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Diffusion Processes in Ti–Si Systems during Silicide Formation

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Two methods of creation of the $\text{TiSi}_2(\text{C}54)$ stable phase are reviewed, and their comparison is considered. The formation of the structure of $\text{TiSi}_2(\text{C}54)$ nanosize films on monocrystalline Si is studied. As shown, the $\text{TiSi}_2(\text{C}54)$ formation is carried out faster ($\cong 55$ s) by low-energy thermion deposition (LETD) of Ti on mono-Si than by magnetron sputtering with post-annealing of 150 s and more. As noted, the electrical-resistivity value for $\text{TiSi}_2(\text{C}54)$ nanosize film deposited by LETD is equal to $\rho_v = 13.5 \mu\Omega\text{-cm}$, and with magnetron sputtering, it is equal to $\rho_v = 24 \mu\Omega\text{-cm}$. A phenomenological model for titanium disilicide formation on mono-Si by low-energy thermion deposition of titanium is proposed.

Розглянуто дві методи формування стабільної фази $\text{TiSi}_2(\text{C}54)$. Вивчено формування структури нанорозмірних плівок $\text{TiSi}_2(\text{C}54)$ на монокристалічному кремнії. Показано, що формування $\text{TiSi}_2(\text{C}54)$ відбувається швидше ($\cong 55$ с) за допомогою низькоенергетичної термоіонного осадження (НТІО) Ti на монокристалічний Si, аніж магнетронним напорошенням із подальшим відпалом (150 с і більше). Встановлено, що величина електричного опору для нанорозмірної плівки $\text{TiSi}_2(\text{C}54)$, одержаної за допомогою НТІО, складає $\rho_v = 13,5 \mu\text{Ом}\text{-см}$, а при магнетронному напорошенні та подальшому відпалі — $\rho_v = 24 \mu\text{Ом}\text{-см}$. Запропоновано феноменологічну модель для формування дісиліциду титану на монокристалічному кремнії при НТІО титану.

Рассмотрены два метода формирования стабильной фазы $\text{TiSi}_2(\text{C}54)$. Изучено формирование структуры наноразмерных плёнок $\text{TiSi}_2(\text{C}54)$ на мо-

нокристаллическом кремнии. Показано, что формирование $\text{TiSi}_2(\text{C}54)$ происходит быстрее ($\cong 55$ с) при помощи низкоэнергетического термоионного осаждения (НТИО) Ti на монокристаллический Si, чем магнетронным напылением с последующим отжигом (150 с и более). Установлено, что величина электрического сопротивления для наноразмерной плёнки $\text{TiSi}_2(\text{C}54)$, полученной при помощи НТИО, составляет $\rho_v = 13,5$ $\mu\text{Ом}\cdot\text{см}$, а при магнетронном напылении и последующем отжиге — $\rho_v = 24$ $\mu\text{Ом}\cdot\text{см}$. Предложена феноменологическая модель для формирования дисилицида титана на монокристаллическом кремнии при НТИО титана.

Key words: silicides, $\text{TiSi}_2(\text{C}54)$, diffusion, phase formation, low-energy thermion deposition.

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1. INTRODUCTION

Titanium disilicide has been widely used in complementary metal–oxide–semiconductor technology as contacts and gate electrodes mainly because of its low resistivity, good thermal stability, and manufacturing simplicity [1]. Although extensive investigations of formation of the titanium silicides have been carried out by many research groups, process parameters such as cleanliness of the silicon wafer, deposition conditions of the titanium film, and annealing conditions are still of great interest from a fundamental and practical point of view [2]. A fundamental investigation of diffusion processes in silicide films is one of the driving forces in the development of semiconductor technology as diffusion determines the structural properties of materials and thus its electrical performance in integrated circuit devices (IC).

An important factor for obtaining the nanosize silicide films is the reduction of both energy supply and the number of manufacturing operations. For current technologies of the integrated circuit production, the low energy thermion deposition of nanosize titanium silicide layers is a promising method. At the same time, ion-stimulated technologies (*e.g.*, LETD method) are currently receiving applications in microdevice fabrication. These technologies allow a better control of the condensation process, an appropriate modification of the structure of thin films and a good control of the metallization properties.

In a given work, we used two different deposition methods for obtaining $\text{TiSi}_2(\text{C}54)$ layers: low-energy thermion deposition of Ti on monocrystalline Si and magnetron sputtering of titanium followed by vacuum annealing.

The aim of this work is to study the influence of deposition conditions on diffusion and phase transformation of $\text{TiSi}_2(\text{C}54)$ nanosize films.

2. EXPERIMENTAL SECTION

We used two different deposition methods to study the diffusion processes and phase transformation in Ti–Si system.

Method I. The used deposition approach was low energy thermion deposition based on the ionization of Ti vapour at a pressure of $2 \cdot 10^{-4}$ Pa [3]. The method leads directly to Ti silicide layer formation during the deposition. The ion acceleration voltage of $U = 4$ kV leads to an average energy of the Ti ions of $E_i = z_i e U \cong 8$ keV ($z_i = 2$ is the degree of Ti ionization) and to a specific power of the silicon surface bombardment of $3.6 \text{ W} \cdot \text{cm}^{-2}$. The flux current was 0.9 mA/cm^2 , and the flux density of the titanium ions was $2.5 \cdot 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$. In this case, Ti deposition on naturally oxidized Si(100) substrates with a SiO_2 film thickness of 1.5–2.0 nm was carried out for 10–55 sec. Before deposition, the substrate was heated to 500 K and during the LETD process, temperatures from 550 to 700 K depending on deposition time were achieved.

Method II. Alternatively, the conventionally used magnetron sputtering deposition is considered. In this case, a 30 nm thick Ti film was grown on Si(100) at room temperature. The substrate was cleaned by a 5% HF solution for 4 min. The deposition rate of titanium was 0.1 nm/s. Film thickness was determined using a quartz resonator with an accuracy of about 10%. The as-prepared samples were post-annealed for 30 s in the temperature range of 720–1220 K in a vacuum furnace (*VUP-5m*) at a pressure $\cong 1 \cdot 10^{-4}$ Pa.

The thickness of the obtained films was measured by a linear optical interferometer (LOI-02a). X-ray phase analysis of the deposited layers has been made employing a DRON-2.0 XRD system with a monochromatic CuK_α beam and a Debye camera. The phase analysis was carried out by determining the interplanar distances and comparing it with standard data [4]. Electrical properties were measured using conventional four probe equipment.

3. RESULT AND DISCUSSION

3.1. Ti–Si Formation by Low-Energy Thermion Deposition

For a range of deposition time $\tau \leq 20$ s, the results of X-ray phase analysis for samples deposited by LETD shows that the deposition rate is larger than the reaction rate of titanium with silicon (Fig. 1). Therefore, a pure α -Ti layer is formed (Table). Beginning from $\tau \leq 30$ s, the Ti_5Si_4 phase is formed additionally to the α -Ti phase. According to [1], the formation of the thermodynamic unstable phase Ti_5Si_4 can be induced by the presence of oxygen. In this case, the oxygen in the thin SiO_2 layer causes this process.

For deposition times longer than $\tau = 30$ s, the inclusions of Ti_5Si_4 are

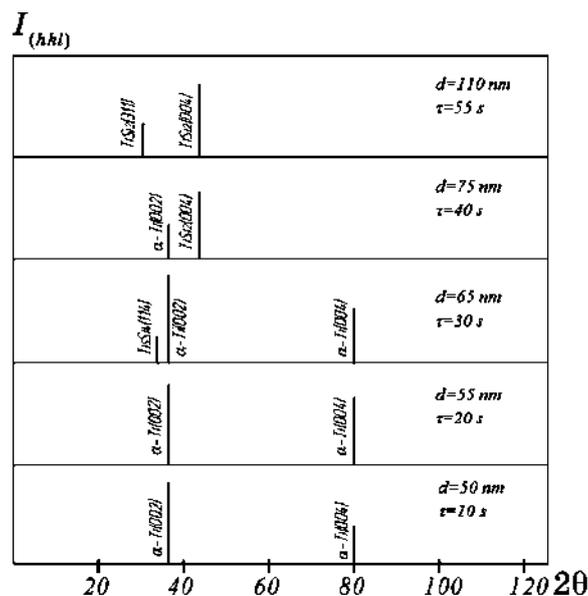


Fig. 1. Dish diagram of X-ray diffraction patterns of the LETD deposited films measured by a Debye camera. For $\tau \geq 55$ s, the desired TiSi_2 phase is observed.

TABLE. Phase composition of films deposited by LETD of titanium on Si(100).

Phase	Deposition time τ , s	Film thickness d , nm
α -Ti	10	50
α -Ti	20	55
α -Ti, Ti_5Si_4	30	65
α -Ti, $\text{TiSi}_2(\text{C}54)$	40	75
$\text{TiSi}_2(\text{C}54)$	45	85
$\text{TiSi}_2(\text{C}54)$	50	95
$\text{TiSi}_2(\text{C}54)$	55	110

dissolved and thermodynamically stable TiSi_2 layers are formed. Additionally, the α -Ti phase is observed in small quantities. For $\tau \geq 45$ s, only the $\text{TiSi}_2(\text{C}54)$ titanium disilicide phase can be found (Fig. 1).

Diffusion interaction of metals with monocrystalline Si does not occur uniformly at the entire surface area when SiO_2 exists on the interface [5]. During the deposition process of Ti ions on Si substrate, the SiO_2 film is dissolved and begins the reactive diffusion between Si substrate and deposited titanium film. In case of the structure (Ti/ SiO_2 thin layer/Si substrate), we can therefore propose that, at the initial

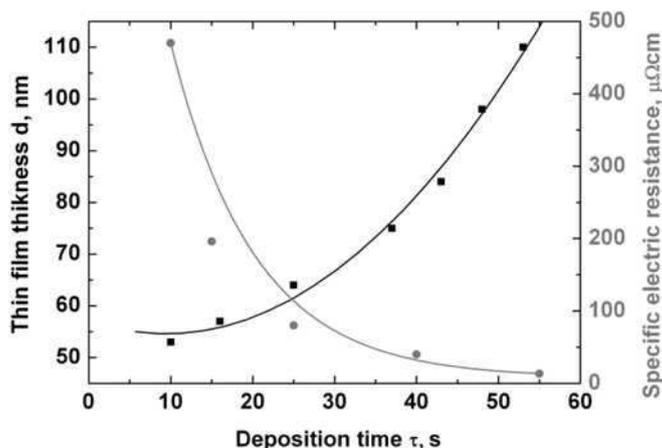
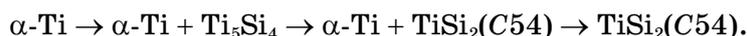


Fig. 2. Dependence of film thickness d (black squares, left scale) and specific resistivity ρ (gray circles, right scale) on the thermion deposition time τ . The lines are a guide to the eye.

stage of reactive diffusion, separated nuclei of the silicide phases form at the interface of the metallic film. With ongoing deposition process, a continuous layer of TiSi_2 is gradually formed by diffusion of Ti and growth processes. The thin layer of SiO_2 is completely dissolved for deposition times longer than 40 s, and a continuous film is formed.

The film thickness d and the electric resistivity of the $\text{TiSi}_2(\text{C54})$ stable phase depend on the deposition time τ . The measured values are shown in Fig. 2. The decrease of the specific electric resistance with deposition time τ accompanied with an increase of the silicide film thickness with τ supports the conclusion that a continuous stable phase of $\text{TiSi}_2(\text{C54})$ is formed. For 55 s, the electrical resistivity is $\rho_v = 13.5 \mu\Omega\cdot\text{cm}$.

Based on the X-ray phase analysis, the kinetics of formation of the $\text{TiSi}_2(\text{C54})$ on $\text{Si}(100)$ by LETD method can be summarized as follows:



According to [3], ion bombardment has no substantial influence on the formation temperature of TiSi_2 films. However, it can change the formation conditions of the silicide phase nuclei, and it leads to an acceleration of silicide formation without the appearance of an intermediate metastable phase of $\text{TiSi}_2(\text{C49})$, which is in agreement with our XRD results (Fig. 1). Theoretically, this can be explained by irradiation-induced generation and penetration of Frenkel's defects (interstitials and vacancies) inside the film that change the character of Ti diffusion towards the reaction front. Such a radiation-stimulated diffu-

sion of Ti in the film provides fast mass transport towards the silicide-silicon boundary and evidently it must cause nucleation of the silicide phase. The vacancies concentration for this case is determined by the following formula [6]:

$$c_v(x) = c_{v_0} + \Phi \frac{E_i}{E_d} \frac{\omega x_0}{D_v} \left(1 - \frac{x}{x_p} \right); \quad (1)$$

c_{v_0} is the equilibrium thermal vacancy concentration; Φ is the ion flow; E_i is the ion energy; E_d is the displacement energy; ω is the average atomic volume in the silicide; x is the film depth; D_v is diffusion coefficient of vacancies; x_p is the position of the diffusion front.

With the assumption that $c(x)$ satisfies the diffusion equation with varying diffusion coefficient, it is obtained [6] as follows:

$$\frac{d}{dx} \left[D(x) \frac{dc(x)}{dx} \right] = 0. \quad (2)$$

Supposing that Ti diffuses into silicide by vacancy mechanism, then $D(x)$ has to be proportional to the local vacancy concentration: $D(x) \propto c_v(x)$. On the contrary, the equilibrium value of the diffusion coefficient D_0 is achieved by satisfying the equilibrium conditions:

$$D(x) = \frac{D_0}{c_{v_0}} c_v(x). \quad (3)$$

Based on the work of Larikov *et al.* [6], the diffusion coefficient of Si on stage of continuous layer formation of $\text{TiSi}_2(\text{C54})$ is determined as $D = 4,5 \cdot 10^{-16} \text{ m}^2/\text{s}$.

3.2. Ti–Si Formation by Magnetron Sputtering Technique and Post-Annealing

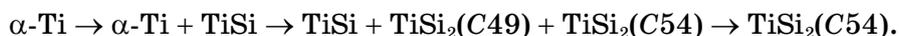
30 nm thick Ti films were deposited on monocrystalline Si by magnetron sputtering and afterwards post-annealed for 30 s. From X-ray diffraction analysis, it was found that, in the temperature range 720–870 K, there was no silicide phase formation. For higher annealing temperature of 920 K, TiSi and α -Ti phase were formed. This is in contradiction to the observation by Makogon *et al.* [7], where they have observed a stable phase formation of $\text{TiSi}_2(\text{C54})$ even at 920 K. But it is to be noted that, in the present case, the presence of impurities such as C and O_2 retards the diffusion of Ti and Si atoms and thus the silicide formation. This is supported by the fact that for vacuum annealing the impurities from residual atmosphere diffuse preferentially in the film along grain boundaries. They can accumulate on the interfaces of α -Ti–

Si, α -Ti– α -Ti and create inclusions. For such low annealing temperature (720–920 K), diffusion of silicon in titanium films runs along the grain boundaries, and therefore, the aggregation of impurities there would block the rapid formation of TiSi_2 (C54). This causes the changes in mechanisms of silicide phase formation at initial stages of solid state reactions and requires increased annealing times and temperature.

By increasing the annealing temperature to 1220 K, the intensity of interdiffusion processes between silicide film atoms in the films and silicon substrate increases. At 1220 K, we observed TiSi phase in small quantities apart from TiSi_2 (C49) metastable phase and TiSi_2 (C54) stable phase by using an annealing time of 30 s. For annealing times of 150 s and more, TiSi and TiSi_2 (C49) phases are dissolved, and only TiSi_2 (C54) phase is found.

Tu and Mayer [5] have done an experiment to explain the silicide formation process at high temperatures. As shown, for high-temperature reactions, phonon energy between high-melting metals (*e.g.*, Ti, W, Co) and Si is big enough to destroy the covalent bonds of Si. The destroyed Si bonds allow Si to diffuse through the films to the metals. A high concentration of structural defects in metallic films considerably simplifies the silicon diffusion. At 1220 K, the thermal activation of point defects (vacancies, divacancies) plays the active role in diffusive mass transfer.

By magnetron sputtering with post-annealing, the intermediate phases TiSi, TiSi_2 (C49) appear at the beginning stage of phase formation. For higher temperatures and longer annealing times, the TiSi_2 (C54) stable phase is formed. In comparison to LETD, the unstable TiSi_2 (C49) can be observed. The kinetics of formation of TiSi_2 (C54) on Si(100) by annealing can be summarized as:



The determined specific electrical resistance for the TiSi_2 (C54) is $\rho_v = 24\mu\Omega\text{-cm}$, which is higher than that for a LETD process.

4. CONCLUSIONS

Comparison of structural and electrical properties of Ti–Si films prepared by LETD and magnetron sputtering followed by vacuum annealing is presented. As shown, the formation of TiSi_2 (structural phase C54) runs faster ($\cong 55$ s), when using LETD, compared to the conventional annealing method (> 150 s). In case of LETD, the structural modification of Ti–Si thin films was described, using the diffusion model of Si and Ti atoms in a silicide layer by vacancy mechanism. In this case, low-energy treatment results in radiation-stimulated defects (of

Frenkel's type), which accelerate the diffusion processes of the silicide phase formation of $\text{TiSi}_2(\text{C}54)$ on $\text{Si}(100)$.

Furthermore, it was found that the specific electrical resistance of $\text{TiSi}_2(\text{C}54)$ deposited by LETD is $\rho_f = 13.5 \mu\Omega\cdot\text{cm}$. For sputtering, it is higher with $\rho_f = 24 \mu\Omega\cdot\text{cm}$. Thus, one can conclude that the LETD technique forms in a shorter time thin films with less defects.

The use of a less energy consuming supply is additionally a more effective method for silicide film production in the IC manufacturing.

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