Effect of Fluorine Incorporation on the Thermal Stability of PtSi/Si Structure

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Abstract—The effect of fluorine incorporation on PtSi/Si structure is studied systematically. It is observed that the fluorine incorporation from ion implantation improves the high-temperature stability of the PtSi/Si structure. The optimum implantation energy is determined to be the energy at which the maximum percentage of the as-implanted fluorine ion locates at the PtSi/Si interface region. The SIMS analysis shows that the fluorine atom piles up at the PtSi/Si interface. The XPS analysis indicates that the fluorine atoms at the PtSi/Si interface are bonded to the silicon atoms in a form of SiF_2 or SiF_3. A fluorine-buffer (FB) model is proposed to explain the effect of fluorine incorporation. It is postulated that the Si–F layer acts as a buffer layer to change the PtSi/Si interface energy and preserve the integrity of the silicide layer at high temperature. Fluorinated Schottky junctions are fabricated and the electrical characteristics show that the sustainable process temperature can be improved from 650°C for the unfluorinated Schottky junctions to higher than 800°C for the fluorinated Schottky junctions.

I. INTRODUCTION

PLATINUM SILICIDE (PtSi) has been widely used for its stable features as well as low resistivity. With the progress of VLSI technology, thin-film silicides become increasingly important. Formation of low-resistance contact, low sheet-resistance diffused region, and polycide gate and interconnection line is crucial for the VLSI circuit performance. PtSi can form stable ohmic and Schottky contacts to silicon at temperatures lower than 600°C. It consumes less silicon than the refractory metals during silicide formation [1]. It is suitable for SALICIDE process [2]. It has also been reported that using Pt or PtSi as a barrier film, high-quality shallow junctions with junction depths of less than 100 nm (both n^+-p and p^+-n junctions) can be fabricated using furnace annealing at tem-

peratures lower than 750°C [3], [4]. All of these indicate that PtSi should be a choice for application to very large scale bipolar and MOS integrated circuits. However, high-temperature stability of PtSi has always been questionable.

The often quoted high-temperature instability of PtSi on silicon apparently arises from the fact that the lowest eutectic point in the Pt–Si system occurs at 830°C [5]. Even after the complete consumption of metal to form silicide at low temperature, platinum diffusion into silicon substrate from PtSi at a temperature of 700°C or higher has been reported [6]. The high-temperature instability of PtSi has also been observed in the degradation of the PtSi/n-Si Schottky junction. Annealing of such a junction to a temperature of 650°C or higher will cause large reverse leakage current and nonideal forward current–voltage characteristics [7]. One effort to improve the high-temperature instability associated with the PtSi/Si structure is to produce a film with Si/Pt atomic ratio higher than that in the eutectic to bypass the eutectic composition and hence the instability [8]. It is shown that the co-sputtered silicon-rich alloy prevents agglomeration of the silicide, but increases the resistivity and decreases the Schottky-barrier height of the film. Electrical properties such as forward and reverse current–voltage characteristics still degrade after high-temperature annealing. Furthermore, the technique is not compatible with the modern VLSI process.

Recently, the effect of fluorine incorporation on the MOS device has become an attractive research field. Sequential experiments on the dielectric properties, the radiation hardness, and the hot-carrier immunity of the fluorinated MOS device has been pursued by Yale, Stanford, and Hitachi groups [9]–[16]. With fluorine incorporation at appropriate conditions, the interface state density and the interface radiation hardness of the SiO_2/Si interface and the hot-carrier resistance of the MOSFET device are improved significantly. One drawback is that a higher dose of fluorine causes degradation in charge to breakdown [10]. Other effects associated with fluorine incorporation on MOS devices are studied by other groups. It is observed that fluorine plays a major role in the penetration of boron into and through the gate oxides of p-channel MOSFET's which employ p^+-doped polysilicon gates [17]–[20]. It has also been suggested that fluorine atoms may be trapped by group V dopants in n-type

TABLE I
EXPERIMENTAL CONDITIONS USED TO DETERMINE THE OPTIMUM IMPLANTATION CONDITION FOR THE
HIGH-TEMPERATURE STABILITY IMPROVEMENT OF THE PtSi/Si STRUCTURE BY BF_2^+-ION
IMPLANTATION

Sample Structure	PtSi(300 Å)/Si					
BF_2^+ energy (keV)	38	75	100	125		
F^+ effective energy (keV)	15	30	40	50		
BF_2^+ dose (1/cm^2)	5×10^{13}	2×10^{14}	5×10^{14}	1×10^{15}	2×10^{15}	
Annealing temperature (°C)	400	700	750	800	830	850
Annealing time	60 min					

silicon due to high electronegativity of fluorine atoms. Fluorine atoms prevent the As^+–Si^- and P^+–Si^- pairs forming, the formation and dissociation of which cause diffusion enhancement and extended defects. However, the formation of As^+–F^- and P^+–F^- pairs reduces the dopant activation [21].

In the authors' previous work, it was observed that implanting fluorine-contained ions (such as F^+ or BF_2^+) through the Pt/Si (Implantation Through Metal, ITM) or PtSi/Si (Implantation Through Silicide, ITS) structure allows the PtSi/Si structure to withstand a higher process temperature, up to 800°C, without degradation [22]. This high-temperature stability was confirmed by sheet resistance measurement, scanning electron microscopic (SEM) inspection, and Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS) analyses. Secondary ion mass spectroscopy (SIMS) analysis indicates that the implanted fluorine atoms pile up at the PtSi/Si interface. The high-temperature stability should be correlated to the fluorine pileup. In this work, the effect of fluorine incorporation on the PtSi/Si structure is studied systematically. The optimum condition of fluorine implantation is determined. A fluorine-buffer (FB) model is proposed to explain the improvement of high-temperature stability. Fluorinated Schottky junctions were fabricated and compared to unfluorinated Schottky junctions.

Both ITM and ITS samples were processed. Because the results of the ITS scheme are similar to those of the ITM scheme, only the ITM scheme is reported and discussed in detail. Nonetheless, some results different for the ITS and ITM schemes will be stated in the text.

II. EXPERIMENTS AND RESULTS

A. BF_2^+ Implantation

In [22], the authors have clarified the effect of ion implantation on the high-temperature stability of PtSi film by implanting different species of BF_2^+, F^+, and B^+ separately at equivalent energies and doses into the PtSi/Si samples. It was concluded that the improvement of the high-temperature stability is attributed to the fluorine ions with the boron ions playing no role. Similar results could be obtained by implanting F^+ or BF_2^+ ions if the fluorine ions had the same effective energy. Because the beam current of BF_2^+ ions is at least one order of magnitude higher than that of the F^+ ions when BF_3 gas is used as the ion

source, BF_2^+ were employed to introduce fluorine at first to determine the optimum implantation condition.

The starting material was n-type (100) oriented 0.8–2.7-Ω · cm phosphorus-doped silicon wafer. The wafers were first cleaned by the standard RCA cleaning process. Platinum film of about 300 Å thickness was deposited in an electron-beam evaporation system with a base pressure of less than 5×10^{-6} torr and a deposition rate of 1 Å/s. Before loading into the deposition chamber, wafers were immersed in dilute HF solution (HF : H_2O = 1 : 50) for 1 to 2 min to remove the surface oxide grown during cleaning, and the silicon surface was passivated by hydrogen and/or fluorine at the same time which can prohibit oxidation in air [23]. After Pt deposition, BF_2^+ ions were implanted into the wafers at different energies from 38 to 125 keV to different doses from 1×10^{14} to 5×10^{15} cm^{-2}. The corresponding fluorine energy was determined by multiplying the BF_2^+ energy with the ion mass ratio of $F^+/BF_2^+ = 19/49$ to be from 15 to 50 keV. Wafers were first annealed in N_2 ambient at 400°C for 60 min to form PtSi and the unreacted Pt was selectively etched by boiling in dilute aqua regia. Wafers were then cut into six pieces and five of them were further annealed in N_2 ambient for 60 min at 700, 750, 800, 830, and 850°C, respectively. Table I summarizes the key experimental conditions.

The sheet resistance (R_s) of each sample was measured by a four-point probe. For each sample before degradation, the deviation of R_s over five measurements is within 1–2 Ω/□. Figs. 1 and 2 show the R_s–annealing temperature relation of the samples implanted with BF_2^+ ion at 38 and 75 keV (effective F^+ energy of 15 and 30 keV), respectively; the R_s–temperature data of the unimplanted samples are also included for comparison. For the unimplanted samples, the R_s value starts to increase at 750°C. For the samples implanted with BF_2^+ ion at 38 keV, the R_s value remains stable up to 800°C but increases drastically at higher temperatures independent of the implanted dose. For the samples implanted with BF_2^+ ion at 75 keV, a different tendency was observed. For the two lower dose sample sets, R_s–temperature relation is similar to that of the 38-keV implanted samples. As the implanted dose becomes higher than 1×10^{15} cm^{-2}, the R_s value becomes clearly more stable. Fig. 3 shows the R_s–temperature relation of the samples implanted with BF_2^+ ion
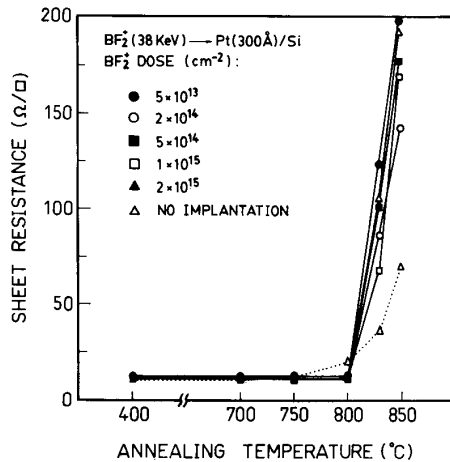
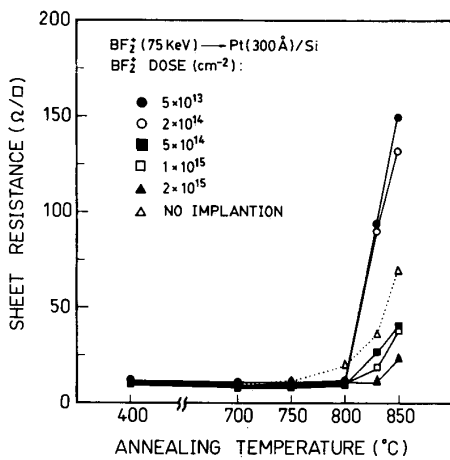Fig. 1. R_s-temperature relation of the Pt(300 Å)/Si samples implanted with BF_2^+ ions at 38 keV to various doses.

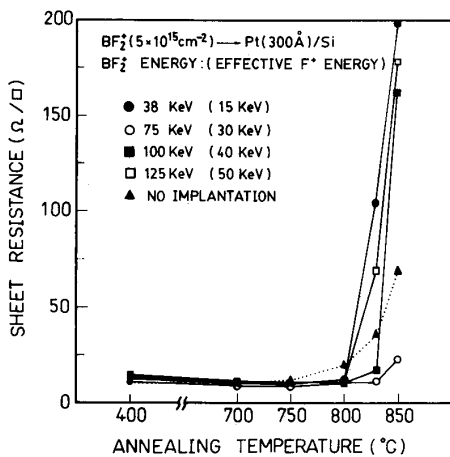Fig. 2. R_s-temperature relation of the Pt(300 Å)/Si samples implanted with BF_2^+ ions at 75 keV to various doses.

Fig. 3. R_s-temperature relation of the Pt(300 Å)/Si samples implanted with BF_2^+ ions at 38, 75, 100, and 125 keV, respectively, to a dose of 5 × 10^{15} cm^{-2}.

TABLE II
FLUORINE ION DISTRIBUTION (%) FOR THE Pt(300 Å)/Si STRUCTURE BY
TRIM SIMULATION

Energy (keV)	15	30	40	50
Backscattered	28.54	24.67	23.65	21.83
Within Pt film	67.43	42.46	29.39	19.22
300–600 Å	4.02	23.57	22.52	19.22
>600 Å	0.01	9.30	24.44	39.73

to a dose of 5 × 10^{15} cm^{-2} at energies of 38, 75, 100, and 125 keV (effective F^+ energy of 15, 30, 40, and 50 keV), respectively. It is observed that the 75- and 100-keV implantations give rise to the highest stability. As the implantation energy is increased to 125 keV, the high-temperature stability deteriorates.

The as-implanted fluorine distribution is simulated by the TRIM program [24]. The Pt-film thickness is assumed to be 300 Å. Table II lists the percentage fluorine distribution with the fluorine ion implanted at 15, 30, 40, and 50 keV, respectively. The target is divided into three regions: the Pt film, the Si surface region which will be consumed during silicidation (300–600 Å), and the Si substrate underneath the final PtSi/Si interface (>600 Å). The thickness of the second region is calculated by multiplying the Pt-film thickness by the reacted volume ratio of Pt/Si = 1/1.32 [1]. Because the oxygen contamination is not well controlled in the film's deposition system, the Pt film cannot be converted into PtSi completely. In this work, the final PtSi film thickness of the Pt(300 Å)/Si sample is about 450 Å measured by ellipsometry [25] and TEM cross sections. The consumed silicon is thus about 300 Å thick. With fluorine energy at 15 keV, most of the fluorine ions are confined in the Pt film. During silicide formation, this fluorine might diffuse out of the sample to the ambient and play no role on the high temperature stability. As the fluorine energy increases from 30 to 50 keV, the amount of fluorine ions that penetrate into the Si substrate increases. However, the maximum stable temperature of the 50-keV (F) implanted samples is lower than that of the 30- and 40-keV (F) implanted samples. It is thus assumed that only the fluorine ions located near the Pt/Si interface, especially those located within the second region, will influence the high-temperature behavior of the PtSi/Si structure. This is quite reasonable since during the silicide formation, the fluorine atoms will be pushed ahead by the PtSi phase front to pile up at the interface.

To verify whether the optimum implantation energy is the energy at which the largest amount of fluorine ions is placed within the Si surface region to be consumed, the high-temperature stability of samples with 170 Å of Pt was examined. Table III lists the TRIM simulated percentage fluorine distribution of the fluorine ion implanted into the Pt(170 Å)/Si structure at 15, 20, and 25 keV, respectively. In this case, the silicon consumption is about 170 Å thick. It is observed that 20-keV implantation places the largest amount of fluorine within the region consumed by silicidation. Thus 20 keV should be the op-
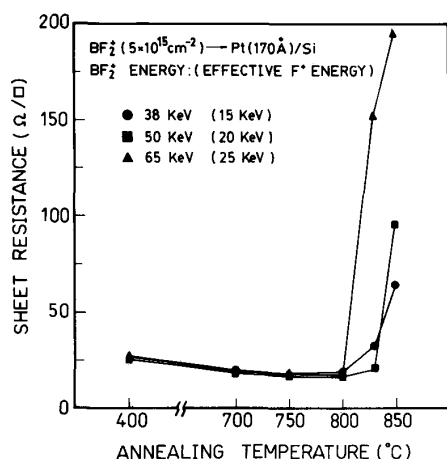
Fig. 4. R_s-temperature relation of the Pt(170 Å)/Si samples implanted with BF_2^+ ions at 38, 50, and 65 keV, respectively, to a dose of 5×10^{15} cm^{-2}.
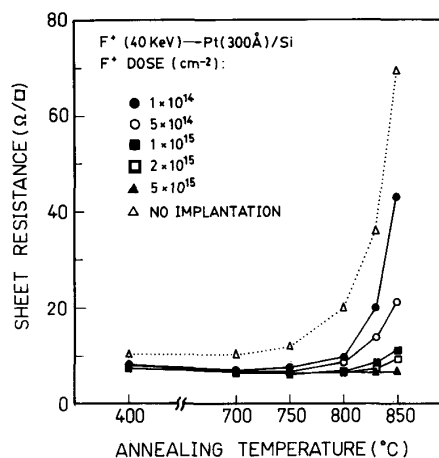

Fig. 5. R_s-temperature relation of the Pt(300 Å)/Si samples with fluorine implantation at 40 keV to various doses.

TABLE III
FLUORINE ION DISTRIBUTION (%) FOR THE Pt(170 Å)/Si STRUCTURE BY TRIM SIMULATION

Energy (keV)	15	20	25
Backscattered	27.79	26.37	24.36
Within Pt film	40.20	26.88	18.18
170–340 Å	22.21	22.74	20.77
>340 Å	9.80	24.09	36.69

timum energy for the Pt(170 Å)/Si structure. Fig. 4 shows the R_s-temperature relation of the Pt(170 Å)/Si samples implanted with BF_2^+ ion at 38, 50, and 65 keV (effective F^+ energy of 15, 20, and 25 keV), respectively. This confirms the criteria of the optimum implantation energy. A similar experimental procedure was also followed for the ITS scheme. The optimum energy of fluorine ion for the PtSi(600 Å)/Si structure was determined to be 50 keV.

B. F^+ Implantation

Fluorine ions alone were implanted into the Pt(300 Å)/Si structure at the optimum energy (40 keV) to further examine the high-temperature characteristics of the fluorinated PtSi/Si structure. The Pt(300 Å)/Si structure was prepared using the same process as that employed in the BF_2^+ implantation experiment. Fluorine ions were then implanted into wafers at 40 keV to various doses ranging from 1×10^{14} to 5×10^{15} cm^{-2}. Following the F^+ implantation, all wafers were cut into smaller pieces and were annealed in N_2 furnace for 60 min at 400, 700, 750, 800, 830, and 850°C, respectively. The unreacted Pt was selectively etched by aqua regia.

Fig. 5 shows the R_s-temperature relation of the fluorine-implanted samples; the R_s-temperature data of the unimplanted samples are also included for comparison. Since the unimplanted samples and the fluorine implanted

samples were not prepared at the same time and a deviation of the Pt film thickness of about $\pm 10\%$ exists in our laboratory, sheet resistances of the unimplanted and fluorine-implanted samples at low temperature are slightly different. For the unimplanted samples, the R_s value increases at temperatures higher than 700°C. As the implanted fluorine dose increases from 1×10^{14} to 5×10^{15} cm^{-2}, the high-temperature stability of the R_s value of the PtSi film is successively improved. It is seen that the R_s value remains stable up to 800°C as the implanted dose exceeds 1×10^{15} cm^{-2} and up to 850°C as the implanted dose is 5×10^{15} cm^{-2}. Such an improvement is stable and reproducible over at least six different experimental lots.

SEM inspection was employed to further characterize the high-temperature stability of the PtSi film. Fig. 6 shows SEM micrographs of the PtSi surface and the corresponding silicon surface after removal of the silicide film of 800°C annealed samples without fluorine implantation and with fluorine implantation to a dose of 1×10^{15} and 5×10^{15} cm^{-2}, respectively. It is shown that severe agglomeration occurs for the unimplanted sample, and the PtSi film becomes discontinuous. For the sample with fluorine implantation to a dose of 1×10^{15} cm^{-2}, the PtSi film is non-uniform and shows some agglomeration, and small pinholes were observed. As the implanted dose increases to 5×10^{15} cm^{-2}, the PtSi film remains smooth after 800°C annealing as seen in the micrograph. The morphology of the silicon surface is consistent with that of the PtSi surface. As the film agglomerates, the PtSi spikes into the silicon substrate; thus the silicon surface becomes rather rough. Fig. 7 shows SEM micrographs of the PtSi surface and the silicon surface after removal of the silicide film of 850°C annealed samples without fluorine implantation and with fluorine implantation to a dose of 5×10^{15} cm^{-2}. The PtSi film of the unimplanted sample has agglomerated to isolated islands which accounts for the dramatic increase of the R_s value. For the sample
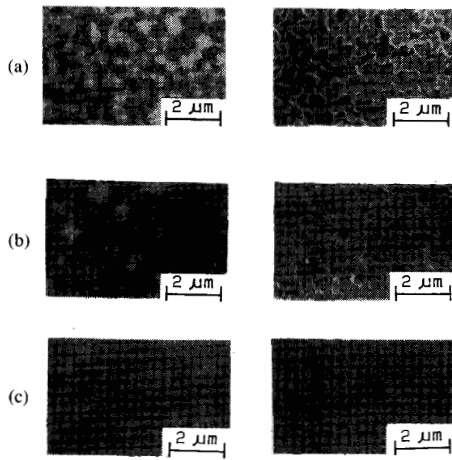
Fig. 6. SEM micrographs of the PtSi surface (left) and the Si surface after removal of the PtSi film (right) of the 800°C annealed samples (a) without fluorine implantation, and with fluorine implantation to a dose of (b) 1×10^{15} cm^{-2} and (c) 5×10^{15} cm^{-2}.
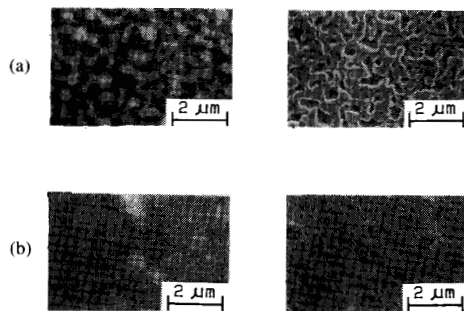

Fig. 7. SEM micrographs of the PtSi surface (left) and the Si surface after removal of the PtSi film (right) of the 850°C annealed samples (a) without fluorine implantation, and (b) with fluorine implantation to a dose of 5×10^{15} cm^{-2}

Fig. 8. AES depth profiles of the samples annealed at 850°C which are implanted with F$^+$ ions to a dose of 1×10^{14}, 1×10^{15}, and 5×10^{15} cm^{-2}, respectively, and the depth profile of an unimplanted sample annealed at 400°C.

Fig. 9. Comparison of the forward $I-V$ characteristics of the Schottky junctions with fluorine implantation to a dose of 5×10^{15} cm^{-2} and annealed at 800°C and the junctions without fluorine implantation and annealed at 400 and 800°C, respectively.

with fluorine implantation to a dose of 5×10^{15} cm^{-2}, the PtSi film becomes nonuniform but still remains continuous.

Fig. 8 shows the AES depth profiles of the samples implanted with F$^+$ ions to a dose of 1×10^{14}, 1×10^{15}, and 5×10^{15} cm^{-2}, respectively, followed by an 850°C annealing; also shown is the profile of an unimplanted sample annealed at 400°C. No platinum penetration into the silicon substrate is observed up to 850°C for the 5×10^{15} cm^{-2} implanted samples. As the implantation dose decreases to 1×10^{15} cm^{-2} or less, the PtSi film agglomerates to discontinuous islands, platinum penetrates into the silicon substrate, and the Si substrate is exposed. The RBS profile indicates similar results. These are consistent with the results of the sheet resistance measurement and the SEM inspection.

C. Schottky-Junction Characteristics

Because the Schottky-barrier height is very sensitive to the properties of the silicide/silicon interface [7], [8], in-
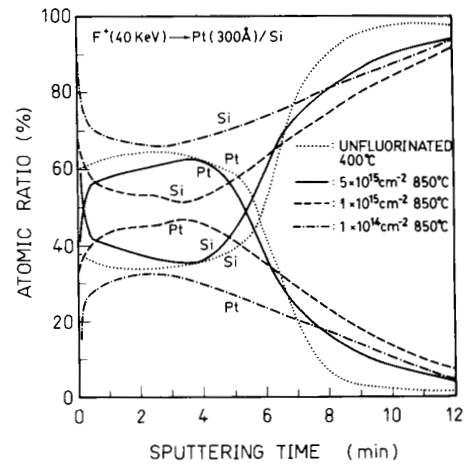
vestigation on Schottky junction is used to evaluate the applicability of the fluorine implantation technique to a typical integrated circuit process for the improvement of high-temperature stability of PtSi film. The junction area was defined by etching a square window through a 4700-Å-thick thermally grown SiO$_2$ layer. The wafer backside was metallized by aluminum. Other processes are the same as those described in Section II-B.

Fig. 9 compares the forward $I-V$ characteristics of the PtSi/n-Si Schottky junction formed by annealing at 800°C with fluorine implantation to a dose of 5×10^{15} cm^{-2} and the unimplanted Schottky junction annealed at 400 and 800°C, respectively. Since the silicide/silicon interface becomes irregular at temperatures higher than 700°C, the 800°C annealed, unfluorinated Schottky junc-
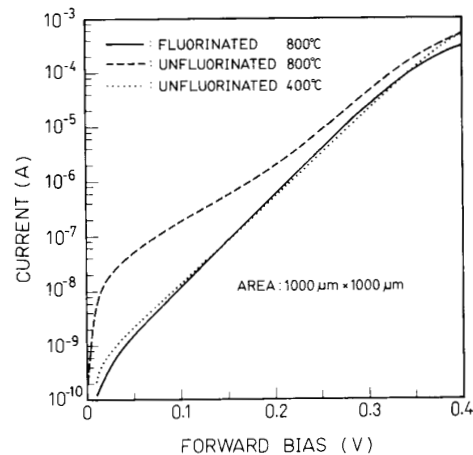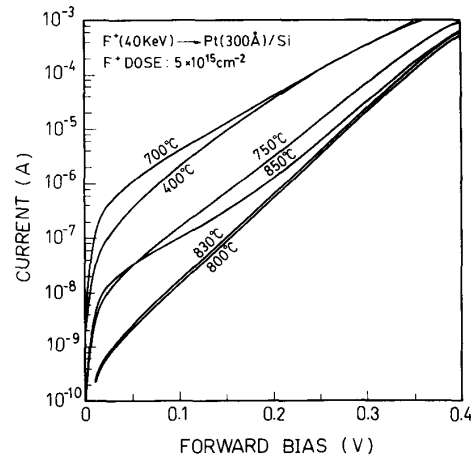
Fig. 10. Comparison of the forward I-V characteristics of the Schottky junctions with fluorine implantation to a dose of 5×10^{15} cm^{-2} and annealed at different temperatures.

TABLE IV
THE MEASURED SCHOTTKY BARRIER (ϕ_{bn}), FORWARD IDEALITY FACTOR (η), AND REVERSE CURRENT DENSITY AT -5 V (J_R) OF THE SCHOTTKY JUNCTIONS WITHOUT FLUORINE IMPLANTATION AND WITH FLUORINE IMPLANTATION TO A DOSE OF 5×10^{15} cm^{-2}
(X: without fluorine implantation. F: with fluorine implantation.)

Annealing Temperature (°C)		400	700	750	800	830	850
ϕ_{bn} (eV)	X	0.866 ±0.002	0.841 ±0.008	0.812 ±0.011	0.797 ±0.011	0.801 ±0.011	***
	F	0.706 ±0.003	0.677 ±0.002	0.786 ±0.003	0.864 ±0.004	0.858 ±0.007	0.833 ±0.005
η	X	1.005 ±0.003	1.054 ±0.002	1.135 ±0.003	1.193 ±0.004	1.194 ±0.004	***
	F	1.376 ±0.037	1.691 ±0.063	1.230 ±0.030	1.054 ±0.009	1.066 ±0.017	1.146 ±0.014
J_R (μA/cm^2)	X	0.034 ±0.007	0.572 ±0.112	1.13 ±0.447	1.97 ±0.814	9.41 ±7.29	46.2 ±23.8
	F	80.0 ±4.5	233.0 ±29.8	9.31 ±3.57	2.56 ±0.53	4.88 ±1.76	202 ±140

tion has degraded severely. For the fluorinated Schottky junction, the interface remains stable up to 800°C. Thus no evident difference is observed between the forward characteristic of the 800°C annealed, fluorinated junction and that of the 400°C annealed, unfluorinated junction. Table IV lists the measured Schottky-barrier height (ϕ_{bn}), the forward ideality factor (η), and the reverse current density at -5 V (J_R) of the Schottky junctions without fluorine implantation and with fluorine implantation to a dose of 5×10^{15} cm^{-2}. These values are obtained by averaging data from at least 10 arbitrarily chosen junctions. Also shown are their standard deviations. The ϕ_{bn} and η values are extracted from the semi-log forward I-V plot using a Richardson constant of 120 (A/cm^2/k^2). The ϕ_{bn} of the 800°C annealed, fluorine implanted junction is close to that of the 400°C annealed, unimplanted junction. This indicates that most of the implantation damages near the silicide/silicon interface has been recovered, and the Schottky barrier is restored to its normal feature. The

ideality factor (η) of fluorine-implanted junctions is lowest after 800°C annealing, but it is slightly higher than that of 400°C annealed, unimplanted junctions. Fig. 10 compares the forward I-V characteristics of the Schottky junctions with fluorine implantation to a dose of 5×10^{15} cm^{-2} and annealed at different temperatures. The degradation of the 830 and 850°C annealed junction is attributed to the local nonuniformity of the PtSi film.

It is observed in Table IV that the J_R of the fluorine-implanted junction is higher than that of the 400°C annealed, unimplanted junction. Even if the fluorine-implanted junction had been annealed at 800°C and the J_R decreased to the lowest value, the J_R would still be two orders of magnitude higher than that of the 400°C annealed unimplanted junction. Fig. 11 shows a TEM cross-sectional view of the surface layer of a fluorine-implanted sample. It is observed that some dislocation loops and bubble-like defects reside in the silicon substrate. The high J_R is thus attributed to these residual defects.
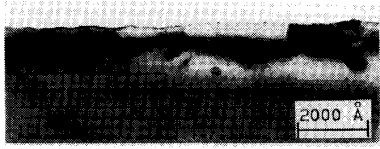
Fig. 11. TEM cross-sectional view of the 800°C annealed sample with fluorine implantation to a dose of 5×10^{15} cm^{-2}.

III. DISCUSSION

In a previous publication [22], the authors have demonstrated by SIMS analysis that the fluorine atoms segregate at the silicide/silicon interface after thermal treatment. In this work, we try to compare the fluorine segregation behavior with different implanting dose and annealing conditions. Before samples were SIMS analyzed, the PtSi film was stripped by boiling in aqua regia to prevent the results from being interfered with by the PtSi film. Since residual Pt signal is still detected at the sample surface, the fluorine concentration is not quantified. Fig. 12 shows the fluorine profiles of the samples with fluorine implantation to a dose of 1×10^{15}, 2×10^{15}, and or 5×10^{15} cm^{-2}, followed by an 800°C anneal. It is expected that both the total dose in the substrate and the interface concentration decrease as the implanting dose decreases. The higher the interface concentration, the better is the thermal stability, as shown by the sheet resistance data. From this observation, we find a direct relation of the thermal stability of fluorinated PtSi/Si structure and the fluorine concentration at the interface. Another interesting phenomenon shown in the fluorine profiles is the kink at about 300 Å below the interface. This could be attributed to the gettering by the residual damage [26] since heavy substrate damage was produced during the high energy implantation. A similar phenomenon was also observed by other workers [27]. This damage gettering behavior can explain why the Schottky barrier and the forward and reverse characteristics of the fluorine-implanted Schottky diode can be recovered after annealing.

The chemical state of such a high-concentration fluorine was further analyzed by the X-ray photoelectron spectroscopy (XPS). The PtSi film was first etched by boiling in dilute aqua regia. A thin native SiO$_2$ layer was grown during the etching process and the subsequent DI water rinsing step. The oxide layer was not removed using the fluorine-containing solution to avoid the interference of residual fluorine contamination from the solution. Instead, the sample was loaded into the chamber, and argon sputtering was employed until the Auger electron signal of oxygen decreased to the background noise level. The XPS analysis was then performed within the sputtered window. A value of 84.0 eV for the Au($4f_{7/2}$) peak was used as reference of calibration for the XPS binding energy. The F$_{1s}$ peak at 686.2 eV corresponds to the SiF$_2$ or SiF$_3$ type species [28], [29]. No atomic or molecular fluorine was detected.

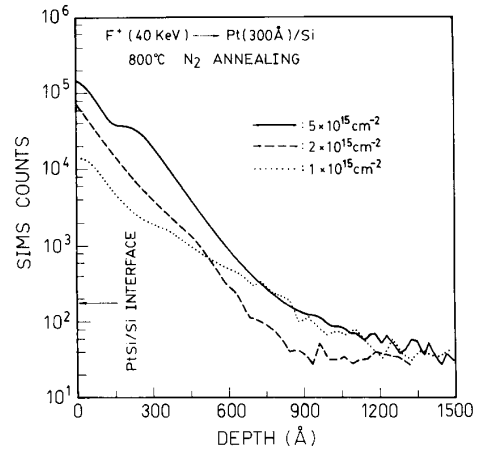The polycrystalline silicide allocated between two other

Fig. 12. Comparison of the fluorine profiles of the 800°C annealed samples with fluorine implantation to a dose of 1×10^{15}, 2×10^{15}, and 5×10^{15} cm^{-2}, respectively.

phases, i.e., the silicon substrate and the ambient, is a structure which is not thermodynamically stable. The driving force for this silicide agglomeration is the reduction of total energy of the system, including that of the silicide grain boundary, the silicide/silicon interface, and the silicide-free surface [30]. The agglomeration process will continue until all the grain boundaries disappear, that is, the islanding of the silicide film, once the thermal energy can be sufficiently applied. As for the fluorine addition to the PtSi/Si system, we can expect that there will be a certain reduction of the total system energy. We are not able to distinguish whether it is a result of the lowered grain boundary energy or the interface energy. Chen et al. [31], [32] argued that the improved thermal stability of NiSi$_2$ system is attributed to the retardation of the growth of NiSi$_2$ grain by the presence of boron and/or fluorine atoms at the grain boundaries. We observed in our experiment that, once the implanting energy is not sufficient to have the fluorine ion reaching the silicide/silicon interface, very little effect on the thermal stability can be obtained. It is evident that the fluorine segregation at the interface, and not at the grain boundaries, plays a dominant role in the stabilization. It was also found that BF$_2^+$ implantation when the whole dose is confined to the silicide layer degrades the thermal stability of CoSi$_2$/Si system [33], which further confirms our conclusion.

Because it is very difficult to explain unambiguously the stabilizing influence from the thermodynamic point of view, kinetic factors determining the transport of material, which causes the agglomeration, should also be considered. Van der hove [30] proposed a silicide dissociation model, which is associated with the solid-phase-epitaxy process [34], to explain the agglomeration phenomenon of the silicide thin film. He suggested that the agglomeration occurs through the dissociation of the silicide at the intersection of the grain boundaries and the

interface. The dissociated silicon atoms grow epitaxially on the silicon substrate, while the metal atoms migrate through the silicide grains and react with the substrate forming new silicide at the bottom of the silicide globule. There are two kinetic limitation processes we can find in this mechanism: one is the silicon epitaxy process, the other is the metal silicide formation process. Both of them require a lot of silicon dangling bonds to which either the silicon or metal atoms can easily bond to. We found in our SIMS measurement and XPS analysis that a lot of fluorine atoms were bonded to the dangling silicon atoms at the PtSi/Si interface because of the strong binding energy of Si–F bond of about 5.73 eV. This means that the silicon dangling bonds, which the agglomeration process demands, are no longer sufficiently supplied. The whole system will necessitate even more thermal energy to break the Si–F bonds making the silicon dangling bonds available for the silicide film to agglomerate. This is the proposed fluorine-buffer effect and it is the fluorine-buffer model (FB model) that explains why the fluorine incorporation at the silicide/silicon interface improves the thermal stability of the system.

In fact, work has been done by other authors dealing with the thermal stability of other silicides, especially $TiSi_2$ [35], [36]. Those results suggest several methods to prevent agglomeration. This includes lowering the process temperature and time, limiting diffusion and grain growth, or using thicker films. Other possibilities include using epitaxial single-crystal films and adding contaminants to the film which inhibit grain growth. Shenai has proposed that the thermal stability of $TiSi_2$ at elevated temperatures is diffusion-controlled. Diffusion of titanium, silicon, dopants, defects, and film contaminants play a critical role. Thus the $TiSi_2$ film formed on single-crystal silicon is thermally stable at much higher post-silicide processing temperatures compared to that formed on polycrystalline silicon under similar conditions. It is believed that the proposed FB model can be applied to other silicide/silicon systems since the high-concentration fluorine can reduce the dissociation of PtSi at grain boundaries and it can also suppress the diffusion of metal and silicon atoms.

It is necessary to clarify that the fluorine addition to the silicide/silicon system can improve the thermal stability, but cannot totally inhibit the silicide film agglomeration because this system is basically not thermodynamically stable. Once a sufficient thermal energy is supplied to the system, i.e., annealing the system at higher temperature and/or for a longer period, the polycrystalline silicide film will eventually degrade. It is worth notice that the outdiffusion of fluorine from silicon substrate, the bonding of fluorine atoms to the dangling bonds of interfacial layer, the gettering of fluorine at the damage sites of the substrate, the breaking of the Si–F bonds, the dissociation of the silicide at the intersections of grain boundaries and the interface, the epitaxial growth of dissociated silicon atoms, and silicide formation at the bottom of the silicide globule are all thermally activated processes. There will be different thermal balance conditions for different thermal treatments. Fortunately, it seems that the fluorine addition to the PtSi/Si system favors the practical thermal ranges for the integrated circuit process. To make the system thermodynamically stable, epitaxial silicide may be a very promising solution [37], [38].

The FB model can also be applied to the observation of sheet resistance of the fluorinated samples as shown in Figs. 1–5. To retard the agglomeration of the silicide film, the fluorine concentration must be increased to a certain level. As the implantation dose decreases, the FB effect decreases, and the high temperature stability degrades. Besides the implantation dose, the implantation energy also plays an important role on the FB effect. The results of low energy implantation are similar to those of low dose implantation because of insufficient fluorine incorporation into the silicon substrate. Higher implantation energy introduces more fluorine atoms into the silicon substrate; however, the fluorine projected range may be too large to be far away from the silicide/silicon interface. During annealing, the formation of an efficient FB layer competes with the degradation of the silicide film. If the amount of the fluorine atoms located near the interface is not large enough, the silicide film degrades before the embedded fluorine can pile up at the interface to form the FB layer. This is consistent with the optimum implantation condition proposed in Section II-A.

IV. CONCLUSION

In this work we studied the effect of fluorine incorporation on the thermal stability of the PtSi/Si structure. Fluorine-containing species (F^+ and BF_2^+) were implanted into the Pt/Si and the PtSi/Si structures followed by annealing in N_2 ambient from 400 to 850°C. During the annealing, the fluorine atoms in the Si substrate move toward the PtSi/Si interface and pile up there. The fluorine atoms bond to silicon atoms to form SiF_2- or SiF_3-type compound. Such a highly fluorinated layer acts as a fluorine-buffer layer to change the PtSi/Si interface energy (and/or the silicide grain boundary energy) which in turn improves the high-temperature stability of the PtSi/Si structure. In the experimental conditions of this work, the higher the implanted fluorine dose, the better the high temperature stability. The implantation energy also plays an important role. The optimum implantation energy is the energy at which the maximum fraction of the implanted fluorine ions is placed near the PtSi/Si interface in the Si substrate. Higher energy introduces more fluorine into the Si substrate but their distribution may be too far away from the PtSi/Si interface so that when the PtSi/Si structure is annealed the PtSi film may have degraded before the fluorine-buffer layer is formed. The optimum implantation energy for different Pt or PtSi thickness may be predicted by the TRIM simulation. Fluorine-implanted Schottky junction was fabricated to examine the applicability of the fluorinated scheme to the integrated

circuit process. The Schottky-barrier height and the forward ideality factor of the fluorinated junctions remain comparable to those of the typical PtSi/Si Schottky junction, but the fluorine-implanted Schottky junction is able to sustain a process temperature as high as 800°C. Although the residual defect will increase the reverse current of the fluorine-implanted Schottky junction, it will not affect the PtSi contacted n^+-p or p^+-n junction if the residual defect is confined within the heavily doped region. The FB model can also be employed to explain the superior high-temperature performance of the CoSi$_2$ and TiSi$_2$ film grown on the BF$_2^+$-implanted Si substrate as compared to those grown on the unimplanted Si substrate [39], [40]. The fluorine implantation scheme will be a valuable technique in the future for the improvement of the integrated circuit reliability.

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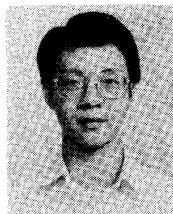
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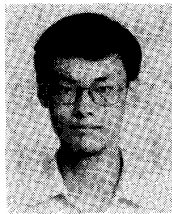
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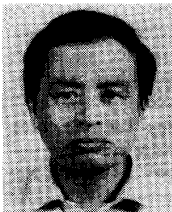
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