Fullerene Sensitized Silicon for Near- to Mid-Infrared Light Detection

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Detection of light in the near- to mid-infrared (IR) spectral range is a technology in demand for many applications such as optical data transmission (1.55 μm), contrast enhancement for imaging systems in foggy environments, and quality control. Most of the optoelectronic devices on the market are based on the rather expensive III–V compound technology and, as a result, the monolithic integration into the well-established and cheap silicon-based complementary metal oxide semiconductor (CMOS) production process is still an unachieved goal. Here, we report on a novel light-sensing scheme based on a silicon/fullerene-derivative heterojunction that allows the realization of optoelectronic devices for the detection of near- to mid-IR light, which is fully compatible with CMOS technology. Despite the absence of light absorption by silicon and the fullerene-derivative in the IR. a heterojunction of these materials absorbs and generates a photocurrent (PC) in the near- to mid-IR. In this spectral range it is proposed that the IR PC is caused by an interfacial absorption mechanism.

In essence, an inherent disadvantage of silicon for optoelectronic IR applications is its transparency beyond a wavelength of 1.1 μm. To overcome this disadvantage, several technologies such as the heteroepitaxial growth of (polycrystalline) germanium on silicon[1–3] or the usage of near-IR (NIR)-photoconductive and soluble nanoparticles have been developed.[4,5] In the latter case, the facile solution processing of a guest material to the silicon-based host is of particular interest.[5]

In this work, the soluble C_{60} derivative methano-fullerene [6,6] phenyl-C61 butyric acid methyl ester (PCBM) as guest material has been chosen (see inset of Fig. 1, where the chemical structure is depicted). In contrast to pristine C_{60}, PCBM exhibits a solubility of up to 5 wt% in common organic solvents due to functionalization of the fullerene cage with a butyric acid methylester sidegroup.[6] For polycrystalline C_{60} thin films processed into field effect devices, the electron mobility is of the order of $1\,\mathrm{cm^2\,Vs^{-1}}$ [7,8] and for the spin-cast PCBM thin films it is approximately one to two orders lower in magnitude.[9] The microscopic charge-carrier mobility of PCBM is only weakly temperature dependent and a highly conductive state of PCBM under a filamented current density at 15 K has been reported.[10]

In this Communication is shown that a p-Si/PCBM heterojunction features a PC for photon energies from ~0.55 to 1.1 eV (2.25–1.12 μm). The investigated samples have a layered structure (Fig. 1). On top of a boron-doped p-Si wafer (boron concentration 10^{15}–$10^{16}\,\mathrm{cm^{-3}}$) the PCBM film is deposited by spin-coating, resulting in a PCBM film thickness of 140 nm. By thermal evaporation of Al the electrical front- and back-contacts to the PCBM thin film and to the p-Si wafer are formed. To ensure an Ohmic contact of the Al to the p-Si wafer, the Al/p-Si contact is alloyed at 580 °C in a nitrogen/hydrogen atmosphere.[11]

In Figure 2, the current-density–voltage (*J*–*V*) characteristics of an Al/p-Si/PCBM/Al heterojunction is presented at room temperature and 77 K. At 297 K a current rectification ratio of 3×10^4 for a bias variation from −1 to +1 V is observed. Similar values for pristine C_{60}/silicon heterojunction diodes have been obtained by Chen et al.[12] Upon cooling, the reverse dark current density at −2 V bias decreases from $3 \times 10^{-6}\,\mathrm{A\,cm^{-2}}$ at 297 K to the pA $\mathrm{cm^{-2}}$ region at 77 K, while the current rectification increases to $\sim 10^7$ for a bias variation from −1 to +1 V. From an Arrhenius plot of the dark current in reverse bias at −1 V (see inset in Fig. 2a) an activation energy of 0.45 eV is found for the temperature range from 297 to 240 K.

At a sample temperature of 77 K and under broadband-IR illumination with a tungsten lamp that is spectrally restricted by a high-energy-cut-off silicon filter, a *J*–*V* characteristic typical for a photovoltaic device is observed (Fig. 2). The light intensity (measured with a calibrated InGaAs detector) behind the Si filter is $3.8 \times 10^{-3}\,\mathrm{W\,cm^{-1}}$, which leads to a short-circuit current (J_{sc}) of $J_{sc} = 15\,\mathrm{nA\,cm^{-2}}$ and a open-circuit voltage of +0.45 V at 77 K. At room temperature a high-resolution *J*–*V* scan around zero bias verifies that a finite short-circuit current of $\sim 10\,\mathrm{nA\,cm^{-2}}$ and an open circuit voltage of ~1 mV is still observable (Fig. 2a and inset).

Under the same experimental conditions as for the *J*–*V* measurements, the PC at various temperatures is spectrally

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DOI: 10.1002/adma.200901383

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resolved using a Fourier-transform IR (FTIR) spectrometer in step-scan mode. To ensure that the PC is measured under equilibrium conditions, the response time of the PC is determined in a separate experiment. After ~5 ms 70% of the saturated PC amplitude is reached, corresponding to a −3 dB roll-off at 200 Hz. Consequently, all step-scan FTIR data are recorded with a chopper frequency of 38 Hz, which is far below the roll-off frequency.

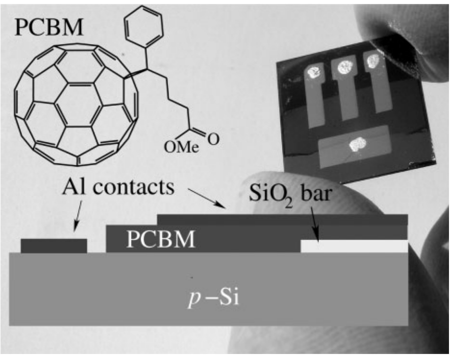

Figure 1. Sample photograph and the schematic cross-section of the Al/p-Si/PCBM/Al heterojunction. The inset shows the chemical structure of the fullerene derivative—PCBM.

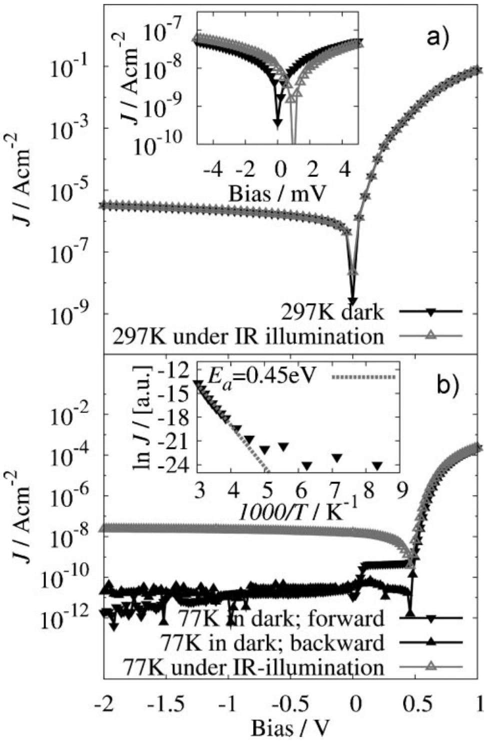

Figure 2. Al/p-Si/PCBM/Al-heterojunction *J–V*-characteristics at 297 K in panel (a) and at 77 K in panel (b), measured in the dark (visualized by the symbols ▼ and ▲) and under broadband-IR illumination (visualized by the symbol △). A tungsten lamp spectrally restricted by a Si filter at room temperature and a low-pass interference filter (cut-off at 0.95 eV) is used as a light source. The bottom inset in panel (a) shows an Arrhenius plot of the reverse dark-current density at −1 V bias. The different bias sweep directions are visualized by the ▲ symbol for a bias sweep direction towards higher voltages (forward) and the ▼ symbol for a bias sweep direction towards lower voltages (backward).

The spectrally resolved PC in the temperature range from 77 to 297 K is shown in Figure 3. Above a threshold photon energy of ~0.55 eV the PC is monotonically increasing up to the absorption edge of the Si filter (at 1.1 eV). By increasing the sample temperature, the magnitude of the PC at 1.1 eV increases and is dominant around 130 K sample temperature. The PC at 1.1 eV is due to the absorption in the p-Si substrate as will be shown below. In order to prevent that the p-Si substrate signal dominates the dynamic range of our experiment, a low-pass interference filter with a cut-off energy at 0.95 eV was used in addition to the Si filter. In this configuration one clearly observes that the magnitude of the PC at each wavelength in the spectral range from 0.55 to 0.95 eV remains almost constant as a function of temperature between 297 and 130 K and is finally increased by a factor two at 77 K (Fig. 3b). At 77 K, a responsivity of 1.4×10^{-5} A W^{-1} is measured at a photon energy of 0.95 eV (see Experimental section for details).

The observed photoresponse as well as the rectifying *J–V* characteristics of the p-Si/PCBM heterojunction can be understood in terms of the electron and hole band discontinuities across the interface, which are sketched schematically in Figure 4. Since the work function of Si is about −4.8 eV[13] and the lowest unoccupied molecular orbital (LUMO) of PCBM is at −4.2 eV,[14] the Fermi level of the p-Si is energetically below the LUMO of the PCBM molecule. Under a positive (forward) bias voltage applied to the Al/p-Si back-contact, electrons are efficiently injected from

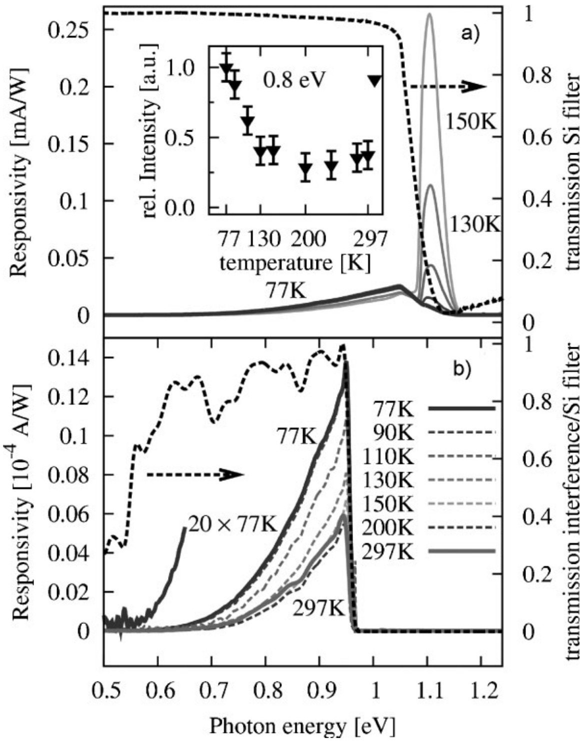

Figure 3. IR photocurrent at 0 V bias of an Al/p-Si/PCBM/Al heterojunction as function of photon energy in the temperature range from 297 to 77 K. In panel (a), the tungsten light source is spectrally restricted by a Si filter and in panel (b) by an additional low-pass filter with a cut-off at 0.95 eV. Filter transmissions are shown by the broken lines in (a) and (b). The inset of (a) shows the normalized temperature dependency of the photocurrent at 0.8 eV photon energy.

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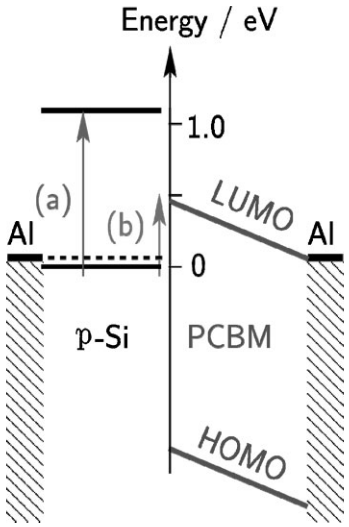

Figure 4. Sketch of the electronic structure of an Al/p-Si/PCBM/Al heterojunction at zero bias. The graph does not take into account possible interfacial layers at the p-Si/PCBM interface. The experimentally observed optical transitions are labeled as processes (a) and (b).

the Al top-contact into the PCBM layer. The electron injection from the PCBM into the Si conduction band (CB) is energetically unfavorable and the current has to traverse the organic/inorganic interface as a recombination current between electrons in the PCBM and holes in the p-Si. When biasing the p-Si/PCBM diode in reverse direction (negative voltage applied to the Al/p-Si back-contact), holes are extracted from the p-Si valence band (VB) into the Al back-contact. However, no efficient direct injection of holes into the p-Si from the PCBM–HOMO (highest occupied molecular orbital) is possible due to the very low intrinsic PCBM hole concentration and the injection barrier for holes from the Al top-contact into the PCBM–HOMO. Thus, in the absence of radiation, only thermally excited carriers can maintain the dark current observed under reverse bias.

Two processes have to be considered in which holes can be injected thermally into p-Si giving rise to the observed reverse dark current: (a) the thermal excitation of electron–hole pairs in the p-Si and a subsequent injection of the electron into the PCBM–LUMO and (b) the direct thermal excitation of electrons from the Si VB into the PCBM–LUMO. For process (a), the expected thermal activation energy equals the indirect Si bandgap, whereas for process (b) an activation energy in the sub-bandgap range of silicon is expected. From the temperature dependence of the reverse dark current between 297 and 240 K, an activation energy of 0.45 eV is determined from the Arrhenius plot, as shown in the inset of Figure 2b. This result indicates that process (a) can be excluded as the dominant mechanism responsible for the observed reverse dark current, which, as a consequence, has to be ascribed to process (b). The observation of process (b) indicates a strong interaction of the PCBM–LUMO with the Si VB states across the interface.

Due to the transparency of both silicon and PCBM in the spectral range below 1.1 eV, the PC response between ~0.55 and 1.1 eV cannot be trivially assigned to a direct absorption in either of the materials. Instead, it is ascribed to a spatial diagonal optical transition from the VB of p-Si to the LUMO of the PCBM thin film [process (b) in Fig. 4]

Upon radiation, the processes labeled as (a) and (b) in Figure 4 can be excited optically. From its energetic position, the strong signal at 1.1 eV shown in Figure 3 is assigned to the excitation of an electron from the Si VB to the CB and its subsequent injection into the PCBM [process (a)]. Since the NIR radiation is incident from the silicon side of the sample, only light with energy in a narrow range around the Si absorption edge contributes to this spectral feature. Radiation at larger energies is absorbed by the Si filter and in the Si substrate, far away from the p-Si/PCBM interface. By lowering the sample temperature, the bandgap of the p-Si substrate is increased above the cut-off energy of the silicon filter at room temperature,[15] resulting in a signal decrease at 1.1 eV. At a sample temperature of 77 K (black graph in Fig. 3) no radiation with sufficient energy to be absorbed in the p-Si substrate passes through the Si filter, thus, the signal due to process (a) is absent at that temperature and only the signal due to absorption across the interface [process (b)] remains.

According to our model one would expect, ideally, that the onset energy of the PC and the activation energy of the reverse dark current are equal. However, experimentally a slightly larger value is observed for the former (~0.55 eV) than for the latter (0.45 eV). Such minute deviation between the PC onset energy and thermal activation energy is commonly observed for heterojunction detectors, as optical methods are less sensitive to spatial variation of the interfacial barrier height than transport measurements.[16–18]

We would like to emphasize that the PC due to process (b) must be distinguished from results for photoemission of electrons from clean metal surfaces as described by the Fowler model.[19] This model has also been applied to Schottky-barrier and heterojunction-internal-barrier detectors,[20,21] and is based on a two-step photoemission process composed of a transition of a charge carrier into an excited state of the electrode and a subsequent injection into the vacuum (for metal surfaces) or into the semiconductor (for Schottky diodes). However, in the p-Si/PCBM device such a two-step process can be excluded for photon energies below the Si bandgap, since no electron states that can be excited exist within the Si bandgap. In addition, the injection of an excited hole from the Si VB into the PCBM at hole energies in the range between 0.55 and 1.1 eV below the Si-VB edge can also be excluded due to the large band offset between the PCBM–HOMO and the Si VB (Fig. 4).

In summary, it has been shown that charge carriers can be directly excited across the interface of a silicon/fullerene-hybrid heterojunction by IR radiation. This excitation process opens a versatile spectroscopic method to investigate the nature of interfaces between semiconducting organic and inorganic heterostructures. Besides its scientific relevance, the simple fabrication process as well as its compatibility with well-established silicon technology makes the presented hybrid approach a promising candidate for widespread applications.

Experimental

Device Fabrication: The heterojunction was manufactured by spin-coating a PCBM solution (3 wt% in chlorobenzene) on top of a p-Si

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substrate after removing the native oxide by an HF dip. The PCBM was purchased at Solenne BV Netherland and used as received. The resulting PCBM film thickness was 140 nm. Light microscopy and atomic force microscopy (AFM) measurements proved a good PCBM thin-film quality with a smooth surface without pinholes. The 80-nm-thick Al contacts to the p-Si and to the PCBM thin film were prepared by thermal evaporation of Al under dynamic vacuum (10^{-6} mbar). To ensure an Ohmic contact of the Al to the p-Si, the contact was alloyed at 580 °C under nitrogen/hydrogen atmosphere. The p-Si was partially covered with a 100-nm-thick thermally grown SiO_2 oxide to prevent shortcuts to the p-Si substrate when contacting the Al PCBM top-contact. All processing steps were performed under N_2 atmosphere in a glove box system (O_2 contents below 1 ppm), to prevent oxygen diffusion into the PCBM thin film and to suppress the formation of a native SiO_2 on the p-Si substrate.

Electrical Characterizations: For the electrical characterizations a Keithley 236 SMU has been used.

Optical Characterization: The PC spectra were measured with a Bruker Vertex 80 FTIR spectrometer operated in step-scan mode, which was equipped with a tungsten lamp and a CaF beam splitter. The samples were mounted in a variable-temperature nitrogen cryostat attached to the sample chamber of the spectrometer and illuminated by the beam leaving the Michelson interferometer of the spectrometer. In the optical path in front of the cryostat, a mechanical chopper (operating at 38 Hz) and a 1-cm-thick Si filter in combination with an interference filter (cut-off at 0.95 eV) was placed. The short-circuit PC of the sample generated by this spectrally limited beam was amplified by a Standford Research Systems Model SR830 lock-in amplifier and fed back into the spectrometer electronics via the input for external detectors. In order to eliminate all spectral features originating from the tungsten source and the optical elements in the light path and the cryostat windows of the spectrometer, the PC spectra were normalized to a reference spectrum measured also at 38 Hz modulation frequency using a pyroelectric detector with a responsivity independent of the wavelength in the spectral range of interest. To precisely estimate the intensity of the IR beam at the sample position, a calibrated InGaAs detector was placed at the sample position inside the cryostat. With the known spectrally resolved IR light intensity at the sample position and the relative responsivity determined by the FTIR spectrometer, it is straightforward to estimate the absolute sample responsivity in [A W^{-1}]. For time-resolved PC measurements, a black-body emitter ($T = 1900$ K) chopped with a mechanical shutter was used as a light source. Similar to the step-scan FTIR experiment, the chopped light beam was spectrally restricted by a Si filter and an additional low-pass interference filter (cut-off at 0.95 eV).

Acknowledgements

This work was supported by the Austrian Science Funds (FWF project number S9710), the Österreichische Forschungsförderungsgesellschaft (FFG project number 818046) and the Austria Wirtschaftsservice. The authors thank K. Hingerl for the critical comments and S. Berkebile for reading the manuscript.

Received: April 24, 2009
Revised: June 15, 2009
Published online: November 20, 2009

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