10 Excitons in Organic-Based Multilayers

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10.1 Introduction

A lot of effort has been devoted in the last few years to the growth of organic crystalline layered structures (including organic quantum wells [QWs] and superlattices): much improvement in the technique of organic molecular beam deposition has led to a variety of good-quality heterostructures based on molecular solids as well as combinations of organic and inorganic semiconductors [1]. The weak van der Waals bonding between organic epilayers and substrates facilitates the epitaxial growth even in the presence of lattice mismatch. The possibility of growing tailor-made systems incorporating different organic crystalline materials with even more flexibility than for multiple quantum wells based on inorganic semiconductors alone opens up a promising field of research from the point of view of fundamental as well as applied physics. It is only natural that the advent of such a new class of organic crystalline materials prompted scientists to investigate their optical properties, and in particular their non-linear and electro-optical properties, in order to understand their possible advantages in comparison with the usual organic or inorganic materials. In this chapter, we review the results of theoretical studies for two types of heterostructures.

In Sect. 10.2, we discuss the optical properties of interacting organic and inorganic nanostructures with resonating Frenkel excitons (FEs) in the organic material and Wannier–Mott excitons (WEs) in the inorganic semiconductor. In a number of cases, rather strong modifications of the optical properties take place that are interesting from the point of view of both fundamental and applied physics. We show that in such heterostructures two regimes can be realized: the strong coupling regime and the weak coupling one. The former can be achieved in structures where the level splitting due to the resonant interaction is large compared to the exciton widths in the inorganic and organic materials. In such a case, new hybrid exciton states appear in which the electronic excitation spends part of its time as an FE and part as a WE. On the one hand, FEs can have a large oscillator strength, which is typical of some organic molecules. On the other hand, WEs can have strong optical non-linearities due to their large Bohr radii and small saturation densities. Hybrid exciton states have properties of both FEs (large oscillator strength) and WEs (small saturation density), which enhances their optical
non-linearities. The latter regime (weak coupling) occurs in structures where
the width of the exciton states in one or both of the subsystems (organic and
inorganic) is large in comparison with the energy splitting. In such a case, the
hybrid excitons do not arise, but the energy transfer from one subsystem to
the other can be very fast. This process could be particularly interesting for
certain applications. Usually, the FE width in organic materials is large com-
pared to that of the WEs in inorganic semiconductors; thus, the case of energy
transfer from the inorganic subsystem to the organic one is of relevance. The
WEs in the inorganic semiconductors can be pumped electrically (as in light
emitting diodes, LEDs) and, consequently, the fast energy transfer to the
organics can be used to pump the latter material. Such a mechanism could
be used, for example, to realize bright organic LEDs bypassing the problems
hindering the electrical pumping of the organic material itself (small car-
rrier mobilities, space-charge formation, charge-injection difficulties, etc.). We
consider different resonance phenomena in hybrid heterostructures and dis-
cuss the theoretical results for quantum-well, microcavity and quantum-dot
configurations.

In Sect. 10.3, we summarize the studies of charge-transfer excitons (CTEs)
at donor-acceptor (D–A) interfaces. The repulsion among CTEs, arising from
their static dipole moments, can be responsible at high excitation densities for
a new kind of phase transition to a conducting state (cold photoconductivity).
Below the threshold for such transition, the CTEs dipole interaction leads
to strong optical non-linearities and, in asymmetric superlattices, to a new
photovoltaic mechanism.

10.2 Excitons in Organic-Inorganic Heterostructures

In this section, we discuss the possibility of obtaining qualitatively new phys-
ical effects, potentially useful also for technological applications, by inge-
niously combining organic with inorganic materials in one and the same hy-
brid structure. Excitons play a fundamental role in the optical properties of
dielectric solids [2,3]; two models are conventionally used to classify excitons:
the Frenkel exciton model (appropriate mainly for molecular solids) and the
Wannier–Mott exciton model (appropriate mainly for semiconductors). The
mean electron–hole distance in a WE is typically large (in comparison with
the lattice constant). On the other hand, the FE is represented as an elec-
tronic state of a crystal in which electrons and holes are placed on the same
molecule. We can say that FEs in organic crystals have radii \( a_F \), comparable
to the lattice constant \( a_F \sim a \sim 5 \text{ Å} \). In contrast, weakly bound WEs in
semiconductor QWs have large Bohr radii \( a_B \sim 100 \text{ Å} \) in III-V materials
and \( a_B \sim 30 \text{ Å} \) in II-VI ones; in both cases \( a_B \gg a \). The oscillator strength
of an FE is close to a molecular oscillator strength \( F \), whereas the oscillator
strength \( f \) of a WE is usually much weaker: in a QW \( f \sim a^3 a_B^2 L^{-1} F \),
where \( L \) is the QW width \( (a_B > L > a) \). Both types of excitons interact with