Fullerene sensitized silicon for near- to mid-infrared light detection

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Here, we report on a novel light sensing scheme based on a silicon/fullerene-derivative (methano-fullerene [6,6] phenyl-C61 butyric acid methyl ester – PCBM) heterojunction that allows the realization of optoelectronic devices for the detection of near- to mid-IR light. Despite the absent absorption of silicon and the fullerene-derivative in the IR a heterojunction of these materials absorbs and generates a photocurrent in the spectral range from 1.1 to 0.55 eV. Besides its scientific relevance, the simple fabrication process of the heterojunction (e.g., the fullerene-derivative is deposited by spin coating on Si) as well as its compatibility with the established complementary metaloxide semiconductor (CMOS) technology makes the presented hybrid approach a promising candidate for widespread applications.

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1 Introduction Many applications such as optical data transmission, contrast enhancement for imaging systems in foggy environments, and quality control demands in a technology for the detection of light in the near to mid infrared. In essence, the inherent disadvantage of silicon for optoelectronic infrared applications is its transparency in the IR ($E_{\text{photon}} < 1.1$ eV). To overcome this disadvantage, several technologies such as the deposition of (polycrystalline) germanium on silicon [1–3] or the usage of in near infrared photoconductive and soluble nanoparticles [4] have been developed. In the latter case, the simple solution processing is of particular interest. In this work as soluble semiconductor the C_{60} derivative methano-fullerene [6,6] phenyl-C61 butyric acid methyl ester (PCBM) has been used (see Fig. 1a where the chemical structure is depicted). In contrast to pristine C_{60}, PCBM is soluble up to 5 wt.% in common organic solvents [5]. PCBM thin films are electron conductors with mobilities in the order of 10^{-2} cm^2/Vs [6]. It is shown that a p-Si/PCBM heterojunction features a photovoltaic effect in the infrared regime from 0.55 to 1.1 eV [7].

2 Experimental The investigated samples have a sandwich type structure (see Fig. 1). On top of a boron doped Si wafer (boron concentration $\approx 10^{16}$ cm^{-3}) the PCBM film is deposited by spin coating.

The resulting PCBM film thickness is ≈ 140 nm. The subsequent evaporation of Al and Au is forming contacts to the PCBM film. Ohmic contacts to the p-Si are maintained by alloyed Al contacts. preparation. In Fig. 2 the current density versus voltage (*I–V*) characteristics at room temperature and
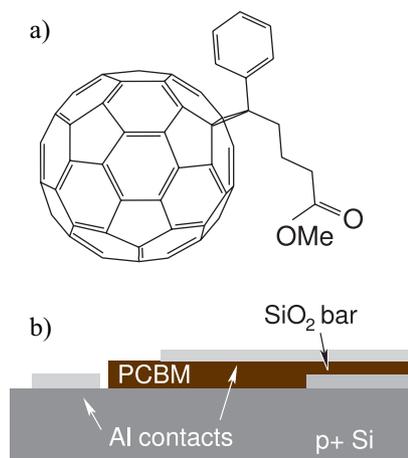

Figure 1 (online color at: www.pss-b.com) (a) Chemical structure of the C_{60} derivative PCBM. (b) Schematic cross section of the Al/p-Si/PCBM/Al heterojunction.

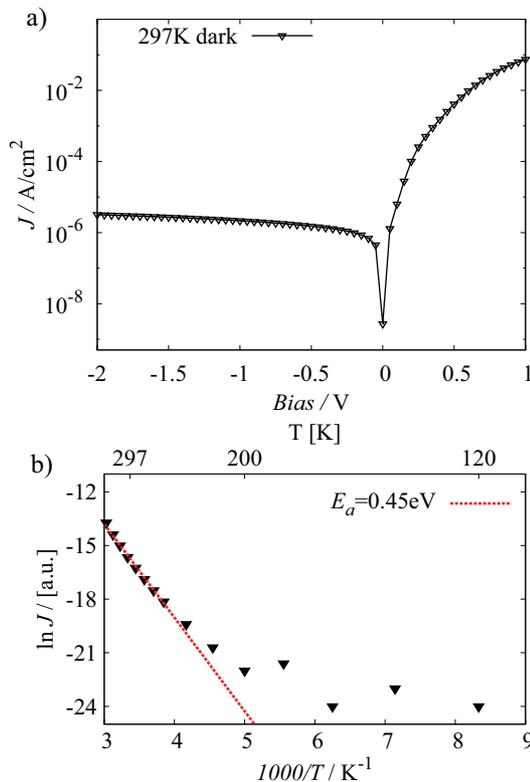© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

a)

b)

Figure 2 (online color at: www.pss-b.com) (a) *I–V*-characteristics at 297 K in dark. (b) Arrhenius plot of the reverse current density at −2 V bias.

Figure 3 (online color at: www.pss-b.com) *I–V*-characteristics at 77 K in dark (black triangles) and under broadband IR illumination (red triangles). As light source a tungsten lamp filtered by a 1 cm thick Si filter at room temperature was used. 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).

and in Fig. 3 at 77 K in dark under broad-band IR illumination are presented. At 297 K the *I–V*-characteristics exhibit a current rectification ratio of 3×10^4 for a bias variation from −1 to +1 V. AFM studies confirmed a homogeneous film formation [8] of the PCBM on top of the hydrophobe p-Si surface. A non-homogeneous PCBM thin film formation (e.g., pinholes) is causing shorts and an illdefined *I–V*-characteristics.

Upon cooling, the reverse dark current density at −2 V bias decreases from 2×10^6 A/cm^{-2} at 297 K to the sub-nA/cm^{-2} region at 77 K with an increased current rectification of $\approx 10^7$ for a bias variation from −1 to +1 V. From an Arrhenius plot of the reverse dark current density at −2 V bias for the temperature range from 297 to 240 K, an activation energy of $\Delta E \approx 0.45$ eV is found (see Fig. 2b).

Under broadband NIR-illumination from a tungsten lamp spectrally restricted by a high-energy cut-off Si filter and 77 K sample temperature, an *I–V*-characteristics typically for a photovoltaic device is observed (see Fig. 3). At zero bias (short-circuit condition) the current is in the range of 20 nA/cm^2 and at +0.5 V bias the current vanishes (open-circuit condition).

Under the same experimental conditions as for the *I–V* measurements, the NIR photocurrent (PC) at various temperatures is spectrally resolved using a Fourier-transform spectrometer. The spectrally resolved PC is normalized to
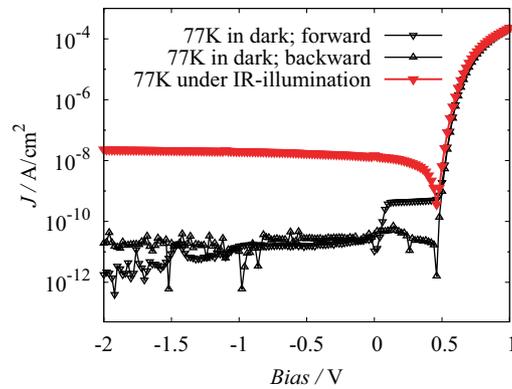
the absolute incident light intensity by the usage of a calibrated InGaAs photodiode.

The PC is monotonically increasing in the spectral range from 0.55 to 1.1 eV (see Fig. 4). At 115 K sample temperature, an additional PC around 1.1 eV is observed, which is dominant for temperatures above 150 K. To prevent that the PC around 1.1 μm is dominating the dynamic range of the experiment, a low pass interference filter (cut-off at 0.95 eV) in addition to the Si filter is placed in the optical path (see Fig. 4b).

The PC from 0.55 to 1.1 eV the PC is weakly temperature dependent and is decreased by approximately 60% at room temperature compared to the PC at liquid nitrogen temperature.

3 Discussion The interaction of fullerenes with semiconductors and metals is strong and complex. In particular, at the interface of a silicon/fullerene heterojunction, a silicon fullerene LUMO state mixing with an accompanying (at least partial) charge transfer has been reported [9, 10]. Similarly, fullerenes on metals are very likely to be chemisorbed which entails a charge transfer and accounts for an additional bonding beyond van der Waals interactions. Especially low workfunction metals as Al, form an Ohmic contact to fullerene thin films [11]. The observed photoresponse as well as the *I–V*-characteristics of the p-Si/PCBM heterojunction can be understood in terms of the electron and hole band discontinuities across the interface. Since the work function of Si is about −4.8 eV [9] and the LUMO of PCBM is at −4.2 eV [11], 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 the Ohmic Al/PCBM top-contact into the PCBM layer. The electron injection from the PCBM into the Si conduction band (CB) is energetically
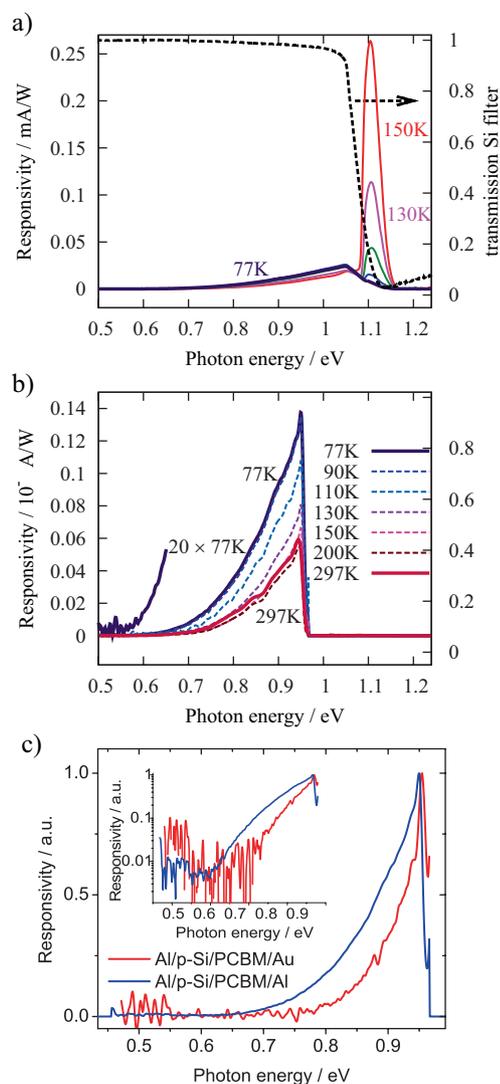
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Figure 4 (online color at: www.pss-b.com) IR photocurrent of an p-Si/PCBM heterojunction as function of photon energy from 297 to 77 K. In graph (a) and (b) the PCBM thin film is contacted with Al and in (c) with Al and Au, respectively. The p-Si is contacted with alloyed Al. The tungsten light source is spectrally restricted by a Si filter in (a) and in (b) and (c) by an additional low-pass interference filter with a cut-off at 0.95 eV.

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, holes are extracted from the p-Si valence band (VB) into the Al back-contact. In the absence of radiation, only thermally excited carriers can maintain the dark current observed under reverse bias. Two processes are considered by which holes are injected thermally into p-Si. (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 at the p-Si/PCBM interface with the subsequent injection of holes and electron in the bulk of the

p-Si and PCBM, respectively. 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 Fig. 2b an activation energy of ≈ 0.45 eV is determined. This result indicates that process (a) can be excluded as the dominant mechanism responsible for the observed reverse dark current. Further, the observation of process (b) also indicates a strong interaction of the PCBM–LUMO with the Si VB states across the interface. Upon radiation, processes (a) and (b) can be excited optically. From its energetic position, the strong signal at 1.1 eV shown in Fig. 4a is assigned to an VB to CB absorption in the p-Si and a subsequent electron injection into the PCBM. Since the NIR radiation is incident to 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 band-gap of the p-Si substrate is increased above the cut-off energy of the at room temperature maintained silicon filter [12], resulting in a signal decrease at 1.1 eV. At a sample temperature of 77 K, no radiation with sufficient energy to be absorbed in the p-Si substrate passes through the Si filter and the signal due to process (a) is absent at that temperature. Due to the transparency of silicon as well as the of pristine 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 an optical absorption process at the p-Si/PCBM interface. To further confirm this concept the ohmic Al contact to the PCBM thin film has been replaced by a Au. Au forms an non-ohmic electron contact to PCBM. The electron injection is inferior compared to Al but not the electron extraction [11]. A non-ohmic contact can lead to a photocurrents in the sub-bandgap regime of the semiconductor by internal photo-emission [13]. In case the contacts to the PCBM are influencing the IR response, a change from the ohmic Al contact to Au should enhance and/or change the onset of the observed PC. The PC for the sample with Au contacts was by a factor 20 lower as the with Al contacts but the onset of the PC remains at ≈ 0.55–0.6 eV (see Fig. 4). A more complete study is in progress, but in the present state it can be concluded that the used metal to the PCBM thin film is not (or just in a minor way) influencing the onset and/or shape of the IR response. Hence internal photoemission from the metal to the PCBM is not present and the p-Si/PCBM heterojunction absorbs in the IR. In Ref. [7], we proposed as absorption mechanism the presence of joint-density of states between the VB of p-Si and the LUMO of the PCBM. But other mechanism as the excitation of charged centers at the heterojunction [14] cannot be ruled out.

4 Conclusion In summary, it has been demonstrated that a silicon/fullerene heterojunction absorbs and generates a photocurrent in the spectral range from 0.5 to 1.1 eV (the principal absorption of Si). As manifestation of the strong

interaction of fullerenes with the Si surface, the PC originates from an absorption mechanism at the heterojunction. Besides its scientific relevance, the simple fabrication process as well as its compatibility with the well established complementary metaloxide semiconductor (CMOS) technology, makes the presented hybrid approach a promising candidate for widespread applications.

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