

Distribution and segregation of arsenic at the SiO₂/Si interface

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The segregation and pile-up of arsenic atoms at the Si/SiO₂ interface in steady state was investigated in detail by a combination of grating incidence x-ray fluorescence spectroscopy (GI-XRF) measurements, electrical measurements, etching on the nanometer scale, and measurements of the step heights by interferometry. Using GI-XRF measurements and removal of the highly doped segregation layer by a sensitive etching process it was possible to distinguish clearly between the piled-up atoms and the arsenic atoms in the bulk over a large range of implantation doses, from 3×10^{12} to 1×10^{16} cm⁻². The samples were annealed at different temperatures from 900 °C to 1200 °C for time periods long enough to make sure that the segregation reflects an equilibrium state. With additional step height measurements at line-space structures, the thickness of the layer with the piled-up arsenic and the shape of the segregation profile was determined. Electrical measurements indicated that the segregated arsenic atoms are deep donors with an electrical activity that increases eventually to full electrical activation for high sheet concentrations of the segregated atoms. The measured data can be modeled as a steady state of neutral arsenic atoms in the segregation layer with positively charged substitutional arsenic atoms and free electrons. For the highest concentration, a saturation of the sheet concentration of segregated arsenic atoms was observed that correlates with the increase in electrical activation. For the use in process simulation programs, a three-phase segregation model was adapted and calibrated. © 2008 American Institute of Physics. [DOI: 10.1063/1.2956700]

I. INTRODUCTION

Due to the continuous shrinking of the dimensions of semiconductor devices and the corresponding increase of the dopant concentration, dopant activation becomes one of the dominant problems. One of its limiting factors is the segregation and pile-up of dopants at the SiO₂/Si interface.¹⁻⁸ Experimental results have shown that the piled-up dopants are immobile^{1,3} and can be removed by a dip in hydrofluoric acid.⁴ It was also found that the segregation occurs on the silicon side of the interface⁵⁻⁷ in a region larger than 1 nm.^{6,7} Since the work of Sai-Halasz *et al.*,¹ it was believed that the segregated arsenic atoms are electrically inactive. Only recently, Frühauf⁹ suggested that 10–20% of the segregated arsenic atoms are electrically active.

Despite considerable efforts, the physical nature of this effect is still under discussion and reliable experimental data are scarce. Dabrowski *et al.*¹⁰ proposed a trapping/pairing model for arsenic at the interface guided by *ab-initio* calculations. Ravichandran and Windl¹¹ indicated on the basis of

ab-initio calculations that hydrogen should strongly enhance the possible number of trapping sites for arsenic segregation at the interface. A model without the need of trapping sites was presented by Komarov *et al.*⁸ They suggested a cluster model in which the pile-up at the interface is caused by a reduction of point defects in a few nanometers wide region at the interface. In contrast, Ferri *et al.*⁷ assumed a distribution of unspecified traps at the interface.

Even today, the reliable characterization of dopant profiles at interfaces is a major challenge, especially when the concentration changes by more than an order of magnitude on the nanometer scale. Measurements by secondary ion mass spectroscopy (SIMS), e.g., suffer from ionization probabilities that vary strongly at the interface. As for any other characterization method based on sputtering for depth profiling, an artificial broadening of the profile is caused by ion-beam mixing. Our approach to characterize the concentration profile at the interface is based on grating incidence x-ray fluorescence spectroscopy (GI-XRF) in combination with etching of the silicon and step height measurements using an interferometry profilometer. With this method it is possible to determine the sheet concentration of piled-up dopant atoms and the dopant concentration below the piled-up region on

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TABLE I. Summary of annealing conditions.

Implanted dose	Furnace annealing		RTP		
	900 °C	1000 °C	1000 °C	1100 °C	1200 °C
$3 \times 10^{12} \text{ cm}^{-2}$		30 min			
$1 \times 10^{13} \text{ cm}^{-2}$		30 min	30 min		40 s
$3 \times 10^{13} \text{ cm}^{-2}$	6 h	30 min			
$1 \times 10^{14} \text{ cm}^{-2}$	2, 6, and 10 h	10 and 30 min			
$3 \times 10^{14} \text{ cm}^{-2}$	6 h	30 min	25 and 60 min	3 and 9 min	30 and 90 s
$1 \times 10^{15} \text{ cm}^{-2}$	2 and 6 h	10 and 30 min			
$3 \times 10^{15} \text{ cm}^{-2}$			7 and 30 min	30 min	6 and 30 s
$3 \times 10^{16} \text{ cm}^{-2}$	2 and 6 h	10 and 30 min			

unpatterned wafers.¹² Determination of the arsenic profile at the interface on the nanometer scale becomes possible by combining the results of such measurements with step height measurements on suitable line-space structures.

Various samples doped with different doses and annealed at different temperatures were investigated. Results of these measurements were compared with electron energy loss spectroscopy (EELS) and Z-contrast measurements. Based on the experimental data obtained we propose a model describing the relation between the sheet concentration of segregated arsenic atoms and the concentration of substitutional atoms in the bulk nearby.

II. EXPERIMENTAL DETAILS

All experiments were performed with *p*-type 150 mm Czochralski (100)-oriented Si wafers with resistivities of 4–10 $\Omega \text{ cm}$. In addition to bare wafers for the GI-XRF measurements, some wafers with line-space patterns were used to characterize the depth distribution of the segregated arsenic atoms. The latter wafers were fabricated by spin-coating of photoresist and subsequent patterning by standard lithography.

Before the implantation of arsenic, the native oxide was removed by an HF dip to avoid oxygen knock-on. Arsenic was then implanted with an energy of 32 keV and doses from 3×10^{12} to $1 \times 10^{16} \text{ cm}^{-2}$. After the implantation, the photoresist was removed from the wafers with the line-space pattern by ashing and all wafers were cleaned with a 5:1 (vol) mixture of 96% H_2SO_4 and 30% H_2O_2 at 140 °C for 20 min.

After removal of the regrown surface oxide by an additional HF dip, a wet thermal oxide was grown at 700 °C. The standard process used resulted in 2–4 nm thick oxides on unimplanted wafers. The oxidation times required varied from 10 to 20 min. On the implanted wafers, the resulting oxide thicknesses ranged approximately from 4 to 30 nm, depending on the implantation dose and the oxidation conditions. On the wafers patterned before ion implantation, the enhanced oxide growth occurred only in the implanted areas. This lead to oxide-filled trenches in the silicon which reflected the mask pattern. After oxidation, the wafers were annealed either in a horizontal furnace in an N_2 ambient or by rapid thermal processing (RTP) in argon. For the furnace processes (900 and 1000 °C), the ramp rates were 5 K/min during ramping up and -2 K/min during cooling down. Due to the annealing, the oxide thickness increased by about 1–2

nm. The ramp rate of the RTP processes (1000–1200 °C) was 50 K/s. The annealing conditions are summarized in Table I. For several implant conditions and temperatures, two annealing times were used to make sure that the experimentally found segregation to the interface reflects a steady-state condition and is not affected by transient effects like segregation during the initial oxidation, snow-plowing during solid-phase epitaxial regrowth (SPER), or a too slow exchange between the segregated arsenic atoms and the arsenic atoms in the bulk.

The GI-XRF measurements were performed using an ATOMIKA 8300W. The excitation source was a long fine focus x-ray tube with a Mo anode operated at 50 kV and 20 mA. The fluorescence signal was measured as a function of the glancing angle. At large glancing angles, the fluorescence signal is a measure for the sheet concentration of dopant atoms in the sample, since at these angles the penetration depth of the x-ray beam becomes deep enough to excite all arsenic atoms with almost the same x-ray intensity. All simulations of the angular dependence of the fluorescence signal were based on the model of Weisbrod *et al.*¹³

In order to obtain chemical concentration profiles unambiguously, GI-XRF measurements were combined with etching of layers on the nanometer scale and measurements of the thicknesses of the layers removed. Etching of oxide layers but also of highly doped silicon layers was achieved by immersing the samples into HF. Variations of the thickness of the etched layers were achieved via the etch time and via the concentration of HF. In this respect, the method differs from the approach of Bennett *et al.*¹⁴ in which depth profiling was achieved by repeated growth and removal of a thin oxide layer. Thicker silicon layers after removal of the segregation layer were taken off in the present work by anodic oxidation and removal of the grown oxide by diluted HF.¹⁵ The electrolyte used for the anodic oxidation was 0.1 M HCl. A constant current density of 0.32 mA/cm^2 was applied for 90 s between the sample and a Pt anode, leading to the growth of thin oxides with thicknesses of a few nanometers. The oxides were removed with diluted HF (1%). This procedure was repeated in order to remove thicker layers. The anodic oxidation was performed locally with an apparatus similar to that described by Ryssel *et al.*¹⁶ The thickness of the removed silicon layer was determined by measuring the step height with a Micromap-512 interferometry profilometer

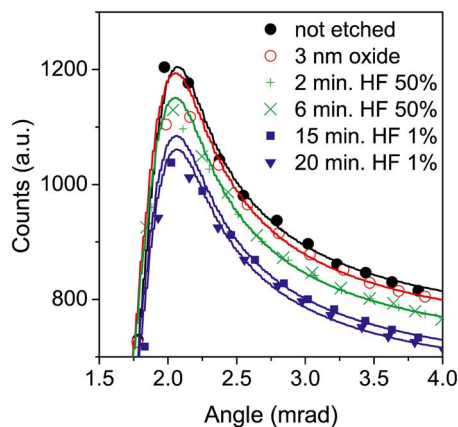


FIG. 1. (Color online) Fluorescence signal as a function of the incidence angle for a sample implanted with $1 \times 10^{16} \text{ cm}^{-2}$ and annealed for 360 min at 900 °C. The symbols refer to different etching procedures prior to the GI-XRF measurements, and the lines are the respective simulations for the final estimate of the arsenic profile.

with a 10 $\times$ objective operated in wave mode. The method is applicable for step heights exceeding about 5 nm.

The same profilometer operated in phase mode with a 50 $\times$ objective was used to measure the topography of the line-space structures which resulted from the local oxide variation. For these measurements, trenches with a width of 40 μm were used. Since the root-mean-square (rms) roughness of the internal mirror of the profilometer exceeded 1 nm, measurements had to be corrected for the distortion caused by the mirror topography. This was achieved by measuring the topography of a flat silicon wafer at five different positions. The average of these measurements is an approximation for the topography of the internal mirror and was subtracted from measurement of the line-space structure. With this setup, the measurement is applicable for step heights exceeding 0.5 nm. The accuracy of the measurements is about $\pm 0.3 \text{ nm}$.

The four-point probe (4PP) measurements were performed using a Prometrix OmniMap RS50/e. Complementary Hall-effect measurements were performed with an Accent HL5500 system after patterning the samples with a “Greek cross” van der Pauw geometry¹⁷ by photolithographic definition and etching. For arsenic, a Hall-effect scattering factor of 1 was assumed.¹⁸ The ellipsometer measurements were performed using a PLASMOS EST 2/3 at a wavelength of 632.8 nm, an incident angle of 70°, and a polarizer angle of 45°.

III. RESULTS AND DISCUSSION

A. Grating incidence total x-ray reflection combined with etching

Since we found that the angular dependence of the fluorescence signal in GI-XRF measurements is not sufficient to extract arsenic depth profiles unambiguously,¹² such measurements were combined with etching processes on the nanometer scale. Figure 1 shows as an example the results of GI-XRF measurements on a sample implanted with a dose of $1 \times 10^{16} \text{ cm}^{-2}$ arsenic and annealed in a furnace for 360 min at 900 °C. The symbols refer to the various etching proce-

dures discussed below that were applied before the GI-XRF measurements, the lines to the respective simulations. All etching procedures were performed locally on the same wafer within a circle of 2 cm diameter.

In a first step, part of the oxide was removed until a residual oxide of less than 4 nm remained. To this end, the samples were etched repeatedly in diluted HF (1%) for 1 min. The thickness of the residual oxide was determined each time by ellipsometry. Based on the etch rate of about 7 nm/min extracted from these measurements, the etch time of the last etching process was selected appropriately. The sample of Fig. 1 had an initial oxide thickness of 33.8 nm. From the measured dose loss and the thickness of the removed oxide, it can be estimated that the mean arsenic concentration in the oxide was about $1 \times 10^{20} \text{ cm}^{-3}$. All other samples investigated had thinner initial oxides, and the GI-XRF measurements did not indicate a significant dose loss associated with the partial removal of the oxide. As a consequence, it was not possible to conclusively determine arsenic concentrations in the oxide from these measurements.

The local removal of highly doped silicon layers was achieved by additional etch steps after the oxide was thinned to a residual thickness of less than 4 nm. After etching with concentrated HF (50%) for 2 min, the sheet concentration of arsenic in the sample decreased significantly. However, the same process with the etch time extended to 6 min did not lead to a further decrease in the sheet concentration of the residual arsenic. Using diluted HF (1%) instead, a considerably larger reduction was achieved after 15 min, which increased significantly for an etch time of 20 min. The thicknesses of the silicon layers removed were on the order of 1 nm. The procedure used to characterize these thicknesses is described in detail in the next section.

From the thickness of the etched layer, an etch rate of about 0.2 nm/min can be estimated for an arsenic concentration of approximately $1.4 \times 10^{21} \text{ cm}^{-3}$. In similar experiments with etching times of several hours it was found that the etch rate reduces to 0.08 nm/min for an arsenic concentration of $6 \times 10^{19} \text{ cm}^{-3}$, and to 0.03 nm/min for an arsenic concentration of $8 \times 10^{18} \text{ cm}^{-3}$.

The rate at which arsenic is removed during etching is equal to the etch rate times the arsenic concentration at the surface of the residual silicon. After the removal of the segregation layer, the arsenic removal rate drops considerably. This drop was taken as an indication that the segregation layer was removed. For samples implanted with doses of up to $1 \times 10^{15} \text{ cm}^{-2}$, this criterion is sufficiently accurate to determine the sheet concentration of segregated arsenic atoms, which is basically identical to the sheet concentration of arsenic in the removed layer. For higher doses, the arsenic removal rate does not drop sharply enough when the segregation layer has been etched off, and corrections are required as discussed in Sec. III C.

After removal of the piled-up arsenic, thicker silicon layers had to be removed to measure a significant arsenic dose loss with GI-XRF. As described above, this was achieved by anodic oxidation and removal of these oxide layers with diluted HF. Since the thickness of the layers removed exceeded 5 nm, they could be characterized directly by an interferom-

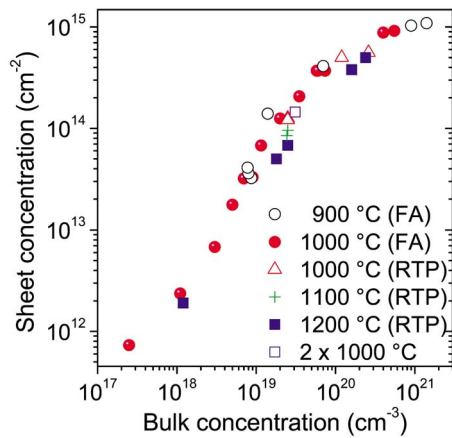


FIG. 2. (Color online) Sheet concentration of arsenic in the pile-up layer as a function of the total arsenic concentration in the bulk below the pile-up region. The values were obtained after furnace annealing (FA) or rapid thermal processing (RTP) from GI-XRF measurements combined with etching. Also shown is the data point for a sample (2×1000 °C) that was processed twice as described in Sec. III D.

etry profilometer. Figure 2 shows the sheet concentration of arsenic atoms in the pile-up layer as a function of the total arsenic concentration below the pile-up region for all samples characterized. Although the data points for all temperatures lie remarkably well on a curve, there is a slight dependence on temperature which is discussed in Sec. III H.

The segregated atoms in the pile-up region can be assumed to be in steady state with the electrically active, substitutional atoms. From the GI-XRF measurements in combination with anodic oxidation one obtains the total arsenic concentration in the bulk below the segregation layer. For the highest implanted doses, the total concentration comprises substitutional arsenic atoms and arsenic atoms in inactive complexes, presumably arsenic-vacancy complexes.¹⁹ To obtain the concentration of substitutional arsenic atoms $C_{As_s^+}$, complementary 4PP sheet resistance measurements were performed before and after the anodic oxidation. Using the procedure for the pile-up layer discussed in Sec. III G in analogy, the concentration of electrically active arsenic atoms in the removed layer was estimated from the sheet resistance measurements. The results were corroborated by Hall-effect measurements on selected samples. It was found that the active and total concentrations agreed for all but the highest dose of 1×10^{16} cm⁻². For the latter, as an example, an active concentration of 1.2×10^{20} cm⁻³ was obtained after annealing at 1000 °C for 10 min from the sheet resistance measurements while the total concentration obtained from GI-XRF was 6.5×10^{20} cm⁻³.

B. Profile of the segregated atoms

To calculate concentration values from the measurements of the sheet concentrations of arsenic atoms before and after etching steps, information about the thickness of the removed layers is required. Measurements of the topography near the edges of the locally etched areas indicated that the transition between etched and unetched regions spans several tens of micrometers. Therefore, for the thin layers in the segregation region with thicknesses on the nanometer

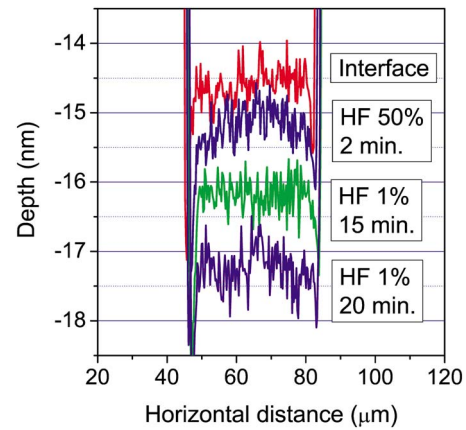


FIG. 3. (Color online) Interferometry measurements on 40 μ m wide line-space structures on a sample implanted between about 45 and 85 μ m with an arsenic dose of 1×10^{16} cm⁻² and annealed for 360 min at 900 °C. The curve denoted “interface” is the base line for the step height measurements. The lines below refer to different etching procedures prior to the interferometry measurements.

scale, a reliable characterization of the step height directly at the locally etched areas by atomic force microscopy or interferometry was not possible.

As an alternative, wafers with the arsenic implanted locally into line-space patterns were used to obtain the information required. Because of the much higher oxidation rate of the implanted regions, more silicon is consumed there so that the implanted regions appear as trenches after the removal of the grown oxide in HF. While etching in HF additionally removes silicon layers with thicknesses on the order of a nanometer at the bottom of the trenches, only negligible silicon etching is expected in the unimplanted areas.²⁰ As a consequence, the unimplanted areas can be taken as reference point for the step-height measurements while the implanted areas are expected to have a comparable etching behavior as unpatterned wafers. Within the 40 μ m wide trenches, step height measurements with a resolution of 0.3 nm were possible with the interferometry profilometer.

Figure 3 shows as an example the results of the step height measurements on a patterned wafer that was otherwise processed identically to the one for which the angular dependence of the fluorescence signal is shown in Fig. 1. As on the unpatterned wafer, localized areas were etched in 1% HF until a residual oxide of less than 4 nm remained on the implanted areas. The step height measured thereafter served as a base line for the characterization of the following etching procedures applied as described in the previous section. Etching with concentrated HF (50%) acid led to an increase of the step height by about 0.5 nm. Alternatively, etching in diluted HF (1%) for 15 or 20 min led to increases of about 1.6 and 2.8 nm, respectively.

An important point in the interpretation of the step height measurements is to assess the influence of residual oxides. Although oxide layers are transparent for the light used ($\lambda=510$ nm), some influence on interferometer measurements can be anticipated. This influence was investigated experimentally as well as by simulations. In order to investigate the influence of residual oxides experimentally, samples with line-space structures were etched repeatedly as

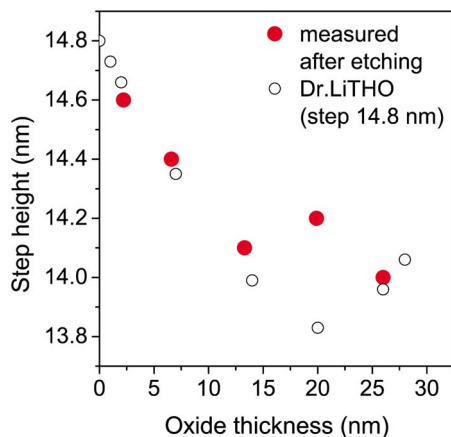


FIG. 4. (Color online) Step height as a function of the residual oxide thickness in a trench as obtained from experiments and simulations with the lithography simulator Dr. LiTHO (Ref. 21).

described in the previous section in diluted HF (1%) to remove the oxide successively. After each etching step, the depth of the trench was measured with the interferometry profilometer while the thickness of the residual oxide was measured by ellipsometry on a nearby implanted area of appropriate size. Figure 4 shows the measured step height as a function of the residual oxide thickness. To complement the experimental study, the setup of the interferometer profilometer was simulated with the lithography simulator Dr.LiTHO using the waveguide approach.²¹ In the calculations, a simplified trench structure with a sharp interface and a step height of 14.8 nm was used. For the complex refractive index $n^* = n - i \times k$, values of $1.4618 - i \times 0.0$ and $4.2326 - i \times 0.0473$ were assumed for oxide and silicon, respectively.²² The simulation results are likewise shown in Fig. 4. By combining the experimental information and the simulation results, it can be estimated that residual oxides with thicknesses below about 10 nm result in a measurement error of about 0.06 nm per nanometer of residual oxide. This would give less than 0.2 nm for a residual oxide thickness of 3 nm. We are aware that the accuracy of the ellipsometry measurements and of the simulations is limited for such thin oxides because the refractive index is not known accurately and cannot be determined independently in the ellipsometer measurements. However, by comparison of ellipsometer measurements to electrical measurements and transmission electron microscopy (TEM) measurements made on similar oxides earlier, it can be estimated that the error in the ellipsometer measurements should be less than ± 0.5 nm. Overall, it can be concluded that the effect of residual oxides on the step height measurements is within the error limits of the interferometer profilometer measurements.

A second point to be addressed is the influence of the regrowth of the native oxide on the etched surfaces. Ellipsometry measurements indicated that oxides of similar thicknesses grow within the time between etching and profilometer measurements on implanted and unimplanted surfaces so that no additional correction to the step heights measured are necessary.

Combining the step height measurements with the corresponding GI-XRF measurements of the sheet concentrations

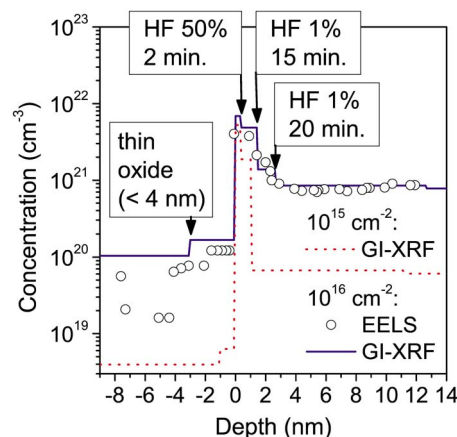


FIG. 5. (Color online) Concentration profile of arsenic at the interface determined by combining the results from the step height measurements and GI-XRF measurements for samples implanted with doses of 1×10^{15} and 1×10^{16} cm^{-2} before annealing them at 900 °C for 360 min and 1000 °C for 30 min, respectively. Also shown are the results from EELS measurements (Ref. 23) for the sample implanted with a dose of 1×10^{16} cm^{-2} and annealed for 360 min at 900 °C.

removed results in the concentration profile in Fig. 5. Only the concentration profile between -3 and 0.5 nm is not unambiguously defined since the residual oxide and a thin silicon layer are removed in the same step. The estimate given is based on a partition of the removed arsenic sheet concentration between oxide and silicon under the assumption that the arsenic concentrations in either layer is by about the same factor higher than in the respective neighboring oxide and silicon layers. From the 20 min etching step in 1% HF it can be estimated that the segregation layer extends about 2.7 nm. Figure 5 shows also the results of EELS described in Ref. 23. EELS and GI-XRF profiles agree within the error limits.

For comparison, the result for the sample implanted with 1×10^{15} cm^{-2} arsenic and annealed at 1000 °C for 30 min is also shown in Fig. 5. For these conditions, the pile-up region extends to about 1.1 nm. No significant difference in the step height between the base-line topography and after additionally etching could be measured for the sample implanted with 1×10^{14} cm^{-2} arsenic, indicating that the thickness of the pile-up region is smaller than 0.5 nm.

Previously we investigated the topography of the line-space structure with atomic force microscopy (AFM) measurements.²⁴ However, it turned out later that the removal of the native oxide before the implantation has an influence on the results, resulting in an error of about 1 nm in the position of the Si/SiO₂ interface.

C. Correction of the sheet concentration of segregated atoms

The values for the sheet concentration of arsenic in the pile-up layer shown in Fig. 2 were obtained from the dose loss associated with the removal of this layer. Based on the insufficient experimental information available, one can only speculate about the atomic configurations of the arsenic atoms in the segregation layer. The most simple assumption compatible with the model presented in Sec. III H is to assume that the total bulk concentrations of the arsenic-related

defects like substitutional arsenic or arsenic-vacancy complexes extrapolates continuously into the segregation layer. Then, in order to obtain the net sheet concentration of piled-up arsenic atoms, their contributions have to be subtracted.

For the sample implanted with a dose of $1 \times 10^{16} \text{ cm}^{-2}$ in Fig. 5, as an example, the sheet concentration within the 2.8 nm segregation layer is $1.09 \times 10^{15} \text{ cm}^{-2}$. The total concentration of arsenic in the bulk amounts to $8.5 \times 10^{20} \text{ cm}^{-3}$. This corresponds to a sheet concentration of $2.4 \times 10^{14} \text{ cm}^{-2}$, i.e., 22% of the total dose, within the segregation layer. The contribution of the extrapolated bulk concentration to the total sheet concentration of arsenic in the segregation layer decreases rapidly with the implantation dose. For the sample implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ in Fig. 5, it is already less than 2%, and insignificant for even lower doses.

For the highest doses, as mentioned in Sec. III A, one expects no sharp drop of the rate by which arsenic is removed after the segregation layer has been etched off. Extending the etching leads to a loss in the residual sheet concentration of arsenic in the sample which is approximately given by the bulk concentration of the arsenic below the segregation layer times the thickness of the additionally removed silicon layer. However, this amount is deduced again from the total sheet concentration of removed arsenic during the correction described above so that the corrected sheet concentration of segregated arsenic atoms should be only insignificantly affected by a prolonged etching.

In the remainder of this article, all references to the sheet concentration of segregated arsenic atoms refer to these corrected values $N_{\text{As seg}}$.

D. Influence of implantation and solid-phase epitaxial regrowth

Additional experiments were performed in order to clarify whether the segregation observed reflects an equilibrium property of the interface. Alternatives might be snowplowing during the SPER of the surface-near layer amorphized by the implantation or the existence of residual defects that remain near the surface after SPER.

As a first test, selected samples were characterized after implantation, after oxidation, and after the subsequent annealing. As an example, the corresponding concentration profiles for a sample implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and annealed at 1000°C for 30 min are depicted in Fig. 6. As expected, no enhanced arsenic concentration at the interface could be measured after the implantation. In agreement with tabulated data, the projected range of the as-implanted profile amounts to about 25 nm. After oxidation, the shape of the profile has not changed significantly, but $1 \times 10^{14} \text{ cm}^{-2}$ of the arsenic atoms have piled up at the interface. A pile-up during SPER was also observed by van den Berg *et al.*²⁵ After annealing at 1000°C for 30 min, the amount of piled-up dopant atoms has further increased to $4 \times 10^{14} \text{ cm}^{-2}$. Since an annealing time of 10 min at the same

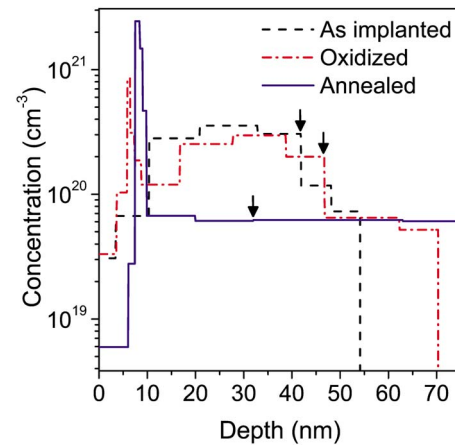


FIG. 6. (Color online) Arsenic profiles after implantation, oxidation, and annealing as determined from GI-XRF measurements and etching for a sample implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and annealed at 1000°C for 30 min. The arrows indicate the depths up to which the silicon was etched off by anodic oxidation. The deeper parts of the profiles result from reverse engineering of the GI-XRF profiles.

temperature resulted in the same sheet concentration of segregated arsenic atoms, it can be concluded that a steady state has been reached.

As a further test of whether ion implantation or SPER introduced traps near the surface, one sample was processed and characterized twice. This means that the sample was implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$, oxidized, annealed at 1000°C for 30 min, and characterized. Due to the characterization, the layer with the segregated atoms and an additional layer of about 10 nm was removed. Thereafter, the oxidation, annealing, and characterization was repeated on the same sample. The corresponding value of the sheet concentration of the piled-up arsenic has been added to Fig. 2 ($2 \times 1000^\circ\text{C}$). One difference between the first and second processing is that no SPER occurs during the second processing. In addition, if residual defects were responsible, they would have been present already after the first processing. Since no significant differences between the first and second characterization results could be found, it can be concluded that the segregation effect is an intrinsic property of the interface and not related to transient effects like SPER or residual defects resulting from processing.

E. Influence of intrinsic point defects

If the segregated arsenic atoms assumed interstitial sites or were present as complexes with vacancies, one would expect a significant change of the dose of segregated atoms under nonequilibrium conditions. To test for such effects, three wafers, implanted with a dose of $3 \times 10^{14} \text{ cm}^{-2}$, were furnace annealed at 900°C in inert and oxidizing atmospheres. The first wafer (A) was annealed in N_2 for 6 h, the second one (B) in dry O_2 for 6 h, and the third wafer (C) first in dry O_2 for 6 h followed by an anneal for 6 h in N_2 . During the oxidation steps of wafers B and C, the oxide thickness increased from 3.8 to 79 nm. Based on the work of Dunham and Plummer,²⁶ one can estimate that the oversaturation of self-interstitials was around 10 during the oxidation. Under such conditions, one should measure a significantly higher

sheet concentration of segregated arsenic in wafer B in comparison to wafers A and C if the segregation mechanism involves self-interstitials, or a significantly smaller value if the segregation mechanism involves vacancies. However, the sheet concentrations of segregated arsenic atoms (A: $1.4 \times 10^{14} \text{ cm}^{-2}$, B: $1.8 \times 10^{14} \text{ cm}^{-2}$, C: $1.8 \times 10^{14} \text{ cm}^{-2}$) are very similar, and simulations indicated that the bulk concentrations should be within a factor of 2. Although the experiments are not fully conclusive, it can be said at least that they brought no clear evidence that the segregated arsenic atoms were on interstitial sites or in complexes with vacancies.

F. Influence of hydrogen

Previously, Ravichandran and Windl¹¹ concluded from their *ab-initio* calculations that hydrogen would reduce the formation energy of the segregated arsenic atoms. In consequence, the sheet concentration of segregated arsenic atoms should increase in a hydrogen-containing atmosphere. In order to test this hypothesis, two samples implanted with $3 \times 10^{14} \text{ cm}^{-2}$ arsenic were oxidized and annealed in different atmospheres at 1000 °C for 10 min by RTP. One sample was annealed in a nitrogen atmosphere, and the other in a mixture of 30% hydrogen and 70% argon. The sheet concentrations of piled-up arsenic and the concentrations below the piled-up region were determined by GI-XRF and etching as described above. Since both samples had identical values of $1.2 \times 10^{14} \text{ cm}^{-2}$ for the sheet concentration of segregated arsenic at the interface and of $2.9 \times 10^{19} \text{ cm}^{-3}$ for the concentration of arsenic below the interface, it can be concluded that the presence of hydrogen during annealing has at most a secondary effect on the segregation behavior of arsenic.

G. Electrical activity of the piled-up atoms

Four-point probe and Hall-effect measurements were performed on selected samples annealed at 1000 °C for 10 or 30 min before and after the removal of the segregation layer to investigate the question whether the segregated arsenic atoms are electrically neutral, as suggested by Sai-Halasz *et al.*,¹ or partially activated as suggested recently by Frühauf.⁹

An important aspect of the following discussions is the conversion between sheet concentrations and mean concentrations within the segregation layer. This requires the thickness of the segregation layer. Unfortunately, as discussed in Sec. III B and indicated in Fig. 7, only for the implantation dose of $1 \times 10^{15} \text{ cm}^{-2}$ is a direct thickness determination available for an anneal at 1000 °C. From the closeness of the sheet concentrations after implantation with a dose of $1 \times 10^{16} \text{ cm}^{-2}$ and annealing at 900 °C for 360 min or at 1000 °C for 10 or 30 min, we assume that the segregation layer has a similar thickness after either of the annealings. From the concentration profile in the segregation layer shown in Fig. 5 and the total segregated dose, an effective thickness of 1.8 nm is estimated. For an implantation dose of $1 \times 10^{14} \text{ cm}^{-2}$, it is only known that the thickness of the segregation layer is smaller than 0.5 nm. The dashed line in Fig. 7 is an empirical power-law fit in the form

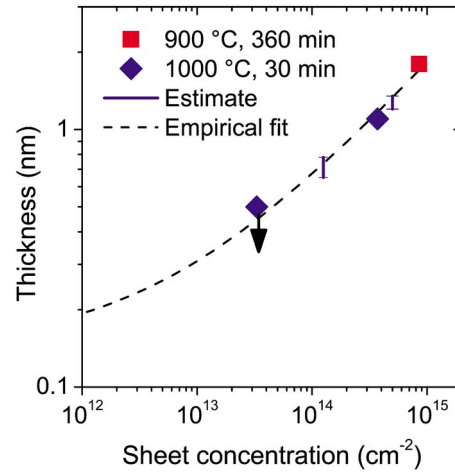


FIG. 7. (Color online) Effective thickness of the segregation layer as a function of the sheet concentration of segregated arsenic atoms. The arrow for the sheet concentration of $3 \times 10^{13} \text{ cm}^{-2}$ indicates that the layer thickness is smaller than 0.5 nm. The dashed line is an empirical power-law fit based on a minimum layer thickness of a monolayer of 0.14 nm.

$$\Delta t = 0.14 \text{ nm} + 1.69 \text{ nm} \sqrt{N_{\text{As,seg}} / 10^{15} \text{ cm}^{-2}} \quad (1)$$

for the effective thickness Δt of the segregation layer as a function of the sheet concentration of segregated arsenic atoms $N_{\text{As,seg}}$. It is based on the assumption that the layer thickness should not fall below the thickness of a monolayer (0.14 nm). It should be noted also that the usage of a similar fit based on the assumption that the thickness would not fall below two monolayers has only insignificant effects on the conclusions.

As a first characteristic of the removed segregation layer, its sheet conductance is shown in Fig. 8. It corresponds to the difference

$$\Delta \sigma_s = \frac{1}{R_s^0} - \frac{1}{R_s^{\text{bulk}}} \quad (2)$$

between the inverse of the sheet resistance R_s^0 of an unetched sample and the inverse of the sheet resistance R_s^{bulk} of the

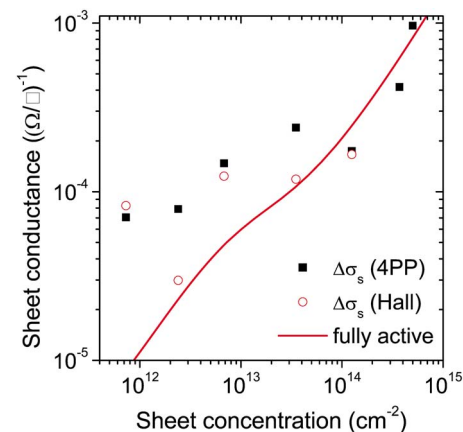


FIG. 8. (Color online) Sheet conductance of the segregation layer as a function of the sheet concentration of segregated arsenic atoms. The experimental data were obtained from four-point-probe measurements (4PP) and Hall-effect measurements (Hall). Also shown is a simulation assuming that all segregated atoms are activated.

TABLE II. Summary of electrical measurements on samples annealed at 1000 °C before (b.r.) and after (a.r.) removal of the segregation layer. An asterisk indicates that the value was estimated.

Implantation dose (cm ⁻²)	3 × 10 ¹⁴	1 × 10 ¹⁵	3 × 10 ¹⁵	1 × 10 ¹⁶	1 × 10 ¹⁶
Annealing time (min)	30	30	30	10	30
R_s^0 (4PP, b.r.) (Ω/□)	352 ± 19	107 ± 6	30.1 ± 1	26.6 ± 1	22 ± 1
R_s^0 (Hall, b.r.) (Ω/□)	353 ± 18	—	—	—	22 ± 1
μ_{Hall}^0 (b.r.) (cm ² /Vs)	91 ± 19	—	—	—	46 ± 7
R_s^{bulk} (4PP, a.r.) (Ω/□)	375 ± 19	112 ± 6	31.0 ± 1	26.4 ± 1	22 ± 1
R_s^{bulk} (Hall, a.r.) (Ω/□)	375 ± 19	113 ± 6	—	27 ± 1	22 ± 1
$\mu_{\text{Hall}}^{\text{bulk}}$ (a.r.) (cm ² /Vs)	85 ± 13	63 ± 3	—	48 ± 3	44 ± 7
Segregation layer:					
C_{As^+} (cm ⁻³)	2 × 10 ¹⁹	6.7 × 10 ¹⁹	1.2 × 10 ²⁰	1.6 × 10 ^{20*}	1.6 × 10 ^{20*}
$N_{\text{As}^{\text{seg}}}$ (cm ⁻²)	1.25 × 10 ¹⁴	3.7 × 10 ¹⁴	5 × 10 ¹⁴	9.2 × 10 ¹⁴	8.8 × 10 ¹⁴
Δt (nm)	0.65–0.78*	1.1	1.2–1.35*	1.8*	1.8*
Calculated characteristics:					
$R_s^{\text{bulk}}(n=C_{\text{As}^+})$ (Ω/□)	363–364	109	30.3	26.8	22.2
R_s^{bulk} (all active) (Ω/□)	395–397	116	30.9	27.8	22.8
$N_{\text{As}^{\text{seg}}}$ (cm ⁻²)	(1.05–1.23) × 10 ¹³	1.63 × 10 ¹⁴	(5.4–5.5) × 10 ¹⁴	—	—
C_{As^+} (cm ⁻³)	(1.5–2.1) × 10 ²⁰	1.6 × 10 ²¹	(4.1–4.7) × 10 ²¹	—	—
Mobility (cm ² /Vs)	48–54	12.8	9.9–10.1	—	—
Electrical activity	8.4%–9.8%	33%	100%	—	—

same sample with the segregation layer removed. Also shown is an estimate of the sheet conductance

$$\Delta\sigma_s = q \times n \times \mu(C_{\text{As}^+}) \times \Delta t, \quad (3)$$

expected for a segregation layer under the assumption that the layer is fully activated. Since the electron concentration n exceeds the intrinsic concentrations in our experiments by orders of magnitude, it corresponds to the concentration of active arsenic atoms C_{As^+} which, in turn, is given by the sum of substitutional arsenic atoms C_{As^+} and segregated arsenic atoms $N_{\text{As}^{\text{seg}}}/\Delta t$. The mobility model of Masetti *et al.*²⁷ was used to describe the concentration dependence of the mobility $\mu(C_{\text{As}^+})$, and q stands for the elementary charge.

A comparison between the experimental data and the estimated sheet conduction of a fully activated segregation layer indicates an increasing discrepancy with decreasing sheet concentrations of segregated arsenic atoms. While the calculated estimate decreases continuously, the experimental data decrease only down to a limiting value σ_s^0 of about $7 \times 10^{-5} \text{ (}\Omega/\square\text{)}^{-1}$. This can be explained by a conductive layer, such as surface states, that forms at the interface independently of the arsenic segregation. An additional point that makes a quantitative analysis problematic for the small and medium sheet concentrations is the apparent discrepancies between the 4PP and Hall-effect data for the samples with segregated sheet concentrations of 2.4×10^{12} and $3.5 \times 10^{13} \text{ cm}^{-2}$. For sheet concentrations of segregated atoms exceeding $1 \times 10^{14} \text{ cm}^{-2}$, for which the simple analysis indicates in part an incomplete ionization, a more careful analysis seems possible. The details of the measurements are listed in Table II. Whenever both are available, there is an excellent agreement between the 4PP sheet resistance measurements performed in Erlangen and the sheet resistance

values that resulted from the Hall measurements (Hall) in Toulouse. This increases the credibility of the conclusions to be drawn later from the differences which would otherwise be within the nominal precision and accuracy of the measurement equipment.

Extending Eqs. (2) and (3) by a segregation-independent “parallel” layer with a sheet conduction of $\sigma_s^0 = 7 \times 10^{-5} \text{ (}\Omega/\square\text{)}^{-1}$, the removal of the segregation layer with a thickness Δt , a mean electron concentration $n = C_{\text{As}^+}$, and a mean mobility $\mu(C_{\text{As}^+})$ leads to an increase of the sheet resistance from R_s^0 to

$$R_s^{\text{bulk}} = \frac{1}{1/R_s^0 - q \times C_{\text{As}^+} \times \mu(C_{\text{As}^+}) \times \Delta t - \sigma_s^0}. \quad (4)$$

Because of the dominant impurity scattering, the mobility is assumed to depend primarily on the concentration C_{As^+} of the electrically active arsenic atoms in the layer. Hall-effect measurements allow, in principle, to determine the mobility. However, because of the extremely thin layers removed, no reliable determination was possible for our samples. As an alternative, the mobility model of Masetti *et al.*²⁷ was used to estimate the mobility for a certain concentration of electrically active arsenic atoms.

For each of the implant doses, several characteristic data were calculated: the expected value of the bulk sheet resistance under the assumption that the segregated atoms are electrically inactive so that the only active atoms in the segregation layer are the substitutional atoms ($n = C_{\text{As}^+}$), the expected value of the bulk sheet resistance under the assumption that all segregated atoms are electrically active in addition (all active), as well as the sheet concentration of electrically active segregated atoms $N_{\text{As}^{\text{seg}}}$ and the respective

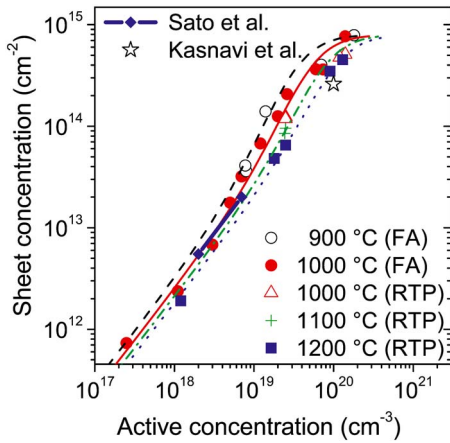


FIG. 9. (Color online) Sheet concentration of piled-up arsenic as a function of the arsenic concentration below the pile-up region. The lines were calculated with the model presented in Sec. III H.

mobility to explain the increase from R_s^0 to R_s^{bulk} within the mobility model consistently. The electrical activity corresponds to the ratio of the sheet concentrations of the electrically active segregated arsenic atoms and the total arsenic atoms. Ranges in sheet concentration, mobility, or electrical activation result from the estimated ranges of the effective thickness of the segregation layer.

For the implantation dose of $1 \times 10^{16} \text{ cm}^{-2}$ annealed for 10 min, a rather unexpected decrease in sheet resistance after removal of the segregation layer was observed. Similarly unexpectedly, for the sample annealed for 30 min, four-point-probe measurements and Hall measurements agreed in equal values before and after removal of the sheet resistance. The analysis of the expected sheet resistances for active and inactive segregated atoms indicates that the measured changes are within the precision of the measurements so that no reliable conclusion can be drawn from the experiments with the dose of $1 \times 10^{16} \text{ cm}^{-2}$.

For the implantation doses from 3×10^{14} to $3 \times 10^{15} \text{ cm}^{-2}$, significant increases in sheet resistance were observed upon removal of the segregation layer. In all these cases, the expected increase in sheet resistance for inactive segregated atoms is considerably smaller than the measured increase. There is a trend toward a higher electrical activation with increasing implantation dose up to complete ionization for the implantation dose of $3 \times 10^{15} \text{ cm}^{-2}$. The results agree excellently with the work of Frühauf,⁹ who found an electrical activation of 10–20% for a corrected segregated sheet concentration (see Sec. III C) of $2.4 \times 10^{14} \text{ cm}^{-2}$ estimated from his Fig. 1.10c. The full electrical activation of the piled-up arsenic atoms above a certain sheet concentration with electron concentrations around $4 \times 10^{21} \text{ cm}^{-3}$, if confirmed, could have important implications for the formation of low-resistivity contacts on *n*-type silicon.

H. Modeling the pile-up of arsenic

The relationship between the corrected sheet concentration of piled-up arsenic atoms and the background concentration of substitutional, active arsenic atoms is shown in Fig. 9. It is approximately linear below a background concentra-

tion of about $5 \times 10^{18} \text{ cm}^{-3}$. For higher concentrations, until a sheet concentration of segregated arsenic atoms of about $2 \times 10^{14} \text{ cm}^{-2}$ is reached, the increase is approximately quadratic. For even higher background concentrations, a reduction of the slope and finally a saturation become apparent.

Experimental data summarized previously by Dabrowski *et al.*²⁸ for phosphorus showed a similar linear/quadratic behavior, which was explained by trapping of dopants and the formation of dopant pairs at the interface. At least for our data, we suggest a simpler mechanism based on the assumption that the segregated arsenic atoms are deep donors.

The electrical data summarized in Sec. III G allow a reasonable assumption that the majority of the segregated atoms are electrically neutral for substitutional arsenic concentrations up to about $3 \times 10^{20} \text{ cm}^{-3}$. These defects As_{seg}^0 can be thought to result from the reaction



between positively charged substitutional arsenic atoms As_s^+ and free electrons e^- . In steady state, the concentration of segregated arsenic atoms in the interface layer

$$C_{\text{As}_{\text{seg}}} \approx C_{\text{As}_{\text{seg}}}^0 \propto C_{\text{As}_s^+} \times n \quad (6)$$

is then approximately equal to the concentration of neutral segregated arsenic atoms, which, in turn, is proportional to the product of the substitutional concentration of arsenic atoms $C_{\text{As}_s^+}$ and the electron concentration n . The latter can be approximately calculated from the assumption of charge neutrality and is then given by

$$n = C_{\text{As}_s^+}/2 + \sqrt{(C_{\text{As}_s^+}/2)^2 + n_i^2}. \quad (7)$$

For substitutional arsenic concentrations below n_i , the electron concentration equals approximately $n \approx n_i$ and the concentration of segregated atoms (6) increases linearly with the substitutional arsenic concentration. When the substitutional arsenic concentration exceeds the intrinsic carrier concentration significantly, the electron concentration approaches the concentration of substitutional atoms $n \approx C_{\text{As}_s^+}$ so that the concentration of segregated atoms (6) increases quadratically with the substitutional arsenic concentration.

At substitutional arsenic concentrations, for which the segregated sheet concentration exceeds a level of about $2 \times 10^{14} \text{ cm}^{-2}$, a reduction of the slope and finally a saturation is apparent in Fig. 9. This saturation correlates for the 1000 °C data discussed in Sec. III G with the increase of the electrical activity of the segregated arsenic atoms from low to full electrical activity. A plausible explanation for the saturation could be that positively charged segregated arsenic atoms are energetically less favorable than neutral ones. It then remains to identify the reason for the increase in electrical activation. For shallow donors such an effect is well known. As outlined in the recent review of Altermatt *et al.*,²⁹ it is caused by the merging of the impurity band of the interacting donor states with the conduction band. For the shallow substitutional atoms, the transition occurs for a concentration around $1 \times 10^{19} \text{ cm}^{-3}$. For a deep donor with its

tightly bound electron, it is reasonable to assume that the transition would occur at a considerably higher concentration.

For an implementation into existing process simulation programs, the three-phase model suggested first by Lau *et al.*³⁰ and Orłowski³¹ can be adapted. It considers the trapping of atoms to and their emission from an interface layer with a maximum sheet concentration $N_{As}^{\max}$ of sites that can be occupied. This maximum sheet concentration can be used to pragmatically model the saturation which we otherwise ascribe to the electrical activation of the segregated arsenic atoms. In analogy to Eq. (5), but now with the total area concentration of segregated atoms $N_{As,seg}$ replacing the area concentration $N_{As,seg}^0$ of neutral segregated atoms, the relation between the species involved can be described in steady state by

$$t \times \exp(-E_t/k_B T) \times C_{As^+} \times n/n_i \times (N_{As}^{\max} - N_{As,seg}) = e \times \exp(-E_e/k_B T) \times N_{As,seg}. \quad (8)$$

Therein, $t \times \exp(-E_t/k_B T)$ and $e \times \exp(-E_e/k_B T)$ are thermally activated rates governing the trapping to and emission from the pile-up region. From Eq. (8), the sheet concentration of segregated atoms can be expressed in the form

$$N_{As,seg} = \frac{N_{As}^{\max} \times C_{As^+} \times n/n_i}{C_{As^+} \times n/n_i + e/t \times \exp[-(E_t - E_e)/k_B T]}. \quad (9)$$

With the electron concentration given by Eq. (7), the linear and quadratic increase follows directly as long as the denominator in Eq. (9) is dominated by the second term which is only a function of temperature. For the highest concentrations of substitutional arsenic, the denominator in Eq. (9) will be dominated by the first term and the sheet concentration of segregated arsenic atoms approaches its maximum value.

The lines shown in Fig. 9 were obtained from Eq. (9) with the parameters $N_{As}^{\max} = 8 \times 10^{14} \text{ cm}^{-2}$, $e/t = 3.2 \times 10^{21} \text{ cm}^{-3}$, and $E_t - E_e = 0.25 \text{ eV}$ determined from the experiments, and n_i taken from Morin and Maita.³²

Also shown in Fig. 9 are the previous experimental results of Sato *et al.*⁴ and Kasnavi *et al.*⁵ In the work of Sato *et al.* the arsenic atoms, segregated to the surface during an annealing process at 900 °C, were removed by soaking the respective samples in HF. The sheet concentration of arsenic in a particular sample was obtained from sheet resistance measurements after subjecting it to a high-temperature long-time drive-in during which the arsenic atoms were largely activated. Since the concentration of substitutional arsenic atoms could not be measured directly, the respective numbers were estimated from simulations using a simple analytical solution for postimplantation diffusion profiles. Considering the uncertainties in the analysis, the agreement with our experimental results is excellent. Soaking in HF was also used in the work of Kasnavi *et al.*⁵ to remove the segregation layer after annealing at 1050 °C. The dose loss associated was obtained from SIMS analyses of etched and unetched samples. The respective value is about a factor of 2 smaller than an estimate based on our experiments. Although this is

still a good agreement, it can possibly be explained by a too small process time in the work of Kasnavi *et al.* to guarantee that steady state between segregated and substitutional arsenic atoms was already established.

The last work to be discussed in this context is that of Oh and Ward.³³ Since it is not clear whether solid solubility in their work refers to the concentration of electrically active or total concentration, which differ for arsenic by roughly 1 order of magnitude,^{34,35} an evaluation of the otherwise parameterized model is problematic. On the other hand, it is clear that the total trap density $\sigma_{\max} = 2 \times 10^{14} \text{ cm}^{-2}$ in their work is by a factor of 4 smaller than what would be consistent with our analysis.

IV. CONCLUSION

The segregation of arsenic at the interface between silicon and silicon dioxide was investigated by GI-XRF measurements in combination with etching and electrical measurements. Information about the thickness of the etched silicon layers was obtained from interferometry measurements on line-space structures. It was found that the method is suitable to resolve the profile of the arsenic atoms with a resolution on the order of a nanometer.

The thickness of the pile-up region was found to depend on the sheet concentration of arsenic segregated at the interface, which itself is a monotonically increasing function of the substitutional arsenic concentration. After annealing at 900 °C for 360 min, the pile-up extended to a depth of about 2.7 nm for an implant dose of $1 \times 10^{16} \text{ cm}^{-2}$, and to about 1.1 nm in a sample implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and annealed at 1000 °C for 30 min. For an arsenic dose of $1 \times 10^{14} \text{ cm}^{-2}$ annealed at 1000 °C for 30 min, the segregation layer was estimated to be thinner than 0.5 nm.

By varying the annealing time, it was verified that the pile-up at the interface reflects a steady-state condition. Additional experiments were carried out to confirm that the pile-up was an intrinsic property of the interface. Hydrogen was not found to affect the pile-up under the conditions studied. Similarly, an oversaturation of self-interstitials by 1 order of magnitude induced by an oxidation process was not found to have a significant influence.

With GI-XRF it was possible to investigate a large range of implantation doses and to determine the sheet concentration of piled-up arsenic atoms as well as the total arsenic concentration below the pile-up region. To obtain the concentration of electrically active arsenic atoms, the GI-XRF measurements were complemented by electrical measurements. The experimental data indicated that the sheet concentration of segregated atoms increases at first linearly with the concentration of electrically active arsenic atoms below the pile-up region. For concentrations above the intrinsic charge carrier concentration, the dependence becomes quadratic and finally, for the highest arsenic concentrations, a saturation was observed. This saturation was found to be consistent with an increase in the electrical activation of the segregated arsenic atoms which was tentatively explained by

assuming that the segregated arsenic atoms are deep donors and that their impurity band merges for the highest concentrations with the conduction band.

To explain the linear/quadratic relationship, it was assumed that the piled-up arsenic atoms are, for our long annealing times, in steady state with the electrically active, substitutional arsenic atoms and the free electrons. Within this model, the observed linear and quadratic relationships reflect the dependence of the electron concentration on the concentration of electrically active atoms. The saturation was explained tentatively by the activation of the segregated atoms which is expected to make the segregated atoms energetically unfavorable. The model was parameterized for the three-phase model available in commercially available process simulation programs and is able to predict the segregation of arsenic to the silicon/silicon dioxide interface in steady state within a wide range of experimental conditions.

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