Structural and Electrical Changes in Polycrystalline Silicon Thin Films That Are Heavily In Situ Boron-Doped and Thermally Oxidized with Dry Oxygen**

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In this paper, we investigate some particular aspects of changes in the thermal behavior polycrystalline silicon films deposited by low pressure chemical vapor deposition (LPCVD). The results will concern changes in both the structural and electrical properties of heavily (2 x 10^{20} cm^{-3}) in situ boron-doped thin films before and after thermal-oxidation treatments. Secondary ion mass spectrometry (SIMS), transmission electron microscopy (TEM), and four-point-probe resistivity (FPPR) measurements were carried out on submicrometer layers (= 300 nm) deposited at two interesting temperatures T\text{O}_2 = 520 °C and T\text{O}_2 = 605 °C. The thermal-oxidation experiments are performed under dry O_2 at three oxidation temperatures T\text{ox} = 840, 945, and 1050 °C for several durations. Remarkable changes in the behavior of doping profile, grain growth, and electrical conductivity were observed. While the kinetic-oxidation analyses reveal the presence of a "differential oxidation rate (DOR)" between the two layers, recrystallization effects show a similar behavior, called "differential growth mechanism (DGM)", between the same layers. These observations seem to be characteristic of the in situ heavily boron-doped films, consistent with results of a previous study.

Keywords: LPCVD Si layers, Oxidation, Boron, SIMS, Diffusion

1. Introduction

Polycrystalline silicon films obtained by low pressure chemical vapor deposition (LPCVD) have been extensively investigated over the last three decades.[1-18] Considerable interest has been generated with the introduction of this material in VLSI processing materials. This opportunity has provided an important field of application in the microelectronics industry. The most attractive application is the manufacture of the polysilicon bipolar integrated transistor, which has a shallow emitter junction and that the final doping profile obtained is generally flat over the whole film depth, and there is no need for a post-doping anneal, often necessary when the implantation mode is used.

In this study, we present some results of qualitative and quantitative investigations of structural and electrical properties at high levels of boron-doping concentrations, and the evolution of some specific factors of these layers, such as grain boundary structures, defects related to impurity segregation, impurity clustering, and vacancy complex formation that occurs when the solid solubility limit is reached.

2. Experimental Methods

2.1. Sample Preparation

Thin polysilicon films were supplied by Motorola laboratories of Toulouse (France). They were obtained in an isothermal hot-wall LPCVD reactor, from decomposition of...
silane (SiH₄) with a controlled-rate reaction of a SiH₄–3 % BCl₃–N₂ gas mixture. The gas flow was set according to the following proportions: 0.1 L/min of SiH₄ against 0.09 L/min of 3 % BCl₃–N₂, in order to maintain a constant boron atom supply in the chemical reaction of the deposition process. This was also to ensure appropriate interaction with the growth rate during the cycle of film formation. The film deposition pressure was set at 400 mtorr, and the films were simultaneously doped in situ with boron at the same pressure. At the flow rate of BCl₃ employed, the final boron content is around 5 %.

The film thicknesses measured by a mechanical Talystep profilometer (Taylor-Hobson 1661 with ±5 nm accuracy) were found to be approximately close to 290 nm for films deposited at temperature Tₓ = 520 °C and 280 nm for those deposited at Tₓ = 605 °C. Previous studies have shown that the first deposits correspond to a heterogeneous polycrystalline structure, with large grain size (dG = 30 to 40 nm) due to the high proportion of crystalline silicon (c-Si) nuclei. The polycrystalline layers were deposited on bare or oxidized substrates of lightly doped (resistivity q ~ 10 Ω cm) monocrystalline (111) silicon. The thickness of the thermal oxide of the oxidized substrates, labeled (poly/SiO₂), was 100 nm. In contrast, the bare substrates, labeled (poly/c-Si), contained only a native oxide layer of 1–1.5 nm unavoidably present at the poly/mono-Si interface.

After deposition steps, the polycrystalline silicon films are subjected to thermal-oxidation treatments under a dry oxygen flow of 1.8 L/min at atmospheric pressure (pure O₂ containing less than 5 ppm of water vapor). Then, the oxide layers grown on the polycrystalline films were removed with an appropriate solution of hydrofluoric acid prior to electrical and structural characterization.

A systematic study of the oxidation-kinetics of these films has already been published. In this work, we present the second half of results obtained with the remaining poly-silicon layers, which were used for resistivity, transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS) investigations.

2.2. Measurement Techniques

2.2.1. Four-Point Probe Resistivity (FPPR) Technique

The sheet resistivity was measured using a classical probe set having four probe arranged in a square (LAAS Laboratory in Toulouse, France). The average resistivity before and after the thermal-oxidation process was calculated from repeated measurements performed over the whole surface of the samples. Particular care was taken to avoid the probe's points penetrating the surface of the sample. The details of this experimental technique have been described previously, and particularly in the work reported by Laplume.

2.2.2. SIMS Technique

SIMS has been extensively used in measuring impurity diffusion profiles and is suitable for studying many elements such as boron, phosphorus, and arsenic. The main advantage is the high sensitivity, with a concentration detection limit of 1 × 10⁻¹⁵ cm⁻³, and the capability of measuring total dopant profiles in less than the 100 nm range. But, it needs standards.

In-depth boron concentration profiles were obtained using CAMECA IM 5300 SIMS microanalyzer equipment belonging to the INSA Laboratory in Toulouse (France). The primary ion bombardment beam was a net 10 keV O₂⁺ of 25 µm diameter with an oriented incident angle of 30° from the sample normal. This beam is distributed over an area of 250 × 250 µm². Under ion impacts, the film surface will be sputtered, and the resulting secondary ions are then collected through a circular area of 70 µm diameter and focused on a double magnetic prism, which ensures their mass filtration. Typically, these sputtered ions are detected with appropriate positive secondary ion detection equipment to optimize boron sensitivity. At the output, all sidewall and redeposition contributions are minimized. The depth profile is calibrated against as-grown polysilicon thickness, and the boron concentration profile is calibrated against concentration in reference samples. Under these experimental conditions (i.e., taking into account the repeatability error from run to run, the depth scale error in estimating the crater depth, the variation of the erosion rate as a function of depth layer, and the matrix effect) we can conclude that the measured values are within 10 % of the nominal fluence. As mentioned above, the lowest limit of boron concentration that can be measured is of the order of 1 × 10⁻¹⁵ cm⁻³.

2.2.3. TEM Observations

Plan-views of TEM observations were obtained from samples chemically etched from the bottom to the top after stripping off the grown oxide SiO₂. Then, the remaining polysilicon layer was observed using a Temscan microscope with an accelerating energy of 200 keV, in the LMSM Laboratory of University of Paul Sabatier in Toulouse (France). More details of this experimental technique have been described elsewhere.
3. Results

3.1. General Aspects of the SIMS Profiles

In this section, a description of the major features of the results obtained directly from SIMS profiles will be presented.

Figure 1a illustrates the SIMS profiles, before the oxidation process, of the films deposited according to the experimental procedure given in Section 2. The dopant concentration appears to be homogeneous and remains constant over the whole thickness of the film. The average concentration value seems to be constant and equal to \(2.2 \times 10^{19}\) cm\(^{-3}\). Obviously, it shows no evident dependence of dopant concentration profile on the film depth \(W\), and the deposition temperature \(T_d\). However, this behavior is not observed on the in situ phosphorus-doped films, which appear totally inhomogeneous (Fig. 1b).\[17\]

![SIMS Profiles of as-grown polysilicon films deposited on oxidized monocrystalline silicon substrates (100 nm) at two deposition temperatures \(T_d\).](image1)

Fig. 1. SIMS profiles of as-grown polysilicon films deposited on bare (280 nm polyc-Si) or oxidized (290 nm poly/SiO\(_2\)) monocrystalline silicon substrates (100 nm) at two deposition temperatures \(T_d\). a) B-LPCVD in situ boron-doped films. b) P-LPCVD in situ phosphorus-doped films.

Figures 2–4 show the boron concentration within the film and the underlying single-crystal silicon substrates, after the oxidation processes, for films deposited at \(T_d = 605\) °C and \(T_d = 520\) °C. For the higher \(T_d\), the concentration is always less than in films deposited at the lower \(T_d\). This difference tends to decrease when \(T_{ox}\) increases. Beyond \(T_{ox} = 1050\) °C, this phenomenon becomes inverted, except for films deposited directly on bare substrates (polyc-Si), where there is no oxide barrier to prevent the diffusion process. Indeed, if we consider the relative difference between SIMS profiles of layers deposited at \(T_d = 605\) °C and those deposited at \(T_d = 520\) °C as a function of the oxidation temperature \(T_{ox}\), the variation of this relative difference may be approximately considered, at first sight, to be similar to another phenomenon, called “differential oxidation rate (DOR)”, pointed out during kinetic oxidation analyses of these same layers.\[19\] This last phenomenon is seen to increase with \(T_{ox}\) until \(T_{ox}\) reaches a temperature of 1000 °C, and then decrease. In a recent work, Tompkins et al.\[29\] pointed out the presence of a heating-up phenomenon and saturation effect occurring as the limiting step of crystallization. Thus, according to these observations, we believe that the film microstructure plays an important role in the interaction of the dopant with the grains and grain boundaries and therefore in dopant diffusion behavior.

The thinner native oxide of (polyc-Si) samples is always broken up during heat treatments even at the lowest \(T_{ox}\) (Figs. 2b, 3b, and 4b). But the thicker thermal oxide of the (polyc/SiO\(_2\)) samples holds up well at the beginning and only begins to be broken up if \(t_{ox}\) is sufficiently long.

![SIMS Profiles of in situ boron-doped (B-LPCVD) polysilicon films deposited on an oxidized (290 nm poly/SiO\(_2\)) monocrystalline silicon substrate at \(T_d = 520\) °C or 605 °C and oxidized at \(T_{ox} = 840\) °C under dry oxygen for \(t_{ox} = 61\) min.](image2)

a) B-LPCVD/SiO\(_2\), \(T_d = 520\) °C, \(t_{ox} = 61\) min.

b) B-LPCVD/c-Si, \(T_d = 520\) °C, \(t_{ox} = 61\) min.

Fig. 2. a) SIMS profiles of in situ boron-doped (B-LPCVD) polysilicon films deposited on an oxidized (290 nm poly/SiO\(_2\)) monocrystalline silicon substrate at \(T_d\) = 520 °C or 605 °C and oxidized at \(T_{ox} = 840\) °C under dry oxygen for \(t_{ox} = 61\) min. b) As for (a), except with a bare (280 nm poly/c-Si) monocrystalline silicon substrate.
4. The boron SIMS profile, obtained from layers deposited at temperatures
(Td) = 520 °C or 605 °C and oxidized at (Tox) = 945 °C under dry oxygen for (tox) = 12 min 45 s. b) As for (a), except with a bare (280 nm poly/c-Si) monocrystalline silicon substrate.

(Figs. 2a, 3a, and 4a). After rupture, we can see a classical characteristic Gaussian-like profile in the underlying single-crystal silicon. This behavior is also observed in the case of boron-implanted films.[6]

The initial distribution of dopant present in the films evolves with the thermal-oxidation process. In almost all cases, we can see a boron concentration pile-up near both the polysilicon film surface and the film/oxide-substrate interface, while, in the intermediate region, the boron concentration decreases. This new redistribution of dopant may be attributed to the combination of both the thermal-activation process and the oxide natural-attraction effect. Presumably, these effects are responsible for the driving diffusion phenomenon of the dopant from the bulk to the two interface sides.

The oxidation temperature effect is shown in Figures 2–4. The boron SIMS profile, obtained from layers deposited at (Td) = 520 °C and oxidized at (Tox) = 840 °C (see Fig. 2) for (t tox) = 61 min, presents an accumulation peak concentration of around 3 × 10^{20} cm^{-3}, occurring near the polysilicon surface over a depth of 10–80 nm. This is followed by an almost-flat region of (2–2.5) × 10^{20} cm^{-3} for a thickness of 100 nm, and finally by a peak concentration of around 3.5 × 10^{20} cm^{-3} at the film/oxide-substrate interface. For layers deposited at (Td) = 605 °C, the profile is similar to that observed for layers deposited at (Td) = 520 °C. Concentration values were found to be (2–2.5) × 10^{20} cm^{-3}, 1 × 10^{20} cm^{-3}, and (1.5–2.5) × 10^{20} cm^{-3} for the surface, bulk, and interface regions, respectively.

Figure 3 shows the boron SIMS profile for layers also deposited at temperatures (Td) = 520 °C and 605 °C but oxidized at (Tox) = 945 °C for (t tox) = 12 min 45 s. Again, very similar results to those observed in Figure 2 are obtained. Likewise, in Figure 4 we present, for the same layers, the results of boron SIMS profiles for (Td) = 1050 °C and (t tox) = 12 min. The predominant features remain identical to those given above but the attractive effect seems to be more pronounced upon long oxidation times (t tox) and high temperatures (Tox). When (t tox) is short, this loss appears to be relatively weak. The boron concentration values of the three characteristic regions are equal to (2–3) × 10^{20} cm^{-3}, (4–6) × 10^{19} cm^{-3}, and (5–50) × 10^{20} cm^{-3}, respectively.

3.2. FPPR Results

Values of resistance measurements have been obtained using a classical four-point probe. This technique is becoming a routine evaluation for diffusion profile measurements and for checking procedures by comparison to other meth-
ods, such as the SIMS technique. In this section, in addition to the thermal-oxidation effect, we are also interested in examining the effect of the deposition temperature \( T_d \) and the film thickness \( W_p \) on the resistivity variations. Figures 5a and b show the resistivity variations of the two layers versus \( t_{ox} \) at \( T_{ox} = 840^\circ \text{C} \) and \( 945^\circ \text{C} \). For \( T_{ox} = 1050^\circ \text{C} \), because most of the polysilicon film is consumed during the thermal-oxidation process, we were not able to carry out resistivity measurements on the remaining very thin layers after removal of the grown oxide. Compared to the as-grown resistivity, it is clear that \( \rho \) values of the oxidized films are mostly equal or slightly higher, except for the case with \( T_d = 605^\circ \text{C} \) and \( t_{ox} > 350 \text{ min} \), which presents an opposite behavior at the two oxidation temperatures \( T_{ox} \). This variation is in good agreement with previous studies.\(^{18,20,21}\)

These figures illustrate well the effect of the thermal-oxidation parameters (\( T_{ox} \) and \( t_{ox} \)) on the resistivity evolution. After 1 h 46 min and 5 h annealing treatments, it seems that \( t_{ox} \) does not appreciably affect the resistivity of films deposited at \( T_d = 605^\circ \text{C} \). On the other hand, for films deposited at \( T_d = 520^\circ \text{C} \), \( \rho \) decreases when \( t_{ox} \) increases at \( T_{ox} = 945^\circ \text{C} \), but increases at \( T_{ox} = 840^\circ \text{C} \). So, the effect of \( T_{ox} \) on the resistivity behavior is characterized by an increase of \( \rho \) with \( t_{ox} \) until \( t_{ox} \) reaches 1000 \text{ sec}. This evolution appears clearly at long enough times \( t_{ox} \). In particular, whereas this evolution appears to be too slow for layers deposited at \( T_d = 605^\circ \text{C} \), for those deposited at \( T_d = 520^\circ \text{C} \) this variation seems to be markedly enhanced, where it increases to overtake the value reached by those deposited at \( T_d = 605^\circ \text{C} \). Once again, the relative difference of resistivity variations, also called the "relative differential of resistivity variation (DRV)" between the two layers as a function of \( T_{ox} \), and especially at long oxidation times, shows the same behavior as indicated above.

In Figure 5c, we plot the resistivity values versus the film thickness \( W_p \) between 15 and 300 nm. We notice that for \( W_p > 50 \text{ nm} \), \( \rho \) remains constant and equal to \( 3 \times 10^3 \Omega \text{ cm} \). For the lowest thicknesses, a particular behavior appears to be linked to \( T_d \). The value of \( \rho \) increases strongly when \( T_d = 520^\circ \text{C} \) and decreases also strongly when \( T_d = 605^\circ \text{C} \).

After oxidation treatment of the sample at \( 945^\circ \text{C} \), the variation of resistivity with thickness changes according to the temperature of deposition \( T_d \) (either \( 520^\circ \text{C} \) or \( 605^\circ \text{C} \)). On one hand, at \( T_d = 605^\circ \text{C} \) and for \( W_p < 50 \text{ nm} \), \( \rho \) remains constant at nearly the same value as obtained before thermal-oxidation treatment, while for \( W_p > 50 \text{ nm} \), \( \rho \) values reach a limit of \( 1 \times 10^2 \Omega \text{ cm} \). On the other hand, at \( T_d = 520^\circ \text{C} \), the thickness–resistivity behavior is quite different before and after the oxidation process.

3.3. TEM Observations

Figures 6a–h show the effect of grain growth during the thermal-oxidation treatments. At \( T_d = 520^\circ \text{C} \) and before the oxidation process, the as-deposited films are initially largely amorphous, with crystalline grains varying in size and scattered sparsely throughout the film. On the other hand, at \( T_d = 605^\circ \text{C} \), the films are completely crystallized. During the oxidation process, the amorphous phase of the first layers (\( T_d = 520^\circ \text{C} \)) appears to transform to a structure where crystallinity is clearly enhanced; Figures 6d and h confirm this evolution and indicate a textured structure. The average grain size is estimated to be 40 nm. When \( T_{ox} \) increases, the majority of the smaller grains appear to have grown such that most of the grain sizes are now approx-
Fig. 6. TEM images of films deposited at $T_d = 520^\circ$C (top row) or $T_d = 605^\circ$C (bottom row). First, as deposited (a,e) and, second, after dry O$_2$ oxidization of the films at: b,f) $T_{ox} = 840^\circ$C for 61 min; c,g) $T_{ox} = 945^\circ$C for 12 min; d,h) $T_{ox} = 1050^\circ$C for 12 min.

approximately 80–90 nm. Meanwhile, during the same process, films deposited at $T_d = 605^\circ$C indicate a slow grain growth evolution.

Qualitatively, the variation of the relative difference between the two rates of grain growth seems to confirm the presence of a “differential growth mechanism (DGM)”. This behavior is also pointed out by Tompkins et al.[29] They suggest that grains are seen to grow from small nuclei until an equilibrium condition is reached, where the films are totally occupied by crystalline material.[29]

4. Discussion

4.1. FPPR Analysis

At first sight, the resistivity results of these layers show a particularly singular resistivity variation, in which sometimes they present insulating behavior and sometimes a conducting one. So, in all likelihood, these singular values can be attributed, on the one hand, to a particular difference in microstructure of the as-deposited layers at the film/oxide–substrate interface.[8,20,21] On the other hand, these changes may be clear evidence of the presence of some deep modifications in the film microstructure that occur during the thermal-oxidation treatments.

4.2. TEM Observations

The structural properties have been studied throughout the crystallization process of two selected layers deposited at $T_d = 520^\circ$C and $T_d = 605^\circ$C. The first layers have an amorphous state. Therefore, they present poorly developed grains (G) with the number of grain boundaries (GB) less than in the second fine-grained polysilicon layers, which have a polycrystalline microstructure state. These deliberately selected values of $T_d$ should be suitable to specify the magnitude of the effects of the grains and the grain boundaries on the dopant diffusion behavior. However, these observations have been found to be insufficient to separate the two effects. Because of the presence of a “differential growth mechanism (DGM)”, probably due to a non-uniform enhanced recrystallization effect, this microstructural difference becomes very small (see Figs. 6d,h) and therefore tends to disappear during the course of annealing heat treatments.
4.3. SIMS Profiles

We are particularly interested in the redistribution of the boron atoms within the film itself, and especially when it is annealed under dry oxygen ambient. Often, this situation is not directly taken into account because usually these layers are used as diffusion source materials, in order to introduce junctions into the underlying single-crystal silicon on which these films are deposited. In this study, both dopant redistribution in the film and diffusion in the underlying substrate will be considered. First, we would like to point out the following.

- The dopant peaks observed at the polysilicon surface are similar to what is seen in boron-implanted films. But, in the case of boron-implanted films, these peaks generally correspond to those of the as-implanted ones. For the in situ boron-doped films, there are no boron peaks in the as-grown films, therefore, it is not possible to attribute them to the same sources. The boron peak in this case may be the result of segregation in the polyoxide that occurred during the thermal-oxidation steps. The presence of a newly formed polyoxide layer may acts as a preferential sink to precipitate boron atoms. Globally, boron peaks remain near both the poly-Si surface and poly-Si/SiO₂ interface for all oxidized samples.

- In spite of this, boron diffusion behavior under these specific conditions has not been completely investigated. Until now, no analytical model has been developed. Improved attempts were still required to obtain a better understanding of the effect of thermal oxidation on the diffusion characteristics. In this work, we attempt to give an analysis based on the boron diffusion mechanisms that takes into account the effect of grains and grain boundaries.

At high concentration levels, diffusion in polysilicon can be described by mechanisms involving impurity diffusion and its interactions with the grains (G) and the grain boundaries (GB). In the grains, the diffusion process will be characterized by the coefficient \( D_G \) and in the grain boundaries by the coefficient \( D_{GB} \). If we assume that the realistic boron diffusion coefficient \( D_p \) is equal to a linear combination of these two terms, and we can express \( D_p \) by Equation 1. Diffusivities inside the grains and along the grain boundaries may be determined by solving Fick’s diffusion equations, using an implicit, finite-difference method.

\[
D_p = D_G + D_{GB} \tag{1}
\]

In order to have a quantitative approximate value of \( D_{GB} \), we can separately calculate the value of \( D_G \) and compare the obtained results, using Equation 1, to the reliable published values of \( D_G \) (the available experimental data of \( D_p \) approximately similar to our conditions are those published by Horiuchi and Blanchard). For \( D_p \), the diffusion model is based on the criterion of the concentration-dependence effect, well-known in single-crystal silicon. Indeed, when impurity concentration is high, the diffusion profiles deviate from the predictions of simple diffusion theory, and the impurity diffusion is affected by factors not considered in Fick’s simple diffusion laws (FDLs). Since the SIMS profile measurements reveal concentration-dependent diffusion effects, Fick’s diffusion equation with concentration-dependent diffusivities is applied to the high-concentration diffusions. The concentration-dependent diffusivities are determined by a Boltzmann–Matano (BM) formulation.

Now, if we refer to the classical diffusion profile behavior in single-crystal silicon, we can see that the situation of constant diffusion coefficient prevails only when the doping concentration is less than the intrinsic carrier concentration \( n_i \) at the diffusion temperature \( T_{ox} \). Obviously, under our high dopant concentration, it is stated that the diffusion coefficient \( D_p \) becomes a function of concentration \( C \). Indeed, if the value of \( D_p \) changes with concentration, and if the concentration changes with the film depth, \( D_p \) will also change with the depth of the samples. Different expressions for the diffusion concentration dependence have been given in the literature. In order to determinate \( n_i \), we must first solve numerically the empirical Equation 2 with Equation 3 and also note that Wolf and Tauber have used a relationship similar to what is used (Eq. 4), where \( D_i \) is the intrinsic diffusion coefficient in single-crystal silicon, \( C \) the boron concentration, \( p \) the electrically active boron concentration, and \( \beta \) an unknown parameter, which in theory is given by \( D' / D^0 \). Also, the diffusion temperature dependence coefficient is modeled only with an Arrhenius-like relationship (Eq. 5), as is given by Post et al. [5]

\[
n_i^2 = 1.5 \times 10^{33} (T_{ox})^3 \exp \left( \frac{-1.2 + \Delta E_g}{kT_{ox}} \right) \tag{2}
\]

\[
\Delta E_g = -7.1 \times 10^{-13} (n_i/T_{ox})^{1/2} \tag{3}
\]

\[
D_g = D_i \left( 1 + \frac{C}{C^* + 4 n_i^*} + \frac{\beta p}{n_i} \right) \frac{1}{1 + \beta} \tag{4}
\]

\[
D_p = D_0 \exp \left( \frac{-E_g}{kT_{ox}} \right) \tag{5}
\]

We see that, if we divide the polysilicon thickness into three regions with average boron concentrations of around \( 3 \times 10^{21} \text{ cm}^{-3} \), \( 1.7 \times 10^{20} \text{ cm}^{-3} \), and \( 3.5 \times 10^{20} \text{ cm}^{-3} \), respectively, at the surface, in the bulk, and at the interface of the films, and using an appropriate computer program, we find a range of values of the diffusion coefficient in the grains \( D_g \) equal to \( (2.73-1.82) \times 10^{14} \), \( (3.72-1.86) \times 10^{13} \), and \( (4.24-3.32) \times 10^{13} \) cm² s⁻¹ for the three oxidation temperatures \( 840 \), 945, and 1050 °C, respectively. Therefore, the es-
Estimated values of diffusion coefficient in the grain boundaries \( D_{gb} \) is found to be equal to \( 5.73 \times 10^{-14} \), \( 1.79 \times 10^{-13} \) and \( 1.00 \times 10^{-12} \) cm\(^2\) s\(^{-1}\) for the same three oxidation temperatures 840, 945, and 1050 °C respectively. All our calculation steps are summarized in Table 1. Then, if we use the estimate values of \( D_p \) (given above), and with the known values of \( E_p \) reported in the literature, we find that the pre-exponential factor \( D_0 \) agrees well (see Table 1) with what is reported elsewhere.[22,31]

According to what is reported in the literature, the predicted boron diffusivity along the grain boundaries, with low concentration doping level, is -100 times faster than in the bulk material.\(^{[23]}\) In the case of high concentration doping level, we found that at \( T_{ox} = 945 \) °C and 1050 °C, the grain boundary diffusivity \( D_{gb} \) is still comparable to \( D_b \) (\( D_{gb} = D_b \)). In recent work, Nédélec et al.\(^{[38]}\) have found comparable values for boron-implanted polysilicon layers. In another publication, Losee et al.\(^{[36]}\) have reported a value of \( D_{gb} \leq 10 D_b \) for phosphorus diffusion polysilicon, which is significantly lower than what has been reported elsewhere in the literature.\(^{[31]}\) The variation of the estimated diffusivity as a function of the inverse of \( T \) permits us to calculate the activation energies of \( D_{gb} \) and \( D_b \) (see Fig. 7). Values of the order of 2.00 eV and 3.42 eV were found for \( D_{gb} \) and \( D_b \), respectively. This order of values of measured diffusivities is equal to a range close to that given in the literature.\(^{[5,38]}\)

Also, because thermal oxidation activates recrystallization of the amorphous phase of films deposited at \( T_d = 520 \) °C, the film structure evolves considerably and tends to be close to those deposited at \( T_d = 605 \) °C. As a consequence, only small differences are observed between diffusivity of films deposited at temperatures \( T_d = 520 \) °C and \( T_d = 605 \) °C.

Diffusion of boron in the poly-Si is also affected by the solid-solubility limit.\(^{[37,39]}\) When this solid-solubility limit is exceeded, boron diffusivity is drastically reduced. The formation of boron precipitates, which reduces the boron diffusivity, has been suggested for samples with high levels of in situ boron doping. In single-crystal silicon, boron solid solubilities vary exponentially with the oxidation temperature \( T_{ox} \), whereas the solid-solubility values in polysilicon films have only a small temperature dependence.\(^{[5]}\) These differences are probably caused by the interaction of boron with the grain boundaries. The dopant either precipitates or forms complex compounds with silicon, such as SiB, in order to establish an equilibrium at high temperatures \( T_{ox} \). This equilibrium is achieved very quickly at high temperatures.

So, with this assumption at high \( T_{ox} \), which is consistent with what is published in the literature,\(^{[32]}\) cluster formation is strongly reduced at lower temperatures, whereas declustering is fast enough to maintain cluster equilibrium in the diffusion process. This seems to be in good agreement with other studies, which suggest that cluster equilibrium is attained fast compared with diffusive redistribution.\(^{[32]}\) This works well because the reduction of the diffusion coefficient at or above cluster equilibrium "freezes" that part of the impurity distribution, and also because, at high doping levels, the concentration gradient of the mobile atoms almost vanishes.

5. Conclusion

In this study, various characterizations of structural and electrical properties of heavily in situ boron-doped...
LPCVD-Si thin films have been undertaken. The results indicate that the subsequent thermal-oxidation processes yield a significant modification of the film properties initially established, whatever the film deposition temperature $T_d$. From these changes it can be stated that:

- Differential effects of oxidation rate, growth mechanism, resistivity variation (DOR, DGM, DRV), and other heating-up and saturation phenomena are found to have similar behavior.
- Results of qualitative and quantitative investigations of dopant diffusion calculations indicate that the value of the boron grain boundary diffusivity $D_{gb}$ is of the same order as the boron diffusivity in the grains $D_e$. And, boron precipitation in grain boundaries for high doping levels (at the limit of solubility) was also found to be one of the main causes of the strong reduction in the diffusion coefficient in the grain boundaries.

- Resistivity measurements obtained from classical resistance analysis present values indicating a limitation of the electrically active carrier concentration.

In addition, we believe that diffusion study is complicated by not only the presence of precipitation, structural defects, and high-concentration level effects, but also by other complex induced factors such as oxygen migration due to O$^{16}$ bombardment during SIMS measurements, and epitaxial alignment of the poly-Si with the substrate after the rupture of oxide barrier.

Another promising way to study the fundamental physical processes involved in situ heavily boron-doped and oxidized polysilicon thin films, in which the realistic diversity of these structures is taken into account, would be the introduction of statistical factors (Monte Carlo methods) for a better description of the random distribution of grains and grain boundaries of each structure.

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