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ABSTRACT

Contactless measurement of important semiconductor parameters has become a popular trend of current semiconductor technology. Here we will describe an improved version of radio frequency photoconductive decay (RFPCD) operating in the ultra-high frequency (UHF) region. This work will show that the improved technique is capable of measuring samples ranging in size from submicron thin films to large silicon ingots. The UHF region is an ideal compromise for volume penetration and lifetime resolution with system response of 10 ns or less.

INTRODUCTION

Because of the increased demand for production diagnostics, the development of new and improved contactless techniques has become a focus of the Electro-optical Characterization Team at the National Renewable Energy Laboratory (NREL). The contactless measurement of minority-carrier (low-injection) or recombination (high-injection) lifetimes is an important diagnostic tool in photovoltaic devices. Techniques requiring contacts severely limits the accuracy and applicability of the diagnostic technique in most cases. Reliable ohmic contacts require metal deposition in vacuum and post-deposition processing. Contamination caused by the contact is always a concern, and contact removal adds another somewhat expensive processing step. Thus, ohmic contact deposition is not a prudent operation for samples that are to be turned into devices. For spring-loaded contact schemes, the ohmicity of the contact is often a problem when the measurement accuracy is influenced by nonlinear contact behavior. Thus, in the production environment, contactless diagnostics are almost mandatory unless a diagnostic substructure can be tolerated in the final device. Therefore, in evaluating the minority-carrier lifetime of ingots, wafers, and films prior to processing, a contactless technique is almost always required.

The well-known microwave-reflection technique is the standard of the silicon industry and is the standard for the contactless measurement of minority-carrier lifetime. The technique is limited to small-signal measurements (low injection) and low- to moderate-conductivity materials. In this work, we will describe experimental results from a second-phase measurement system based on a contactless system described earlier [1]. The early system was adequate for thin films and small bulk samples, but was not useful for large wafers or ingots. The Phase II measurement system can function for samples of arbitrary physical size, ranging from thin films to ingots with volume of hundreds of cm^3. This paper will describe RFPCD measurements on a variety of popular photovoltaic materials ranging from submicron films to silicon ingots.

OTHER CONTACTLESS TECHNIQUES

Microwave Reflection

Microwave reflection is based on the reflectance of free carriers, and thus both the background dark conductivity and light-induced excess carriers are sensed by the detection system. At the popular test frequencies in the gigahertz (GHz) range, the microwave reflection is a very nonlinear function of sample conductivity [2].
One may write the reflected microwave power as the first term of a Taylor series:

$$\Delta P = P_{in} \frac{dR(\sigma)}{d\sigma} \Delta\sigma, \quad (1)$$

and define the derivative $dR/d\sigma$ as the sensitivity factor $A(\sigma)$. As $R(\sigma)$ is a nonlinear function of conductivity, transients measurements are interpretable only in the small signal range, i.e., when $\Delta\sigma << \sigma$ and the higher-order terms in the Taylor expansion can be neglected. Thus:

$$\frac{\Delta P}{P_{in}} = A(\sigma)\,\Delta\sigma, \quad (2)$$

The calculations of Kunst and Beck show that for the low conductivity range (from 10^2 to 10^{-1} $ohm^{-1}cm^{-1}$), the 30-GHz sensitivity factor varies as:

$$A(\sigma) = 1 - B\sigma, \quad (3)$$

where B is a prefactor that is a linear function of the microwave frequency ω. In this case, $R(\sigma)$ changes from about 0.99 at 10^{-2} $ohm^{-1}cm^{-1}$ to about 0.90 $ohm^{-1}cm^{-1}$, for a typical wafer ($\varepsilon = 12$) that is about 330 μm thick. A reflectivity minimum occurs at about 1.0 $ohm^{-1}cm^{-1}$, and thus A = 0 in this range. At larger conductivities, $R(\sigma)$ begins to increase to a value near unity at σ= 10 $ohm^{-1}cm^{-1}$. In this conductivity range, the sensitivity factor varies as:

$$A(\sigma) = C\,\sigma^{-1.5}, \quad (4)$$

Here, prefactor C contains the test frequency as $\omega^{-0.5}$. At conductivities greater than 10 $ohm^{-1}cm^{-1}$, the reflectivity

is nearly 1.0 and thus the technique fails. In summary, the limitations of the microwave reflection technique are:

(1) Measurements can only be made over a limited range of conductivites.

(2) The reflection is a nonlinear function of σ and thus only small signal (low injection) TRMC measurements can be interpreted.

Radio Frequency Decay

In analyzing the techniques that are based on the interaction of electromagnetic (EM) waves with free carriers, one needs to calculate the penetration depth of the wave. This is needed as a function of EM frequency and material conductivity. The "skin depth" or 1/e penetration depth of the EM wave is calculated from classical EM theory as:

$$\delta = \frac{C}{\sqrt{\sigma\ \omega}}, \quad (5)$$

Here, δ is the skin or penetration depth, ω is the radiation frequency, σ is the conductivity of the material, and C is a constant. Recent work has used radio frequencies (RF) to measure transient conductivity induced by pulsed light sources and extract the minority-carrier lifetime [3,4]. A coil driven at RF produces eddy currents in a sample under test. These eddy currents in turn produce an additional RF voltage in the driving coil that tracks the excess-carrier decay. At the operating frequency of 424 MHz used in the present work, the penetration depth of the RF varies from 1000 µm at 10 $ohm^{-1}cm^{-1}$ to 20,000 µm at 0.1 $ohm^{-1}cm^{-1}$. The author recently applied the UHF technique to a variety of silicon wafers that were both lightly and heavily doped as well as single and polycrystalline [5]. These measurements were successfully made over a wide range of injection levels. The limitation of this Phase I technique was that it did not function with samples that were physically large, such as large silicon wafers or ingots. A second-generation measurement system has recently been developed that does not have the latter limitation [6]. Measurements with the Phase II system will be described here, applying the technique to a variety of photovoltaic materials, ranging from silicon ingots to thin, submicron films of CdS.

The new technique uses a three-turn drive coil (diameter of 5 mm) to induce eddy currents in a semiconducting sample. These eddy currents, in turn, induce an additional voltage in the drive coil, and that voltage is a function of the sample conductivity. The induction coil is a component of a high-frequency circuit operating at a fixed frequency of 424 MHz. The dark conductivity of the sample is nulled by the electronic tuner. Circuit analysis shows that the output of the RF detector can be made linear over at least three orders of magnitude of sample conductivity. Thus, the high- and low-injection lifetimes can be analyzed. This feature is advantageous for several reasons to be described. We are able to measure minority-carrier or recombination lifetimes in a large variety of materials including silicon, germanium, GaAs, InGaAs [7], CdS, and recently, SiC [8]. Silicon wafers have been measured in the conductivity ranges from conductivities of 100 $ohm^{-1}cm^{-1}$ to those less than 0.01 $ohm^{-1}\ cm^{-1}$. First, the lifetime at various injection levels may be an important parameter in modeling device operation. Finally, when a single Shockley-Read-Hall (SRH) defect dominates the lifetime, the ratio of high- to low-injection lifetime is a function of the ratio of capture cross sections of electrons and holes of the particular defect [9]. This distinctive ratio may be used to identify the impurity controlling the lifetime.

The primary light source used for these measurement is a yttrium aluminum garnet (YAG) laser with a full width half maximum (FWHM) of 3.0 ns at a wavelength of 1.064 µm. Our system has a doubler producing 532-nm and a tripler producing 355-nm light pulses. In addition, the tripler is used to run an optical parameteric oscillator (OPO) that can span a wavelength range from 400 nm to 2.0 µm. An advantage of the OPO is that it can be tuned to the onset of absorption for most semiconductors, so that uniform generation in the sample volume is produced. The output pulse energy is continuously controllable by directing the laser beam through a pair of crossed polarizers. Other light sources include pulsed-light-emitting diodes and a xenon flashlamp. For silicon lifetime measurements, the fundamental YAG wavelength of 1064 µm produces nearly uniform volume generation ($\alpha \sim 5\ cm^{-1}$) and surface effects are minimized. To measure the surface recombination velocity (S) in silicon, the 532 nm and 355 nm source produce near surface absorption accentuating the effect of S and allowing a calculating of S to be made.

EXPERIMENTAL RESULTS

Sample Size Independence

The following data illustrate the system capability for handling samples that vary orders of magnitude in volume.

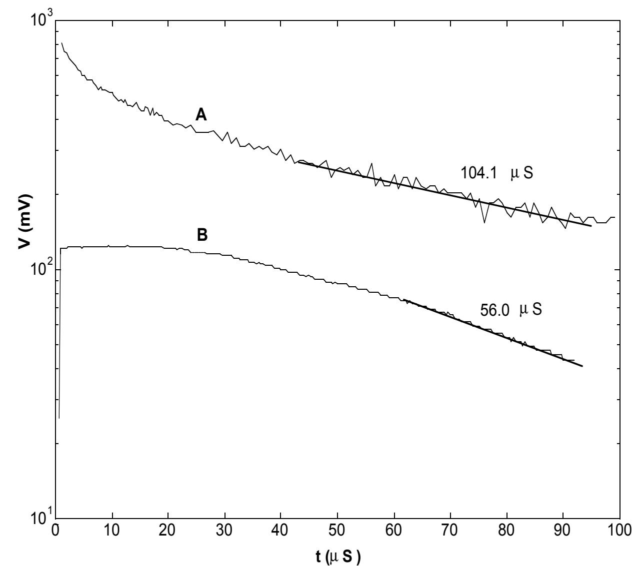

Fig. 1. Curve A: the photoconductive decay of a silicon ingot grown by the float zone technique. Curve B: the decay of a silicon "needle" that has been cut from a float zone ingot.

Fig. 1 illustrates the feature of sample size independence of the Phase II system using data (Curve A) from a silicon ingot grown by the float-zone technique. The ingot is about 6 in. in length and 1.5 in. in diameter. A long-term lifetime of 104 μs is seen from the data fit. The excitation wavelength here is 1064 nm and the sample surface is unpassivated. The initial, faster decay may be caused by diffusion of minority carriers away from the sensing coil.

To compare data from a large sample to a very small sample, Curve B of Fig. 1 shows data from a small silicon "needle" that has physical dimensions of 92 μm x 83 μm x 1.38 cm. This sample was cut from a quality float zone wafer using a dicing saw. The sample was then etched, cleaned, and surface passivated using a wet oxidation process. Because of the high surface-to-volume ratio of these samples, the surface-recombination effects are expected to dominate all other processes. Here, we observe high- and low-injection lifetimes as modeled in the literature [9].

Lifetime Measurement in a Passivating Solution

A second advantage of RFPCD (or UHFPCD) techniques is that silicon can be immersed in iodine-methanol solutions and inductively coupled to the measurement system [4]. Detailed data on a variety of passivated silicon wafers were recently described [5]. The time required to null dark conductivity for samples of similar physical size is typically less than 1 min. using manual techniques. Automated techniques could greatly reduce that time. The ease of nulling makes the technique a candidate for production-line quality control and diagnostics. On the other hand, because of the contactless nature of the measurement, extending the sample temperature to cryogenic temperatures is not extremely difficult, bypassing the general problem of good low-temperature contacts. A Phase IB system has produced lifetime measurements down to 80 K. A representation of data from a variety of sample types will be presented in the remainder of this manuscript.

To illustrate measurement in solution, Fig. 2 shows the results of lifetime studies on a very high quality float zone wafer grown at the UniSil Corporation. The wafer is undoped and the conductivity is less than 0.01 ohm^{-1} cm^{-1}. The wafer was cleaned in hydrofluoric acid, rinsed in deionized water, and placed in methanol that was saturated with iodine. The methanol/iodine (M-I) solution has been shown by Kimmerling and coworkers [4] to reduce the surface recombination velocity to minimal values. Prior to M-I treatment, a lifetime of several hundred microseconds was measured on this wafer and surface recombination was the dominant process. Because of the strong response of this wafer, the 1064 nm laser beam was attenuated well below the minimum pulse energy provided by crossed polarizers. The latter energy has been measured at about 50 μJ/pulse. Because of the low background doping, high-injection conditions were observed even at these attenuated pulse energies. Fig. 2 shows an initial decay time of 8.44 ms followed by a plateau region for which the lifetime is 53.5 ms. The initial decay is Auger recombination produced by the high injection of excess carriers. The 53.5 ms lifetime is indicative of a saturated SRH defect level for which the recombination rate is dominated

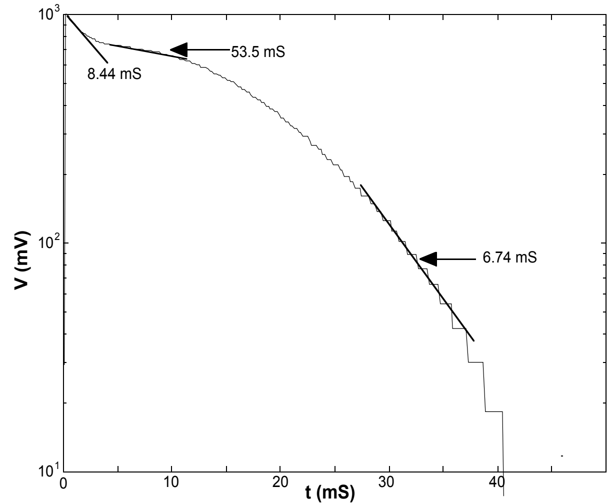

Fig. 2. The photoconductive decay of a high quality float zone ingot immersed in a solution of methanol saturated with iodine.

by the majority-carrier capture rate. Finally, the low-injection region is observed with a lifetime of 6.7 ms. Thus, this wafer has three distinct lifetime regions as the carrier decay is observed over about two orders of magnitude of injection level. These data indicate the value of a measurement system that is linear over several orders of magnitude in order to sort out the variety of recombination processes that are active.

Lifetime as a Function of Excitation Wavelength: Surface Recombination

When surface passivating solutions are not available or convenient, the separation of surface and bulk effects can be accomplished by changing the excitation wavelength during the measurement. As the absorption depth decreases, the effect of surface recombination becomes pronounced in the initial decay. An analytical expression described the initial decay in terms of the bulk lifetime and surface recombination velocity S for a bulk material of infinite thickness. The result has been derived as [2]:

$$\tau_0 = \frac{\tau_b}{1 + \alpha S \tau_b}, \qquad (6)$$

Here, τ_0 is the initial decay time, τ_b is the asymptotic or bulk decay time, α is the absorption coefficient, and S is the surface recombination velocity in cm/s.

As an example, we measured a p-type wafer, provided by Siemens Solar, with a conductivity of about 0.1 ohm^{-1} cm^{-1}. The wafer was sawed from an ingot and subjected to both caustic and texture etches. Fig. 3, Curve A shows the photoconductive decay of the wafer using YAG 1064-nm wavelength pulses. The incident-pulse energy is approximately 1 mJ and the beam diameter is 5 mm. We see from the data that a typical, two-component SRH behavior is active with a high-injection lifetime of 17.6 μs and a low-injection lifetime of 11.6 μs. Curve B shows the photoconductive decay of the same wafer using a 532-nm wavelength.

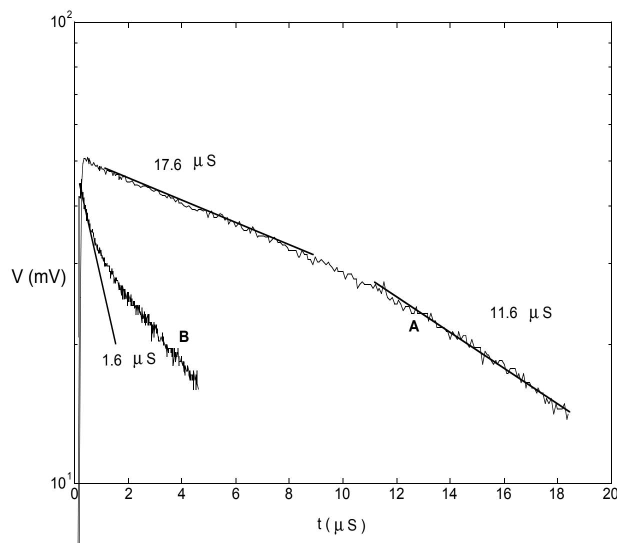

Fig. 3. The photoconductive decay of a solar cell grade Czochralski grown wafer. Curve A: λ=1064; Curve B: λ=532 nm.

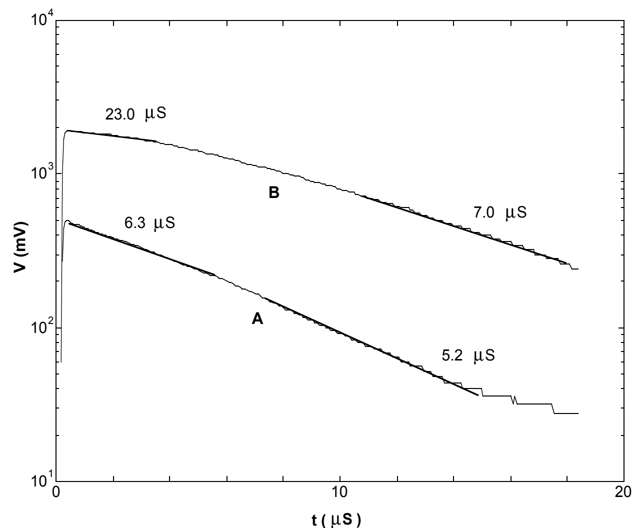

Fig. 4. The photoconductive decay of a In(0.53)Ga(0.47)As/ InP double heterostructure at low injection: Curve A and high injection: Curve B.

A lifetime of 1.6 μs at t = 0 is observed because the excess carrier density is generated near the front surface. The 1/α, or generation length, is about 1 μm in this case and the surface recombination dominates the decay until electrons diffuse into the bulk. At longer times, the lifetime becomes 4.8 μs which is likely a low-injection value. Applying the experimental lifetime values and the absorption coefficient of 8.9×10^3 cm^{-1}, the calculated surface recombination S is 64 cm/s.

Thin Film Measurement

Thin films are an important component of current photovoltaic activity and lifetime characterization of these materials is very useful. The thermophotovoltaic program addresses energy conversion from relatively low-temperature sources (2000°C to 3000°C) and uses small bandgap semiconductors to match the blackbody spectra of the latter.

As an example of the utility of the RFPCD measurement system for thin film lifetime characterization, measurements were made on thin films of In(0.53)Ga(0.47)As that is lattice matched to InP. The data of Fig. 4 were obtained from a double heterostructure of n-InP/n-InGaAs/n-InP grown on an InP substrate. The film thickness is 1.75 μm and the background electron concentration is 1.27×10^{15} cm^{-3}. Using the 1064-nm YAG laser-excitation source, the data of Curve A were obtained with very low energy pulse excitation. The low-injection lifetime of 5.2 μs is slightly increased in the initial portion of the curve owing to partial SRH center saturation. Curve B shows the RFPCD decay at slightly higher pulse energies, with an initial decay time of 23.0 μs followed by a lower injection lifetime of 7.0 μs. These data again illustrate the value of measuring lifetime over a wide range of injection levels to obtain values that are commensurate with the actual device injection conditions.

CONCLUSION

The Phase II UHFPCD measurement system was shown to be compatible with a wide range of sample sizes ranging from ingot to thin films. The system response was shown to be linear over at least two orders of magnitude of carrier injection. Because of the ease of operation and the ability to accomodate large samples sizes, the Phase II system is quite adaptable to a production environment.

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REFERENCES

[1] R.K. Ahrenkiel, AIP Conference Proceedings, **353**, AIP, 1996, p. 161.
[2] M. Kunst and G. Beck, *J. Appl. Phys.* **60**, 1986, p. 3558.
[3] E. Yablonovitch, *Solid St. Electron* **35**, 1992, p. 261.
[4] H. M'Sand, G.J. Norga, J. Michel, and L.C. Kimmerling, AIP Conference Proceedings **306**, Eds. R. Noufi and H. Ullal, AIP Press, 1994, p. 471.
[5] R.K. Ahrenkiel, AIP Conference Proceedings **394**, 1997, p. 225.
[6] R.K. Ahrenkiel (patent applied for).
[7] R.K. Ahrenkiel, T. Wangensteen, M.M. Al-Jassim, M. Wanlass, and T. Coutts, AIP Conference Proceedings **321**, AIP Press, 1994, p. 412.
[8] W.A. Doolittle, A. Rohatgi, R.K.Ahrenkiel, D. Levi, G. Augustine, and R. Hopkins (submitted for publication).
[9] R.K.Ahrenkiel, B.M. Keyes, and D.J. Dunlavy, *J. Appl. Phys.* **70**, 1991, p. 225.