

Sensing infrared light with an organic/inorganic hetero-junction

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Organic and inorganic semiconductors are diverse in many of their physical properties but the combination of these can feature unexpected as well as unique physical properties. Here we report on an organic/inorganic hetero-junction which can readily be utilized for sensing infrared light. The used materials are highly boron doped crystalline silicon (100) and a soluble buckminster fullerene derivative. Despite the missing light absorption of silicon as well as the of the fullerene derivative for a wavelengths beyond 1.3 μm and 720 nm respectively, a hetero-junction of these materials absorbs in the infrared and generates a primary photo-current in the wavelength range from 1.3 to 3 μm . The simple preparation of the hetero-junction by a solution process of the fullerene derivative on top of the silicon wafer substrate, is technologically attractive in an economically viable way.

1. Introduction

Here we report on a novel light sensing device based on a silicon/fullerene hetero-junction that allows the realization of optoelectronic devices for the NIR which are fully compatible with CMOS technology. In essence, the inherent disadvantage of silicon for optoelectronic infrared applications is its transparency beyond a wavelength of 1.1 μm . To overcome this disadvantage, several technologies such as the hetero-epitaxial growth of (polycrystalline-) germanium on silicon or the usage of in near infrared photo-conductive and soluble nano-particles [1] have been developed. In the latter case, the facile solution processing is of particular interest. Potential soluble semiconductors are organic conjugated polymers and fullerene derivatives. The strengths of this material- class are the solubility, excellent optical properties and the per se tunable chemically structure. In this work, the

soluble C_{60} derivative methano-fullerene [6,6] phenylC₆₁ butyric acid methyl ester (PCBM) has been chosen (see left graph in Fig.1 where the chemical structure is depicted). In contrast to C_{60} , PCBM is soluble up to 5 weight percent in common organic solvents.

In this paper it is shown that a p-Si/PCBM hetero-junction features a photo-voltaic effect in the infrared regime between photon energies from 0.4 to 1.1eV (3-1.3 μm) [2].

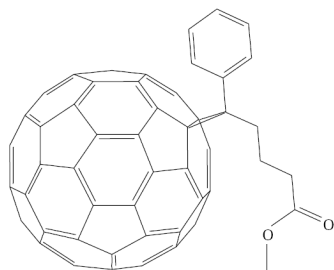


Fig. 1. shows the chemical structure of the fullerene derivative – PCBM [2].

2. Experimental Methods

The investigated samples have a layered structure (right graph in Fig. 1) and the hybrid hetero-junction is manufactured by spin-coating a PCBM solution (3 weight % in chlorobenzene) on top of a p-Si substrate. The resulting PCBM film thickness is 140nm. Subsequently a 100 nm thick aluminum contact is evaporated under dynamic vacuum (10^{-6} mbar) on top of the PCBM thin-film as well as directly to the p-Si substrate. For the electrical characterizations a Keithley 236 SMU has been used. The photo-current spectra were measured with a Bruker 113v Fourier transform spectrometer. The short circuit photo-current generated in the sample was amplified by a Stanford Research Systems SR570 low-noise current amplifier and fed back into the spectrometer electronics via the input for external detectors.

3. Results

In Fig. 2 the current-density versus voltage (IV) characteristics are presented at room temperature and at 80K. At 295K the IV-characteristics exhibit a current rectification ratio of $8 \cdot 10^5$ for a bias variation from -1 to +1 V. Upon cooling, the reverse dark current-density at -2 V bias decreases from $5 \cdot 10^{-7}$ A/cm² at 295 K to the sub nA/cm² region at 80K. From an Arrhenius plot of the reverse dark current-density at -2 V (see inset in the top graph of Fig. 2), an activation energy of $E_a=0.3\text{eV}$ is found. In dark and at 80K, the IV-characteristics features two

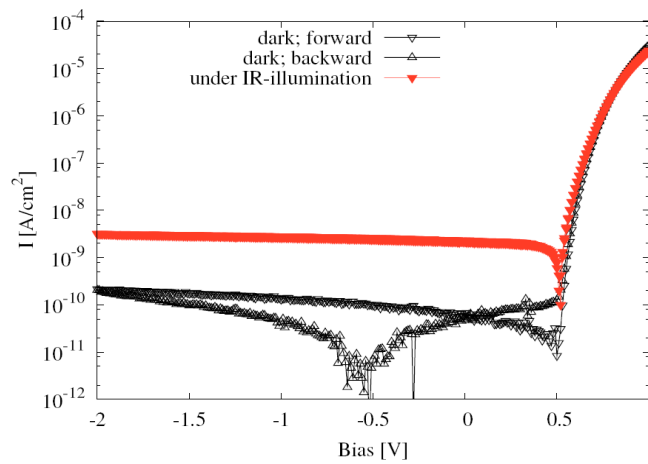
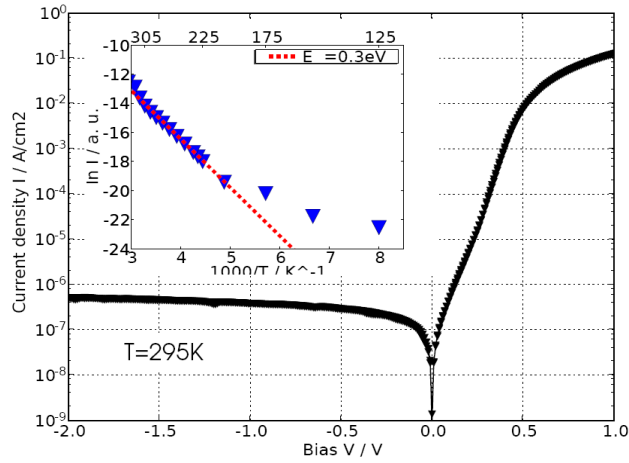


Fig.2. Current-density versus voltage (IV) characteristics of an Al/p-Si/PCBM/Al hetero-junction at 295K (top graph) and at 80K (bottom graph). The inset shows an Arrhenius plot of the reverse current-density at -2V bias. In the bottom graph the IV-characteristics at 80K under broadband IR illumination (red triangles) is shown [2].

distinct current minima, at -0.5 , V and at $+0.5$ V bias voltage for opposite sweep directions. This hysteresis behavior is attributed to trapped charges in the PCBM thin-film. At a sample temperature of 80K and under broadband NIR illumination from a tungsten lamp spectrally restricted by a Si filter, an IV-characteristics typically for a photo-voltaic device is observed (see bottom graph in Fig. 2). Under the same experimental conditions as for the IV measurements, the NIR photo-current at various temperatures is spectrally resolved using a Fourier-

transform spectrometer. Above 220K sample temperature, a photo-current solely around 1.1eV is observed (red graph in Fig. 3). Reducing the sample temperature, the photo-current at 1.1eV is decreasing, and a spectral monotonically increasing photo-current in the energy range from 0.4eV to the cut-off of the at room temperature maintained Si filter is measured. Upon cooling the signal to noise ratio increases and saturates at temperatures below 150K. The onset and the spectral shape of the photo-current between 0.4 and 1.1eV is only weakly temperature dependent.

The interaction of fullerenes with semiconductors and metals is strong and complex. In particular, fullerenes on bare silicon are very likely to be chemisorbed which entails a charge transfer and accounts for an additional bonding beyond van der Waals bonding [3,4]. Low work-function metals as Al or Ca, form an ohmic electron injecting contact to fullerene thin-films [5]. As Al is also ohmic to p-Si too, it is concluded, that the observed rectification if the IV-characteristics is due to the p-Si/fullerene interface.

Under an applied positive (forward) bias voltage, electrons are efficiently injected from the ohmic Al top-contact into the PCBM layer and recombine with 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. But this hole-current is limited by the hole blocking properties of the PCBM thin-film and the Al top contact receptively. Out of the temperature dependence of the reverse dark current between 305K and 205K, an activation energy E_a of 0.3eV is determined from the Arrhenius plot, shown in the inset of Fig. 2. This result indicates and manifests a strong interaction of the PCBM-LUMO with the Si VB states across the interface. E_a is interpreted as the height of a band-offset (barrier) between the Si VB and the LUMO of the PCBM thin-film.

The strong PC at 1.1eV is assigned to the excitation of an electron from the Si VB to the CB and its subsequent injection into the PCBM. Due to the transparency in the spectral range below 1.17eV of the silicon and PCBM respectively, the photo-current response between 0.4eV and 1.1eV cannot be trivially assigned to a direct absorption in either of the materials. Instead, it is ascribed to an (in real space indirect) optical transition from the VB of p-Si to the LUMO of the PCBM thin-film. The onset of the IR photo-current at 0.4eV is consistent with by the Arrhenius plot estimated barrier height E_a of 0.3eV.

4. Conclusions

In summary, it has been shown that by infrared radiation charge-carriers can be directly excited across the interface of a silicon/fullerene hybrid hetero-junction. Besides its scientific relevance, the simple fabrication process as well as its compatibility with the well established silicon technology makes the presented hybrid approach a promising candidate for widespread applications.

Acknowledgments

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