Condensed-matter physics

Online title: Light tailors the electronic properties of a model semiconductor

Print title: Light tailors the properties of a model semiconductor

Hitting the semiconductor material black phosphorus with intense laser light is shown to alter the behaviour of its electrons. The discovery opens a route to time-dependent engineering of exotic electronic phases in solids. See p.XXX

The atoms in a crystalline solid are arranged in space with periodicity and symmetry that are inherited by the physical properties of the material. These properties can therefore be modified by altering crystal structure — for example, with pressure, strain or chemical substitution. But for many technological applications, controlling the properties of a crystal in time is just as important as changing them in space. Such temporal engineering has been successful in systems comprising groups of ultracold atoms arranged in lattices by means of intersecting laser beams [1], and in some solids [2–4], but it is yet to be implemented in semiconductors — until now. On page XXX, Zhou *et al.* [5] report that the physical properties of black phosphorus (Fig. 1a), a model semiconductor, can be tailored through irradiation with intense laser light.

The behaviour of electrons in a periodic crystal was first described in 1929 by Swiss–American physicist Felix Bloch [6]. His theory reveals that these electrons have a range of allowed energy levels in the solid, owing to their wave-like nature, and the pattern of these levels is called the crystal's electronic band structure. The forbidden range of energies between the 'valence' band (at low energies) and the 'conduction' band (at high energies) is known as the band gap.

The way that electrons occupy these bands determines how they move through a material: metals have partially empty bands, whereas insulators and semiconductors have fully occupied bands, with band gaps that are large and small, respectively (Fig. 1b). Electrical conductivity can therefore be controlled by engineering the occupation of the band structure, and by manipulating band gaps — and now it is possible to do this in a time-dependent way.

The necessary mathematical tools to extend Bloch's theory to incorporate time had actually already been devised in the 19th century by French mathematician Gaston Floquet [7]. In the framework of Floquet's theory, driving a solid with an intense electromagnetic field that oscillates in time, such as that associated with intense laser light, results in new energy levels appearing at integer multiples of the photon energy [8], making the crystal band structure resemble a ladder of 'sidebands' known as the Floquet–Bloch states (Fig. 1c). Under certain conditions, gaps open up at the crossing between the original bands and the sidebands [9]. A 2009 prediction that such gaps would appear in irradiated graphene marked the birth of Floquet engineering of crystals [10], but the theory found experimental confirmation only three years ago [2]. Zhou *et al.* have now broadened the scope of Floquet engineering by implementing it in a semiconductor.

For real crystals, the first challenge is tracking dynamical changes in the band structure while the solid is being optically excited with intense laser light, and the second is distinguishing the electronic states created by Floquet engineering from those arising from other effects. Zhou and colleagues overcame these challenges by using a technique called time- and angle-resolved photoemission spectroscopy. In doing so, they revealed a marked change in the shape of the valence band of black phosphorus when they irradiated it. They also found that they could manipulate the position and width of the light-induced band gaps by varying the energy, intensity and polarization of the light.

Floquet theory is consistent with many of the authors' experimental findings, such as the dependence of the size of the band gap on the laser fluence (a measure of its energy per unit area). Other effects were, however, unexpected. Zhou *et al*. found that the effects of Floquet engineering were largest when the energy of the photons was nearly equal to the material's band gap. This finding is at odds with theoretical predictions suggesting that this 'resonant' excitation disrupts Floquet–Bloch states by allowing the laser to heat the material [11, 12]. Intriguingly, Zhou *et al*. showed that the band structure changed even when impurities were added to black phosphorus to modify the occupation of the bands and to prevent electrons from traversing the band gap by absorbing the energy of the photons. This indicates that the changes were not a result of the valence band being depleted of charge carriers, so must have arisen through Floquet engineering.

The physical properties of black phosphorus have a key role in the behaviour reported by Zhou and colleagues. The material has a large charge-carrier mobility, a band gap that is easy to modify, and its crystal structure is a puckered honeycomb lattice comprising pairs of layers that are 'armchair' shaped (AC) in one direction and zig-zagged (ZZ) in the other [13]. This asymmetry is known to be responsible for the anisotropic optical properties of black phosphorus, but the authors found that the outcome of Floquet engineering also depends strongly on the relative orientation of the light polarization with respect to these directions. Specifically, the light-induced band gap became substantially narrower when the direction of the laser light polarization was switched from the AC axis to the ZZ axis. This indicates that Floquet–Bloch states can be precisely adjusted by varying the periodicity of the electromagnetic wave in time as well as the periodicity of the crystal in space.

Zhou and colleagues' study demonstrates that near-resonance excitation is a viable strategy for tailoring the electronic properties of crystals, despite the detrimental effects of heating by the laser. The approach is particularly successful when combined with the authors' careful use of impurities to pinpoint the effects of Floquet engineering. This strategy can now be extended to other families of semiconductor and insulator, such as transition metal dichalcogenides, group IV chalcogenides, lead-halide perosvkites and correlated oxides.

Aside from the possible technological advantages of optically controlling the electronic properties of solids in time, the authors' advance could also motivate fundamental research designed to implement quantum mechanical models in systems that can be easily tuned. Such efforts are typically undertaken in laser-controlled lattices of ultracold atoms, but solid-state systems offer a more versatile experimental platform. Zhou and colleagues' observation that Floquet–Bloch states are influenced by the crystal lattice symmetry of black phosphorus represents an example of the exotic electronic phases that emerge when optical perturbation is combined with solid-state materials.

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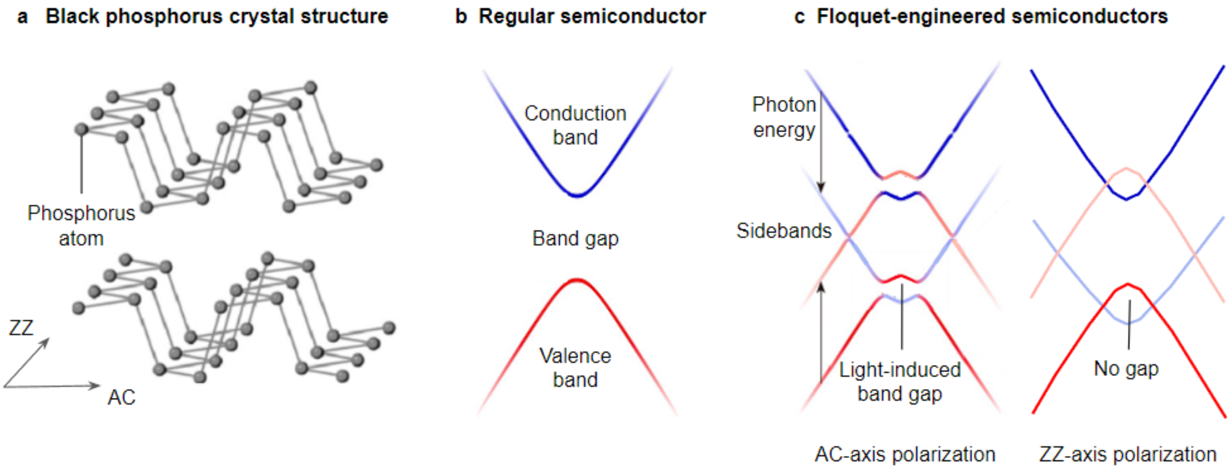

Figure 1 | Modifying the electronic properties of black phosphorus. a, Black phosphorus is a semiconductor material with a bilayer crystal structure that is 'armchair' shaped (AC) in one direction and zig-zagged (ZZ) in the other. **b**, The energies of electrons in a regular semiconductor are restricted to a valence band and a conduction band, with a 'band gap' in between. **c**, Zhou *et al.* irradiated black phosphorus and showed that the light induced new energy levels to appear at integer multiples of the photon energy, creating 'sidebands', as well as band gaps at the crossing between the original bands and the sidebands. These sidebands appeared when the light was polarized in the AC direction only, not in the ZZ direction. This type of modification is known as Floquet engineering, and it can be used to control the transport of electrons in a material and realize new electronic phases. (Adapted from Figs 1 and 4 of ref. 5.)

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