Nonlinear transient photovoltaic response in Al/C_{60}/Au devices: Control of polarity with optical bias

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We report fast (nanosecond) transient photovoltaic response and steady-state photovoltage of rectifying Al/C_{60}/Au sandwich devices. The transient photovoltage changes polarity at a critical light intensity, which can be varied and controlled by applying steady-state light as bias. This ability to change the polarity of the transient photovoltaic response and to control the intensity at which the polarity changes sign offers potential for use in applications in the area of fast nonlinear optoelectronic detectors.

The photovoltaic effect, which occurs at a metal-semiconductor interface when illuminated, is a well-known phenomenon which has been widely applied to solar energy conversion and photodetection.[1] As a novel semiconductor, the photovoltaic response of C_{60} has been extensively studied in recent years. Miller *et al.*[2] reported that solvent-cast films of C_{60} on noble-metal electrodes show the photovoltaic response typical of *n*-type semiconductors. Yonehara and Pac[3] reported that C_{60} thin films sandwiched between Al and Au electrodes exhibit rectification after exposing the cell to air. Sariciftci *et al.*[4] reported rectifying heterojunctions (diodes) fabricated from C_{60} and a π-conjugated polymer. More generally, the photoelectronic properties of undoped C_{60} films have been investigated through a variety of spectroscopies[5–13] including the photoconductivity measurements.[5–9]

In this letter, we report the transient photovoltage (PV) of Al/C_{60}/Au sandwich cells in the nanosecond time regime and the spectral dependence of the steady-state (cw) photovoltaic response. These devices are rectifying diodes which exhibit photovoltaic response. We focus on the transient PV which changes polarity at a critical intensity (I_c) of the pulsed excitation; I_c can be varied by applying cw light as bias.

The Al/C_{60}/Au device was constructed by successive vacuum depositions of the bottom Al electrode, the C_{60} film, and the top semitransparent Au electrode on an alumina substrate. In order to achieve high temporal resolution, we incorporated this device on to a microstripline configuration.[14] A 600-μm-wide Al microstripline was deposited on to the top half surface of the substrate, and then exposed to air in order to obtain the rectifying junction, as demonstrated by Yonehara and Pac.[3] Thin film of C_{60} was deposited on top of the air-exposed Al electrode by evaporating purified C_{60} powder from a quartz crucible.[15] A 600-μm-wide semitransparent Au microstripline was then deposited on to the other top half surface of the C_{60} film with a small overlap area ($\approx 3\times10^{-3}$ cm^2) between the top and bottom electrodes. This small overlap area minimizes the overall capacitance and thereby enhances the temporal resolution (measured as $\approx$2 ns from the rise time of the transient PV). Finally, an Au ground plane was deposited on the back surface of the substrate to form a microwave transmission line with 50-Ω impedance.[16] All measurements were carried out at room temperature under a pressure of less than 10^{-4} Torr. The current-voltage (I-V) response of the device was measured with a Keithley 467 picoammeter/voltage source.

Excitation pulses for the transient PV measurements were obtained from a PRA LN105A dye laser system pumped with a PRA LN1000 N_2 laser. The pulse width was about 30 ps at $\hbar\omega$=2.92 eV. One of the electrodes was grounded and the other connected to the EG&G PAR 4400 boxcar system. The transient PV data were taken with a sampling gate width of 2 ns.

The cw photovoltaic response was measured by a standard modulation technique; the excitation light from a 500-W tungsten-halogen lamp was modulated at frequency of 20 Hz, and the photovoltaic response was detected by a lock-in amplifier. The light intensity incident on the semitransparent Au electrode was about 0.4 mW/cm^2 at $\hbar\omega$=2.5 eV. Data were taken with spectral resolution of about 5 nm, and normalized to the spectral response of the detection system after correcting for transmission through the semitransparent Au electrode.

Figure 1 shows the I-V characteristics of the Al/C_{60}/Au sandwich cell in the dark and under the cw illumination at $\hbar\omega$=2.5 eV. The inset shows the same data on semilog scales. The device exhibits rectification, with forward bias corresponding to positive voltage applied to the Al electrode, consistent with the previous report.[3]

Figure 2 displays the transient PV at various pulse intensities I_L. We set $t=0$ at the peak of the transient PV for high light intensities. The Au electrode was grounded and illuminated by the pulsed excitation; the Al electrode was connected to the boxcar. The inset compares the intensity dependence of the transient PV at $t=0$ obtained with the cell without cw illumination with that under cw bias light of $\sim1.5\times10^{15}$ photons/cm^2 s at $\hbar\omega$=1.6 eV.

As the incident light intensity is increased, the magnitude of the positive transient PV initially increases and then

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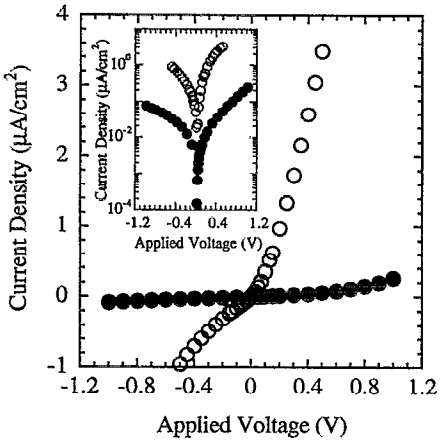

FIG. 1. The I-V characteristics of Al/C_{60}/Au sandwich cell in the dark (●) and under the cw illumination on the semitransparent Au electrode with an incident intensity of 0.4 mW/cm^2 at $\hbar\omega$=2.5 eV (○). The inset shows the same data on semilog scales.

goes through a maximum at $I_L \approx 1.7\times10^{14}$ photons/cm^2 (curve a). When the intensity increases above that level, the transient PV decreases and changes sign from positive to negative at a critical intensity, $I_c \approx 4.2\times10^{14}$ photons/cm^2. At I_c, the transient PV consists of an initial negative component followed by a positive component (curve c). When the intensity further increases above I_c, the negative transient PV increases continuously. A similar transient PV response was previously observed by Moses[14] in the Au/a-Se/Au sandwich cell. When the Al electrode was grounded and the Au electrode connected to the boxcar, we observed similar photovoltaic response with reversed polarity, i.e., a negative PV

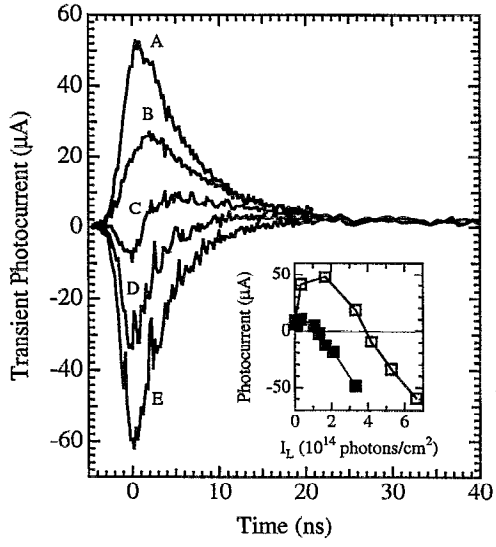

FIG. 2. The fast transient photovoltaic response of the Al/C_{60}/Au cell at various pulse intensities I_L of (a) 1.7×10^{14}, (b) 3.3×10^{14}, (c) 4.2×10^{14}, (d) 5.2×10^{14}, and (e) 6.6×10^{14} photons/cm^2 at $\hbar\omega$=2.92 eV. The inset compares the intensity dependence of the transient PV at t=0 obtained with the cell without cw illumination (□) with that under cw bias light of $\sim1.5\times10^{15}$ photons/cm^2 s at $\hbar\omega$=1.6 eV (■). The lines are plotted as a guide to the eye.

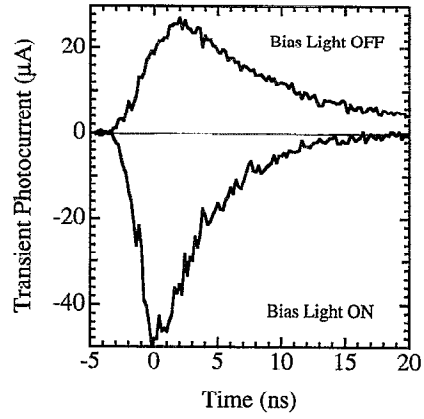

FIG. 3. The transient PV under an incident pulse intensity of 3.3×10^{14} photons/cm^2 at $\hbar\omega$=2.92 eV (top curve) is compared with that under cw optical bias (bottom curve).

at $I_L < I_c$ and a positive PV at $I_L > I_c$. The observed polarity of the transient PV indicates that the Al electrode is negative at $I_L < I_c$, and positive at $I_L > I_c$, with respect to the Au electrode.

The Au/C_{60}/Au cells under similar configurations show symmetric and linear I-V characteristics. They exhibit negligible photovoltaic response, indicating that the photovoltaic response occurs at the interface between C_{60} and the air-exposed Al electrode.

The inset of Fig. 2 shows that the value of I_c can be varied by applying cw light as bias. The cw bias intensity of $\sim1.5\times10^{15}$ photons/cm^2 s at $\hbar\omega$=1.6 eV reduces I_c from $\sim4\times10^{14}$ to $\sim1.2\times10^{14}$ photons/cm^2. Moreover, it also reduces the magnitude of the transient PV at low incident pulse intensities.

Figure 3 shows the transient PV in response to an incident pulse intensity of 3.3×10^{14} photons/cm^2 with and without the cw optical bias. As can be clearly seen, the cw bias light switches the transient PV from positive to negative.

The spectral dependence of the cw PV of the same device used in the transient PV measurement is shown in Fig. 4, together with the optical absorption of C_{60} film. The inset displays the phase of the signal. The cw PV action spectrum closely follows the absorption spectrum, and is similar to the cw photocurrent action spectrum of air-exposed C_{60} film measured in the surface-cell configuration.[7,8] However, the magnitude of the cw PV shows a sharp minimum at $\hbar\omega \approx 2.3$ eV, at which the phase of the lock-in signal changes by approximately 180° (see the inset). This result indicates that the internal electric field changes polarity at $\hbar\omega \approx 2.3$ eV. Since the applied bias voltage can change the internal field distribution, the photon energy at which the internal field changes polarity is expected to vary with the bias voltage. As expected, we have observed that the phase of the cw photocurrent under the forward bias changes sharply by approximately 180° at higher energy than at 0 V, e.g., at $\hbar\omega \approx 2.35$ eV under 0.3-V bias. However, the phase of the cw photocurrent at −0.3 V (reverse bias) decreases only gradually at $\hbar\omega < 2.3$ eV, and at $\hbar\omega > 2.3$ eV it is almost same as those under 0- and 0.3-V bias.

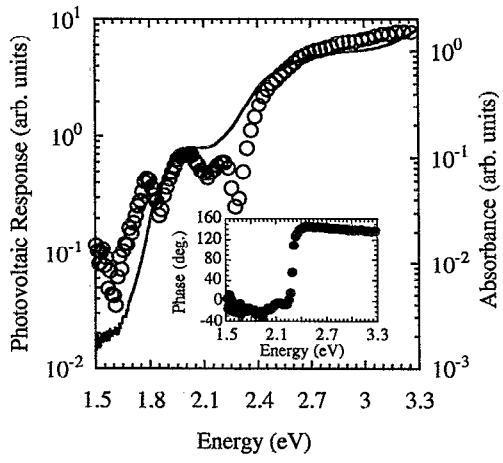

FIG. 4. The spectral dependence of the cw PV (○), together with the optical absorption (solid line): The inset displays the phase of the PV response (●).

The peaks observed at $\hbar\omega<2.3$ eV in Fig. 4 appear at the same energies as the known structure in the low-energy tail of the absorption spectrum of C_{60}.[11] Giro *et al.*[9] also reported such peaks at similar energies in the cw photocurrent action spectrum of the Al/C_{60}/Al cell. Thus, the structure in the photoresponse at $\hbar\omega<2.3$ eV can be associated with vibronic transitions assigned from the detailed studies of the absorption spectrum.[11]

The underlying mechanism responsible for the PV response reported here is not clear. Recently, Sarkar and Halas[17] have reported the Dember effect in C_{60} sandwiched between silver electrodes. Since the electrons are more mobile in C_{60} than the holes, under steady state, a potential difference (Dember photovoltage) builds up across the film with the illuminated electrode positive relative to the dark electrode. Although the polarity of the transient PV observed at $I_L<I_c$ is consistent with that of the Dember photovoltage, the reversed polarity at $I_L>I_c$ cannot be explained by the Dember effect. Moreover, the observation of a fast PV response, limited only by the temporal resolution of the detection system (~2 ns), is incompatible with a relatively slow buildup of the PV expected from the Dember effect since it depends on diffusion of photocarriers. Therefore, it seems that our observations cannot be explained by the Dember effect alone and necessitate the existence of other source for a built-in potential.

Since Au/C_{60} and Al/C_{60}, when not exposed to air, have been reported to form ohmic contacts,[3–5] the rectification observed in Fig. 1 arises from a thin aluminum oxide insulating layer at the interface between Al and C_{60}. Yonehara and Pac[3] suggested that an inversion layer may form at the Al/C_{60} interface as reported for Al/SiO_2/Si cells.[1] However, this model would not predict the reversal of the transient PV polarity at I_c, shown in Fig. 2. It appears that the transient PV could result from a complicated built-in potential at the Al/C_{60} interface, which is strongly dependent on the light intensity and changes polarity at a certain critical intensity. The polarity reversal of the cw PV at $\hbar\omega\approx2.3$ eV, shown in Fig. 4, may arise when a sufficient flux of low-energy ($\hbar\omega<2.3$ eV) photons reaches the Al/AlO_x/C_{60} interface. For higher-energy photons, that critical flux level could not reach the Al/AlO_x/C_{60} interface due to the short absorption depth.

In summary, we have investigated the transient photovoltaic response in the nanosecond regime and the spectral dependence of the cw photovoltaic response in Al/C_{60}/Au sandwich cells. The transient PV changes polarity at a critical intensity which can be varied and controlled by applying cw bias light. We find that the magnitude of the cw PV shows a sharp minimum at $\hbar\omega\approx2.3$ eV, at which the phase of the lock-in signal changes by approximately 180°, indicating that the cw PV also changes polarity at this energy. The change in polarity of the transient PV as a function of the incident light intensity and the ability to vary the critical intensity at which polarity changes sign can be viewed as features of a light-controlled nonlinear detector which might find use in applications in the area of fast optoelectronic switches.

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[1] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1982).
[2] B. Miller, J. M. Rosamilia, G. Dabbagh, R. Tycko, R. C. Haddon, A. J. Miller, W. Wilson, D. W. Murphy, and A. F. Hebard, J. Am. Chem. Soc. **113**, 6291 (1991).
[3] H. Yonehara and C. Pac, Appl. Phys. Lett. **61**, 575 (1992).
[4] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, C. Stucky, and F. Wudl, Appl. Phys. Lett. **62**, 585 (1993).
[5] J. Mort, K. Okumura, M. Machonkin, R. Ziolo, D. R. Huffman, and M. I. Ferguson, Chem. Phys. Lett. **186**, 281 (1991).
[6] M. Kaiser, J. Reichenbach, H. J. Byrne, J. Anders, W. Maser, S. Roth, A. Zahab, and P. Bernier, Solid State Commun. **81**, 261 (1992).
[7] C. H. Lee, G. Yu, D. Moses, V. I. Srdanov, X. Wei, and Z. V. Vardeny, Phys. Rev. B **48**, 8506 (1993).
[8] C. H. Lee, G. Yu, B. Kraabel, D. Moses, and V. I. Srdanov, Phys. Rev. B **49**, 10 572 (1994).
[9] G. Giro, J. Kalinowski, P. D. Marco, V. Fattori, and G. Marconi, Chem. Phys. Lett. **211**, 580 (1993).
[10] J. H. Weaver, J. Phys. Chem. Solids **53**, 1433 (1992), and references therein.
[11] A. Skumanich, Chem. Phys. Lett. **182**, 486 (1991).
[12] M. K. Kelly, P. Etchegoin, D. Fuchs, W. Krätschmer, and K. Fostiropoulos, Phys. Rev. B **46**, 4963 (1992).
[13] G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Caudano, J. P. Vigneron, Ph. Lambin, and A. A. Lucas, Phys. Rev. Lett. **67**, 2171 (1991).
[14] D. Moses, Philos. Mag. B **66**, 1 (1992).
[15] V. I. Srdanov, A. P. Saab, D. Margolese, E. Poolman, K. C. Khemani, A. Koch, F. Wudl, B. Kirtman, and G. D. Stucky, Chem. Phys. Lett. **192**, 243 (1992).
[16] D. H. Auston, in *Picosecond Optoelectronic Devices*, edited by C. H. Lee (Academic, New York, 1984), Chap. 4.
[17] D. Sarkar and N. J. Halas, Solid State Commun. **90**, 261 (1994).