

A SURVEY ON OPTICAL AMPLIFIERS IN BROADCAST OPTICAL NETWORKS

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Abstract

Inorganic semiconductors permeate virtually every sphere of modern human existence. Micro-fabricated memory elements, processors, sensors, circuit elements, lasers, displays, detectors, etc are ubiquitous. However, the dawn of the 21st century has brought with it immense new challenges, and indeed opportunities—some of which require a paradigm shift in the way we think about resource use and disposal, which in turn directly impacts our ongoing relationship with inorganic semiconductors such as silicon and gallium arsenide. Furthermore, advances in fields such as nano-medicine and bioelectronics, and the impending revolution of the ‘ubiquitous sensor network’, all require new functional materials which are bio-compatible, cheap, have minimal embedded manufacturing energy plus extremely low power consumption, and are mechanically robust and flexible for integration with tissues, building structures, fabrics and all manner of hosts. In this short review article we summarize current progress in creating materials with such properties. We focus primarily on organic and bio-organic electronic and optoelectronic systems derived from or inspired by nature, and outline the complex charge transport and photo-physics which control their behaviour. We also introduce the concept of electrical devices based upon ion or proton flow (‘ionics and protonics’) and focus particularly on their role as a signal interface with biological systems. Finally, we highlight recent advances in creating working devices, some of which have bio-inspired architectures, and summarize the current issues, challenges and potential solutions. This is a rich new playground for the modern materials physicist.

Introduction

Inorganic semiconductors such as silicon and gallium arsenide have fuelled the high technology, photonics and computer revolutions of the past five decades. Devices containing semiconductor processors, memory elements, detectors, sensors, circuitry, light emitting diodes, photodiodes, etc. control or assist virtually every facet of our modern life: healthcare, energy, entertainment, transport, communications, even thinking! In the developed world particularly, there is a whole

generation that cannot conceive of life without a mobile phone or computer. Many of these modern-day essentials are deliberately designed to be obsolete within a few years of purchase, and a very small proportion are recycled or even capable of being recycled. This is leading to a number of extremely unfortunate and undesirable outcomes: for example, massive amounts of often toxic electronics waste, and rapid depletion of already scarce elements such as gallium and indium (‘endangered elements’). This is simply unsustainable. Furthermore, the processing of

inorganic semiconductors is an energy intensive business. If you think about the manufacturing chain of events that turns a humble pile of sand into a GHz silicon processor, the problem becomes all too apparent. The energy expended in manufacturing just one chip processor exceeds the total energy used by a modern laptop over its typical 3 year lifespan. In an energy-constrained, carbon sensitive world, this will become unacceptable. There is no doubt that the 'silicon age' has delivered a discontinuous advance in humankind's technological ability, but how much longer can it last, and what is next?

Additionally, concepts such as the 'ubiquitous sensor network' [1] with visions of stand-alone sensing and control systems deployed to manage energy consumption, health and medical interventions, internal and external environments and communications, will require components of extremely low power consumption and which can be integrated into a range of hosts—building fabric, biological tissue, natural environments, etc. Bio-compatibility, low embedded energy, low power consumption (or even self-powered), minimal environmental footprint and mechanical flexibility are all key requirements of the functional materials making up these devices and indeed their architectures. It is not clear how, or even if, our current toolkit of inorganic semiconductors can meet these requirements. The revolutions in so-called 'bioelectronics' and 'nanomedicine' which promise splendours such as in situ real-time health monitoring with integrated biosensors, tissue repair, targeted drug delivery, cellular-level control and stimulation, pose even greater

materials challenges—for example, how does one interface a complex biological system with control circuitry in order to 'read or write' an electrical signal [2–4]? Biology is dominated by ion gradients and currents, membrane electric potential gradients and local chemical reactions. As well as being hostile to biological tissues, semiconductors are electronic. As such, new concepts such as high fidelity ionto-electron transduction and 'ionics' (electrical circuits and elements based on the flow of ions) become relevant and necessary [5, 6]. The recent demonstration by the Rolandi group (to be discussed in detail later in the review) of a biologically inspired 'bioprotonic field-effect transistor' made from a proton conducting polysaccharide is one of the first examples of this new kind of electrical device, and a major advance

Nature, of course, through millions of years of evolution, presents an almost limitless supply of materials, concepts and architectures to address these critical challenges. A desire to understand and then mimic the natural world is part of our 'scientific-DNA'. For example, artificial photosynthesis is a popular but hugely challenging concept as a potential solution for future clean energy (trees can do it, so why can't we?), powerful computational systems based upon neural networks are established and effective 'artificial decision makers', and synthetic nano-and-micro engines can mimic the elegant functionality of cellular motors. In the semiconductor space, organic electronic and optoelectronic materials are coming of age, their evolution driven by the imperatives described above in applications such as displays, lighting, plastic electronics and sensors

[7]. Metallic and semiconducting polymers, organic small molecules and dendrimers contain delocalized π -electron systems, akin to proteins and other functional biological macromolecules, which confer electrical conductivity, and optical and transport gaps of order a few eV. These materials are often photo-conductive and can be engineered to have high photoluminescent and electroluminescent quantum yields. Photo-excitations in organic semiconductors are 'excitonic' in nature—characteristically low dielectric constants mean weak screening of the electron-hole (e-h) electrostatic interactions,

and the pair remain Coulombically bound (the exciton) with a typical binding energy of 100s of meV. In an inorganic semiconductor photo-excitation leads to the spontaneous creation of a free electron and hole. The excitonic nature of organic semiconductors is a defining feature of their physics and an essential functional element of natural chromophores and proteins. Does the exciton limit or enhance our ability to make use of naturally inspired photo-active materials?

Furthermore, organic conductors and semiconductors can display 'hybrid' electrical physics, i.e. current flow via

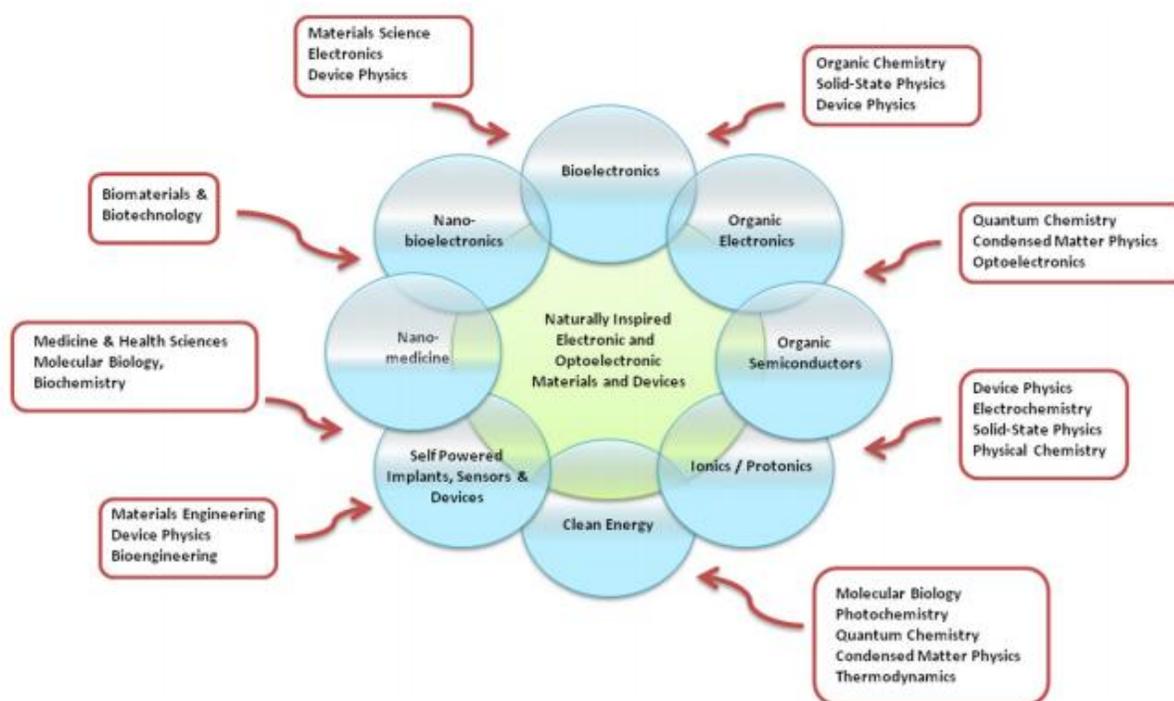


Figure 1. The diverse elements of science and engineering that intersect with or utilize advanced functional electronic and optoelectronic materials inspired by nature. Many of the sub-fields listed are mature—such as organic optoelectronics, whilst others are newly emerging, such as bioelectronics. The classical fields of physics, chemistry, engineering, materials science and biology feed these multi-disciplinary endeavours, and physics in particular has a pivotal role to play.

ions/protons and electrons/holes. This is not a common feature in either synthetic or natural

compounds, the classic synthetic example being poly(3,4-ethylenedioxythiophene) doped with

poly(styrenesulfonate) (PEDOT : PSS) [4]. Mostert and coworkers recently reported hybrid behaviour in the natural pigment melanin—for over four decades considered to be one of the first examples of an amorphous organic semiconductor [8]. It appears that the complex electrical physics of these important bio-macromolecules is dominated by the transport of protons (also to be discussed later in the review in detail). It is true to say that the underlying physics of organic (and bioorganic) semiconductors is significantly more complex and less well understood than their inorganic counterparts. This inherent complexity is in part due to the molecular nature of organic systems (providing strong correlations at the electronic level) and the high levels of structural disorder which renders traditional condensed matter physics approaches such as band theory somewhat ineffective, especially when considering room temperature properties. However, the rationale design of new, high performance materials requires a deep understanding of the underlying structure–property relationships, and this is driving a ‘renaissance’ in the basic physics of natural and bioinspired-synthetic functional systems.

This Report on Progress in Physics examines the current state-of-the-art of advanced functional electronic and optoelectronic materials and devices inspired by, or indeed derived from, nature. In particular, we will focus upon organic and bio-organic systems with semiconducting or photo-active properties. Application areas of interest include light energy conversion and light detection, electronic and computing

components, sensors and particularly bioelectronics and bionanoelectronics for interfacing the biological world with conventional control systems. This is not an exhaustive list, but gives a flavour of the diversity and opportunity. The report will cover a broad range of topics from materials to device architectures and pay particular attention to the underlying electrical and photo-physics as we examine the specific challenges of achieving pre-requisite basic device characteristics such as low power consumption, fast response, high carrier mobilities and high photoluminescent quantum yields. The field is by its very nature highly multidisciplinary, and is emerging as a key frontier in advanced functional materials. The principles of optoelectronics, condensed matter, quantum and solid-state physics, along with synthetic organic and physical chemistry, materials science and engineering, biomaterials and applied biotechnology are all essential elements of this challenging endeavour. The interactions between these diverse fields and various application areas are shown in figure 1. Not all of the subelements of the science are at the same stage of maturity, and so naturally there will be some degree of ‘imbalance’ between subjects covered in the review. Furthermore, we have taken the approach of providing more detail where the physics is better understood—and also highlighted those areas where more attention is needed. In summary, this report seeks to provide a brief overview of the current status, highlight some of the key issues and summarize the early adoption application areas. Language and nomenclature are diverse as befits a modern

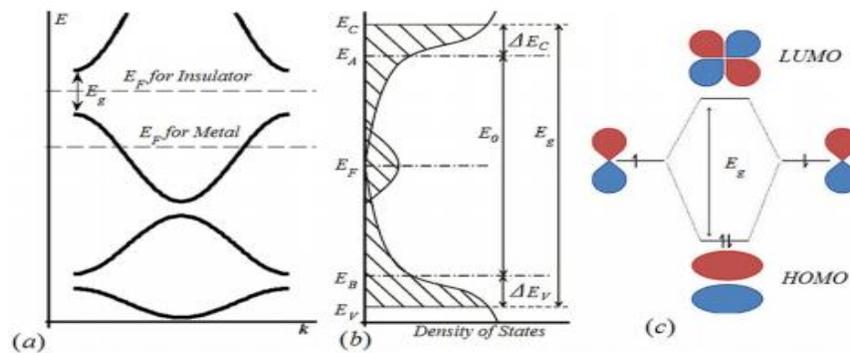


Figure 2. (a) An idealized electronic band structure for a crystalline material, where E is the energy, k the reciprocal lattice vector for the Brillouin zone (crystal unit cell), E_F the Fermi energy (depicted here for both an insulator and metal) and E_g is the energy gap between the valence and conduction bands (for an insulator). Electrons fill up the lowest bands first to E_F (which is the electronic chemical potential at $T = 0$). (b) The density of states for an amorphous semiconductor. There are several energy levels defined as: E_V (E_C) the valence (conduction) mobility edge, E_B (E_A) is the valence (conduction) level, E_F is the Fermi energy, E_0 is the optical gap, E_V (E_C) is the energy gap between the valence (conduction) level and mobility edges, and E_g is the mobility gap. (c) An Idealized electronic picture for the ethene molecule using MO theory. The p_z orbitals from each carbon atom are combined to form a new electronic 'Molecular Orbital'. The HOMO is separated from the LUMO by an energy gap, E_g which is completely analogous to the traditional band gap.

frontier subject where traditional physics interacts with, and contributes to, an emerging field.

Physics of electrical conduction in organic and bio-organic conductors

In this section we briefly review the relevant physics that underpins electrical conduction in organic and bio-organic conductors. From the most fundamental of perspectives, the charge transport properties of any material are described by the simple conductivity (σ) equation:

$\sigma = en\mu$, (1) where e is the fundamental charge, n is the conductive charge density and μ is the mobility of the conductive charge carrier. The study of transport ultimately is based upon understanding σ in terms of n and μ and their interplay. In the case of organic and bio-organic conductors one must frame this analysis in the context of the defining physics, namely, the 'molecular nature' of organic solids, the interactions of strongly correlated π - electrons in organic semiconductors, high levels of

structural and energetic disorder, and the possibility of ions/protons contributing to or even dominating conduction. We consider these concepts in the foregoing discussion.

Electrons and holes

Band theory of electron transport.

A logical place to begin this discussion is with the classical view of electron/hole conduction in a standard semiconductor. This is historically what has defined the language and nomenclature of transport physics. Crystalline materials are usually modelled with an electronic Hamiltonian that reflects the underlying periodicity of the crystal [9], which leads to the concept of delocalized electronic charges. An idealized energy spectrum for a banded solid is shown in figure 2(a) and from this emerge the natural concepts of the band gap and conduction and valence bands. The position of the Fermi energy E_F , determines whether a material is a metal or an insulator. In a metal E_F slices through an energy band, and in an insulator (or semiconductor), E_F lies in-

between bands. Thus, in order to excite an electron into an unoccupied (conductive) band, one needs to cross the energy gap E_g . In this model, the difference between an insulator and a semiconductor is merely a matter of degree, where E_g for a semiconductor is considered to be 1 to 3 eV, and for an insulator higher. Thus, the key to understanding σ is to examine how E_g impacts the carrier density available for conduction. In the first instance, the relationship between E_g and n is given by a Boltzmann description: $n \sim \exp(-E_g/2k_B T)$, (2) where k_B is Boltzmann's constant and T is temperature. Note here that the activation energy is $E_g/2$ since for every electron excited to the conduction band, a hole is left behind in the valence band which acts as the counter charge carrier [9]. This process can be enhanced by photo-conduction with light of energy $>E_g$. The mobility μ is controlled by the shape of the bands (band shape affects the group velocity of the charges [9]) and n can be manipulated by doping. However, the salient point is that the basic characteristic of a crystalline semiconductor is a dependence of σ on T in a Boltzmann fashion with an E_g of 1–3 eV.

Modification of band theory

Mott–Davis model. When solids are amorphous, disorder forces localization of the electronic states. Anderson famously described the formation of these localized states in a periodic system [10] and a simple

schematic of the underlying problem is depicted in figure 3. Essentially, Anderson demonstrated that at a specific value for V_0/B a transition occurs between delocalized and localized transport (the Anderson transition), leading to a

major change in μ . This model was exemplified for the case of amorphous semiconductors—most famously by Mott and Davis [11], which lead to the concept of an extended density of states as shown in figure 2(b). The key to understanding the electronic structure of an amorphous semiconductor is to realize that electrons in the gap between the so called 'mobility edges' (shaded area in figure 2(b)) occupy localized states. In order for an electron to move from a fully occupied localized state to an unoccupied localized state requires an activation energy resulting in a conductivity described by: $\sigma = A \exp - B T n$, (3) where A is the usual pre-exponential factor (related to μ), B is the activation energy depending on the wavefunction shape and density of states of the material, and n is determined by the temperature range. At 'reasonable' temperatures $n = 1$, but at low temperatures $n = 1/4$. When the mobility edge (EC) is crossed by the application of high temperatures or strong electric fields, the conductivity changes character to: $\sigma = \sigma_{min} \exp -(EC - EF) / k_B T$, (4) where σ_{min} is the minimum metallic energy and encapsulates μ . This quantity is important since it is substantially higher than A , and as the name suggests metallic (band like) transport becomes the main mechanism. Thus, in amorphous conducting solids, by changing the temperature (or electric field in electrical switching experiments (see [12] for an original example)) one sees fundamentally different physics. This was an argument relied upon as we shall see later by McGinness et al in categorizing the natural pigment melanin as an amorphous semiconductor [13]. T

The density of states as shown in figure 2(b) also explains the optical 'tail' observed in amorphous semiconductors. In very broad terms, in crystalline semiconductor systems (figure 2(a)), absorption of the light occurs if the incoming electromagnetic radiation is of energy equal to or greater than the energy gap E_g . At this point a very sudden and large increase in the conductivity is seen. In an amorphous semiconductor there is a gradual increase in conductivity with the energy of the photo-excitation [14]. This is due to progressive depopulation of the occupied, localized states below the mobility edge to unoccupied 'band' states above: another 'quirk' of amorphous semiconductors of relevance to the organic/bio-organic semiconductor discussion

Future perspectives: opportunities and challenges

In this Report on Progress in Physics we have reviewed in brief the status of bio-inspired and bio-compatible electronic and optoelectronic materials and devices. The focus has been largely on organic and bio-organic conductors and photoactive systems, although the subjects of natural dielectrics and substrates have also been addressed. Research efforts in this emerging field are motivated by a number of factors: the need for more sustainable high tech materials; the requirements of interfacing with biological systems in bionanomedicine and bioelectronics; and the drive towards cleaner energy solutions. Traditional organic electronics and optoelectronics provide much of the chemical and physical 'foundation elements' for the field which is highly multi-disciplinary. The physics of organic and bio-organic semiconductors is dominated by a number of

intrinsic features: high degrees of energetic and structural disorder; the molecular nature of organic solids; strong electronic correlations; electrical conduction within extended π -conjugated networks; hybrid electronic–ionic (protonic) transport; and the excitonic nature of photoexcitations.

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