Directed Growth of $C_{60}$ Nanowhiskers for Millimetre-Wave Detectors

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Abstract. The formation of $C_{60}$ nanowhiskers via the liquid-liquid interfacial precipitation technique presents a low-cost means of fabricating nanostructured fibres for use as active or passive elements in a number of possible applications. Recent measurements [9] have reported encouraging electrical characteristics that indicate the possibility of using $C_{60}$ nanowhiskers to realise electronic devices with switching or sensing capabilities. In this work, we focus on one application in particular – millimetre-wave power detectors. Traditional detectors based on Schottky junctions have difficulty impedance matching over very wide video bandwidths, in addition to insensitivity to very low power signals and high susceptibility to thermal and shot noise. $C_{60}$ nanowhiskers offer the possibility of realising low-cost, robust, sensitive millimetre-wave detectors with significantly reduced shunt capacitance and improved noise performance. Before this can be achieved, however, techniques are needed to control growth parameters and eliminate assembly through in-situ growth. Here, results are presented showing the influence of DC electric fields on $C_{60}$ molecules and nanowhiskers. Early indications suggest that alignment parallel to DC electric fields is possible.

Keywords: $C_{60}$, fullerenes, millimetre-wave detectors, nanowhiskers, nanotubes, self-assembly.

1. Introduction

The molecule $C_{60}$, discovered by Kroto et al. [1] in 1985, was the first observed example of a closed-form, stable arrangement of carbon atoms. The $C_{60}$ molecule is
a class of fullerene (buckminsterfullerene) consisting of 60 carbon atoms arranged in a ‘cage’ lattice, formed through adjacent arrangements of pentagons and hexagons. The structure conveniently takes on the shape of a FIFA football and is commonly referred to as a buckyball. The chemistry of fullerenes was developed further through the important discovery of carbon nanotubes by Iijima [2] at NEC in 1991. Carbon nanotubes (CNTs) can be visualised as elongated cylinders of hexagonally arranged atoms, capped at either end with fullerene hemispheres. Diameters have been reported in the range \( \sim 0.42 \text{ nm} \) [3] to tens of nanometres, with lengths of up to several centimetres [4].

The structural symmetry of CNTs underpins a variety of desirable physical properties, including high mechanical strength [5] and low resistivity, indicative of ballistic electron transport [6, 7]. This situation arises as CNTs are 1-dimensional conductors, resulting in fewer scattering events compared with bulk conductors.

Recently, Miyazawa et al. [8] reported a technique for growing needle-like structures of \( \text{C}_{60} \) from solution at room temperature. The structures, termed “\( \text{C}_{60} \) nanowhiskers”, grew in arbitrary directions, with uniform lengths of up to several hundred microns. In contrast to CNTs, which can be visualised as rolled-up sheets of graphene, \( \text{C}_{60} \) nanowhiskers contain no long-range hollow structure. In simplified form, they can be considered as linear arrangements of polymerised \( \text{C}_{60} \) molecules.

Electrical characterisation on individual, suspended \( \text{C}_{60} \) whiskers has been carried out in [9], and early measurements have indicated low DC resistivity at room temperature and the possibility of non-linear I–V characteristics.

The reported electrical attributes and expected high mechanical strength at nanoscale dimensions, make \( \text{C}_{60} \) whiskers suitable candidates for use in applications with electronic and mechanical functionality. In this paper, focus is applied to the former and, in particular, the possibility of using \( \text{C}_{60} \) whiskers to realise low-cost, high performance millimetre-wave power detectors. To achieve low-cost, a system is proposed that avoids assembly by using in-situ growth. Before this can be achieved, however, techniques need to be developed to control growth parameters, such as growth location and direction as well as final dimensions. We present results of early investigations on the influence of electric fields on \( \text{C}_{60} \) whiskers during growth; the aim being to demonstrate alignment between opposite pairs of electrodes.

2. Millimetre-wave power detection

Conventional millimetre-wave power detectors rely on semiconducting diodes to extract the power of the incident signal through its relationship with induced voltage. Millimetre-wave detectors are becoming increasingly more widespread as they can be used in a number of applications, including pollution monitoring, vehicle radar systems and object detection. Devices based on semiconductor diodes, however, suffer from a number of disadvantages which degrade signal detection under certain conditions. Applications which require high performance signal detection rely on alternative technologies; however, these are not widespread due to constraints on cost and practicality. The following sections will discuss millimetre-wave detector applications and related theory.
2.1. Applications

Many companies are involved in the modelling, design and manufacture of systems operating at millimetre-wave frequencies (e.g. from 30 to 300 GHz) and above. To date, these frequencies find only limited commercial applications (e.g. 77 GHz car radars, for autonomous cruise control). However, frequency figures-of-merit for diodes or transistors and their associated interconnects continue to increase. As a result, it is inevitable that new and ubiquitous applications will emerge above circa 100 GHz for the civil market. For example, future European Community directives on air pollution monitoring will require cheap, but high performance, sensors to detect low levels of pollutants using their signature absorption bands; examples include: ozone at 110 GHz, nitric oxide at 150 GHz, sulphur dioxide at 204 GHz and chlorine monoxide at 278 GHz. High resolution radiometric imaging at 94 GHz and 140 GHz has many important applications, including aircraft landing systems, locating victims trapped in fires and finding weapons concealed under clothing. Also, above circa 100 GHz, sophisticated security tagging/identification systems are possible that are both easy to conceal and extremely difficult to forge. Ultra-high data rate optical communications – using a ‘radio-fibre’ type of system – could transform the way information networks are distributed (British Telecom has been investigating picocellular systems at 180 GHz). Some research groups are also working on sensors for sub-cellular probing. This could potentially lead to new developments in medical imaging.

For applications such as car radar and radiometric imaging, the detector needs to be able to operate efficiently over very wide video bandwidths and, therefore, optimal impedance matching must be maintained across this bandwidth. Moreover, all the above applications rely on the need for a very sensitive (or “quiet”) detector, in order to simplify systems architectures and to make them affordable. While technologies exist for implementing quiet detectors they are either not appropriate for mass production (e.g. resonant-tunnelling diodes, (RTDs)) or require superconducting technologies incorporating cryostat-based cooling (e.g. superconductor-insulator-superconductor (SIS) junction detectors); this latter option requires a great deal of DC power, is too bulky for portable applications and is very expensive.

2.2. Conventional signal detection

Generally, detection of microwave and millimetre-wave power is through the use of semiconductor diodes, as illustrated in Fig. 1 in such an arrangement, most of the input RF signal power is absorbed by the 50 Ω input load resistor. This impedance matched resistance makes the input impedance less dependent on the diode impedance. However, some of the input RF signal power is converted to a DC current that flows through the diode. This current develops an output voltage across resistor R.

At relatively high input signal power levels (e.g. >+10 dBm), this circuit is simply half-wave rectifying the input RF signal (e.g. as an envelope detector). The RF carrier is short circuited to ground by the capacitor C, while the signal envelope appears across R.
At low input signal power levels (e.g. \(< -30\) dBm), the output voltage is directly proportional to the square of the of the input RF signal’s voltage amplitude (i.e. directly proportional to the input RF signal power). This phenomenon requires that the diode is operating at the knee of its I–V characteristic, shown in Fig. 2, and zero-bias Schottky diodes are used for this purpose [10].

The general I–V relationship for a diode is given by the standard diode equation.

\[
i = I_S \left( e^{\frac{qV}{nkT}} - 1 \right),
\]

where \(I_S\) – Diode reverse saturation current, \(q\) – electron charge, \(v\) – voltage across the diode junction, \(k\) – Boltzman’s constant, \(T\) – absolute temperature, \(n\) – diode ideality factor between 1.05 and 1.2.

\[
v = V_{in} - V_{out}, \quad \text{where} \quad V_{in} = V_s \cos \omega t,
\]

\[
\therefore i = I_S \left( e^{\frac{qV_s \cos \omega t}{nkT}} - e^{\frac{-qV_{out}}{nkT}} - 1 \right).
\]
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\[ V_{out} = \frac{1}{2\pi} \int_{0}^{2\pi} (iR) \, d\theta, \quad \text{where} \quad \theta = \omega t, \]

\[ \therefore V_{out} \cdot e^{\frac{kT}{nkT}} = I_{S}R \frac{2\pi}{2\pi} \int_{0}^{2\pi} \left( e^{\frac{qV_{s}\cos\omega t}{nkT}} - e^{\frac{qV_{out}}{nkT}} \right) \, d\theta. \]

After applying a Taylor’s expansion to both sides, and then integrating each term over one RF cycle, it can be shown that for small signals:

\[ V_{out} = I_{S}R \left[ \frac{nkT}{4(nkT + qI_{S}R)} \left( \frac{qV_{s}}{nkT} \right)^{2} + \text{higher even powers of} \left( \frac{qV_{s}}{nkT} \right) \right]. \]

The odd powers vanish because the odd $\cos\theta$ terms integrate to zero over one RF cycle. Therefore, in this ‘square law’ region of small signal operation, the detected DC output voltage is proportional to $V_{s}^{2}$. In practice, an additional series resistance (e.g. the 60 $\Omega$ resistor shown) may be used to dampen the series resonance from the diode’s combined parasitic shunt capacitance (both junction and packaging) and associated bond wire inductance [10].

RF signal detectors are commonly implemented using semiconductor Schottky junctions. At millimetre-wave frequencies, simple detectors suffer from a number of problems, namely: difficulty impedance matching over very wide video bandwidths, low sensitivity to very low power signals and poor immunity to thermal and shot noise. Furthermore, there may be a need to forward bias the diode to achieve the required level of optimal non-linearity.

As a way of minimising the effects of shunt parasitic capacitance, the point-contact (known historically as the “Cat’s Whisker”) diode is used at millimetre-wave frequencies. This technology can be susceptible to mechanical shock as the whisker has to touch one of many exposed semiconductor islands, arranged in a 2-dimensional matrix.

Moreover, the shot noise will still be present. For this reason, superconductor-insulator-superconductor (SIS) junction detectors can be used if performance is paramount. However, as with all superconducting technologies, the requirement to incorporate cryostat-based cooling makes this a rather unattractive option; especially for portable or space applications.

3. $C_{60}$ nanowhiskers: potential for use in RF detectors

As mentioned, a technique for the formation of $C_{60}$ nanowhiskers, through a process known as liquid-liquid interfacial precipitation (LLIP), was developed by Miyazawa and co-workers in [8]. From initial findings, a number of interesting observations on the physical properties of these nanowhiskers were reported.

Microscopy revealed $C_{60}$ whisker growth to be in arbitrary directions, to a range of dimensions, depending on the duration of growth. Diameters were found to remain
constant along individual lengths, varying from hundreds of nanometres to tens of
microns across separate whiskers. C\textsubscript{60} whiskers with sub-micron diameters will hereon
be referred to as nanowhiskers.

High strength was inferred from the curvature of a number of nanowhiskers; how-
ever, this is likely to be an artefact of growth, rather than an indicator of response to
external loading. Instead, from a statistical standpoint, the smaller the dimensions
of the nanowhisker, the greater its strength is likely to be, due to decreased defect
density. Other than this, we cannot comment further on the mechanical strength
of C\textsubscript{60} nanowhiskers. As will be covered in more detail later, the structure of C\textsubscript{60}
nanowhiskers resembles a “pearl-chain” arrangement, as depicted in Fig. 3. Me-
chanical strength will thus depend on the nature of intermolecular bonding between
adjacent molecules.

![Figure 3: “Pearl-chain” arrangement of C\textsubscript{60} molecules
through successive polymerisations along an axial path.
Inter-chain polymerisations can also take place,
resulting in a more robust 3D network.](image)

Room temperature electrical characterisation using a two-terminal tungsten probe
revealed low DC conductivity and increasingly non-linear I–V characteristics with
decreasing whisker diameter from 5 \( \mu \)m to 2 \( \mu \)m [9]. However, as data was collected
using only two terminals, objective proof that the characteristic relates to the intrinsic
properties of the whiskers remains elusive. Nevertheless, as a fullerene structure, such
an assumption is not unsupported, as both semiconducting and metallic behaviour
has been confirmed in another class of fullerene: carbon nanotubes.

The low temperature DC conductivity indicates the possibility of a charge trans-
port mechanism related to ballistic progression. Certainly, as nanowhisker dimensions
decrease, electrical behaviour will tend to approach that prevalent in a 1-dimensional
conductor. As there will now be fewer scattering events, the thermal noise properties
of C\textsubscript{60} nanowhiskers may be superior to those associated with conventional (semi-)
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conductors. Moreover, if intrinsic I–V non-linearity exists, there will ideally be no need for a Schottky junction to create non-linear behaviour, and hence, no shot noise. The potentially lower noise component in C$_{60}$ nanowhiskers will increase their room temperature sensitivity to millimetre-wave signals.

The properties of C$_{60}$ nanowhiskers outlined above suggest the possibility of its exploitation as an excellent (sub-)millimetre-wave signal detector. The uniformity and relatively long length of C$_{60}$ nanowhiskers allow them to be placed such that associated parasitic shunt capacitance can be almost negligible.

Figure 4 shows a possible means of implementing a C$_{60}$ nanowhisker within a millimetre-wave detector circuit. The nanowhisker is shown suspended between metallised electrodes, raised from the substrate plane. As such, instead of a Schottky junction, having a sub-micron (e.g. 0.2 μm) epitaxial layer of n-doped GaAs, the electrode separation in air for detectors based on the C$_{60}$ nanowhisker can easily be 200 μm. As a first order of approximation, this translates into a four orders of magnitude reduction in the associated shunt parasitic capacitance. This would allow extremely wide video bandwidths of operation, as well as relaxing the output impedance matching circuit requirements.

![Fig. 4. Schematic, showing a possible arrangement for a C$_{60}$ nanowhisker within a detector circuit.](image)

The possibility of manufacturing a low-cost and potentially very sensitive millimetre-wave signal detector is a very important driver. Of course, the existing ad hoc method of manufacturing C$_{60}$ nanowhiskers and their handling has to be addressed for future large volume production. If ballistic conduction of free electrons can be achieved in the smallest nanowhiskers, the thermal noise properties are likely to be far superior to those associated with conventional (semi-)conductors. If intrinsic I–V behaviour is sufficiently pronounced, there will be no need for forward biasing to achieve the optimal response, further reducing the noise figure of the detector.

By exploiting the above features, it may be possible to implement a very sensitive RF signal detector for millimetre-wave applications. To this end, this paper presents some of the work that has been carried out at Imperial College London, to investigate methods of growing C$_{60}$ nanowhiskers in situ under the influence of electric fields.
4. Carbon nanotubes: interesting parallels

A number of processes have been established to grow CNTs in sufficiently large quantities to be economically viable. A combination of selected growth parameters and post-growth processing allows dimensions (and hence properties) to be tailored at the outset. The following sections discuss methods of CNT growth and recently developed techniques for achieving directional control.

4.1. Carbon nanotube growth

CNT growth via established techniques, such as laser ablation, arc deposition and chemical vapour deposition (CVD), requires the use of metal catalysts. As such, complicated and damaging purification post-treatments are needed to remove traces of these elements from the final product. C$_{60}$ nanowhiskers offer an interesting alternative to CNTs as growth via the LLIP method is carried out at room temperature and without the need for catalysts.

4.2. Controlling growth direction

A number of approaches have been demonstrated for achieving directional control of CNTs grown via CVD processes. These have involved, among others, the use of catalyst-patterned vertical microposts [11] and electric fields [12]. In the latter, both AC and DC fields have been shown to induce polarity between the ends of growing CNTs, resulting in aligning moments that direct growth parallel to field lines.

In parallel with such efforts, a number of techniques have been developed to positioning and process CNTs, post-synthesis. Most positioning techniques employ dielectrophoresis [13], however, success has been achieved in selective processing of random dispersions of CNTs to create, most notably, suspended structures [14, 15].

5. Growth of C$_{60}$ nanowhiskers

Growing C$_{60}$ nanowhiskers via the LLIP technique is relatively straightforward. Achieving directional alignment and dimensional control are, however, non-trivial issues that require substantial investigation before C$_{60}$ nanowhiskers can be reliably implemented in electronic applications. As mentioned, electric fields have successfully been applied to control the growth direction of CVD nanotubes. The fields polarise growing tubes and direct growth parallel to electric field lines.

The following provides a discussion of preliminary work that has been conducted on the growth of C$_{60}$ nanowhiskers and attempts made to direct growth using electric fields.

5.1. Experimental

Growth solutions are prepared as follows: C$_{60}$ powder with a purity of 99+\% (M.E.R. Corp., USA) is ultrasonically dissolved in toluene to achieve a solution of
0.2–0.3% concentration by weight. The C$_{60}$-toluene solution is then transferred to separate growth vials in volumes of 8 ml, to which equal volumes of IPA are gently added. Differences in surface tension between IPA and the C$_{60}$-toluene solution lead to the formation of a well-defined liquid-liquid interface in each vial (Fig. 5a). Growth of C$_{60}$ nanowhiskers results from room temperature polymerisation reactions occurring within this region. Although UV irradiation can enhance the propensity for growth, nanowhiskers can grow in the absence of UV. A nucleation stage is required before C$_{60}$ nanowhiskers can form. This stage usually occurs within 24 hours. All nanowhiskers grown in subsequent experiments were obtained after a period of 72 hours.

Fig. 5. a) Growth vial showing liquid-liquid interface, illustration of a C$_{60}$ dimer (middle, left), including microscope image of deposits on a glass slide after 72 hours growth (bottom); b) SEM image showing a random arrangement of C$_{60}$ (nano)whiskers and bulk C$_{60}$ deposits.
5.2. Growth mechanism

The pressure within the interface region is believed to induce a series of 2+2 cycloaddition polymerisation reactions (Fig. 6) between neighbouring C_{60} molecules leading to the formation of thin, long C_{60} nanowhiskers.

![Fig. 6. Reaction mechanism responsible for the polymerisation of C_{60} molecules into chains.](image)

A prerequisite is a surface from which nucleation and growth can occur. Without this, nucleates would settle at the base of the vial and exhibit no subsequent growth. Polymerisation between adjacent chains is believed to lead to the growth of larger diameter whiskers. Figure 5b shows an arbitrary arrangement of C_{60} nanowhiskers and bulk C_{60} crystals on the surface of a Si die placed through the liquid-liquid interface during the growth period.

5.3. Microscopy

C_{60} nanowhiskers grown at the interface between IPA and C_{60}-toluene have a range of dimensions and broadly random orientation. There is a tendency for growth to be directed parallel to the interface plane; however, this is not always the case.

C_{60} nucleates do not tend to grow into nanowhiskers from the glass walls of the growth vials; as such a separate nucleation surface is required. If this surface penetrates the interface at an angle, nanowhiskers have also been observed to grow preferentially in the plane perpendicular to the surface (i.e. at angles deviating from the interface plane). There are, therefore, preferential growth planes, within which nanowhisker orientation is random. Furthermore, it is plausible that rotation about the fixed end (i.e. when root bonding is weak or when nanowhisker mass is sufficient), may give the impression of growth in other directions.

A “nest” of nanowhiskers and larger diameter fibres deposited on a copper wire penetrating the liquid-liquid interface is shown in the SEM image in Fig. 7. It is seen that straight, long nanowhiskers of varying diameter are readily formed at the interface.

Insight into growth mechanisms is provided through scans with an atomic force microscope (AFM) on a selection of nanowhiskers grown on a Si die. Figure 8 shows nanowhiskers with branching and “onion-skin” growth features. Scans over smaller ranges revealed striations on some nanowhiskers, indicating that one mechanism for diameter growth is via cross-polymerisation between adjacent, narrower chains.
5.4. Directed growth within electric fields

As C$_{60}$ molecules are electron-deficient, they are likely to experience forces within electric fields. To confirm this, an experiment was carried out in which clusters of C$_{60}$ were electrophoretically deposited onto a conductive surface. The clusters were created by adding acetonitrile to an equal volume of C$_{60}$-toluene solution. The die to be plated contained a chromium/gold (Cr/Au) seed layer exposed through an opening in a sputtered silicon dioxide mask. After immersion in the solution, a DC potential
of 150 V was applied between the sample and an inert platinum electrode (Fig. 9a) for 5 minutes. The sample was then removed from the solution, rinsed and dried in air. Figure 9b shows clusters of C\textsubscript{60} that have been deposited onto the conductive area.

Fig. 9. a) Scheme for electrophoretic deposition of C\textsubscript{60} clusters within a mixture of acetonitrile and C\textsubscript{60}-toluene solution; and b) deposited C\textsubscript{60} clusters (tip has peeled from the substrate).
If C\textsubscript{60} molecules experience forces within electric fields, the next question to ask is whether or not this is also true of C\textsubscript{60} nanowhiskers. To investigate this possibility, DC potentials were applied between alternate sets of interdigitated planar Au electrodes on dies placed through the liquid-liquid interface, where they remained suspended during growth. Figure 10 shows “nests” of C\textsubscript{60} nanowhiskers that have preferentially deposited onto positive electrodes (anodes) following a 72 hour growth period at an applied DC potential of 150 V.

Although an interesting result, the placement of C\textsubscript{60} nanowhiskers on separate anodes as seen in Fig. 8 is still arbitrary. In order to bring in-situ growth of C\textsubscript{60} nanowhiskers one step closer to reality, a degree of control over the direction of growth must at least be achieved. Furthermore, growth across opposite sets of electrodes would be an important aspect.

In attempts to achieve directed growth within DC electric fields, dies with a similar electrode arrangement to that depicted in Fig. 10 were placed perpendicular to liquid-liquid interfaces. Alternate pairs of electrodes were thus arranged vertically about the regions of growth, minimising the effect of coincidental aligned growth parallel to the interface plane. In some cases, dies removed after 72 hours showed evidence of aligned C\textsubscript{60} nanowhisker growth between opposite electrodes at an applied potential of 150 V (Fig. 11) [16]. The reproducibility of such results was low, however, as successful alignment and positioning is likely to be heavily dependent on die positioning. Moreover, the process of inserting dies through liquid-liquid interfaces tends to introduce considerable variability in growth conditions from one sample to the next.

Another factor affecting reproducible alignment within electric fields involves the presence of significant surface tension forces at die-liquid boundaries. Such forces can hinder aligning moments within electric fields. To improve matters, modified dies were fabricated with suspended electrodes formed in thick (8–10 \( \mu \)m) electroplated nickel (Ni) with a thin surface coating of Au.
Due to the greater electrode thickness and the absence of an insulating substrate directly beneath suspended electrodes, arcing occurred at field strengths greater than 0.05 V/μm. The arcing disrupted the liquid-liquid interface, preventing subsequent growth of C₆₀ nanowhiskers. At field strengths below 0.05 V/μm, no signs of alignment have so far been observed. In separate experiments, AC potentials were applied between suspended electrodes at 10 V RMS and frequencies of 5 kHz and 5 MHz. Unfortunately, no evidence of alignment was seen here either. Despite the absence of substrate material beneath electrodes, surface tension forces at electrode-liquid interfaces may still have been sufficient to reduce the effect of aligning moments at the reduced field strength.

6. Conclusions

C₆₀ nanowhiskers grown via the LLIP technique are an interesting alternative to CNTs in a number of applications as they can be grown at room temperature and without the need for catalyst materials. Growth experiments under DC electric fields have shown that nanowhiskers can be polarized and, as a consequence, will experience forces in the presence of such fields. Early results indicate a tendency towards electric field directed growth of C₆₀ nanowhiskers between planar electrodes on thermally oxidized Si dies under a field strength of 3.75 V/μm. Surface tension forces at die-liquid interfaces act to mitigate electric field induced aligning moments, introducing variability in the growth direction. Dies with suspended electrodes eliminated surface boundaries between electrodes, however, a lower arcing threshold limited the maximum field strength that could be applied. Consequently, no clear evidence of electric field aligned growth was observed between such electrodes.
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This early work suggests that the in-situ growth of C60 nanowhiskers for sensitive millimetre-wave signal detectors will be very challenging. Although DC electric fields are seen to influence the growth direction of C60 nanowhiskers, further work is necessary to improve the degree of alignment and to exercise control over growth dimensions.

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