processing temperature. Cacialli and co-workers patterned poly(*p*-phenylene vinylene) (PPV), an electroluminescent polymer that is increasingly being used in polymer light emitting diodes and photovoltaic cells.

Although the future of thermochemical lithography seems promising, a number of challenges still have to be addressed. Like other scanning probe techniques, thermal patterning can modify a surface, but not necessarily the entire thickness of the film. The sub-surface heat conduction is largely isotropic, and for thicker films this may result in larger features with overhanging profiles that are undercut during removal of the untreated polymer or subsequent processing steps. The mechanical collapse of nanoscale resist features with high aspect ratios, often due to capillary forces associated with wet processing, has also been a challenge. Line edge roughness[10] — due to spatial and temporal temperature fluctuations, resist chemistry and other chemical processes — could also limit the ultimate resolution of thermochemical lithography.

Throughput will be another significant challenge, and although thermochemical lithography is unlikely to compete with optical methods in this regard, write speeds have increased from less than a micron per second to more than a millimetre per second[9]. It remains to be seen if the ultimate limit on the write speed will depend on the reaction rates of the material being patterned or on the thermal transport properties of the overall system.

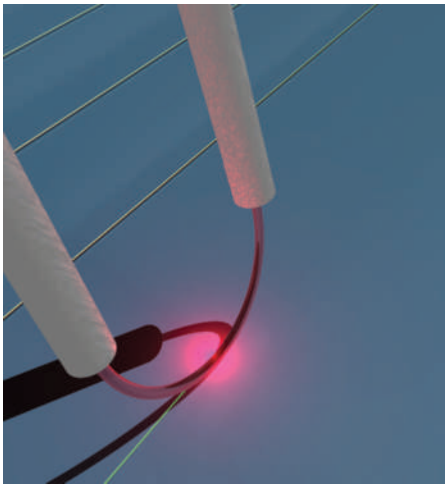

Figure 1 | Artist's impression of thermochemical lithography. Cacialli and co-workers were able to produce features with line widths as small as 28 nm by scanning a heated wire over a polymer surface[7]. The wire, which is made of platinum and rhodium, has a diameter of 5 µm and is heated by passing a current through it.

A robust system for thermochemical patterning will also require tight tolerances on a number of parameters. For example, the contact force between the tip and the sample influences not only the thermal heat transfer but also the mechanical or thermomechanical deformation of the film. Atomic force microscopy systems can maintain precise force feedback control, but only if the tip geometry, spring constant and angle of attack of the probe are maintained throughout the duration of the scan. The probe temperature will also need to be precisely calibrated and controlled, as reaction rates are often exponentially related to temperature. Other practical aspects to explore include Joule expansion of the material and the effect of wetting films that form between the tip and the sample.

The field of thermochemical lithography is young and holds much promise for patterning unique materials at the nanoscale. Although factors such as the limit on throughput might restrict its usage, its simplicity and applicability to a wide range of materials means that it will find its niche in the nanopatterning tool set. ❐

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SPINTRONICS

Shedding light on nanomagnets

The magnetism of semiconductor nanocrystals can be controlled by shining light on them, which could have applications in information storage and processing.

Igor Žutić and Andre Petukhov

A fridge magnet is a simple example of a non-volatile device, because it does not need power to remain stuck to the fridge door. Its magnetic state, which can be considered as stored information, is maintained indefinitely. Advances in non-volatile magnetic storage, using metal-based structures, have allowed a 1,000-fold increase in the capacity of computer hard drives over the past decade. However, this is only a small indication of the possible advances using magnetic materials. Control of magnetism in a wider class of materials, including non-metallic nanostructures, has the potential to have an even broader impact, dramatically altering the way we process and transfer information[1,2].

Most electronic devices operate by manipulating the charge of the electron. However, in magnetic devices one has to look beyond the charge and focus instead on the spin of the electron and the associated magnetic moment. The spins of a group of electrons will, in general, point in different directions (for example 'up' or 'down'). A net magnetization results when more of these spins point in one direction than another. Ferromagnets such as iron have a built-in magnetization, and paramagnets develop one when a magnetic field is applied. In antiferromagnets, on the other hand, neighbouring spins point in opposite directions and there is no net magnetization. Controlling the microscopic state of a bulk magnet is a tall

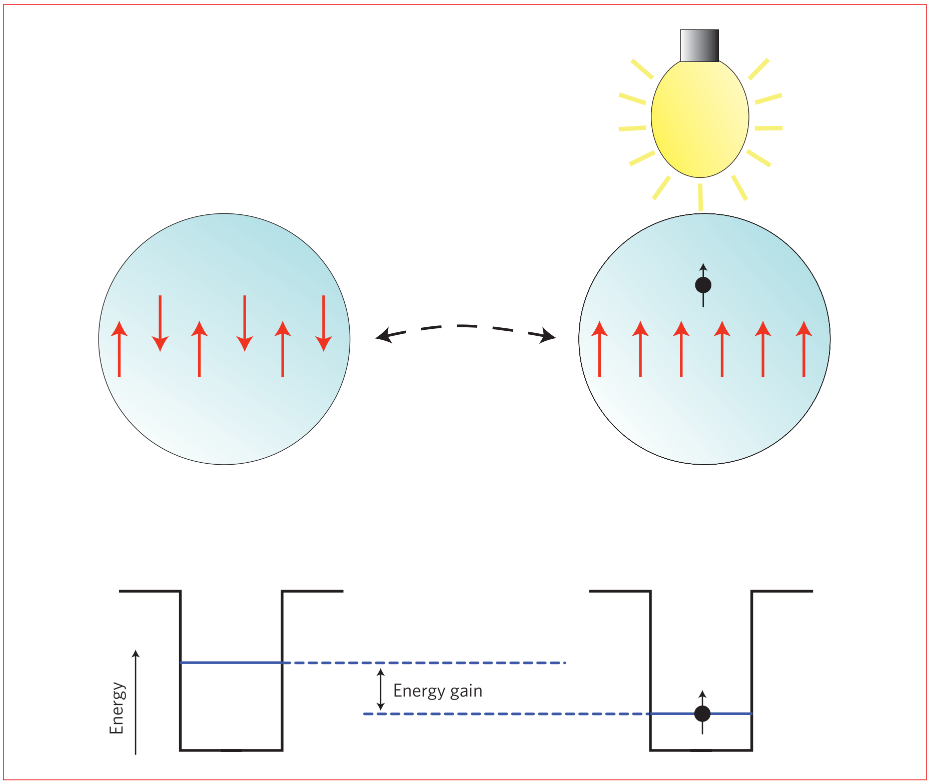

Figure 1 | Carrier-mediated magnetism in ZnO nanocrystals doped with Mn. The spins of neighbouring Mn ions point in opposite directions (top left), even in an applied magnetic field (not shown). The nanocrystal can be represented as a square-well potential, and the spin arrangement has a particular energy level (bottom left). When light from an ultraviolet lamp is applied (top right), the spin of a single photoexcited electron (black arrow) aligns the Mn spins, giving the maximum possible magnetization. This state, which is known as a magnetic polaron, has lower energy (bottom right) than the original state, and the energy difference between these two states can be seen as a red shift in the light emission from the nanocrystal. The original state can be recovered simply by exposing the nanocrystal to air.

challenge. However, on page 681 of this issue, Daniel Gamelin and co-workers at the University of Washington in Seattle demonstrate that a single photoexcited electron can produce a dramatic increase of magnetization in nanomagnets, even at room temperature[3]. Nanomagnets can, it seems, do new tricks.

This new trick was done with solution-processed semiconductor nanocrystals, also known as colloidal quantum dots. These nanocrystals, which typically have sizes of several nanometres, self-assemble over the course of a chemical reaction. They therefore represent a bottom-up approach to building nanostructures, offering inexpensive paths to devices such as solar cells, light emitting diodes and lasers. This type of fabrication can be contrasted with that of epitaxial quantum dots[4–6], which are made by a top-down approach common to conventional electronics. The carriers (electrons and holes) in both colloidal nanocrystals and epitaxial quantum dots are confined in all three dimensions, and therefore are restricted to a set of discrete energy levels. Electrons can make transitions between these levels, emitting or absorbing light as they do, which is why nanocrystals and quantum dots are sometimes called artificial atoms[4]. These materials also have optical, electrical and magnetic properties that depend on their size, in the same way that the tone of a guitar string depends on its length.

Gamelin and colleagues[3] started with pristine ZnO nanocrystals, and doped them to tailor their properties[7,8]. First, magnetic Mn^{2+} dopants replaced some Zn^{2+} ions, maintaining charge neutrality, but introducing five unpaired spins for each Mn^{2+} ion added to the nanocrystal. Charges were then introduced by illuminating the nanocrystals with an ultraviolet lamp, promoting electrons to higher energy levels and leaving behind trapped holes. This photodoping effectively circumvents the problems[8] associated with the more conventional approach of introducing impurities, and has the added benefit that it can be reversed simply by exposing the nanocrystal to air.

Before photodoping, many of the spins introduced by the Mn^{2+} ions displayed antiferromagnetic ordering, and an applied magnetic field of 5 T (which is enormous) was only able to align a small number of these spins. Remarkably, however, a combination of a 5 T field and just one extra photodoped electron per nanocrystal (courtesy of the ultraviolet lamp) was sufficient to align all the spins, thereby producing the maximum possible room-temperature magnetization (Fig. 1). Although photo-enhanced magnetism[1,4] has been demonstrated in quantum dots and much larger Mn-doped semiconductor junctions before, it was limited to cryogenic temperatures (and the junctions required large numbers of photoexcited carriers). How then can we understand the findings of Gamelin and colleagues?

The spin of the photodoped electron is spread throughout the nanocrystal and, like a good-will messenger, mediates a ferromagnetic coupling between all Mn spins, convincing many disgruntled neighbours to get aligned. The magnetic field on its own is, by comparison, less effective, acting like a policeman trying to enforce spin order externally. The collection of aligned spins is analogous to a magnetic molecule with a large magnetization, known as a magnetic polaron[9]. The aftermath of the electron's mediation is a net gain in magnetization, in this case corresponding to a more stable magnetic configuration in a lower energy state (Fig. 1). This is similar to carrier-mediated magnetism in bulk-like systems, where extra carriers can also be created electrically[1] or thermally[10].

What could be next for these 'enlightened' nanomagnets? The reversible control of magnetism demonstrated by Gamelin and colleagues requires a substantial magnetic field, as nanocrystals, similar to atoms with net spin, are too small to support ferromagnetism. However, this is not a fundamental limitation. It may be possible to achieve a finite magnetization in a zero field by doping the nanocrystals with holes rather than electrons, because the spins of holes are more effective in promoting ferromagnetic alignment of impurity spins. Recent results have shown that the addition of both electrons and holes can lead to substantial zero-field magnetization[11]. However, since electrons and holes recombine quickly, on a timescale of nanoseconds, the effect is transient in contrast with the stable electron-mediated magnetism described here[3]. It may also be possible to cause magnetic polarons (Fig. 1) to magnetically interact with each other and pass along spin-dependent information. Finally, other means of manipulating magnetization could be pursued such as changing the nanocrystal shape to shift its energy levels and alter the spin alignment[12].

With these and other nanoscale building blocks in place, one could pursue the more complex goal of processing information, as opposed to just storing it[1]. Indeed, it has been shown that magnetic quantum dots could have an important role in this regard[13]. As a bonus, the nanocrystal work discussed here[3] contributes to the vigorous debate on the origins of magnetism in bulk doped ZnO (ref. 14). In both the bulk and nanoscale cases, there is a direct connection between the presence of carriers and the measured magnetic signal. Charging nanomagnets may thus shed new light on many other magnetic structures. ❐

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BIOMOLECULAR COMPUTING

Molecules that reason

DNA reactions can be used to implement simple logic programs.

Darko Stefanovic

Many recent advances in our understanding of the synthetic capabilities of nucleic-acid-based molecules have been inspired by the dream of harnessing DNA to perform useful computations[1]. On page 642 of this issue, Tom Ran, Shai Kaplan and Ehud Shapiro of the Weizmann Institute of Science continue this trend by using cascading reactions of remarkable speed and complexity to carry out computation in a unique manner[2]. The reactions are physical manifestations of programs in a simple logic programming language.

A continuous theme throughout the six decades of computing research has been automated reasoning. This has been inspired in part by a desire to achieve a hallmark of human intelligence by synthetic means, and in part by the mundane need to prove that the behaviours of complex engineered systems are safe, correct and so on. Although general-purpose theorem provers have remained specialist tools, a restricted form of automated reasoning, called logic programming, has become an important, if not yet mainstream, programming paradigm. First conceived in the early 1970s (ref. 3), it was quickly turned into a practical programming system (Prolog)[4], but it was not given a competitive implementation on electronic computers until 1983 (ref. 5). Shapiro co-authored an influential text[6] on Prolog and its semantics in 1986.

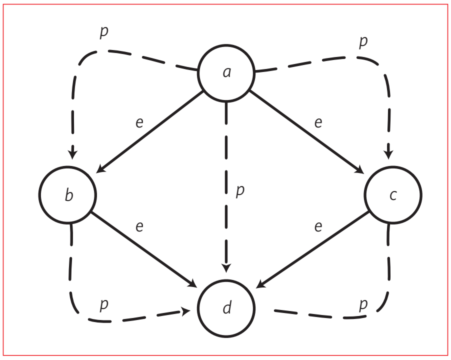

Figure 1 | Model of the logic program $\{e(a,b).\ e(a,c).\ e(b,d).\ e(c,d).\ p(X,Y) \leftarrow e(X,Y).\ p(X,Y) \leftarrow e(X,Z),p(Z,Y).\}$, which describes a directed graph with edges from *a* to *b*, from *a* to *c*, from *b* to *d* and from *c* to *d*. The edge relation *e* is explicitly represented in the program facts. The path relation *p* is implicit in the program rules and is effectively recomputed on each query: there is a (non-empty) path from node *X* to node *Y* whenever there is an edge from *X* to *Y*, or whenever there is an edge from *X* to some *Z* and a path from *Z* to *Y*. For instance, the query $p(a,d)?$, which asks if there is a path from *a* to *d*, is answered in the affirmative by the program.

In logic, a proposition, *p* or *q*, such as 'Socrates is Greek', is a statement that may be true or false. In logic programming we use elementary propositions (or facts) and implications (or inference rules) to answer queries. Inference rules, such as *p* implies *q*, are written $q \leftarrow p$. The right-hand side of a rule can mention multiple propositions to express conjunction: for example, $w \leftarrow p,q,r$ means that *p*, *q* and *r* together imply *w*. Finally, a query, *p*?, such as 'Is Socrates Greek?', is a proposition (or a number or conjunction of propositions) that we seek to prove using the facts and rules in our program. The possible answers are yes, meaning that the proposition(s) in the query have been proven, or no, which means that they could not be proven (which is different from disproving them).

To illustrate this, consider the program $\{a.\ b.\ c.\ d.\ e \leftarrow a,b.\ f \leftarrow e,c.\}$ and the query $d,f?$. In the program *a*, *b*, *c* and *d* are the known facts, and $e \leftarrow a,b$ and $f \leftarrow e,c$ are the rules. The query is a conjunction, so we proceed to prove its two subgoals *d* and *f*. To prove *d* we observe that it is a fact asserted in the program. To prove *f* we observe that it can be reduced to two further subgoals *e* and *c* using a rule asserted in the program. We take up the subgoal *e* and reduce it to *a* and *b*, whereupon all the remaining subgoals, *a*, *b* and *c*, are proved as facts in the program. When no subgoals remain, the proof is complete.

Now consider the program $\{a.\ b.\ c.\ d \leftarrow a.\ d \leftarrow b,c.\}$ and the query *d*?. There are two distinct ways of proving *d*: we can prove the subgoal *a* or we can prove two subgoals *b* and *c*. Sequential implementations of logic