Electronic conduction properties of Au/C$_{60}$/p-Si and C$_{60}$/Au/p-Si sandwich structures: I–V and transducer characteristics

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Abstract

Gold-fullerite [C$_{60}$]-silicon (p-type) sandwich structures have been fabricated in order to investigate intrinsic cross-sectional and planar electronic conductive properties, in particular the C$_{60}$/p-Si p–n heterojunction. The turn-on voltage of this p–n heterojunction lies in the range 0.25–0.27 V. The I–V characteristics of the Au/C$_{60}$/p-Si structure are mostly defined by the bulk specific resistance of the fullerite crystal film itself ($\approx 6 \times 10^7$ $\Omega$ cm). I–V curves in the C$_{60}$/Au/p-Si structure are shown to be ohmic. Au/C$_{60}$/p-Si sandwiches irradiated with swift (300 MeV) heavy ions, ($^{84}$Kr$^{14+}$) to a total fluence $\approx 10^{10}$ ion/cm$^2$ yield structures which are sensitive to ambient air pressure, specifically in the case of a transverse contact configuration, and if one of the contacts is located on the irradiated part of the fullerite film. The sandwich-structure sensitivity to pressure is $\approx 5 \times 10^{-6}$ Pa$^{-1}$. This exceeds the sensitivity of conventional silicon pressure transducers by almost three orders of magnitude.

Keywords: A. Fullerenes; A. Thin films; A. Heterojunctions; C. Scanning and transmission electron microscopy; D. Radiation effects and pressure

1. Introduction

Following discovery of the closed fullerene molecular clusters [1,2] there have been applications of fullerite (the C$_{60}$ crystal) in the fabrication of light, humidity, temperature and pressure sensors [3–6]. To this end the aims and objectives of our work lie specifically in a combination of well known silicon properties with the new fullerite technologies, and in the fabrication of new devices at the nanometric level. Here, we shall describe phenomenological results from experimental studies of the I–V characteristics and conducting properties of Au/C$_{60}$/p-Si and C$_{60}$/Au/p-Si sandwich structures for cross-sectional and planar contact configurations. We reveal a p–n heterojunction in the Au/ C$_{60}$/p-Si structure, between the fullerite film and the silicon substrate. A simple model and equivalent circuit are suggested to describe I–V characteristic of this C$_{60}$/p-Si diode. The pressure dependence of the I–V characteristics of a Au/C$_{60}$/p-Si structure has also been examined for a
sample irradiated with swift (300 MeV) $^{84}$Kr$^{14+}$ ions, in order to probe additionally the influence of radiation damage on the conducting properties of fullerite.

Studies of the influence of isotropic ambient air pressure on intrinsic I–V curves are also described, since one of the most important applications of the C$_{60}$/p-Si diode structure can be in pressure (transducive) sensor devices. Capacitive and conductive (resistive) sensors are rather well understood, particularly the former, where there is a smaller influence on the signal from background noise.

Here, we shall be more concerned with the existence of a C$_{60}$/p-Si (diode) interface heterojunction and its implications, which suggests that, in principle, a true transistor might be fabricated.

Because of the appearance of a diode between the fullerite film and the silicon substrate we shall refer to such structures, fullerite-on-silicon, as FOS systems.

2. Experimental

P-type silicon wafers (455 $\mu$m thick, resistivity $\sim$0.04 $\Omega$·cm), were cut on {111} and {100} planes. They were then cleaned in the normal way $\pm$ 5 min. acetone in an ultrasonic bath, rinsing in DI water of 17 M$\Omega$, 5 min methanol in ultrasonic bath, rinsing in DI water, exposure to a 5H$_2$O/1H$_2$O$_2$/1HCL mixture for 15 min at 80°C, rinsing in DI water, 1 min. HF of 1 wt% at ambient temperature, rinsing in water, and finally drying with an N$_2$ gun. Two types of sample were prepared:

(a) Planar C$_{60}$ films (250 nm) were evaporated onto (111) oriented p-Si wafers, onto which a $\sim$5 nm thick Au layer had previously been deposited (Fig. 1).

(b) Planar C$_{60}$ films (100 nm) were evaporated onto 5 nm Au layers pre-evaporated onto (100) oriented p-Si wafers.

One such Au/C$_{60}$/p-Si sample had been pre-irradiated with 300 MeV $^{84}$Kr$^{14+}$ ions at the Ion Beam Laboratory (IBL) at the Hahn-Meitner Institute (Berlin) to a fluence $\sim 10^{10}$ ion/cm$^2$.

To measure cross-sectional lateral conductivities and I–V characteristics three contact pads were fabricated. Two dots were deposited on top of the gold or fullerite film (front side) and one on the silicon substrate side using silver paste (see Fig. 1). Surface contacts (interchangeable) were labelled ‘1’ and ‘2’, and the base contact as ‘S’. The thin layer of C$_{60}$ was deposited by vacuum evaporation: ($T_e = 600$ °C, $t_e = 20$ min. $P = 10^{-6}$ Torr, $\sim 0.2$ nm/s evaporation rate). Cross-sectional and tilt SEM images of a C$_{60}$/Au/p-Si sample are shown in Fig. 2(a) and (b), respectively. The thin ($\sim$5 nm) gold film layer in C$_{60}$/Au/Si was, as expected [7,8], intermittent (see SEM cross section in Fig. 2(a)).

It is assumed to be the same for the fullerite film (roughness-height of asperities-determined by SEM $\sim$10 nm). The grain size in the fullerite film was $\sim$25–75 nm (see Fig. 2(b)).

3. Results and discussion

The current–voltage measurements were usually performed between ‘1-S’; ‘2-S’; and ‘1-2’ contacts, the free contact being usually disconnected. Both contacts on the surface of sandwich structure were located on the...
unirradiated area. Fig. 3(a) shows the two basic FOS-structure current/voltage curves between ‘1-S’ and ‘2-S’ contacts. The I–V characteristics clearly have an asymmetric diode-type shape for both contact pairs, thus displaying basic rectifying properties. The rectification ratio is \( I_{\text{forward}}/I_{\text{reverse}} = 10^7 \) at \( V = 0 \pm 1.75 \) V. These observations support the argument for a p–n heterojunction, assuming no penetration of gold through the fullerite to the silicon. This confirms earlier RBS observations [9] for sharp border contact systems in Pd/C\(_{60}\)/Pd; Cr/C\(_{60}\)/Cr; Pd/C\(_{60}\)/Cr, C\(_{60}\)/Au/Si.

Shottky-barrier heights in Au/p-Si and Au/n-Si structures are 0.35 and 0.82 eV, respectively [10,11]. For Ag/p-Si and Ag/n-Si corresponding values of 0.54 and 0.78 eV are reported [10].

In this work, the forward voltage threshold \( (V_t = 0.25 \pm 0.27 \) V) is quite clear (Fig. 3). An Au/C\(_{60}\)/Al diode structure has also been described (\( V_t = 0.4 \) V) [12]. This value corresponds well with the model of an ideal metal–semiconductor junction where the Shottky-barrier height is \( \psi_{\text{ms}} = \psi_{\text{m}} - \psi_{\text{s}} = 0.4 \) eV and \( \psi_{\text{m}}(\text{Au}) = 5.1 \) eV [10], \( \psi_{\text{s}}(\text{C}60) = 4.7 \) eV [13] are work functions for gold and fullerite, respectively.

We rule out any contribution from the silver paste to our observations. Indeed silver is considered to be the best conductor. It has a low specific resistivity, crystallizes easily, is widely used in VLSI fabrication and as ohmic contacts in screen printing [14,15].

The value \( \rho_{\text{Fe}} \) corresponds to the resistivity of C\(_{60}\) single crystal as had been reported in Refs. [16,17]. The value \( \rho_{\text{Fe}} \) is much low compared with \( 10^{14} \) Ω cm, early reported by J. Mort et al., for 1.5 μm thick sublimated films of C\(_{60}\)/C\(_{70}\) [18] and with own results for polycrystalline C\(_{60}\)/C\(_{70}\) film \( (10^{13}–10^{14} \) Ω cm) [19,20].

The I–V characteristics for contacts ‘1–2’ are shown in Fig. 4. There is a clear voltage dependent hysteresis, which may be due to charge accumulation in the high resistive fullerite layer. The average I–V curve for contacts ‘1–2’ is shown also.

The values for current in the I–V curve correspond to the reverse currents of individual p–n-junctions for terminals ‘1’ and ‘2’, respectively, suggesting the presence of two p–n junctions, one of them being reverse biased for different voltage polarity on the two contacts. The slight asymmetry of the average \( I_{\text{reverse}}(V) \) curves is most likely due to the different contact areas of the two pads.

### 3.1. Basic FOS structure; an equivalent circuit

The general equivalent circuit suggested in Fig. 5 is based on analysis of the I–V characteristics described. The special case of different polarities (different applied voltages on terminals ‘1’, ‘2’ and ‘S’) is not included.

It is useful to trace current paths in Fig. 5 starting from terminal ‘1’ to either terminals ‘S’ or ‘2’. The current might flow directly to ‘2’ via the high ohmic surface metallization \( R_m \) and high ohmic bulk resistance of the fullerite in the lateral direction \( R_{\text{fb}} \) or, laterally, through the fullerite in a transverse direction \( R_{\text{fs}} \) and diode \( D_{\text{FS}} \). Any diode leakage resistance \( R_{\text{fs}} \) is ignored for simplification.

The current might pass transversely through the bulk resistance of the silicon substrate \( R_{\text{bs}} \) to terminal ‘S’ below...
it, or terminal ‘2’, depending on the voltage at these terminals. With terminal ‘2’ disconnected a current can flow from terminals ‘1’ to ‘S’—and vice versa—when terminal ‘S’ is disconnected, the flow is through the structure laterally from ‘1’ to ‘2’.

We tentatively explain the I–V characteristics for terminals ‘1-S’ (‘2-S’) and ‘1-2’ as follows:

(a) If \( V_1 = 0 \) and \( V_S > 0 \), then terminal ‘2’ is disconnected. This corresponds to a forward bias \( D_{FS1} \). The current passes through \( R_{bs} \) and thus the forwarded diode \( D_{FS1} \) and \( R_{bs} \). For \( R_{bs} \gg R_{bs} \), then the I–V curve for forward bias is defined by the barrier height (\(-0.27 \text{ eV}\)) and the value of \( R_{bs} \) (see Fig. 3).

(b) If \( V_1 > 0 \) and \( V_S = 0 \), then terminal ‘2’ is disconnected. This corresponds to a reverse bias of \( D_{FS1} \). The current passes through \( R_{bs} \), the reverse diode \( D_{FS1} \) and \( R_{bs} \). The I–V curve for a reversed bias is then defined by the resistance of the reverse diode \( D_{FS1} \) and by the diode leakage resistance \( R_{gs} \) (Fig. 3(a)). The same situation arises when terminal ‘1’ is disconnected and voltage is applied to terminals ‘2’ and ‘S’.

(c) When \( V_1 = 0 \) and \( V_S > 0 \), terminal ‘S’ is disconnected. This corresponds to forward bias of \( D_{FS1} \) and reversed bias of \( D_{FS2} \). The current flows into terminal ‘1’ through both diodes, because \( R_{bs} \gg R_{bs} \), \( R_{bs} \gg R_{bs} \) and \( R_{bs} \gg R_{bs} \). The I–V curve is defined by the reversed diode \( D_{FS2} \) (see Fig. 4). If \( V_1 \gg 0 \) and \( V_S = 0 \), terminal ‘S’ is disconnected, and the I–V curve is defined by the reversed diode \( D_{FS1} \).

(d) Finally, for \( V_1 = 0 \), \( V_2 \gg 0 \) and \( V_S \gg 0 \), the n–p–n transistor structure is clear, where \( D_{FS1} \) is the emitter, \( D_{FS2} \)—the collector, and the p-Si substrate is the base.

Our purpose here has been to demonstrate that construction of a good transistor based on C\(_{60}\)/p-Si heterojunctions can be realized. We note, however, that in practice a much smaller gap between terminals ‘1’ and ‘2’ is necessary (<\(< 1 \text{ mm}) in these experiments). Nevertheless our Au/C\(_{60}\)/p-Si structure can readily be exploited as an adjustable non-linear resistor.

3.2. Electrical conduction in C\(_{60}\)/Au/p-Si sandwich structures

I–V characteristics for transverse and lateral configuration of contacts in this structure are shown in Fig. 6. The slight asymmetry is probably due to a masking of the Au/C\(_{60}\) Schottky barrier as a consequence of the very high resistance vested in the fullerite film, implying an ohmic contact only.

The transverse current path through terminals ‘2-S’ is defined by the specific resistance of the fullerite film under the contact (\( r_F = 5.5 \times 10^7 \Omega \text{ cm}\)). Larger values of current (Fig. 6) are due to larger silver paste contact areas (\( r_{cont} = 1.45 \text{ mm}\)). The lateral current path through terminals ‘1-2’ is also defined by the specific resistance of the fullerite film, which is of the same order as that in the transverse plane. We conclude, therefore, that C\(_{60}\)/Au/p-Si structures will be of value not only in studies of the electrical conductivity of fullerite but also in environmental applications, particularly in the design of pressure and chemical sensors based on fullerite.

3.3. Response of Au/C\(_{60}\)/p-Si sandwich structures to the pressure of ambient air

Intrinsic physical properties of this FOS structure, in particular its sensitivity to pressure, can be exploited so that it becomes a transductive sensor. The forward current/
voltage characteristics of this irradiated sample are displayed in Fig. 7.

Measurements were made between contact ‘1’, connected to the substrate, and contact ‘2’, located on an irradiated area of the sample. The terminal configuration corresponds to Fig. 7 with contact ‘1’ short circuited. The I–V characteristics of the sample in a vacuum chamber were measured at normal pressure and at a low pressure of ambient air (Fig. 7). Once again diode characteristics are evident, in contrast to the unirradiated sample and the opening voltage for the p–n junction $V_{tirr}$ is less than $V_f = 0.27$ V for the unirradiated sample. The reverse current, however, is greater than that for the unirradiated sample.

What we have here, then, is a dependence upon ambient air pressure for the irradiated sample which is not found in the unirradiated sample. It is noted, however, that the I–V reverse curve also does not depend on pressure. The fundamental origin for this singular and sensitive transducer effect must lie in the p–n junction and in ion beam modification of the polycrystalline fullerite film. There are possible reasons for this:

(a) Bajwa et al. [21] describe aggregation into dimers and/or polymeric C$_{60}$ (fluence $<10^{12}$ ion/cm$^2$) and amorphization of C$_{60}$ (fluence $\sim 10^{14}$ ion/cm$^2$) for irradiation of fullerite films with 110 MeV $^{58}$Ni ions. Our 300 MeV $^{84}$Kr$^{14+}$ ions are both heavier and more energetic. Polymerization and fragmentation of C$_{60}$ with a fluence $\sim 10^{13}$ ion/cm$^2$, therefore, both seem likely, leading in turn to a decreasing resistance of the fullerite film. In this case-forward bias ($V_f < 0$, and no diode $D_{FS1}$ in the structure) the current path from terminal ‘S’ could be through the opened diode $D_{FS2}$, then through the reduced resistance of irradiated C$_{60}$ film to terminal ‘2’. The I–V curve is then defined by diode $D_{FS2}$.

(b) The same authors [21] describe a shrinking fullerite band gap with increasing ion fluence, which means that it is possible to alter the potential barrier between Si-p-type and irradiated (n-type) zones of the fullerite film. The smaller the band gap the lower is the potential barrier of the p–n heterojunction, as is evident in Fig. 7, where the threshold voltage $V_{tirr}$ is less than $V_f = 0.27$ V. Irradiation with swift heavy ions consequently leads to changes in the I–V curve of the Au/C$_{60}$/p-Si structure by reducing the height of the potential barrier in the C$_{60}$/p-Si contact system and increasing the conductivity of the irradiated part of the fullerite film.

The irradiated fullerite film sensitivity to pressure can be explained in several ways. First there is likely to be an increase in film porosity due to both fragmentation of C$_{60}$ and amorphization, rendering the film sensitive to humidity-adsorption and desorption. In these circumstances, the conductivity of the film falls at reduced pressures due to removal of moisture in the pumping-out process. This is seen in the I–V curve for the diode $D_{FS2}$ as an increase of base resistance.

In addition, as radiation induced part-polymerization proceeds the distance between each such zone naturally decreases, as does the distance between fullerene molecules, which are bound by van der Waals interactive forces. This leads to internal strain in the crystallites and external strains between them, which all bears down on the active number of conducting electrical chains and thus on sensitivity isotropic pressure.

Since the forward current, $I_{forward}$, depends on the applied isotropic pressure, it is useful to estimate the overall sensitivity. The divergence in forward I–V curves for different pressures starts at a voltage $V_{tirr} \sim 0.15$ V and appears distinctly at the voltage 0.4 V, (Figs. 7 and 8). It should be noted (see Fig. 8) that the specific resistance of the irradiated C$_{60}$ film ($\rho_{FS} = 1.9 \times 10^8$ Ω cm) is less than that for the unirradiated ($\rho_{FS} = 6 \times 10^7$ Ω cm).

The pumping-out process leads to increasing specific resistance, i.e. $\rho_{FS}(P_1) = 3.48 \times 10^7$ Ω cm, (Fig. 8), and we
make an estimate of the intrinsic transducing sensitivity $S$ in the following way:

$$|S| = |g(P_0) - g(P_1)||g(P_0)(P_0 - P_1)|^{-1},$$

where $g(P_0)$ and $g(P_1)$ are the gradients of the I–V characteristics for $P_0$ and $P_1$, respectively (Fig. 8). The final value for $|S|$ is $5 \times 10^{-6}$, almost three orders of magnitude greater than that for conventional silicon pressure sensing devices.

4. Conclusion

The experiments, we have described, using C$_{60}$ in layered sandwich structures, constitute a new step into the experimental nanometric unknown. We have demonstrated a new silicon-fullerite heterojunction with a threshold voltage of 0.25–0.27 V and a rectification ratio $\sim 10^3$. There is a sharp difference of conductivity between transverse and lateral current pathways through the fullerite film, which may be attributed on the one hand to grain boundary trapping of electrons (lateral direction) and, on the other, to complex current transverse pathways through individual fullerite microcrystals. As is the case for all heterojunctions, there is the possibility of changing the threshold voltage by varying the dopant level in the silicon substrate, and the type of conductivity. Preliminary deposition of a gold layer onto a p-Si substrate leads to ohmic contact between the p-Si and C$_{60}$ films—a potentially useful step towards the production of high resistance semiconductor based on fullerite.

There is a strong dependence of conductivity on ambient air pressures for C$_{60}$/p-Si junctions irradiated with swift heavy ions. At present we can only speculate as to the physical origin for this phenomenon and clearly more extensive experimental studies are called for. Nevertheless, we consider that there is rich potential for rapid exploitation of the device because of the high transducing sensitivity ($|S| = 5 \times 10^{-6}$ Pa$^{-1}$).

Combination of silicon and fullerene technologies leads to an entirely new family of electronic, sandwich systems. We refer to these as FOS (Fullerite on Silicon) devices. More specifically, in the present context, we affirm that combination of p–n and ohmic junctions on a p-Si substrate will lead to the assembly of more complicated circuitry, in which fullerite supplies the basic semiconducting properties exploited. It is rather clear that FOS structures are likely to be more attractive in transducer applications than their classical silicon counterparts because of their particularly pronounced diode and resistive properties.

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