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Tungsten Thin-Film Deposition on a Silicon Wafer: The Formation of Silicides at W–Si Interface

S. V. Plyushcheva, G. M. Mikhailov, L. G. Shabel'nikov, and S. Yu. Shapoval

Institute of Technological Problems of Microelectronics and High Purity Materials, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

e-mail: plush@iptm.ru

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Abstract—The interphase boundary formed in the process of tungsten thin-film deposition on a silicon wafer is investigated. These films are produced via (1) a CVD technique relying on hydrogen reduction of tungsten hexafluoride, (2) the same technique supplemented with plasmochemical action, and (3) magnetron deposition used for comparison purposes. It is shown that a nanometer tungsten silicide W_5Si_3 layer is formed at the tungsten–silicon interface only under gas-phase deposition. The effect of annealing on the specimen composition and surface resistance is investigated. It is shown that the formation and growth of a silicide WSi_2 layer commences at 700°C for CVD films and at above 750°C for films obtained with plasmochemical deposition; this results in a drastic increase in their electrical resistance. Under optimal conditions, tungsten films of 8×10^{-6} Ω cm resistivity are produced.

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INTRODUCTION

The employment of tungsten as a current-carrying material for metallization of ICs is of growing interest owing to its unique properties; as electronic devices become smaller, this material continues to withstand progressively greater current densities. Despite the fact that a tungsten layer has higher electrical resistance than an aluminum layer, in the production of semiconductor ICs, the former offers a number of advantages to the process of metallization [1–4]. Tungsten films are to a smaller degree prone to electromigration, and they differ but little in their thermal-expansion coefficient from silicon and silica, which are most often used in technology.

A metal film is deposited directly on silicon; therefore, in some cases, when the occasion requires, in the process of manufacturing devices, a silicide layer is produced under a later thermal treatment or the metal layer is left unchanged. Knowledge of the basic laws that govern film–substrate interface interactions in the specific structures and feasibility of control over these processes with the use of various growth methods and different film growth conditions serve as a physical foundation in the manufacture of electronic devices. Moreover, the conditions at the interlayer boundary, by and large, dictate the useful life of the devices.

The aim of this paper is to investigate the chemical interactions occurring at the tungsten–silicon interface in the process of tungsten thin-film deposition onto a silicon wafer with the use of various techniques of obtaining these films with a low electrical resistance.

EXPERIMENTAL

Tungsten films on silicon were obtained via the CVD technique by the hydrogen reduction of tungsten hexafluoride (in a thermal process with the activation energy of 70.32 kJ/mol) and gas-phase deposition with the plasmochemical stimulation of hydrogen. In the latter case, the activation energy is 15.91 kJ/mol. The specimens produced with magnetron deposition were taken for comparison. High-resistance ⟨100⟩-oriented silicon wafers were taken as substrates. These wafers were prepared by the conventional procedure [5].

The isothermal annealing of all the specimens was performed in hydrogen in the range from room temperature to 900°C in 50°C steps in the course of 30 min in the interior of an SUOL tube-furnace equipped with a precision temperature regulator. Hydrogen was cleaned by filtering with the use of a Palladii 0.5 installation equipped with palladium filters.

The film thickness was measured with a Talystep profilometer. The steps were formed both by masking a substrate in the process of metal film deposition and also by partially stripping the film out of the substrate surface. The electrical resistance of the films was measured according to the four-point probe method.

The chemical interaction of silicon substrate surface layers and a tungsten film was investigated with Rutherford backscattering spectrometry (RBS) and thin-film x-ray diffractometry (TFXRD) [6–8]. The special features of the TFXRD technique are the specimen position with a low-angle primary x-ray beam and the

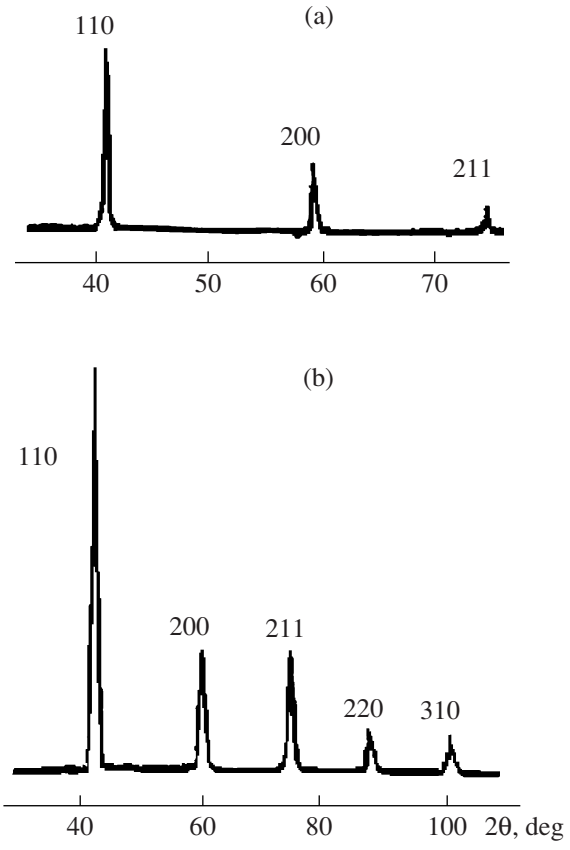

Fig. 1. Diffraction patterns of tungsten films deposited on silicon; the diffraction patterns are obtained with the use of (a) conventional and (b) TFXRD techniques.

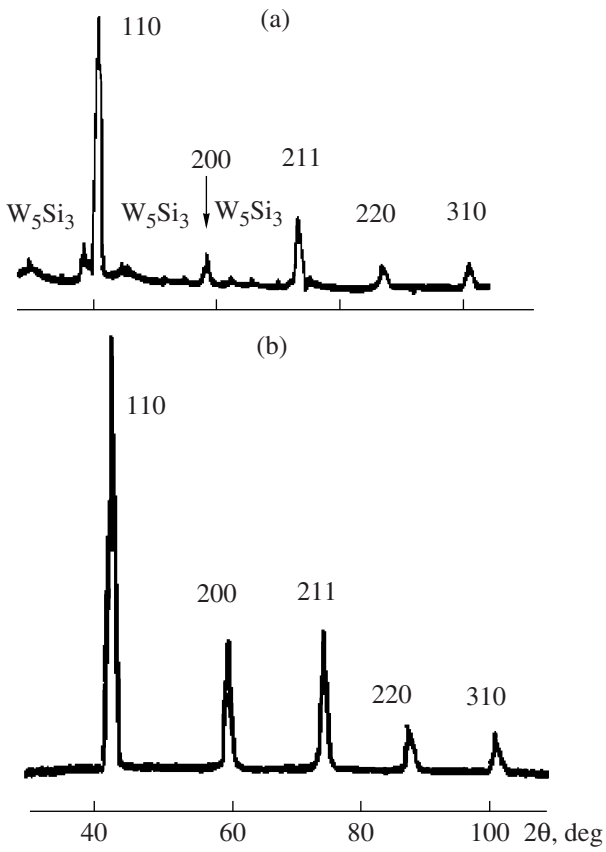

Fig. 2. Diffraction patterns of tungsten films obtained on silicon with the use of (a) plasmochemical deposition of tungsten and (b) magnetron deposition of tungsten at 100–200°C.

detection of diffracted radiation as an x-ray detector rotates.

Figure 1 presents the diffraction patterns of tungsten films deposited on silicon; these patterns are obtained with the conventional recording procedure with the use of the TFXRD scheme. As is seen from the figure, the application of the TFXRD scheme ensures a substantial increase in the diffraction line intensity for the film specimens.

RESULTS AND DISCUSSION

The tungsten layer deposition begins with interaction in accordance with the reaction [9]

$$2WF_6 + 3Si = 2W + 3SiF_4. \quad (1)$$

Then, the tungsten layer growth occurs owing to hydrogen reduction according to the reaction

$$WF_6 + 3H_2 = W + 6HF. \quad (2)$$

It is thought that no silicide layer can occur under conventional temperatures of 250 to 400°C. However, the Auger and RBS spectra for the tungsten layers obtained under the interaction between WF_6 and hydrogen show that these layers are not uncombined tungsten [9, 10]. The well-discernible tails of the silicon distribution are almost universally present in the spectra of these layers in the vicinity of the interface. This confirms that silicon penetrates to a large measure into a tungsten layer. In [9, 10], the details on characteristics of the observed tails were omitted.

The diffraction patterns show that, inside the tungsten films, a WF_6 layer localized at the film–substrate interface is formed; this holds for the tungsten films obtained by gas-phase deposition from a WF_6–H_2 mixture both in the case of true thermal deposition and also for the plasmochemical technique (Fig. 2). There is no silicide layer in the films produced with magnetron deposition at temperatures between 100 and 300°C (Fig. 2b) or with gas-phase deposition of tungsten onto silica substrates; all this provides the basis to assume that silicide arises by the interaction between tungsten hexafluoride and silicon according to the reaction

$$10WF_6 + 21Si = 2W_5Si_3 + 15SiF_4. \quad (3)$$

The thermodynamic calculations performed support the possibility of reaction (3). The Helmholtz energy (ΔG) of tungsten silicide W_5Si_3 formation is close to

The Helmholtz energy of reaction products formed at W–Si interface

Reaction	–Δ*G*, kJ/mol			
	298 K	373 K	473 K	573 K
$WF_6 + 3H_2 \longrightarrow W + 6HF$	0.92	25.95	58.73	91.25
$2WF_6 + 3Si \longrightarrow 2W + 3SiF_4$	657.20	664.74	671.85	678.55
$10WF_6 + 21Si \longrightarrow 2W_5Si_3 + 15SiF_4$	687.34	692.36	698.64	704.08

this value of tungsten formation according to reaction (1) (see table). Moreover, as is known, the heterogeneous interaction between tungsten and silicon escapes detection up to 600°C.

The XRF analysis of annealed specimens does not show a change in their composition up to 700°C. The diffraction patterns for pre- and postannealed tungsten films are shown in Fig. 3. The growth of silicide phase 700°C is observed at annealing temperatures up to 700°C; this is confirmed by an increase in its diffraction peak intensity with a rise in temperature. Irrespective of the film growth technique, strong peaks of tungsten disilicide WSi_2 of tetragonal modification show up in the specimens annealed at 800°C.

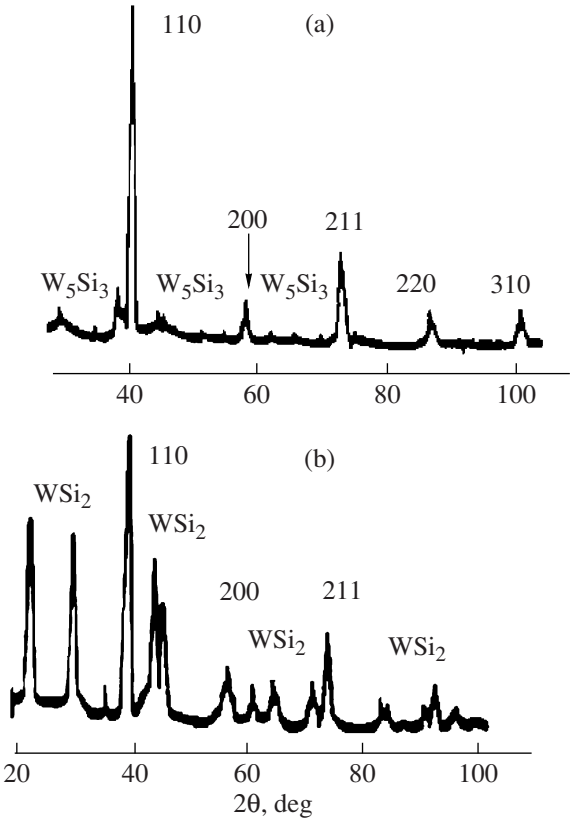

Fig. 3. Diffraction patterns of CVD tungsten films obtained on silicon: (a) before and (b) after annealing.

Comparing the diffraction patterns produced with the different techniques, we found that, in the case of plasmochemically deposited films, the silicide layer thickness (<10 nm) was much less than the ones obtained by conventional thermal gas-phase deposition (~20 nm). Conceivably, this might be due to activated hydrogen in the reduction reaction of tungsten hexafluoride. Being favorable to the course of reaction (2), activated hydrogen makes silicide formation difficult, because tungsten silicide WF_6 is divided among reactions (2) and (3). The part played by active hydrogen was mentioned in (9) as well. Conceivably, the activation of a gaseous mixture with the use of an rf discharge results in weakening the interaction between WF_6 and silicon; this may happen owing to competition between deposition reactions (1) and (3) [5].

Internal strains in the tungsten films were measured according to the TFXRD technique (Fig. 4). In the initial stage, a CVD specimen shows the linear relationship $\varepsilon(\sin^2\psi)$; this points to a uniform state of stresses. The film deformation found by extrapolation to $\sin^2\psi = 0$ corresponds to compression. After the film was annealed, a decrease in stresses and change in their sign were revealed; in accordance with Fig. 4, the stresses correspond to expansion. In films obtained with magnetron deposition, a nonuniformly stressed state is observed; after annealing, this state becomes uniform and the internal stresses show a substantial rise in value.

The grain-boundary angles in the texture were measured with the use of 110 reflection in the diffraction pattern shown in Fig. 5. The half-width of the curve $I_{110}(\omega)$ serves as the measure of misorientation for

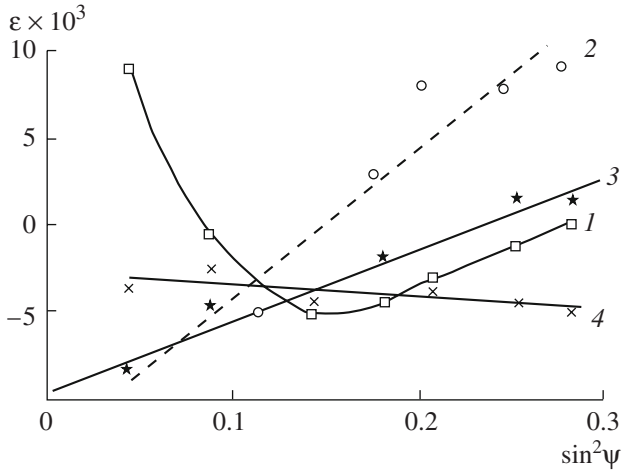

Fig. 4. The deformation given by $\varepsilon = \frac{\Delta d}{d(211)}$ vs. $\sin^2\psi$, where($\psi = \Theta - \omega$): *1*, *2*) magnetron deposition at 750°C before and after annealing, respectively; (*3*, *4*) CVD deposition at 600°C before and after annealing, respectively.

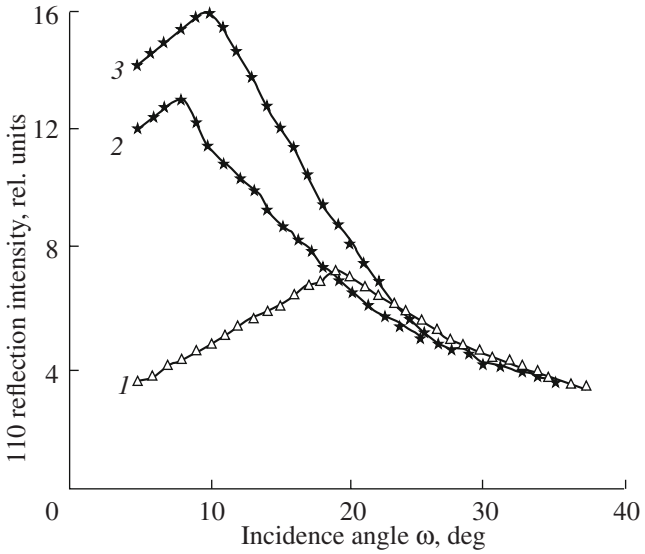

Fig. 5. Intensity of 110 diffraction reflection vs. x-ray incidence beam angle: (*1*) initial specimen, (*2*) specimen annealed at 600°C, and (*3*) specimen annealed at 800°C.

grains in a textured film. The films obtained with magnetron deposition show a more pronounced texture as compared to the films produced by gas-phase deposition. The TFXRD technique made it possible to measure internal strains in the tungsten films and grain-boundary angles between ⟨110⟩ axes of grains in the texture and the normal to the substrate surface; it was revealed that, after annealing, the half-width of the curves narrows; this effect is attributable to a decline of microstresses in film grains or to a growth in their size.

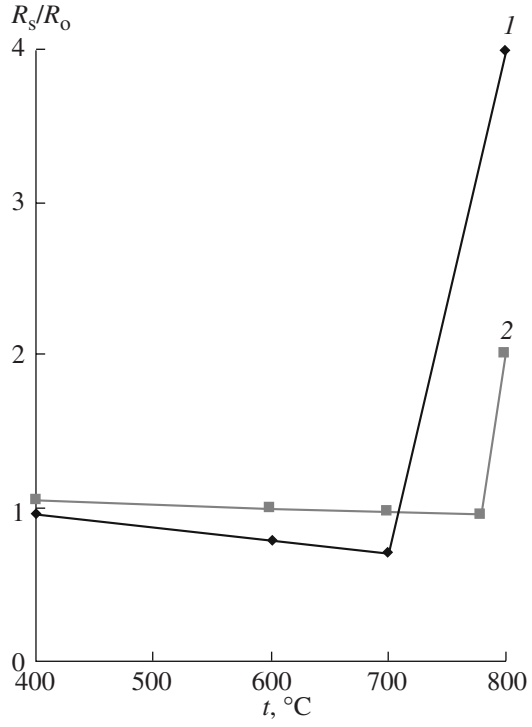

Fig. 6. Relative electrical resistance of tungsten layers vs. annealing temperature; the films were produced using (*1*) CVD technique and (*2*) CVD technique supplemented with activation of hydrogen.

In CVD films and in films obtained with the CVD technique supplemented with rf activation of hydrogen, the effect of annealing on the film composition and electrical resistance was investigated. As a rule, the films produced at 350–400°C and deposited with no stimulation show a lower electrical resistance as compared with films obtained at a temperature of about ~100°C under plasma-stimulated deposition. Upon the thermal treatment of films in hydrogen, the surface resistance shows a certain decrease with increasing temperature; then, at a temperature above 700°C, a jump in the electrical resistance occurs.

The electrical resistance versus annealing temperature is presented in Fig. 6 for various specimens. The specimens obtained under plasmochemical stimulation of hydrogen show a growth in the electrical resistance at a higher temperature (800°C). One can suppose that the shift into a higher temperature range is caused by the kinetics of formation of silicides and related to a lower thickness of the self-restricted film obtained under plasmochemical deposition. This layer with the active film–substrate interaction is thought to be the major contributor of nucleation centers of silicide growth under annealing. The rise in annealing temperature up to 700°C results in a slight reduction of the electrical resistance; this phenomenon may be due to a decrease in the number of defects in the film. Using the results of the x-ray investigations, we can ascribe a drastic increase in the electrical resistance to the appearance tungsten disilicide of the tetragonal phase.

The performed investigations made it possible to optimize the growth processes and to produce thin tungsten layers with a resistivity of 8×10^{-6} Ωcm, which is close to the resistivity of the bulk metal.

CONCLUSIONS

Tungsten films were obtained on a silicon wafer with the use of various techniques: the W–Si interfaces were investigated.

The gas-phase deposition of tungsten layers was performed from a mixture of tungsten hexafluoride and hydrogen; it was shown that tungsten silicide W_5Si_3 is formed at the interface in accordance with the reaction

$$WF_6 + Si \longrightarrow W_5Si_3 + SiF_4.$$

In the case of plasmochemical deposition of tungsten, the activation of hydrogen makes the reaction of silicide formation difficult; as a consequence, these specimens have a thinner W_5Si_3 film (below 10 nm). Annealing in hydrogen at a temperature up to 650°C leaves the tungsten film composition unaltered. The

reduction of the electrical resistance is correlated to a decrease in the defect density, internal strains, and microstresses in the film; this is supported by x-ray diffraction results.

The formation and growth of silicide WSi_2 commences at 700°C in the films obtained with gas-phase deposition; in the case of the films obtained with plasmochemical deposition, this is true at a temperature above 750°C; the formation of WSi_2 is accompanied by a drastic growth in the electrical resistance of these films.

The obtained thin tungsten films have a resistivity of 8×10^{-6} Ωcm, which is close to the resistivity of the bulk metal.

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