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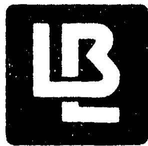

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

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Determination of Surface Recombination Velocity and Bulk Lifetime in Detector Grade Silicon and Germanium Crystals

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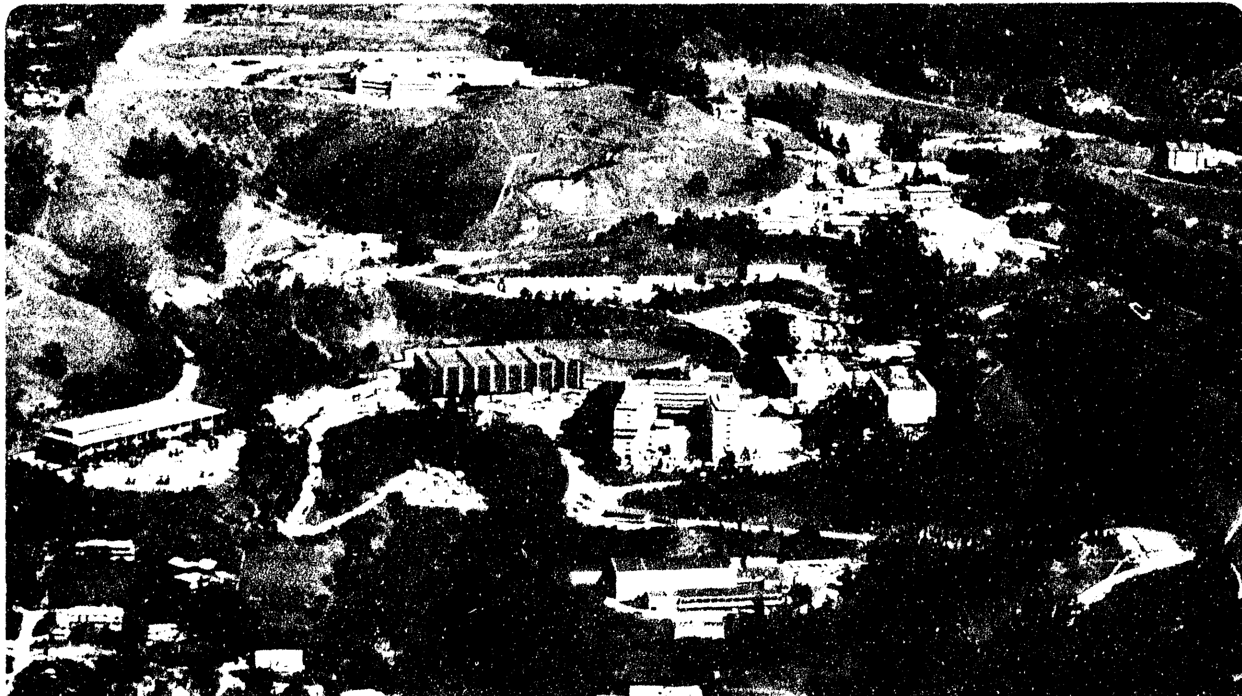

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Engineering Division
Lawrence Berkeley Laboratory
University of California, Berkeley CA 94720

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Engineering Division, Lawrence Berkeley Laboratory[1]
University of California, Berkeley CA 94720

Abstract

The utility of a noncontact photoconductive decay (PCD) technique is demonstrated in measuring the bulk lifetime, τ_B, and surface recombination velocity, S, in detector grade silicon and germanium crystals. We show that the simple analytical equations which relate the observed effective lifetimes in PCD transients to τ_B and S have a limited range of applicability. The noncontact PCD technique is used to determine the effect of several surface treatments on the observed effective lifetimes in Si and Ge. A degradation of the effective lifetime in Si is reported as a result of the growth of a thin layer of native oxide at room temperature under atmospheric conditions.

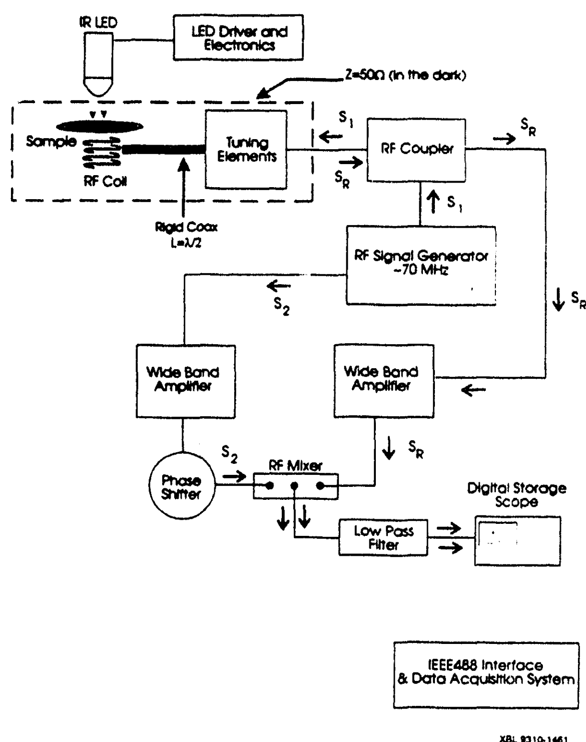

Fig. 1 Schematic of the experimental setup.

I. INTRODUCTION

Realization of the ideal performance of semiconductor radiation detectors depends in part on the optimization of key material parameters such as the bulk lifetime (τ_B) and surface recombination velocity (S). These two parameters affect the spectral background, energy resolution and entrance window dead layers in semiconductor detectors [1]. Measurement of the values of τ_B and S during detector fabrication procedures provides useful feedback for the development of optimum fabrication processes. Of the several available techniques to determine the free carrier lifetime in semiconductors, noncontact photoconductive decay (PCD) measurements are the most suitable for a fabrication environment since they require minimal sample preparation, can be used on line in between processing steps, and are nondestructive [2].

In this paper, we evaluate and utilize a noncontact PCD technique to measure the decay times of free carriers in detector grade floating-zone Si and high purity Ge, as part of an effort to develop a simple characterization tool which will aid in detector process development. Furthermore, we evaluate the limitations of different data analysis schemes which are used to interpret PCD transient data and we describe the proper use of such techniques. Two examples are described in which the PCD technique is used to measure the growth of native SiO_2 on Si after chemical etching and the effect of amorphous Ge deposition on the measured effective lifetime of Ge.

II. EXPERIMENTAL SETUP

The design of our noncontact lifetime measurement system is based on an inductively coupled photoconductive decay (ICPCD) technique described previously in the literature [3,4]. A block diagram of the system is shown in Fig. 1. The sample is placed on top of a 4-turn radio coil having a diameter of approximately 2 cm. The sample is inductively coupled to the coil and the measurement system by effectively behaving like a single turn secondary coil. The coil/sample combination is connected to a variable capacitor tuning element via a rigid coaxial cable with a length equal to half the wavelength of the applied 75 MHz RF signal. The section of the apparatus shown in the dashed box of Fig. 1 is a simple capacitance matching network that is tuned to present a 50 Ω impedance in the 20 dB coupler. The generated RF signal is split into two parts with amplitudes S_1 and S_2. S_1 goes to the 20 dB coupler and then into the branch of the system containing the sample. The output signal from the coupler, S_R, which is subsequently amplified by the wide band amplifier, is dependent on any impedance "mismatch" that the sample load presents to the coupler. With the sample in place, the capacitance matching network is tuned, using an RF vector voltmeter, so that the sample load to the coupler is 50 Ω. Connecting the load to the

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coupler, the phase shifter is adjusted to produce a minimum signal out of the mixer. The light from the IR LEDs excites free carriers in the semiconductor and increases sample conductivity. This in turn decreases the load impedance creating an impedance mismatch at the coupler and thus an increased RF signal out of the coupler. Once the optical source on the sample is turned off, the RF signal envelope from the coupler decays with a time constant that is proportional to the photoconductive decay of the carriers in the semiconductor sample. The output from the mixer is proportional to:

$$S_2 S_R(t)[\cos(\Delta\phi) + \cos(2\omega t + \Delta\phi)] \quad (1)$$

where ω is the resonant frequency and $\Delta\phi$ is the phase difference between S_2 and $S_R(t)$. The mixer output signal passes through a low pass filter to eliminate the higher harmonics and is then stored in a digital oscilloscope.

An array of infrared LEDs (λ_o = 875 nm, FWHM = 100 nm) was used to excite free carriers in the silicon samples. The measurements were performed at low LED power levels (~10–100 mW) to ensure a low level injection ($\Delta n << n_o$). The optical pulsewidths were 100–500 µs and the pulse rise/fall time was less than 250 ns. For the thicker germanium samples, a strobe light was used as the excitation source with a maximum output of 40 W. This source had a broadband spectral output with approximately Gaussian pulses having FWHM ≈15 µs. Filters were used to adjust the light intensity and ensure a low level injection. The measured PCD transients were fitted and the characteristic effective lifetimes, τ_{eff}, were extracted from them. The relationship of τ_{eff} to τ_B and S is discussed in the next section.

III. DATA ANALYSIS

Surface recombination of photogenerated carriers influences the PCD transients extensively and introduces complications in the analysis of the transients [5]. When surface effects are eliminated, then PCD transients are governed by a single decay constant which is the bulk lifetime. That is, the nonequilibrium conductivity decays according to the function $\exp(-t/\tau_B)$. In reality, however, finite surface recombination rates result in multiexponential PCD transients [5–7] The exact solution to the equations governing the decay of photoexcited carriers in a semiconductor with finite surface recombination velocities gives rise to PCD transients that decay according to:

$$\sigma = \sigma_o \sum_1 a_j e^{-\frac{t}{\tau_j}}, \quad (2)$$

and the characteristic times are given by:

$$\frac{1}{\tau_j} = \frac{1}{\tau_B} + \alpha_j^2 D, \quad (3)$$

where D is the diffusion coefficient, and α_js are given by the solutions to the transcendental equation:

$$\cot\left(\frac{\alpha_j L}{2}\right) = \frac{2D}{SL}\left(\frac{\alpha_j L}{2}\right) \quad (4)$$

where L is the sample thickness.

Figure 2 shows a calculated PCD transient for a typical silicon sample ($\tau_B = 10^{-3}$, S = 30,000 cm/sec, D = 32 cm²/sec, L = 500 µm).

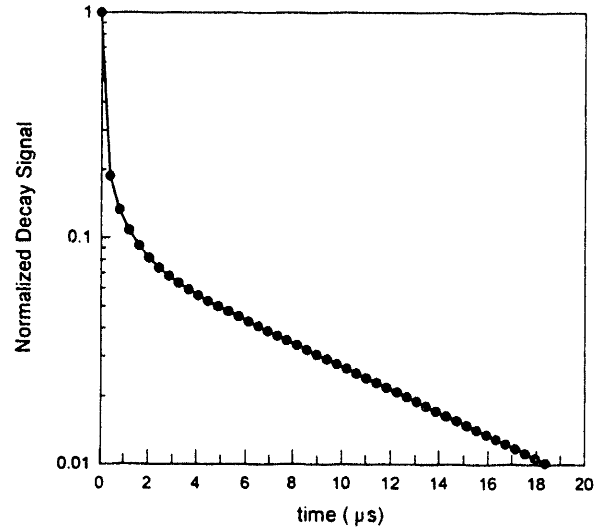

Fig. 2 Calculated PCD transient for a typical Si sample.

The first term in the series solution (2), which contains the longest effective lifetime, is the dominant decay mode in the multiexponential transients. This dominant term is labeled the effective lifetime, τ_{eff}, of the PCD transient. The terms governed by shorter decay times die out quickly, resulting in the initial sharp drop of the transients [6,8] Simple analytical expressions can be derived for the observed τ_{eff} based on the values of material parameters such as τ_B, S, D, and sample thickness L [8]:

$$\text{if } S<<2D/L \text{ then } \quad \frac{1}{\tau_{eff}} = \frac{1}{\tau_B} + \frac{2S}{L}, \quad (5)$$

$$\text{if } S>\pi D/L \text{ then } \quad \frac{1}{\tau_{eff}} = \frac{1}{\tau_B} + \frac{\pi^2 S^2}{(SL+2D)^2} D, \text{ and} \quad (6)$$

$$\text{if } S>>2D/L \text{ then } \quad \frac{1}{\tau_{eff}} = \frac{1}{\tau_B} + \frac{\pi^2 D}{L^2} \quad (7)$$

A PCD experiment, however, allows the measurement of only the sample thickness and effective lifetime. The extraction of τ_B and S from a PCD transient is possible if the appropriate equation is applied to analyze the data. In the case of Equation 5, the determination of τ_B and S is straightforward:

the effective lifetime of samples of varying thickness, but identical surface conditions, is measured and the plot of $1/\tau_{eff}$ vs. $1/L$ will yield τ_B and S. However, the range of applicability of Equation 5 is limited. For instance, with typical Si wafers having thicknesses in the range 200-1000 µm, the application of Equation 5 is only appropriate if the surface recombination velocities are lower than 100 cm/sec. Such low values of S are typically only observed on highly passivated Si surfaces. Consequently, the limitations imposed by Equations 5–7 necessitate some prior knowledge of the parameters under investigation. Proper data analysis in PCD experiments requires solving the equations governing the decay of photo-excited carriers and fitting the observed transients with the appropriate multiexponential decays. This method of analysis requires the introduction of additional fitting parameters which may, in certain situations, introduce unavoidable uncertainties in the measured variables. Nevertheless, the ICPCD technique can be used effectively to investigate the influence of various surface treatments on S by comparing the effective lifetimes of samples of equal thickness that have been through different surface treatments, providing the surface processes do not alter the bulk lifetime.

IV. RESULTS

To demonstrate the effectiveness of the ICPCD technique, we report on our measurements of the degradation of the effective lifetime in Si due to native oxide growth on Si. The growth of the native oxide on silicon surfaces at room temperature under atmospheric conditions after dilute HF etching has generated great interest recently from the silicon industry, because the thin native oxide films (10–50 Å) influence the growth of high quality epitaxial silicon [9–12]. The well studied thermodynamics which control the growth of thermal oxide on silicon is inadequate in describing the kinetics of native oxide growth [9]. Several investigators have used ellipsometry to measure the growth rate of the native oxide on silicon [9, 11–13] and they have found that the oxide grows logarithmically with time on a freshly etched Si surface, saturating at a thickness of approximately 10–50 Å over a 24 hour period, depending on ambient conditions. The growth of native oxide is associated with the creation of surface states due to breakage of Si-Si and Si-H bonds in favor of the formation of Si-O and Si-OH bonds [10]. A decrease in the band-to-band photoluminescence intensity in HF treated Si over time has also been ascribed to a decrease of the surface lifetime due to native oxide growth [10]. We have measured this change in the surface lifetime of Si due to oxide growth using the ICPCD system. The test sample was a 1 mm thick, 4 cm^2 square, high resistivity, floating-zone Si (p-type, $N_A - N_D \sim 10^{11}$ cm^{-3}). The sample was etched in HNO_3:HF (3:1) for one minute followed by an isopropanol quench and then given a two minute HF:H_2O (1:5) etch, followed by a one minute DI water rinse. The sample was then placed in the ICPCD measurement system and the PCD transients were measured over time. (During the course of the experiment, the room temperature was 22±2°C and the humidity was 52±3%.) Figure 3a shows a typical normalized PCD transient from these samples. The output of the infrared LED signal is also shown in this figure demonstrating the relatively sharp turn off time of the optical source. Each transient was curve fitted and an effective lifetime was extracted. Figure 3b shows the decay part of the transient fitted with an exponential function having an effective decay time of 140 µs. Figure 4 shows the effective lifetime as a function of time after etching for the silicon samples.

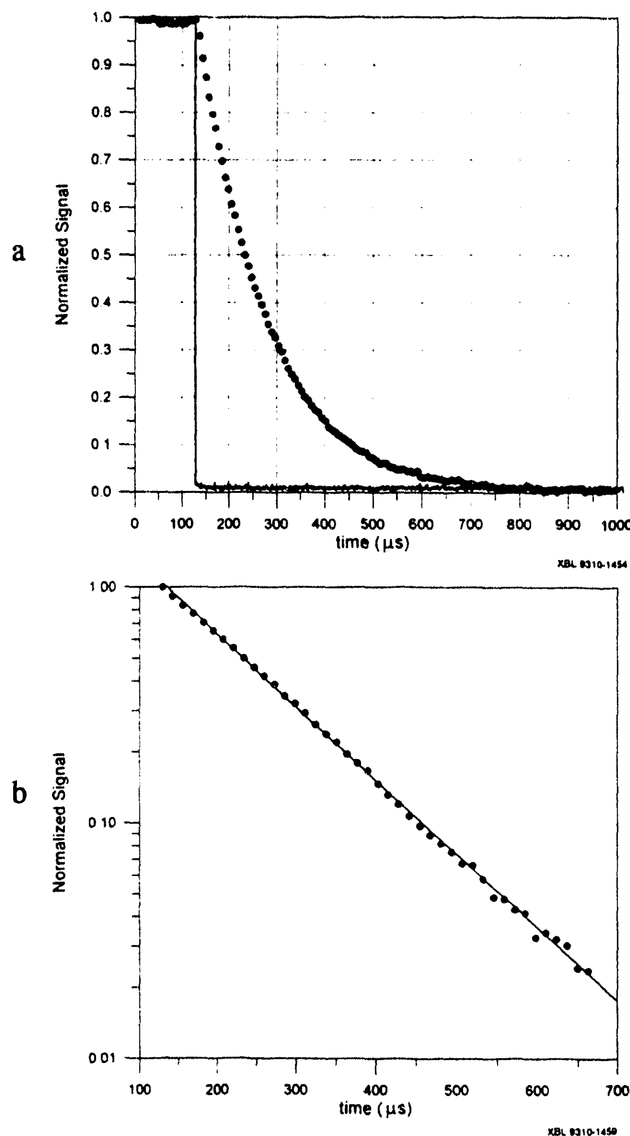

Fig. 3 (a) Normalized PCD transient of a 1mm thick Si sample (•••). The output signal of the LED array is also represented (—). (b) The decay part of the transient curve fitted by an exponential function with a characteristic time equal to 140 µs.

HF treatment of silicon surfaces results in the removal of the native oxide and produces hydrogen termination of the dangling Si bonds, which passivates the surface and decreases the surface recombination velocity [9,10]. Accordingly, we measured a relatively large effective lifetime in the silicon immediately after HF etching (715 µs) which subsequently

decreases logarithmically with time, indicating the growth of the native oxide. Two distinct regions are evident in the curve in Fig. 4, which suggests a layer-by-layer growth of native oxide [10]. After 400 minutes, the measured effective lifetime asymptotically approaches 24 μs and does not decrease further. The increase in the surface recombination velocity, due to the growth of the native oxide on freshly etched Si samples, results in a measurable decrease in the observed effective lifetime of Si. To insure the stability of Si detectors over time, we are currently employing the ICPCD system to investigate different Si surface passivation schemes that would result in a consistent and stable τ_{eff} after standard HF treatments.

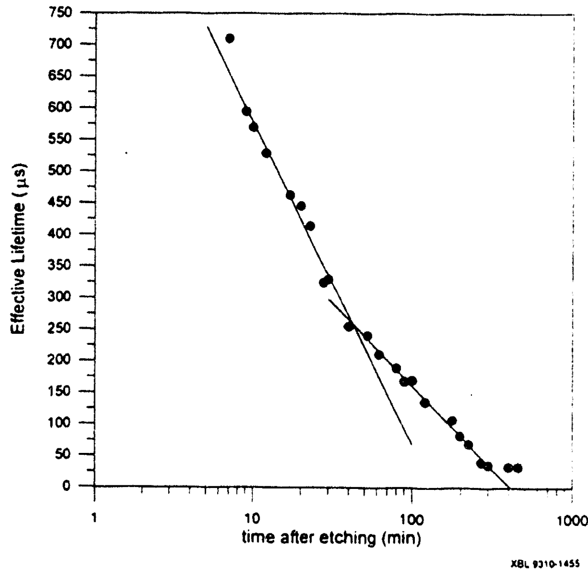

Fig. 4 Decay of the effective lifetime in silicon after HF treatment due to native oxide growth.

In addition to the previously described measurement of τ_{eff} in oxidized Si, we have also measured τ_{eff} as a function of sample thickness, L, in order to extract the material parameters S and τ_B. Silicon wafers of varying thickness were cut (0.025 cm $< L <$ 0.183 cm) and were given similar chemical treatments as described above. The wafers were stored at room temperature under atmospheric conditions for one day to allow the growth of the native oxide. The PCD transients were measured using the ICPCD measurement system and τ_{eff} was obtained for each thickness. Figure 5a shows $1/\tau_{eff}$ vs. $1/L$ using the experimental data and the fit obtained by modeling the exact solutions to the equation governing the decay of the photoexcited carriers in Si [8]. The parameters used in the fitting curve were: τ_B = 2500 μs, D = 28 cm^2/sec, and S = 20,000 cm/sec. (The vendor specified bulk lifetime was 3000 μs, which correlates closely with the value for τ_B obtained from the fit.) Similar measurements were performed on Ge samples (p-type, N_A - N_D ~10^{10} cm^{-3}, 0.09 $< L <$ 1.0 cm), and are shown in Fig. 5b. The fitting parameters for the Ge were τ_B = 5000 μs, D = 80 cm^2/sec, and S = 1300 cm/sec. The dramatic difference in S between the Si and Ge samples is due to the higher surface state density resulting from the thin native oxide layer on the silicon surface.

Finally, we investigated the utility of the ICPCD technique for monitoring surface conditions resulting from detector processing by comparing the effective lifetimes of a 4mm thick Ge sample before and after the deposition of 600 Å amorphous Ge. The samples were chemically treated as described previously; the measured τ_{eff} before the deposition of the amorphous Ge was 3.0±0.3 x 10^{-3} seconds. After sputtering 600 Å of amorphous Ge on both surfaces of the wafer, τ_{eff} decreased to 2.3±0.3 x 10^{-4} seconds, due to the large concentration of traps on the Ge surface created by the amorphous layer. The effective lifetime increased back to its original value of 2.9±0.3 x 10^{-3} seconds after the amorphous layer was subsequently etched away.

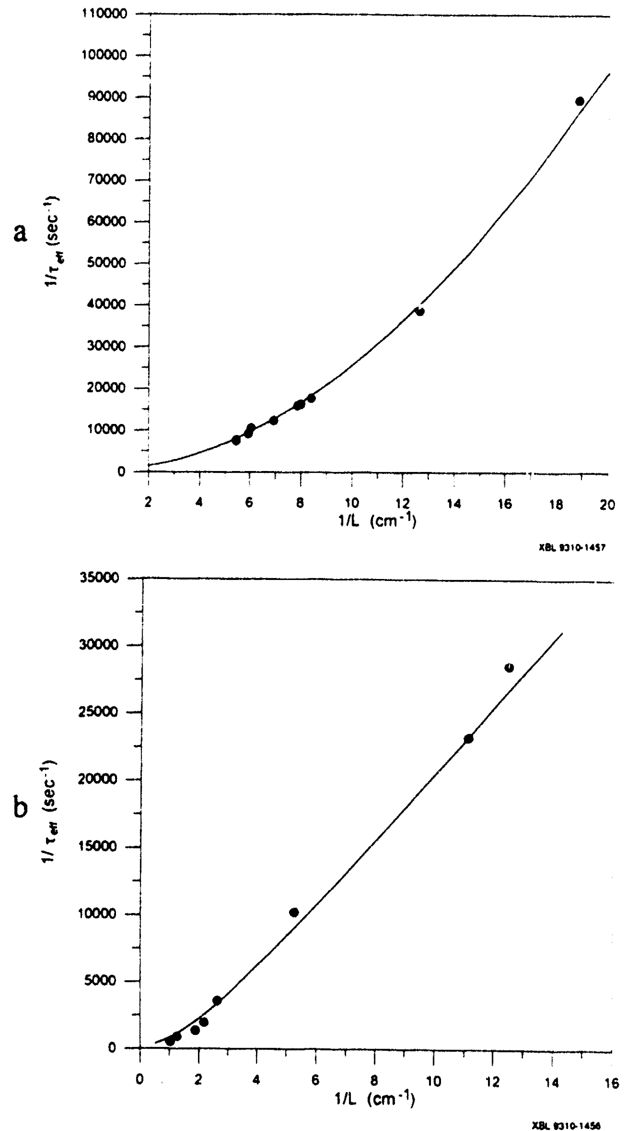

Fig. 5 Plot of $1/\tau_{eff}$ vs. $1/L$ using the experimental data (•••) and the calculated results (—) for (a) Si, and (b) Ge.

V. CONCLUSION

We have evaluated the utilization of a noncontact photoconductive decay measurement technique to determine the

effective lifetime of detector grade high purity Si and Ge crystals. The technique is ideally suited for use in a detector fabrication environment, because it does not require extensive sample preparation and is nondestructive. Furthermore, we have identified the inherent limitations which exist in the analysis of PCD transients using simple analytical expressions that relate the observed τ_{eff} to τ_B and S. The ICPCD technique is shown to be effective in the measurement of the degradation of τ_{eff} as a function of native oxide growth on Si, and for estimating τ_B and S as a function of processing conditions of high purity detector grade Si and Ge. We are incorporating the ICPCD technique as an aid in the optimization of key processing steps in the fabrication of Si and Ge radiation detectors.

VI. REFERENCES

[1] D.C. Joy, "The energy dispersive x-ray detector: a quantitative model," *Rev. Sci. Instrum.*, vol. 56(9), pp. 1772-1779, Sept. 1985.

[2] D.K. Scroder, *Semiconductor Material and Device Characterization*, New York:John Wiley and Sons, 1990, Chapter 8, pp. 359-447.

[3] E. Yablonovitch and T. Gmitter, "A contactless minority lifetime probe of heterostructures, surfaces, interfaces and bulk wafers," *Solid State Elect.*, vol. 35, pp. 261 267, March 1992.

[4] H.W. Curtis and R.L. Verkuil, "High signal to noise oscillator for contactless measurement of photoinduced carrier lifetimes," *Lifetime Factors in Silicon*, ASTM STP 712, 1980, pp. 210-224.

[5] W. Shockley, *Electrons and Holes in Semiconductors*, New York:Van Nostrand, 1950, p. 318.

[6] K.L. Luke and L. Cheng, "Analysis of the interaction of a laser pulse with a silicon wafer: Determination of bulk lifetime and surface recombination velocity," *J. Appl. Phys.*, vol. 61, pp. 2282-2293, March 1987.

[7] M. Morin, M. Koyanagi and M. Hirose, "A semi analytical approach to compute the decay of optically generated carriers in silicon wafers," *Jpn. J. Appl. Phys.*, vol. 32, pp. L816-L819, June 1993.

[8] N. Derhacobian, J.T. Walton, P.N. Luke, Y.K. Wong and C.S. Rossington, "Proper interpretation of photoconductive decay transients in semiconductors," submitted to *J. Appl. Phys.*, October 1993.

[9] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami and M. Ohwada, "Growth of native oxide on a silicon surface," *J. Appl. Phys.*, vol. 68, pp. 1272-1281, August 1991.

[10] T. Konishi, K. Uesugi, K. Takaoka, S. Kawano, M. Yushimura and T. Yao, "Characterization of HF treated Si(111) surfaces," *Jpn. J. Appl. Phys.*, vol. 32, pp. 3131-3134, July 1993.

[11] M. Morita and T. Ohmi, "In-situ control of native oxide growth for semiconductor processes," in *Mat. Res. Soc. Symp. Proc.*, vol. 259, San Francisco, CA, April 1993, pp. 19-29.

[12] C. Okado, H. Kobayashi, I. Takahashi, J. Ryuta and T. Shingyouj, "Growth of native oxide and accumulation of organic matter on bare Si wafers in air," *Jpn. J. Appl. Phys.*, vol. 32, pp. L1031-L1033, August 1993.

[13] F. Lukes, "Oxidation of Si and GaAs in air at room temperature," *Surf. Sci.*, vol. 30, pp. 91-100, March 1972.

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