Electronic devices from diamond-like carbon

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Abstract
This paper reviews the work carried out over the past few years on the
application of diamond-like carbon (DLC) materials to electronic devices.
The use of such materials is still in its infancy due to their high defect state
density and associated low mobilities. To date, the major effort in the
electronic field has been in their attempted use as cold cathode field emitters
where their low threshold field has attracted much attention. However,
attempts have also been made to produce metal semiconductor metal
structures, diodes, a-C/c-Si heterostructures and thin film transistors with
varying degrees of success. A brief review of work carried out on the use of
DLCs in solar cell manufacture will also be presented but it seems at this
early stage in their development that the most promising area for future
development will be in the field of microelectromechanical structures where
their friction, stiction and wear properties make them prime candidates for
use in moving mechanical assemblies.

1. Introduction

Over the past few years carbon based materials have become
increasingly interesting for use in electronic applications.
These range from the rather unsophisticated heat sink
requirements for power semiconductors, through disposable
electronics for consumer goods, to UV sensors and dosimeters
and the highly sophisticated large area flat panel displays.
Each one of these potential applications depends upon the
production of high quality, reproducible and well characterized
material; each particular application being determined by the
material available. Of these potential materials thin film
amorphous carbon has many attractive features for electronic
use: a bandgap which can be varied from $\sim$0.5 eV up to
$\sim$4.0 eV, potential to produce n, p and intrinsic material,
and large area deposition at room temperature. Amorphous
carbons containing significant amounts of sp^3 bonding are
known as diamond-like carbon (DLC). This is because of
the presence of the sp^3 bonds which confer the diamond-
like properties of chemical inertness, mechanical hardness
and wider bandgap than one would find in an sp^2 bonded
material [1]. The most common form of DLC is hydrogenated
amorphous carbon (a-C:H) which is typically grown by plasma
enhanced chemical vapour deposition (CVD).

It has not been possible to grow a pure 100% sp^3 bonded
a-C, which would correspond to 'amorphous diamond' and
be totally analogous to amorphous silicon. The highest sp^3

content so far is $\sim$85%. This material, because of its high
percentage of tetrahedral bonding, is known as tetrahedrally
bonded amorphous carbon (ta-C). ta-C can be grown using
several different techniques involving energetic ions or plasma
beams. These include mass selected ion beam (MSIB) [2],
the filtered cathodic vacuum arc (FCVA) [3] and pulsed laser
deposition [4]. By addition of hydrogen to the growing films,
then highly sp^3 bonded films containing substantial amounts
of hydrogen can also be formed. These are termed ta-C:H by
analogy with ta-C.

The use of amorphous carbon thin films in electronic
devices, however, has been limited by their high defect state
density and their associated low mobilities. Their main
application in the electronic field has been in their use as
cold cathode field emitters where their low threshold field has
attracted much attention [5]. However, attempts have also
been made to produce metal semiconductor metal structures
(MSMs) [6], diodes [7], a-C/c-Si heterostructures [8] and
thin film transistors [9], with varying degrees of success.
The utilization of carbon thin films in solar cells has also
been attempted [10, 11] and work on microelectromechanical
systems (MEMS) [12] has just begun. The aim of this paper
is to review this work and comment on future opportunities.

2. Metal semiconductor metal structures

The initial research in this area was carried out by Egret
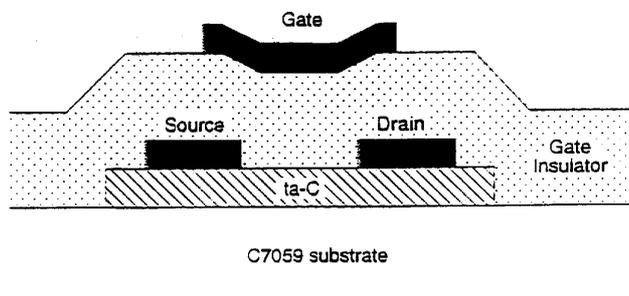*et al* in 1996 [6] where they investigated the merits of

Figure 1. Top gate coplanar TFT structure.

metal/a-C:H/metal MSMs for use as an alternative structure for the pixel switches in active matrix addressed liquid crystal displays (AMLCDs). Conventionally, thin film transistors (TFTs) are used as the pixel switches in AMLCDs but two terminal switches offer a number of advantages over TFTs, such as fewer mask steps and a potentially larger optical aperture, e.g. Philips initial high quality AMLCDs used Si-rich silicon nitride diodes as the switches. The MSM is a sandwich structure operated in the high field conduction region. a-C:H based MSMs were shown to have sharper switching characteristics than either SiN or Ta_2O_5 based MSMs but not as sharp as those made at Philips using their Si-rich a-SiNi$_x$:H alloy. However, the room temperature deposition capability gives them a significant advantage in that they can be utilized for switches in plastic based displays. The manufacture of TFTs using DLC has also been attempted. Both ta-C and ta-C:H have been used as the active channel material.

3. Thin film transistors

The use of as-grown undoped ta-C which, as indicated previously is slightly p-type, was first investigated as the channel material. Ta-C has a sp^2-rich surface layer present as a consequence of the sub-plantation deposition process. Such a layer exists both on the top of the film (because of the sub-plantation) and also at the substrate/film interface due to high incident ion energies. The thickness of both these layers are dependent upon ion energy used during deposition [13]. The first series of experiments addressed the problem that this layer would lead to a pinning of the Fermi level so a TFT structure that would allow easy removal of the sp^2-rich layer was chosen. A top gate coplanar structure was therefore adopted as shown in figure 1. At that time there was also uncertainty as to whether the sp^2-rich layer would instantly re-form once removed, so a scheme was devised whereby the sp^2-rich layer could be removed and the gate insulator subsequently deposited all within the same pump down sequence. A RIE process to remove the sp^2 layer using nitrous oxide as the etching gas was adopted and immediately silane was then added [9] to deposit the gate insulator. Subsequently, it was discovered that the sp^2 layer once removed did not re-form.

A typical undoped ta-C TFT did indeed operate in the p-channel accumulation mode (figure 2) confirming the p-type nature of the as-grown ta-C but the on/off ratio was only approximately 2–3 orders and the hole mobility was estimated to be 10^{-5}–10^{-6} cm^2 V^{-1} s^{-1}.

This indicates that extended state transport is not the dominant conduction mechanism and hopping in the band tails
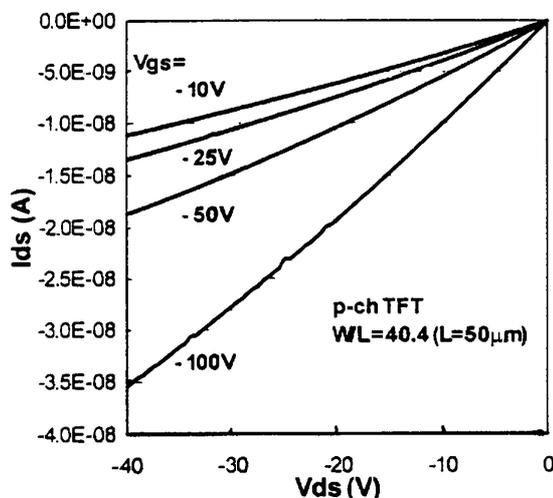

Figure 2. Drain transfer characteristics for a p-channel top gate TFT.
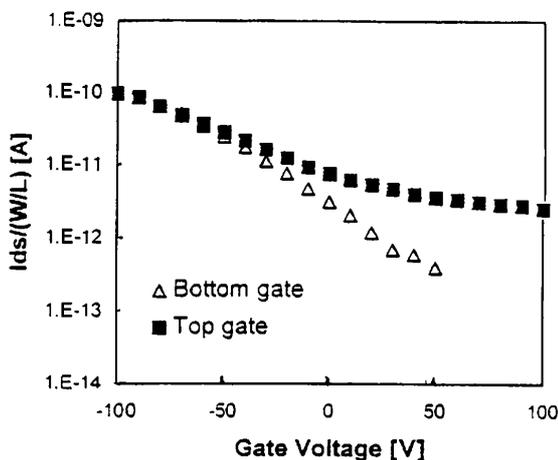

Figure 3. Comparison between a bottom gate and top gate TFT.

is more likely. In such a process, the main factor in controlling the mobility is the degree of localization of tail states. In highly sp^3 bonded material, a high degree of localization of π states at the band edges has been predicted by McKenzie [14]. In an effort to improve TFT performance, two alternative solutions were attempted: (i) to investigate bottom gate structures and (ii) to investigate n-channel devices as these have been found to have significantly higher mobilities than p-channel devices made using a-Si:H.

Bottom gate TFTs were produced by depositing the ta-C films onto thermal oxide covered c-Si wafers. The effect was to reduce the off-current but gave no improvement in the on-current as shown in figure 3. The improvement in the off-current is due to the fact that we are using thermal oxide as the gate insulator in this instance.

N-channel devices were then produced by adding nitrogen to the films during deposition as previously described [15]. Both top gate and bottom gate structures have been produced and these operate in the n-channel enhancement mode as expected. However the best of these only gave a maximum field effect mobility value of ~5×10^{-7} cm^2 V^{-1} s^{-1}.

In an effort to try to understand these results, a series of scanning tunnelling microscopy experiments [16] were carried

out to probe the density of states in the bandgap of the ta-C films and these indicated that the valence band tail is steeper than the conduction band tail, which is in marked contrast to that observed in a-Si:H. This would explain the lower mobility values for the n-channel devices.

Addition of hydrogen to ta-C films has previously been shown to reduce the ESR spin density by approximately five times and therefore, in a final effort to increase the mobility, TFTs were produced using plasma beam source deposited ta-C:H as the active channel material in a bottom gated structure. This had the effect of increasing the on/off ratio by a factor of two.

The best mobility obtained to date for any a-C based TFTs is $\sim 10^{-4}$–10^{-5} cm^2 V^{-1} s^{-1}. This was measured on a bottom gate p-channel TFT using a thermal oxide as the gate insulator and a ta-C film with 50/50 sp^3/sp^2 bonding. Much more work is needed in order to reduce the DOS before amorphous carbons can be utilized in practical thin film transistor structures.

4. Solar cells

The use of DLC in the manufacture of solar cells is not new. In 1982 Moravec and Lee [17] investigated the use of DLC as the antireflective coating on silicon solar cells. They reported a 40% efficiency improvement over un-coated cells. The photovoltaic behaviour and spectral response of n-type (nitrogen-doped) tetrahedral amorphous carbon (ta-C)/p-type crystalline silicon heterojunction photodiodes were first reported by Veerasamy *et al* [8]. Abrupt step junction type characteristics were observed with ta-C films ranging in thickness from 40 to 160 nm. The photovoltage increases and the prominent peak in responsivity shifts from 800 nm to longer wavelengths of 1000 nm as the doping in the ta-C films was increased, indicative of a widening of the depletion region in the Si. Use of the responsivity versus wavelength data with the Donnelly and Milnes model for an abrupt heterojunction was successful in predicting the depletion width in the Si and the doping level in the higher doped ta-C. Secondary ion mass spectroscopy studies confirmed the abrupt nature of the junctions. Further work on ta-C:N/c-Si (p-type) hetero-structures was carried out by the group in Singapore [18] where they reported open circuit voltages of 0.27 V and short circuit current densities of 5.05 mA cm^{-2} under AM1 illumination.

Perhaps more usefully, the use of DLC films as one of the active semiconductor layers in thin film solar cells has also been investigated. In 1998 Lee and Lim [11] reported the use of B doped a-C:H as the p-type window layer in an a-Si:H based solar cell. Conventionally, a-SiC window layers have been used since p-type a-S:H absorbs too much of the incident solar insolation as its bandgap shrinks with addition of boron. The p-type DLC is an alternative material for this application with a potential bandgap of greater than 3 eV. However, the p-type doping of DLC is not well characterized or understood. Lee and Lim used a mercury sensitized photo-CVD technique in an attempt to produce p-type a-C:H for such an application. Their work has confirmed what others had already shown that addition of boron to a-C:H undoubtedly increases the conductivity.
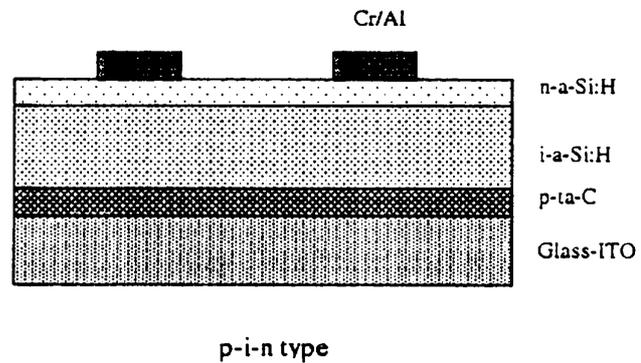

Figure 4. Structure of proto-type ta-C/a-Si:H heterojunction solar cell.

The optical gap increases slightly until a B incorporation of 3600 ppm where $E_{gopt} \sim 3.8$ eV. Above this level of B incorporation, however, the bandgap shrinks. Although this material has a wider bandgap than the conventionally used a-SiC the conductivity of the material still remains of the order of 10^{-7} S cm^{-1} which is far too high for its use as a window layer material. Thus they proposed a compromise structure where they utilized a p-a-C:H/p-a-SiC double layer to overcome the high resistivity problems associated with the p-a-C:H whilst improving the performance over that of the standard 2.6 eV bandgap a-SiC because of the lower absorption losses associated with the wider bandgap carbon film. The combination of <15 A layer a-C:H with $\sim$40 A layer of a-SiC led to an increase in the short wavelength response over conventional devices and the V_{oc} improved from 0.766 V to 0.865 V for the double layer device. They extended their work later to consider how the current is transported through the p-type a-C:H layer by studying the temperature dependence of the dark current–voltage characteristics of their cells. These indicate that carriers transport predominantly through the film by thermionic emission at $T > 300$ K and by hopping at lower temperatures. They suggest that the improvement in cell operation with the addition of the a-C:H layer is associated with a lowering of the Schottky barrier height by inserting the carbon layer between the SnO$_2$ transparent contact and the p-a-SiC:H enhancing V_{oc} and the short wavelength response. Finally, last year we reported the use of ta-C as the window layer in an a-Si:H solar cell [10]. The structure is shown in figure 4.

Preliminary results on this structure are encouraging and the short circuit current is significantly better than a p–i–n a-Si:H cell made in house. However, the open circuit voltage of 0.25 V is much less than a typical a-Si:H p–i–n cell. This low value is thought to be associated with trapping of the photo-generated holes in the defect states in the ta-C window layer.

Although the use of wide bandgap carbon films as the window layer in a-Si:H based cells has now been investigated by the above groups, the production of an all carbon based thin film solar cell has only just been reported in Japan by Krishna *et al* [19]. Here they use n–C/p–C junctions, the structure of which is shown in figure 5.

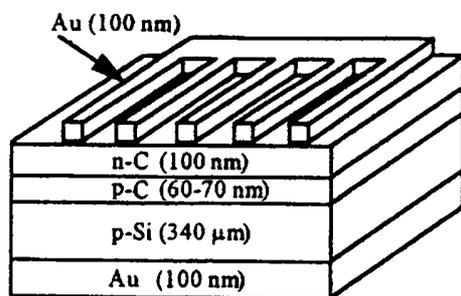The J–V plot under AM0 conditions is shown in figure 6. The material used however is not DLC but rather material
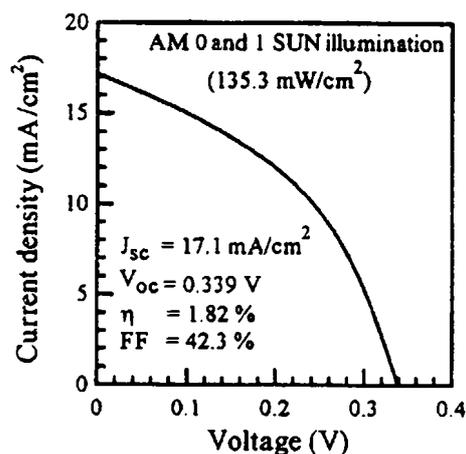
Figure 5. n-C/p-C solar cell [19].

Figure 6. *J–V* plot under AM0 conditions for structure shown in figure 5.

Figure 7. DLC comb structure (after Sullivan and Friedmann, Sandia Labs [12]).

produced by (a) pyrolysis of camphor giving a p-type material of bandgap 0.7 eV and (b) ion beam sputtering of camphor which seems to give an n-type material with a bandgap of 1.05 eV. However, the conversion efficiency of 1.82% and open circuit voltage of 0.339 V are encouraging and further work is ongoing to improve these results.

5. Microelectromechanical systems

Finally and potentially most importantly in this area, the use of DLC films for the manufacture of MEMS has just begun. A high surface smoothness (a few nanometre rms roughness is typical), high hardness and chemical inertness in combination with a low coefficient of friction make DLC an ideal candidate for MEMS applications. MEMS are currently under consideration for numerous microsensor and microactuator applications. Sensors detect physical and chemical signals. Actuators can drive microcomponents, including optical mirrors and displays, photonic lattices, fluids and turbines. Biological applications are now also under investigation. Most current MEMS are based on silicon microelectronics technology and, although entirely suitable for many applications, the physical limitations of silicon can limit MEMS uses. Therefore the MEMS field is now
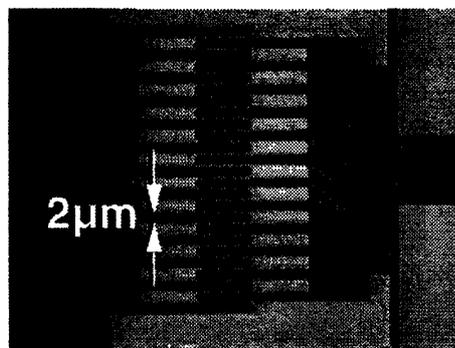
extending to new materials, including diamond, silicon carbide and metals. Some diamond film on silicon devices have been made in laboratories in the USA and examples of their applications include gas flow and chemical sensors and piezoelectric pressure sensors. The diamond films used for such applications were difficult to fabricate and too rough to be able to utilize them in the tiny devices envisioned for next generation MEMS. However, a major breakthrough has recently been achieved by the workers at the Sandia Labs in Albuquerque [12] who have used a pulsed laser deposited ta-C film to manufacture a simple proof-of-principle comb structure. The advantages of this material for MEMS applications are that it is extremely smooth, very hard (with hardness approaching that of diamond itself), low coefficient of friction and low stiction, as ta-C (unlike silicon) is not hydrophilic. Also a major advantage for numerous potential MEMS applications is that it is entirely biocompatible so that it can be used, for example, for in-body drug dispensing units without any chance of allergic reaction.

A major potential application for DLC based MEMS is in a particular class of MEMS known as moving mechanical assemblies (MMAs), for example, tiny pumps, motors and turbines. Many of the more visionary applications of MEMS such as tiny weather satellites and deep spacecraft require MMAs that will operate for at least several years if not decades. Because of their size such devices must operate at speeds of the order of 400 000 rpm. At such speeds, silicon based components would wear out in hours or even minutes. The DLC material however is much more wear resistant (>10 000 times more wear resistant than polysilicon).

Until the work at Sandia, however, the use of ta-C for such applications was limited by the high internal compressive stress exhibited by the films. Friedmann and Sullivan [12] have recently reported that they can produce highly sp^3 films with zero stress. They have achieved this by post deposition annealing the films at 600 °C for 2 min.

The world's first proof-of-principle DLC micromachine is shown above in figure 7 where the comb structure drives a tiny diamond piston. The drive is powered by a tiny alternating electrical current. As the two sets of comb teeth repel and attract each other, one comb slides back and forth. The DLC reduces stiction—a combination of stickiness and friction.

The use of DLC in such MEMs would seem potentially one of the most significant applications in the near future.

The design of surface acoustic wave devices based on DLC material is also ongoing in several labs [20] including ours. In this type of device to realize the required high velocity waves there are several possibilities. One of the prime candidates is to utilize piezoelectric films on high velocity substrates. ZnO/sapphire and AIN/sapphire have been previously investigated but the idea of using ZnO/diamond structures should in theory enable gigahertz operation because of the higher sound velocities possible in diamond [21]. However, because of the roughness of polycrystalline CVD diamond it is difficult to successfully deposit the interdigitated arrays on top of the films. DLC has a similar sound velocity to diamond and its smoothness means that depositing the top electrodes is not a problem. It is also amorphous and has no grain boundaries (unlike in CVD diamond) which can scatter the phonons. It also has the added advantage of room temperature deposition capability. Recently, preliminary results on ZnO/nitrogenated a-C:H structures have shown that velocities up to 7000 m s^{-1} are attainable in such systems and recent calculations indicate that ta-C should have even higher acoustic velocities [22]. However, much more work is needed to optimize performance in these systems.

6. Conclusions

The use of the various diamond-like carbons in electronic devices is still in its infancy. The application of such films continues to be limited by their high defect state density and their associated low mobilities. To date, the major effort in the electronic field has been in their use as cold cathode field emitters where their low threshold field has attracted much attention. However, attempts have also been made to produce MSMs, diodes a-C/c-Si heterostructures and TFTs with varying degrees of success. Solar cells have also been attempted but perhaps the potentially most interesting future area will be in the field of MEMS where their friction, stiction and wear properties make them prime candidates for use in MMAs.

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