Review of Progress in QUANTITATIVE NONDESTRUCTIVE EVALUATION

Volume 5B

Review of Progress in QUANTITATIVE NONDESTRUCTIVE EVALUATION

Volume 5B

Edited by
Donald O. Thompson
Ames Laboratory (USDOE)
Iowa State University
Ames, Iowa

and
Dale E. Chimenti
Materials Laboratory
Air Force Wright Aeronautical Laboratories
Wright-Patterson Air Force Base
Dayton, Ohio

PLENUM PRESS • NEW YORK AND LONDON

The Library of Congress has cataloged the first volume of this title as follows:

Review of progress in quantitative nondestructive evaluation–Vol. 1– –New York: Plenum Press, 1982–
v.: ill.; 28 cm.
Annual.
Vols. 2– published in 2 pts.: A and B.
Vol. 1– are the Proceedings of the 8th, 1981– Air Force/Defense Advanced Research Projects Agency Symposium on Quantitative Nondestructive Evaluation.
ISSN 0743-0760 = Review of progress in quantitative nondestructive evaluation.
1. Non-destructive testing–Congresses. I. United States. Air Force. II. United States. Defense Advanced Research Projects Agency. III. Air Force/Defense Advanced Research Projects Agency Symposium on Qua, titative Nondestructive Evaluation.

TA417.2.R48	620.1'127–dc19	84-646699
Library of Congress	[8502]	AACR 2 MARC-S

Library of Congress Catalog Card Number 84-646699
ISBN 0-306-42269-7

Second half of the proceedings of the Twelfth Annual Review of Progress in Quantitative Nondestructive Evaluation, held June 23–28, 1985, in Williamsburg, Virginia

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

Printed in the United States of America

VOLUME 5B

CHAPTER 5: ELECTRONIC MATERIALS AND DEVICES

CHAPTER 6: COMPOSITE MATERIALS

Section A: Process Control

Section B: Properties and Defects

Section C: Defects

CHAPTER 7: MATERIALS CHARACTERIZATION

Section A: Properties

Section B: Acoustoelasticity and Stress

Section C: Processes

Section D: Deformation

Section E. Porosity

REVIEW OF THE ACCURATE DETERMINATION OF OXYGEN IN SILICON

Li Yuezhen and Wang Qimin

Shanghai Institute of Metallurgy
Academia Sinica
Shanghai, China 200050

INTRODUCTION

One of the important problems in characterizing the quality of single crystal silicon is the determination of its oxygen content. There are many experimental methods for determining the oxygen content in silicon, for example, infrared absorption method, gas-fusion method, α-particle activation analysis and photon activation analysis. Among these methods the ir absorption method is the simplest and is non-destructive. However, the ir absorption method for measuring the oxygen content in silicon must be first calibrated by the other methods. In 1957, Kaiser et al. [1,2] first established the calibration curve for determining the oxygen content in silicon. Baker [3] suggested another calibration curve in 1970, which was in coincidence with the result of ^{3}He activation analysis by Gross [4]. ASTM adopted Baker's calibration curve as the standard in 1971. This calibration relationship between the ir absorption coefficient and the oxygen concentration has a large uncertainty. Moreover, the calibration constant would be probably high. In 1977, according to Graff's data [5], a standard was proposed in West Germany (DIN), but the calibration constant is much lower than Baker's data. However, Yatsurugi et al. [6] in 1973 obtained another calibration curve, but they paid no attention to it. Owing to the experimental dispersion in the above mentioned literatures, we established two more accurate calibration curves in 1981 [7] and in 1983 [8], one for 300K, the other for 78K, using inert-gas fusion method and α-particle activation analysis for determining oxygen in silicon. Due to the improvements of the specimen preparation and the ir and the gas-fusion technique, our results are better than those in the literature cited. In 1983 Iizuka [9], using α-particle activation analysis and in 1984 Rath [10], using photon activation analysis, respectively recalibrated the ir absorption curve for determining the oxygen content in silicon at 300K. Within the experimental error their results are consistent with our results.

The above mentioned results obtained by various authors are summarized in the following, and a new method for selecting the ir oxygen-free reference sample used in ir absorption difference method is presented. Finally the key points and the precision of our inert-gas fusion experiment as compared with other works are discussed.

COMPARISON OF EXPERIMENTAL RESULTS

300K Ir Oxygen-determining Calibration Curves and Calibration Constants

Baker's calibration curve is shown in Fig. 1. Figure 2 is Graff's calibration curve. It can be seen from Fig. 1 and Fig. 2 that the experimental dispersion is large. Figure 3 shows our result, the precision will be discussed below. Figure 4 shows Iizuka's calibration

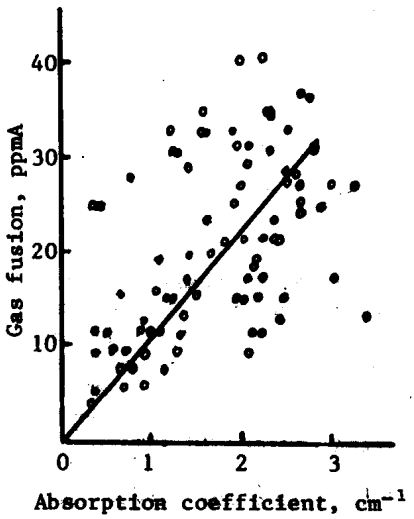

Fig. 1. Baker's calibration curve.

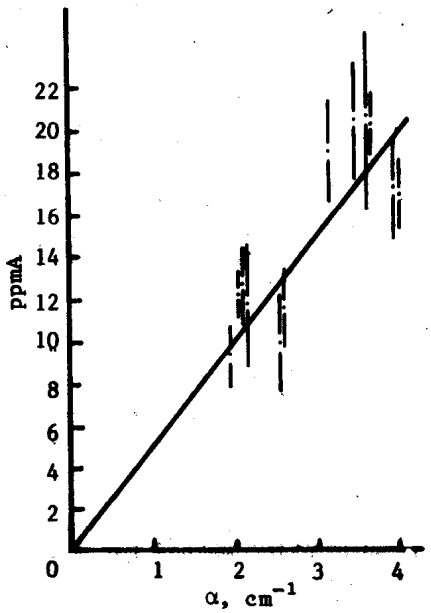

Fig. 2. Graff's calibration curve.

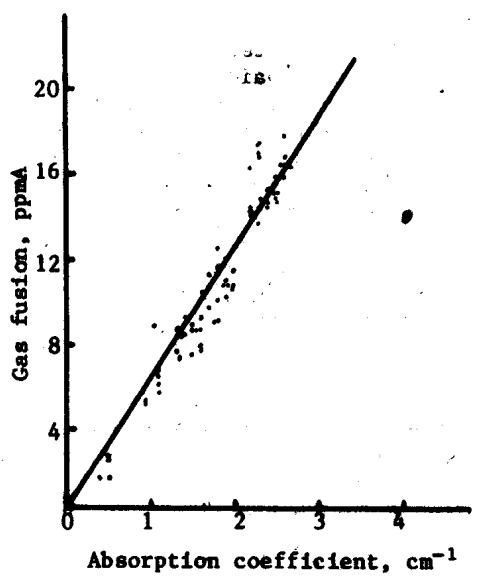

Fig. 3. Our calibration curve.

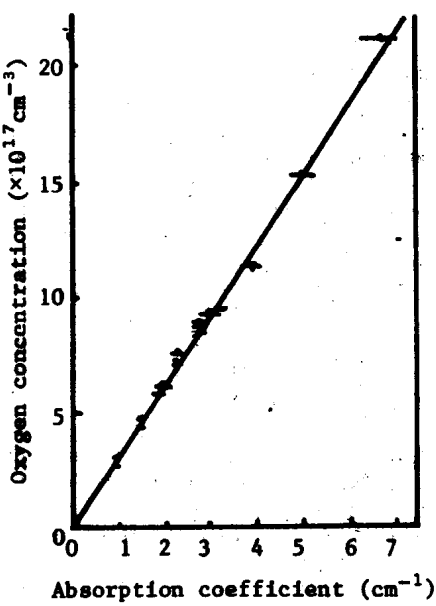

Fig. 4. Iizuka's calibration curve.

curve using α-particle activation analysis and Fig. 5 shows Rath's calibration curve using photon activation analysis. Figure 6 indicates the comparison of the experimental results obtained by various authors. It can be seen that Baker's calibration curve tends toward a high value of oxygen concentration, whereas Graff's calibration curve tends to a low value. Kaiser's result is slightly lower than ours. The calibration curves of Iizuka, Yatsurugi and Rath results are nearby our result. The comparison of calibration constants by various authors is shown in Table I.

Table I. The Comparison of Calibration Constants

Author	Gas analysis ppmA / Absorption coefficient α cm^{-1}	Activation analysis ppmA / Absorption coefficient α cm^{-1}
Baker	9.63 ± 2.29	8.1
Graff	4.9 ± 0.2	5.9
Ours	6.2 ± 0.1	6.2 ± 0.4
Iizuka, Yatsurugi	---	6.06 ± 0.04
Rath	---	6.0 ± 0.4

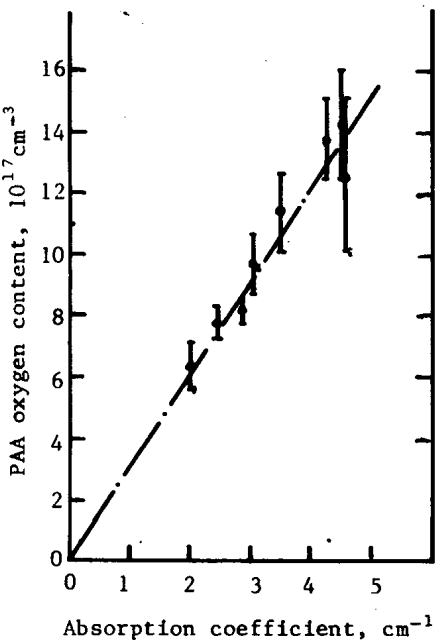

Fig. 5. Rath's calibration curve.

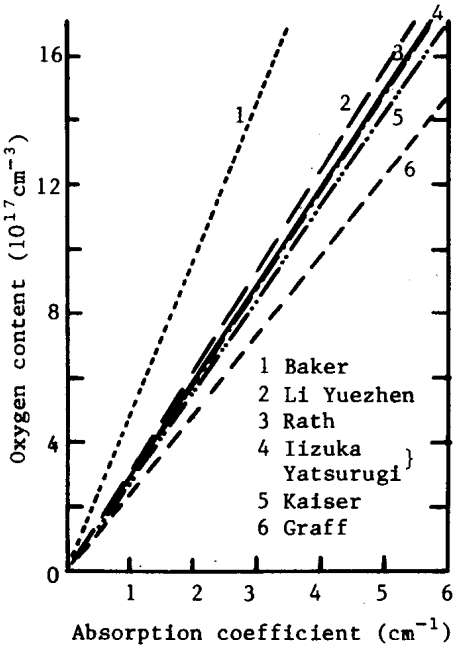

Fig. 6. Comparison of various calibration curves.

78K Ir Oxygen-determining Calibration Curves and Calibration Constants

Because low-temperature measurement can increase the sensitivity (5), the measuring sensitivity of the oxygen content at 80K can be twice that at 300K. Therefore, we carried out the measurements at 78K using ir absorption difference method. ASTM has set a standard that the calibration constant for 78K ir measuring oxygen content is 4.81 ppmA/cm^{-1} [11,12], but the calibration constant obtained by Graff in 1973 is 1.9 ppmA/cm^{-1} (5). The difference between them is rather large. Figure 7 shows our 78K calibration curve. The calibration constant obtained by us is 2.6 ppmA/cm^{-1}. The comparison of the 78K calibration curves among ASTM, Graff and ours is shown in Fig. 8. From Fig. 7 and Fig. 8, it can be seen that the experimental dispersion in Graff's curve is larger than ours.

A NEW METHOD FOR SELECTING IR OXYGEN-FREE REFERENCE SAMPLE

Using the air-reference method, there is an uncertainty in the absorption coefficient ranging from 0.6 to 1.05 cm^{-1} due to the intrinsic absorption of oxygen in Si-O-Si, whereas in the difference method there is no such uncertainty. Therefore, we have developed a new method for selecting the ir oxygen-free reference sample, which is more convenient, simple and reliable than other methods. This method utilizes the air reference method to measure the ir characteristics of the Si-O-Si absorption band at 78K after which we can distinguish the characteristic absorption of interstitial oxygen from the three photon absorptions of silicon. Thus, the ir oxygen-free sample can be found.

DISCUSSION

The gas-fusion method is a direct method for calibrating the ir absorption coefficient, but it is difficult to control. In order to improve the experimental accuracy, we adopted two procedures: careful preparation of the test specimen and accurate control of the ir and gas-fusion conditions.

Preparation of the Test Specimen

Specimens were prepared as 0.7 x 0.7 x 0.5 cm dice, weighing approximately 0.57 g. They were cut from CZ or FZ n-type and p-type of single

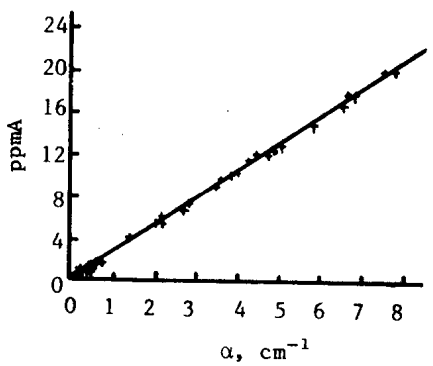

Fig. 7. The relationship between ir absorption coefficient and oxygen content at 78K.

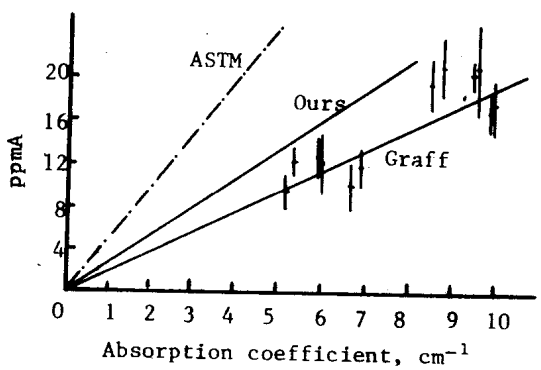

Fig. 8. The comparison among the calibration curves of ASTM, Graff and ours.

crystal silicon <111> orientation. The six faces were carefully polished with syton (colloidal silica) and then the pieces were cleaned by sequential immersion in basic and acidic hydrogen peroxide. Before the inert-gas fusion analysis, each piece was measured by the ir difference method. The area exposed is a circle 5 mm in diameter, thus there is no influence of inhomogeneous distribution of oxygen content. An oxygen content, corresponding to 1.2 ppmA oxygen for each dice, in a surface oxide film of average thickness 14Å was deduced from the gas-fusion result.

Control of the Gas-fusion Condition

We have used the Ni-Sn bath to extract carbon monoxide formed in the reduction process. In order to maintain a stable operating temperature (1690 ± 30°C), it was necessary to keep the relative positions of the inductive coil and the graphite crucible the same. When the graphite crucible was outgassed sufficiently at 2100°C, the blank of the gas analysis was stable and was reduced to lower than 0.1 μg.

Comparison of Results

In Fig. 3, 67 pairs of data points from gas-fusion analysis and ir absorption measurement were fitted to the regression line. The calculated value of the calibration constant is 6.2 ppmA, and the correlation coefficient is $r = 0.965$. The standard deviation of the residuals is 1.16 ppmA in our experiment and about 3.85 ppmA in Graff's data. In our diagram, it covers 68% experimental points within the range of ±1.16 ppmA, while in Graff's diagram it covers 68% experimental points in the range of ±3.85 ppmA.

Low temperature (78K) measurement of the ir absorption coefficient can increase the sensitivity of determination and can improve the measuring accuracy, especially for specimens of low oxygen content. Thirty-one data points from the ir difference method at 78K were measured (Fig. 7). Fitting these points by the regression method into a straight line, the calculated value of the calibration constant is 2.59 ppmA/cm^{-1}. The deviation of the slope is 0.19, so that $y = (2.59 \pm 0.19)x$, and the correlation coefficient $r = 0.999$. The residual standard deviation is $s = 0.275$ ppmA, while the s of Graff is 2.31. Our diagram (Fig. 7) covers 95% of the experimental points within the range of ±0.55 ppmA, while in Graff's diagram, 95% of the experimental points in the range of ±4.62 ppmA are included.

Two samples of the high, middle and low oxygen content crystal respectively were chosen for ir measurement at 300K by eight laboratories. The results are that for oxygen concentrations less than 1.15 ppmA the multilaboratory precision (RIS%) is of ±10.1%, while for concentrations above 1.15 ppmA the RIS% is of ±6.4%, which are better than ASTM results.

CONCLUSION

According to our results, the calibrating formula for 300K is

$$N_o = 3.1 \times 10^{17} \times \alpha \text{ atoms/cm}^3$$

or

$$N_o = 6.2 \times \alpha \text{ ppmA}$$

while that for 78K is

$$N_o = 1.3 \times 10^{17} \times \alpha \text{ atoms/cm}^3$$

or

$$N_o = 2.6 \times \alpha \text{ ppmA}$$

where α is the ir absorption coefficient.

REFERENCES

1. W. Kaiser, P. H. Keck and C. F. Lange, The Phys. Rev., 101, 1264 (1956).
2. W. Kaiser and P. H. Keck, J. Appl. Phys., 28, 882 (1957).
3. J. A. Baker, Solid-State Electronics, 13, 1431 (1970).
4. C. Grass, et al., J. Electrochem. Soc., 116, 248c (1969).
5. K. Graff, E. Grallath, S. Ades, G. Goldback and G. Tolg, Solid-State Electronics, 16, 887 (1973).
6. Y. Yatsurugi, N. Akiyama, Y. Endo and T. Nozaki, J. Electrochem. Soc., 120, 975 (1973).
7. Li Yuezhen, He Huannan et al., "A New Calibration Curve for Measuring Oxygen Content of Single Crystal Silicon by 9 μ Infrared Absorption Method" Shanghai Institute of Metallurgy, Academy of Sciences of China, May 1981; Li Yuezhen, He Huannan et al., Chinese Journal of Semiconductor 4, 81 (1983); He Huannan, Li Yuezhen, Zhao Guandi, Yan Ronghua, Lu Qingren, Qi Mingwei, Talanta, 30, 761 (1983).
8. Li Yuezhen, Shen Jinyuan and Wang Qimin, Materials Letters, 2, 101 (1983).
9. T. Iizuka, Shin Takasu, M. Tajima, T. Arai, M. Nozaki, N. Tnoue and M. Watanabe, in "Defects in Silicon", The Electrochemical Society, Softbound, Proceedings 83-9, p. 265.
10. H. J. Rath, P. Stallhofer and D. Huber, J. Electrochem. Soc., 131, 120 (1984).
11. 1979 Annual Book of ASTM Standards, Part 43, F121-79.
12. 1981 Annual Book of ASTM Standards, Part 43, F121-80.