

# Minority carrier lifetime in polycrystalline silicon solar cells studied by photoassisted Kelvin probe force microscopy

Masaki Takihara,<sup>1,a)</sup> Takuji Takahashi,<sup>1</sup> and Toru Ujihara<sup>2</sup><sup>1</sup>*Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan*<sup>2</sup>*Department of Crystalline Material Science, Nagoya University, Nagoya 464-8603 Japan*

(Received 27 February 2008; accepted 21 June 2008; published online 14 July 2008)

We have proposed a method to evaluate minority carrier lifetime through photovoltage measurements by photoassisted Kelvin probe force microscopy and have applied it to characterize a polycrystalline silicon solar cell. The results indicate that the lifetime significantly decreases in the vicinity of a grain boundary of the polycrystalline material. The photovoltage distribution around the grain boundary is also discussed by considering a contribution of both the intrinsic surface potential and the lifetime. © 2008 American Institute of Physics. [DOI: 10.1063/1.2957468]

The minority carrier lifetime is one of the most important parameters to determine the solar cell performance. Conventionally, microwave photoconductivity decay ( $\mu$ -PCD) is used to evaluate the minority carrier lifetime,<sup>1,2</sup> but  $\mu$ -PCD is very sensitive to a sample surface, and an appropriate surface passivation process is required to obtain a correct value of the lifetime in the bulk.<sup>3</sup> In addition, a grain boundary in a polycrystalline material may influence the lifetime, but spatial resolution in the  $\mu$ -PCD method is not high enough to investigate it directly.

In this paper, we describe a method to evaluate the minority carrier lifetime through photovoltage measurements by Kelvin probe force microscopy<sup>4</sup> (KFM) operating under light illumination, named photoassisted KFM (P-KFM).<sup>5,6</sup> In this method, a sample surface is illuminated by a modulated light and the minority carrier lifetime is extracted from a temporally averaged photovoltage at various modulation frequencies. This method enables us to evaluate a bulk recombination lifetime  $\tau_b$  independently of surface recombination lifetime  $\tau_s$  without any surface passivation process as well as to investigate a spatial distribution of  $\tau_b$  at high spatial resolution. We also discuss a contribution of the lifetime and the intrinsic surface potential to photovoltage distribution around the grain boundary.

A  $p$ - $n$  junction as a solar cell structure was fabricated on a  $p$ -type polycrystalline silicon substrate with phosphorus doping to create a surface  $n$ -layer of approximately 500 nm in thickness. We neither formed a surface electrode nor carried out any surface passivation process before the lifetime measurements by P-KFM.

For the minority carrier lifetime measurements, we modulated an incident light to illuminate a sample surface as indicated in Fig. 1(a), and Fig. 1(b) shows an expected waveform of the photovoltage based on the following assumptions: Carrier recombination occurs both at a surface and in a bulk, and the recombination rate at the surface is very fast compared with that in the bulk because we do not perform any surface passivation process; free photocarriers generated in the  $n$ -type surface layer as well as photoinduced surface charges quickly recombine at the surface because of the fast surface recombination rate, while most photocarriers in the  $p$ -type bulk substrate are not so mobile and they recombine

at a bulk recombination rate, that is, the carrier lifetime. As shown in Fig. 1(b), the waveform of photovoltage is divided into three regions: (i) Photovoltage rises very fast at an onset of the modulated light and is constant during the illumination period. (ii) At an end of the light illumination, the photovoltage drops instantaneously due to quick extinction of the photocarriers in the surface  $n$ -layer at the surface recombination rate  $1/\tau_s$ , where  $\tau_s$  is much shorter than the modulation period  $T$  in our experiments. (iii) The photovoltage gradually decays during the off period at the bulk recombination rate  $1/\tau_b$ , where  $\tau_b$  is the minority carrier lifetime in the  $p$ -type bulk substrate. Since a response in photovoltage measurements by KFM is slow, P-KFM gives a temporally averaged photovoltage over the whole period of the on and off states of the light illumination. From the above assumptions, the temporally averaged photovoltage  $V_{av}$  as a function of the modulation period  $T$  is given by

$$\begin{aligned} \frac{V_{av}}{V_{max}} &= \frac{1}{T} \int_0^T (V) dt \\ &= \frac{1}{T} \left\{ \int_0^{T/2} dt + \int_{T/2}^T (1-r) e^{-(t-T/2)/\tau_b} dt \right\} \\ &= \frac{1}{2} + \frac{\tau_b}{T} (1-r) (1 - e^{-T/2\tau_b}), \end{aligned} \quad (1)$$

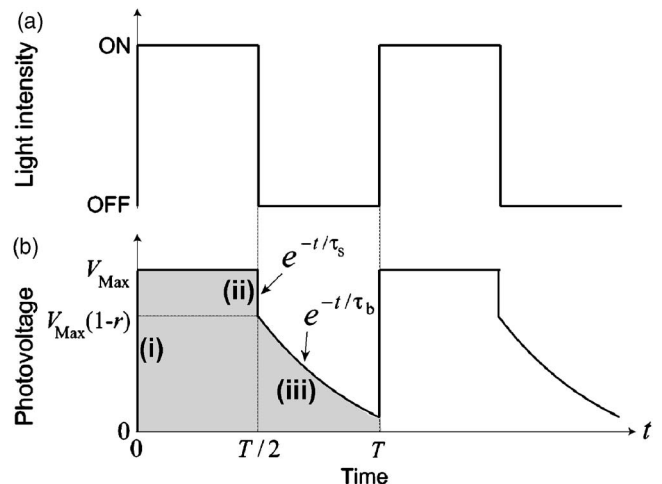


FIG. 1. Schematic illustration of waveforms of (a) light intensity and (b) corresponding photovoltage as a function of time  $t$ .

<sup>a)</sup>Electronic mail: takihara@iis.u-tokyo.ac.jp.

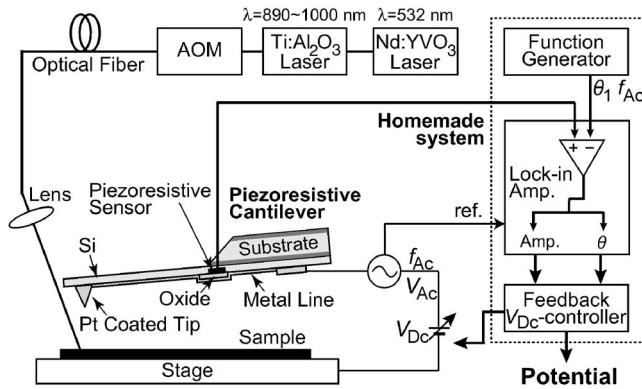


FIG. 2. Experimental setup of our P-KFM system.

where  $V_{\max}$  is the photovoltage under the continuous light illumination. The photovoltage drop at the end of the light illumination, that is, a contribution of the photocarriers in the surface  $n$ -layer to the total photovoltage, is represented by  $r$ . From a value of  $V_{av}$  at a short modulation period (i.e., a high modulation frequency) where the photovoltage decay by the bulk recombination is negligible, we can estimate a value of  $r$  because the photovoltage during the off period is  $(1-r)V_{\max}$  and therefore  $V_{av}$  should be  $(1-r/2)V_{\max}$ . Then,  $\tau_b$  is numerically obtained by substituting the empirical value of  $V_{av}$  at a certain modulation period  $T$  into Eq. (1).

Our P-KFM shown in Fig. 2 consists of a commercial AFM system (SPI4000/SPA 300HV, SII NanoTechnology Inc., Japan) and some external electronics to obtain an accurate surface potential value. This system operates in a high vacuum (typically,  $10^{-5}$  Pa) at room temperature and in an intermittent contact mode with a piezoresistive cantilever (PRC400, SII NanoTechnology Inc., Japan). The oscillation amplitude of the cantilever in the intermittent contact mode operation was set to be around 100 nm. A monochromatic light at a wavelength of 910 nm from a tunable Ti:Al<sub>2</sub>O<sub>3</sub> laser system was modulated by an acousto-optic light modulator with a duty ratio of 50%, and we confirmed that the temporally averaged intensity of the modulated light was kept to be half of the continuous light intensity in the whole range of the modulation frequency we used. Then it was transmitted through an optical fiber and focused on a sample surface just beneath a Pt-coated KFM tip, as shown in Fig. 2. For the photovoltage measurements by KFM, an intrinsic surface potential was measured under the dark condition first, and secondly the surface potential under the light illumination was measured. Then we calculated the photovoltage as a potential change between those potential values.

Figure 3(a) shows an optical micrograph of the surface of our sample. In this figure, surface orientation as well as a type of boundary characterized by the electron backscattering diffraction (EBSD) method were indicated. Figure 3(b) shows the temporally averaged photovoltage  $V_{av}$  as a function of the modulation frequency measured at point A, indicated in Fig. 3(a), under a light intensity of 6 mW/cm<sup>2</sup>. This  $V_{av}$  is normalized by  $V_{\max}$ , that is, the photovoltage under the continuous light illumination. As shown in Fig. 3(b),  $V_{av}$  is saturated at the high modulation frequency where the photovoltage decay due to the bulk recombination during the off period of the light illumination [region (iii)] is negligible because of the shorter modulation period  $T$  than the lifetime  $\tau_b$ . We consider, however, that the instant photovoltage drop

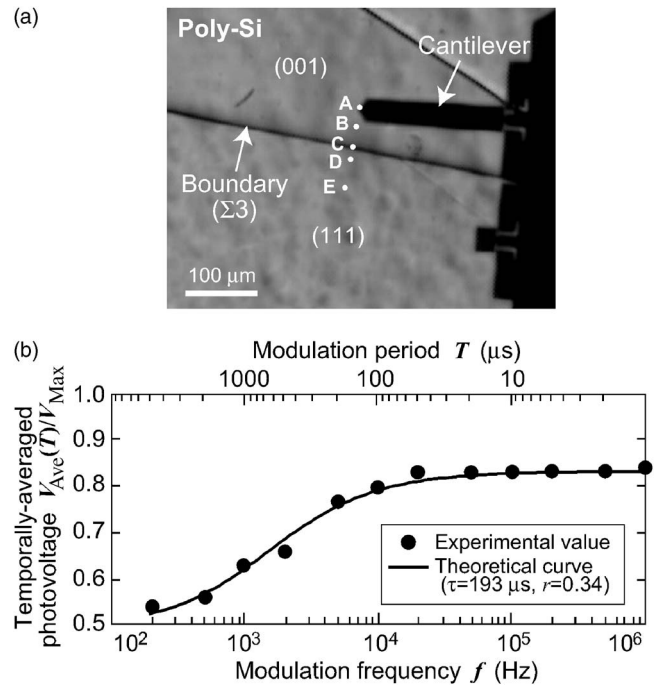


FIG. 3. (a) An optical micrograph of the polycrystalline silicon solar cell sample and (b) the temporally averaged photovoltage  $V_{av}$  normalized by  $V_{\max}$  (the photovoltage under continuous illumination) as a function of the modulation frequency  $f$  ( $=1/T$ :  $T$  is the modulation period) measured at point A indicated in (a).

at the end of the light illumination due to the fast surface recombination [region (ii)] still occurs even in this high frequency region because  $V_{av}$  is not saturated at 1.0, as shown in Fig. 3(b). Note here that an intermediate plateau in this frequency range indicates that the carrier diffusion velocity is not high enough to sweep all the photocarriers out; otherwise the photovoltage decay should be dominated by a single decay rate determined by the surface recombination, and  $V_{av}$  should simply reach 1.0 in the high frequency region without showing any plateaux. From a value of  $V_{av}$  in this high frequency region, we can estimate a value of  $r$  as mentioned before. In Fig. 3(b), for instance,  $V_{\max}$  and  $V_{av}$  at the high frequency were 284 and 236 mV, respectively, and then  $r$  was estimated to be 0.34. As also described before,  $r$  represents the contribution of the photovoltage generated in the surface  $n$ -layer. Since the surface  $n$ -layer is very thin, the number of photocarriers as well as the generated photovoltage in this layer are always smaller than those in the bulk  $p$ -type substrate, but due to a saturation feature of the photovoltage relative to the number of photocarriers the  $r$  value is expected to increase as an increase in the illumination power. In fact, the  $r$  values at the central area of the (001) grain in Fig. 3(a) (The point is not shown.) were estimated to be 0.22, 0.27, 0.30, and 0.39 under the light intensity of 0.6, 3.0, 4.2, and 6.0 mW/cm<sup>2</sup>, respectively. This result is very consistent with our expectation. Consequently, we consider that the measured lifetime by our method is less influenced by the contribution of the photocarriers in the surface  $n$ -layer and that its value well represents the bulk carrier lifetime  $\tau_b$  in the  $p$ -type substrate, although further investigation will be needed to surely judge whether the measured lifetime is completely free from the surface effects or not.

Figure 3(b) also indicates the theoretical curve of Eq. (1) calculated with  $r=0.34$  and  $\tau_b=193 \mu\text{s}$ , and this curve fits

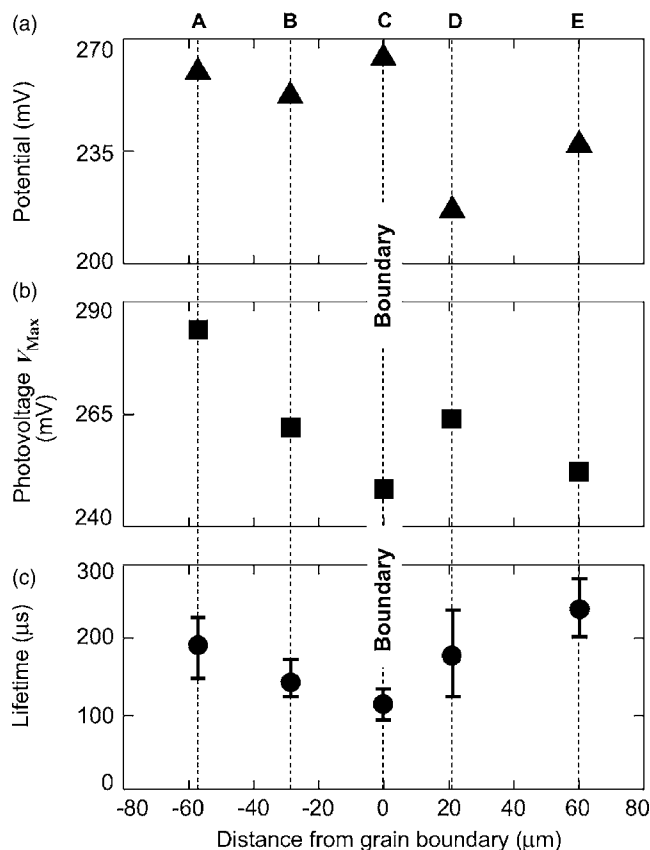


FIG. 4. (a) Intrinsic surface potential under dark condition, (b) photovoltage during continuous light illumination at a wavelength of 910 nm, and (c) lifetime at points A–E indicated in Fig. 3(a).

very well with the empirical values. By considering both the incident light intensity and the photoabsorption coefficient of the sample, we have confirmed that the carrier injection level is regarded as a low-injection level, and therefore, the measured decay time  $\tau_b$  corresponds to the minority carrier lifetime.<sup>7</sup> Thus the minority carrier lifetime  $\tau$  at point A was determined to be 193  $\mu$ s. We have performed similar measurements on the other points indicated in Fig. 3(a), and the estimated carrier lifetime as well as the intrinsic surface potential and  $V_{\max}$  are summarized in Fig. 4. Note here that the intrinsic surface potential in this figure actually means the contact potential difference between the sample and the Pt-coated KFM tip and that a high or low potential area repels or attracts the electrons, respectively. As shown in Fig. 4(c), the lifetime gradually decreases as the measuring point moves toward the grain boundary, and the lifetime at point C in the most vicinity of the grain boundary is approximately half of those at points A and E. The photovoltage at point C is also degraded, as shown in this figure. The similar degradation of photovoltage near the grain boundary has consistently been observed in our previous study.<sup>6</sup> These facts suggest that this  $\Sigma$ 3 grain boundary acts as a carrier

recombination site and/or a leakage pass and degrades the solar cell performance.

Now we compare the photovoltage within the single grains. The photovoltage at point A is higher than that at point B, while the intrinsic surface potentials at those points are comparable. This photovoltage difference is simply interpreted from the lifetime difference between them. On the other hand, the photovoltage at point D is higher than that at point E even though the lifetime at point D is shorter than that at point E. This photovoltage difference is attributable to the intrinsic surface potential distribution: the electrons are easy to accumulate near point D because of the low potential, and they enhance the photovoltage there. Consequently, we can consider that the overall performance for photovoltage generation at point D is superior to that at point E.

Our experimental results clearly indicate that the P-KFM method allows us to investigate the distribution of the minority carrier lifetime very well, together with the intrinsic surface potential and the photovoltage at high spatial resolution, and that P-KFM becomes a very powerful tool to characterize the photovoltaic performance in the solar cell.

In conclusion, we have proposed a method to obtain the bulk carrier lifetime through the photovoltage measurements by P-KFM and have found the lifetime decreasing in the vicinity of the grain boundary in the polycrystalline silicon solar cell material. This result indicates that the grain boundary degrades the solar cell performance by acting as a carrier recombination site and/or a leakage pass. We also discussed the photovoltage distribution within the single grains by considering the intrinsic surface potential and the carrier lifetime.

The authors would like to express their sincere thanks to Professor Yoshio Oshita and Dr. Koji Arafune of Toyota Technological Institute for measurements with the EBSD method. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), by the New Energy and Industrial Technology Development Organization (NEDO), and by Special Coordination Funds for Promoting Science and Technology MEXT, Japan. The authors express their appreciation to the reviewer for valuable comments that improved our manuscript.

<sup>1</sup>C. Swiatkowski, A. Sanders, K. D. Buhre, and M. Kunst, *Appl. Phys. Lett.* **78**, 1763 (1995).

<sup>2</sup>M. E. Rodriguez, A. Mandelis, G. Pan, J. A. Garcia, V. Gorodokin, and Y. Raskin, *J. Appl. Phys.* **87**, 8113 (2000).

<sup>3</sup>J. Schmidt and A. G. Aberle, *Prog. Photovoltaics* **6**, 259 (1998).

<sup>4</sup>M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe, *Appl. Phys. Lett.* **58**, 2921 (1991).

<sup>5</sup>T. Igarashi, T. Ujihara, and T. Takahashi, *Jpn. J. Appl. Phys., Part 1* **45**, 2128 (2006).

<sup>6</sup>M. Takiyara, T. Igarashi, T. Ujihara, and T. Takahashi, *Jpn. J. Appl. Phys., Part 1* **46**, 5548 (2007).

<sup>7</sup>W. M. Bullis and H. R. Huff, *J. Electrochem. Soc.* **143**, 1399 (1996).