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LETTER TO THE EDITOR

n-type doping of highly tetrahedral diamond-like amorphous carbon

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Abstract. The ability to control the electrical resistivity of semiconducting tetrahedral amorphous carbon (ta-C) films is reported. Phosphorus is incorporated during film growth from a plasma formed with a cathodic vacuum arc by using a phosphorus-containing carbon cathode. By changing the P content in the cathode from 0–1% mass the room temperature resistivity of the films can be changed from 10^7 Ω cm to 5 Ω cm. Electron energy-loss spectroscopy shows that incorporation of P does not change the amorphous tetrahedral nature of the carbon films deposited by the vacuum arc method.

The filtered cathodic arc is an efficient source of hydrogen free carbon plasma which can be used to deposit extremely hard and resistive thin films on a variety of substrates. These films have been denoted tetrahedral amorphous carbon (ta-C) or 'amorphous diamond' due to the high proportion of tetrahedral bonds (>90%) which give a structure analogous to amorphous silicon [1] and properties similar to those of diamond [2]. Work, to date, on the electronic properties of ta-C has been limited to studies of the intrinsic material, which is weakly p type. In order to realize the promise of this material as a new type of wide-band-gap amorphous semiconductor the ability to dope it must be realized. Here we report initial results which show that successful n-type doping of ta-C can be achieved with the incorporation of phosphorus.

Hydrogenated amorphous silicon (a-Si:H) has become an important semiconductor because of its high sensitivity to light, and the ability to deposit it at low temperatures and over large areas. Solar cells and large transistor arrays for switching display elements in portable computers and television sets are examples of where it is widely used. However a-Si:H suffers from instability problems, e.g. the Staebler–Wronski effect and shift in threshold voltage associated with transistors under prolonged gate bias. Both these effects are thought to be associated with the incorporated hydrogen. Also, at elevated temperatures, the hydrogen evolves and degrades electrical performance. An amorphous semiconductor which could operate at higher electric fields and temperatures would therefore be useful in its own right. The use of another group IV material such as carbon would at first sight seem to be a viable alternative. The equivalent tetrahedral form of amorphous carbon (ta-C) is produced by cathodic

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arc deposition [3] *in the absence of hydrogen*. The tetrahedral bonding is stabilised by compressive stress [1]. Undoped or intrinsic ta-C has recently been shown to have semiconducting properties by forming heterojunctions with Si [4]. The possibility of forming an amorphous semiconductor using unhydrogenated ta-C has been confirmed by optical absorption measurements and study of the density states using space charge limited current flow [6]. The Fermi level in the undoped material was found to lie about 0.2 eV above the valence band. The density of states at the Fermi level is of the order of 10^{18} cm^{-3} eV^{-1} and decreases exponentially with increasing energy. The optical band gap of the material lies in the range 1.9–2.2 eV.

The ion flux emitted by a cathodic arc is closely, related to the composition of the cathode [5]. Therefore, in order to produce doped ta-C from ionized phosphorus and carbon, cathodes were fabricated from a mixture of 1%, 0.5% and 0.2% by mass of 9.999% pure red phosphorus powder in 99.999% pure graphite powder. The powders were ultrasonically mixed and compressed into a 50 mm diameter disc under 20–30 MPa pressure.

A cathodic arc was struck with the phosphorus-containing carbon disc as the cathode. The vacuum base pressure was 10^{-5} Pa and care was taken to eliminate water vapour and oxygen from the system. The arc voltage of 32–35 V at a current of 60 A was significantly larger than the 19–24 V observed for a pure graphite cathode. In order to eliminate micronsized solid particles also emitted from the cathode, the plasma was passed through a 90° curved solenoid with an axial magnetic field of 30 mT [6]. Films of 30–35 nm thickness were deposited at a rate of 1–2 nm s^{-1} onto {100} silicon, Si_3N_4 and fused silica. The species P^+, P and P_2 were observed by a mass spectrometer in the deposition chamber.

The advantage of introducing the phosphorus at the cathode is that it enables phosphorus-containing carbon films to be grown from ionic species. The phosphorus and carbon ions are emitted from the cathode with 20–50 eV kinetic energy [7] and are further accelerated by the bias voltage of the substrate. Under these conditions a significant fraction of the phosphorus ions will be implanted a few monolayers beneath the surface of the growing film.

A typical current–voltage curve measured across a film deposited from a 1% phosphorus-containing carbon cathode on Si_3N_4 is shown in figure 1(*a*) (identical results are obtained on fused silica substrates). The linearity of this curve clearly demonstrates that there is an ohmic contact between the phosphorus-containing carbon film and the gold contact. The resistivity of the film was calculated to be 5 Ω cm at room temperature. This is more than six orders of magnitude lower than the resistivity of undoped ta-C on the same substrates, which is typically 10^7 Ω cm. To verify that the reduction in resistivity was due to phosphorus doping, carbon cathode sources with varying P concentrations were used to deposit films on fused silica substrates under identical conditions. The variation of the I–V characteristics as a function of P concentration in the cathode is seen in figure 1(*b*). The progressive reduction in the resistivities with increasing P in the plasma source formed from the vacuum arc is evidence of the ability to dope ta-C in a controllable manner.

The conductivity of the phosphorus-containing film deposited using a 1% cathode was measured as a function of temperature between 130 K and 330 K. The Arrhenius plot (curve a) in figure 2 shows that the dark conduction in the phosphorus-containing film is thermally activated with an activation energy of 0.12 eV in the temperature range 200 K to 330 K. At temperatures below 160 K, the conductivity had an additional component which is attributed to activated conduction in the tail states

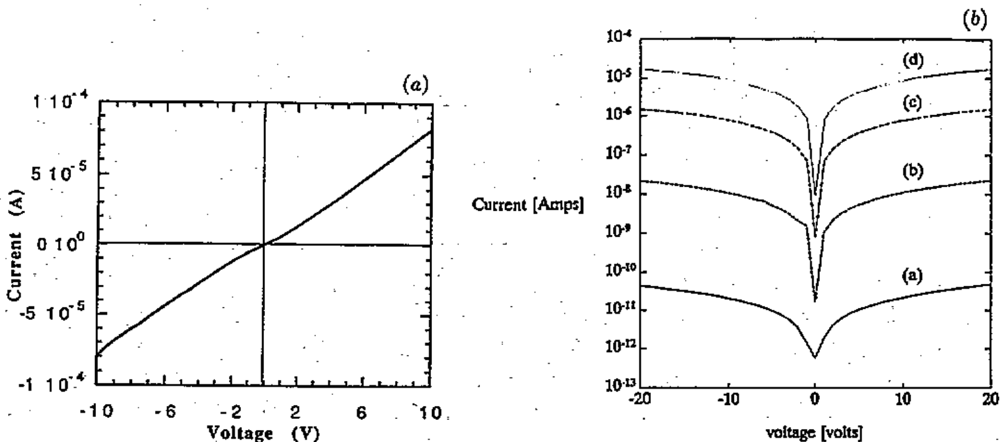

Figure 1. (*a*) Ohmic current–voltage curve for a phosphorus-containing ta-C film deposited on Si_3N_4. Electrical contact to the film was made through 25 nm thick gold coatings which were thermally evaporated under a vacuum of 10^{-4} Pa. A shadow mask was used to restrict the fold contacts to a 5 mm wide strip containing the 0.5 mm gaps across which the measurements were made. Leakage current through the Si_3N_4 was less than 10^{-13} A. (*b*) Ohmic I–V characteristics as a function of P content (by mass) in the carbon cathode: curve a, undoped film—0% P in cathode, curve b, 0.2% P, curve c, 0.5% P, curve d, 1% P.

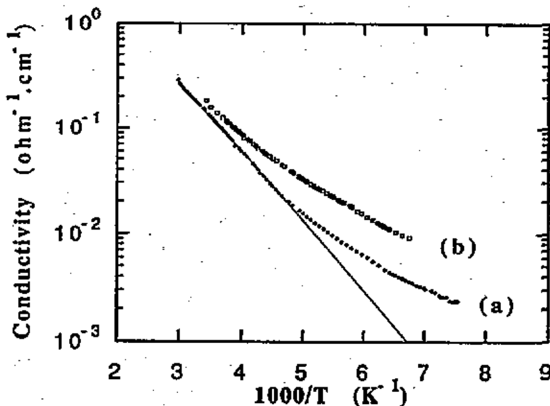

Figure 2. Arrhenius plots of the conductivity of a phosphorus-containing film (1% P in cathode) for temperatures between 130 K and 330 K: curve (a), in the dark and curve (b), under light. An activation energy of 0.12 eV is calculated for curve (a) from a linear fit to the data between 200 K and 300 K. The measurement structure was identified to that described in figure 1.

[8]. Curve b in figure 2 shows the Arrhenius plot which is obtained when the sample is exposed to AM-1 light. The photoconductive component of the conductivity is larger than the thermally activated conduction component only for temperatures below 200 K, which is typical of a doped semiconductor. In order to further verify that inclusion of phosphorus in the films can lead to a controllable change in conductivity, the activation energies of the films deposited using cathodes containing 0%, 0.2%, 0.5% and 1% phosphorus on fused silica substrates were obtained from the Arrhenius plots of conductivity shown in figure 3(*a*). The measured activation energies and resistivity clearly decrease as the phosphorus content increases. The temperature at which conduction through activation into tail states starts to dominate also moves, as expected, to lower temperature values as the phosphorus content increases. It should be noted that the undoped (0%) activation energy is considered to be relative to the valence band based on our previous studies. This means that with inclusion of P at the 0.2% level the Fermi level in the ta-C moves from 0.25 eV above the

valence band to 0.18 eV below the conduction band. This is not unreasonable since as discussed below, it is estimated that 0.2% P in the cathode will correspond to more than 10^{16} cm^{-3} active carriers. Verification of this transition in the Fermi level across the middle of the band gap by reducing the P content has proved practically difficult due to the cathode fabrication process. However, we have verified that the Fermi level moves in such a manner in ta-C by incorporation of nitrogen in the gas phase, which allows much smaller quantities to be included in the ta-C films. When nitrogen is incorporated the Fermi level transition across the mid-gap is seen as an initial increase in the activation energy with a low nitrogen fraction, followed by a lowering of the activation energy as the nitrogen content increases. Details of the changes in conductivity characteristics of ta-C with nitrogen incorporation will be reported at a later date [14]. The optical band gaps of the ta-C films remain unchanged at 1.9–2.0 eV with the inclusion of phosphorus, as can be seen from figure 3(*b*) which shows the Tauc plot derived from the optical absorption measurements on an undoped film and one deposited from a 1% phosphorus cathode (maximum P concentration). The results in figure 3 are consistent with the Fermi level in the ta-C moving closer to the band edge as more phosphorus is incorporated.

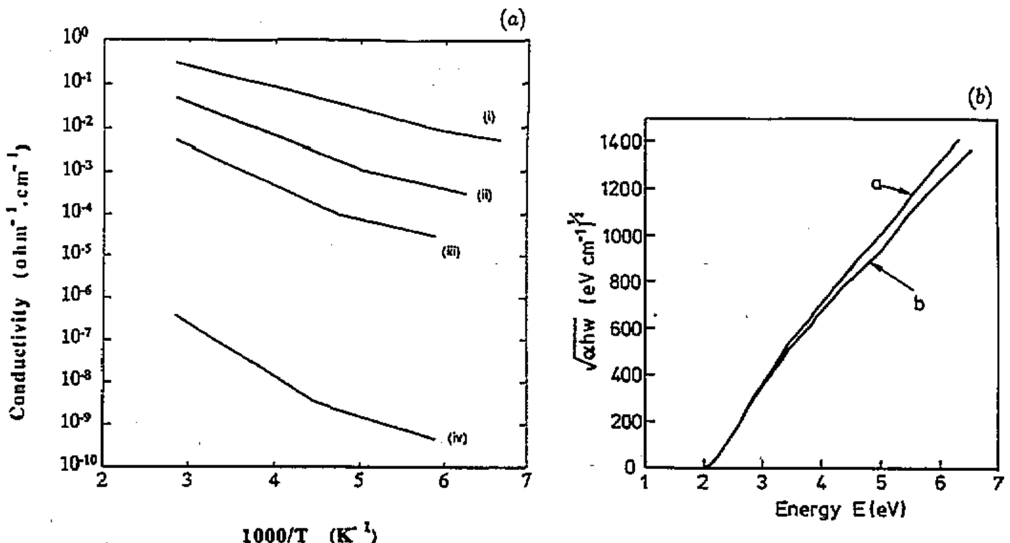

Figure 3. (*a*) Arrhenius conductivity plots of ta-C films deposited from cathodes containing varying amounts of phosphorus: (curve i), 1%, (curve ii), 0.5%, (curve iii), 0.2% and (curve iv), 0% (undoped film). The measured activation energies in the higher-conductivity regions are (i) 0.12 eV, (ii) 0.15 eV, (iii) 0.18 eV and (iv) 0.25 eV. (*b*) Tauc plots from the optical absorption data for films deposited from a 1% P cathode (curve a) and a pure carbon cathode containing no P (curve b). Extrapolation of the linear portions of both curves to the energy axis give a common optical band-gap value of 1.9–2.0 eV.

Preliminary Hall effect measurements on the sample deposited from a 1% P cathode gave a Hall voltage consistent with conduction by electrons. This is different from observations in other amorphous semiconductors such as n-doped a-Si:H where the Hall voltage shows an anomalous change in polarity. However, there are other amorphous semiconductors based on Ge alloys which show correct Hall polarity [12]. The Hall mobility measured at room temperature is 0.4 cm^2 V^{-1} s^{-1}, which

is significantly higher than that reported for a-Si:H [13]. If we assume that the correct polarity for the Hall voltage and the higher Hall mobility justifies ta-C being considered as a material with a relatively large mean free path for carriers so that the standard relationships apply, the carrier density at room temperature estimated from the Hall voltage is of the order of 10^{17} cm^{-3}. The carrier density when combined with the conductivity gives an electron mobility in the extended states of around 10 cm^2 V^{-1} s^{-1}. These values must however, be taken with some caution. More work on the Hall effect in ta-C with p-type dopants and measurements of thermopower is necessary before any conclusions can be drawn on whether there is anomalous behaviour.

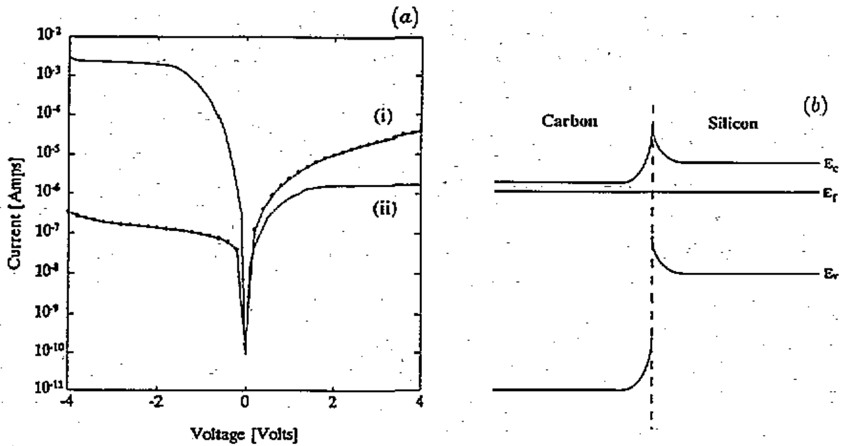

Figure 4. Current–Voltage curves on heterojunctions between ta-C and 1–5 Ω cm n-type silicon: (curve i), undoped ta-C; (curve ii), phosphorus-containing ta-C. Also shown is the band diagram proposed to explain the polarity of the rectifying junction between phosphorus-containing ta-C and n-type silicon, taking a typical band gap to be 2.2 eV [11]. The energy difference between the conduction band and the Fermi level is taken to be 0.1 eV in ta-C and 0.3 eV in silicon. The Fermi level in ta-C was estimated on the basis of a 10^{17} cm^{-3} carrier density and a density of states of 10^{18} cm^{-3} at the conduction band edge calculated from space charge limited current data [6]. Contact to the film was made through 1 mm diameter vacuum evaporated gold contacts to form Au/carbon film/Si sandwich structures. The silicon substrates were pressure contacted onto a large metal base which was held at earth potential. The bias voltage was applied to the gold contact and the current–voltage characteristic measured using a Hewlett Packard 4140B pA meter/DC voltage source.

Heterojunction diodes which are formed by depositing ta-C on silicon [4] can give useful information about the band structure and defects in the material. The current–voltage curve of an n-type silicon to undoped ta-C heterojunction diode is shown as curve i in figure 4(*a*). At positive voltages, the junction is forward biased and there is majority carrier (electron) injection from the silicon into the ta-C. In contrast, curve ii in figure 4(*a*) shows that when the film contains phosphorus the polarity of the device is reversed. Injection of electrons now occurs from the phosphorus-containing film into the n-type silicon, as would be expected if incorporation of phosphorus has moved the Fermi level in the carbon film close to the conduction band [9]. This shows that an n–n isotype heterojunction has been formed as represented by the band diagram in figure 4(*b*). Note that for forward voltages greater than 2 V the current

injection from the phosphorus-containing film into the silicon is limited by resistance at the gold–carbon interface.

A free-standing film was analysed by transmission electron microscopy and parallel electron energy-loss spectroscopy (PEELS). The diffraction pattern showed diffuse rings characteristic of an amorphous material. The PEELS data at the carbon K edge around 288 eV also showed a peak which is consistent with the material being completely amorphous. The plasmon energy, which is related to the valence electron density, was found to be 30.9 eV. Detailed structural investigation of ta-C has shown that a plasmon energy of 30.5 eV corresponds to more than 90% tetrahedral bonding in the film [1, 10]. The nearest-neighbour carbon–carbon distance and bond angle determined using the radial distribution function [1] are 0.154 nm and 109° for the ta-C film containing the maximum phosphorus, providing further evidence that the predominantly tetrahedrally bonded microstructure of the films is maintained. Energy dispersive spectroscopy (EDS) in a scanning electron microscope operated at 2 keV confirmed the presence of phosphorus in films deposited from a 1% P cathode on Si_3N_4. No other impurities were detected. These results indicate that the material retains essentially the same structure as ta-C. The fact there was sufficient phosphorus in the films for detection by EDS, but an insufficient amount for detection by PEELS suggests that the atomic fraction of phosphorus in the films is between 0.1% and 1%. Using a carrier density of 10^{17} cm^{-3} from the Hall measurements and a density of 3 g cm^{-3} for the ta-C [1], a doping efficiency of the order of 10^{-3} to 10^{-2} is estimated at room temperature.

The dramatic increase in the conductivity of ta-C films containing phosphorus, together with the fact that the highly tetrahedral amorphous structure of intrinsic ta-C is retained, shows that ta-C films have been successfully doped. The properties of heterojunctions with silicon, together with the progressive reduction in resistivity with increasing P fraction and activation energy measurements, are consistent with shallow n-type doping of ta-C by incorporation of phosphorus during growth.

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