Coherent manipulation of single spins in semiconductors

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During the past few years, researchers have gained unprecedented control over spins in the solid state. What was considered almost impossible a decade ago, in both conceptual and practical terms, is now a reality: single spins can be isolated, initialized, coherently manipulated and read out using both electrical and optical techniques. Progress has been made towards full control of the quantum states of single and coupled spins in a variety of semiconductors and nanostructures, and towards understanding the mechanisms through which spins lose coherence in these systems. These abilities will allow pioneering investigations of fundamental quantum-mechanical processes and provide pathways towards applications in quantum information processing.

In the past few decades, the application of nuclear magnetic resonance and electron spin resonance to large spin ensembles has yielded substantial information on spin dynamics in semiconductors. Experimental advances since the 1990s have allowed researchers to increase their control over single charges, providing a pathway for studies of single spins. Early experiments on single spins confined in semiconductor quantum dots highlighted the opportunity for controlling individual quantum states in a solid.

When quantum information processing became a realistic prospect in the late 1990s, Daniel Loss and David DiVincenzo proposed a quantum computing scheme based on spins in quantum dots[1], and Bruce Kane developed a proposal for a silicon-based quantum computer[2]. It was apparent from these and other theoretical concepts that, in a future quantum computer, the spins must be initialized, manipulated and read out one by one[3]. At about the same time, other researchers were independently developing 'toolkits' of sensitive spin-manipulation techniques to investigate fundamental quantum-mechanical processes in nanostructures such as decoherence on the atomic scale. Ultimately, around the start of this century, spintronics emerged[4], a field that seeks to encode classical information in the spin state of electrons. Both spintronics and quantum information processing have been major driving forces towards the control of single-spin systems.

Here we review experimental progress towards full control of the quantum states of single and coupled spins in different semiconductor systems. We also discuss the mechanisms that lead to the loss of spin coherence in these systems.

Single spins in semiconductors

Single-spin systems in semiconductors broadly fall into two categories: atomic impurities and quantum dots. Atomic impurities are routinely added to semiconductors to control the electrical properties (doping). When the concentration of impurities is very low, the possibility of addressing individual impurities arises. Atomic impurities may have nuclear spin, or they can act as a potential trap for electrons or holes. Often they do both, as in the case of phosphorus in silicon. If two or more impurities are present, or if there is a combination of impurities and lattice defects such as a vacancy, more complicated 'centres' can be formed that often have excellent properties for single-spin studies. One prime example is the nitrogen–vacancy (N–V) colour centre in diamond, which consists of a substitutional nitrogen atom next to a missing carbon (the vacancy) (Fig. 1). This N–V centre has a paramagnetic electron spin and a strong optical transition at a visible wavelength, which allows optical imaging of single spins.

Quantum dots, by contrast, behave like atoms in many ways, but they are fabricated in the laboratory. By engineering the electronic band structure, reducing the size of the semiconductor crystal in one or more dimensions, or applying electric fields, charge carriers can be confined to a small region of the crystal. If the region is roughly the same size as the wavelength of the charge carrier, the energy levels will be quantized as in real atoms. Many atomic properties, such as shell structure and optical selection rules, have analogues in quantum dots, giving rise to their nickname 'artificial atoms'[5–7]. In contrast to real atoms, however, quantum dots allow flexible control over the confinement potential and tend to be easier to excite optically. Quantum dots with large tunnel coupling (that is, strong overlap of their electronic wavefunctions) can form 'artificial molecules'. Such covalent bonding transforms the single-dot orbitals into molecular-like orbitals that span both quantum dots. As a consequence, spins in neighbouring coupled quantum dots overlap strongly and will form two-particle wavefunctions such as spin singlet and triplet states[8].

Quantum dots come in various sizes and in a range of materials. Here we mainly focus on the two types of quantum dot in which coherent dynamics have been observed at the single-spin level. In the first type, confinement is achieved through the application of electric fields, and measurements typically involve the transport of charge carriers through the device. Quantum dots with a tunable number of electrons are routinely fabricated from a two-dimensional electron gas (2DEG) that confines the charge carriers to a plane. Confinement in the remaining two dimensions is achieved by electric fields, either through metallic surface gates above the 2DEG (Fig. 1a) or, if a small pillar has been prepared by etching, from the edges. Gallium arsenide (GaAs) has been the material of choice for many years for these devices, as the high level of control has led to high-purity, flexible devices. More recently, motivated by the detrimental effect of lattice nuclear spins on the coherence times of electron spins, quantum dots have also been studied in materials such as silicon and carbon that can be isotopically purified to obtain a lattice that is free of nuclear spins.

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The second type of quantum dot is defined in the semiconductor during the growth of the crystal. For instance, small islands of semiconductor material such as indium gallium arsenide (InGaAs) can be created within a matrix of a semiconductor with a larger bandgap, such as GaAs (Fig. 1b). The difference in bandgap confines charge carriers to the island. Once the material is grown, the bandgap profile is fixed. However, changes to the overall potential, and potential gradients on top of the bandgap profile, can be induced by electric or magnetic fields. Another example of growth-defined dots is nanocrystal quantum dots, whose small size confines charge carriers. Double dots can be formed in nanocrystal dots by growing shells of different materials around the core.

Optical transitions in this second type of quantum dot typically have a large oscillator strength, and many studies use only optical techniques. Recent years have also seen the advent of hybrid systems, in which both electrical transport and optical excitation and detection are possible[9].

Experiments on single spins in quantum dots

In the 1990s, measurements of electron transport through single quantum dots yielded information about spin states[10]. The past five years have seen tremendous progress towards the control of single spins[8]. Single-spin dynamics was first studied in a series of pioneering experiments[11] at the NTT Basic Research Laboratories in Atsugi, Japan, in 2001 that made use of fast voltage pulses on gate electrodes. Toshimasa Fujisawa, Seigo Tarucha and co-workers found that if a transition between two states was forbidden by spin-selection rules, the corresponding decay time (more than 200 μs) was more than four orders of magnitude greater than for transitions not involving a change of spin (about 10 ns). In a second experiment, they made a single electron oscillate coherently between orbitals in neighbouring coupled dots[12]. The orbital ('charge') coherence of this oscillation was found to disappear in just a few nanoseconds, whereas theory was predicting coherence times of several microseconds for the spin degree of freedom[13–15].

In 2004, Leo Kouwenhoven and co-workers at the Kavli Institute of Nanoscience in Delft, the Netherlands, combined the pulse schemes of Fujisawa's group with a fast charge sensor that could tell exactly when an electron was entering or leaving the dot. By making the tunnelling rate of the electron from the dot dependent on its spin state, they could determine the spin state by measuring the charge on the dot over time (Fig. 2a). Two variations of this spin-to-charge conversion were demonstrated to work in single-shot mode[16,17]. Again, relaxation times for a single electron and for two-electron spin states were found to be of the order of a millisecond. A few years later, even longer electron spin relaxation times, of up to a second, were found at magnetic fields of a few tesla by Marc Kastner's group at the Massachusetts Institute of Technology in Cambridge[18].

Coherent control over two-electron spin states

Two electrons in neighbouring quantum dots with a significant tunnel coupling form a two-particle spin wavefunction, which can be a spin singlet or a spin triplet. The energy difference between these states can be described as an effective exchange splitting, $J(t)$. Control over this exchange splitting allows dynamical control of the two-electron spin states. If two electrons with opposite spin orientation in neighbouring dots are initially decoupled, turning on the coupling will result in a precession of the two spins in the singlet–triplet basis. This leads to periodic swapping of the two spin states at integer multiples of the time interval $\pi\hbar/J$ (where $\hbar$ is $h/2\pi$ and h is Planck's constant), whereas the electrons are entangled for intermediate times[1]. In fact, the state swapping occurs for arbitrary initial states of the two spins. This two-spin control, appropriately called a SWAP operation, is an essential ingredient for many proposals for quantum computing with spins in dots[19–21]. If logical quantum bits (qubits) are encoded in more than one spin, control over the exchange splitting is sufficient to build up any quantum gate[22]. The exchange operation has several benefits: the control is fully electrical, the interaction can be turned on and off, and the resultant gate operation times can be very short (less than a nanosecond).

The first step towards the exchange operation was the observation by Tarucha's group[23] of Pauli spin blockade in a double quantum dot. The presence of double-dot singlet and triplet states became apparent when the current was suppressed in one bias direction (Fig. 2c). It was later found that this current blockade can be lifted by fluctuating fields from the nuclear spins that cause mixing of the singlet and triplet spin states[24,25]. In 2005, by using the strength of the exchange interaction to control the mixing, Charles Marcus's group at Harvard University in Cambridge, Massachusetts, demonstrated coherent oscillations of two spins[26]. Although it was not yet possible to probe arbitrary input states, this experiment demonstrated the essence of the SWAP gate.

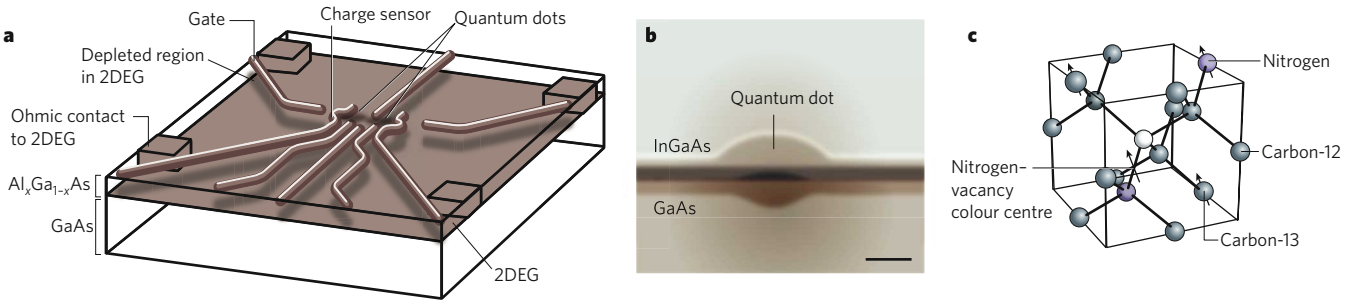

Figure 1 | Single-spin systems. Studies of the coherence of a single spin require a system in which the spin is localized and isolated from environmental disturbances. In semiconductors, such systems are either impurity atoms or quantum dots, which act as artificial atoms. In the three systems on which this article mainly focuses, the level of experimental control is so high that the dynamics of a single spin can be studied and manipulated. **a**, A quantum dot defined in a two-dimensional electron gas (2DEG). The electrons are confined in the third dimension by electric fields from the surface gate electrodes. Electron spins can be manipulated using magnetic resonance or a combination of electric fields and a position-dependent effective magnetic field. Interactions between spins in neighbouring tunnel-coupled dots are mediated by the exchange interaction. These quantum dots are typically measured at temperatures below 1 K. **b**, A quantum dot defined by growth. The semiconductor of the island has a smaller bandgap than that of the surrounding matrix, thereby confining charge carriers to the island. Spins can be created and controlled optically. Additional gates can be used to apply an electric field to the structure to change the number of carriers on the quantum dot. Measurements are typically carried out at around 4 K. Scale bar, 5 nm. **c**, A nitrogen–vacancy (N–V) colour centre in diamond, consisting of a substitutional nitrogen atom next to a missing carbon atom. The N–V centre (in the negatively charged state) comprises six electrons that form a spin triplet in the electronic ground state. Strong optical transitions to excited states, in combination with spin-selection rules, allow optical initialization and read-out of the electron spin. Coherent control of the spin has been demonstrated with high fidelity at room temperature using magnetic resonance. The N–V centre interacts with nearby electron spins by means of magnetic dipolar coupling, and through hyperfine interaction with nearby nuclear spins. Also, non-local coupling between N–V centres may be established by using the optical transition; photons then act as mediators of the interaction.

Single-spin rotations

A year after the coherent two-spin experiments, the Delft group, now headed by Lieven Vandersypen, demonstrated single-spin control[27] through magnetic resonance. In this technique, an oscillating magnetic field is applied perpendicular to the static magnetic field. When the frequency of the oscillating field is matched to the energy difference of the two spin states, the spins are rotated coherently.

Although electric fields do not couple directly to the spin, a coupling between the two can be mediated through a position-dependent effective magnetic field. By 'shaking' the electron in this field gradient, an oscillating effective magnetic field is imposed on the electron that can coherently rotate the spin (see, for example, ref. 28). A few examples of this approach have already been demonstrated in a quantum dot by exploiting a gradient in the nuclear spin polarization[29], a field gradient from a micromagnet[30], and the spin–orbit coupling[31]. In the last case, coherent control has been achieved on a timescale similar to that obtained with magnetic resonance (about 100 ns for a single rotation). In comparison to magnetic resonance, electrical control has the important advantage that it allows spins to be easily addressed locally, because electric fields are much easier to confine to small regions of space than magnetic fields.

Experiments on optically measured quantum dots

The physics of optically measured quantum dots is very similar to that of those studied electrically, but the experimental techniques differ markedly. Experiments on quantum dots in group III–V and group II–VI semiconductors, such as InGaAs dots in a GaAs matrix, make use of optical-selection rules in these materials. Shining circularly polarized light onto the material excites electron–hole pairs with specific spin. This has become a standard method for exciting packets of spin-polarized electrons in semiconductors and studying their coherent behaviour[32].

In a quantum dot, the same technique applies but with limited space for charge carriers. With proper tuning, the number of excited electron–hole pairs in the dot can be limited to one. In this way, a single electron and single hole can be created with well-defined spin states, in addition to any permanent charge carriers in the dot. The spin-selection rules also work the other way: when an electron–hole pair recombines, the polarization of the emitted photon tells us what the spins of the electron and the hole were. Optical-selection rules thereby allow the initialization and read-out of the spin states (Fig. 2d).

Optical techniques have been used to probe the stability of electron spins. In 2004, Jonathan Finley and co-workers at the Walter Schottky Institute in Munich, Germany, optically pumped electron–hole pairs that had a specific spin orientation into a large number of quantum dots. They then removed the holes by rapidly changing the electrical potential of the dots[33]. After a variable time, they reinserted a hole into each dot to allow recombination, and monitored the polarization of the emitted photons, which reflects the spin of the captured electrons. In these ensemble measurements, the electron spin could be found in the same orientation even after 20 ms. Finley and co-workers have recently repeated the spin relaxation measurements for single holes[34]. For a long time, it was thought that these hole spins would lose their orientation quickly as a result of strong spin–orbit coupling in the valence band. However, Finley's data pointed to very long hole-spin relaxation times of up to 300 μs, as predicted by a recent theory from Loss and co-workers at the University of Basel, Switzerland, that takes into account the confinement potential and strain[35]. Future experiments will seek to obtain coherent control of the hole spin state and determine the spin coherence time.

The spin orientation of electrons can also be inferred from the Kerr effect, in which the linear polarization of an incident laser beam is rotated in proportion to the spin polarization of electrons. This powerful technique has become a standard method for studying spin dynamics in semiconductors. It has recently been extended to the single-spin limit by the group of David Awschalom at the University of California, Santa Barbara[36], and subsequently by the group of Atac Imamoglu at ETH Zurich, Switzerland[37]. With this single-spin sensitivity, time-resolved observation of the precession of a single spin in a magnetic field has been achieved[38].

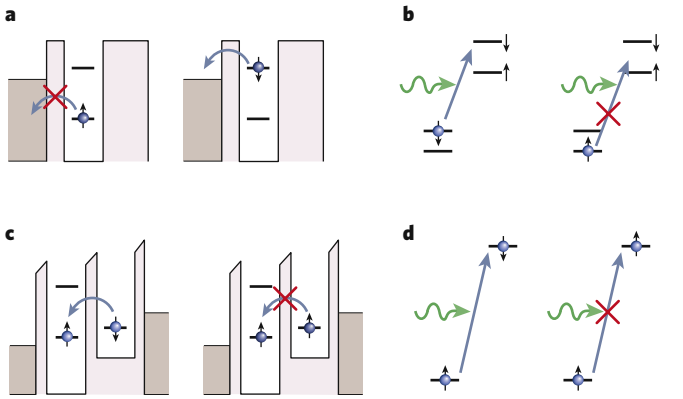

Figure 2 | Single-spin read-out. Studying a single spin is difficult because the magnetic moment of a spin is very small. Several spin read-out techniques have been developed in which the spin information is transferred to quantities that are more easily measured, such as electric charge or the polarization of light. This conversion requires that a transition between two states depends on the initial spin state; several examples of such transitions that are used in experiments are shown. **a**, **b**, Conversion of spin-state information into electric charge or photons by exploiting the energy difference between spin states. In **a**, an electron can tunnel from the quantum dot to the reservoir only if it is in the spin-down state. Measurement of the charge on the dot yields the spin state. **b**, A colour centre or quantum dot is optically excited and subsequently emits a photon only if it is in the spin-down state. The laser light is not resonant for the other spin state. Using a sensitive photon counter, the spin state can be determined after several optical cycles[65]. **c**, **d**, Spin read-out by spin-selection rules. The Pauli principle forbids two electrons with the same spin orientation to occupy a single orbital. Therefore, if one electron occupies an orbital, a second electron cannot enter if it has the same spin. Transitions that conserve spin (such as tunnelling and electric dipole transitions) can thus be blocked for certain spin states, hence the name 'Pauli spin blockade'. **c**, In a double quantum dot, the transition from the right dot to the left dot is blocked if the two electrons involved have the same spin. The second electron needs to go into a higher orbital, which is energetically not available. **d**, Circularly polarized laser light excites electrons with a certain spin orientation out of the valence band to the lowest orbital in the conduction band in a quantum dot. If an electron with the same spin orientation is already present in that orbital, the transition is forbidden.

Optical techniques also allow the coherent manipulation of spins. One method that has been proposed in the context of quantum information processing makes use of Raman transitions of spins in a microcavity[39]. Alternatively, single spins may be manipulated using the a.c. Stark effect[40], in which an intense laser pulse at a frequency slightly below the optical transition renormalizes the energy of the optical transition. When circularly polarized light is used, only one of the two spin states is affected by the laser pulse, resulting in an energy shift between spin up and spin down. This shift, known as the a.c. Stark shift, acts as an effective magnetic field along the light propagation direction; the magnitude of this field depends both on the detuning of the laser with respect to the optical transition and on the intensity of the pulse. Awschalom's group recently used the a.c. Stark effect to manipulate a single electron spin[41]. Short laser pulses were shown to induce rotations of the spin over an angle up to 180° in a time interval as short as 30 ps. This is about three orders of magnitude faster than any magnetic or electrical manipulation on single spins in quantum dots achieved thus far and is an important improvement in the context of quantum error correction.

Loss of spin coherence in quantum dots

In this discussion, we distinguish between energy relaxation processes (typically characterized by a spin relaxation time, T_1) and phase relaxation processes (characterized by a spin coherence time, T_2). By definition, T_1 sets a bound on T_2 such that $T_2 \leq 2T_1$. For successful quantum error correction, T_2 must exceed the spin manipulation time by several

orders of magnitude. A third timescale, T_2^*, is often used to denote the time after which the electron phase is randomized during free evolution. If the spin manipulation time is less than T_2^*, the fidelity of the control can be severely reduced, which adds a second requirement for quantum information application.

Quantum coherence of spins in semiconductor quantum dots is limited by coupling to other degrees of freedom in the environment. Electrons or holes can couple to states outside the quantum dot (Fig. 3a), and fluctuations in the electrical potential can indirectly lead to decoherence of the spin (Fig. 3b).

The absence of inversion symmetry in the lattice and the presence of electric fields or confinement asymmetries lead to coupling between spin and the motion of electrons (Fig. 3c). This spin–orbit coupling mixes the spin eigenstates. Except for small energy splitting, spin relaxation in group III–V quantum dots is typically dominated by spin–orbit coupling in combination with phonon emission that takes away the excess energy. Measurements of the spin relaxation time in many different devices have confirmed the theoretically predicted dependence on magnetic field and temperature[8]. However, the phase of localized electron spins is much less sensitive to the spin–orbit coupling[15]. The spin decoherence time, T_2, of electrons in group III–V quantum dots is typically limited by the nuclear spins (Fig. 3d).

The hyperfine interaction with the nuclear spins has two effects on the electron spin[42]. First, each nuclear spin exerts a tiny effective magnetic field on the electron spin. The sum of the fields of the roughly 1 million nuclear spins in a quantum dot, known as the Overhauser field, can be large (up to several tesla) if the nuclear spins all point in the same direction. The magnetic moment associated with the nuclear spins is small, so the thermal polarization is tiny even at millikelvin temperatures. However, the Overhauser field still fluctuates around this tiny average. A simple estimate tells us that for n nuclear spins, the statistical variation is of the order of $\sqrt{n}$, which corresponds to an effective magnetic field of a few millitesla for a typical group III–V quantum dot. Such a field causes the phase of the electron spin to change by π in roughly 10 ns. A measurement usually lasts tens of seconds, during which time the nuclear spins change orientation many times. One measurement therefore yields an average over many different nuclear spin configurations, leading to random phase variations between successive measurements. This leads to a dephasing time, T_2^*, of about 10 ns (refs 13, 14), a timescale that was first verified in optical experiments[43,44].

The Overhauser field changes slowly relative to the spin manipulation time, because the nuclear spins interact weakly both among themselves and with their surroundings. For example, recent optical experiments indicate that, in certain circumstances, nuclear spin polarizations in quantum dots can sometimes survive for up to an hour[45]. Simple spin-echo techniques can therefore be used to eliminate the effect of the quasi-static Overhauser field, provided that the electron spin can be manipulated on a timescale that is short compared with the spin precession time in the Overhauser field. There are two approaches to achieving this. The most straightforward is to make the manipulation time very short, either by using the exchange energy in two-spin systems or by optical manipulation using the a.c. Stark effect. Alternatively, the Overhauser field can be made smaller. One way of doing this is to narrow the distribution of the Overhauser fields by bringing the nuclear spins to a specific and stable quantum state[46–48]. Another option is to polarize all of the nuclear spins. Nuclear spin polarizations of up to 60% have been measured in quantum dots[44,49], but it is anticipated that a polarization far above 90% is required for a significant effect[50].

Another effect of the nuclear spins on the electron spin coherence comes from flip-flop processes[42], in which a flip of the electron spin (say from spin up to spin down) is accompanied by a flop of one nuclear spin (from spin down to spin up). In a first-order process, this leads to spin relaxation (the electron spin is flipped). If the electron spin is continuously repolarized, for example by optical pumping, the nuclear spins will all be flopped into the same spin state. After many such flip-flop events, a significant nuclear spin polarization can arise. This process is called dynamical nuclear polarization. If there is a large energy mismatch between the electron spin splitting and the nuclear spin splitting (because there is an external magnetic field, for instance), this first-order process is strongly suppressed. Second-order processes — in which two nuclear spins exchange their state by two flip-flops with the electron spin — are still possible. Through these virtual flip-flops, the nuclear spins can change orientation much faster than is possible with the magnetic dipolar interaction with nearby nuclear spins. This effectively leads to spin diffusion. The observed T_2 of about a microsecond is thought to be compatible with this picture, although firm experimental evidence isolating the different causes of nuclear field fluctuations is still lacking[8].

Spins of holes in the valence band of group III–V semiconductors have wavefunctions that have zero weight at the position of the nuclei, so the contact hyperfine interaction should not affect the coherence of holes. Richard Warburton and co-workers have recently initialized single hole spins in quantum dots at zero magnetic field[51] by adapting a procedure that was previously demonstrated on single electron spins[52].

The detrimental effect of the nuclear spins on the coherence in quantum dots has also spurred research into materials systems that contain

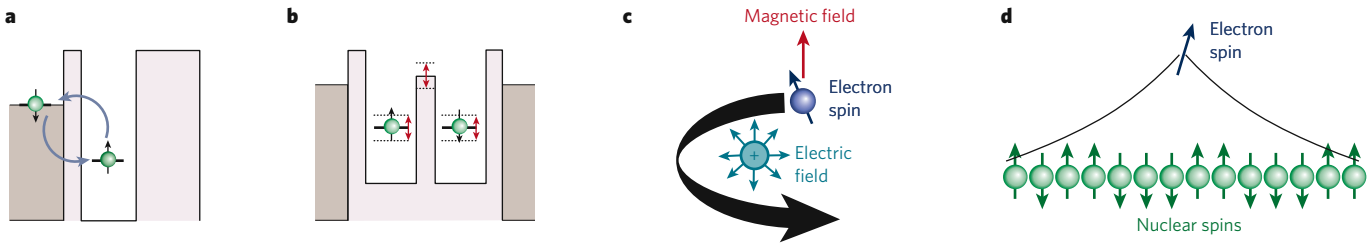

Figure 3 | Spin decoherence in quantum dots. The coherence of spins in quantum dots is affected by several mechanisms. **a**, Co-tunnelling. Although energy conservation forbids first-order tunnelling of charge carriers to states outside the dot at higher energy, second-order tunnelling processes (co-tunnelling) — in which a charge carrier tunnels from the dot to a reservoir and is replaced by a different charge carrier from the reservoir — are allowed[83]. The charge carrier from the reservoir will in general not be in the same spin quantum state as the one that first occupied the dot, so this process causes spin coherence to be lost. By increasing the energy difference between the dot and the reservoir states, and also making the tunnel coupling between them small, co-tunnelling processes can effectively be suppressed. **b**, Charge noise. Fluctuations in the electrical potential (charge noise) do not couple directly to the spin but can influence the spin dynamics indirectly. For example, the energy splitting, J, between singlet and triplet states in a double quantum dot depends strongly on the height of the tunnel barrier between the dots and the alignment of the levels in the dots. Any changes in the electrostatic environment can lead to changes (indicated by red arrows) in the barrier height and level misalignment, which modify J and therefore induce random phase shifts between the singlet and triplet states[84,85]. Charge switching and gate-voltage noise are two possible causes for such changes[86]. **c**, Spin–orbit coupling. The coupling between the spin and orbital of charge carriers leads to mixing of the spin states in a quantum dot. As a result of this coupling, any disturbance of the orbitals leads to phase fluctuations of the spin state. **d**, Nuclear spins. The charge carriers in the dot couple to the nuclear spins of the host material. These nuclear spins exert an effective magnetic field, and allow spin flip-flop processes that lead to spin relaxation and decoherence.

fewer or no nuclear spins. Two prominent examples are carbon and silicon, which can both be purified isotopically to yield a zero-spin lattice. Single and double quantum dots have been studied in these systems for several years, with control now approaching the level of GaAs systems[53–57]. Experiments probing the spin coherence times in silicon and carbon quantum dots are expected in the near future.

Coherent control of magnetic dopants

In contrast to non-magnetic nanostructures, individual magnetic-ion spins can be doped within group II–VI semiconductor quantum dots and measured through their exchange coupling to the electrons and holes. Statistically, it is possible to find an ion-impurity spin that is randomly doped at the centre of a single quantum dot. Using self-assembled quantum dots consisting of cadmium telluride and zinc telluride, Lucien Besombes *et al.*[58] isolated an individual paramagnetic manganese ion within individual dots. The micro-photoluminescence spectrum of an exciton (an electron–hole pair) was observed to split into six equally spaced lines owing to the quantization of manganese with a spin of 5/2. The next step was to apply a gate bias and change the charge state of the dot by pulling in either one electron or one hole. In this case, the coupling between the manganese ion and either the hole or the electron splits the six-line spectrum into twelve lines[59], in agreement with models based on spin exchange interactions within diluted magnetic semiconductors[60].

Dilute doping of group III–V semiconductors with manganese ions produces a unique environment for single-ion spin physics. Because the manganese states rest within the bandgap, it is not necessary to isolate a single manganese impurity within a single quantum dot, as the ions themselves act as recombination centres. In analogy with atomic physics, they form their own 'ideal' quantum dot states. The spin state of the manganese ion is independent of the electronic exciton and can be read out directly from the polarization of the manganese neutral acceptor emission[61]. In the absence of an applied magnetic field, the orientation of the magnetic ions is controlled by a dynamic interaction with optical injected electron spins. This mechanism is similar to dynamic nuclear polarization between electron spins and nuclear spins through the hyperfine interaction. After the manganese ions are partially aligned, a mean field interaction between the manganese ions, mediated by heavy hole states, favours a parallel alignment of the magnetic moments, creating a zero field splitting of the manganese-ion spins. The measurements indicate that single manganese-ion spins have longer coherence times than their electronic counterparts, motivating further studies of coherent control of manganese spins in semiconductors.

Coherent control of spins in diamond

Spins in diamond have recently become a leading candidate for solid-state quantum control, owing to their long coherence times and strong optical transitions, as well as the enormous progress that has been made in the growth and engineering of diamond as a unique semiconductor[62]. Ensemble experiments in the late 1990s indicated that spins of impurity centres in diamond can have very long coherence times, even at room temperature[63]. A more recent series of experiments demonstrated high-fidelity coherent control over electron spins and nuclear spins at room temperature at the single-spin level.

Most work is focused on the N–V centre (Fig. 1c) because of its attractive properties for quantum coherent operation[62]: the N–V centre's electronic-level structure allows both optical cooling and optical read-out of the electron spin. In 1997, following progress in confocal microscopy and the availability of diamond samples with a low concentration of N–V centres, Jörg Wrachtrup and co-workers reported the first study[64] of a single N–V-centre spin. In the seven years that followed, Fedor Jelezko, Wrachtrup and co-workers demonstrated single-shot read-out of the N–V electron spin at 1.5 K using resonant laser excitation[65] (Fig. 2b), coherent control of a single spin using magnetic resonance[66], and a two-qubit gate involving the host nuclear spin of the N–V centre[67]. In a parallel development, materials research achieved the growth of diamond using the chemical vapour deposition (CVD) method. With CVD, control over the number of impurity atoms increased enormously, resulting in the availability of very clean layers of diamond. Moreover, diamond nanocrystals of various sizes that contain N–V centres or other colour centres can now be grown[68]. These crystals have the advantage that they are small and light, and can be positioned onto other materials. This may facilitate interfacing spins in diamond with optical components such as fibres and cavities[69].

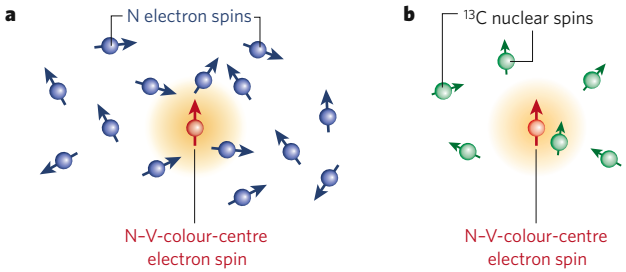

Figure 4 | Control and coherence in diamond. Spins in diamond are unique among solid-state systems in that single spins can be coherently controlled with high fidelity even at room temperature. The amount of impurity spins has a strong influence on coherence properties. **a**, Schematic representation of a nitrogen–vacancy (N–V) centre surrounded by electron spins of nitrogen impurities. In this case, the coherent dynamics of the N–V-centre spin are determined by the nitrogen atom's electron spins; the influence of nuclear spins is negligible because their magnetic moment is three orders of magnitude smaller than that of the electrons. Because an electron spin bath is easily tunable with a magnetic field, these systems allow detailed investigation of spin decoherence models and tests of quantum control in a tunable spin bath[73]. **b**, Schematic representation of an N–V centre surrounded by nuclear spins of carbon-13 in an ultrapure diamond. Nuclear spins that are much closer to the N–V centre than the others (within the orange sphere) stand out from the rest of the nuclear spins and can be individually distinguished and controlled[78].

The coherent evolution of impurity spins in diamond is dominated by magnetic interactions (Fig. 4). Whereas in quantum dots many nuclear spins have identical coupling to the electron spin, the highly localized nature of an impurity spin makes the magnetic interactions strongly dependent on the distance between spins. Other couplings such as a spin–orbit interaction have a much weaker effect at impurities than in quantum dots because of the much larger electronic-level splittings.

For impurity concentrations down to about 1 p.p.m., magnetic dipolar coupling between impurity electron spins dominates spin coherence in diamond[63,70] (Fig. 4a). In some cases, two spins are much closer to each other than to the rest of the spins, in which case the dynamics become a simple two-spin evolution. One example is an N–V centre in close proximity to a single nitrogen impurity, in which case the nitrogen spin can be polarized and read out through the N–V centre[71,72].

In general, an N–V centre will be coupled to many nitrogen spins, which can be viewed as a 'spin bath'. Even in this case, the spin of the N–V centre can be controlled with high fidelity, allowing investigation of decoherence induced by the spin bath. Analogous to an electron spin in a quantum dot that is coupled to a nuclear spin bath, the nitrogen electron spins influence the evolution of the N–V centre in two ways. First, the magnetic dipolar field from the bath shifts the energy splitting between the N–V centre's spin states (analogous to the Overhauser field in quantum dots). It has recently been shown[73] that the interactions within the bath, leading to the fluctuations of the dipolar field, are strongly suppressed when a magnetic field is applied, in which case single-spin flips do not conserve energy. The second effect of the spin bath comes from flip-flop processes with the N–V electron spin. In contrast to a nuclear spin bath (where the spin splitting is tiny), the electron spin bath can be tuned into energy resonance with the N–V-centre electron spin. Resonant flip-flop processes then provide a strong additional decoherence path, leading to much shorter spin coherence times.

Because the spin coherence in diamond is dominated by magnetic interactions, it is not strongly temperature dependent, except at low

temperatures and high magnetic fields, at which the bath spins polarize thermally; this occurs for electron spins in a field of 8 T at a few kelvin. Recent experiments on a diamond with a high concentration of nitrogen electron spins show that when all of the electron spins are thermally polarized, the fluctuations in the spin bath are completely frozen out and the spin coherence time reaches the same high value as in ultrapure diamond[74].

In most diamonds studied thus far, the positions of the impurity spins were random, affected only by growth parameters. In 2005, single N–V centres were deliberately created by ion-implanting nitrogen[75,76]. This approach may lead to fundamental studies of spin coherence in diamond by designing different spin environments, as well as allow pathways for engineering spin qubits into future scalable quantum information-processing systems.

In diamonds where the impurity concentration is very low (below 1 p.p.m.), the presence of the few nuclear spins of the carbon-13 isotope (which has a natural abundance of 1.1%) becomes apparent. These nuclear spins also constitute a spin bath, which limits the N–V centre's coherence time to a few hundred microseconds[70,71]. Because a single N–V spin can be rotated using magnetic resonance in less than 10 ns, more than 10,000 error-free operations can be performed, which is within the commonly assumed threshold for quantum error correction. As in the case of impurity electron spins, if a few nuclear spins are much closer to the N–V centre than the other nuclear spins, their individual coupling to the N–V-centre spin can be detected[77] (Fig. 4b). Mikhail Lukin's group at Harvard University demonstrated that these nuclear spins can be used to store quantum information for much longer than the electron spin's coherence time[78]. The quantum state of the N–V electron spin can be mapped onto, or retrieved from, the nuclear-spin memory through a combination of state-dependent precession of the nuclear spin and fast optical reinitialization of the N–V-centre spin. Experiments have shown that even on a 20-ms timescale, the nuclear spin shows no sign of decoherence[78], suggesting that nuclear spins may have coherence times of seconds or even longer. By extending the control to multiple nuclear spins, a small quantum memory can be created that will operate at room temperature.

As well as long spin coherence times, N–V centres also have a strong optical transition. Lifetime-limited optical linewidths have been observed[79], and the optical preparation of a coherent superposition of spin states has been demonstrated in coherent population trapping experiments on single N–V centres[80]. These results may, in the future, be extended to dynamical all-optical control of single spins in diamond.

Optical control opens the door to schemes for creating entangled states of spins at large distances[81], in a similar way as was recently demonstrated for atom traps[82]. Such long-distance entanglement is also a crucial ingredient for applications in quantum communication.

Outlook

After enormous progress in recent years, researchers can now initialize, control and read out single spins in semiconductors in a few specific systems, with others likely to be added to the list within a few years. The coherence times of electron spins in materials with few or no nuclear spins, as well as the coherence times of hole spins, are expected to be much longer than for electron spins in group III–V semiconductors. Carbon-based materials, such as carbon nanotubes and graphene, are being heavily investigated; diamond has already shown its potential for quantum coherence studies (at room temperature) with a level of single-spin control that meets the quantum information-processing error-correction threshold.

The emphasis of this research area will shift in the coming years from single-spin control to the creation and manipulation of entangled states of two or more spins, as well as the development of sophisticated quantum control techniques. This will lead the way for more studies on fundamental issues such as decoherence and the role of measurements in quantum mechanics. At the same time, protocols for quantum information processing may be tested in systems with few spins. These are exciting times for 'spin doctors', as they continue to drive a rapidly expanding field that has a promising future. ■

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