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TECHNICAL NOTE

Carbon fiber polymer-matrix structural composite as a semiconductor and concept of optoelectronic and electronic devices made from it

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Abstract. An epoxy-matrix composite with continuous crossply carbon fibers was found to be a semiconductor in the through-thickness direction, with a tunable energy gap of 10^{-2}–10^{-1} eV (infrared). The higher the pressure during composite fabrication by lamination, the higher the interlaminar stress and the greater the energy gap, which is the activation energy for electron jumping from one lamina to the adjacent one in the composite. The semiconducting behavior involves the contact electrical resistivity between adjacent laminae in the composite decreasing reversibly with increasing temperature. The concept of optoelectronic and electronic devices made from carbon fiber polymer-matrix composites is provided. Devices include solar cells, light emitting diodes, lasers, infrared detectors and transistors. Thus, a new dimension is added to smart structures and a new field of electronics ('structural electronics') is born.

1. Introduction

Polymer-matrix composites with continuous carbon fiber reinforcement are widely used as lightweight structural materials for aircraft and sporting goods, in addition to less common use in automobiles and civil structures. Because of their importance as structural materials, work in this field has mostly concerned the mechanical properties.

Because carbon fibers are electrically conducting while the polymer matrix is not, studying the electrical properties of the composites provides a means of investigating the structures [1–5] and monitoring the damage [6–9] of the composites. Applications that relate to the electrical conductivity include electromagnetic interference (EMI) shielding [10–14] and lightning protection (static discharge), which are valuable for aircraft. Because the continuous fibers increase in the degree of alignment upon tension of the composite in the fiber direction, the electrical conductivity of the composite increases in the fiber direction and decreases in the through-thickness direction (less chance for adjacent fiber layers to touch one another) upon tension of the composite in the fiber direction, thus providing the composite with the ability to sense its own strain [6, 7, 9, 15]. This strain sensing ability is useful for structural vibration control and dynamic load monitoring.

Although the applications mentioned above are important, they are limited in scope, as electronic and optoelectronic devices, such as transistors, diodes, lasers and solar cells, are not included. These devices require semiconductors—just electrical conductivity is not enough. The composites have not been found to be semiconducting, prior to this work.

2. The semiconducting phenomenon in carbon fiber composites

In this paper, we report the first observation of semiconducting behavior in fiber composites. This behavior occurs in the through-thickness direction of a continuous crossply carbon fiber polymer-matrix composite laminate. This direction is not insulating because there are contacts between fibers of adjacent laminae; fibers are not exactly straight and the polymer matrix is not perfectly uniform in distribution [8, 9]. The composite is a semiconductor with a narrow and tunable energy gap in the infrared region. The energy gap is the activation energy for an electron to jump from one lamina to another. Tuning can be achieved by adjusting the amount of pressure on the laminate during composite fabrication. The origin of the tuning ability

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relates to the effect of the interlaminar stress on the energy gap and the effect of composite fabrication temperature on the interlaminar stress. The interlaminar stress includes curing and thermal stresses, both of which are different between the longitudinal and transverse directions of a lamina (crossply). When the amount of pressure on the laminate during composite fabrication is increased, the thickness of the polymer matrix between adjacent laminae is decreased, so that the fiber volume fraction increases and the interlaminar stress is increased. A higher stress leads to a greater energy gap. Thus, the energy gap is tunable by varying the pressure on the laminate during composite fabrication.

3. Experimental details

This section provides the experimental support of the phenomenon described in the last section.

Two laminae of unidirectional carbon fiber epoxy-matrix prepregs (table 1) in the form of strips crossing one another, with one strip on top of the other (figure 1), were fabricated into a composite at the overlapping region of the two laminae by applying pressure and heat to the overlapping region (without a mold). The pressure was provided by a weight, which was varied in order to vary the pressure. A glass fiber epoxy-matrix composite spacer was placed between the weight and the junction (the overlapping area region of the two strips). The heat was provided by a Carver hot press. A Watlow model 981C-10CA-ARRR temperature controller was used to control the temperature and the ramping rate. Each of the samples was put between the two heating platens of the hot press and heated linearly up to $175 \pm 2\,^{\circ}C$ at the rate of $2.5\,^{\circ}C\ min^{-1}$. It was then cured at that temperature for 10 h and subsequently cooled linearly to $50 \pm 2\,^{\circ}C$ at the rate of $0.18\,^{\circ}C\ min^{-1}$. After that, the sample was reheated up to $150 \pm 2\,^{\circ}C$ and then cooled back to $50 \pm 2\,^{\circ}C$. Both the reheating and the subsequent cooling were linear and at the rate of $0.15\,^{\circ}C\ min^{-1}$. Still after that, the sample was heated linearly up to $150 \pm 2\,^{\circ}C$ again at the rate of $1\,^{\circ}C\ min^{-1}$ and then cooled linearly back to $50 \pm 2\,^{\circ}C$ at the rate of $0.15\,^{\circ}C\ min^{-1}$. All the time, the contact electrical resistance and the temperature of the sample were measured respectively by a Keithley 2001 multimeter and a T-type thermocouple, which was put just beside the junction. Electrical contacts were made to the four ends of the two strips, so as to measure the contact electrical resistivity (resistance multiplied by contact area, which is the area of the overlapping region) between the two laminae in the composite, using the four-probe method (figure 1). The epoxy at the ends of each prepreg strip was burned out to expose the carbon fibers for the purpose of making electrical contacts. These exposed fibers were wrapped by pieces of copper foil, with silver paint between the copper foil and the fibers. The electric current flowed from A to D, such that the dominant resistance was the contact resistance, as the volume resistance of the strips was negligible in comparison. The voltage between B and C is the voltage between the two laminae.

Figure 2 shows the variation of the contact resistivity ρ_c with temperature during reheating and subsequent cooling, both at $0.15\,^{\circ}C\ min^{-1}$, for samples cured at 0 and

Table 1. Carbon fiber and epoxy matrix properties (according to ICI Fiberite).

10E - Torayca T-300 (6 K) untwisted, UC-309 sized	
Diameter	7 μm
Density	1.76 g cm^{-3}
Tensile modulus	221 GPa
Tensile strength	3.1 GPa
976 Epoxy	
Process temperature	350 °F (177 °C)
Maximum service temperature	350 °F (177 °C) dry
	250 °F (121 °C) wet
Flexural modulus	3.7 GPa
Flexural strength	138 MPa
T_g	232 °C
Density	1.28 g cm^{-3}

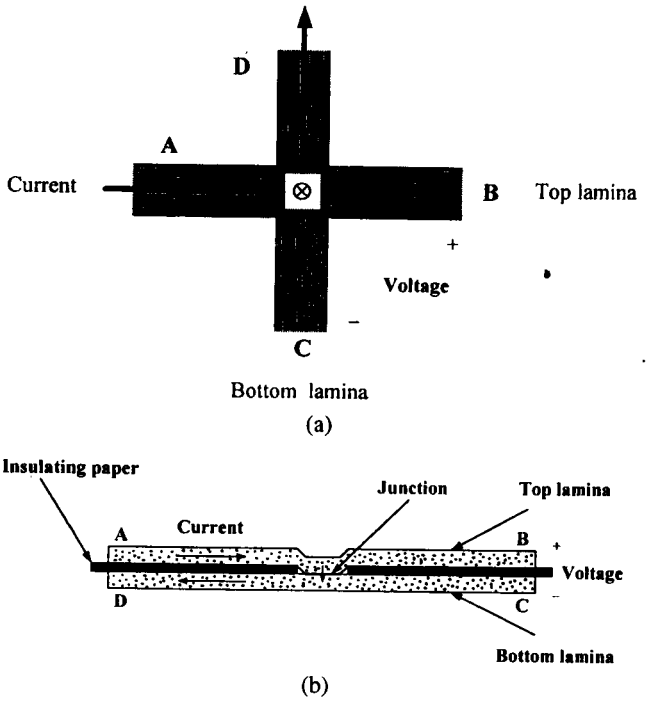

Figure 1. Composite configurations for testing contact resistivity as a function of temperature. (a) Crossply. (b) Unidirectional.

0.33 MPa. The corresponding Arrhenius plots of log contact conductivity (inverse of contact resistivity) versus inverse absolute temperature during heating are shown in figure 3. From the slope (negative) of the Arrhenius plot, which is quite linear, the activation energy can be calculated by using the equation

$$\text{slope} = -\frac{E}{2.3k}$$

where k is the Boltzmann constant and E is the activation energy. The linearity of the Arrhenius plot means that the activation energy does not change throughout the temperature variation. It also indicates semiconductor behavior. This activation energy is the energy gap for electron jumping from one lamina to the other. Electronic excitation across this gap enables conduction in the through-thickness direction.

A slightly concave shape is present in the Arrhenius plots obtained during heating as well as cooling (figure 3). This shape means that the activation energy increases slightly with increasing temperature. On the other hand, the interlaminar

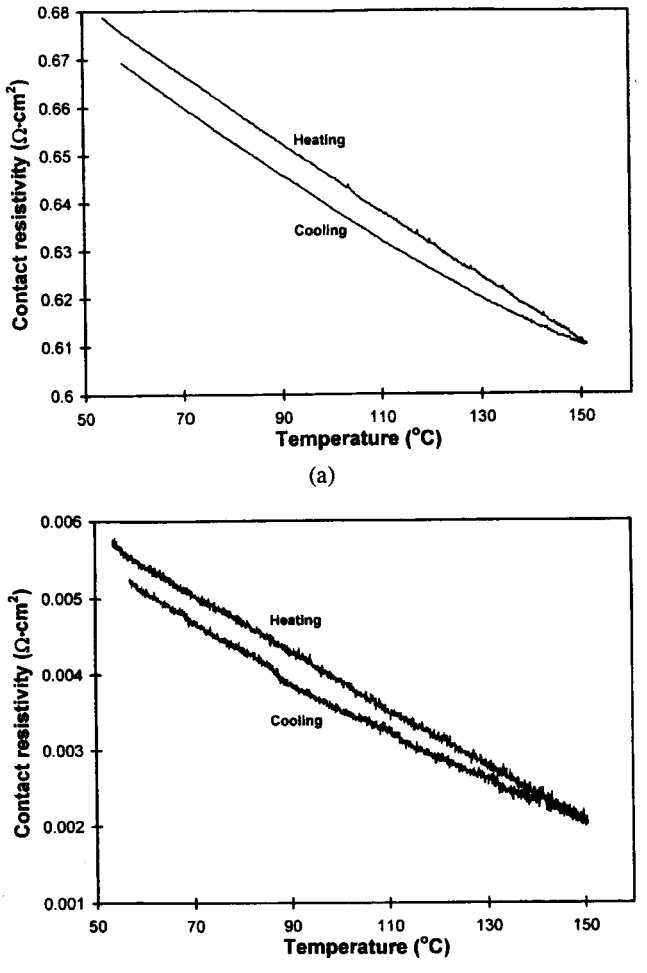

Figure 2. Variation of contact electrical resistivity with temperature during heating and cooling at 0.15 °C min^{-1} (a) for sample made without any curing pressure and (b) for sample made with a curing pressure 0.33 MPa.

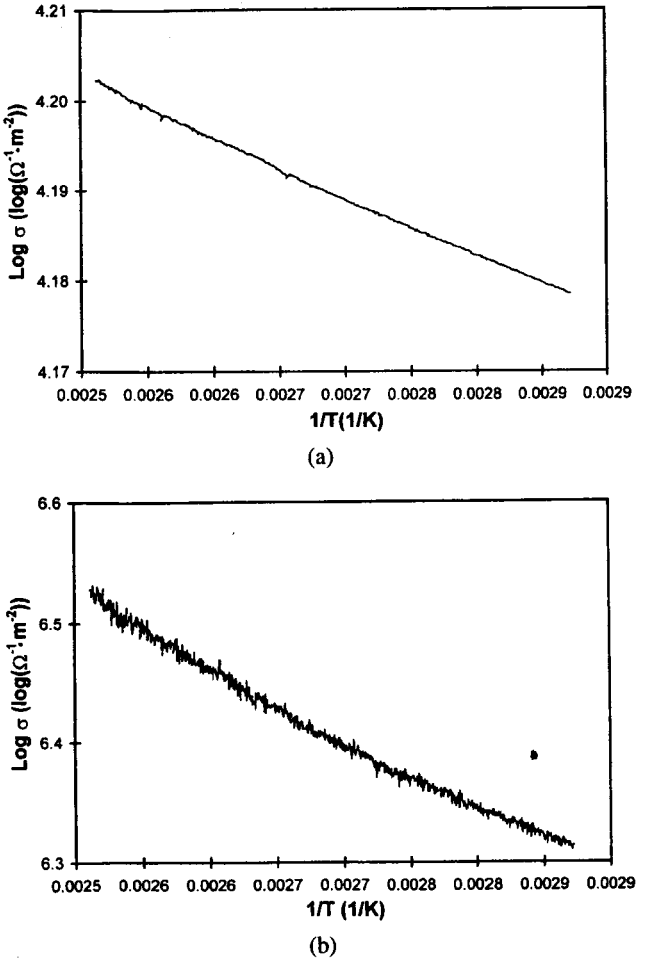

Figure 3. Arrhenius plot of log contact conductivity against inverse absolute temperature during heating at 0.15 °C min^{-1} (a) for sample made without any curing pressure and (b) for sample made with curing pressure 0.33 MPa.

thermal stress decreases with increasing temperature, as explained in the next paragraph. Thus, this curvature suggests that the thermal stress is not dominant in affecting the activation energy. The origin of the curvature is believed to be the loss of moisture during heating.

The activation energies, thicknesses and room temperature contact resistivities for samples made at different curing pressures and composite configurations are shown in table 2. All the activation energies were calculated based on the data at 75–125 °C. In this temperature regime, the temperature change was very linear and well controlled. From table 2 it can be seen that, for the same composite configuration (crossply), the higher was the curing pressure, the smaller was the composite thickness (because of more epoxy being squeezed out), the lower was the contact resistivity, and the higher the activation energy. A smaller composite thickness corresponds to a higher fiber volume fraction in the composite. During curing and subsequent cooling, the matrix shrinks while the carbon fibers essentially do not, so a longitudinal compressive stress will develop in the fibers. For carbon fibers, the modulus in the longitudinal direction is much higher than that in the transverse direction. Thus, the overall shrinkage in the longitudinal direction tends to be less than that in the transverse direction. Therefore, there will be an interlaminar stress in the two crossply layers in a given direction. This stress accentuates the barrier for the electrons to jump from one lamina to the other. The greater the interlaminar stress, the higher the barrier, which is the activation energy. After curing and subsequent cooling, heating will decrease the thermal stress, due to the CTE (coefficient of thermal expansion) mismatch between fibers and matrix. However, the thermal stress is probably smaller than the curing stress, so the activation energy does not decrease upon heating (figure 3). Therefore, the higher the curing pressure, the larger the fiber volume fraction, the greater the interlaminar stress, and the higher the activation energy, as shown in table 2.

The activation energy increased gradually with increasing curing pressure from 0 to 0.19 MPa, but increased abruptly from 0.02 to 0.12 eV when the curing pressure was increased from 0.19 to 0.33 MPa. The abrupt increase at high pressure is probably not due to the interlaminar stress abruptly increasing, but is probably due to another phenomenon that occurred at the high curing pressure of 0.33 MPa. This phenomenon has not been investigated, but one possibility is the pressure increasing the anisotropy of the matrix and thereby accentuating the barrier for electron jumping from one lamina to the other.

The curing pressure for the sample in the unidirectional

Table 2. Activation energy (energy gap) for various composites. The standard deviations are shown in parentheses.

Composite configuration	Curing pressure (MPa)	Composite thickness (mm)	Contact resistivity ρ_{c0} (Ω cm^2)	Activation energy (eV)		
				Heating at 0.15 °C min^{-1}	Heating at 1 °C min^{-1}	Cooling at 0.15 °C min^{-1}
Crossply	0	0.36	0.73	0.0131 (2×10^{-5})	0.0129 (3×10^{-5})	0.0125 (8×10^{-6})
	0.062	0.32	0.14	0.0131 (4×10^{-5})	0.0127 (7×10^{-5})	0.0127 (4×10^{-5})
	0.13	0.31	0.18	0.0168 (3×10^{-5})	0.0163 (4×10^{-5})	0.0161 (2×10^{-5})
	0.19	0.29	0.054	0.0222 (3×10^{-5})	0.0223 (3×10^{-5})	0.0221 (1×10^{-5})
	0.33	0.26	0.0040	0.118 (4×10^{-4})	0.129 (8×10^{-4})	0.117 (3×10^{-4})
Unidirectional	0.42	0.23	0.29	0.0106 (3×10^{-5})	0.0085 (4×10^{-5})	0.0081 (2×10^{-5})

composite configuration was higher than that of any of the crossply samples (table 2). Consequently, the thickness was the lowest. As a result, the fiber volume fraction was the highest. However, the contact resistivity of the unidirectional sample was the second highest rather than being the lowest, and its activation energy was the lowest rather than the highest. The low activation energy is consistent with the fact that there was no CTE or curing shrinkage mismatch between the two unidirectional laminae and, as a result, no interlaminar stress between the laminae. This low value supports the notion that the interlaminar stress is important in affecting the activation energy. The high contact resistivity for the unidirectional case can be explained in the following way. In the crossply samples, the pressure during curing forced the fibers of the two laminae to press on to one another and hence contact tightly. In the unidirectional sample, the fibers of one of the laminae just sank into the other lamina at the junction, so pressure helped relatively little in the contact between fibers of adjacent laminae. Moreover, in the crossply situation, every fiber at the lamina–lamina interface contacted many fibers of the other lamina, while, in the unidirectional situation, every fiber had little chance to contact the fibers of the other lamina. Therefore, the number of contact points between the two lamina was less for the unidirectional sample than the crossply samples. Figure 2 also shows a small irreversible decrease in the room temperature contact resistivity after a heating–cooling cycle. This may be due to some degree of permanent decrease of the moisture content during heating. The irreversibility vanished when the temperature change was small (e.g., temperature changing from 20 to 100 °C). The larger the temperature change, the more significant the irreversibility. The slight irreversibility is consistent with the fact that the activation energy obtained during cooling was slightly less than that obtained during heating (table 2). Table 2 also shows that the heating rate essentially did not affect the activation energy.

4. Concept of optoelectronic and electronic devices made from carbon fiber composites

Graphite is a semi-metal in the in-plane direction and an insulator in the out-of-plane direction [16]. In the in-plane direction, there are electron and hole carriers in equal concentrations, as the energy bands overlap. A carbon fiber differs from graphite in that it is not completely crystalline. The carriers in a carbon fiber in the fiber axis (which tends to be the in-plane direction) can be electrons and/or holes, as the crystallinity differs among different types of carbon fiber and the band structure changes with crystallinity. When a carbon fiber is doped by intercalation (i.e., chemical reaction that forms a layered compound or intercalation compound in which the dopant or intercalate resides between the carbon layers), the carrier concentration increased due to the charge transfer between intercalate and carbon [17]. If the intercalate is an electron acceptor, such as bromine, the hole concentration increases and the intercalation compound becomes a hole metal (a metal with holes as carrier) in the in-plane direction [17]. If the intercalate is an electron donor, such as cesium and potassium, the electron concentration increases and the intercalation compound becomes an electron metal (a metal with electrons as carriers) in the in-plane direction [17].

The electrical behavior of a carbon fiber polymer-matrix composite in the fiber direction is governed by the fibers, so in this direction, the composite is either a semi-metal (if not intercalated) or a metal (if intercalated). The metal form is much more conducting than the semi-metal form, so it is preferred. In contrast, the composite is a semiconductor in the through-thickness direction.

The combination of metallic behavior and semiconducting behavior in different directions of the composite makes the composite uniquely attractive for devices, as the metallic behavior allows the carbon fibers to serve as ohmic electrical contacts and interconnections that are built in to the semiconductor. (In contrast, a conventional semiconductor such as silicon requires a metal thin film deposited on its surface to serve as an electrical contact or interconnection.) The metallic behavior does not interfere with the semiconducting behavior because the two kinds of behavior occur in different directions. Current is passed to the composite through a carbon fiber lamina (metallic), which spreads the current throughout the lamina. Then the current continues to flow in the through-thickness direction (semiconducting) from one lamina to the adjacent one, which is also metallic.

Depending on whether the fibers are n-type or p-type, the composite semiconductor is either n-type or p-type. In other

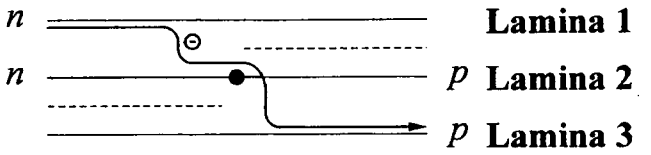

Figure 4. Conceptual design of a pn junction made from carbon fiber composite. Solid lines are laminae. Dashed lines are insulating interlayers. Arrow indicates electron path. The hole path is the same but opposite in direction. The solid circle is an electrical connection.

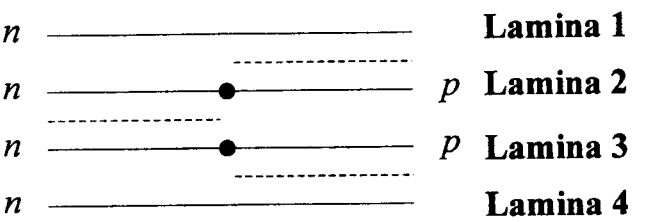

Figure 5. Conceptual design of an npn junction made from carbon fiber composite. Solid lines are laminae. Dashed lines are insulating interlayers. Solid circles are electrical connections.

words, the major carrier in the fibers in the fiber direction is also the major carrier in the composite in the through-thickness direction. By doping the fibers, the semiconductor is doped.

The possibility of having composites in the form of n-type and p-type semiconductors implies the possibility of having pn junctions (diodes), and pnp and npn junctions (transistors). A pn junction can be a carbon fiber composite with three laminae. One of the two outer laminae is n-type, while the other outer lamina is p-type. The inner lamina is partly n-type and partly p-type, such that the two parts are electrically connected, as illustrated in figure 4. Under forward bias of the junction (p-type outer lamina positive relative to the n-type outer lamina), electrons flow from the outer n-type lamina to the n-type part of the inner lamina, while holes flow from the outer p-type lamina to the p-type part of the inner lamina, thus giving rise to an electric current from the p-side to the n-side. The electrons meet the holes at the junction of the n and p parts of the inner lamina and recombine, thereby causing the emission of electromagnetic radiation of energy equal to the energy gap (infrared). This allows the pn junction to serve as a light emitting diode. The reverse phenomenon is that electromagnetic radiation directed at the junction of the n and p parts of the inner lamina under forward bias generates electron–hole pairs. Electrons separate to the n-side while holes separate to the p-side, resulting in a current. This allows the pn junction to serve as a solar cell and as a detector of electromagnetic radiation. Since the energy gap is small and the carrier concentration is high (provided by the metal), it is possible for the Fermi energy to be above the bottom of the conduction band in the n-side and below the bottom of the top of the valence band in the p-side in equilibrium. Upon forward bias of the pn junction, population inversion occurs in the junction (i.e., occupied electron states at a higher energy than the unoccupied electron states). As a result, radiation is emitted from the junction and the pn junction is a semiconductor laser. As shown in figure 4, insulating interlayers need to be placed in some interlaminar regions in order to direct the current flow. The concept illustrated in figure 4 can be extended to provide npn and pnp junctions, which are transistors. Figure 5 illustrates an npn configuration. Electrical contacts to the two n sides of the npn transistor can be made using laminae 1 and 4 (figure 5). Electrical contact to the np junction inside the npn transistor can be made using lamina 2; that to the pn junction inside the npn transistor can be made using lamina 3.

The semiconductor of this paper works up to at least the composite fabrication temperature, which can be as high as 300 °C, depending on the particular polymer matrix. This high temperature capability is as good as or superior to that of conventional semiconductors.

The fabrication of the semiconductor devices of this paper is inexpensive, as it does not require any clean room, high temperature furnace, thin film deposition, photolithography or single-crystal wafer. The fabrication is essentially the same as that of carbon fiber structural composites. Fabrication by lamination is recommended.

Only rather crystalline (graphitic) carbon fibers can be intercalated. An example is the mesophase-pitch-based carbon fibers made by Amoco (e.g., Thornel P-100 and P-120). These fibers are expensive and are therefore not commonly used for structural composites. Therefore, the number of laminae of such fibers should be kept to be a minimum in a composite—just enough to make the required devices. To save cost and enhance durability, carbon fibers that are not intercalated but naturally either n-type or p-type may be used instead of intercalated fibers. These laminae should be at the exterior side of the structural composite if the devices to be made are optoelectronic devices, such as solar cells, light (infrared) emitting diodes and lasers, as carbon is a good reflector and absorber of electromagnetic radiation. For electronic devices such as transistors, these laminae can be anywhere.

This paper shows that a carbon fiber polymer-matrix composite can be an electronic/optoelectronic material in addition to being a structural material. It is multifunctional. This means that the body of an aircraft made with carbon fiber composite can be a solar panel, light emitting diodes, lasers, transistor circuits, etc. These devices are not embedded in the body; rather, the body itself is these devices. This allows structures to exhibit an aspect of smartness that is different from conventional smartness related to sensing, actuation and self-healing. This aspect of smartness encompasses abilities to generate electric power (solar cells), absorb infrared radiation (solar cells), detect infrared radiation, emit infrared radiation (lasers and light emitting diodes), amplify signals (transistors) and process signals (circuits). These abilities are particularly attractive for aircraft and spacecraft. The ability to generate electric power is also relevant to buildings, for which low-cost solar cells are much needed.

A circuit involves not just diodes and transistors, but also resistors and capacitors. Diodes and transistors require semiconductors, but resistors and capacitors do not. Carbon fibers themselves can serve as resistors. The electrical resistivity of a carbon fiber that is not intercalated and not crystalline can be quite high, like $10^{-3}\ \Omega\ \mathrm{cm}^{-1}$. The use of a high dielectric constant material as an interlayer between laminae provides a capacitor (a parallel-plate capacitor).

Since the structure can be large and the number of laminae in the composite can be substantial, a high capacitance can be attained.

This paper provides the basis of a new field of electronics, which we call 'structural electronics'. By this, we mean electronics built from structural composites.

5. Conclusion

Carbon fiber epoxy-matrix composite was found to be a semiconductor in the through-thickness direction, with a tunable energy gap of 10^{-2}–10^{-1} eV (infrared). The tuning was achieved by adjusting the pressure during composite fabrication. The higher the pressure, the higher the fiber volume fraction, the higher the interlaminar stress, and the greater the energy gap, which is the activation energy for an electron to jump from one lamina to another. The semiconducting behavior involves the contact resistivity between adjacent laminae in the composite decreasing reversibly with increasing temperature (preferably below the composite fabrication temperature).

The concept for optoelectronic and electronic devices made from carbon fiber polymer-matrix composites is summarized below. Carbon fiber polymer-matrix composite is a semi-metallic or metallic in the fiber direction. The metallic behavior occurs if the fibers are intercalated. Intercalation with an acceptor gives fibers that are a hole metal, so that the composite is a p-type semiconductor in the through-thickness direction. Intercalation with a donor gives fibers that are an electron metal, so that the composite is an n-type semiconductor in the through-thickness direction. Thus, the composite is a metal in the fiber direction and a semiconductor in the through-thickness direction. The metallic behavior allows the fibers to serve as built-in electrical contacts and interconnections for pn, pnp, npn and other junctions, which constitute devices such as solar cells, light emitting diodes, lasers and transistors.

The technology described in this paper allows carbon fiber polymer-matrix composites to serve as both structural and optoelectronic/electronic materials. Thus, a carbon fiber structural composite can generate electric power, absorb/emit radiation (infrared), and amplify and process signals. This adds a new dimension to smart structures, in addition to providing a new field of electronics called structural electronics.

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