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# Formation of platinum-based silicide contacts: Kinetics, stoichiometry, and current drive capabilities

G. Larrieu, E. Dubois,<sup>a)</sup> X. Wallart, and X. Baie

*Institut d'Electronique de Microélectronique et de Nanotechnologie, IEMN/ISEN UMR CNRS 8520, Cité Scientifique, Avenue Poincaré, 59652 Villeneuve d'Ascq Cedex, France*

J. Katcki

*Institute of Electron Technology, Al. Lotników 32/46, 02-668 Warsaw, Poland*

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A detailed analysis of the formation of Pt<sub>2</sub>Si and PtSi silicides is proposed, based on x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electrical characterizations. Published kinetics of the Pt<sub>2</sub>Si and PtSi transformations under ultrahigh vacuum condition are consolidated on the basis of XPS measurements performed during an *in situ* annealing at a constant heating rate. At room temperature, an incomplete Pt<sub>x</sub>Si reaction is clearly identified by XPS depth profiling. Using rapid thermal annealing at 300, 400, and 500 °C, the sequential Pt–Pt<sub>2</sub>Si–PtSi reaction chain is found to be completed within 2 min. Outdiffusion of silicon to the top surface is shown to be responsible for the formation of a thin SiO<sub>2</sub> capping layer at 500 °C. Pileup of oxygen occurring at the Pt<sub>2</sub>Si/Pt reaction front is clearly identified as an inhibiting factor of the silicidation mechanism. Another incomplete reaction scheme limited to the unique formation of Pt<sub>2</sub>Si is exemplified in the case of ultra thin silicon-on-insulator films. Finally, current drive measurements on PtSi Schottky contacts have allowed us to identify 300 °C as the optimum annealing temperature while TEM cross sections demonstrate the formation of a smooth and continuous PtSi/Si interface at 300 °C. © 2003 American Institute of Physics.

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## I. INTRODUCTION

Very thin films of metal silicides play an increasing important role in silicon integrated circuit technology as metal-oxide-semiconductor field-effect-transistors (MOSFETs) are shrunk below 0.1 μm of gate length.<sup>1</sup> Titanium, cobalt, and nickel silicides are commonly used in the semiconductor industry. The interesting properties of metal silicides, directly related to their utility in silicon technology, include thermal stability, low resistivity, and reduced silicide/silicon specific contact resistance. In order to further pursue down-scaling of MOSFETs in the 10–20 nm range of gate lengths, a significant effort must be devoted to the development of alternative architectures<sup>2</sup> that solves the many issues associated to the use of high κ dielectrics<sup>3</sup> and to the design of improved source/drain (S/D) regions. S/D are commonly based on a highly doped extension that provides the necessary configuration to obtain an excellent ohmic contact with a typical specific contact resistivity around 10<sup>-7</sup> Ω cm<sup>2</sup>. This last value is representative of the best midgap silicides.<sup>4</sup> A deeper insight in the challenges imposed to the S/D regions reveals tremendous constraints imposed to the dopant profiling and to the contact resistances. For instance, the lateral S/D doping steepness (1 nm/decade), the silicide thickness (5 nm), and the specific silicide/silicon contact resistance (2.4 × 10<sup>-8</sup> Ω cm<sup>2</sup>) are expected to reach very low targets in the

perspective of a 10 nm physical gate MOSFET.<sup>2</sup> One possible solution to obtain a reduced specific contact resistance is to adopt a dual silicide approach according to which silicide materials with very low Schottky barriers to holes ( $\phi_{bp}$ ) and electrons ( $\phi_{bn}$ ) are integrated in *p*-type and *n*-type MOSFETs, respectively. Even more exciting, a MOSFET architecture using low Schottky barrier (ideally 0 eV) contacts has been recently proposed<sup>5-7</sup> in order to replace the conventional ohmic contacts on highly doped S/D. Pt and Ir based silicides (low  $\phi_{bp}$ ) and rare earth silicides like ErSi<sub>2</sub> (low  $\phi_{bn}$ ) are probably the best candidates for that purpose.<sup>8,9</sup> These perspectives reactivate a great deal of interest on platinum silicide. Much of the recent work on Pt<sub>2</sub>Si and PtSi has focused on the kinetics and stoichiometry under ultrahigh vacuum (UHV) annealing conditions.<sup>10-13</sup> In this article, we propose a detailed study of the Pt silicidation mechanisms using various annealing conditions like UHV and rapid thermal annealing with a particular attention on the interface reaction at room temperature, on the influence of oxygen during silicidation reaction and on the optimum conditions to obtain the lowest specific contact resistance. After a description of the preparation techniques and measurement procedures in Sec. II, the kinetics and composition of Pt<sub>2</sub>Si and PtSi silicides are critically analyzed using x-ray photoelectron spectroscopy (XPS) in Sec. III. Finally, Secs. IV and V provide electrical measurements and transmission electron microscopy (TEM) observations that consolidate the results of physical analysis.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: emmanuel.dubois@isen.iemn.univ-lille1.fr

## II. PREPARATION TECHNIQUES AND EXPERIMENTAL PROCEDURES

### A. XPS analysis

The samples have been analyzed by XPS, using a Physical Electronics 5600 spectrometer fitted in an UHV chamber (base pressure  $1 \times 10^{-10}$  Torr). We use a monochromatized Al x-ray source ( $h\nu = 1487$  eV) and the detection angle is  $45^\circ$  with respect to the sample surface normal. For depth profile analysis, we use an Ar<sup>+</sup> ion gun with an ion energy of 1 keV and a beam raster of  $5 \times 5$  mm<sup>2</sup>. Concentration profiles are obtained using standard sensitivity factors provided by the manufacturer.<sup>14</sup> Sputter profiling induces the knock-on effect resulting in a smearing of the depth resolution. This is why, in order to minimize this effect, we have chosen a moderate ion energy of 1 keV. Under our experimental conditions, the induced broadening lies probably around 2 nm.<sup>15</sup> However, the following analysis of the XPS results (Sec. III) does not rely on thickness measurements from the depth profiles neither on a precise research of interface positions. Hence, the conclusions are not affected by this parasitic effect.

### B. Sample preparation

Samples consist of pieces cut from (100) Si bulk or silicon-on-insulator (SOI) substrates (*p* type doped 4–10  $\Omega$  cm). A first degreasing step was performed in acetone followed by a rinse in isopropyl alcohol. A standard RCA cleaning step was subsequently applied to remove any possible surface contamination. Before being loaded into the vacuum deposition system, the surface oxide was removed by an HF:H<sub>2</sub>O(1:100) dip for 30 s followed by a rinse in deionized water. Pt films were deposited by electron beam evaporation. The base vacuum before deposition was  $2 \times 10^{-8}$  Torr. A gentle surface etch was realized *in situ* using Ar sputtering at 60 eV during 20 s. Unless otherwise specified in the following of this paper, silicidation steps at various temperatures were processed by rapid thermal annealing (RTA) system (Jipelec).

### C. Electrical measurements

The accurate determination of the barrier height of a silicide/silicon Schottky contact is a difficult task when this barrier is very low. A first reason is related to the silicon resistance connected in series with the Schottky contact. In the case of a weakly doped substrate, the silicon resistivity governs the current–voltage characteristic making the specific contact resistance hardly detectable. Another source of difficulty is the high level of reverse current flowing in through the Schottky junction that precludes an accurate discrimination between conduction and displacement currents when a capacitance–voltage method is considered.<sup>16</sup> Using internal photoemission measurements, the square root of photocurrent yield established by Fowler theory<sup>17</sup> becomes superlinear when applied to low Schottky barriers. In that specific case, the determination of the Schottky barrier height according to this method is therefore questionable. Another serious issue is related to the nature of the current transport

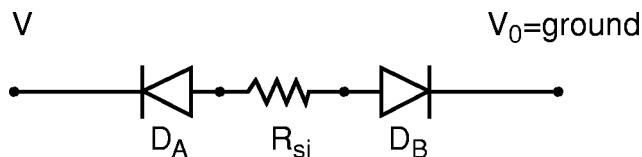


FIG. 1. Equivalent lumped circuit corresponding to two back-to-back Schottky diodes ( $D_A$  and  $D_B$ ) separated by the silicon series resistance  $R_{si}$ .

mechanisms that involve a complex combination of the thermionic emission and field emission as outlined in the article by Crowell and Rideout.<sup>18</sup> A direct consequence is that the activation energy method in reverse mode can become less accurate because the slope of the  $\ln(J_R/T^2) - 1/T$  plot does not necessarily reflect the real barrier height.<sup>19–21</sup> In order to circumvent the aforementioned problems, an alternative method that characterizes the current drive capability of a Schottky contact has been set up. To reproduce the lateral configuration of the source/drain contacts of a MOSFET, measurements are performed between two Schottky contacts separated by a micrometer gap. This configuration also holds the advantage to eliminate any contribution of parasitic resistance associated with another type of metal–semiconductor interface (e.g., contact at the back side of the sample). The lumped equivalent circuit corresponds to two back-to-back Schottky junctions separated by the series resistance associated to the silicon gap as reproduced in Fig. 1. When an external voltage  $V$  is applied on a circuit terminal, one Schottky junction is forward biased while the second operates in reverse mode. Because a forward current increases exponentially with the applied voltage, this configuration ensures that the measured current is representative of the reverse biased junction providing that the silicon series resistance is negligible. Two criteria can be used to evaluate Pt-based silicides in terms of current performance. The first one is the maximum current drive when the contribution of the silicon series resistance is negligible compared to the Schottky contact resistance. In order to further justify the relevance of this parameter, Fig. 2 shows a typical Arrhenius plot for different voltages applied to the Schottky system depicted in Fig. 1. At a given applied bias (e.g., 0.5 V), two modes of operation can be distinguished. In the high temperature region, the silicon series resistance clearly governs the current, resulting in a pure ohmic behavior. In the low temperature region, the current is limited by the thermionic and field emission currents flowing over and through the Schottky barrier, respectively. The second criterion is the transition temperature between regimes governed by the silicon series resistance or by the Schottky contact resistance. Its determination is also illustrated in Fig. 2 at a given applied bias. For a same substrate type and doping, a low transition temperature reflects a low Schottky specific contact resistance and therefore a low value of the barrier height. In order to illustrate the relevance of this parameter, electrical simulations of the system formed by the two back-to-back Schottky junctions have been performed. The current–voltage model is taken from Crowell and Rideout’s theory<sup>18</sup> extended to include the effect of image charge induction.<sup>16</sup> The voltage at each node of the lumped circuit given in Fig.

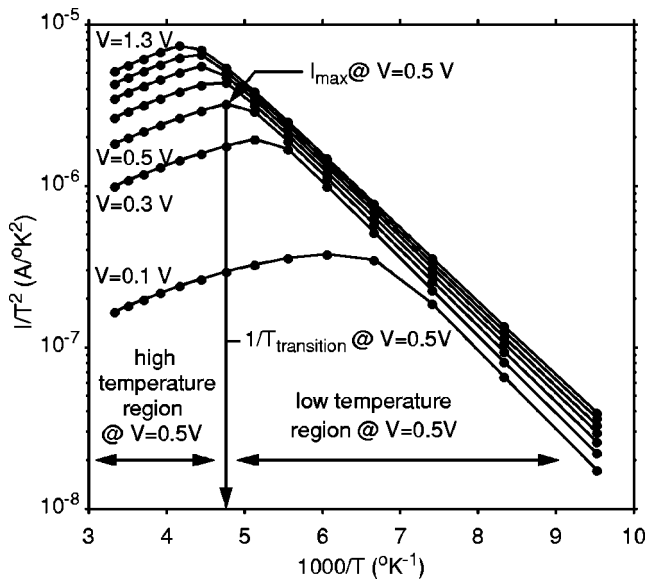


FIG. 2. Typical Arrhenius plot obtained for two back-to-back diodes on a weakly doped silicon substrate. The maximum current drive and the transition temperature are reported for a given value of the applied bias.

1 is then determined by solving a nonlinear numerical system using a conventional Newton–Raphson procedure. Figure 3 represents the temperature dependence of the voltage drop across each element of the circuit for different values of the Schottky barrier height. For a low temperature, the total applied voltage matches the voltage drop across the reverse biased junction  $D_A$  indicating that the current flowing through the circuit is limited by this Schottky contact. As the temperature increases, the voltage drop across the silicon series resistance also increases up to a point corresponding to the transition temperature for which the external bias is equally distributed across  $D_A$  and  $R_{Si}$ . The careful inspection of Fig. 3 reveals that the transition temperature decreases when the Schottky barrier is reduced. As a conclusion, this parameter proves to be useful to classify Schottky contacts with respect to their barrier height and thus to estimate the quality of the silicide/silicon interface.

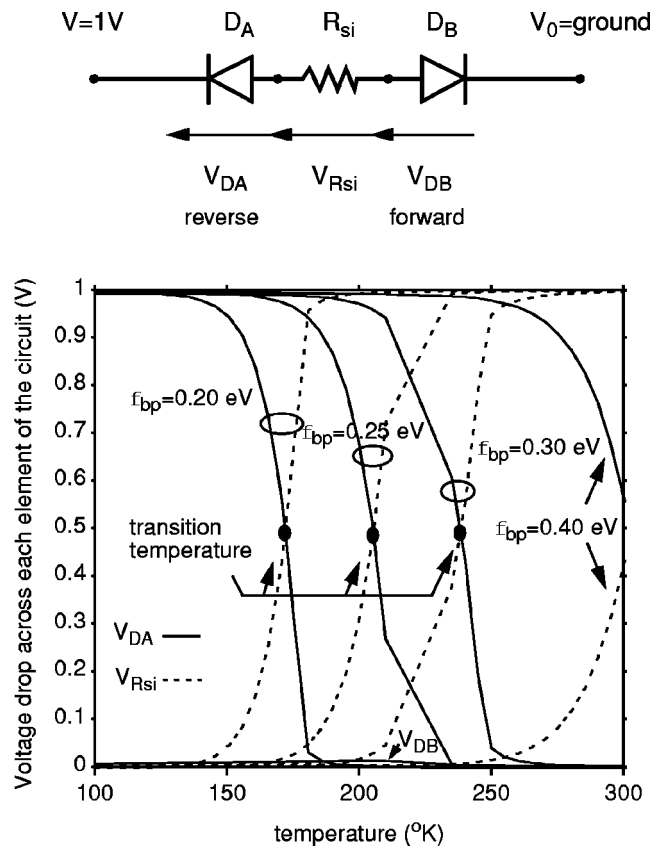


FIG. 3. Results of electrical simulation showing the voltage drop across each element of the equivalent lumped circuit formed by the two Schottky contacts and the silicon series resistance. The Schottky barrier height is taken as a parameter. A low transition temperature is relevant of a low Schottky barrier height.

### III. XPS ANALYSIS

#### A. Kinetics of platinum silicidation

Pt-Si intermixed layers can present three distinct types of composition PtSi, Pt<sub>2</sub>Si, and Pt<sub>3</sub>Si, but only the two first are stable forms.<sup>22</sup> Several studies have demonstrated that the platinum silicidation reaction is a two-step process governed by different energies of activation.<sup>11,12</sup> In the first reaction, Pt diffuses into Si to form an intermediate compound Pt<sub>2</sub>Si, and

TABLE I. Typical activation energies related to Pt to Pt<sub>2</sub>Si and Pt<sub>2</sub>Si to PtSi reactions.

Reference	Reaction (1): Pt <sub>2</sub> Si formation Pt diffusion into Si				Reaction (2): PtSi formation Si diffusion into Pt <sub>2</sub> Si			
	$D_{Pt/Pt_2Si}$ $D = D_0 \cdot \exp(-E_A/kT)$		Si consumption/Pt <sub>2</sub> Si expansion		$D_{Pt/Pt_2Si}$ $D = D_0 \cdot \exp(-E_A/kT)$		Si consumption/PtSi expansion	
	$D_0$ (cm <sup>2</sup> /s)	$E_A$ (eV)	nm of Si per nm of Pt	nm of Pt <sub>2</sub> Si per nm of Pt	$D_0$ (cm <sup>2</sup> /s)	$E_A$ (eV)	nm of Si per nm of Pt	nm of PtSi per nm of Pt
a	—	1.3 ± 0.2	0.66	1.43	—	1.5 ± 0.2	1.32	1.97
b	—	1.55 ± 0.05			—	1.72 ± 0.05		
c	3.7 × 10 <sup>1 ± 1.55</sup>	1.50 ± 0.15			2.7 × 10 <sup>1 ± 1.95</sup>	1.70 ± 0.22		

<sup>a</sup>Reference 22.

<sup>b</sup>Reference 11.

<sup>c</sup>Reference 12.

in the second reaction Si diffuses into Pt<sub>2</sub>Si to form a stable PtSi layer. These two reactions are known to occur sequentially: reaction (1) necessitates the complete consumption of the initial Pt layer before reaction (2), corresponding to the transformation of the Pt rich phase (Pt<sub>2</sub>Si) into platinum monosilicide (PtSi),<sup>22</sup> starts. Both reactions are thermally activated. Table I summarizes typical measured values of the activation energy and of the pre-exponential diffusion coefficient in previously published experiments.<sup>11,12,22</sup> Accounting for the most recent data proposed by Stark *et al.*,<sup>12</sup> these activation energies are  $1.50 \pm 0.15$  eV and  $1.70 \pm 0.22$  eV, for the first and second reactions, respectively. In order to analyze the silicidation kinetics of each transformation, the same authors used Rutherford backscattering spectroscopy spectra analysis in conjunction with *in situ* ellipsometric measurements. Starting from a Pt overlayer of 23 nm and for an annealing step performed at a constant heating rate of 5 K/min, the conversion of Pt into Pt<sub>2</sub>Si was found to be completed at 261 °C while the transformation of Pt<sub>2</sub>Si into PtSi was obtained at 335 °C. Within the frame of this work, a similar type of annealing has been conducted into the XPS chamber under UHV condition. The initial Pt layer was 20 nm thick and the temperature was ramped from 20 to 550 °C in 120 min, corresponding to an average heating rate of 4.4 K/min. Only the top surface of the sample was analyzed by XPS during the annealing in order to detect the change of surface composition over  $3\lambda$ ,  $\lambda$  being the escape depth of 2.5 nm.<sup>23</sup> Figure 4(a) shows the temperature-dependent concentration corresponding to the Pt 4*f* and Si 2*p* emission lines. In order to accurately determine the characteristic temperature at which each transformation is completed, we have detected the most abrupt changes in chemical shift corresponding to the Pt 4*f* core level. Figure 4(b) shows a selection of Pt 4*f* spectra recorded during the annealing. As long as the annealing temperature is less than 245 °C, the position of Pt 4*f*<sub>7/2</sub> peak is clearly centered at 71 eV, a binding energy relevant to elemental (metallic) Pt. The following spectrum recorded at 258 °C exhibits a sharp chemical shift of 1.5 eV that indicates that the Pt to Pt<sub>2</sub>Si reaction front has reached the top surface. Spectra measured at temperatures up to 311 °C are also characterized by the same Pt 4*f*<sub>7/2</sub> peak at 72.5 eV. At 324 °C, an additional 0.1 eV shift in the binding energy is clearly detected at 72.6 eV. Finally, from 338 °C to higher annealing temperatures, the Pt 4*f*<sub>7/2</sub> peak remains centered at 72.7 eV indicating that the Pt<sub>2</sub>Si intermediate phase has been fully converted into PtSi. In conclusion, reaction (1) (Pt<sub>2</sub>Si formation by Pt diffusion into Si) and reaction (2) (PtSi formation by Si outdiffusion into Pt<sub>2</sub>Si) are found to take place in the 245–258 °C and 324–338 °C intervals, respectively. Despite different heating rates and a thickness of the Pt overlayer that slightly differs, the temperatures related to the end of both silicidation reactions are found to be in excellent agreement with results published by Stark *et al.*<sup>12</sup> In order to get a more accurate determination of these characteristic temperatures, Fig. 5 represents the variations of the thickness of the formed Pt<sub>2</sub>Si and PtSi silicide layers as a function of temperature, accounting for the two different

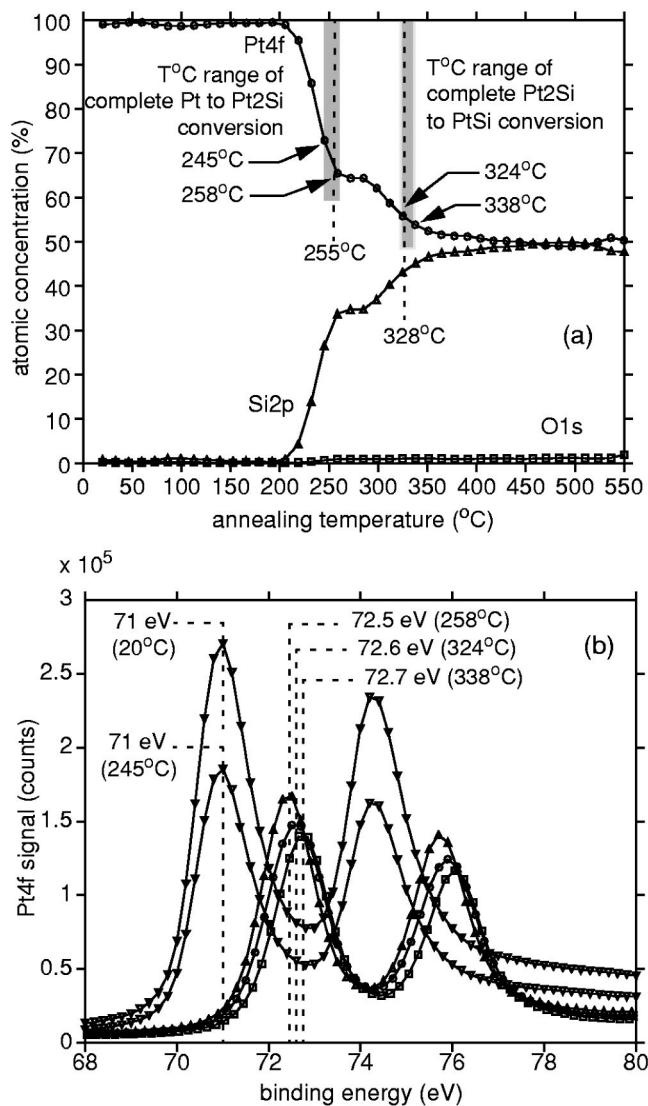


FIG. 4. Kinetics of silicidation reactions: (a) atomic concentration recorded by XPS during *in situ* annealing at a constant heating rate (4.4 K/min) under UHV condition. The temperature ranges at which the reaction fronts of the Pt<sub>2</sub>Si and PtSi reactions reach the top surface are indicated. The most probable temperature of completion of each reaction (255 and 328 °C) is extracted from Fig. 5. (b) Pt 4*f* spectra recorded at some specific temperatures around the Pt<sub>2</sub>Si and PtSi transitions.

heating rates, i.e., 5 K/min. in Ref. 12 and 4.4 K/min in this work. These curves have been obtained using a classical growth rate equation given by

$$\begin{aligned}
 d_x^2 &= \int_0^t D_x dt = \int_{T_0}^{T_x} D_x (dT/dt)^{-1} dT \\
 &= D_{0x} (dT/dt)^{-1} \frac{k_B}{E_{Ax}} \left\{ T_x^2 \exp\left(-\frac{E_{Ax}}{k_B T_x}\right) \right. \\
 &\quad \left. - T_0^2 \exp\left(-\frac{E_{Ax}}{k_B T_0}\right) \right\}, \quad (1)
 \end{aligned}$$

where  $x$  stands for 1 or 2 for the first or the second reaction, respectively.  $T_x$  is the temperature at which each one of the above reactions is fully completed.  $E_{Ax}$  is the activation energy,  $D_x$ , the temperature-dependent diffusivity, and  $D_{0x}$  the

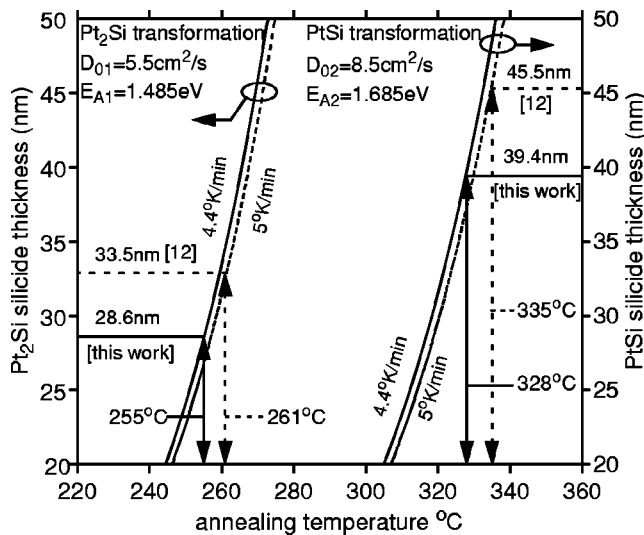


FIG. 5. Thickness of the  $\text{Pt}_2\text{Si}$  and  $\text{PtSi}$  phases accounting for different heating rates. The pre-exponential diffusion coefficients are fitted to match results published in Ref. 12 using an annealing ramp of 5 K/min. In the present experiment performed at 4.4 K/min, the temperatures of complete silicidation (255 and 328 °C for  $\text{Pt}_2\text{Si}$  and  $\text{PtSi}$  transformations, respectively), are extracted using  $D_{01}=5.5 \text{ cm}^2/\text{s}$ ,  $D_{02}=8.5 \text{ cm}^2/\text{s}$ ,  $E_{A1}=1.485 \text{ eV}$ , and  $E_{A2}=1.685 \text{ eV}$ .

pre-exponential diffusion coefficient.  $T_0$  is the starting temperature set at 20 °C. Given the large error bars associated to results of previously published work<sup>12</sup> (e.g., the min–max values of  $D_{0x}$  vary over 3 decades), the following procedure has been used to better estimate the most probable characteristic temperatures of complete silicidation in the present experiment.

- (i) Assuming that the average activation energies  $\langle E_{A1} \rangle = 1.485 \text{ eV}$  and  $\langle E_{A2} \rangle = 1.685 \text{ eV}$  are the most representative of the silicidation experiments conducted by Stark *et al.*,<sup>12</sup> the mean pre-exponential diffusion coefficients  $\langle D_{01} \rangle$  and  $\langle D_{02} \rangle$  must be set to 5.5 and 8.5  $\text{cm}^2/\text{s}$  in order to match the final thickness of the  $\text{Pt}_2\text{Si}$  and  $\text{PtSi}$  phases, 33.5 and 45.3 nm reached at temperatures of 261 and 335 °C, respectively.
- (ii) Considering that the above values of  $\langle E_{A1} \rangle$ ,  $\langle E_{A2} \rangle$ ,  $\langle D_{01} \rangle$  and  $\langle D_{02} \rangle$  also hold in the case of our experiment, the characteristic temperatures are found to be 255 and 338 °C (Fig. 5) to match the final thickness of the  $\text{Pt}_2\text{Si}$  and  $\text{PtSi}$  phases, established at 28.6 and 39.4 nm, respectively.

## B. Platinum silicide at room temperature

It has been reported that Pt can react with silicon at room temperature resulting in the formation of an intermixed Pt–Si layer. Using high resolution cross-sectional TEM analysis, Donaton *et al.*<sup>24</sup> observed the formation of a continuous, smooth and uniform 3 nm thin  $\text{PtSi}$  layer obtained after Pt deposition and selective chemical etching, on top of which a thin layer of silicon oxide was formed. XPS experiments confirmed the same characteristics of silicide bonds before and after a subsequent rapid thermal annealing at 450 °C. One of their conclusions was that the sputtering tech-

nique used to deposit Pt provides sufficient energy to sputtered atoms to initialize the silicidation reaction. In contrast, other works also report the presence of Pt–Si bonds when Pt is evaporated on a clean silicon substrate kept at low temperature, i.e., without bringing any notable source of energy to activate the silicidation mechanism.<sup>25</sup> In order to investigate the initial interfacial reaction, a 15 nm thick Pt layer was evaporated following the procedure described in Sec. II B. It is worth noting that the sample was not heated during this deposition step. An XPS depth profile was recorded on that sample in order to detect a possible reaction between Pt and Si. The original photoemission measurements of the Pt 4*f* and Si 2*p* core levels have been fitted using a standard linear least squares procedure<sup>14</sup> to identify the chemical states of each element (Si and Pt) that appear in the depth profile. Figure 6(a) shows the resulting decomposition of the Pt 4*f* profile into two Pt 4*f*( $\text{Pt}_x\text{Si}$ ) and Pt 4*f*(Pt) contributions. The extracted basis of spectra used to calculate the two deconvolved depth profiles is given in Fig. 6(c). The Pt 4*f* spin–orbit doublet ( $4f_{5/2}, 4f_{7/2}$ ) exhibits a chemical shift of 1.5 eV from 71 to 72.5 eV that reveals the activation of a silicidation reaction involving the formation of a  $\text{Pt}_x\text{Si}$ -like layer.<sup>10,26,27</sup> This result is consolidated by Fig. 6(b) that gives the decomposition of the Si 2*p* profile into its two Si 2*p*( $\text{Pt}_x\text{Si}$ ) and Si 2*p*(Si) expected contributions. The corresponding basis of spectra is also shown in Fig. 6(d) revealing a chemical shift from 99.2 to 99.8 eV of the Si 2*p* emission line, which is again attributed to the presence of silicide-like bonds.<sup>10,27</sup> Figure 6(e) gives a summarized picture of the Si and Pt concentration depth profiles depending on the chemical environment of each element. It can be concluded that silicide is formed although it is not possible to determine the exact composition nor to conclude on the uniformity of the silicide layer. Nevertheless, the variations of the individual Si 2*p*( $\text{Pt}_x\text{Si}$ ) and Pt 4*f*( $\text{Pt}_x\text{Si}$ ) profiles over a period covering 30–80 min of sputtering time does not seem indicative of a stable stoichiometric composition. However, these profiles can be affected by the knock-on effect induced by the sputtering as suggested by the observed tail of the Pt signal at long sputtering time and hence do not allow us to go further in the analysis of the interfacial compound.

## C. Platinum silicide formation at 200 °C

Because the silicidation reactions involving Pt are governed by a diffusion mechanism, a significant part of the initial Pt layer can react at a relatively low temperature. Zhou *et al.*<sup>11</sup> have found that the two major reactions (formation of  $\text{Pt}_2\text{Si}$  and  $\text{PtSi}$ ) are preceded by an initial transformation taking place between 100 and 200 °C and characterized by a very low activation energy of  $0.19 \pm 0.043 \text{ eV}$ . In the present contribution, we have investigated the silicidation reaction obtained by RTA at 200 °C for 2 min, starting from an initial Pt layer of 15 nm. Figure 7 gives the corresponding atomic concentration depth profile obtained by XPS analysis. Over the range of 30–50 min of sputtering time, the concentrations of Pt and Si clearly outline a zone of reaction over which a partial transformation of Pt into  $\text{Pt}_x\text{Si}$  ( $x \sim 2$ ) takes place. More surprisingly, we find a significant presence of

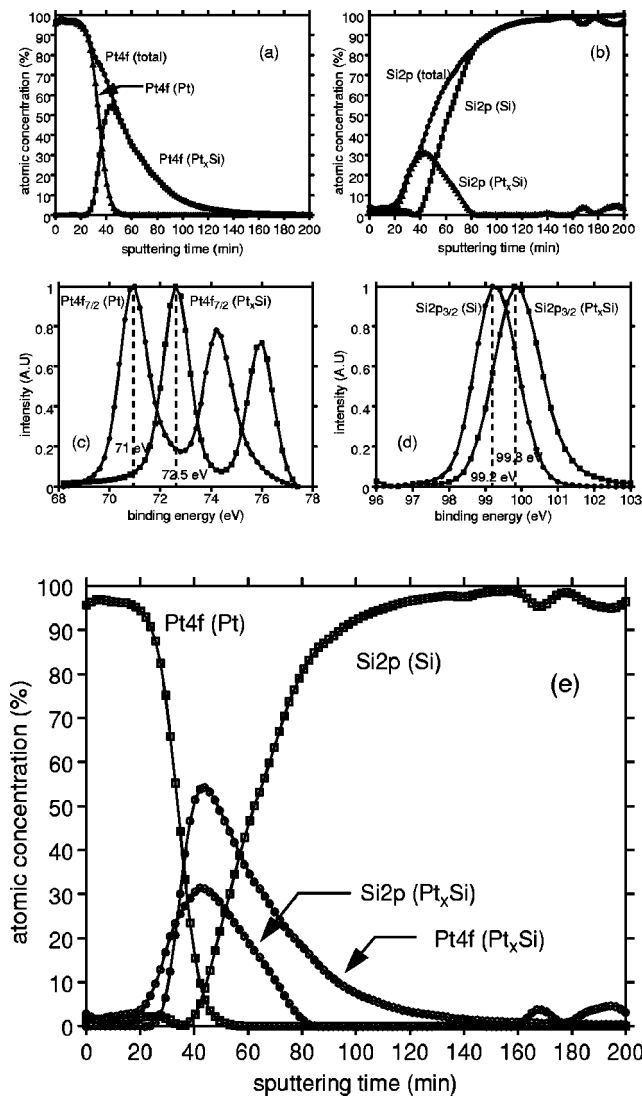


FIG. 6. XPS analysis of the initial Pt–silicide reaction occurring at room temperature: (a) Pt 4*f* depth profile deconvoluted into its Pt 4*f*(Pt<sub>*x*</sub>Si) and Pt 4*f*(Pt) contributions; (b) Si 2*p* depth profile deconvoluted into its Si 2*p*(Pt<sub>*x*</sub>Si) and Si 2*p*(Si) contributions; (c) extracted basis of spectra used in the deconvolution of the Pt 4*f* profile shown in (a): 71 and 72.5 eV are relevant of metallic and silicide-like binding energies; (d) extracted basis of spectra used in the deconvolution of the Si 2*p* profile shown in (b): 99.2 and 99.8 eV are relevant of elemental silicon and Pt<sub>*x*</sub>Si-like binding energies; and (e) summary of atomic concentration depth profiles obtained from Pt 4*f* and Si 2*p* photoemitted electrons according to their chemical environment.

silicon close to the initial surface between 10 and 20 min of sputtering time, indicating that the reaction front is probably not as sharp and uniform as assumed for ellipsometric measurements.<sup>12</sup> In this region, the Si 2*p*<sub>3/2</sub> photoemission line is essentially centered at a binding energy of 100 eV attributed to silicide-like bonds.

#### D. Platinum silicide formation above 300 °C

As outlined previously, Pt reacts first with Si to form Pt<sub>2</sub>Si and only after all Pt has been consumed in this way, the second reaction of Pt<sub>2</sub>Si to PtSi starts. For annealing temperatures above 300 °C, the diffusivities  $D_1$  and  $D_2$  of the two sequential Pt to Pt<sub>2</sub>Si and Pt<sub>2</sub>Si to Pt silicidation mechanisms are large enough to ensure that both reactions are fully

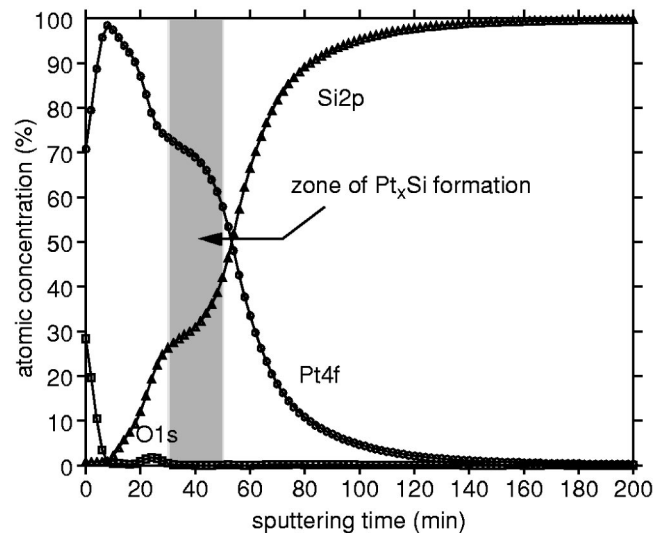


FIG. 7. XPS atomic concentration depth profile obtained from a sample annealed by RTA at 200 °C for 2 min. The shaded zone corresponds to a reacted Pt<sub>2</sub>Si phase covered by metallic Pt.

completed when a sufficiently thin layer of Pt is considered. Starting from an initial Pt layer of 15 nm, the Pt<sub>2</sub>Si reaction takes less than 3 s at 300 °C while the full silicidation into PtSi requires less than 120 s. These times of reaction have been obtained using the conventional square-root dependence of the silicide thickness with time described by Eq. (1). Their calculation accounts for the average diffusion parameters determined with the help of Fig. 5 and based on the results of Stark *et al.*<sup>12</sup> From the above analysis, the PtSi silicidation mechanism is expected to be fully completed within the 2 min of annealing performed at 300, 400, and 500 °C starting from the same 15 nm thick Pt overlayer. XPS depth profiles have been recorded for these three annealing conditions and are presented in Figs. 8, 9, and 10, respectively. Stoichiometric PtSi is obtained sufficiently far from

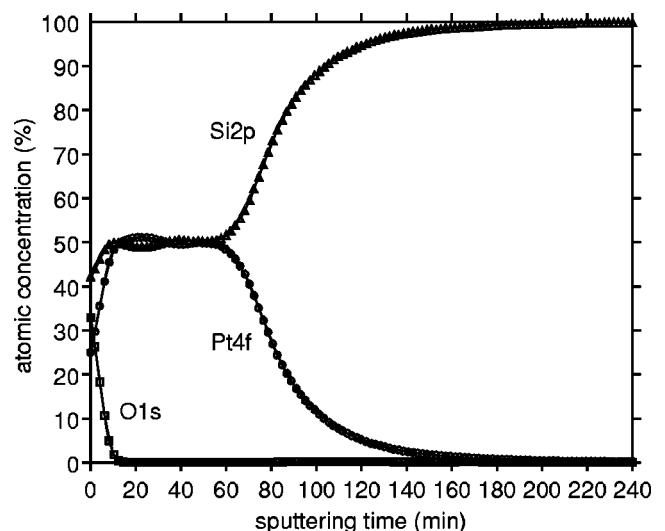


FIG. 8. XPS atomic concentration depth profile obtained from a sample annealed by RTA at 300 °C for 2 min. The PtSi silicidation reaction is fully completed as shown by the stoichiometric Pt and Si concentrations. The Pt overlayer is 15 nm.



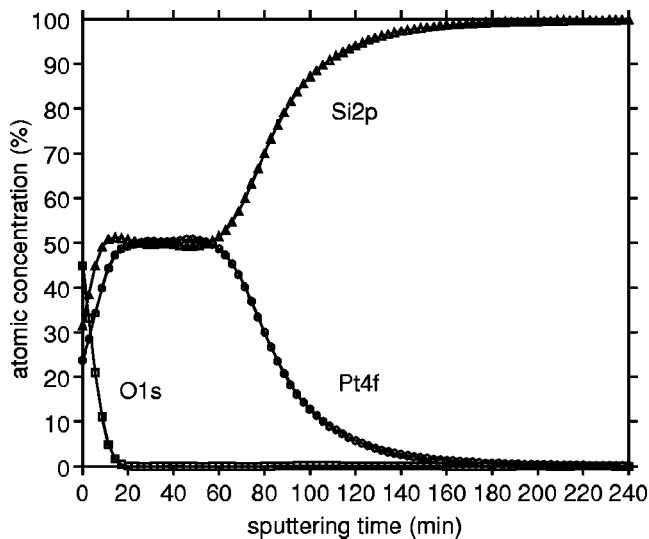


FIG. 9. XPS atomic concentration depth profile obtained from a sample annealed by RTA at 400 °C for 2 min. The Pt overlayer is 15 nm.

the top surface. For the three annealing conditions and at a typical sputtering time of 50 min relevant to platinum monosilicide, the Pt 4f<sub>7/2</sub> emission line is centered at 72.7 eV resulting in a chemical shift of 1.7 eV<sup>26,27</sup> with respect to metallic Pt (71 eV). Consistently, the Si 2p emission peak is displaced from the 99.2 eV emission position of clean p-Si(100) to 100.1 eV relevant of PtSi formation. One important feature that can be observed when the annealing temperature reaches 500 °C (Fig. 10) is the significant increase of oxygen concentration present at the top surface. This effect is attributed to silicon outdiffusion, the diffusion species during PtSi formation. From a quantitative viewpoint, the ratio between the surface atomic concentrations of oxygen and silicon is close to 2:1 indicating that the top layer could be composed of silicon dioxide. At the beginning of the sputtering phase, a careful inspection of Fig. 10(c) reveals that the dominant peak of the Si 2p emission line is centered around 103.8 eV, while a secondary peak is centered at 100.1 eV. The first binding energy is consistent with the presence of SiO<sub>2</sub>,<sup>28,29</sup> whereas the second peak is typical of PtSi-like bonds. As the sputtering process proceeds, the Si 2p peak at 103.8 eV vanishes while the 101.1 eV emission line clearly increases as the PtSi layer is uncovered during depth profiling. Considering now the O 1s photoemission spectra of Fig. 10(b), it can be observed that the initial peak position located at 533.1 eV<sup>29,30</sup> slightly moves to a lower binding energy of 532.4 eV before disappearing when sputtering reaches the PtSi layer. The above range of O 1s peak positions are also characteristic of the presence of the SiO<sub>2</sub> and consolidate the interpretation based on the analysis of the Si 2p spectra.

**E. Incomplete silicidation reaction due to oxygen pileup**

Crider and co-workers<sup>22</sup> established that the growth rates and phase growth sequence of Pt<sub>2</sub>Si and PtSi silicides were not affected by chemical etching with fluoridric acid, by sputter cleaning with Ar or by the presence of nitrogen under a partial pressure of 10<sup>-7</sup> Torr during the Pt deposition step.

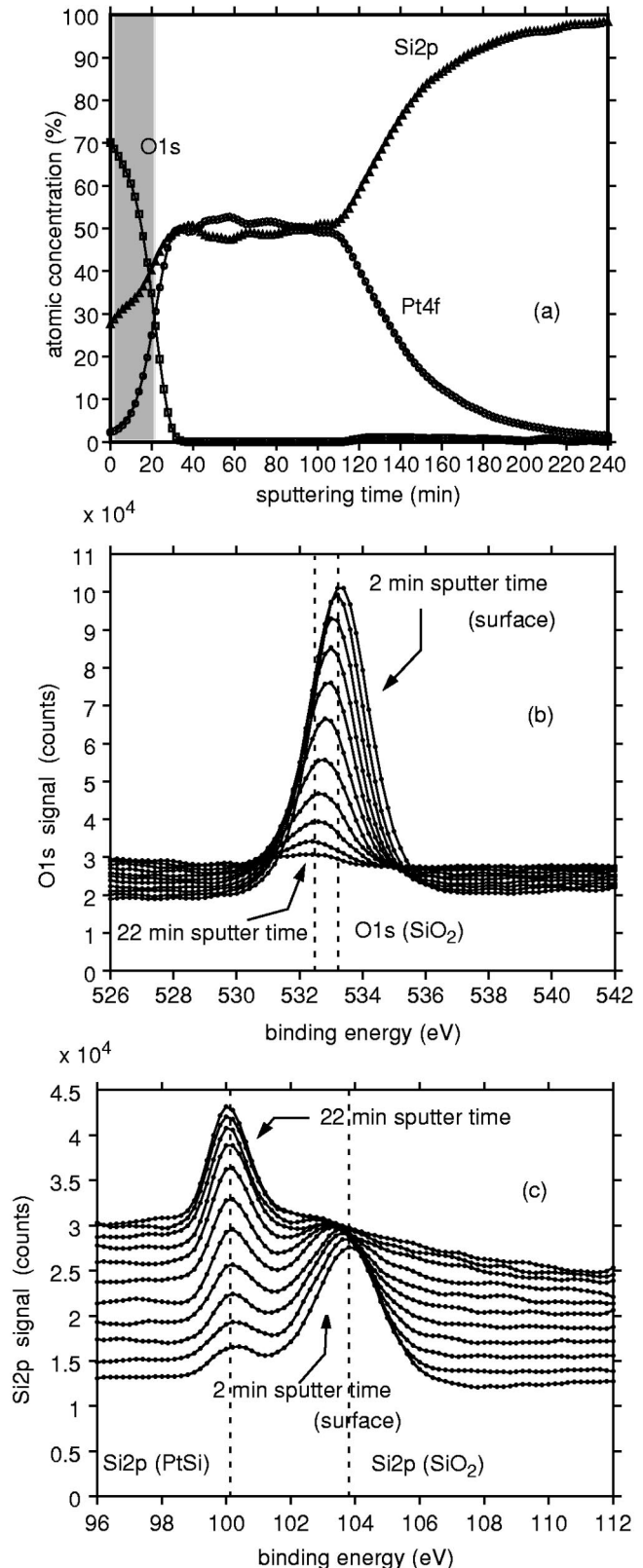


FIG. 10. XPS analysis of a sample annealed by RTA at 500 °C for 2 min starting from a 15 nm Pt overlayer: (a) atomic concentration depth profile showing stoichiometric PtSi covered by SiO<sub>2</sub> formed by Si outdiffusion and oxidation; (b) series of O 1s spectra recorded close to the surface: the O 1s peak centered in the 532.4–533.1 range indicates the presence of SiO<sub>2</sub>; (c) series of Si 2p spectra recorded in the shaded zone of (a): the Si 2p peak centered at 103.8 eV (top surface SiO<sub>2</sub>) vanishes rapidly while the second peak centered at 100.1 eV dominates when the stoichiometric PtSi phase is reached.

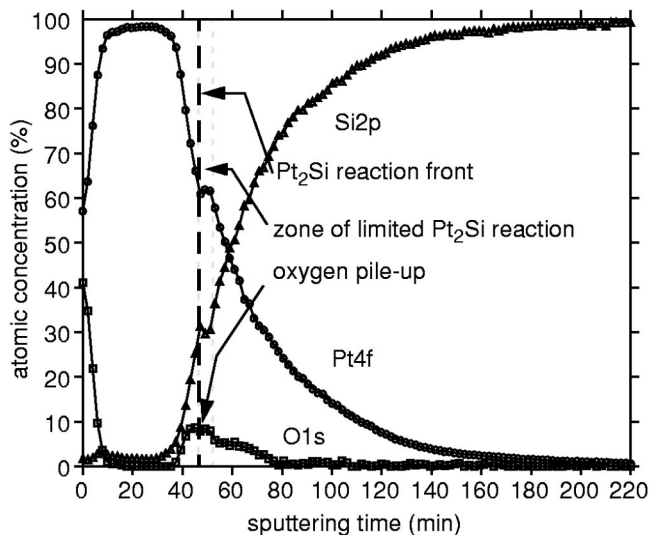


FIG. 11. XPS atomic concentration depth profile of a sample annealed at 300 °C during 30 min in a conventional tubular oven under  $N_2$  flow but exposed to ambient oxygen during the introduction phase. The diffusion of  $O_2$  into Pt stops the  $Pt_2Si$  reaction front.

In contrast, a significant decrease in both  $Pt_2Si$  and  $PtSi$  diffusivities was observed when the Pt film was evaporated under  $10^{-8}$  Torr of oxygen partial pressure. In this last case, the simultaneous existence of Pt,  $Pt_2Si$ , and  $PtSi$  can be observed because oxygen is known to pile up at the advancing  $Pt_2Si$  front.<sup>22</sup> Within the frame of this study, a 15 nm thick layer was deposited under the same cleaning and evaporation conditions than previous samples for which no abnormal silicidation reaction is observed. The annealing was performed in a conventional tubular oven at a temperature of 300 °C under a continuous flow of nitrogen. Because the introduction of the sample is made under ambient atmosphere, a significant amount of oxygen is present in the heating pipe at the beginning of the silicidation reaction. Figure 11 shows the resulting XPS depth profile obtained after a 30 min annealing step. A significant concentration of oxygen is observed within the top Pt film with a clear accumulation peak occurring at a depth corresponding to a sputter time of 50 min. A probable zone of quasistoichiometric  $Pt_2Si$  is obtained sufficiently far from the top surface. A definite phase growth front corresponding to the oxygen peak position may be clearly identified in this profile. In the present experiment, oxygen is not introduced during the deposition step as it was the case in Refs. 22 and 31. This anomalous and partial  $Pt_2Si$  silicidation reaction is attributed to oxygen diffusion into the Pt film. Thus, two competitive diffusion processes take place in opposite directions: oxygen present in the oven enclosure tends to diffuse into the Pt film while the  $Pt_2Si$ -Pt reaction front proceeds to the top surface. In a sufficiently thin Pt film (e.g., 15 nm), oxygen rapidly piles up at the Pt/ $Pt_2Si$  interface,<sup>32</sup> and acts as diffusion barrier for Pt. As a consequence, an annealing at 300 °C as long as 30 min is not sufficient to ensure the completion of the first  $Pt_2Si$  silicidation reaction. It is worth noting that experiments conducted in the RTA furnace (Secs. III C and III D) are not disturbed by oxygen penetration because samples are introduced at

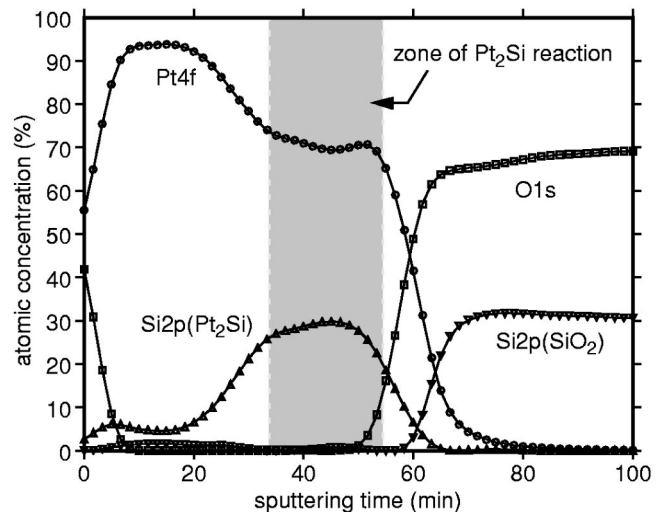


FIG. 12. Silicidation of a thin (8 nm) SOI film: XPS atomic concentration depth profile after annealing by RTA at 300 °C for 2 min. The  $Pt_2Si$  reaction is stopped after the complete consumption of silicon (SOI) layer.

room temperature and also because a primary vacuum is realized before the introduction of the  $N_2/H_2$  (97:3) gas flow and before activating the heating ramp.

#### F. Incomplete silicidation reaction due to a limited silicon source

The absence of a sufficient source of silicon atoms to complete the first  $Pt_2Si$  reaction is another possible cause for an abnormal termination of the silicidation mechanisms. In order to highlight this scenario, a 20 nm thick Pt film was evaporated on top of a very thin SOI layer and subsequently RTA annealed at 300 °C for 2 min. The full initial stack consists of the Pt overlayer, a 8 nm silicon SOI film, a buried oxide (BOX) of 400 nm, and finally the silicon back substrate. From Table I, the silicon thickness consumed by the  $Pt_2Si$  reaction is theoretically 13.2 nm. Therefore, this reaction is expected to terminate prematurely due to the default of one species (Si) in the active SOI film. Figure 12 perfectly illustrates this phenomenon through the XPS depth profile recorded across the Pt/ $Pt_2Si$ /SiO<sub>2</sub> stack after annealing. The original measurements of the Si 2p photoemission line has been fitted using a linear least squares algorithm in order to identify the chemical states of silicon. Excluding the 7 first minutes of sputtering characterized by an intermixed PtO layer, an unreacted Pt layer is clearly observed and characterized by a  $Pt 4f_{7/2}$  peak centered at 71 eV, indicative of a metallic state. A second zone where a silicidation reaction takes place is clearly identified in the 30–50 min sputtering interval. Over this region, chemical shifts of 1.5 and 0.6 eV are observed for the  $Pt 4f_{7/2}$  and Si 2p<sub>3/2</sub> peak positions, as expected. Finally, the deeper part of the depth profile corresponds to the BOX region for which the peak positions of Si 2p<sub>3/2</sub> (103.8 eV) and O 1s (533.1 eV) are consistent with the presence of oxide. In summary, special care must be taken for typical situations where thin SOI films, widely used in aggressive MOSFET architectures, are combined with a Pt silicidation step.<sup>5–7</sup> This discussion also consolidates the se-

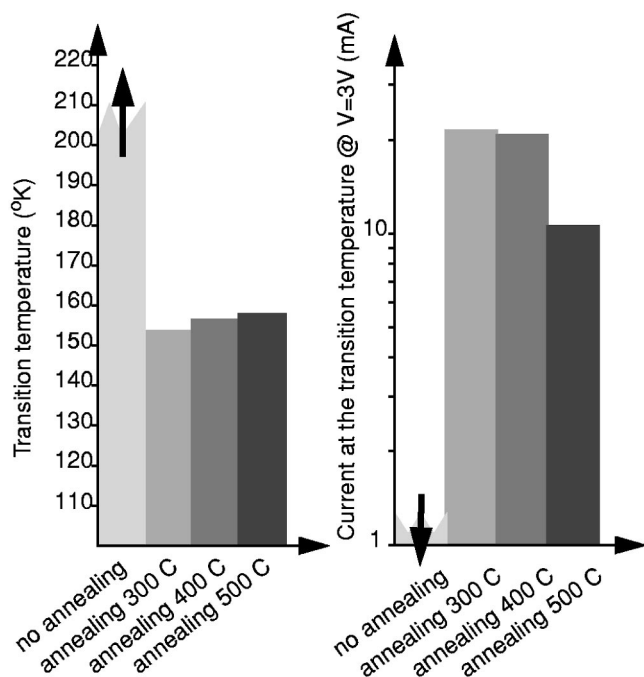


FIG. 13. Electrical characterization of Pt-based silicide contacts obtained at different temperatures (RTA treatment at 300, 400, and 500 °C). A low transition temperature and a high current drive are relevant of the best silicide obtained at 300 °C.

quential nature of Pt-based silicide reactions according to which the formation of the PtSi is possible only after the completion of the initial Pt<sub>2</sub>Si transformation.

#### IV. ELECTRICAL MEASUREMENTS

Electrical measurements of Pt-based silicide contacts have been conducted to determine the annealing conditions that provide the lowest Schottky barrier to holes and, therefore, the lowest specific contact resistance that characterizes the carrier transport through the silicide/silicon interface. Both the transition temperature and the corresponding current level defined in Sec. II C have been extracted from current–voltage characteristics measured in the 170–300 K temperature range. This information is reported in Fig. 13 for different annealing conditions. First of all, the silicide contact formed at ambient temperature exhibits a very low current drive consistently associated to a very high transition temperature. This behavior is attributed to the noncontinuous and nonhomogeneous nature of the silicidation reaction deduced from the XPS depth profile in Fig. 6. The best electrical performance is obtained at an annealing temperature of 300 °C. For thermal treatments realized at higher temperature (400 and 500 °C), a slight decrease of the current drive is observed in conjunction with an increase of the transition temperature. This last performance degradation is attributed to silicon outdiffusion that forms a thin oxide layer with oxygen available at the top surface. This interpretation is corroborated by the corresponding XPS depth profiles of Figs. 9 and 10(a).

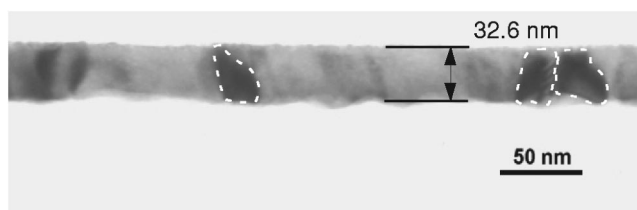


FIG. 14. TEM cross sections of a sample annealed at 300 °C by RTA for 2 min starting from a  $15 \pm 1$  nm Pt overlayer. A smooth and regular PtSi/Si interface is obtained. The thickness of the formed PtSi phase is in agreement with published expansion factors (see Table I).

#### V. TEM CROSS SECTIONS

TEM cross sections have been realized on a sample annealed by RTA at 300 °C starting from a  $15 \pm 1$  nm Pt overlayer. The corresponding images presented in Fig. 14 show a homogeneous PtSi film on which the vertical orientation of grains can be distinguished. No preferential site of growth can be observed and the silicide/silicon interface is smooth. The thickness ratio is  $d_{\text{Pt}}/d_{\text{PtSi}} \sim 0.5$  which is consistent with the theoretical target given in Table I ( $1/1.97 = 0.507$ ) and close to values found in the literature.<sup>33</sup>

#### VI. CONCLUSION

In summary, we have proposed a detailed study of Pt-based silicides obtained at room temperature, annealed in UHV or thermally activated by rapid thermal processing up to a temperature of 500 °C. XPS analysis was extensively used to characterize the kinetics and stoichiometry of the Pt<sub>2</sub>Si and PtSi phases. A remarkable agreement with kinetics parameters obtained by Stark *et al.*<sup>12</sup> has been obtained under UHV conditions. We have confirmed pileup of oxygen occurring at the Pt<sub>2</sub>Si/Pt reaction front as an inhibiting factor of the silicidation. The incomplete silicidation of an ultrathin SOI film has been clearly outlined, providing on the same occasion a confirmation of the sequential nature of the disilicide/monosilicide reactions. Finally, current drive measurements on PtSi Schottky contacts have allowed us to identify 300 °C as an optimum annealing temperature.

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