BORON ACTIVATION AND DIFFUSION IN POLYCRYSTALLINE SILICON WITH FLASH-ASSIST RAPID THERMAL ANNEALING

Ву

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To my family, for their endless support and encouragement

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LIST OF ABBREVIATIONS

APT	Atom probe tomography
BIC	Boron interstitial cluster
BiCMOS	Bipolar CMOS
CMOS	Complementary Metal-oxide-semiconductor
c-Si	Crystalline silicon
CVD	Chemical vapor deposition
FIB	Focused ion beam
FIM	Field-ion microscopy
fRTP	Flash-assist rapid thermal processing
iRTP	Impulse rapid thermal processing
НВТ	Heterojunction bipolar transistor
LEAP	Local electrode atom probe
MOSFET	Metal-oxide-semiconductor field-effect transistor
PFET	p-type field-effect transistor
Poly-Si	Polysilicon, or polycrystalline silicon
PTEM	Plan-view transmission electron microscopy
RTA	Rapid thermal annealing
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SPER	Solid phase epitaxial regrowth
SOI	Silicon-on-insulator
TED	Transient enhanced diffusion
TEM	Transmission electron microscopy
TOF	Time-of-flight

XTEM Cross-sectional transmission electron microscopy

Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

BORON ACTIVATION AND DIFFUSION IN POLYCRYSTALLINE SILICON WITH FLASH-ASSIST RAPID THERMAL ANNEALING

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The rigorous scaling in dimensions for future generations of transistor fabrication demands ever steeper requirements for dopant solubility with minimal diffusion. Advanced annealing techniques such as flash-assist rapid thermal processing now allow effective anneal times up to three orders of magnitude less than conventional methods. At the same time, advanced characterization techniques can now provide three-dimensional compositional analysis of materials systems. While there has been extensive research for flash annealing of B doped crystalline Si, the effects on polycrystalline Si have been less studied, but is of equal importance. It continues to be prevalent in device fabrication for current and future technologies.

The morphology and evolution of grains in heavily B-doped poly-Si is studied under high temperature millisecond annealing conditions using plan-view transmission electron microscopy. High activation with low thermal budgets has allowed study of a very fine-grained microstructure of highly activated B doped poly-Si. 3D atom probe tomography allowed direct quantitative measurement of the segregation coefficient of B to the grain boundaries, and its diffusion behavior has been accurately modeled. Activation, mobility, and deactivation of B in flash annealed polycrystalline Si was also

explored using Hall effect. By combining electrical, compositional and microstructural measurements, a model has been developed to describe the activation, mobility, and diffusion behavior of B in poly-Si films with average hole concentrations greater than 5×10^{19} cm⁻³.

CHAPTER 1 MOTIVATION

The semiconductor industry has seen tremendous innovation over the past halfcentury as it attempts to keep pace with Moore's Law; the observation and prediction of transistor density growth by Intel co-founder Gordon Moore, who stated that the number of transistors on a chip would double each year¹. In an attempt to fulfill Moore's Law, the industry has managed to double transistor density at a pace of roughly every 18-24 months. As transistor dimensions scale well into the nanometer and even angstrom level, suppressing diffusion has required incredible innovation in thermal processes. The effects of these advanced thermal processes on electrical properties and diffusion in polycrystalline Si, a widely used material for transistor fabrication, must be explored.

1.1 Introduction

Silicon (Si) is the second most abundant element in the Earth's crust², making up roughly one-fourth of its total weight. Due to its relatively low cost as a semiconductor, it has been the primary material used in the fabrication of devices for integrated circuits³ (IC) as well as photovoltaics⁴.

Like many solid materials at room temperature, Si can exist in a single crystalline (c-Si) or polycrystalline form (poly-Si). For electronics applications, the Si is processed to ultra high purities and formed into a single-crystalline state. Oftentimes, processing conditions do not allow the deposition of single-crystalline Si due to lack of a crystalline "seed" surface to grow epitaxially from. In such a case, poly-Si must be used instead.

Since the primary difference between c-Si and poly-Si is the presence of grain boundaries, it is important to understand the effect these boundaries have on the material system. Furthermore, due to aggressive scaling in integrated circuits, variability

and device yield become of increasingly greater concern when grain sizes and device dimensions become comparable. Therefore, it is pertinent to understand the role of grain boundaries in polysilicon as it pertains to current and next-generation processing conditions in integrated circuits.

1.2 Improving the Heterojunction Bipolar Transistor

Oftentimes in device fabrication processing, use of single-crystalline silicon for some structures is simply unfeasible due to the lack of a crystalline surface to act as a seed for epitaxy^{5, 6}. One such example is in the case of high-performance SiGe:C heterojunction bipolar transistors, where poly-Si forms the elevated extrinsic base in the base layer of the structure and is deposited over oxide⁵. Improving the transit frequency, $f_{T,}$ and the maximum oscillation frequency, f_{MAX} , has proven to be challenging due to compensating effects for a given thermal budget. A low thermal budget aids in delivering the highest transit frequencies due to reduced diffusion in the base, thereby allowing a thin base width⁷. However, because of increased base resistance due to lower activation using a low thermal budget, f_{max} is reduced.

With this in mind, the application of millisecond annealing using flash-assist rapid thermal processing (fRTP) to B-doped poly-Si presents itself very favorably^{7, 8}. High temperature annealing (up to 1350°C) allows greater B solubility⁹, and therefore lower resistance, while short annealing timescales significantly limits diffusion⁸. The typical pulse width¹⁰ for flash annealing is on the order of 1 ms. While the scope of this research focuses on the electrical properties of poly-Si in its application as the elevated extrinsic base in bipolar CMOS technology⁵, the results presented form a fundamental basis for understanding the effect of millisecond annealing on sheet resistance, activation, and mobility of heavily B-doped poly-Si films. This is then verified with

microstructural and compositional analysis using three-dimensional analytical techniques.

1.3 Objectives and Statement of Thesis

The goal of this work is to explore the effect of millisecond annealing on the electrical and chemical properties of B doped poly-Si. The low thermal budgets allowed by using flash-assist rapid thermal processing (fRTP) explores a new regime in microstructure and dopant activation—specifically suppressed grain growth with very high levels of dopant activation.

The results of this research have provided a number of scientific contributions. Using transmission electron microscopy, the mechanism for grain growth in heavily B doped poly-Si films under flash annealing has been verified to be of lattice dislocation motion. Activation, mobility, and deactivation measurements using Hall effect of heavily B doped poly-Si films with flash annealing up to 1350 °C led to creation of a mathematical model relating grain size, activation, and mobility for hole concentrations greater than 5×10¹⁹ cm⁻³. A model was also developed for quantitative values for grain boundary segregation of B, which was previously thought to not occur. This was achieved by using flash annealing to create a highly activated yet very fine microstructure of poly-Si. This fine microstructure allowed for direct evidence of B segregation using 3D atom probe tomography, a powerful analytical technique with a limited field of view. The measured segregation data then allowed for accurate simulation of B diffusion through the polycrystalline film. Finally, the work has been able to apply 3D atom probe tomography to commercially fabricated field-effect transistor devices, revealing B segregation to the gate oxide and verification of surface recombination velocity of point defects.

CHAPTER 2 LITERATURE SURVEY

2.1 Doping in Poly-Si

The fundamental property of a semiconductor is its ability to behave as both an insulator and a conductor depending on the impurities that are added¹¹. For Si, the most common p-type dopant is B. Doping is typically incorporated into the material by two processes. In-situ doping refers to incorporation of dopant either during crystal growth or during deposition of material. Poly-Si is typically deposited from a gas-phase source using chemical vapor deposition (CVD). Dopant atoms are typically incorporated automatically into the lattice using this method up to a certain concentration. Another method of introducing dopant atoms into Si is via ion implantation, where dopant atoms are ionized and accelerated under a high potential and forced into the substrate material. This process causes significant damage to the crystalline lattice and an annealing step is required to repair the damage and incorporate the dopant atoms onto substitutional lattice positions in order to contribute to conduction. The thermal treatment gives rise to diffusion, and so annealing techniques such as flash annealing have been developed in order to reduce the effective time of the anneal.

2.1.1 In-situ doping

Poly-Si is typically deposited in a low-pressure chemical vapor deposition chamber, with the decomposition of silane (SiH_4) via the reaction¹²

$$SiH_4(g) \rightarrow SiH_4(s) \rightarrow Si(s) + 2H_2$$
 (2-1)

Low-pressure deposition reduces unwanted gas phase reactions as well as improves film uniformity. Doping the films with B involves addition of diborane gas (B_2H_6) to silane during deposition. First, diborane undergoes thermal decomposition

$$B_2H_6(g) \to 2BH_3(g) \tag{2-2}$$

The actual incorporation of B into Si is thought to proceed by¹³

$$BH_3(g) \rightarrow BH_3(s) \rightarrow B(s) + (3/2)H_2 \tag{2-3}$$

The amount of B incorporation has been seen to depend linearly with diborane/silane ratio¹⁴.

An advantage for n-situ doping is that it allows for direct incorporation of B into the crystal lattice, thereby removing the need for an annealing step in order to activate the dopant onto a lattice position. However, for poly-Si the activation is not complete due to some amount of dopant in an inactive state at the grain boundaries. Varying the diborane/silane ratio has also been shown to effect the microstructure of the asdeposited film¹⁵.

2.1.2 Ion implantation

Ion Implantation is the most common method of doping for integrated circuit technology. The technique involves accelerating dopant ions under an electric field and implanting them directly into the semiconductor substrate. The process allows for very good control, precision, uniformity, and repeatability, however, the crystal suffers significant radiation damage¹⁶, which must be repaired by way of an annealing step.

There are two stopping mechanisms for which the accelerated ion comes to rest within the material. The first is called nuclear stopping, which represents elastic collisions between the ions and the recoiled atoms of the lattice. The second, termed electronic stopping, describes the electrostatic interactions between the ions and the outer shell electrons of the semiconductor. Nuclear stopping is a process that creates Frenkel pair defects. A Frenkel pair describes a pair of point defects created when a Si atom is displaced into an interstitial position and the vacancy it left behind. Collisions are elastic and require a conservation of momentum. 15 eV of energy is required to displace an atom of Si off of its lattice position. The amount of damage is therefore a function of incoming ion energy, the ion's mass, implanter current, and substrate temperature.

The sum total of energy loss by nuclear and electronic stopping determines the range the ion travels within the material. The ion distribution is of a Gaussian shape, with a projected range R_p and a straggle ΔR_p .

2.1.2.1 Amorphization

Beyond a critical damage density^{17, 18}, the Si crystal undergoes a first order phase transformation into an amorphous phase¹⁹. The minimum ion dose necessary to induce amorphization is dependent on the ion's mass, its energy, dose rate, and the temperature of the substrate²⁰.

2.1.2.2 Activation via solid phase regrowth

In Si, one way to increase activation of dopant is to first create an amorphous layer and implant the dopant into it. Implantation into the amorphous phase and subsequent annealing allows the crystal to repair from the underlying seed and incorporate the dopant into the lattice during this regrowth, termed solid phase epitaxial regrowth (SPER)²¹⁻²³. This allows much higher solubility, and thereby activation, than equilibrium solubility since regrowth can occur at relatively low annealing temperatures.

Preamorphization and regrowth can similarly be applied to a polycrystalline structure. It has been shown that the regrowth rate varies significantly for different crystallographic orientations²⁴ and so in a polycrystalline structure, the growth of the

amorphous-crystalline interface can be very rough, with some areas showing full regrowth while others exhibiting very little. It has also been shown that at sufficiently high implantation doses, c-Si regrows as poly-Si²⁵.

One of the drawbacks to the preamorphization and regrowth process is the generation of excess interstitials from the implantation process, which manifest themselves as end-of-range (EOR) defects^{16, 26} at a distance slightly beyond the amorphous-crystalline interface. The dissolution kinetics of EOR defects releases interstitials and creates a supersaturated environment, which significantly enhances B diffusion^{27, 28}.

2.2 Diffusion of Boron in Silicon

A consequence of the thermal processes in microelectronics fabrication is diffusion of B through the material. For poly-Si, this can be very rapid due to the enhanced diffusivity of B in the grain boundaries^{29, 30}. In order to understand diffusion of B in poly-Si one must first understand the mechanisms for B diffusion in single crystalline silicon (c-Si), and before that, one must first understand the basic concept of diffusion.

Thermodynamically, the process of diffusion is driven by the gradient of the concentration profile, or more specifically, the reduction of the gradient in chemical potential. For ideal mixtures, these are equivalent. At its most fundamental level, the driving force is simply an availability of sites as atoms diffuse in the lattice by random walk. Areas with low concentrations of dopant atoms have more available sites to occupy, and so there is a net motion of atoms from higher concentration to lower concentration.

In the case of B doped Si, this flux, *J*, of B from high concentration to low concentration can be described by Fick's 1st law in one-dimension by,

$$J = -D\frac{\partial C}{\partial x} \tag{2-4}$$

where *D* represents the diffusivity in dimensions of length² per time, such as cm^2/s , and *C* is the concentration. In order to predict how the diffusion changes with respect to time, Fick's 2nd law can be derived from Fick's first law using mass balance,

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}J = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}C\right) = D\frac{\partial^2 C}{\partial x}$$
(2-5)

The diffusivity, D, can be described by the Arrhenius expression

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2-6}$$

where D_0 is the pre-exponential factor, E_a is the activation energy, *k* is Boltzmann's constant, and *T* is the absolute temperature.

Unfortunately, diffusion of B in Si is not so simplistically behaved as to be a function of only the concentration gradient. However, it has been well studied for a wide range of concentrations and annealing conditions, and so can be built upon for application to a polycrystalline microstructure under millisecond annealing conditions.

2.2.1 B diffusion and point defects

It is widely accepted that the mechanism for dopant diffusion in Si is governed by the interactions between dopants and point defects such as interstitials and vacancies³¹. The available reactions for B diffusion in Si can be described via the equations³¹

$$B + V \Leftrightarrow BV$$
 (2-7)

$$B + I \Leftrightarrow BI \tag{2-8}$$

$$B + I \Leftrightarrow B_i \tag{2-9}$$

$$B \Leftrightarrow B_i + V \tag{2-10}$$

where *V* represents a Si vacancy and *I* represents a Si self-interstitial. Eq. (2-7) describes diffusion via a vacancy mechanism, (2-8) by an interstitial mechanism, and (2-9) by an interstitialcy kick-out mechanism. Eq. (2-10) describes a dissociative reaction known as the Frank-Turnbull mechanism³² whereby a B atom on a substitutional lattice position moves into an interstitial position, leaving behind a vacancy. It is expected that in an environment of excess interstitials, Eq. (6) would dominate, while conversely, Eq. (2-10) would apply in an environment of excess vacancies.

It has been shown that B diffuses by almost a purely interstitialcy mechanism³³, where a Si self-interstitial supplants a substitutional B atom via a kick-out process, thus allowing it to diffuse through the crystal. As the B atom later supplants a Si atom on the lattice, a new Si interstitial is generated and the process repeats. The concentration for interstitials can drastically increase above the equilibrium concentration due to many processes, such as generation of Frenkel pairs from ion implantation^{27, 34}, generation of interstitials via oxidation of the surface³⁵, and even release of interstitials from high concentrations of Si-B clusters³⁶. This supersaturation of interstitials relative to the equilibrium concentration^{32, 37} of interstitials therefore represents an enhancement factor to the diffusivity of B, and can be expressed by

$$D_{B} = D_{B}^{*} \frac{C_{I}}{C_{I}^{*}}$$
(2-11)

where D_B^* represents the diffusivity of B at an equilibrium concentration of interstitials.

This supersaturation of interstitials represents a non-equilibrium system and so there is a driving force to remove the excess interstitials. The diffusivity enhancement has been termed transient enhanced diffusion²⁸ (TED), referring to the time transient required for the system to return to equilibrium, and the enhancement ratio C_l/C_l^* to return to unity. For ion implantation processes, this time transient arises due to the formation of extended defects, primarily {311} rod-like defects¹⁶ whose dissolution kinetics release a steady stream of interstitials into the system²⁷. Excess interstitials typically diffuse to and annihilate at the surface³⁸⁻⁴⁰, although they may recombine with vacancies or form boron-interstitial clusters (BIC)⁴¹.

For a polycrystalline structure, the grain boundaries may be thought of as effective surfaces for point defect recombination⁴². In fine-grained poly-Si structures, as is the case when small thermal budgets such as flash annealing do not allow for significant grain growth, the surface area available for recombination can be very high. The effect of this environment will be explored when discussing diffusion of B in the polycrystalline structure.

2.2.2 B diffusion in polycrystalline Si

It has been shown that grain boundaries in poly-Si act as an effective sink for vacancies, and postulated that the same is true for interstitials⁴³. Polycrystalline films of CoSi₂ deposited on Si have been shown to generate an interstitial undersaturation⁴⁴. In fine-grained poly-Si structures, as is the case when small thermal budgets such as flash annealing do not allow for significant grain growth, the surface area available for recombination can be very high, thus reducing enhanced diffusivity effects arising from processes that create a supersaturation of interstitials discussed previously.

However, the presence of grain boundaries has a profound impact on diffusion in a polycrystalline structure due to an enhancement in B diffusivity in the grain boundary²⁹ that is several orders of magnitude greater than in the bulk. Dopants such as As and P have been shown to segregate to grain boundaries in poly-Si⁴⁵⁻⁴⁸, but reports on B segregation to the grain boundary are conflicting^{3, 45-47, 49, 50}. Results seem to suggest that segregation is only seen at very high concentrations (>1.3 at%) Nevertheless, it has been demonstrated that diffusion of B in poly-Si is significantly faster than in bulk c-Si, suggesting an enhanced diffusivity within or near the grain boundaries themselves.

The modeling aspect for this behavior^{45, 51-54} has been well studied for As and P. Mathematically, the diffusion in a polycrystalline structure is described by splitting the diffusion equations into diffusivity of the dopant within a crystallite (D_i) and diffusivity of the dopant within a grain boundary (D_i^{gb}). The differential equations are

$$\frac{\partial C_i^g}{\partial t} = \frac{\partial}{\partial x} D_i \frac{\partial C_i^g}{\partial x} + \tau^{-1} \left(C_i^g p_{seg} - C_i^{gb} \right)$$
(2-12)

$$\frac{\partial C_i^{gb}}{\partial t} = \frac{\partial}{\partial x} D_i^{gb} \frac{\partial C_i^{gb}}{\partial x} - \tau^{-1} \Big(C_i^g p_{seg} - C_i^{gb} \Big)$$
(2-13)

where the subscript *i* denotes the diffusing impurity species, and the segregation coefficient, $p_{seg} = C_i^{gb}/C_i^g$ is maintained at steady state. The two concentrations are coupled by a kinetic reaction term, where τ represents the rate of segregation. The model describes diffusion in terms of a random walk, whereby if the dopant encounters a grain boundary, it takes much larger steps due to the increased diffusivity, but may also jump back into the grain. τ represents the rate for this process occuring, while p_{seg} describes the tendency for the diffusing atom to remain in the boundary. In this work, this diffusion model is extended to B diffusion in poly-Si using direct chemical analysis of B segregation to the grain boundaries. Flash annealing and heavy doping create an ideal environment for B segregation. Prior work regarding dopant segregation was mainly inferred from electrical measurements^{45, 53}, and thus may not accurately be able to detect low segregation at large grain sizes where its influence is expected to be minimal on conduction.

2.3 Flash-Assist Rapid Thermal Annealing

To meet future metrics for dopant activation and limited dopant diffusion, thermal processing has evolved to ever increasing ramp-up and cooling rates in order to reduce the effective annealing times at high temperatures. Conventional rapid thermal processing (RTP) heats wafers by use of incandescent tungsten lamps to allow ramp rates up to 350°C-s⁻¹, however, this is no longer sufficient for the needs of future technology nodes. In fact, it has been shown that heating rates beyond 100°C-s⁻¹ give no improvement with regard to diffusion⁵⁵. This is due to the inability for conventional RTP to minimize the soak and cooling times of the anneal.

Power, spectral distribution, and response time govern the performance for lampbased heating of Si. The use of an argon arc lamp allows much higher power and response time than tungsten lamps. Tungsten lamps operate at 3500K, which represents a power of 10³ W. In contrast, the argon plasma in an arc lamp operates at 12000K, resulting in a power of 10⁶ W, which allows four orders of magnitude improvement in ramp rates over tungsten lamps. With regard to spectral distribution, only 40% of the radiation generated from the tungsten lamp is below the band gap absorption of Si, while over 95% of the radiation emitted from the arc lamp is absorbed⁵⁶. The thermal response time for the arc lamps is also roughly a magnitude

faster¹⁰ (25 ms vs. 300 ms) due to the smaller thermal mass of argon compared to tungsten. This allows for a much faster transition from heating to cooling with the arc lamp.

Flash-assist RTP (fRTP) allows annealing times in the millisecond regime by use of an argon arc lamp¹⁰. A schematic of the Mattson Vortek argon arc lamp is shown in Figure 2-1. In a two arc lamp system, the bottom arc lamp heats the bulk wafer to an intermediate temperature, similar to a spike anneal. The wafer is then "flashed" from the second arc lamp above, describing the discharge of a capacitor bank through the arc lamp at a rate much faster than the thermal conduction rate of the wafer. Only the near surface of the wafer gets heated to the high flash temperatures due to time constant of the flash, which is only ~1 ms which is much faster than the time constant of the wafer¹⁰ (10-20ms). The heating and cooling rates from the flash are on the order of 10^6 °C-s^{-1} . Because the flash only heats the near surface of the wafer, the bulk acts as a heatsink allowing for substantial cooling rates. After returning to the intermediate temperature, the bulk wafer further cools through normal radiative cooling at ~150 °C-s⁻¹. Figure 2-2 compares the time-temperature profiles of conventional RTP to flash-assist RTP.

Experiments in this study were done using a Mattson Millios[™] millisecond anneal system.

2.4 Electrical Properties of Poly-Si

For semiconductors, conductivity arises from doping the material with certain impurities, which occupy substitutional sites on the lattice and either donate an electron (n-type) or accept an electron (p-type). B, an element from group III in the periodic table with three valence electrons, is the most common p-type acceptor dopant used in Si.

Conduction in p-type Si occurs via holes since the removal of an electron results in a positively charged hole.

The conductivity of the semiconductor can be described by the equation

$$\sigma = qn\mu_e + qp\mu_h \tag{2-14}$$

where *q* is the elementary charge of the electron $(1.602 \times 10^{-19} \text{ C})$, *n* and *p* represent concentrations of electrons and holes, respectively, while μ_e and μ_h represent their respective electron and hole mobilities. Even at low B doping levels (~10¹⁶ cm⁻³), conduction via holes dominates and the impact from electron conduction can be ignored since the intrinsic carrier concentration in Si at room temperature is only 1×10¹⁰ cm⁻³.

For both single crystalline Si (c-Si) and polycrystalline Si (poly-Si), the effect of dopant concentration on resistivity is essentially the same. Greater concentrations of carriers equate to lower resistance. In fact, at significantly high doping levels, the resistivity of poly-Si is comparable to that of c-Si⁴⁹. This is due to degradation in carrier mobility for c-Si with increasing doping concentration due to increased scattering from high concentrations of ionized impurities. While the mobility is overall less in poly-Si, it has been seen to rise^{57, 58} with increasing doping concentration above 10¹⁸ cm⁻³. Figure 2-3 depicts the effects of doping concentration on carrier mobility for c-Si and poly-Si. The presence of grain boundaries in poly-Si has a significant impact on the mobility of carriers^{57, 58}.

⁵⁷Seto proposed a model to explain the measured Hall mobilities in poly-Si by treating grain boundaries as trapping sites for carriers due to their disorder and incomplete atomic bonding. This leads to accumulation of charge and formation of potential barriers that carriers must surmount in order to move from crystallite to

crystallite. This theory has been proposed to explain mobility⁵⁸ and resistivity¹⁵ measurements in poly-Si prior to his work, and has been confirmed using optical absorption and electron spin resonance measurements⁵⁹. Figure 2-4 illustrates the formation of potential barriers using energy band diagrams.

In Seto's model⁵⁷, for a grain size *L* with a uniformly distributed carrier concentration *N/cm*³, there exist Q_t/cm^2 of traps at an energy E_t to the intrinsic Fermi level (Figure 2-4c). The charge distribution in Figure 2-4b shows that all of the mobile carriers a distance (0.5*L*-*l*) cm from the grain boundary are trapped by trapping states, where *l* represents the edge of the space charge region created due to the trapping sites. The quantity (0.5*L*-*l*) therefore equals half the width of the space charge region. The potential across this region can then be calculated from Poisson's equation

$$\frac{d^2 V}{dx^2} = \frac{qN}{\varepsilon}, \qquad I < |\mathbf{x}| < 0.5L$$
(2-15)

where ε is the dielectric permittivity of poly-Si. Assuming dV/dX = 0 at x = I and integrating twice gives the potential with respect to *x*,

$$V(x) = (qN/2\varepsilon)(x-l)^2 + V_{v0}, \ l < |x| < 0.5L$$
(2-16)

where V_{v0} is the potential of the valence band edge. The Fermi level represents zero energy and energy is positive toward the valence band.

There are two possible conditions depending on the doping concentration. The first represents a lowly doped condition where $LN < Q_t$, where the traps are partially filled and the crystallite is depleted of carriers. *I* is therefore zero and Eq. (2-16) becomes

$$V(x) = (qN/2\varepsilon)x^{2} + V_{v0}, |\mathbf{x}| \le 0.5l$$
(2-17)

and the potential barrier height, V_B , is the difference between V(0) and V(0.5L), therefore

$$V_{\scriptscriptstyle R} = qL^2 N/8\varepsilon \tag{2-18}$$

This shows that the potential barrier height V_B increases linearly with N, the carrier concentration. At some doping concentration, $LN > Q_t$ and all of the traps are filled, resulting in a potential barrier height

$$V_{\rm B} = qQ_t^2 / 8\varepsilon N \tag{2-19}$$

and l > 0. Beyond this doping concentration, the potential barrier decreases rapidly as 1/N. This is illustrated in Figure 2-5.

Seto was able to calculate the potential barrier energy, E_{B} , experimentally via the slope of mobility vs. 1/kT from Hall measurements for various doping concentrations. Using Eq. (2-9), the trapping density Q_t was calculated and found to be about 3.34×10^{12} cm⁻², or roughly equal to the Si surface state density in c-Si. The trap state energy was found to be 0.37 eV above the valence band edge. A plot of the potential barrier energy vs. doping concentration is given in Figure 2-6. At a doping concentration of 5×10^{19} cm⁻³, the calculated potential barrier is only 5 meV.

This work will expand on Seto's research by studying higher B doping concentrations, where the grain boundary potential barrier should be very small and scattering by ionized impurities may begin to play a more significant role in the overall mobility of the poly-Si film.



Figure 2-1. Mattson Vortek Argon Arc Lamp



Figure 2-2. Time-temperature profile comparison. A) conventional RTP. B) flash-assist RTP. The flash anneal heats only the wafer surface.



Figure 2-3. Room temperature hole mobilities at various B doping concentrations in poly-Si⁵⁷.



Figure 2-4. Modeling grain boundary potential barrier. A) Simple model for poly-SI crystal structure. B) Charge distribution at the grain boundary. C) Band structure for poly-Si at the grain boundaries⁵⁷.



Figure 2-5. Dependence of the potential barrier height on doping concentration⁵⁷.



Figure 2-6. Activation energy for overcoming the grain boundary energy barrier for various B doping concentrations⁵⁷.

CHAPTER 3 ANALYTICAL TECHNIQUES

This chapter details the various analytical techniques used in this work. It serves to educate the reader with some basic background knowledge of the capabilities and limitations of each technique, so as to better interpret the results.

3.1 Four Point Probe

The Four Point Probe, as suggested by its name, uses four probes to measure resistivity in a material. A schematic for the probes is given in Figure 3-1. A current is supplied through the outer probes (1-4) and a voltage drop is measured through the inner probes. By measuring the voltage drop through the inner probes (2-3), the resistance of the outside probes themselves can be neglected since practically no current flows through the inner probes.

For a cubic three-dimensional conductor with length *I*, and cross sectional area *A*, (Figure 3-2) the resistance can be described as the resistivity multiplied by the length and divided by the cross-sectional area. By grouping the resistivity with the thickness of the sample, a sheet resistance R_s allows description of resistivity in terms of "squares" (*I=w*). The unit for R_s is ohms, however, it is commonly referred to as ohms/square.

$$R = \frac{\rho l}{A} = \left(\frac{\rho}{t}\right) \frac{l}{w} = R_s \frac{l}{w}$$
(3-1)

For probes of uniform spacing *s*, the resistivity can be described as,

$$\rho = 2\pi s \left(\frac{V}{I}\right) \tag{3-2}$$

where the current emanates from the probe tips in a spherical fashion. If the conducting layer is very thin compared to the probe spacing, as is typical for ion implanted layers

and in-situ doped poly-Si films, the current spreads in rings, and so the resistivity takes on the form

$$\rho = \frac{\pi t}{\ln 2} \left(\frac{V}{I} \right) = 4.532 \left(\frac{V}{I} \right) \times t$$
(3-3)

where *t* is the thickness of the conducting layer. For poly-Si grown on oxide, this is simply the thickness of the grown film. For ion-implanted crystalline Si, *t* equals x_j , the junction depth.

The resistivity measurement is important for semiconductors because it relates to the carrier density and mobility according to

$$\rho = \frac{1}{q\mu_e n + q\mu_h p} \tag{3-4}$$

where *q* is the charge of the electron/hole, μ_e and μ_h represent the carrier mobility of electrons and holes, respectively, and n and p represent the concentration of electrons and holes. However, mobility and carrier concentration have a complex relationship in crystalline Si, while in poly-Si the presence of grain boundaries adds yet another layer of complexity to both terms. Therefore, while four-point probe measurements are simple and quick, they can only give cursory measurements for resistivity in poly-Si films, and serve as verification for Hall effect measurements.

3.2 Hall Effect

Hall effect measurements allow for more in-depth understanding of electronic properties for materials beyond simple resistivity measurements. In the case of semiconductors, it can measure carrier mobility as well as carrier density, For crystalline Si, dopant solubility, or the occupation of a dopant atom on a substitutional lattice site, is for the most part determined by the annealing temperature^{9, 60}. The same is true for
poly-Si, however, the presence of grain boundaries adds a further layer of complexity by allowing energetically favorable sites for dopant segregation⁴⁵, which lead to potential barriers that impede carrier mobility⁵⁷.

The Hall effect arises when a magnetic field is applied perpendicular to a moving carrier. The field causes a deflection in the moving carrier that is perpendicular to both the magnetic field and the plane the carrier was traveling in. This deflection is produced by the Lorenz force¹¹, and introduces a potential difference across the sample resulting in an electric field. This is depicted in Figure 3-3 using an electron as the carrier. This potential difference is known as the Hall voltage, V_H . In semiconductors, both electrons and holes deflect to the same side of the sample due to opposite charges as well as opposite velocities.

Measurement of the Hall voltage is done using the van der Pauw technique^{61, 62} illustrated in Figure 3-4. A constant current is forced through opposing contacts (1-3) and the Hall voltage is measured across (2-4). The magnitude of the Hall voltage, V_{H} , relates to both the current traveling through the sample and the applied field through the relation

$$V_H \Big| = \frac{IB}{qn_s} \tag{3-5}$$

where *q* is the elementary charge of the carrier (1.602×10^{-19} C), *l* is the current applied, *B* is the magnitude of the magnetic field, and *n*_s is the sheet density of the carriers. For the experiments conducted here, a constant current of 1.0 mA is applied across the sample while the Hall voltage is measured and averaged for both positive and negative magnetic fields at 0.4 T, 0.7 T, and 1.0 T.

The Hall voltage then allows determination of the sheet number, n_s , which allows for calculation of the mobility, μ , through the relation

$$\mu = \frac{1}{qn_s R_s} \tag{3-6}$$

Calculation for sheet resistance, R_s , can also be accomplished using the van der Pauw technique through the relation,

$$\exp\left(\frac{nR_A}{R_S}\right) + \exp\left(\frac{nR_B}{R_S}\right) = 1$$
(3-7)

where R_A and R_B are characteristic resistances determined from measurements according to Figure 3-5. For p-type semiconductors, where *p* represents the active hole concentration, the Hall coefficient is defined as

$$R_H = \frac{1}{qp} \tag{3-8}$$

Due to the complex energy band structure of the material giving rise to changes in effective mass of holes, as well as lattice scattering, and ionized impurity scattering⁶³, correction factors need to be applied to Hall effect measurements in order to obtain accurate mobilities and sheet numbers^{63, 64}. This correction factor is known as the Hall factor, *r*, and relates to the Hall coefficient, R_H , by

$$R_H = \frac{r}{qp} \tag{3-9}$$

Therefore, active doses must be multiplied by the Hall factor, *r*, while Hall mobility must be divided by *r* to determine the true conductivity mobility. ⁶³For hole concentrations above 1×10^{20} cm⁻³, which represents all of the material in this work, the Hall factor used is 0.7.

Measurements for this study were done using a Lakeshore 7507 Hall Effect system at 20 °C.

3.3 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry, or SIMS, is a chemical analysis technique, which allows compositional analysis of thin films. The surface of the film is sputtered using a primary ion beam, which in turn ionizes and ejects secondary ions. A mass spectrometer then separates the secondary ions by their mass-to-charge ratio by varying the strength of the magnetic field. This is illustrated in Figure 3-6.

SIMS is among one of the most sensitive techniques for compositional analysis of impurities, being able to detect down into the parts-per-billion^{65, 66} (ppb) range, however this is dependent on how efficiently the impurity atom ionizes. The depth resolution for SIMS can be as good as ~1 nm/decade⁶⁷, however, this depends on a number of factors. A mixing zone that is produced between the primary ions and the sputtered secondary ions limits the depth resolution. As such, the use of heavier primary ions, lower primary ion energy, and smaller angle of incidence can reduce the depth of this mixing zone and improve the depth resolution.

The concentration versus depth profiles from SIMS are generated from calibrations to known standards. This is because the secondary ion yield for a given species changes depending on the primary ion being used, as well as the substrate being sputtered⁶⁵. Therefore, relative sensitivity factors (RSF) are used to convert an ion yield per second into a relative concentration. Finally, the depth can be determined from the sputtering time by measurement of the final crater depth using a profilometer.

In this work, SIMS is used to quantify the B concentration profiles in poly-Si films after their initial in-situ growth and following ion implantation, as well as measure any

subsequent diffusion following flash-assisted rapid thermal annealing. A 3 kV Cs⁺ primary beam was used and concentration profiles were generated from the detection of CsB^{-} secondary ion clusters. This method eliminates the surface yield enhancement seen when measuring B profiles using an O⁺ primary beam⁶⁸.

3.4 3D Atom Probe Tomography

Atom probe tomography (APT) is an extension from Field Ion Microscopy (FIM), a point-projection microscope invented in 1951 by Erwin Müller^{69, 70}. In 1955, Müller and Bahadur of Pennsylvania State University were the first persons to resolve individual atoms of tungsten (W) by cooling a sharp tip with radius <50 nm to 78K and using He as the imaging gas⁷¹. By positively biasing the W tip, an electric field on the order of 15-60 V-nm⁻¹ can be generated. The field generated is given by $F = V/\beta R$, where *F* is the electric field, *V* is the voltage applied, *R* is the tip radius, and β is a geometric factor⁷². The imaging gas adsorbs onto the tip, and then loses an electron to the tip surface via tunneling⁷³. The newly created positive ions of the imaging gas are then repelled from the tip surface orthogonal to the local curvature and are detected in two-dimensions on a microchannel plate, biased at ground⁷¹. In FIM, the imaging gas ions form the projection image of the surface of the sample tip.

In 1956, an important discovery was made that allowed FIM to evolve into atom probe tomography (APT). When Müller began raising the dc voltage of the W tip, and thereby increasing the electric field, he began noticing the atoms on the surface of the specimen tip themselves ionizing and ejecting from the surface. This was termed field desorption⁷⁴, or field evaporation, which describes the sublimation of the atoms under a high electric field, and is a material property. Different materials have different minimum values for field evaporation to occur.

With this discovery, FIM underwent a radical evolutionary shift. No longer was an imaging gas necessary to provide imaging of only the sample surface, but the ionization of the samples themselves allowed a layer-by-layer analysis of the specimen being analyzed.

The addition of a time-of-flight (TOF) detector⁷⁵ dramatically shifted the scope of the instrument from one of simply atomic imaging, to that of a tool for three-dimensional imaging with materials analysis capabilities. TOF detectors allow calculation of each individual ion's (and their isotope's) mass-to-charge ratio, allowing their unique identification. From here, the addition of modern computing power and a two-dimensional position sensitive detector has allowed the atom probe to evolve into a three-dimensional tool for materials characterization⁷⁶⁻⁷⁹.

APT was traditionally limited to primarily refractory metals, with high conductivity and the ability to withstand the high electric fields necessary for field evaporation. Specimens were biased to just below the required electric field for evaporation, and then the specimen voltage was pulsed at about .1-.2 of the standing voltage to induce field evaporation one ion at a time and allow TOF calculations for each atom. The advent of pulsed laser assisted atom probes has allowed the application of APT to semiconducting materials such as Si^{72, 80-82} by using the laser as a thermal aid for overcoming the field evaporation barrier. Laser pulses operate as fast as 500 khZ allowing rapid data collection. In fact, recent advancements in laser technology has allowed detailed analysis of even insulating materials such as oxides using femtosecond laser pulses and ultraviolet wavelengths⁸³⁻⁸⁶. Figure 3-7 illustrates operation of a pulsed-laser atom probe⁸⁰.

3D APT allows a ~10⁶ magnification for a 50 nm tip radius and 50 mm flight length. The best achievable spatial resolution is on the order of 0.02 nm; in fact, (200) planes in Si have been resolved using spatial distribution maps^{67, 71, 80, 81}. This has allowed APT to play an important role in materials research. Indeed, the relatively recent innovations that allow analysis of electronic materials has led to many important findings, such as dopant segregation to grain boundaries in polycrystalline Si^{46, 47, 87}, gate oxide segregation⁸⁸, as well as direct imaging of dopant-defect interactions^{89, 90} and clustering^{87, 91, 92}. As a purely chemical analysis technique, it is used as an aid to understanding the physical reasons for electronic properties in materials, but separate electrical measurements must be made to validate any inferences from the atom probe data.

Traditionally, thin wires for bulk metallic specimens were sharpened to a ~50 nm radius using electropolishing⁷¹. However, electronic device structures are complex, and often require site-specific sample preparation methods. The evolution of increasingly diminutive transistor dimensions has lessened the disadvantages inherent in the relatively limited analysis volume from APT. Indeed, site-specific analysis has been achieved for many types of transistors; ranging from patterned structures to study lateral As diffusion⁹³, to high-electron mobility AlGaN/GaN HEMTs⁹⁴, and even FinFET structures^{95, 96}.

This type of high-precision sample preparation is achieved using state-of-the-art dual-beam focused-ion beam (FIB) systems with high-resolution scanning electron microscope (SEM) capabilities and in-situ micromanipulation. The general procedure has been well-documented in the literature⁹⁷ and will be briefly discussed here.

In order to prevent implantation damage to the sample surface from the Ga⁺ beam of the FIB, a thin ~50 nm layer of Ni is deposited on the sample surface. Figure 3-8 documents the lift-out procedure for MOSFET device fabricated on silicon-on-insulator (SOI) using SEM imaging in the FIB. After locating the region of interest, ~100 nm Pt is deposited in-situ using a gas-injection source to mark the area and further protect the sample from ion beam damage. Two cuts are made at 30° to the sample normal to form a wedge. An in-situ micromanipulator removes the wedge and transfers the sample to a Si coupon with a 6×6 array of pillars. The wedge is sectioned off at a pillar and then sharpened to a final tip radius ~50 nm using annular milling. The lift-out method can be employed for both blanket wafers as well as devices requiring site-specificity.

3.5 Transmission Electron Microscopy

The transmission electron microscope (TEM) is used in this work to image the microstructure of flash annealed poly-Si, which produces grain sizes on the order of ~20-100 nm. It allows extremely high magnification imaging by transmitting a beam of electrons through an ultrathin sample and generating an image from the transmitted beams. The principle behind such large magnifications comes from the fact that the de Broglie wavelength⁹⁸ of an electron is many orders of magnitude smaller than the wavelength of light, and can be described by (3-10), where λ is the de Broglie wavelength, *h* is Planck's constant, and *p* is the relativistic momentum of the electron, described by the electron to a certain velocity. A typical TEM may operate at an accelerating voltage of 200 kV, which accelerates an electron to 70% of the speed of light, producing a wavelength of only 2.5 pm.

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_0 eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0 c^2}}}$$
(3-10)

The source for electrons is typically a tungsten filament biased such that the work function of the filament is exceeded and electrons are generated via thermionic emission. Next, a series of electromagnetic condenser lenses focuses the electrons into a coherent, monochromatic beam. The first lens determines the spot size while the second lens determines the beam diameter on the sample. The beam passes through the sample and undergoes a series of elastic and inelastic scattering processes. For elastic scattering, Bragg's law (3-11) states that electrons scattered by the same atomic spacing, *d*, will scatter at the same angle, Θ ,

$$\lambda = 2d\sin\Theta \tag{3-11}$$

where λ is the wavelength of the incident beam. The diffracted beams create a diffraction pattern of the material, which is a function of the sample orientation, crystal structure, lattice spacing, and structure factor.

A final objective lens focuses the transmitted beams into an image, often projected onto a phosphor screen or a CCD camera. The use of an objective aperture can allow imaging from only a single diffracted beam, allowing increased contrast along specific crystallographic orientations. Figure 3-9 depicts a ray diagram for the electron beam as it moves through a series of lenses to produce the final image. Polycrystalline structures such as the ones imaged in this study do not produce diffraction patterns with individual spots, but instead due to the random orientation of the crystallites, diffraction rings are observed. Transmission electron micrographs produced in this study were taken in the bright field mode. Because imaging in a TEM requires the transmission of electrons, specimens must be made incredibly thin so as to be electron transparent. For Si, typically this thickness is ~200 nm. For 120 nm poly-Si deposited on 12 nm SiO₂, the preparation of plan-view TEM (PTEM) samples involves a backside polish followed by a backside etch until the desired thickness is achieved.

Poly-Si samples were cored into 3 mm discs and subsequently polished using SiC paper at 250 and 600 grit to a thickness of ~100 μ m. Then, samples were thinned down to electron transparency using drip acid etching. The perimeter of each disc was covered with wax so as to confine the etch to the center of the disc. The acid used was a 3:1 volume ratio of 70% HNO₃: 49% HF. The etch chemistry can be described according to the equations⁹⁹,

$$Si(s) + 4HNO_3(l) \Leftrightarrow 3SiO_2 + 4NO(g) + 2H_2O$$
(3-12)

$$SiO_2(s) + 6HF(l) \Leftrightarrow H_2SiF_6(l) + 2H_2O$$
 (3-13)

Essentially, the nitric acid serves to oxidize the Si surface and then the hydrofluoric acid etches the resulting SiO₂ away.

Alternatively, cross-sectional orientation samples (XTEM) were prepared using a dual-beam focused-ion beam (FIB). The sample surface is first protected with ~60 Å graphitic C, and then marked using in-situ gas injection Pt for further protection from the Ga⁺ ion beam operating at 30 kV. XTEM samples ~100 nm in thickness were produced by continual focused ion beam milling, and subsequently removed and placed onto C grids using micromanipulators¹⁰⁰.

The TEM images in this study were taken with a JEOL 200CX microscope operating at 200 kV using bright field imaging mode.



Figure 3-1. Schematic representation of four-point probe measurement.



Figure 3-2. Sample geometry for deriving sheet resistance from resistivity.



Figure 3-3. Illustration demonstrating the Hall voltage V_H arising due to the Lorenz force from application of a magnetic field, *B*.



Figure 3-4. Illustration of the van der Pauw Hall Effect geometry.



Figure 3-5. Determining characteristic resistance R_A and R_B using van der Pauw technique.



Figure 3-6. Illustration of ion analysis from secondary ion mass spectrometry.





(Source: T. F. Kelly, International Conference on Frontiers of Characterization and Metrology for Nanoelectronics, 2007)



Figure 3-8. Sample preparation for APT using the lift-out method for a MOSFET on SOI. A) In-situ micromanipulator removes wedge formed from angular cuts in front and behind using the ion beam. B) transfer of a portion of the wedge to a pillar for sharpening via annular milling. C) final tip sharpened showing placement of the device layer in the center of the tip.



Figure 3-9. Ray diagram demonstrating the path of the electron beam traveling from source to final image in a TEM.

CHAPTER 4 GRAIN GROWTH IN B-DOPED POLY-SI

4.1 Thermodynamics of Grain Growth

The microstructure of poly-Si is directly related to its electrical performance and reliability. Grain growth in poly-Si has been extensively studied¹⁰¹⁻¹¹⁰ for a variety of doping and annealing conditions. The effect of millisecond flash annealing on heavily B-doped poly-Si is studied here.

While it is known that films doped with As and P show significant grain growth enhancement^{101, 103}, films doped with B have little effect^{101, 104, 108} over a doping concentration range of 1×10^{19} - 1×10^{21} cm⁻³. Interestingly, it was found that B has a compensating effect on grain growth enhancement in As and P doped films^{104, 109}. It is believed that grain growth is a diffusion-controlled process and the effect of impurities is due to changes in the vacancy concentration¹⁰⁴ due to shifts in the Fermi level, as well as a change in the grain boundary energy due to dopant segregation or cluster formation.

Mei¹⁰¹ developed a model for grain growth based on thermodynamic principles. The driving force, F, for grain growth is due to the energy difference between atoms at either side of the boundary, and the interfacial energy between two grains. This interfacial energy drives the grain boundary to minimize its area, and can be expressed by

$$F = \frac{a\lambda b^2}{L} \tag{4-1}$$

where λ is the grain boundary energy, *b* is the lattice constant, *L* is the grain diameter, and *a* is a geometric factor. If growth is diffusion controlled, then the grain boundary mobility should be directly proportional to the Si self-diffusivity.

$$\mu = \frac{D^g}{kT} \tag{4-2}$$

Eq. (4-3) describes the grain boundary mobility, μ , where D^g is the self-diffusivity of Si. The product of the mobility and driving force equals the boundary migration rate, which describes the growth rate

$$\frac{dL}{dt} = \mu F = \frac{a\lambda b^2 D^g}{LkT}$$
(4-3)

By integration, the grain size L can be determined in terms of the initial grain size L_0 , where

$$L = \left[L_0^2 + \frac{2ab^2}{kT} \lambda D_{Si} t \right]^{1/2}$$
(4-4)

assuming the grain-boundary energy and Si self-diffusivity does not vary with time. It has been shown that for primary grain growth, such as the case for B doped poly-Si, grain sizes are limited to the thickness of the film^{101, 111}.

This thickness effect is due to the variation in grain boundary energy when the grains come in contact with the oxide layer. As grains grow larger, this effect becomes more pronounced since more grain surface mobility is slowed at this interface. This effect has been modeled using

$$\lambda = \frac{\lambda_0}{1 + h \frac{2}{Al}} \tag{4-5}$$

where A is the grain boundary area per volume (3/L), *I* is the thickness of the film and *h* is a fitting constant that was experimentally determined to be 6.

4.2 Experimental Conditions

120-nm poly-Si films deposited on 12 nm SiO₂ were doped in-situ to a total dose of 2.5×10^{15} cm⁻². Half of the samples were then preamorphized using Ge⁺ implantation at 40 keV to a dose of 5×10^{14} cm⁻², creating a 60 nm continuous amorphous region. The samples receiving the Ge⁺ preamorphization were then further ion implanted with B⁺ to bring the total dose of the film to 4.9×10^{15} cm⁻². Cross-sectional TEM micrographs of the as-deposited and as-implanted poly-Si films are shown in Figure 3-1. Their corresponding initial doping profiles as measured by SIMS are shown in Figure 3-2.

The films were then annealed using a flash-assist rapid thermal annealing to peak temperatures of 1150 °C, 1250 °C, and 1350 °C. The intermediate pre-flash temperature was 850 °C. An example of a typical temperature profile from the Mattson Millios[™] tool used is shown in Figure 3-3. The pulse width is approximately 1.0 ms. For reference, samples were also annealed using conventional rapid thermal annealing at 988 °C for 5 s.

Following annealing, samples were prepared for plan-view transmission electron microscopy (PTEM) in order to measure grain size distributions. This was done by coring 3 mm discs from each wafer and backside mechanical polishing until ~100 μ m thickness. Samples were then further thinned from the backside using an acid etchant of 75% HNO₃ (70% conc) to 25% HF (49% conc) until electron transparent. Films were imaged using a JEOL 200CX TEM operating at 200 keV.

4.3 Results and Discussion

PTEM revealed as-deposited films as having a very fine microstructure with an average grain diameter of 19 nm. Upon flash annealing, grains became more refined and coarsened to an average diameter of 52 nm in the in-situ doped case and 59 nm in samples with the additional Ge⁺ and B⁺ implant at 1350°C. The amorphous region showed full regrowth at the pre-flash temperature, so there was no regrowth of any amorphous phase during the flash part of the anneal. Secondary grain growth was not observed, and was not expected based on previous literature^{105, 106}.

Grain growth enhancement has been reported to be correlated to hole concentration¹⁰⁴, with slightly greater enhancement at temperatures above 1100 °C¹¹². In Hall effect measurements, it was shown that implanted samples that are flash annealed using a 950 °C pre-flash temperature have an approximately 25% lower hole concentration. Despite a slightly higher thermal budget, grain size measurements for this anneal condition fell in between that of the in-situ doped sample and the implanted sample using an 850 °C pre-flash temperature. This confirms the model proposed by Kim¹⁰⁴, which predicts enhancement as a function of hole concentration, but even their model shows the enhancement to only be up to 25% at 1000 °C for the narrow range of hole concentrations studied here. The significant overlap in error bars between the insitu doped and implanted samples implies that there is not a significant difference in grain growth between the two doping concentrations, and this has been confirmed experimentally¹⁰¹ for B concentrations between 1×10^{19} - 1×10^{21} cm⁻³ at annealing temperatures between 900-1200 °C. However, Hall measurements shown later reveal that these minor differences in grain size reveal themselves in mobility values.

PTEM micrographs and grain size distributions for each anneal condition can be seen in Figure 3-4 for the in-situ doped film and in Figure 3-5 for the implanted film annealed using an 850 °C pre-flash temperature. Figure 3-6 shows the PTEM and grain size distributions for the implanted samples using a 950 °C pre-flash temperature.

Assuming a grain boundary energy^{101, 113} of 1.0 J/m², the model for grain growth was fit to the experimental measurements using an activation energy of 4.7 ± 0.1 eV, This corresponds well with the activation energy for Si self-diffusion³⁷, which was reported to be 4.7 eV in the temperature range 800-1100 °C. A value of 5.1 eV¹¹⁴ has also been reported for temperatures above 1100 °C. The constant *a*, which represents the geometric factor multiplied by the Si self-diffusion pre-exponential was calculated to be 2.5×10⁶ cm²-s⁻¹. The model is plotted along with average grain size measurements in Figure 3-7. Model matches well for both flash annealing and RTA conditions.

Because of the similarity in activation energy for grain growth to that of Si selfdiffusion, the grain growth mechanism in these heavily B-doped poly-Si films under flash annealing appears to be the same as that of the mechanism for lattice dislocation motion. It has been shown that grain boundaries in poly-Si are primarily made up of arrays of dislocations, both simple edge and partial dislocations as well as stacking faults¹¹⁵. If the motion of point defects is the primary mechanism for grain growth in these films, then the behavior of the boundaries can be described by dislocation climb¹⁰⁴. Enhancement in grain growth from n-type dopants has been attributed to the effect of an increase in the concentration of charged vacancies¹⁰⁵ on the Si selfdiffusivity. It has been demonstrated¹¹⁶ that heavy doping of B induces a shift in the

Fermi level, which reduces the number of charged vacancies. This likely explains why B does not enhance grain growth in the way P and As doping do.



Figure 4-1. Cross-sectional transmission electron micrograph of poly-Si film. A) asdeposited poly-Si film. B) after Ge⁺ preamorphization implant and B⁺ implant.



Figure 4-2. SIMS profiles for initial B concentrations for as-deposited and with additional Ge^+ and B^+ implant



Figure 4-3. Temperature profile for a 1350 °C flash anneal with a pre-flash temperature of 950 °C.



Figure 4-4. PTEM and grain size distribution for in-situ B doped poly-Si. A) asdeposited. B) 1150 °C flash. C) 1250 °C flash. D) 1350 °C flash. E) 988 °C RTA.



Figure 4-5. PTEM and grain size distribution for Ge⁺ and B⁺ implanted poly-Si. A) 850 °C iRTP (no flash). B) 1150 °C flash. C) 1250 °C flash. D) 1350 °C flash. E) 988 °C RTA.



Figure 4-6. PTEM and grain size distribution for Ge⁺ and B⁺ implanted poly-Si using 950 °C pre-flash temperature (iRTP). A) 1150 °C flash. B) 1250 °C flash. C) 1350 °C flash.



Figure 4-7. Average grain sizes for in-situ doped and additionally implanted poly-Si with flash annealing.

CHAPTER 5 MOBILITY, ACTIVATION, AND DEACTIVATION OF B-DOPED POLYSILICON WITH FLASH ANNEALING

5.1 Poly-Si in HBT Technology

As microelectronics processing begins to adapt advanced annealing methods such as millisecond flash annealing^{8, 10}, it is important to understand the effect of these processing conditions beyond that of crystalline Si. Poly-Si has many applications in CMOS device fabrication⁶ and continues to play a crucial role in devices such as heterojunction bipolar transistors (HBT)^{5, 7}.

When compared to c-Si, the most obvious separation is the presence of grain boundaries. Grain boundaries primarily act as scattering sites and potential barriers⁵⁹ leading to reduced carrier mobility in polysilicon⁴⁹. However, at sufficiently high doping levels, the resistivity of polysilicon can approach that of single-crystalline silicon⁴⁹ due to the reduced carrier mobility in both environments from high concentrations of active, ionized impurities, which also act as scattering sites. Additionally, the existence of grain boundaries is often a lower energy state for dopants to segregate to and deactivate^{45,} ¹¹³. This has been reported for As^{45, 46} and P⁴⁵, but is less often seen for B except at very high concentrations^{3, 47}.

One of the advantages of the presence of grain boundaries is their ability to act as recombination centers for point defects⁴³. It has been shown that grain boundaries act as an effective sink for vacancies, and this may also be true for interstitials. While millisecond annealing techniques such as flash and laser annealing have allowed very high activation with minimal diffusion, the observance of post-annealing dopant deactivation is also of concern. For As, the deactivation is attributed to formation of As clusters with vacancies¹¹⁷ in c-Si. In poly-Si, As segregation to the grain boundaries^{45, 53}

was seen with cyclical anneal cycles. In the case of B, deactivation has been found to occur due to the presence of {311} defects present in the end-of-range following preamorphizing implants that have not been dissolved with the minimal thermal budget of millisecond annealing¹¹⁸⁻¹²⁰. This mechanism for deactivation should be minimized in a polycrystalline structure if the grain boundaries are significant sinks for excess interstitials.

Oftentimes in device fabrication processing, use of single-crystalline silicon for some structures is simply unfeasible due to the lack of a crystalline surface to act as a seed for epitaxy^{5, 6}. One such example is in the case of high-performance SiGe:C HBTs, where poly-Si forms the elevated extrinsic base in the base layer of the structure and is deposited over oxide⁵. A schematic is illustrated in Figure 5-1. Improving the transit frequency, f_T , and the maximum oscillation frequency, f_{MAX} , has proven to be challenging due to compensating effects for a given thermal budget. A low thermal budget aids in delivering the highest transit frequencies due to reduced diffusion in the base, thereby allowing a thin base width⁷. However, due to the increased base resistance under these thermal processing conditions, f_{max} is reduced.

With this in mind, the application of flash annealing to B-doped poly-Si presents itself very favorably^{7, 8}. High temperature annealing (up to 1350°C) allows greater B solubility⁹, and therefore lower resistance, while short annealing timescales significantly limits diffusion⁸. The typical pulse width¹⁰ for flash annealing is on the order of 1 ms. While the scope of this paper focuses on the electrical properties of poly-Si in its application as the elevated extrinsic base in bipolar CMOS technology⁵, the results

presented form a fundamental basis for understanding the effect of millisecond annealing on sheet resistance, activation, and mobility of heavily B-doped poly-Si films.

5.2 Experimental Methods

120 nm polysilicon films were deposited by low-pressure chemical vapor deposition on 12 nm of oxide over bulk Si wafers and in-situ doped with B during film growth. The total dose of the in-situ doped film is 2.5×10^{15} cm⁻² and represents an environment below solid solubility at higher flash temperatures. Some films are additionally doped via ion implantation using first a Ge⁺ pre-amorphization implant at 40 keV to a dose of 5×10^{13} cm⁻². This forms a continuous amorphous layer of 60 nm. After pre-amorphization, an additional 10 keV B⁺ implant is added to bring the total dose to 4.9×10^{15} cm⁻², as measured by SIMS. In this case, for all annealing temperatures, the peak concentration of B is above solubility. As-deposited and as-implanted profiles for both samples are shown in Figure 5-2.

Films were then flash annealed using an impulse rapid thermal process to a preflash temperature (iRTP) of 850 °C and flashed to temperatures of 1150°C, 1250°C, and 1350°C. For comparison, a 950 °C iRTP was also investigated. Finally, the effect of an RTA anneal at 988 °C for 5 s prior to annealing with the flash system was examined.

In c-Si, the use of an RTA pre-anneal has been shown to improve sheet resistance by removing EOR defects from implantation¹²⁰. Also, because poly-Si gates for CMOS are typically doped at the source-drain implantation step, the significantly reduced diffusion seen with flash annealing leads to "poly depletion"³⁰ in the gate, which can become the dominant effect in gate capacitance. Because diffusion in poly-Si is significantly greater than in crystalline Si due to the presence of grain boundaries²⁹, a short, lower temperature RTA allows sufficient dopant to reach the poly/gate oxide

interface. It is hoped that activation can be further improved using flash annealing in addition to conventional RTA.

Post-flash annealing was carried out using 30 min furnace anneals under N_2 ambient between 400-800°C to study thermal stability of the dopant. Hall measurements were only done on 850 °C iRTP samples annealed at 650 °C and above because noticeable deactivation did not begin to occur until that temperature.

Electrical measurements were done with a Lakeshore 7507 Hall measurement system using the Van Der Pauw method⁶¹. Doping levels were sufficiently high such that good ohmic conduction ($r \ge .99$) was achieved using indium-gallium contacts. Due to the high concentration of dopant in the material, sheet number measurements were calculated using a Hall Scattering Factor of 0.7^{63} . Prior work¹²¹⁻¹²³ for Hall measurements in polycrystalline structures has demonstrated that for sufficient doping, the Hall constant should be accurate in measuring the carrier concentration within the grains. This is because when doping far exceeds the carrier trap density, as is the case in the films studied here, the potential barrier at the grain boundary is very small (~5 meV)⁵⁷.

5.3 Electrical Activation and Mobility

Sheet resistance measurements are displayed in Figure 5-3 for both the asdeposited in-situ doped samples as well as the implanted samples using an 850°C and 950°C pre-flash temperature. Values for samples that were pre-annealed by RTA are also plotted. By effectively doubling the dose of the dopant, sheet resistance values fall roughly 40-50% for all flash temperatures. No difference was observed in sheet resistance by using a 950 °C pre-flash temperature. Sheet resistance improves linearly with RTA pre-anneal and exponentially with only flash anneal. This is due to both

activation and mobility improvements with flash annealing, whereas an RTA pre-anneal grows the grains appreciably prior to flash. This is verified in Figure 5-4 where mobility values are clearly seen to be set by the RTA pre-anneal. Grain size measurements reported previously reveal that the 988 °C 5s RTA anneal is roughly equivalent to a 1250 °C flash anneal in terms of grain growth. Further mobility improvements at 1350 °C flash temperatures are likely compensated by the increase in carrier concentration leading to a reduction in expected mobility due to ionized impurity scattering.

Active sheet number values, shown in Figure 5-5, increase linearly with flash temperature. Despite the increased activation with temperature, mobility values continue to rise. This is due to grain growth, which was verified with plan-view transmission electron microscopy (PTEM). While both the in-situ doped and implanted samples show almost identical microstructures for a given anneal condition, there is a slight improvement in mobility for the implanted sample with roughly twice the dose. In c-Si, such a high activation would lead to a lower mobility due to ionized impurity scattering. Seto's⁵⁷ measurements for hole mobility shows an increasing trend from $5 \times 10^{18} - 5 \times 10^{19}$ cm⁻³ doping concentrations. The active concentrations shown here are above 1×10^{20} cm⁻³, up to as high as 4×10^{20} cm⁻³. This represents a concentration regime outside of his work. Kamins⁵⁸ reported a peak mobility in poly-Si at a hole concentration of 2.5×10¹⁸ cm⁻³, and reduced mobility for concentrations above that regime. However, a major difference in their work is the grain size in the films; Seto reported an average grain size of 20 nm while Kamins reported grain sizes as large as 500 nm in a 5 µm film. The finer grain microstructure in Seto's film more accurately resembles the microstructure of the films in this study. The prevalence of so many

boundaries may act as a significant source for resistivity, and so it should follow that a higher concentration of active B, which effectively lowers the grain boundary potential barrier^{15, 57, 59} can also improve the hole mobility. At larger grain sizes, it is likely that other factors that increase resistance such as impurity scattering play a more significant role.

Unlike the n-type dopants As and P, B has been shown to enhance grain growth only slightly, and this enhancement does not vary noticeably with B concentration^{101, 104}. Also, B doped poly-Si films do not undergo secondary grain growth, where grain sizes grow beyond the film thickness^{105, 106} driven by the surface energies of certain grain orientations. This type of grain growth has been previously seen to occur significantly with P and less so with As doped poly-Si¹⁰⁴⁻¹⁰⁹. Due to millisecond annealing times with flash annealing, grain sizes in this study do not grow appreciably, beginning with an average grain size of 19 nm and reaching a grain size of 59 nm at 1350°C. There was not a significant difference in microstructure for samples that received the Ge preamorphization implant, additional B implant, or 950 °C iRTP anneal.

For implanted samples, there is a roughly 25% lower sheet number measured for samples flash annealed from a 950 °C iRTP temperature instead of 850 °C iRTP. Further reductions in activation were seen with RTA pre-annealed samples. These values are plotted in Figure 5-5. This effect was not significant in the in-situ doped samples, suggesting that this is an effect from the additional implants. Possible causes for this reduced activation can be attributed to defect induced cluster formation or segregation to grain boundaries.

Preamorphization by ion implantation and solid phase epitaxial regrowth (SPER) has been used extensively in c-Si to improve activation of dopant by direct incorporation into substitutional sites on the lattice during regrowth. The solubility levels achieved using this process²² is of the order of a few 10²⁰ cm⁻³ and almost independent of temperature²³, however, there have been reports that suppression of regrowth by using a low pre-flash temperature allows higher activation when regrowth occurs during the high temperature "flash" portion of the temperature profile^{124, 125}. This is not the case seen here since the amorphous layer shows full regrowth with only the 850 °C iRTP anneal. Because SPER allows activation above equilibrium values, thermal processing after regrowth can lead to a deactivation simply as a return to equilibrium.

Figure 5-6 compares the sheet number values for flash annealed samples to RTA samples. 850 °C and 950 °C data points represent the spike anneal from the iRTP while 988 °C represents the 5s conventional RTA. They are plotted together as RTA since their anneal times are significantly longer than the flash. Also plotted are the calculated theoretical activation curves based on solubility data for c-Si⁹. It is evident that because of SPER, activation prior to flash is above solid solubility for the implanted case. This difference in initial solubility benefit from the lower iRTP temperature accounts for greater activation when flash occurs.

The larger differences at higher flash temperatures suggests a separate pre-flash deactivation process, most likely attributable to cluster formation. Creation of the amorphous layer from ion-implantation has been known to deactivate B due to the interstitials generated at the end-of-range leading to boron-interstitial cluster formation¹²⁶. However, the high temperature activation does not follow either path of

typical boron-interstitial-cluster (BIC) dissolution⁴¹. Similar behavior to that reported here was seen with flash-annealed samples in crystalline Si¹²⁷, and is suggested to be formation of a less stable cluster, which dissolves at high temperatures.

Figure 5-7 shows work from Castillo-Camillo¹²⁷ involving flash annealing of crystalline Si with similar conditions studied here in poly-Si. B was implanted at 1 kV to a dose of 1×10^{15} cm⁻². A Ge preamorphizing implant was also done at 30 kV to a dose of 1×10^{15} cm⁻² and subsequently flash annealed to temperatures between 1000 °C – 1300 °C using a 700 °C iRTP. Similar to the results in poly-Si, activation begins above solid solubility at lower temperatures due to solid phase regrowth. However, at the highest flash temperature, activation is below theoretical levels and this was attributed to cluster formation. This is in contrast to the results from this study in poly-Si, which suggests that cluster formation may be reduced in a polycrystalline structure, where excess interstitials may be absorbed by the grain boundaries.

5.4 Electrical Deactivation and Mobility

Post-flash deactivation measurements were made for 850 °C iRTP samples only. Sheet resistance measurements for samples flashed to 1350 °C are shown in Figure 5-8. Significant rise in sheet resistance was seen only above 650 °C for constant 30 min anneals. Grain size measurements confirm that there is no detectable increase in average grain size for samples annealed at 800 °C for 30 min, allowing for activation and mobility measurements at a constant grain size.

Activation values are plotted in Figure 5-9 for all flash temperatures. Values for activation converge at 800 °C, but implanted samples retain roughly 50 percent more activated dopant. This is unexpected and will require further study. The number of deactivated carriers can be calculated by subtracting the final activation value from the

initial activation value. For all flash temperatures below 1350 °C, the calculated activation energy for deactivation is roughly 1.0±0.2 eV. For 1350 °C flash temperatures, both the in-situ doped and implanted samples retain more activation at 650 °C, but follows the same trend at 700 °C and above. This is likely to be related to grain boundary segregation, since the lower flash temperatures have smaller grains. Segregation values tend to be higher at lower temperatures⁴⁵ due to more available grain boundary surface area.

Mobility measurements following deactivation anneals are shown in Figure 5-10. Because there was no measurable grain growth from these anneals, the mobility gains are directly related to the reduction in active ionized impurities. The lowest average hole concentration measured is 5×10¹⁹ cm⁻³, which corresponds to an estimated grain boundary potential barrier of only 5 meV according to Seto's model⁵⁷. Therefore, mobility gains from deactivation can be solely attributed to less ionized impurity scattering.

Modeling for mobility in poly-Si has been done by using Mathiessen's formula¹²⁸ to combine scattering terms from majority carrier scattering, $\mu_{i,maj}$, grain boundary potential boundary scattering, μ_{Eb} , and a third extracted term describing the influence of grain size, denoted as μ_{GB} . The overall mobility can be expressed as,

$$\mu = \left(\frac{1}{\mu_{i,maj}} + \frac{1}{\mu_{Eb}} + \frac{1}{\mu_{GB}}\right)^{-1}$$
(5-1)

Majority carrier scattering has been well studied¹²⁹, and can be described by

$$\mu_{i,maj} = \mu_0 + \frac{\mu_{max} - \mu_0}{1 + \left(N/C_{ref,1}\right)^{\alpha_1}} - \frac{\mu_1}{1 + \left(C_{ref,2}/N\right)^{\alpha_2}}$$
(5-2)

where *N* is the concentration of holes, and the other parameters are given in Table 5-1. The influence of minority carrier scattering is ignored here due to the heavy doping concentration of the material.

Next, scattering by the grain boundary due to the formation of potential barriers was modeled by Seto⁵⁷ and was discussed in Chapter 2. At the doping concentrations studied here, the magnitude of grain boundary potential barrier formed is almost inconsequential, however, it is included to better represent the poly-Si environment at lower concentrations. The mobility term, μ_{Eb} , can be described by

$$\mu_{Eb} = Lq \left(\frac{1}{2\pi m * kT}\right)^{1/2} \exp\left(\frac{-E_B}{kT}\right)$$
(5-3)

where *L* is the grain size, *q* is the elementary charge, and E_B represents the energy barrier required for a carrier to pass over the grain boundary, given by

$$E_B = \frac{qQ_t^2}{8\varepsilon N} \tag{5-4}$$

where *N* is the average hole concentration, Q_t represents the trap state density $(3.34 \times 10^{12} \text{ cm}^{-2})^{57}$, and ε is the dielectric permittivity of poly-Si.

Finally, given the mobility terms for majority carrier scattering and potential barrier scattering, a fitting term representing the influence of the grain size on the overall mobility in poly-Si was extracted. μ_{GB} is of the form $Aexp(-\beta)$, where

$$A = 1.8 \times 10^{12} L^2 + 1.7 \times 10^6 L + 25$$
(5-5)

and

$$\beta = 1.78 \times 10^{20} N \exp(-3.34 \times 10^5 L)$$
(5-6)

Applying Mathiessen's formula, Figure 5.10 plots the mobility behavior with deactivation for each initial flash condition for the in-situ doped and implanted samples, while the models are generated with the grain sizes measured from PTEM. Sheet numbers have been converted to an average concentration within the film. The model agrees well with the experimental data. Mobility values measured here for poly-Si are roughly half that of c-Si¹²⁹ for a given active carrier concentration, suggesting that both impurity concentration and microstructure play a role in determining mobility in these films.

5.5 Summary

Hall measurements for flash annealed poly-Si samples have provided significant insight into the activation and mobility behavior for heavily B-doped films. Activation improvements with lower iRTP temperatures have been attributed to the above equilibrium activation achievable using the SPER process. Reduced activation from increasing pre-flash thermal budget was therefore shown to be attributed to a reduction in pre-flash activation following regrowth of the amorphous layer.

Mobility measurements upon activation and deactivation verify that mobility is a function of both active concentrations of dopant as well as microstructure. The linear behavior in mobility improvement with flash annealing suggests the compensating effect between increasing grain size (improved mobility) and increasing activation (reduced mobility). By holding microstructure constant, deactivation studies show increases in mobility values due to less ionized impurity scattering. Mobility values have been accurately modeled over the deactivation temperature range of 650 °C to 800 °C. It has been shown that Seto's model, which assumes grain boundary scattering to be the dominant reason for resistivity, cannot apply completely in such highly doped material.
The difference in mobility between poly-Si and c-Si values¹²⁹ suggest that both ionized impurity scattering and grain boundary scattering contribute to the overall mobility in poly-Si films.

(p-type Si)
470.5
470.5
44.9
29
0.719
2.0
2.23×10 ¹⁷
6.10×10 ²⁰

 Table 5-1.
 Majority carrier simulation parameters.



Figure 5-1. Schematic showing elevated extrinsic base for a heterojunction bipolar transistor. Epitaxial growth is allowed over the crystalline heavily-doped collector but not over STI.



Figure 5-2. SIMS profile comparison for initial B concentrations for as-deposited and with additional Ge^+ and B^+ implant.



Figure 5-3. Sheet resistance comparison between as-deposited in-situ doped and additionally B implanted poly-Si films at various flash anneal conditions.



Figure 5-4. Comparison of mobility values between flash-only and RTA + flash anneals. Only the 850 °C iRTP measurements are shown.



Figure 5-5. Active sheet number measurements. a) implanted samples and b) in-situ doped samples. Implanted samples show less activation with increased pre-flash thermal budget.



Figure 5-6. Sheet number for 850 °C iRTP flash anneals compared with RTA anneals. Solid and dashed lines represent theoretical activation curves for implanted and in-situ doped samples, respectively.



Figure 5-7. B activation in crystalline Si from flash annealing of a 1 kV B implant to a dose of 1×10¹⁵ cm⁻², and 30 kV Ge PAI. Solid line represents the theoretical activation.



Figure 5-8. Sheet resistance as a function of furnace annealing temperature following 1350°C flash anneal. Furnace annealing duration is 30 min.



Figure 5-9. B deactivation measurements.



Figure 5-10. Hall measured mobility values for 30 min furnace anneals following flash anneals.



Figure 5-11. Hole mobility behavior as a function of grain size from flash annealing. Solid lines represent the model. A) in-situ doped sample. B) w additional B and Ge implant.

CHAPTER 6 B SEGREGATION TO GRAIN BOUNDARIES AND DIFFUSION IN POLYCRYSTALLINE SI WITH FLASH ANNEALING

6.1 Importance of Dopant Segregation

Polycrystalline Si, or poly-Si, has many applications in the field of microelectronic devices, from conventional field-effect transistors⁶, to heterojunction bipolar transistors⁵, and photovoltaics¹³⁰. Due to the ever-shrinking feature sizes in transistors, innovations in annealing beyond conventional rapid thermal processing are necessary to limit diffusion and increase activation of dopants⁷. In particular, flash annealing allows low thermal budgets with high temperatures and very short time scales on the order of 1 ms⁸. The combination of high B concentration with low thermal budgets presents an ideal environment for B segregation to the grain boundaries in poly-Si. The degree of segregation can have a profound effect on B diffusion due to the significantly enhanced diffusivity of impurities within grain boundaries. Also, segregated dopants are electrically inactive and reduce the conductivity of the material. Therefore, it is important to understand the effect of millisecond annealing on B doped poly-Si films.

Three-dimensional atom probe tomography (APT) allows direct analysis of dopant segregation to grain boundaries and other crystalline defects^{89, 90, 131}. In fact, the technique has already been employed to demonstrate segregation of As and P to grain boundaries in a polysilicon gate electrode⁴⁶. However, there have been conflicting reports as to the segregation of B to grain boundaries. Inoue *et al.* has shown that it does not segregate⁴⁶ while atom probe measurements from Thompson *et al.* show significant segregation⁴⁷ at grain boundary triple points. Even prior to 3D APT, B segregation to grain boundaries was debatable. Activation and deactivation with cyclical annealing was seen for As doped poly-Si, but not for B for concentrations below solid

solubility⁴⁵. On the other hand, it has also been reported that at very high concentrations, (>2 at%) B formed precipitates at the grain boundaries of poly-Si³. In this work, a weak but detectable segregation of B to the grain boundaries is reported using 3D APT. Grain growth was found to significantly reduce the amount of segregated B due to the reduction in grain boundary surface area. Values obtained from the experimental data were applied to a poly-Si diffusion model^{51, 52}, which accurately predicts diffusion of B in flash annealed poly-Si. Hall measurements suggest that the segregated B is electrically inactive.

6.2 Experimental Methods

120 nm poly-Si films were deposited by low-pressure chemical vapor deposition on bulk Si wafers with ~12 nm of SiO₂. B doping was done in-situ to a total dose of 2.5 × 10^{15} cm⁻², which amounts to a peak concentration below the solid solubility level⁹ of 3.0 × 10^{20} cm⁻³ for anneal temperatures above 1250 °C. Additionally, some samples were further doped by ion implantation, beginning with a preamorphizing implant using Ge⁺ at 40 keV to a dose of 5.0 × 10^{14} cm⁻², followed by an additional B⁺ implant at 10 keV to bring the total dose of the film to 4.9×10^{15} cm⁻² as measured by SIMS. The preamorphizing implant produced a 60 nm-thick continuous amorphous layer. At this dose, the peak B concentration remains above the solid solubility limit at all flash temperatures. Initial doping profiles are displayed in Fig. 1.

Annealing was carried out for both B doses using an impulse rapid thermal anneal (iRTP) at a ramp rate of 150 °C/s to a pre-flash temperature of 850 °C, and then subsequently flash annealed to 1150 °C, 1250 °C, and 1350 °C with a pulse duration of 1 ms. For comparison, samples were also annealed using a conventional rapid thermal anneal (RTA) at 988°C for 5s.

Specimens were prepared for 3D APT using an FEI Strata DB235 dual-beam focused-ion beam (FIB) using the liftout method⁹⁷. The samples were first coated with 50 nm Ni by sputter deposition to act as a sacrificial buffer layer to Ga beam damage from the FIB. Annular milling produced atom probe tips with a radius of curvature of less than 50 nm. 3D APT was carried out using an Imago LEAP 3000X-Si system equipped with a 532 nm green pulsed laser. The laser pulse energy was set to 1.0 nJ and specimen temperature cooled to 60 K. The laser pulse rate was set to 100 khz with an evaporation rate of 0.5%. Typical datasets ranged between $5-10 \times 10^6$ ions. Concentration profiles for the films were measured using secondary ion mass spectrometry (SIMS), with a Cs⁺ primary beam at 3 keV.

6.3 Results

3D APT reconstructions revealed the presence of local areas of higher concentration than the bulk. By using the volume render function in the reconstruction software, local concentrations less than 1 at% within one standard deviation can be filtered out. This was done in order to aid in locating areas of relatively higher B concentrations. The volume render is illustrated in Figure 6-2, revealing the segregation of B to the grain boundaries. This grain boundary measures 42 nm, which is the average grain size for this sample which was annealed at 988°C for 5 s. In Figure 6-3, a one-dimensional concentration profile across the grain boundary is compared with a profile within the grain. This was done by extracting a concentration profile along the zaxis of a 10 nm x 10 nm x 40 nm data pipe across the grain boundary in the reconstruction. A second data pipe of the same dimensions was inserted into an area within a grain. Segregation of B to the grain boundary is clearly evident.

From Eq. (6-1), the ratio of the peak concentration within the boundary to the concentration within the grain represents the local segregation coefficient, m_{seg} . Because this represents only the local segregation of the dopant to a single grain boundary, an estimate must be made to account for the total amount of segregated B in the film. Assuming spherical grains with a diameter *L*, the volume fraction term, X_{gb} , in (6-2), is estimated using a grain boundary thickness, t_{gb} , of 2*a*, where *a* is the lattice constant¹¹³ 5.43 Å, multiplied by (3/*L*), the surface-area-to-volume ratio¹³². Multiplying the local segregation coefficient, m_{seg} by X_{gb} gives p_{seg} , the segregation coefficient used in prior models for diffusion of dopants in polysilicon^{51, 52, 101}

$$m_{seg} = \frac{C_B^{gb}}{C_B^g} \tag{6-1}$$

$$X_{gb} = t_{gb} \left(\frac{3}{L}\right) \tag{6-2}$$

$$p_{seg} = X_{gb}m_{seg} = \frac{A}{L(t)}\frac{Q_{Si}}{N_{Si}}\exp\left(\frac{G_T}{kT}\right)$$
(6-3)

The equation for p_{seg} used in the PEPPER⁵¹ diffusion model given by Eq. (6-3) has been used as the basis for the experimental results obtained from 3D APT. Q_{Si} is the density of segregation sites available on a grain boundary, previously calculated⁴⁵ to be 2.64 × 10¹⁵ cm⁻² for spherical grains, and N_{Si} is the density of silicon, 5.0 × 10²² cm⁻³. Values for p_{seg} are plotted versus flash temperature for both the implanted and in-situ doped samples in Figure 6-4. The pre-exponential *A* was calculated to be 0.80 ± 0.06, with a heat of segregation, *G_A*, of 0.36 ± 0.2 eV. For comparison⁴⁵, previous values for the pre-exponential published for As and P are 3.02 and 2.46, respectively, and both share a heat of segregation of 0.456 eV at a concentration of 2.0 × 10^{19} cm⁻³. For B, there is significantly less segregation to the grain boundaries when compared to As or P^{45} .

The term *L*(*t*) in Eq. (6-3) represents the grain diameter. Grain growth mechanisms in B doped poly-Si have been well-studied^{101, 102} for furnace anneals, and so the work here is an extension of their model to the millisecond annealing regime. Grain size measurements were taken using plan-view transmission electron microscopy, and fit to a model for grain growth^{51, 101} with flash annealing conditions. This is given by Eq. (6-4), where L_0 is the initial grain diameter, *b* is the lattice constant, λ is the grain boundary energy, and *t* is the duration of the anneal (*t* = 0.001 s for flash anneals). Assuming a grain boundary energy^{101, 113} (λ_0) of 1.0 J/m², the pre-exponential multiplied by the geometric term *a* is calculated to be 2.5 x 10⁶, and the activation energy for grain growth was found to be 4.7 ± 0.1 eV, which is the same activation energy reported for Si self-diffusion of 4.7 eV^{37, 101}. It is important to note that the grain boundary energy, λ , will decrease as the grain size increases,¹⁰¹ representing a change in interfacial energy with the underlying oxide. This was discussed in Chapter 4, and is represented by Eq. (6-5).

$$L = \left[L_0^2 + \frac{2ab^2}{kT} \lambda D_{Si} t \right]^{1/2}$$
(6-4)

$$\lambda = \frac{\lambda_0}{1 + h \frac{2}{Al}} \tag{6-5}$$

Based on previous reports^{101, 133}, no effect on microstructure was expected due to the additional Ge⁺ pre-amorphization and B⁺ implant, and indeed no there was not a

significant effect. There was also no effect seen with regard to transient enhanced diffusion²⁸, which was not expected for a number of reasons. First, even at the lowest flash temperature of 1150 °C, the enhancement factor of C_i/C_i^* in transient enhanced diffusion approaches unity due to the high concentration of intrinsic interstitials for crystalline silicon³⁷, although it is not known how a polycrystalline structure might effect this value. Secondly, it is likely that the significantly greater diffusivity via the grain boundaries overwhelmingly dominates as the mechanism for diffusion.

Diffusion of B in poly-Si is modeled using the Florida Object Oriented Process Simulator¹³⁴ (FLOOPS) using equations based on the PEPPER model⁵¹, which separates the diffusivity of the impurity into two components; diffusivity within the grain (6-6) and diffusivity along the grain boundary (6-7). The two differential equations are coupled with a kinetic reaction term, which drives $C^{gb}/C^g = p_{seg}$ at steady state. τ is a constant that represents the rate of segregation. The extrinsic diffusivity within the grain (6-8) comes from Fair's model¹³⁵ for B diffusivity, which accounts for the enhanced diffusivity with higher B concentration in the films¹³⁵ by way of an enhancement factor of (p/n_i) , where p is the hole density from Hall effect measurements and n_i is the intrinsic hole concentration¹³⁶ at the anneal temperature. The diffusivity along the grain boundary (6-9) was determined previously²⁹.

$$\frac{\partial C_B^g}{\partial t} = D_B^g \frac{\partial^2 C_B^g}{\partial x^2} + \tau^{-1} \Big(C_B^g p_{seg} - C_B^{gb} \Big)$$
(6-6)

$$\frac{\partial C_B^{gb}}{\partial t} = D_B^{gb} \frac{\partial^2 C_B^{gb}}{\partial x^2} - \tau^{-1} \Big(C_B^g p_{seg} - C_B^{gb} \Big)$$
(6-7)

$$D_B^g = 0.037 \exp\left(\frac{-3.46}{kT}\right) + \left(\frac{p}{n_i}\right) 0.76 \exp\left(\frac{-3.46}{kT}\right)$$
(6-8)

$$D_B^{gb} = 0.012 \exp\left(\frac{-2.0}{kT}\right)$$
 (6-9)

Using these equations, the model for B diffusion in poly-Si is overlaid with the respective SIMS profiles in Figure 6-1. For flash anneals, the time-temperature profiles are simulated based off of the temperature profiles generated from measuring the top-surface of the wafer using an optical pyrometer. The wafers experienced a 150 °C/s ramp rate from 20 °C to the pre-flash temperature of 850 °C, followed by the flash, which is represented using a 10^6 °C/s ramp rate and dwell time of 1 ms at the peak flash temperature. The cooling is modeled at -1×10^5 °C/s, -7×10^4 °C/s, and -4×10^4 °C/s from the peak flash temperatures of 1150 °C, 1250 °C, and 1350 °C, respectively. Following the flash, the wafer surface temperatures rise to 900 °C, 920 °C, and 950 °C, for the 1150 °C, 1250 °C, and 1350 °C flash anneals, respectively. The rise in surface temperature is more pronounced for higher flash temperatures. Finally, the wafers cool at 100 °C/s to room temperature. Similarly, temperature profiles for the 850 °C iRTP spike and 988 °C RTA anneal are modeled using 150 °C/s and 75 °C/s ramp rates, respectively, and both cooled at 100 °C/s.

The constant τ^{-1} representing the rate of segregation has been extracted from the model iteratively by fitting to the diffusion profiles. It is shown to have Arrhenius behavior, given in Eq. (6-9), and was found to be independent of anneal time.

$$\tau^{-1} = 6.1 \times 10^{22} \exp\left(\frac{-5.8}{kT}\right) \tag{6-10}$$

As an example, Figure 6-5 depicts the separation of the two concentration profiles, C^g and C^{gb} as the dopant diffuses through the layer for the 1350 °C flash anneal of the in-situ doped sample. At this annealing condition, all of the dopant is below the solid solubility limit for B in crystalline Si⁹. Hall measurement for this sample gives a sheet number of 2.36 × 10¹⁵ cm⁻², which agrees well with the integrated area under the curve for C^g (2.35 x 10¹⁵ cm⁻²) in Figure 6-5.

Hall measurements also revealed that the active dose in the implanted case matches well with the theoretical solubility of B in crystalline Si⁹. However, for the in-situ doped sample, activation does not reach the theoretical value until 1350 °C flash temperatures. These results are shown in Figure 6-6 with comparisons to theoretical activation levels based on solubility data⁹. Because the in-situ doped sample had a lower total dose, segregation to the grain boundary accounted for a noticeable difference from expected activation values. For the additionally implanted samples, the concentration of segregated B to the grain boundary had reached saturation due to the high dose. This is verified in Table 6-1, where the predicted active dose for the in-situ doped samples, calculated by assuming the segregated B is inactive, matches closely with the sheet number values from Hall measurements. The predicted active dose equals the total dose by p_{seg} .

6.4 Discussion

B segregation to grain boundaries was imaged directly using 3D atom probe tomography, and measured segregation coefficients were applied to a diffusion model to accurately predict the diffusion of B in poly-Si. Given solubility constraints, the model allows reasonable estimates for the expected activation levels of the dopant by assuming individual crystallites have the properties of bulk single-crystalline Si. From this, it can be inferred that the B segregated to the grain boundaries is electrically inactive.

Although some prior work did not detect B segregation to grain boundaries, their conclusions were inferred from electrical measurements⁴⁵. 3D APT has allowed direct evidence for B segregation to the grain boundary, while at the same time confirming that for most traditional thermal processing, the amount of segregation is low and may not be detectable electrically. Furthermore, the experimental conditions here create an idealized environment for B segregation. The material is very heavily doped and grain growth is suppressed due to millisecond annealing times. Still, the highest local segregation coefficient measured here is only ~3.0 at the lowest flash temperature of 1150 °C, and drops to as low as ~1.5 with further annealing. It is shown that longer duration anneals and high temperature anneals, both conditions that promote grain growth and solubility, respectively, lead to a significant reduction in the already relatively weak segregation of B to the boundary.

T °C	Predicted Active Dose (cm ⁻²)	Hall Sheet Number (cm ⁻²)
1150	1.5×10 ¹⁵	1.32×10 ¹⁵
1250	2.0×10 ¹⁵	1.90×10 ¹⁵
1350	2.3×10 ¹⁵	2.36×10 ¹⁵

Table 6-1.Comparison between predicted active dose and Hall sheet number for in-
situ B doped poly-Si at various flash temperatures.



Figure 6-1. B concentration profiles. A) in-situ doped and B) additionally B implanted polysilicon films with various annealing conditions. Solid lines represent simulated profiles.



Figure 6-2. 3D atom probe reconstruction using volume rendering. Local concentrations below 1 at% filtered out to highlight the grain. Only B atoms are shown.



Figure 6-3. 1-D concentration profile across the grain boundary. Boundary depicted in Figure 6-2 (squares). For reference, the bulk concentration within the grain is also plotted (circles).



Figure 6-4. *p*_{seg} values from atom probe tomography are plotted for both the in-situ doped (squares) and implanted (triangles) samples.



Figure 6-5. An example of the diffusion model for a 1350°C flash anneal on an in-situ doped sample.

CHAPTER 7 APPLICATION OF 3D ATOM PROBE TOMOGRAPHY TO ANALYSIS OF FIELD EFFECT TRANSISTORS ON SILICON-ON-INSULATOR SUBSTRATES

7.1 Challenges for 3D Analysis of SOI

The ability of atom probe tomography (APT) to provide three-dimensional (3D) compositional mapping with sub-nm spatial resolution^{67, 81, 137} suggests it will be an important technique in the characterization of future generations of aggressively scaled and complex field effect transistors (FETs)¹³⁸. Traditionally limited to the analysis of metallic materials, recently developed pulsed-laser APT instruments have expanded the range of analyzable materials to include semiconductors and insulators¹³⁹ making it potentially capable of compositional analysis of modern FETs on Si-on-insulator (SOI) substrates. It can also potentially complement current two-dimensional characterization techniques, such as scanning spreading resistance microscopy, which uses local nm-scale electrical measurements developed from atomic-force microscopy¹⁴⁰ but is capable of detecting only electrically-active dopants.

However, even with the development of laser-assisted APT to allow analysis of insulating materials, APT of FETs on SOI substrates presents many challenges due to the presence of the SOI layer. Traditionally, APT analysis of layered structures has been performed in a "top-down" orientation^{47, 67, 81, 93, 141}, where each layer is evaporated in series rather than in parallel, as shown in Figure 7-1a. If there is little variability in the evaporation field and thermal conductivity between the layers, performing top-down analysis is straightforward. However, when the variations are large, this can result in sample fracture at the transition from evaporating one layer to another in addition to analysis artifacts.^{142, 143} Here, a cross-sectional orientation method¹⁴⁴ for preparation of APT of p-FETs on SOI substrates is used where the FET is rotated 90° along the

channel to situate the buried-SiO₂ layer along the length of the tip, as illustrated schematically in Figure 7-1b; this results in evaporation of the layers in parallel, rather than in series. It is believed that this cross-sectional orientation aids in thermal dissipation of heat from the pulsed laser during analysis, and also removes the buried-SiO₂ from the field of view of the local electrode. Using this geometry enables the exploration of a critical question in microelectronic processing, namely the lateral segregation of boron to the gate oxide. The goal of this paper is to use this unique geometry in APT to observe boron segregation to the gate oxide at various positions laterally in an SOI device after rapid thermal annealing (RTA).

7.2 Methodology

45 nm gate length p-FETs were fabricated on SOI wafers up through source/drain ion-implantation and pulled prior to an RTA anneal and Ni silicidation. At 15 nm offset to the gate edge masked by thermal oxide spacer, the source/drain extensions were pre-amorphized using 40 keV Xe⁺-implantation to a dose of 5.0×10^{13} cm⁻² followed by a B extension implant performed using BF₂⁺-implantation at 3 keV to a dose of 9.0×10^{14} cm⁻²; the deep source/drain B implant was done using BF₂⁺-implantation at 9 keV to a dose of 2.5×10^{15} cm⁻² at 50 nm offset from the gate edge masked by the SiN_x sidewall spacer. Due to the inherent difficulties in performing APT analysis of insulating materials, the SiN_x sidewall spacers were removed prior to APT sample preparation with a combination of etching in hot H₃PO₄ (85% concentration at 140 °C for 8 min) followed by etching with dilute HF (2% concentration for 20 s). Figure 7-2 shows cross-sectional transmission electron microscopy (XTEM) images of the device structure prior to and after the spacer etch treatment. Samples were then annealed using RTA at 900 °C for 16 or 32 s to study B diffusion/segregation behavior. Prior to APT sample preparation,

300 nm of Si was deposited via plasma-enhanced chemical vapor deposition to allow conformal filling of the space between gate structures and provide a buffer material for focused ion beam (FIB) APT tip preparation.

APT samples in both top-down and cross-sectional orientation were fabricated using the traditional FIB lift-out method⁸; in the case of samples with cross-sectional orientation, a change in sample geometry was used: prior to mounting the wedge onto the microtip coupon array, the wedge was rotated 90° along its long axis placing the APT analysis direction orthogonal to the channel direction (parallel to the Si/buried-SiO₂ interface). This orientation allows the buried-SiO₂ layer to run down the side of the tip, and is thought to provide more area for thermal conduction from the pulsed laser, compared to the traditional top-down orientation where a buried-SiO₂ layer effectively acts as a thermal sink during laser-assisted APT. Following rotation, a 50 nm layer of Ni was deposited on the wedge to protect against Ga⁺-implantation from the ion beam, and the wedge attached to a microtip array for sectioning and sharpening using annular milling. This procedure is shown in the scanning electron microscopy (SEM) images presented in Figure 7-3.

Specimens were analyzed using an Imago © local electrode atom probe LEAP 3000X-Si with a stage temperature of 60 K. A 532 nm green laser was used to aid in field evaporation of the specimen tip. The laser pulse frequency was set to 250 kHz with a pulse energy of 0.5 nJ, and the target evaporation rate was set to 0.2 % of the laser pulse rate. Subsequent reconstructions of the datasets were performed using the Imago © IVAS software suite; typical datasets consisted of 8 - 10×10^6 ions.

7.3 Results and Discussion

3D APT analysis was attempted for both top-down and cross-sectional samples for as-implanted samples and samples annealed at 900 °C for 16 s and 32 s. However, because of specimen tip fracture during analysis, no successful data from top-down samples were collected. This is indicative of the challenges associated with sequential field evaporation of layered structures containing insulating materials. Figure 7-4a presents a reconstructed volume of the gate edge region from an as-implanted crosssectional APT sample displaying individual B atoms; an extracted two-dimensional B concentration contour plot is provided for comparison in Figure 7-4b with an XTEM micrograph of the same region shown in Figure 7-4c. The two-dimensional contour plot was generated by assigning color values to concentration ranges within a 1 nm x 1 nm area.

A small analysis volume of 5 nm × 10 nm × 20 nm at 5 nm from the gate edge was extracted from the total device reconstruction to examine the segregation of B laterally to the gate SiO₂. The B concentration across the gate SiO₂ in this region is plotted at 0.5 nm bin widths in Figure 7-5 for different annealing times at 900 °C; accumulation of B at the gate SiO₂ is clearly evident. The segregation coefficient of boron was calculated to be ~4, which is slightly below the reported values in the literature at the anneal temperature used.^{145, 146} Colby *et al.* reports a segregation coefficient of 5.1 while Pfiester *et al.* estimates a value between 4 and 6 depending on the effective B diffusivity in the oxide. It is important to note that this segregation not only comes from the poly-Si gate doping, but the lateral diffusion from the source drain extension implant, which is observed here directly. This is evidenced by the increasing concentration seen in the channel region with increasing anneal time. It is difficult to determine the exact

mechanism for B accumulation at the gate SiO₂. It may be the result of segregation to the oxidized surface in the implanted region followed by an enhanced lateral diffusion under the gate through the SiO₂¹⁴⁵. It is also possible that because B diffuses by an interstitialcy-kickout mechanism³¹, and both the implant and anneal conditions are conducive for transient enhanced diffusion²⁸, this segregation may occur if the B from the implant diffuses laterally in the silicon and subsequently follows the gradient of implantation induced interstitials up to the gate oxide. This has been proposed to explain the so called reverse short channel effect.^{28, 40} Also, because BF₂⁺ is the implantation species, the incorporation of F from ion implantation has been shown to enhance gate oxide penetration^{145, 147, 148}, the diffusivity of boron within the SiO₂ has been shown to be further enhanced as thickness is reduced.¹⁴⁷ Prior APT work of blanket gate electrode poly-Si implanted with B^+ instead of BF_2^+ revealed B diffusing into the gate oxide⁴⁶, but no accumulation in nor penetration through the SiO₂ was observed following annealing, suggesting that the presence of F is responsible for the results seen here.

Diffusion of B from the source/drain extension and deep source/drain implants was modeled using the Florida Object Oriented Process Simulator (FLOOPS) using a pair diffusion model, which describes the diffusivity enhancement of B in the presence of a supersaturated concentration of interstitials generated from the preamorphizing Xe⁺ implant. The interstitial profile is modeled using SRIM and plotted in Figure 7-6. Only the implanted areas of the simulated device are given this profile, while masked and amorphized regions use the equilibrium value C_i^* . The interstitials then diffuse to the surface where they annihilate with a rate known as the surface recombination velocity,

 $k_{\text{surf.}}$ Reported k_{surf} values vary over five orders of magnitude¹⁴⁹ for the temperature studied here. A k_{surf} value of $3 \times 10^{-4} \text{ s}^{-1}$ was found to be in good agreement with the experimental measurement, which is the same value determined by Agarwal and Dunham¹⁵⁰.

This work shows that 3D APT data allows site-specific analysis from commercially processed devices on SOI wafers when the cross-sectional method is used. However, it is important to note that the analyzed volume in a 3D device reconstruction is $\sim 10^6$ times smaller than the volume analyzed using conventional secondary ion mass spectrometry on a blanket SOI wafer; naturally, the dynamic range and sensitivity will be reduced. However, an additional benefit of using a cross-sectional geometry is that with a sufficiently high ion count, the B concentration can be averaged through the width of the gate, therefore producing more accurate data. Nevertheless, there is a set maximum analysis volume before the tip widens to the point that the buried-SiO₂ layer is in the field of view; it is usually at this point that sample fracture was observed to occur in samples prepared in cross-sectional orientation.



Figure 7-1. Schematic representation comparing two different methods of APT sample orientation of FETs on SOI substrates. A) traditional top-down analysis volume for an atom probe tip centered about the gate. B) cross-sectional orientation.



Figure 7-2. XTEM micrograph of the p-FET structure. A) the as-received structure. B) the structure with SiN_x sidewall spacer and thermal SiO_2 spacer removed after hot H_3PO_4 and dilute HF etching.



Figure 7-3. SEM micrographs of APT sample preparation via FIB milling. A) an in-situ micromanipulator removes an ion-milled wedge from an array of p-FETs, B) the wedge is rotated 90° about the long axis (so the analysis direction lies within the plane of the Si/buried-SiO₂ interface and is perpendicular to the channel direction) coated with ~50 nm of Ni, and mounted/sectioned to a Si microtip. C) the tip is sharpened into final shape via annular milling.



Figure 7-4. 3D Reconstruction of as-implanted p-FET. A) 3D analysis cone rotated to show the B extension implant (red) next to the gate; 5% Si ions shown (Grey). B) 2D contour plot showing concentration values for the B extension implant. C) XTEM micrograph from the same area of the device. An analysis volume outlines the location of the extracted 1D concentration profile.



Figure 7-5. 1D B concentration profiles across the gate SiO₂ region of p-FETs after annealing at 900 °C as measured by APT. as-implanted (●), 16 s of annealing (■), and 32 s of annealing (▲); all concentration profiles were acquired at 5 nm from the gate edge. Error bars represent one standard deviation.



Figure 7-6. Simulated concentration profile for interstitials generated from Xe^+ ion implantation. C_i in the amorphous region is set to C_i^* .



Figure 7-7. 2D concentration map extracted from atom probe reconstruction for a 900 °C 16s anneal. Simulated profiles represent a surface recombination velocity of 3×10⁴ s⁻¹ for interstitials.

CHAPTER 8 CONCLUSIONS AND FUTURE WORK

In this work, flash-assist rapid thermal annealing was used in order to explore the diffusion behavior of B in poly-Si. One of the most controversial questions was whether or not B segregated to the grain boundaries. This type of segregation behavior, already seen for the n-type dopants As and P, is incredibly important with regard to microelectronics processing. First, segregated B is not electrically active, and therefore brings down the expected conductivity of the material. Secondly, diffusion in grain boundaries is known to be much faster than in the bulk. Understanding segregation behavior is crucial to modeling diffusion behavior in poly-Si. It was shown that B does indeed segregate to the grain boundaries under specific thermal conditions, such as flash annealing, which allowed creation of a highly active film with limited grain growth, creating the perfect environment for segregation to occur. The scale of this microstructure was then able to be analyzed using three-dimensional tomographic analytical techniques such as atom probe tomography, which has a limited field of view on the order of 150 nm.

Through the use of transmission electron microscopy, secondary ion mass spectrometry, three-dimensional atom probe tomography as well as Hall effect, a comprehensive model was developed to describe microstructural, electrical, and diffusion behavior of heavily B doped poly-Si films under flash annealing conditions. The results are able to confirm the segregation of B to grain boundaries during flash annealing, while also validating previous work by other groups where segregation was not seen due to longer anneals with noticeable grain growth, which reduces segregation significantly.

Since the majority of the work shown here was done on bulk thin films, the natural progression for research would be to extend 3D APT to actual production devices. Due to instrument limitations at the time of this work, 3D APT had not yet evolved to where analysis of insulating oxides was straightforward. New tools have since been developed that are much more capable in this regard and can make analysis of production devices a possibility without deprocessing of various insulating device structures and relayering with compatible material.

APPENDIX A FLOOPS SIMULATION CODE FOR B DIFFUSION IN POLY-SI

Included here is the simulation code used in FLOOPS in order to simulate the

diffusion profiles from Chapter 6. Values to be edited based on experimental

parameters are noted in [] brackets.

#FLOOPS B Poly-Si Diffusion math diffuse dim=1 umf none col scale

#Bg = B concentration within the grain Bb = B concentration in grain boundary solution add name=Bg solve !negative solution add name=Bb solve !negative

#Creates structure of 120 nm Si on 12 nm of Oxide on top of 1 micron of Si line x loc=0.0 spac=0.001 tag=Top line x loc=0.12 spac=0.001 tag=Oxidetop line x loc=.132 spac=0.001 tag=Oxidebottom line x loc=1.0 spac=0.01 tag=Bottom region silicon xlo=Top xhi=Oxidetop region oxide xlo=Oxidetop xhi=Oxidebottom region silicon xlo=Oxidetop xhi=Oxidebottom init

#Inputs the SIMS profile, in this case, the as-implanted profile. profile name=Boron inf=[as-imp.csv] xscale=1e-3

sel z=1e16+Boron name=Bg sel z=1.0e10 name=Bb sel z=log10(Bg) #Plots and labels the initial grain and grain boundary profiles plot.1d label= "Bg0" sel z=log10(Bb) plot.1d !cle label= "Bb0"

#Diffusion is modeled in three parts: ramp up, flash, and ramp down #This next line defines the kinetic reaction term using values calculated for 850 °C pre-#flash temperature

set Gen "(Bg*[pseg(850°C)] - Bb) * \$tau"

#This line defines τ^{-1} set tau "6.12e22*exp(-5.76/(8.62e-5*(Temp+273)))"

pdbSetString Si Bg Equation "ddt(Bg)- $(0.37 \exp(-3.46)(8.62e-5*(Temp+273)))+[p/n_i(850^{\circ}C)]*0.76 \exp(-3.46)(8.62e-5*(Temp+273)))*grad(Bg) + $Gen" pdbSetString Si Bb Equation "ddt(Bb)-0.012*exp(-1.95)(8.62e-5*(Temp+273))))*grad(Bb) - $Gen"$

rta start.temp=[20] ramp=[150] cool=1e6 dwell.temp=[850] dwell.time=0

#Diffusion during the flash is modeled here with a 1 ms pulse duration.

set Gen "(Bg*[p_{seg}(T_{flash})] - Bb) * \$tau"

pdbSetString Si Bg Equation "ddt(Bg)- $(0.37 \exp(-3.46)(8.62e-5*(Temp+273)))$)*grad(Bg) + \$Gen" pdbSetString Si Bb Equation "ddt(Bb)-0.012*exp(-1.95/(8.62e-5*(Temp+273)))*grad(Bb) - \$Gen"

rta start.temp=850 ramp=1e6 cool=[cooling rate] dwell.temp= [T_{flash}] dwell.time=[.001]

#Ramp down is modeled here, starting at 950 °C, and cooling at 125 °C/s. Initial ramp #down temperature changes with flash temperature.

set Gen "(Bg*pseg(950°C) - Bb) * \$tau"

pdbSetString Si Bg Equation "ddt(Bg)-(0.37*exp(-3.46/8.62e-5*(Temp+273)))+[*p/n*_i(950°C)]*0.76*exp(-3.46/(8.62e-5*(Temp+273))))*grad(Bg) + \$Gen" pdbSetString Si Bb Equation "ddt(Bb)-0.012*exp(-1.95/(8.62e-5*(Temp+273)))*grad(Bb) - \$Gen"

rta start.temp=949 ramp=150 cool=[100] dwell.temp=950 dwell.time=0

#plots the output
sel z=log10(Bg)
plot.1d !cle label = "Bgfin"
sel z=log10(Bb)
plot.1d !cle label= "Bbfin"

APPENDIX B FLOOPS SIMULATION CODE FOR 2D B DIFFUSION OF SOURCE DRAIN EXTENSION IN P-MOSFET ON SOI

Included here is the FLOOPS simulation code used in Chapter 7 in order to obtain

the simulated concentration contours used in Figure 7-7 for diffusion of B from the

source-drain extension and source-drain implants.

#FLOOPS B Source Drain Diffusion #Grid initialization – 2 nm gate oxide on 60 nm Si, 100 nm Buried oxide, on Si line x loc=-0.002 tag=gate_ox spa=0.002 line x loc=0.0 tag=top spa=0.002 line x loc=0.06 tag=ox_top spa=0.002 line x loc=0.16 tag=ox_bottom spac=0.01 line x loc=0.5 tag=bot spa=0.005 line y loc=0.0 tag=left spa=0.002 line y loc=0.1 tag=right spa=0.002 region silicon xlo=top xhi=ox_top ylo=left yhi=right region oxide xlo=ox_top xhi=ox_bottom ylo=left yhi=right region oxide xlo=gate_ox xhi=top ylo=left yhi=right region silicon xlo=ox_bottom xhi=bot ylo=left yhi=right

init

#Mask for source drain extension implant mask clear mask name=extension left=-0.1 right=0.04 #etch oxide rate=0.002 time=1 spac=0.002 aniso mask=extension

#Extension Implant using BF₂ 9e14 3kv implant bf2 energy=3 dose=9e14 mask=extension

#Mask for deep source drain implant mask clear mask name=sd left=-0.1 right=0.066

#Deep Source-Drain Implant using BF₂ 2.5e15 9kV implant bf2 energy=9 dose=2.5e15 mask=sd

sel z=1e17+Boron name=Boron

#Creates profile of interstitials from the Xe preamorphization implant (40 kV 5e13) profile name=Int inf=[Intprofile.csv] xscale=1e-4

#math diffuse dim=1 umf none triplet pdbSetSwitch Si I DiffModel Numeric pdbSetSwitch Si V DiffModel Numeric

Int diffusion after Ural et al. PRL 83 (1999) p3454
#pdbSetDouble Silicon Int D0 {[Arrhenius 5.54e-3 0.85]}
pdbSetDouble Silicon Int Cstar {[Arrhenius [expr 5.0e22*exp(10.2)] 3.83]}

pdbSetDouble Silicon Vac D0 {[Arrhenius 1.756e-3 0.493]} pdbSetDouble Silicon Vac Cstar {[Arrhenius [expr 5.0e22*exp(12.8)] 4.367]}

pdbSetSwitch Silicon Boron DiffModel Pair pdbSetSwitch Silicon Boron ActiveModel None pdbSetDouble Silicon Boron Int Binding {[Arrhenius 8.0e-23 -1.50]} pdbSetDouble Silicon Boron Vac Binding {[Arrhenius 8.0e-23 -0.00]} pdbSetDouble Oxide_Silicon Vac Ktrap 0.00 pdbSetDouble Oxide_Silicon Int Ktrap 0.00

#Sets KSurf, the surface recombination variable at the oxide interface. pdbSetDouble Oxide_Silicon Int Ksurf [Ksurf value] sel z=900 name=Temp

#Sets implanted areas beyond amorphous crystalline interface to interstitial profile from #Xe implant plus C_i and C_v values for 900 °C sel z=(y>0.04)*(x>0.028)*Int+4.726e10 name=Int sel z=3.12e9 name=Vac

sel z=log10(Boron);

#Let FLOOPS set correct equilibrium variables diffuse time=1e-15 temp=900 sel z=EqInt+Int name=Int sel z=EqVac+Vac name=Vac

#Anneal for 16s at 900 °C diffuse time=0.267 temp=900

#2D Plot plot.2d grid sel z=Boron contour val=1e21 contour val=5e20 contour val=1e20 contour val=5e19 contour val=2.5e19 contour val=1e19

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BIOGRAPHICAL SKETCH

Sidan Jin was originally born in Shang-hai, China. He immigrated with his family to America at the age of two and grew up in Miami, FL. He graduated from Miami Killian Senior High School and went on to devote the next nine years of his life as a Florida Gator. He graduated in 2006 with a Bachelor of Science in Materials Science and Engineering, and decided to continue on with his graduate education at the University of Florida and received his Master of Science in 2007. While pursuing his Ph. D. under the advisement of Kevin Jones, Sidan worked on 3D characterization of transistors through a collaboration with IBM and the Semiconductor Research Corporation (SRC). He completed an internship with IBM's East Fishkill facility in 2008 in order to familiarize himself with 3D analysis using the local electrode atom probe. He went on to continue a second project with IBM involving flash-assisted rapid thermal annealing of poly-Si films for heterojunction bipolar applications. After graduating with his Ph. D, he will be joining Intel Corporation in Chandler, AZ.