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High-bandwidth, high-sampling-rate, low-noise, two-probe transient photovoltage measuring system

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In this article, we present a two-probe configuration for measuring transient photovoltage (TPV) signals from photo-electronic semiconductor devices. Unlike in a conventional one-probe system, the two electrodes of the devices under test in this study are both monitored in our new measuring system, giving rise to a significantly enhanced signal-to-noise ratio. Tentative experimental data obtained from N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1′-biphenyl)-4,4′-diamine-based organic semiconductor devices show that the bandwidth and the sampling rate of the system reach 1.5 GHz and 50 GS/s, respectively, without degradation of the noise level. In addition, the study of TPV signals on each individual electrode is allowed. The TPV values measured by the two individual probes are not identically equal to half of the differential TPV and will not cancel each other out as expected. This abnormal phenomenon is due to the photoelectric response of the photo-electronic material. This novel two-probe TPV measuring technique and abnormal TPV behavior might be useful for studying more dynamic processes in photo-electronic semiconductors. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4905576]

I. INTRODUCTION

The transport of excess photo-induced carriers in photosensitive semiconductors determines the power output of photovoltaic devices. Therefore, studies on the transient migration processes of photo-induced charge carriers and the development of related measuring systems are crucial for understanding the photo-electronic physics of semiconductors and optimizing the structural design of photo-electronic devices, such as solar cells and photo-sensors. Compared with traditional semiconductors such as silicon, whose photo-electronic dynamic processes are already well known, organic semiconductors—the competitive candidate material for application in solar cells,[1] light-emitting diodes,[2] thin film transistors,[3] and memory devices[4]—require additional novel measuring techniques for the study of their microscopic photo-electronic dynamics. Previous work based on time-resolved optical methods has revealed that the spatial separation of electrons and holes may occur within 1 ns.[5–7] However, to date, transient electric methods, used to directly measure carrier separation, only provide results slower than 10 ns.[8–10] Among these methods, transient current tools (e.g., time of flight,[11,12] charge extraction,[12] and dark injection[13]) are barely useful in the study of such rapid processes, limited by the RC constant of the external circuit (typically ∼100 ns). By contrast, the transient photovoltage (TPV), which originates from the spatial separation of electrons and holes and works under quasi-open circuit condition, is independent of the external circuit, allowing for the measurement of rapid processes (e.g., interface dissociation of excitons in organic semiconductors[14]) without the limitation of the RC constant of the external circuit. Instead, the shortest response time of a TPV measurement is limited by the bandwidth and sampling rate of the measuring systems.

The bandwidth and sampling rate of a TPV measuring system are critical. First, the bandwidth determines the most rapid rise or fall time that can be measured (rise/fall time ≈ 0.35/bandwidth). Second, detailed features of rapid processes may be lost in a measuring system with an excessively low sampling rate. For instance, the TPVs measured at high (625 MS/s) and low (12.5 MS/s) sampling rates with the improved TPV measuring system proposed in the present work (see below) are compared in Figure 1. The rapid voltage peak that appears in the high-sampling-rate measurement (represented by the blue circle) is not observed in the low-sampling-rate case. Therefore, it is highly desirable to increase the bandwidth and sampling rate. However, the direct use of typical commercial measuring instruments operating at a high bandwidth and a high sampling rate will inevitably result in a worse noise level because at the high sampling rate, not only is the rapid signal of the devices recorded but also the undesirable high-frequency noise of the external circuit is as well. For example, as shown by Figure 1, the noise level increased from ∼1 mV to ∼5 mV as the sampling rate increased from 12.5 MS/s to 625 MS/s. Part of the voltage noise that was incoherent to the TPV could be reduced by simply averaging the results of multiple measurements and is not focused in this work. However, certain noise signals are generated by the electric components of the measuring system itself, which are synchronized to the trigger time of the TPV measurement. Such noise signals

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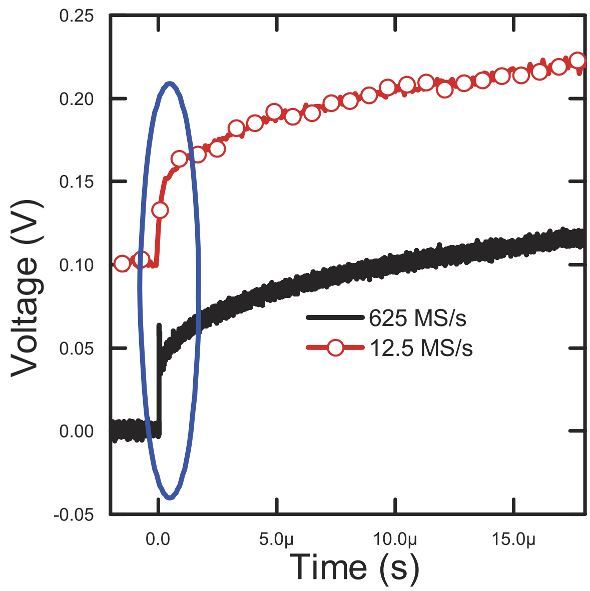

FIG. 1. TPV measured with the proposed two-probe measuring configuration at sampling rates of 625 MS/s (black solid line) and 12.5 MS/s (red squares). A certain voltage offset was used for clear comparison.

are actually coherent to the TPV and cannot be reduced by averaging the results of multiple measurements. Hereafter, this coherent noise is referred to as system noise, and its origin is the focus of the present work.

In this work, the traditional one-probe configuration for TPV measurement[14–16] (only one electrode was monitored by an oscilloscope, and the other was grounded) was promoted to the novel two-probe configuration, which allows for TPV measurements at up to 1.5 GHz (bandwidth) and 50 GS/s (sampling rate) without any degradation in the noise level. This two-probe measuring system is able to measure the TPV of either electrode of a typical sandwich-structured photo-electronic device (a thin photosensitive semiconductor layer sandwiched between two electrodes) independently, where one electrode is transparent to allow ambient illumination into the active layer independently. Moreover, abnormal behavior is observed, i.e., the values of the TPV signals from the two channels (each of which corresponds to one electrode) are not half of the differential TPV and will not cancel each other out as expected, which allows for the observation of new microscopic phenomena exhibited by photo-electronic semiconductors.

II. MATERIALS AND METHODS

The structure of the device under test (DUT) was indium tin oxide (ITO)/*N*,*N*′-Di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB, 750 nm)/Ag (20 nm). ITO is a regular transparent anode material that allows for the transmission of incident ambient light. NPB was chosen because it is a typical hole-transporting organic semiconductor,[17,18] highly demanding extensive TPV investigation by novel measuring tools. Silver is a common high-conductivity electrode material. The device was fabricated by sequential thermal deposition of NPB and Ag at ∼0.3 nm/s onto an ITO-coated glass substrate under a vacuum pressure of $\sim 10^{-5}$ Pa. Regardless of the illumination direction, electrically, ITO (∼20 Ω/sq) and Ag (∼1 Ω) differ only in their conductivities. In fact, under the quasi-open circuit condition (the current of the measuring system $= \frac{\text{TPV}(<1\ \text{V})}{\text{input impedance}(1\ \text{M}\Omega)} < 1\ \mu\text{A}$); ITO and Ag are practically the same. The TPV curves were recorded with one or two Tektronix P6245 active probe(s) (bandwidth 1.5 GHz) connected to a Tektronix DPO71254C oscilloscope (bandwidth 12.5 GHz, sampling rate 50 GS/s). Unless otherwise noted, the bandwidth and sampling rate of the oscilloscope were set to 2 GHz and 50 GS/s, respectively. All the TPV curves shown are the results averaged over 16 measurements. The bandwidth of the entire measuring circuit was 1.5 GHz, limited by the P6245 active probe(s).

III. RESULTS AND DISCUSSION

A. Origin of the system noise in one-probe configuration

The typical configuration for TPV measurements (one-probe configuration) is illustrated in Figure 2(a), where one electrode of the sandwich-structured DUT is grounded and the other is monitored.[14–16] In this case, undesirable noise often appeared within the first few microseconds,[19] as shown in Figure 3 (red circles). The origin of this system noise should be analyzed first. In the present method, the DUT was coupled to the ground, to which many electric components, such as a pulsed laser generator, are also coupled. The pulsed laser generator, which generates laser light pulses together with voltage pulses of over 100 V (and may even exceed 1000 V depending on the equipment model), and other electric components synchronized to the trigger time of the TPV measurement apply an undesirable AC voltage to the ground. This AC noise voltage of the ground is acceptable in the case of low-frequency or DC electric measurements, e.g., I-V measurements, but is harmful to transient electric measurements, e.g., TPV, which are of interest within the scope of the present work. In TPV measurements performed using one-probe configuration, undesirable ground noise was applied to the metal electrode of the DUT, as indicated by the green conducting wire in Figure 2(a), and the response of the DUT could generate additional voltage noise (denoted as $V_{\text{response noise}}$) other than the useful photovoltage signal. Therefore, the voltage-time profile recorded on the oscilloscope can be expressed as

$$V_{\text{oscilloscope}}(t) = TPV(t) + V_{\text{response noise}}(t), \qquad (1)$$

where $TPV(t)$ is the voltage signal of interest and $V_{\text{response noise}}(t)$ is the voltage response to the ground noise, which is a disturbance to the TPV measurement. Moreover, the ground noise voltage (from the pulsed laser generator and any other devices synchronized to the trigger time of the TPV measurement) is highly coherent with the laser pulse as well as the TPV and is therefore impossible to reduce by averaging the data gathered over multiple measurements. If the electric properties of the DUT were not dependent on the laser illumination, the voltage noise $\left(V_{\text{response noise}}(t)\right)$ could be removed by simply subtracting the dark voltage

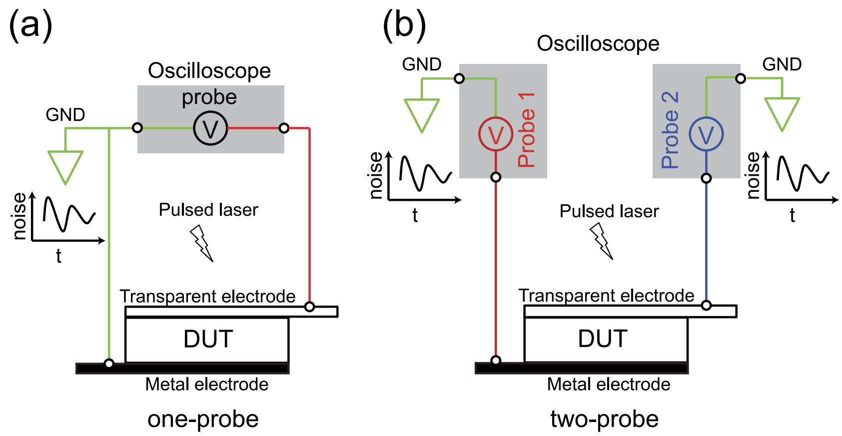

FIG. 2. TPV measuring systems with one-probe (a) and two-probe (b) configurations. The DUT consisted of the active layer of a photo-electronic semiconductor sandwiched between a transparent upper electrode (e.g., ITO or SnO_2:F) and a bottom metal electrode (e.g., Al, Ag, and Au). Each probe in the measuring system was modeled as a voltmeter. As indicated by the green conducting wires, in the one-probe configuration, undesirable ground noise would be coupled to the metal electrode of the DUT; by contrast, in the two-probe configuration, the DUT could be isolated from the ground noise.

signal recorded by the oscilloscope when the DUT was sheltered from laser light (namely, the background voltage $V_{\text{background}}(t) = V_{\text{response noise,dark}}(t)$, as shown in Figure 3, black squares). However, if the DUT conductivity under laser illumination were different from that in the dark, which is generally the case because the device investigated is always expected to behave as a photovoltaic device, the noise measured under laser illumination would be different from the background noise $\left(V_{\text{response noise,dark}}(t) \neq V_{\text{response noise,light}}(t)\right)$. In this case, the noise level could be reduced but still not completely eliminated, as indicated by the blue triangles in Figure 3. Therefore, to reduce the noise in TPV measurements, it is necessary either to identify and eliminate the source of the ground noise or to isolate the DUT from the ground noise. In the present work, the latter option was chosen because of its simplicity and transferability, as shown below.

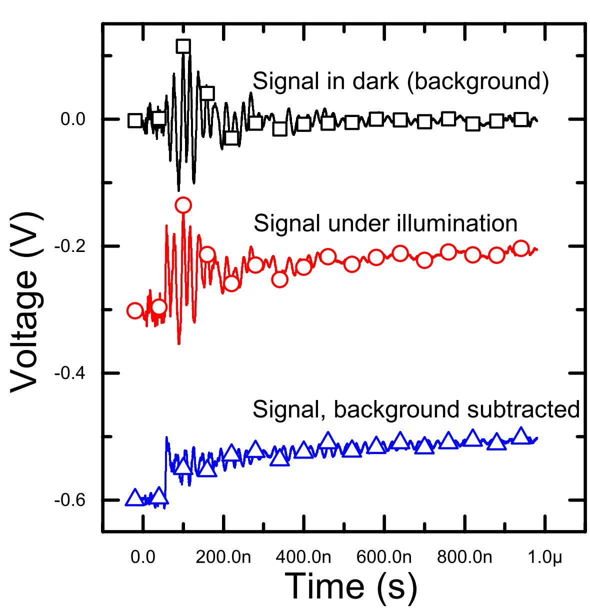

FIG. 3. The ground noise in the dark (background, black squares) and that under illumination (red circles) and the difference between them (blue triangles). The voltages have been offset for a clear comparison.

B. Two-probe configuration

Due to the shortcomings of the one-probe configuration, a two-probe configuration is proposed, as illustrated in Figure 2(b), in which two probes are involved, either of which monitors the voltage potential of one individual electrode of the DUT. The two probes are both grounded, leaving the DUT electrodes completely isolated from the ground and any other undesirable external electric apparatuses.

In this configuration, although the ground noise still exists, the undesirable ground noise voltage is no longer directly coupled to the DUT as in the one-probe configuration but across the input impedance of the probe involved, as indicated by the green conducting wire in Figure 2(b). Moreover, because the two electrodes of the DUT are biased similarly, the differential voltage applied on the DUT will be reduced. As a demonstration, a TPV measurement was carried out in the dark, and the signals from channel 1 and channel 2 of the oscilloscope (denoted as CH1 and CH2, respectively) measured the electric potentials of the two DUT electrodes. In other words, the CH1 – CH2 (differential signal) was equal to the voltage applied to the DUT by the external measuring circuit. As shown in Figure 4(a), the differential voltage applied to the DUT (blue triangles) was reduced remarkably compared to the voltage applied to either individual electrode. Thus, the DUT was practically decoupled from the ground. However, the result remains unsatisfactory because of the phase difference between the ground reference potentials of the two different channels, which is determined by the shape and length of the two ground leads and could not be exactly identical, as illustrated in Figure 4(b). Note that the phase difference of the two ground leads is not a simple time shift but is related to the frequency spectrum of the ground noise. Therefore, this noise could not be eliminated by adjusting the time parameter of the oscilloscope channels.

According to the above-described analysis, to completely remove the effect of ground noise disturbance on TPV, the ground leads of the two probes should be designed to be exactly the same and must be sufficiently short. In addition, the cable should be rigidly fixed to minimize any

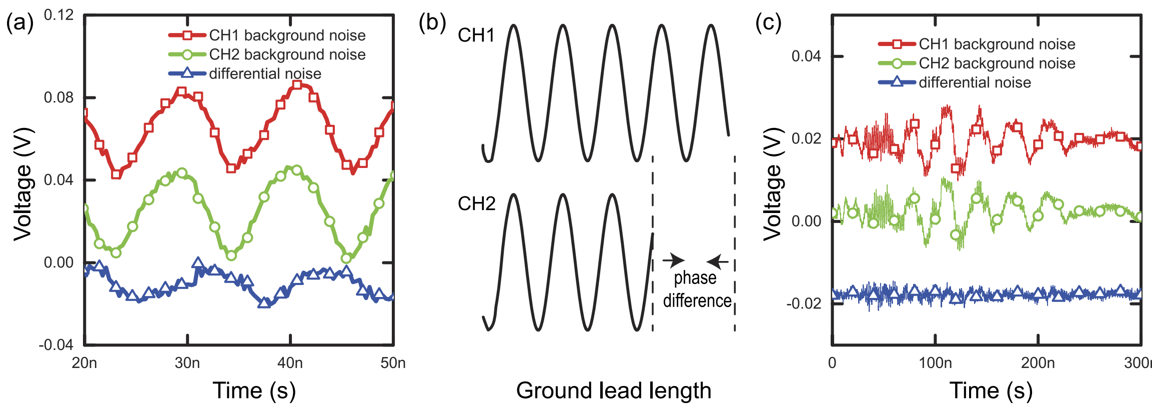

FIG. 4. TPV background noise without the specially designed DUT holder (a), the scheme of the phase difference of the ground noise induced by the different ground lead shapes and lengths (b), and the TPV background noise with the specially designed DUT holder (c). The voltages have been offset in (a) and (c) for a clear comparison.

possible vibration and ensure that the $V_{\text{response noise}}$ remains the same throughout the entire measurement. A special DUT holder was therefore designed, as illustrated in Figure 5. On this holder, the DUT was clamped between the red copper ground conductor and the aluminum base with its electrodes isolated from the ground by an insulating plastic material (polytetrafluoroethene). The two probes were grounded with short ground leads of the same shape (the green part in Figure 5; the distance from the ground socket to the red copper ground neck was ~0.2 cm) to minimize the phase difference between the ground noise sources. With this DUT holder design, the background noise of the two channels and the differential noise that was actually coupled to the DUT were recorded and are shown in Figure 4(c). As indicated, the ground noise of each channel was reduced from ~40 mV (Figure 4(a)) to ~20 mV (Figure 4(c)) due to the reduction in the length of the ground leads, whereas the differential noise was reduced to ~25% of the ground noise of each individual channel (from ~20 mV to ~5 mV). Thus, the DUT was perfectly decoupled from the ground, and the photoelectric response of the DUT to the ground noise was reduced to a satisfactory lower level. In this case, according to the above-described analysis, $V_{\text{response noise}} \approx 0$ in the dark or under illumination. Although the ground noise was still introduced into the two individual probes, the TPVs of the two channels and the difference thereof (CH1 – CH2) could be precisely measured by subtracting the corresponding background voltages

$$TPV_{\mathrm{i}} = V_{\mathrm{i,oscilloscope}} - V_{\mathrm{i,response\ noise}}, \tag{2}$$

where i indicates CH1, CH2, or (CH1 – CH2).

The steps of the measuring procedures can be summarized as follows:

1. With the laser covered, record the voltages of channel 1 and channel 2 of the oscilloscope (denoted as $V_{\mathrm{i,response\ noise}}$, where i = 1 or 2, representing the response of channel 1 or channel 2 to the ground noise, respectively).
2. Under laser illumination, record the voltages of channel 1 and channel 2 of the oscilloscope (denoted as $V_{\mathrm{i,oscilloscope}}$, where i = 1 or 2, representing the sum response of channel 1 or channel 2 to the ground noise and the laser illumination, respectively).
3. Calculate the responses of channel 1 and channel 2 according to Eq. (2). The core for noise reduction in the two-probe configuration is to ensure that $V_{\text{response noise}}$ in the dark remains the same upon laser illumination.
4. The differential voltage equals (CH1 – CH2).

Figure 6 compares the TPVs measured using the one-probe and two-probe measuring systems with the same probe, oscilloscope, and DUT, indicating that the two-probe configuration indeed reduces the TPV noise. The distinct noise appearing in the TPV measured by the one-probe system (black circles) on both rapid (<1 μs) and slow time scales (~10 ms, this noise was originated from the 50 Hz electric power supply, which also resulted in voltage noise to the ground) disappeared in the TPV measured by the two-probe system (red squares). Please note that in our experiment, the shielding did not show an appreciable improvement in the result quality (See Figure S1 in the supplementary material).[20]

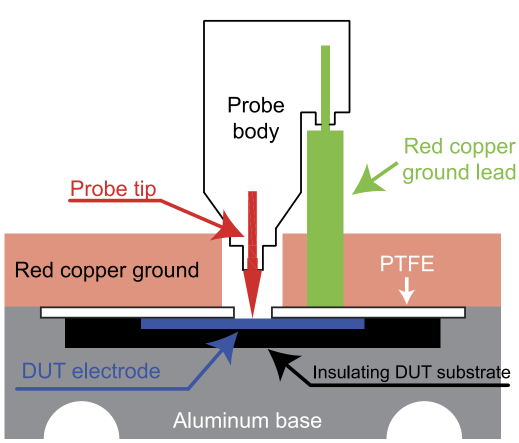

FIG. 5. Scheme of the low-noise DUT holder.

C. TPV of individual electrode

Another advantage of the two-probe configuration is that it allows for the study of the TPV of both channels, which is impossible in the one-probe configuration and may lead to interesting results not previously observed. The TPVs

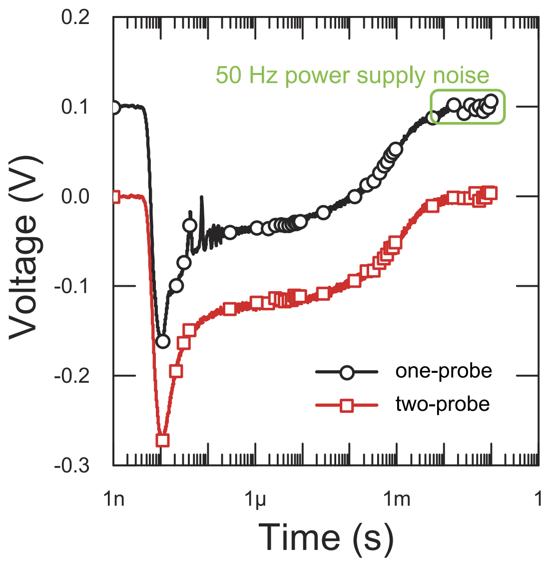

FIG. 6. Comparison between TPVs measured by one-probe and two-probe configurations. Different sampling rates were adopted for different time scales. The sampling rate for less than 10 μs was 50 GS/s. The voltages have been offset for a clear comparison.

measured using the two-probe configuration are shown in Figure 7(a) for the case in which channel 1 and channel 2 were connected to the ITO and Ag electrodes of the DUT, respectively. Because the probes of the two channels are the same (Tektronix P6245, 1 MΩ, ≤1 pF) and equivalent in the measuring circuit, it is expected that the values of CH1 and CH2 would be half the differential TPV and precisely cancel each other out, i.e., CH1 + CH2 = 0. However, the value of CH1 + CH2 is, surprisingly, nonzero in the present experiment, especially within the first 10 μs, as shown in Figure 7(b). Switching the two probes only causes a slight change in the CH1 − CH2 and CH1 + CH2, as illustrated in Figures 7(c) and 7(d), respectively. The value of CH1 + CH2 remains nonzero, indicating that this phenomenon is caused by the DUT itself rather than a defect in the measuring system.

To further confirm that the electric potential of each electrode is physically meaningful, we tried to remove either of the two probes from the DUT. The effect of removing a single probe is shown in Figure 7(e). When channel 1 or channel 2 was disconnected, the external circuit was definitely open, and the result obtained under this condition was almost the same as that in the case in which the TPV external measuring circuit was quasi-open. In other words, CH1 and CH2 had almost no bearing on whether the other electrode was connected to the measuring system. This result further confirms that typical TPV measurements are conducted in a quasi-open circuit condition and that the measured signal is not limited by the RC constant of the external measuring circuit (the RC constant = +∞ for a definitely open circuit, still allowing for the recording of rapid signals <100 ns). Note that the background signal (measured in the dark) was subtracted

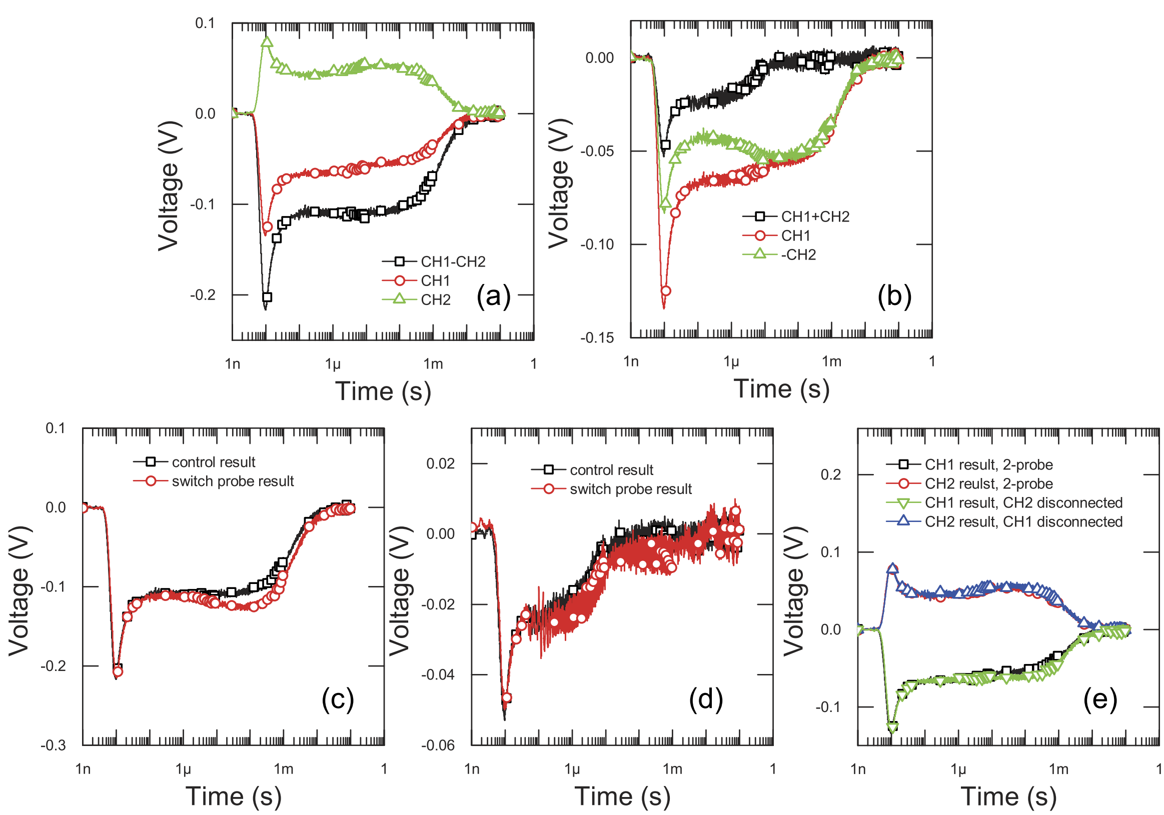

FIG. 7. TPV of the two-probe measuring system. (a) Comparison between CH1 − CH2, CH1, and CH2; (b) comparison between CH1 + CH2, CH1, and–CH2; effect of switching probes on CH1 − CH2 (c) and CH1 + CH2 (d); (e) the effect of removing a single electrode from the TPV measuring circuit. Different sampling rates were adopted for different time scales. The sampling rate for less than 10 μs is 50 GS/s. Note that the common mode noise from the ground of each channel will be doubled in the CH1 + CH2 results while eliminated in the CH1 − CH2 results, resulting in worse quality of the CH1 + CH2 results than of the CH1 − CH2 results.

for all of these TPVs and that the DUT was practically decoupled from the ground noise according to the above discussion, which ensured that the measured TPV was the electric response to laser light incidence. This result indicates that the TPV of each electrode is a photoelectric response of the DUT and is meaningful in device physics in addition to the widely studied differential photovoltage of the two electrodes of photo-electronic devices. The photovoltage of each individual electrode might be related to photo-electronic dynamic processes in photo-electronic semiconductors that have not yet been revealed. Therefore, this technique may lead to a new field in photo-electronic dynamic processes.

IV. SUMMARY

In summary, our systematic analysis of the TPV measuring system demonstrates that the system noise of the TPV measuring system originates from the photoelectric response of the DUT to the ground noise, which is introduced by the electric devices synchronized to the TPV trigger time. Therefore, in this study, the widely used one-probe TPV measuring system, in which one electrode of the DUT is grounded and the other is monitored with an oscilloscope, was upgraded to a two-probe configuration in which each electrode of the DUT was monitored by a probe, allowing for the decoupling of the DUT from the ground. A DUT holder was specially designed to ensure the shapes of the ground leads of two probes were identical, the ground lead lengths were minimized and the probe cables were stiffened. As a result, a high-bandwidth (1.5 GHz) and high-sampling-rate (50 GS/s) TPV measuring system was successfully designed without any degradation of the noise level (~5 mV), allowing for the study of rapid photo-electronic processes (rising edge < 0.23 ns). Moreover, the two-probe configuration allows for the investigation of the TPV of each electrode separately. With this unique advantage, the CH1 + CH2 TPV signal was studied. Although this TPV signal was expected to be zero because the input impedances of the two channels were the same, the real measured result was not zero. This two-probe TPV measuring technique and the abnormal nonzero CH1 + CH2 TPV behavior might lead to the development of a new field of photo-electronic dynamic processes.

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[20] See supplementary material at http://dx.doi.org/10.1063/1.4905576 for comparison of result qualities with or without shielding.