $x = 1.7$ after 30 min at 1000°C. At the same time, the resistivity of WSi_x also decreases from $\simeq$90 Ω/□ for 1500 Å as-deposited film to 5 Ω/□ for the films annealed at 1000°C, the value obtained in a standard homogenization anneal. A scanning electron micrograph (SEM) of 0.5-μm fine lines patterned using e-beam lithography reveals that the integrity of fine line structures, their adhesion to SiO_2, and their vertical profiles remain unchanged after the oxidation process. We suggest that such Si-rich tungsten silicide can be useful as a gate electrode without the polysilicon underlayer, since no extra passivation is necessary and reoxidation and homogenization steps in the FET processing sequence can be accomplished simultaneously.

Introduction

The pursuit of high-speed, high-density and low-power field-effect transistor (FET) technology requires reduction of device dimensions. As dimensions extend into submicron range, some nonscaling effects become important. Such effects arise from the inability to scale certain physical parameters of the materials used to fabricate the structures. One is the resistivity of the gate and interconnect metals. Another is the work function of the gate electrode on silicon. Both of these parameters pose a limit on the extendability of polysilicon as well as polysilicide [1, 2] gate FETs to the linewidths at and below 0.5 μm.

Polysilicide gate, which consists of low-resistivity WSi_2 with an underlayer of polycrystalline silicon (poly-Si) over the thin gate oxide, reduces resistivity by about two orders of magnitude from poly-Si gate. This poly-Si underlayer is necessary for the desirable oxidation properties [3, 4] as well as to preserve gate integrity. Hence, the problem of a proper work function remains, since it is still the work function of n^+ poly-Si ($\phi_m = 4.05$ eV) that sets the mobility of the

Table 1 Tungsten silicide deposition parameters

Temperature	360 ± 10°C
Pressure	200 mT
Time	190–200 s
Helium	400 sccm
Silane	1000 sccm
Tungsten hexafluoride	varied from 10–14 sccm

carriers in the channel for a given threshold voltage [5]. WSi_2 without poly-Si has a work function at midgap between n^+ and p^+ poly-Si and thus would be applicable for submicron CMOS.

The films of stoichiometric WSi_2 prepared by coevaporation of W and Si suffer from adhesion problems when deposited directly on SiO_2 and form volatile oxides [3, 6] without a polysilicon underlayer. It has been reported [7] that LPCVD tungsten silicide adheres well to SiO_2, but only when films are Si-rich. In this paper, we report the study of dry oxidation characteristics of such Si-rich films deposited by LPCVD directly on SiO_2. Previous steam oxidation studies [8] of e-beam coevaporated WSi_3 showed that the resistivity increases for annealing times longer than 20 min at 1000°C. This was attributed to the simultaneous oxidation of metal and silicon. We show that during dry oxidation annealing of LPCVD films, silicon in excess of stoichiometric WSi_2 diffuses through the silicide toward the surface to form a SiO_2 passivating overlayer, and that during this process the resistivity is lowered as it would be during the usual homogenization anneal.

Experiment

The films of WSi_x (with the stoichiometry x varied in the range between 2 and 3) were prepared by LPCVD in a commercial system designed to perform at low pressure and low temperature, with a cold wall [7, 9]. The system can achieve the base pressure of less than 10 mT. The process consists of the reaction of two gases, silane (SiH_4) and tungsten hexafluoride (WF_6). Helium is used as a carrier gas for both reactive gases. The reaction that describes the tungsten silicide deposition process is [10]

$$x\,SiH_4 + WF_6 \rightarrow WSi_x(S) + 6HF(g) + (2x - 3)H_2(g),$$

where $x > 1.5$.

A typical deposition sequence is as follows: First the chamber is purged with helium for 300 s to clean the chamber interior. The helium flow is maintained throughout the process. Then silane is introduced and stabilized. The third step is the actual process step which allows the introduction of tungsten hexafluoride. Process time determines the thickness of WSi_x. Different Si/W ratios (x) are obtained by varying the flow rates of tungsten hexafluoride and silane. After deposition, tungsten hexafluoride is cut off and silane is allowed to flow to react with any residual tungsten hexafluoride. Finally, the chamber is purged with helium to carry away any resultant gaseous products. The parameters used in the deposition are given in **Table 1.** For these considerations the growth rate was measured to be 500–700 Å/min.

The LPCVD WSi_x films deposited on SiO_2 were subsequently oxidized in an open-ended quartz tube furnace

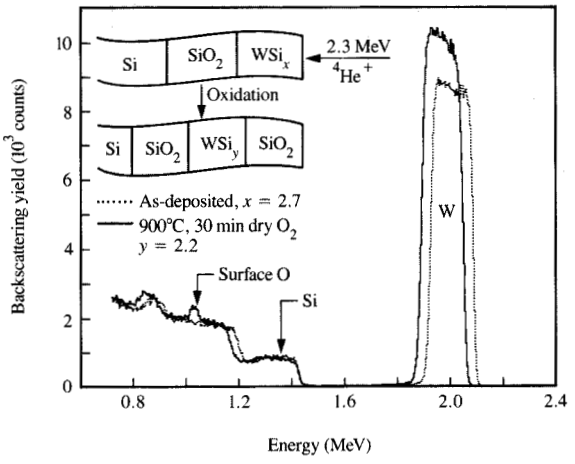

Figure 1

2.3-MeV $^4He^+$ RBS spectra of a silicon-rich WSi_x film (x = 2.7) 1500 Å thick deposited on SiO_2 before and after oxidation at 900°C for 30 min in dry O_2. After annealing, the film loses some of its excess silicon to become WSi_y, with y = 2.2.

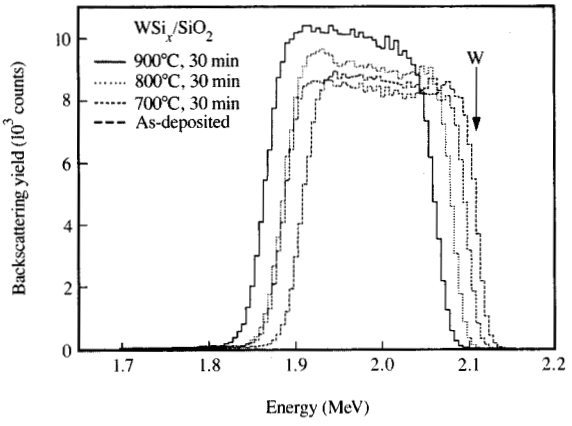

Figure 2

RBS spectra of WSi_x/SiO_2 film (x = 2.7) before annealing and after oxidation at various temperatures. Only tungsten signals are shown.

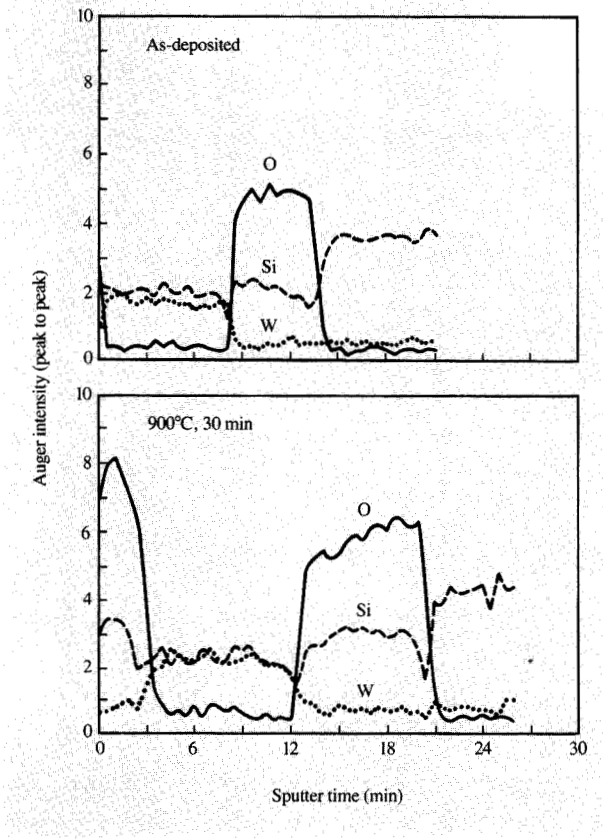

Figure 3

Auger intensities of tungsten silicon WSi_x film deposited on SiO_2 and of the same film annealed at 900°C for 30 min in dry O_2 vs. sputtering time. The spectra clearly indicate a formation of surface SiO_2.

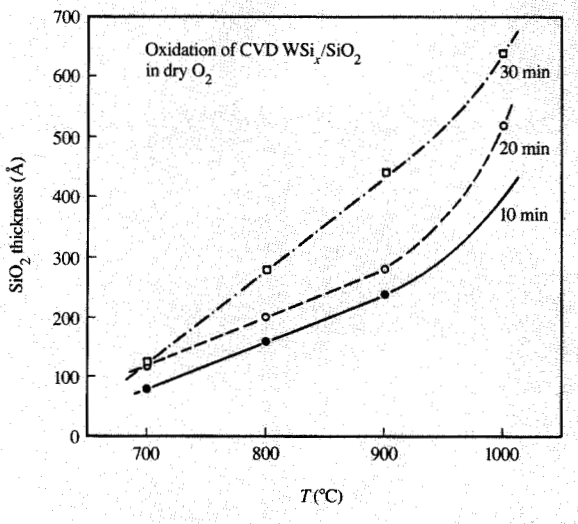

Figure 4

Thickness of the formed SiO_2 overlayer as a function of annealing temperature for three annealing times.

(Marschal type) with a continuous flow of dry O_2. The linear flow rate of O_2 was 4 cm/s and the inner diameter of the quartz tube was 10.2 cm. The oxidation temperatures ranged from 700 to 1000°C, with oxidation times up to 30 min.

Both the stoichiometry and the composition of the as-deposited and the oxidized samples were analyzed with Rutherford backscattering spectrometry (RBS) [11], and Auger analysis was used to back up RBS results. The thicknesses of the WSi_x films were determined from the RBS spectra with the assumption of bulk values for the density of the layers. The thicknesses of the grown oxide layers were obtained by measuring the shift in the tungsten peak after oxidation and comparing it with the calculated shift due to the formation of SiO_2 using surface approximation.* It was also measured with ellipsometry. The resistivities of WSi_x films were measured after removal of the oxide layers using a four-terminal probe.

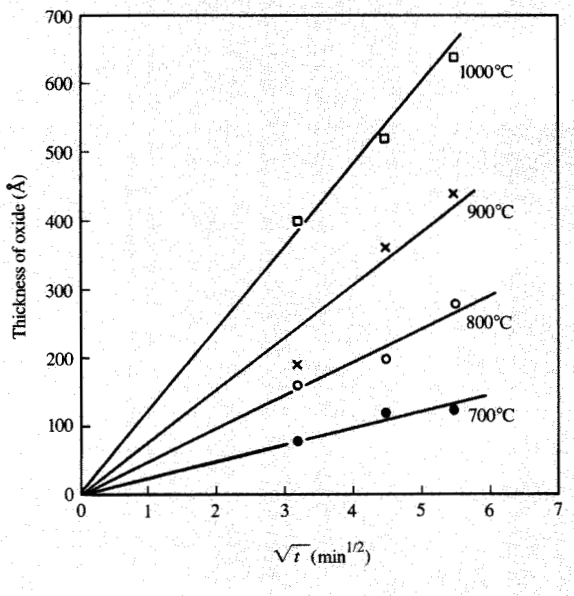

Figure 5

Thickness of the grown oxide as a function of the square root of the oxidation time for several temperatures.

* E. D. Adams, IBM Essex Junction facility, Burlington, VT, private communication.

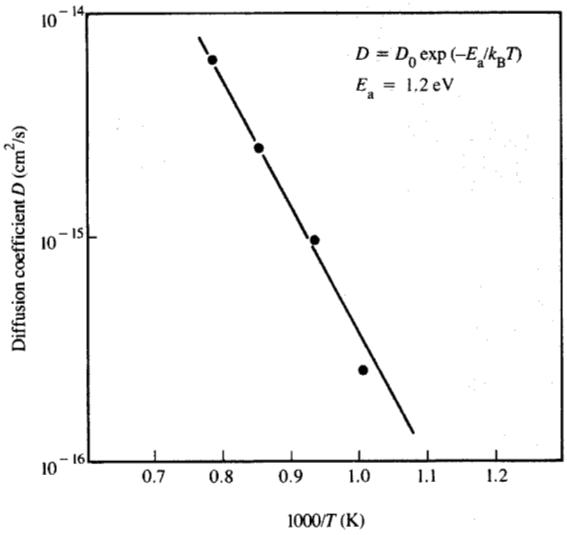

Figure 6

The diffusion coefficient determined from Equation (1) plotted as a function of the reciprocal temperature. The activation energy (E_a) of 1.2 ± 0.1 eV is determined from the fit to the Arrhenius formula.

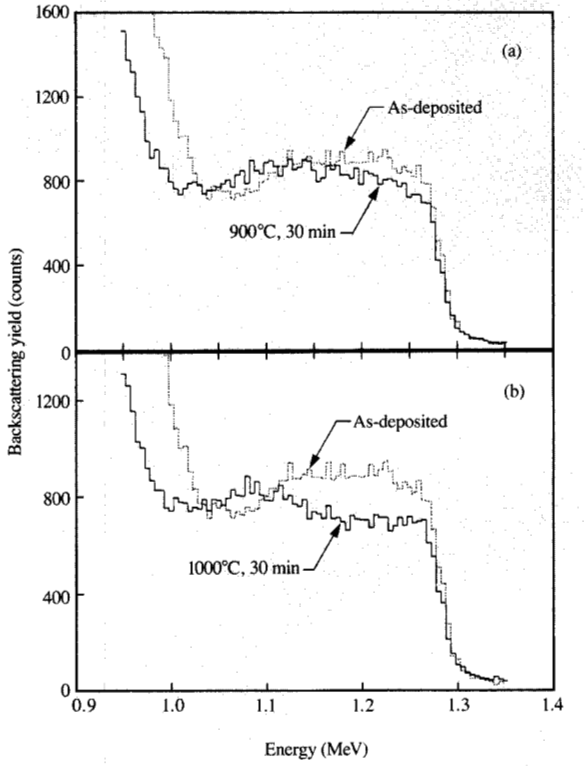

Figure 8

Silicon signals in the RBS spectra of as-deposited WSi_x/SiO_2 films and after annealing for 30 min (a) at 900°C and (b) at 1000°C. The depletion of silicon is observed.

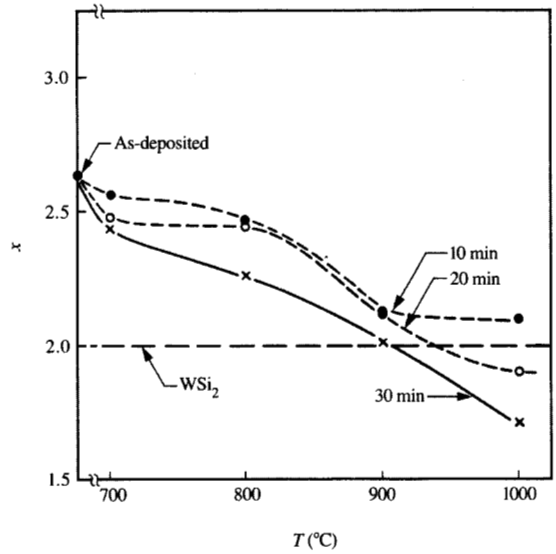

Figure 7

Stoichiometry x of WSi_x as a function of annealing temperature.

Results and discussion

A typical result of the thermal oxidation of Si-rich WSi_x films in a dry O_2 atmosphere is shown in **Figure 1** for a temperature of 900°C. The RBS spectra are presented for an as-deposited film of WSi_x with $x = 2.7$ and for the same film annealed for 30 minutes. We observe that after annealing the stoichiometry x is lowered to become $y = 2.2$, as indicated by the increase in the backscattering yield of the tungsten signal. The growth of the oxide overlayer is indicated by the appearance of a surface oxygen peak as well as by the shift of the tungsten signal toward lower energies. This is displayed in **Figure 2**, where a series of spectra for different annealing temperatures are presented and for simplicity only the tungsten signals are shown. It is apparent that the leading edge of the tungsten signal undergoes parallel displacement during the oxidation anneal. As the intensity of the peak increases, the width remains unchanged, manifesting a depletion of silicon from the silicide. The same oxidation behavior is observed when Si-rich WSi_x is deposited on polysilicon rather than SiO_2. The absence of an overall loss

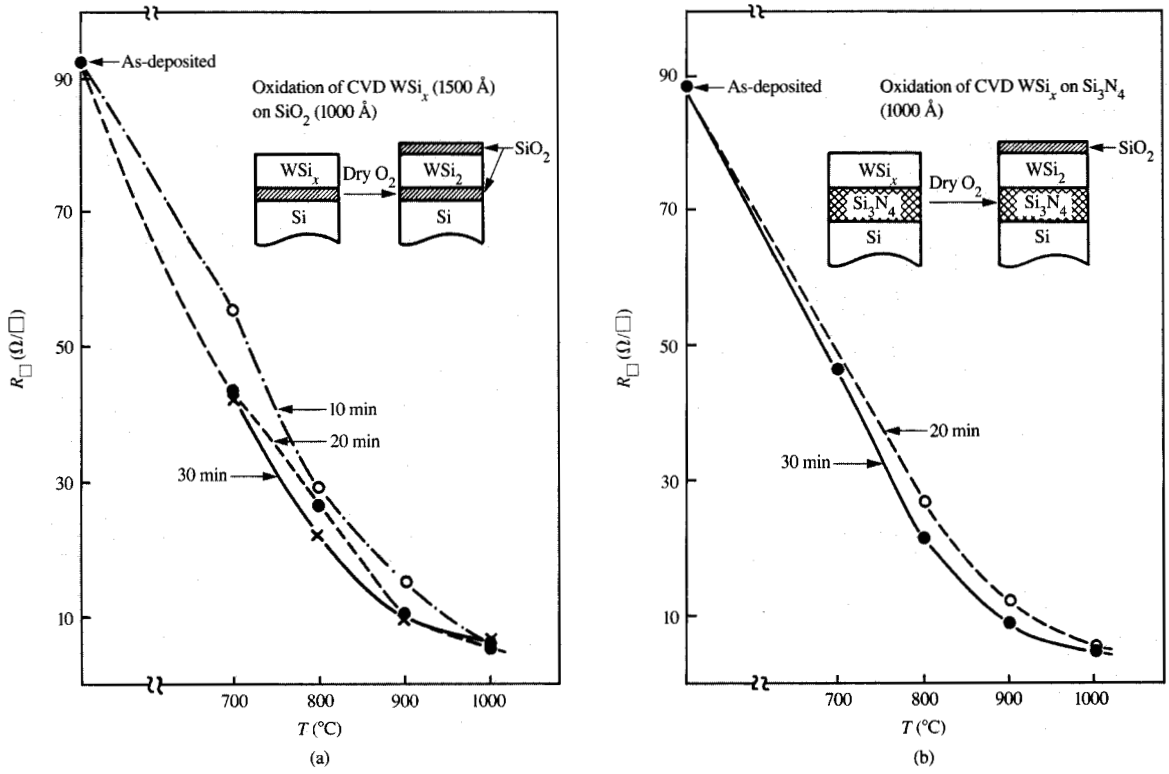

Figure 9

Sheet resistance of (a) Si-rich WSi_x/SiO_2 and (b) WSi_x/Si_3N_4 as a function of oxidation temperature. The resistance was measured using a four-terminal probe after the SiO_2 overlayer was removed.

of W indicates that the formation of volatile W oxides does not take place in this case [3]. The RBS data appear to be consistent with the formation of SiO_2 on the surface of the silicide. The estimate based on the shift of the W peak yields a thickness of SiO_2 equal to 40 Å/channel for the experimental parameters in our measurements (see footnote p. 635), in good agreement with the determination based on the width of the oxygen peak and the ellipsometric measurements.

The growth of surface SiO_2 is confirmed with Auger depth profiling as shown in **Figure 3**, where Auger intensities for films as deposited and oxidized for 30 min at 900°C are shown. It is clear that both silicon and oxygen are present in the surface layer of the annealed film, while there is no evidence for the tungsten and thus for the formation of tungsten oxides or of W_5Si_3 [3, 6].

The growth of SiO_2 is nonlinear in time, as shown in **Figure 4**, where oxide thickness is plotted as a function of temperature for three different oxidation times. Indeed, when plotted as a function of the square root of the oxidation time, the dependence is linear, as shown in **Figure 5** for four different oxidation temperatures: 700, 800, 900, and 1000°C.

The observed parabolic dependence of the oxide growth on time indicates that the oxidation of silicon-rich WSi_x is diffusion-limited.

The thickness, d, of the grown SiO_2 is related to the oxidation time, t, via the diffusion coefficient D of the oxygen diffusing in the oxide as follows:

$$\frac{d}{2} = (Dt)^{1/2}. \tag{1}$$

Therefore, D can be determined from the slopes of the straight lines in Figure 5. The temperature dependence of the diffusion coefficient, which is linear in reciprocal temperature, is displayed in **Figure 6**. This dependence can be fit by the Arrhenius formula

$$D(T) = D_0 \exp\left(\frac{-E_a}{k_B T}\right), \tag{2}$$

where k_B is Boltzmann's constant and T is the absolute temperature. Hence the process is thermally activated, with an activation energy E_a of 1.2 ± 0.1 eV, consistent with the quadratic term in the oxidation of Si. A similar value of E_a is found for WSi_x deposited on polysilicon.

It is usually argued that the mechanism of silicide oxidation is rapid diffusion of silicon through the silicide [12] and oxidation by the oxidant. Oxygen diffusion through the grown SiO_2 and reaction with silicon at the silicide/SiO_2 interface is believed to be the rate-controlling process. The presence of contamination in the silicide may result in lower diffusivity of silicon and thus in higher activation energy. Also, in the case of polysilicide, silicon has to diffuse to the surface from the polysilicon underlayer rather than from the silicide itself. It is not surprising, then, that a typical activation energy for dry oxidation of silicides on polysilicon is about 1.7 eV [7, 13], about 0.5 eV higher than we observe for the Si-rich case.

We infer, then, that during annealing in dry O_2, the excess silicon diffuses toward the surface of the silicide to react with oxygen, and as a result the stoichiometry of silicon-rich WSi_x is a function of both annealing time and temperature, as shown in **Figure 7**. The stoichiometry is observed to decrease monotonically with both time and temperature. The value of $x = 2$ is reached after 30 min at 900°C or 20 min at 950°C. It is interesting to note that in our experiments, WSi_x becomes silicon-deficient after 1000°C anneals for times longer than 20 min. We observe the value of x as low as 1.7 after a 30-min anneal at 1000°C. In addition, at higher temperatures some depletion of the underlying silicon is observed as well, as shown in **Figure 8**. As the excess silicon diffuses out of the silicide, the resistivity of WSi_x is decreased, as shown in **Figures 9(a)** and **9(b)**, where we plot the sheet resistance of WSi_x deposited on SiO_2 and Si_3N_4, respectively. A typical resistance of as-deposited 1500-Å-thick $WSi_{2.7}$ films is about 90 Ω/□. It decreases to a value of 4–6 Ω/□ independently of the underlying insulator. The lowest $R_\square$ is reached at a lower temperature for longer (30-min) anneals than for the shorter (10-min) ones. This sheet resistance value is comparable to a typical value obtained after a standard homogenization anneal practiced in the usual VLSI processing.

Summarizing remarks

We have shown that annealing of silicon-rich WSi_x formed by the CVD process in dry O_2 results in the growth of a SiO_2 overlayer. This passivating SiO_2 film is a result of the diffusion of the excess silicon in the silicide toward the surface and its reaction with oxygen. During the process the stoichiometry of the WSi_x films is decreased, reaching $x = 2$ after a 30-min anneal at 900°C or after shorter anneals at higher temperatures. Further oxidation results in Si-deficient films and some depletion of silicon from the underlying layers. During the dry O_2 anneal, the resistivity of the film is lowered to a value normally attained in a homogenization anneal in VLSI processing using WSi_2. Since a desirable conductivity improvement and formation of the passivating layer can be achieved in one processing step, the use of silicon-rich WSi_x is very attractive in submicron VLSI technology. In addition, while the adhesion to SiO_2 of WSi_2 is a serious reliability concern, it is not an issue for WSi_x. Indeed, as we can see in the scanning electron micrographs of **Figure 10**, patterned 0.5-μm lines of WSi_x retain their good vertical profiles as well as good adhesion after a 900°C, 30-min oxidation anneal in dry O_2.

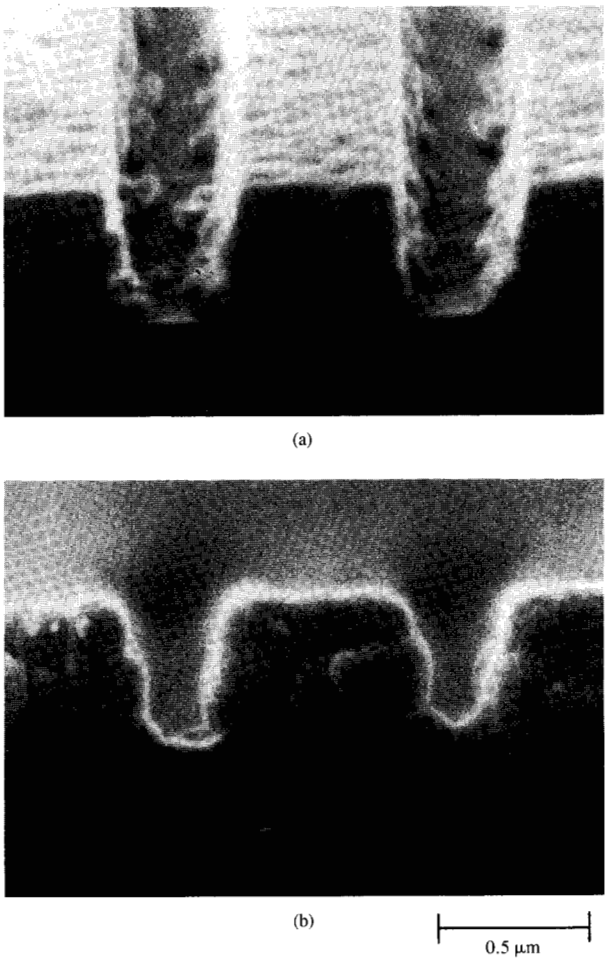

Figure 10

Scanning electron micrographs of 0.5-μm WSi_x lines on SiO_2 after the dry oxidation anneal at 900°C for 30 min: (a) top view of the lines; (b) cross-sectional cut.The integrity of the structure, its vertical profile, and its adhesion remain preserved.

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