Current transport mechanisms in a layered semiconductor

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The layered chalcogenide GaTe is a III–VI compound semiconductor with anisotropic properties. Conductivity studies on single crystals show five different types of transport mechanisms, including weak localization (WL) in 2- and 3-dimensions along the layer planes between 9 and 20 K and between 20 and 50 K, respectively. Across the layer planes, 2- and 3-dimensional Mott-type hopping is observed in the above temperature regimes. The slope of the $G_\parallel$ vs ln T plot under WL enables the accurate determination of the constant $e^2/2\pi^2 \hbar$, which was found to be 1.23 × 10⁻⁵ mhos. Above $T > 80$ K, band conduction is observed in both directions with mobility varying as T^n, due to optical phonon scattering.

CONVENTIONAL mechanisms of current transport such as ohmic conduction are only special cases of many different possible mechanisms. Thus in the quantum transport regime, the current I is no longer proportional to applied voltage V and the resistance R is no longer proportional to sample length L. Different modes of current transport and hence conductivity have their own characteristic dependence on temperature, which is often used to distinguish between them. Metallic conductivity is characterized by a weak negative temperature coefficient, due to increase in scattering of carriers by lattice vibrations (phonons) and hence decrease of mobility with temperature. Semiconductors on the other hand, usually show strong increase in conductivity with temperature due to exponential increase in number of carriers excited across the band-gap, which overwhelms the weaker mobility variation. Other mechanisms studied and reported extensively include Poole–Frenkel hopping, field-emission and tunnelling[1].

Due to disorder present in conductors, other types of behaviour have been postulated and quite a few have been observed experimentally. For example, weak localization reviewed by Lee and Ramakrishnan[2] has been observed in a number of systems. Anisotropy in crystal structure can also give rise to different modes of conduction in different crystallographic directions. It is interesting to note that five different types of current transport over different temperature ranges have been observed in a single material without any structural phase transition[3]. The chalcogenide semiconductor GaTe has a layered structure due to strong covalent Ga–Te bonding within the layer planes and weak van der Waals type of bonding across the layers. It crys-

tallizes in a stable monoclinic phase (space group C_2^2) and has a band-gap of 1.66 eV at 300 K. Thus anisotropy in conduction is expected, but due to difficulties in crystal growth only in-plane properties had been studied before. The crystals have natural stacking faults between the planes as observed from TEM studies and can be easily cleaved between the layers. High quality single crystals were grown by a slow Bridgman technique, the quality being attested to be the low carrier (hole) concentration (2.75–6.5 × 10¹⁵/cm³) and high mobility (450–500 cm²/V.s at 80 K) compared with reports of previous workers such as Manfredotti et al.[4].

Between 9 K and 20 K, the in-plane conductance $G_\parallel$ was observed to vary linearly as given by

$$\Delta G = (\lambda e^2/\hbar) \ln T,$$

characteristic of weak localization in 2-dimensions. From the slope of the plot the value of the constant $e^2/2\pi^2\hbar$ was found to be 1.23 × 10⁻⁵ mhos, which is in excellent agreement with the theoretical value of 1.2306 × 10⁻⁵ mhos. Between 20 K and 50 K, in-plane conductivity $\sigma_\parallel$ varied as $T^{1/2}$ due to weak localization in 3-dimensions.

Transport across the layer planes is dominated by the stacking faults. Between 9 K and 20 K, hopping in 2-dimensions was found with $G_\perp \propto \exp(T/T_o)^{1/3}$, whereas in the 20 K to 50 K regime, hopping in 3-dimensions occurred with $\sigma_\perp \propto \exp(T/T_o)^{1/4}$. Here the exponent is given by $1/(n + 1)$, where n is the number of dimensions. Such hopping behaviour was predicted by Mott[5] for amorphous semiconductors and also observed in MOS structures[5]. It is attributed to phonon-assisted hopping of carriers between states within the band-gap.

Above 80 K conventional band-transport was observed in both directions, but with different temperature dependence of hole mobility $\mu_h \propto T^{-n}$, where $n = 2.05$ in-plane and $n = 3.3$ across the layer plane, due to scattering by optical phonons. It should be noted that the low temperature transport is due to electrons, since holes are immobilized at low temperatures by a deep hole trap as found experimentally. These conductivity variations which are considered to be unique for a single material are summarized in the Table 1.

Another distinct difference is in the sign of the magneto-resistance, which is positive for band transport as expected and negative for weak localization due to suppression of localization effects by the magnetic field. The compa-

Table 1. Different mechanisms of current transport in GaTe

Crystal direction	T 9–20 K	T 20–50 K	$T > 80$ K
Parallel to layer plane	$G_\parallel \propto \ln T$	$\sigma_\parallel \propto \ln T^{1/2}$	$\mu_\parallel \propto \ln T^{-n}$
Perpendicular to layer plane	$G_\perp \propto \exp(T/T_o)^{1/3}$	$\sigma_\perp \propto \exp(T/T_o)^{1/4}$	$\mu_\perp \propto \ln T^{-n}$

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Table 2. Magnetoresistance along and perpendicular to the layer planes at 10 K and 80 K

Crystal direction	$\Delta\rho/\rho$ (in %) $T = 10$ K	$\Delta\rho/\rho$ (in %) $T = 80$ K
Parallel to layer plane	− 7.14	+ 11.5
Perpendicular to layer plane	− 5.18	+ 8.3

rison is given in Table 2. The presence of stacking faults also gave rise to nonlinear I–V characteristics across the layer planes, similar to those due to tunnelling between quantum wells at 10 K, which disappeared at higher temperatures.

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Enhancement of the energy and quantum conversion efficiencies of a photoelectrochemical cell sensitized with a combination of cationic and anionic dyes

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The dye bromopyrogallol red surface complexes to TiO$_2$ and adsorbs the electron-donating cationic dye, acridine orange, binding it to the anionic sulphonate site. The resulting double dye film, when used in a photoelectrochemical cell, shows enhanced incident photon to current and energy conversion efficiencies and a broadened spectral response owing to charge transfer between the dyes and utilization of light absorbed by both the dyes.

SOLAR energy conversion that mimics photosynthesis in utilizing pigments for light harvesting continues to receive much attention and different types of pigment-based artificial light-harvesting systems have been reported[1–9]. One approach to the problem attempts to create reaction centres, linking chromophores, electron donors and/or acceptors by covalent or coordinate bonds. The other, the

practically more successful method, is dye-sensitization of semiconductor nanostructures[2,4]. Attempts have also been made to use coupled electron donor and/or acceptor units to sensitize semiconductors, hoping that this would facilitate the charge separation. The intimate contact between different units, considered necessary for charge transfer is realized via covalent linkages[5,6,10,11]. In this communication, we describe a simple model system where the broadening of the spectral response enhanced charge separation and the consequent increase in the energy and incident photon to current efficiencies (η and IPCE) are more explicitly demonstrated in a photoelectrochemical cell (PEC) by ionic linkage of bromopyrogallol red (B) anions surface-complexed to TiO$_2$ with the acridine orange (A) cations.

TiO$_2$ films were deposited by spraying a dispersion of Degussa P25 (particle size ~ 30 nm) onto conducting tin oxide (CTO) glass plates and sintering at 450°C. On soaking the plate in a solution of the anionic dye, bromopyrogallol red (5,5′-dibromopyrogallol sulphonephthalien) in ethanol (1×10^{-4} M), the dye anchors firmly to TiO$_2$ by complexation involving two of its hydroxyl groups (Figure 1 a). Estimated dye surface concentration (SC) was ~ 90% of the monolayer coverage (dye on the plate is desorbed into a measured volume of 0.02 M NaOH in 80% ethanol and its concentration estimated spectrophotometrically). The second dye, acridine orange (3,6-bis(dimethylamino) acridine hydrochloride), which is cationic gets deposited on top of the first dye, when the plate is soaked in a solution of this dye (1×10^{-4} M in ethanol) or by spreading a measured quantity of the dye solution (0.05 M) on the film. The dye A cation binds to the anionic sulphonate site of B (Figure 1 a), replacing H$^+$ and eliminating HCl. PECs were made from TiO$_2$ films coated with B, A and A–B (A coated on top of B) in the usual manner, interposing the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.03 M I$_2$ in acetonitrile containing 10% ethylene carbonate) between the film and the platinized CTO glass counter electrode. Table 1 gives the
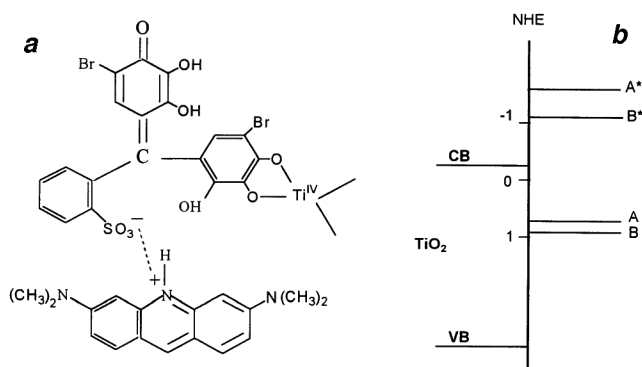

Figure 1. a, Schematic structural diagram showing the surface complexation of bromopyrogallol red (B) to TiO$_2$ and ionic binding of acridine orange (A) cation to the anionic sulphonate group of bromopyrogallol red; b, Energy level diagram indicating the band positions of TiO$_2$, ground and excited levels of the two dyes. VB, Valence band; CB, Conduction band.

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