LBL-37561
UC-404

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials Sciences Division

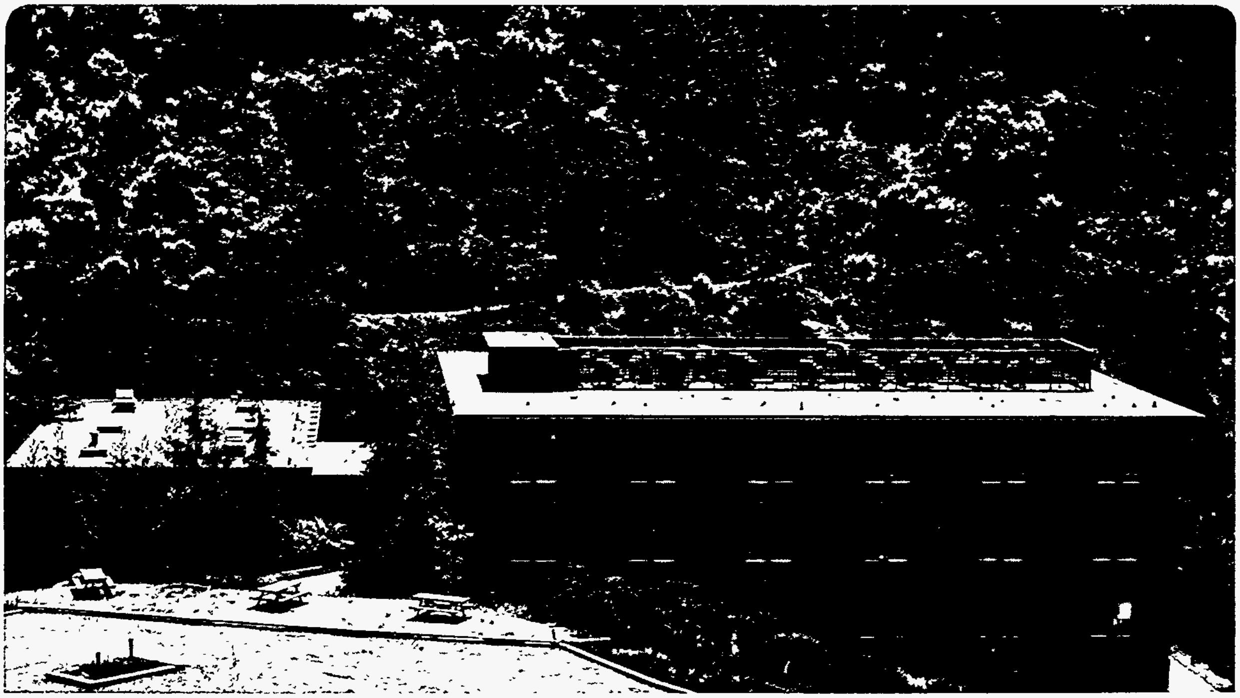
Presented at the 18th International Conference on Defects in Semiconductors, Sendai, Japan, July 23–28, 1995, and to be published in the Proceedings

Microdefects in Nitrogen Doped FZ Silicon Revealed by Li+ Drifting

RECEIVED
NOV 14 1995
OSTI

W.B. Knowlton, J.T. Walton, J.S. Lee, Y.K. Wong,
E.E. Haller, W.v. Ammon, and W. Zulehner

July 1995



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

LBL-37561
UC-404

Microdefects in Nitrogen Doped FZ Silicon Revealed by Li+ Drifting

W.B. Knowlton,[1,2] J.T. Walton,[1] J.S. Lee,[1] Y.K. Wong,[1] E.E. Haller,[1,2]
W.v. Ammon,[3] and W. Zulehner[3]

[1]Department of Materials Science and Mineral Engineering,
University of California, Berkeley
and
[2]Lawrence Berkeley National Laboratory, University of California,
Berkeley, California 94720, USA

[3]Wacker-Chemitronic GmbH, P.O. Box 1140, D-84479 Burghausen, Germany

July 1995

This work was supported by the Director, Office of Biological and Environmental Research, Analytical Technology Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

GK

MICRODEFECTS IN NITROGEN DOPED FZ SILICON REVEALED BY Li^+ DRIFTING

W.B. KNOWLTON[1,2], J.T. WALTON[1], J.S. LEE[1], Y.K. WONG[1], E.E. HALLER[1,2],
W.v. AMMON[3], and W. ZULEHNER[3]

[1]Lawrence Berkeley National Laboratory and [2]Department of Materials Science & Mineral
Engineering, University of California, Berkeley, California 94720, USA
[3]Wacker-Chemitronic GmbH, P.O. Box 1140, D-84479 Burghausen, Germany

Key Words: microdefects, FZ silicon, nitrogen doping, Li drifting, D defects

Abstract. ULSI technology requires ultra-thin device oxides with excellent breakdown integrity. Recent studies have unveiled degraded dielectric breakdown voltage (DBV) performance of the ultra-thin oxides. These findings suggest that one source for poor oxide integrity is the incorporation of native defects from the Si substrate during oxide growth. Primary defect candidates are D defects which exist mostly in the central region of floating zone (FZ) grown Si crystals. Nitrogen (N) doping eliminates D defects, as detected by conventional means, and improves oxide integrity. Results are presented indicating the prevalence of microdefects in the central region of p-type nitrogen doped FZ Si using the method of Li ion (Li^+) drifting in an electric field. A model has been developed based on Li interactions in Si which describes the Li^+ precipitation mechanism. The mechanism establishes that vacancies are the most likely Li^+ precipitation sites. The results are discussed in relation to breakdown mode patterns of polished FZ Si wafers after gate oxide tests.

Introduction

The recently reported spatially dependent lower device yield in the center of FZ and Czochralski (CZ) grown Si, thought to be caused by microdefects, has prompted the development of additional wafer inspection and diagnostic tests. They are used to characterize the distribution and densities of point defects such as A defects (i.e., swirl defects), which are known to be caused by Si self-interstitials (Si_i), and D defects, which are believed to be vacancy clusters [1,2]. These techniques are: X-ray topography or X-ray fine structure analysis (XAFS) of Cu decorated Si wafers, optical microscopy of a Secco etched Si surface, laser particle counting (LPC) of a Si surface after an extended SC1 clean, and voltage stressing of patterned oxidized Si wafers. Each technique has an inherent diagnostic limitation, as discussed below. We also introduce attributes of a Li^+ drifting diagnostic technique.

Cu decoration in conjunction with X-ray topography and XAFS of FZ Si wafers has been successfully used to reveal a region at the wafer periphery of A defects and at the wafer center of D defects [2,3]. However, Cu decoration requires high temperature processing (~1000°C), potentially giving rise to unwanted thermally activated processes. For this reason, other techniques, not requiring high temperature cycles, have been developed to identify point defect distributions in Si wafers.

Yamagishi *et al.* have demonstrated that point defects can be revealed in Si wafers by using a Secco etch and examining the surface morphology of the resultant patterns with optical microscopy [4,5]. The surface morphology of the A defect region is striated while the D defect region shows flow-like patterns called flow pattern defects (FPD). The FPD region has been shown to correlate well with the D defect regions revealed by the Cu decoration technique. The Secco etch technique depends on careful etching of the wafer and some interpretation of the observed FPDs.

The observation that extended cleaning of Si wafers in SC1 led to an increased particle count as detected by laser particle counting (LPC) gave rise to the crystal originated particle (COPS) test.

While the regions of high COPS, found to be etch pits produced during SC1 treatments, have been well correlated with the D defect regions revealed by Cu decoration, the technique is again dependent of the etching process, good wafer cleanliness, and a well calibrated LPC system [6].

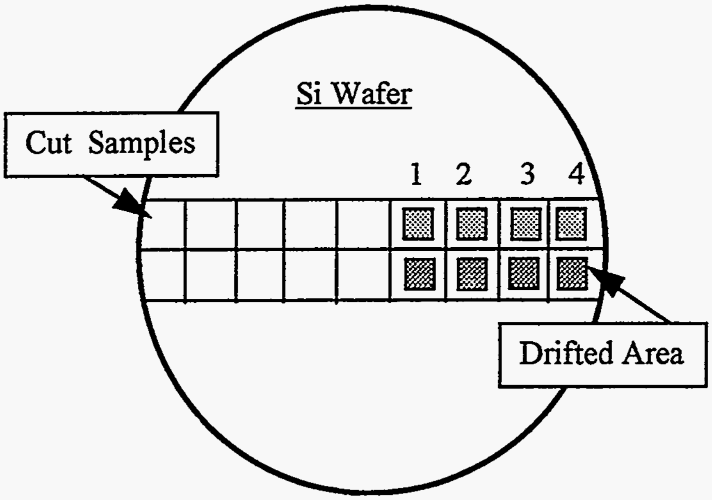


Figure 1: The pairs of samples which were drifted are labeled 1 through 4. Due to detector fabrication restraints, the shaded areas are the active regions.

The three preceding tests described give indirect evidence of the potential for the device yield difficulties noted earlier. A direct approach to the question of device yield is to actually fabricate and test simple devices. The gate oxide integrity test (GOI) does this by determining the dielectric breakdown voltage (DBV) of simple MOS diodes (e.g., [7]). Abe and Kimura showed that a possible correlation exists between FPDs and poor GOI [8]. They postulated that low DBV in SiO_2 was caused by D defects. This has since been shown by others [4,9,10]. A correlation between COPS and poor GOI has also been found supporting the postulation that D defects cause poor GOI [9,11]. Finally, the GOI procedure does require high thermal processing and therefore suffers from the same difficulty as the Cu decoration technique.

In the following, we discuss our results from using Li^+ drifting to detect the presence of microdefects (thought to be vacancies) in the Si lattice, and in particular N doped FZ Si. This technique, as we will show, appears to have a higher sensitivity to D defects than the previously mentioned tests and does not involve high temperature processing.

Li Ion Compensation in Silicon

The properties of Li in Si and Ge were of interest in very early experimental and theoretical semiconductor physics [12]. This early work showed that the pairing between the interstitial Li^+ and the various impurities in the semiconductor was a sensitive probe in determining the nature of these impurities (e.g., O and B) and their distribution in the crystal. It was also found that Li^+ could be used to determine vacancy concentrations. With the subsequent realization that thick semiconductor (both Si and Ge) regions could be made nearly intrinsic by the pairing (i.e., compensation) properties of the interstitial Li^+, fabrication of a variety of thick semiconductor detectors (Si(Li) or Ge(Li)) was initiated at various laboratories. The fabrication of Si(Li) radiation detectors is now the principal application of the Li^+ compensation technique.

Si(Li) detector fabrication is discussed in detail in a previous publication [13]. The procedure begins by Li evaporation onto and diffusion (~ 400°C) into the Si sample. A n^+ contact is formed on the Li deposited side of the sample. On the opposite side, Au is evaporated into a shallow well, etched into the Si thereby producing a Schottky barrier. Li^+ drifting is carried out by applying a reverse bias on the Li diffused sample at ~ 100°C. As the Li^+ drift, they compensate acceptors (e.g., B^-) producing an intrinsic region. The growth rate of the Li^+ compensated region is given by [14,15]:

$$\frac{dW}{dt} = \frac{\mu V}{W} - \frac{W}{\tau_L}. \tag{1}$$

where W is the width of the compensated region, μ is the Li^+ mobility, V is the applied bias, and τ_L is the Li^+ lifetime. The last term is a "loss term" to account for the precipitation of Li^+. The solution to Eq. (1) for constant V, τ_L, and μ is given by:

$$W=W_{max}(1-e^{-2t/\tau_L})^{1/2} \tag{2}$$

where $W_{max}=(\mu V\tau_L)^{1/2}$. When the τ_L is short, then Eq. 2 predicts that $W \leq W_{max}$, independent of the time employed in "drifting" the sample. Furthermore, we have found that many FZ Si crystals either do not Li^+ compensate, or compensate just on the periphery, similar to the delineation that Abe and Kimura observed with X-ray topography of Cu decoration [8].

Recently, we have demonstrated that, in some of these FZ Si crystals, the Li^+ are precipitating [16]. We believe the precipitation sites are vacancies, or D defects. Since it has been reported that N doped Si is free of D defects, it was of some interest to verify this assumption with the Li^+ drifting process and to compare its sensitivity to that of the commonly promoted Si crystal characterization techniques discussed above [4,9,11,17].

Experimental

For our tests, we obtained several 3 mm thick, 103 mm diameter, B and N doped <111> p-type FZ Si wafers from an ingot grown by Wacker-Chemitronic which successfully passed their GOI tests. The concentration of N, C, and O was $3x10^{14}$ cm^{-3}, $\leq 5x10^{15} cm^{-3}$, $2x10^{15}$ cm^{-3}, respectively. Furthermore, the resistivity was 1250 Ω cm, the life time was 900 µs, and the growth rate was 2.5 mm/min. The wafer was cut radially through the center into several 11 mm^2 square samples. To determine the radial driftability (i.e., Si quality) of the wafer, four pairs of samples, with each pair equivalent spatially, were taken from the center position extending to the wafer edge as shown in fig. 1. Sample pairs were used to assess reproducibility. Following Li thermal evaporation, diffusion of Li in an Ar atmosphere at 430°C for 10 minutes was performed. Each sample was Li^+ drifted and fabricated into a *p-i-n* diode structure (i.e., a detector). The active detector regions in the cut samples are shown as shaded squares in fig.1. Alpha particle scans using an ^{241}Am source were performed on each detector to determine if the Li^+ had drifted through the entire volume. The detectors were cut in half and Cu stained to measure the Li^+ drift depth profile (i.e., drift depth with respect to the radial distance from the wafer center).

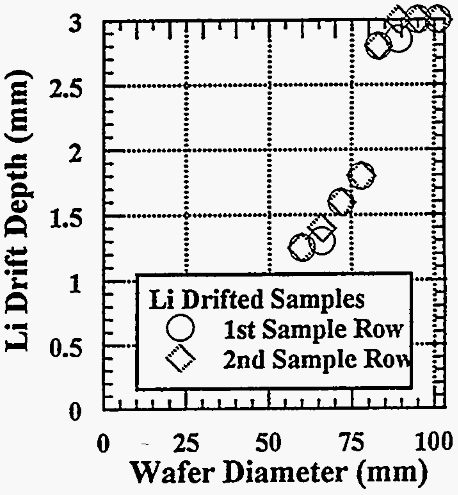


Figure 2: Li^+ drift depths shown for the active regions of samples pairs 1-4.

Results

Samples 1 and 2 did not respond to alpha particle scans indicating that Li^+ did not drift completely through the active region of the samples. Sample 3 responded only partially to alpha particle scans denoting that Li^+ drifted only partly through the active region. Alpha particle scanning of sample 4 showed that the Li^+ drifting was complete in the active region. All the samples respective pairs gave rise to the same results.

Cu staining of the cut samples verified the results obtained from the alpha particle scans. A plot of the Li^+ drift depth as a function of radial distance across the wafer is shown in fig. 2. The plot shows that the Li^+ drift depth is shallow for the sample pairs in the central region of the wafer. Approximately 22 mm from the wafer edge, the Li drift depth increases significantly. Li^+ drifting is complete about 12 mm from the edge. Reproducibility is apparent between sample pairs.

Discussion

From fig. 2, a correlation between Li^+ drift depth and radial distance from the wafer center is clear. The abrupt increase in Li^+ drift depth 12 mm from the wafer edge indicates a circular border separating an outer driftable from an inner predominantly undriftable region. This same effect was seen in Li^+ drifted p-type <111> non-N doped FZ Si wafer in an earlier gettering study [16]. Since that study, a wafer without N from the same ingot was Li^+ drifted and Cu stained. An undriftable central region was found as the results indicate in fig. 3. Furthermore, there is good agreement between the undrifted region in both fig. 2 and 3 with the poor GOI regions reported by von Ammon et al. on similar non-N doped FZ Si wafers [9].

The undrifted regions of both the N doped and undoped N FZ Si are similar suggesting that the N doping has not completely removed the D defects (see fig. 2 and 3). The effect of N doping on the apparently complete suppression of the D defect region was first reported by Abe and Harada using X-ray topography of Cu decorated FZ Si [17]. Yamagishi *et al.* saw the same result using the Secco etch technique [4]. This effect was also seen with the elimination of COPS and FPDs and an increase in GOI [4,9-11]. In O-free Si, N_i pairs having C_{2h} symmetry are the dominant defect [18]. In the D defect region, N pairs are thought to be incorporated into vacancies forming complexes [19]. It has been suggested that the apparent disappearance of the D defect region in N doped Si is attributed to the interaction between Si_i with the N-vacancy (N-V) complexes forming N_i pairs and annihilating vacancies [8,9].

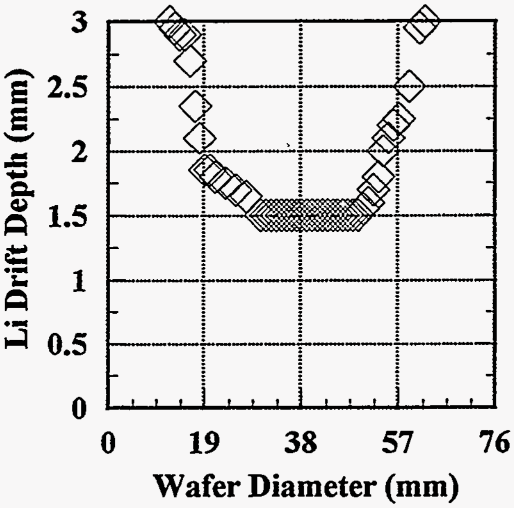


Figure 3: Li^+ drift profile of a <111> FZ Si wafer without N.

Our results suggest that, although the aforementioned N reactions may take place, the D defect regions are still prevalent. In other words, the concentration of D defects has been reduced below the detection limits of X-ray topography of Cu decorated crystals and GOI tests and below the sensitivity of etching techniques with regard to the creation of FPD and COPS, but not below that of the Li^+ compensation method. Subsequent to the tests reported here, we subjected several companion samples from this N doped crystal through our gettering procedure noted above. These samples then compensated, similar to the previous behavior of the non-N doped FZ Si samples after gettering.

Hence, two points can be made in response to the cessation of Li^+ drifting in the central region of N doped FZ Si and the success of our gettering process of N doped FZ Si: first, Li^+ drifting is a more sensitive means to detect microdefects than those described in the introduction, and second, a viable cause for the undriftability of the central region in the N doped FZ Si is the precipitation of Li^+ by D defects.

Conclusion

We have shown that Li^+ drifting is shown to be a more sensitive characterization technique for D defect region identification in N doped p-type FZ Si than X-ray topography of Cu decorated Si, GOI tests, and etching techniques with regard to the creation of FPD and COPS. Our measurements suggest that N doping reduces the D defect concentration but may not eliminate it completely.

We would like to thank Kohei Itoh for his assistance in this study and Amy Barnes for her technical support. This work was supported by the Director, Office of Energy Research, Office of Biological and Environmental Research, Analytical Technology Division, of the US Department of Energy under contract number DE-AC03-76SF00098.

References

[1] L. I. Bernewitz, B. O. Kolbesen, K. R. Mayer and G. E. Schuh, Applied Physics Letters **25,** 277-279 (1974)

[2] P. J. Roksnoer and M. M. B. v. d. Boom, Journal of Crystal Growth **53,** 563-573 (1981)

[3] T. Kitano, Physica Status Solidi **127,** 341-347 (1991)

[4] H. Yamagishi, I. Fusegawa, N. Fujimaki and M. Katayama, Semiconductor Science Technology **7,** A135-A140 (1992)

[5] F. S. d'Aragona, Journal of the Electrochemical Society **119,** 948-951 (1972)

[6] J. Ryuta, E. Morita and T. Tanaka, Japanese Journal of Applied Physics **29,** L1947-L1949 (1990)

[7] B. B. Triplett: *The Seventh International Conference on Silicon Materials Science and Technology*, ed. by H. R. Huff, W. Bergholz and K. Sumino, (The Electrochemical Society, Inc., 1994), pp. 333-345.

[8] T. Abe and M. Kimura: *The Sixth International Symposium on Silicon Materials Science and Technology*, ed. by H. R. Huff, K. G. Barraclough and J.-i. Chikawa, (The Electrochemical Society, Inc., 1990), pp. 105-116.

[9] W. v. Ammon, A. Ehlert, U. Lambert, D. Gräf, M. Brohl and P. Wagner: *The Seventh International Conference on Silicon Materials Science and Technology*, ed. by H. R. Huff, W. Bergholz and K. Sumino, (The Electrochemical Society, Inc., 1994), pp. 136-147.

[10] H. Yamagishi, I. Fusegawa, K. Takano, E. Iino, N. Fujimaki, T. Ohta and M. Skurada: *The Seventh International Conference on Silicon Materials Science and Technology*, ed. by H. R. Huff, W. Bergholz and K. Sumino, (The Electrochemical Society, Inc., 1994), pp. 125-135.

[11] T. Abe and H. Takeno, MRS Proceedings **262,** 3-13 (1992)

[12] H. Reiss, C. S. Fuller and F. J. Morin, The Bell System Technical Journal **XXXV,** 535 (1956)

[13] J. T. Walton, H. A. Sommer, D. E. Greiner and F. S. Bieser, IEEE Transactions on Nuclear Science **NS-25,** 391-396 (1978)

[14] E. M. Pell, Journal of Applied Physics **31,** 291-302 (1960)

[15] A. H. Sher and J. A. Coleman, IEEE Transaction on Nuclear Science **NS-17,** 125-129 (1970)

[16] J. T. Walton, Y. K. Wong, N. Derhocobian and E. E. Haller, IEEE Transactions on Nuclear Science **41,** 1031-1036 (1994)

[17] T. Abe, H. Harada and J.-i. Chikawa, MRS Proceedings **14,** 1-17 (1982)

[18] H. J. Stein: *MRS Proceedings*, ed. by J. C. M. Jr., S. J. Pearton, J. W. Corbett and S. J. Pennycook, (MRS, 1985), pp. 523.

[19] T. Abe, H. Harada, N. Ozawa and K. Adomi, MRS Proceedings **59,** 537-544 (1986)

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720