Nanocrystal self-assembly: a bottom up approach to 2-D semiconductors with electrical non-trivial properties

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Graphene Graphene consists of a honeycomb lattice of carbon atoms; in fact two equivalent triangular sublattices that are interpenetrated. Tight binding theory for a graphene layer was first developed by Wallace in 1946, taking into account the coupling between a C atom and its 3 nearest neighbors (hence of the other sub-lattice). For wave vectors k close to the K Dirac points, the tight-binding E(k) relationship can be developed as $E = \pm v_F\ (k - K)$. Strikingly, the group velocity is independent of the energy E, similar as for photons. Hence, close to the Dirac point, the carriers obey the massless Dirac equation.

Artificial Graphene The emergence of graphene as an unconventional, physically interesting and possibly useful material has raised general interest in the properties of electrons confined in a hexagonal or honeycomb lattice of materials other than C, whether of atomic or nanoscale nature. C.-H. Park et al. and Gibertini et al. proposed to use arrays of metallic gates to impose a honeycomb pattern with a 50 - 100 nm periodicity in a 2-D electron gas. Within the independent particle framework, it was analytically derived that the Brillouin zone is identical to that of graphene, with linear E-k relationships sufficiently close to the Dirac points. The group velocity of the quasiparticles is proportional to (1/periodicity) and (1/effective mass). In order to obtain systems with fast charge carriers It is hence of major importance to reduce the period of the honeycomb lattices far below 50 nm and to use semiconductors in which the charge carriers have a low effective mass.

Honeycomb lattices of semiconductors? It is clear that robust semiconductor lattices that have a honeycomb lattice with a translational period in the nanometer range and low effective carrier mass are of large interest; first of all these systems keep their semiconductor properties but obtain valence and conduction bands with massless Dirac fermions; second, they open the possibility to combine this with the degrees of freedom from the atomic lattice, e.g. a strong spin-orbit coupling. Why are there no reports on 2-D semiconductor superlattices with a honeycomb geometry in which electrons can be confined? The reason is that there is - up to recently - no method available to prepare such systems on the nanoscale. Two-dimensional semiconductors, e.g. semiconductor quantum wells can be prepared by precious gas phase methods (CVD and MBE) and these systems are of tremendous scientific and technological importance[22-28]. However, even with current state-of-the art lithography it is close to impossible to etch a periodic structure with period below 10 nm in such a system.

Our contribution: preparation of 2-D superlattices with honeycomb nanogeometry

In this lecture, it will be shown that 2-D semiconductor superlattices that are atomically coherent and at the same time have a nanoscale periodicity (square and honeycomb) can be prepared by self-assembly in a 2-D reactor plane. Some results are present in figure 2. The procedure to obtain such systems can be summarized as follows;

1. Preparation of suspensions of PbX (X=Se, Te, S) colloidal nanocrystals with a truncated nanocube shape
2. Self-assembly and facet-oriented specific attachment of PbX nanocrystals. This leads to the 2-D superlattices with a honeycomb or square geometry, atomically coherent up to scales of a micrometer.
3. Transformation of the PbX superlattices into CdX or HgX superlattices by ion-exchange

Our contribution: atomistic theory predicts Dirac conduction bands We have performed an atomistic tight-binding study of the electronic bandstructure of these materials (see figure 1). It was found that honeycomb superlattices lead to Dirac-type conduction bands. The bandwidth depends on the degree of quantum coupling and the size of the particles, and is between 10 – 200 meV. Moreover, we found that spin-orbit coupling leads to a spin-splitting of the bands.

References:

W.H. Evers et al., NanoLetters 2012, E. Kalesaki et al. In preparation

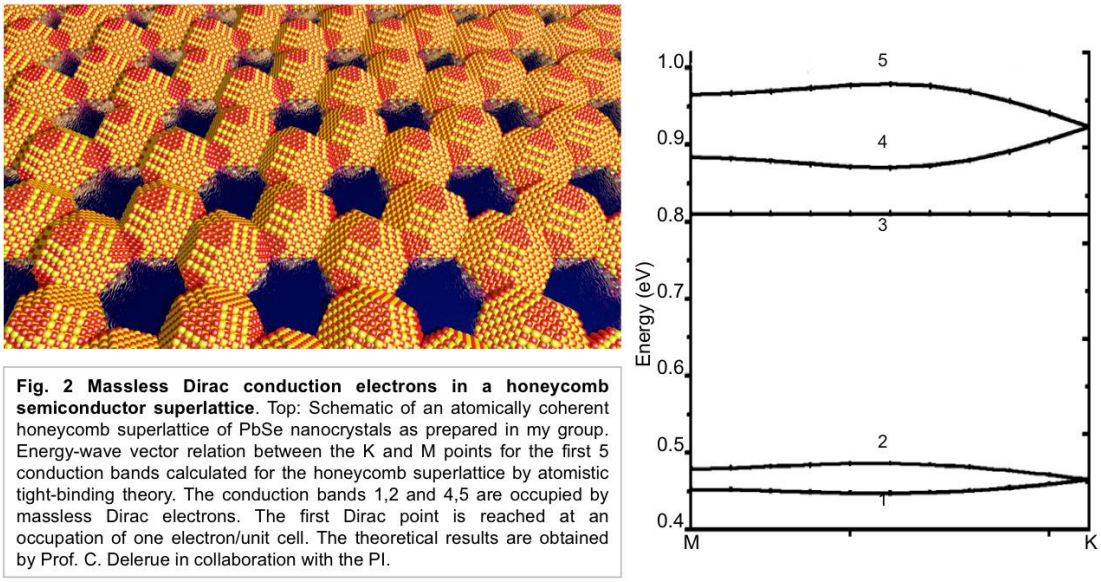

Fig. 2 Massless Dirac conduction electrons in a honeycomb semiconductor superlattice. Top: Schematic of an atomically coherent honeycomb superlattice of PbSe nanocrystals as prepared in my group. Energy-wave vector relation between the K and M points for the first 5 conduction bands calculated for the honeycomb superlattice by atomistic tight-binding theory. The conduction bands 1,2 and 4,5 are occupied by massless Dirac electrons. The first Dirac point is reached at an occupation of one electron/unit cell. The theoretical results are obtained by Prof. C. Delerue in collaboration with the PI.

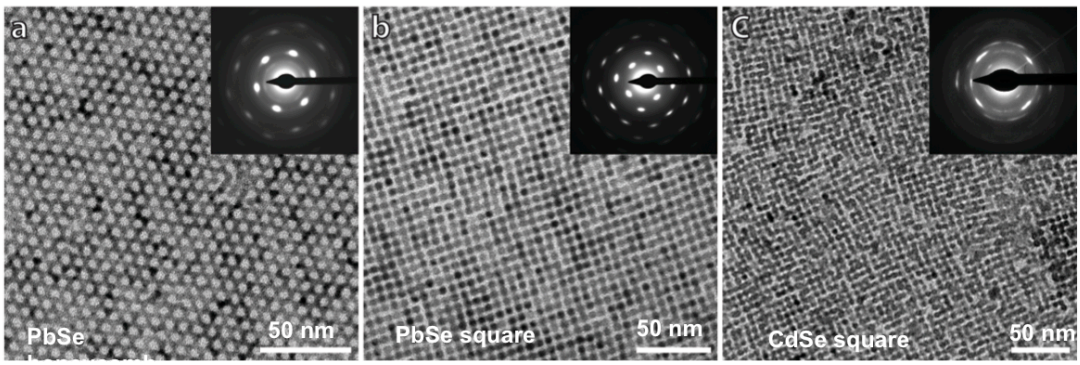

Figure 2: Atomically coherent 2-D semiconductor superlattices formed by nanocrystal attachment
Left: TEM image of a honeycomb PbSe superlattice with electrodiffractogram showing the rocksalt atomic structure, with the [111] direction upright. Center: TEM image of a square PbSe superlattice with electrodiffractogram showing the rocksalt atomic structure, with the [100] direction upright. Right: TEM image of a CdSe superlattice with electrodiffractogram showing the zinc blende atomic structure, with slight disorder.