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The mechanisms of iron gettering in silicon by boron ion-implantation

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INTRODUCTION

TECHNICAL MEMORANDUM

The silicon processing industry has depended on gettering techniques to produce a contamination-free zone in silicon substrates for the manufacture of devices. Advances in cleaning technology and particle-free fabrication environments have reduced the chance of process-induced contamination, but processing engineers depend on gettering strategies to insure high yield in the event of process variations. Giga-scale product manufacturing will require low temperatures, $T < 1000^\circ\text{C}$, as well as metal contamination levels $< 10^{10}\text{cm}^{-2}$.

The concept behind gettering is to introduce a region in the Si wafer which will attract and capture such deleterious elements as Fe during the integrated circuit processing. There are many heat treatments and different processing steps which afford the possibility of intro-

ducing and diffusing unwanted impurities throughout the wafer. Many gettering schemes have been introduced over the years from localized damage at surfaces to oxygen precipitates in the crystal.[1-5] A particularly important gettering agent is the one of bulk substrates which are heavily doped, usually with B, and also contain oxygen precipitates and oxidation crystal defects. The efficacy of a particular gettering scheme is readily apparent to the process engineer, but there is still much uncertainty regarding the various atomistic trapping mechanisms. This uncertainty arises from the experimental difficulties in observing the local motion and trapping of such low levels of impurities.

In this work, high energy boron ion-implantation is used as a model system to study a specific gettering process-the enhanced trapping of Fe at a highly doped B region. Implantation is used to introduce precisely controlled concentrations of B in well defined regions. The gettering effectiveness of this dopant is compared with implanted C, a neutral impurity, and also to damage sites introduced by Si implantation.

We show that a region of high B concentration provides enhanced gettering of Fe, which can be explained by electronic interactions between interstitial Fe and the dopant B ions, controlled by the temperature dependent Fermi level position. Iron, Fe^{0+} , diffuses interstitially and is known to have either a neutral or positive charge state regulated by the Fermi level position in the host silicon.[6] When the Fe species is in the neutral state, no preferential gettering occurs. However, when the Fermi level is below the $E_v + E_t = 0.39\text{eV}$, [6] the positively charged Fe exhibits enhanced gettering.

EXPERIMENTAL PROCEDURE

Twenty $\Omega\text{-cm}$, B-doped Si wafers were implanted with $500\text{keV } ^{54}\text{Fe}$ at a dose of $1\text{E}13\text{ cm}^{-2}$ and were then annealed at 1000 C for 1 hour to fully remove the implantation damage and to uniformly distribute the Fe to an equilibrium concentration of $2\text{E}14\text{ cm}^{-3}$. Then gettering regions were implanted with high energy ^{10}B at doses ranging from $4\text{E}12\text{--}4\text{E}15\text{ cm}^{-2}$. Subsequent heat treatments at temperatures from 600 C to 1000 C were performed in flowing He. A thermocouple was mounted under the boat to monitor the annealing temperature and cooling rate. All samples received an organic clean and HF dip prior to heating and were placed between two silicon wafers to prevent contamination during furnace treatments.

The depletion of Fe from the gettered regions of the silicon samples was monitored by Deep Level Transient Spectroscopy, DLTS, using a BioRad DL8000 spectrometer. The DLTS measured the average Fe concentration $1\text{--}3\mu\text{m}$ from the surface contact. Ti was evaporated through a shadow mask to make the Schottky contacts for the DLTS measurements. The accumulation of Fe in the B-implanted region was detected by secondary ion mass spectrometry, SIMS, using an O_2^+ sputtering beam. High resolution mass detection was necessary to avoid interference of $^{10}\text{B-Si-O}$ trimers (54 amu) with the ^{54}Fe signal.

RESULTS

Si samples which were contaminated with a uniform concentration of $2 \times 10^{14} \text{ Fe cm}^{-3}$, were implanted with 3.3 MeV B, at a dose of $4 \times 10^{14} \text{ cm}^{-2}$ and then annealed for 1 hour at 1000 C. The temperature during cooling decayed as a stretched exponential, dropping to below 200 C within 4 minutes. The total Fe concentration was then measured by DLTS as the sum of the Fe_iB_j pairs, $\text{H}(0.01)\text{eV}$, and Fe_i , $\text{H}(0.46)\text{eV}$, on both the B-implanted side (front) and opposite side (back) of the sample. The results shown in Figure 1, indicate that the Fe has been gettered from the region near the B implant but not from the side opposite the B-implant. SIMS data on a companion sample with the same initial Fe contamination, and with an implant of 1.5 MeV ^{10}B , $6 \times 10^{13} \text{ cm}^{-2}$, followed with 1000 C, 1 hour heat treatment, shows that the Fe has redistributed to the B profile (Figure 2.) The peak concentration of the Fe gettered in the B-region is $\sim 2 \times 10^{16} \text{ cm}^{-3}$ which represents approximately 10% of the total Fe introduced into the sample. The diffusion length for Fe in Si, 1000 C, 1 hour, is more than twice the thickness of the sample; the diffusion length for Fe in Si during the quench, integrating over the full cooling curve, is $67 \mu\text{m}$. [7] Therefore, the DLTS measurements at both surfaces of the samples allows simultaneous monitoring of the diffusion-limited gettering during cool-down (frontside) and Fe solubility at the annealing temperature (backside).

Additional samples which contained the identical uniform Fe concentrations and B-implantation doses, received gettering anneals at temperatures below 1000 C for time periods which allowed for Fe diffusion lengths greater than the thickness of the samples. Representative results are plotted in Figure 3. Fe concentrations at $500 \mu\text{m}$ (backside) are all consistent with the published solubility results. [7,8] In all cases, the Fe has been gettered to well below the solubility limit from the front $3 \mu\text{m}$ of the samples.

The effectiveness of the gettering of Fe by the implanted B region is a function of the B dose. Figure 4 shows the total Fe, which is the sum of the FeB pairs plus the interstitial Fe, remaining in the near surface region of the Si as a function of B dose. The peak concentration of B implanted at 3.3 MeV is $4 \mu\text{m}$ from the surface. The amount of Fe remaining after the gettering treatment decreases with increasing dose, $1 \times 10^{14} \text{ B/cm}^2$, to a value below the DLTS sensitivity, $1 \times 10^{10} \text{ Fe/cm}^3$. At implantation doses $> 1 \times 10^{15} \text{ B/cm}^2$, corresponding to peak B concentration of $3 \times 10^{19} \text{ cm}^{-3}$, extended defects remain in the measurement volume producing broad dislocation signals in the DLTS spectra which prevent the detection of the Fe-related peaks.

It is important to compare the B gettering results with the gettering effectiveness of Si and C, also plotted in Figure 4. [9] The high energy Si implant produces dislocations and provides an example of crystal damage as a gettering scheme. The implanted C provides neutral traps for Fe, and when this data is compared with the B gettering, it illustrates the added effectiveness of the electronic interaction between Fe and B.

DISCUSSION

Our results show that the most effective gettering occurs during the cooling cycle, and that it is associated with the presence of a B-rich region. This gettering behavior can be entirely explained in terms of Fe enhanced segregation into highly doped B regions determined by the difference in the Fermi level positions in the two regions of differing B concentrations.

In the situation where we have Fe distributed throughout Si which has two adjacent regions of differing B concentrations, the higher number of negative ions in the highly doped region will produce a coulomb attraction between B^- and Fe^+ . [6,10] At equilibrium, the ratio of Fe^+ in the highly B-doped region, $[Fe^+]_H$, to the Fe^+ in the region of less B, $[Fe^+]_L$, will be a function of the Fermi level difference, ΔE_F , according to the relation

$$\frac{[Fe^+]_H}{[Fe^+]_L} = e^{\frac{\Delta E_F}{kT}}. \quad (1)$$

In addition, for any given B concentration in Si, the ratio of the number of Fe^+ to the total interstitial iron atoms, Fe^{int} , can be expressed with the Fermi function

$$\frac{[Fe^+]_{H,L}}{[Fe^{int}]_{H,L}} = \frac{1}{2e^{\frac{(E_F - E_V - E_D)}{kT}} + 1} \quad (2)$$

where E_F is the Fermi level, and $E_V + E_D$ is the position of the iron donor level. The mass-action relationship for Fe^+ pairing with B^- is known from previous DLTS results to be

$$[Fe^+B^-] = \frac{[Fe^+][B^-]}{10^{20} \text{ cm}^{-3}} \exp\left(\frac{0.65 \text{ eV}}{kT}\right). \quad (3)$$

Thus, both Fermi level induced Fe redistribution and Fermi level controlled Fe-B pairing provide mechanisms for the enhanced gettering.

The calculation, based on these two equilibrium mechanisms, for the partition coefficient, $[Fe^{int}]_H/[Fe^{int}]_L$, for a highly doped layer, $[B]=1E18 \text{ cm}^{-3}$, adjacent to a low doped region, $[B]=1E15 \text{ cm}^{-3}$, is shown in Figure 5. Above 600 C, there is no effect on the redistribution of Fe. Below 600 C, the partition function increases steeply. The calculation for neutral trapping of Fe at an impurity site is also plotted in Figure 5, and shows the reduction in the partitioning at low temperatures without Fermi level effects. Highly doped layers, $>1E18 \text{ B/cm}^{-3}$, are extremely effective gettering regions, providing partition coefficients for Fe $\sim 10^6$, at low temperatures. Therefore, during Si processing, cooling rates and diffusion lengths become of practical importance.

Si samples with $[Fe^{tot}] = 2E14 \text{ cm}^{-3}$, were implanted with 3.3 MeV B, $1E14 \text{ cm}^{-2}$, and annealed for 1 hour at 1000 C. Measured layers were removed by mechanical polishing from the sample surface before deposition of Schottky barriers. The total $Fe_i + Fe_B$ concentration as a function of depth was determined by DLTS and plotted as the filled circles in Figure 3. To understand these experimental results, the Fermi level was evaluated for the known B profile and was used to determine the local volume concentrations of Fe^0 and Fe^+ for the known Fe profile. Then the diffusion flux, F , could be determined from

$$F = D^0 \nabla [Fe^0] + D^+ \nabla [Fe^+] + \frac{D^+}{kT} [Fe^+] \nabla E_F \quad (4)$$

where D^0 and D^+ are the diffusivities of Fe^0 and Fe^+ in Si.[11] The drift motion of Fe^+ induced by the gradients in the Fermi level is represented by the third term in the equation. This diffusion equation (Eq.4) is coupled with the trapping equation (Eq.3) and solved numerically to determine the redistributed Fe profile for the measured cooling curve. Figure 6 shows these Fe profiles at various temperatures during cooling after a 1000 C anneal. The results reproduce the depletion of Fe from the surface and the accumulation of Fe in the B implanted layer. The final profile is compared with the measured profile, solid points in Figure 6. Therefore, the enhanced gettering of Fe by high dose B ion-implantation is explained entirely by the Fermi level controlled electronic interactions between Fe^+ and B^- . The effective gettering of p/p+ epitaxial silicon wafers is also explained by these results.[1,4,12]

CONCLUSIONS

Understanding and controlling gettering will become more important to future device technologies. In this work we show that regions of high B concentrations are particularly effective gettering agents. This behavior can be entirely understood in terms of Fermi-level-enhanced pairing reactions between Fe and B which becomes operative at temperatures less than 600 C. Such quantitative understanding could have significance for the development of more efficient gettering protocols.

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REFERENCES

- [1] D. Gilles, in *Defect Engineering in Semiconductor Growth, Processing and Device Technology*, edited by S. Ashok, J. Chevallier, K. Sumino and E. Weber, MRS Symposia Proceedings Vol. 262 (Materials Research Society, Pittsburgh, 1992) p. 917.
- [2] K. Graff in *Metal Impurities in Silicon-Device Fabrication*, Springer Series in Materials Science Vol. 24 (Springer-Verlag, New York 1995) p.164.
- [3] B. Shen, T. Sekiguchi, J. Jablonski and K. Sumino, J. Appl. Phys. 76, 4540 (1994).

- [5] D. Gilles and H. Ewe in Ref. 4, p. 772.
- [6] L. C. Kimerling and J. L. Benton, *Physica* **116B**, 297 (1983).
- [7] E. R. Weber, *J. Appl. Phys. A*, **30**, 1 (1983).
- [8] M. Aoki, A. Hara and A. Ohsawa, *J. Appl. Phys.* **72**, 895 (1992).
- [9] W. Skorupa, R. Kogler, K. Schmalz, P. Gaworzewski, G. Morgenstern and H. Syhre, *Nuclear Instruments and Methods in Physics Research*, **B74**, 70 (1993).
- [10] D. Gilles, W. Schroter and W. Bergholz, *Phys. Rev. B* **41**, 5770 (1990).
- [11] S. V. Koveshnikov and G. A. Rozgonyi, *Appl. Phys. Lett.* **66**, 860 (1995).
- [12] M. Aoki, T. Itakura and N. Sasaki, *Appl. Phys. Lett.* **66**, (20), 2709 (1995).

Figure Captions

Figure 1. DLTS, $\tau_1 = 9$ ms, measured at both surfaces of Si after a gettering implant of 3.3MeV, $4E14$ B/cm², and 1000 C, 1 hour anneal. Enhanced gettering is evident at the front surface, but the Fe concentration remains at the solid solubility on the back.

Figure 2. SIMS profiles of both ¹⁰B and ⁵⁴Fe after 1000 C, 1 hour heat treatment. The concentration of Fe redistributed to the B gettering region is approximately 10% of the total Fe contamination in the sample.

Figure 3. DLTS depth profiles of Fe contaminated samples, given 3.3MeV, $1E14$ B/cm² ion-implantation, 1000 C, anneal, followed by 1000 C, 1 hour; 800 C, 2 hour; and 600 C, 18.5 hour anneals. Fe concentration is below the solubility limit at the front of the samples. The Si wafers were thinned by mechanical polishing.

Figure 4. Gettering effectiveness of boron, carbon, and silicon as a function of ion-implantation dose, measured by DLTS. The concentration of Fe remaining in the near surface region is two orders of magnitude less after B gettering at high doses, than after Si gettering.

Figure 5. The calculated partition coefficient of the total Fe concentration redistribution for a region of $[B]=1E18\text{cm}^{-3}$ adjacent to a region of $[B]=1E15\text{cm}^{-3}$ as a function of temperature. The solid line shows the effects of Fermi level controlled Fe⁺ segregation and Fe⁺B⁻ pairing. The dashed line shows neutral trapping of Fe at an impurity site.

Figure 6. The calculated redistribution of Fe during cooling from 1000 C, solved numerically using the partitioning coefficient of Figure 5 and the diffusion flux of Equation 4. The DLTS measurements are shown as solid circles.

Figure 1
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Figure 4
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Figure 5
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Figure 6
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