NANOIMAGING

Hot electrons go through the barrier

Hot electrons can be efficiently injected into a semiconductor using a metallic tip that focuses surface plasmons, and can be used to carry out nanoscale chemical mapping.

P. James Schuck

If the energy of a photon impinging on a metal surface is resonant with the frequency of the collective oscillations of free electrons, or surface plasmons, absorption of light is significantly enhanced. Furthermore, if the metal surface is nanostructured, plasmons can be concentrated in specific locations with a precision of around 10 nm. This large absorption of energy generates excited electrons — known as 'hot' electrons — that have far more energy than they would have in standard thermal equilibrium conditions. The ability to concentrate such large amounts of energy in tight spaces has led to a recent surge in plasmon-based hot-electron research and the emergence of initial applications in molecular sensing, infrared photodetection and artificial photosynthesis[1]. In many of these applications, hot electrons are created on a metal surface and then collected into a semiconductor to produce useful work. However, efficiently extracting hot electrons is difficult and so far the best electron extraction efficiencies reported have been in the order of 1%. Writing in *Nature Nanotechnology*, Enzo Di Fabrizio of the King Abdullah University in Saudi Arabia and co-workers in Italy, Germany and the US have now shown that by appropriately concentrating photonic energy at the apex of a metal tip, hot electrons can be extracted with an efficiency of about 30% and used for nanoscale imaging[2].

The motion of a charge carrier through a metal/semiconductor interface is hampered by the presence of a potential energy barrier known as the Schottky barrier (Fig. 1a). The height of the Schottky barrier depends on the electronic properties of the interfacing materials and hot carriers must possess enough energy to overcome it to move from the metal into the conduction band of the semiconductor. A key benefit of many Schottky barrier-based devices is that the height of the barrier is smaller

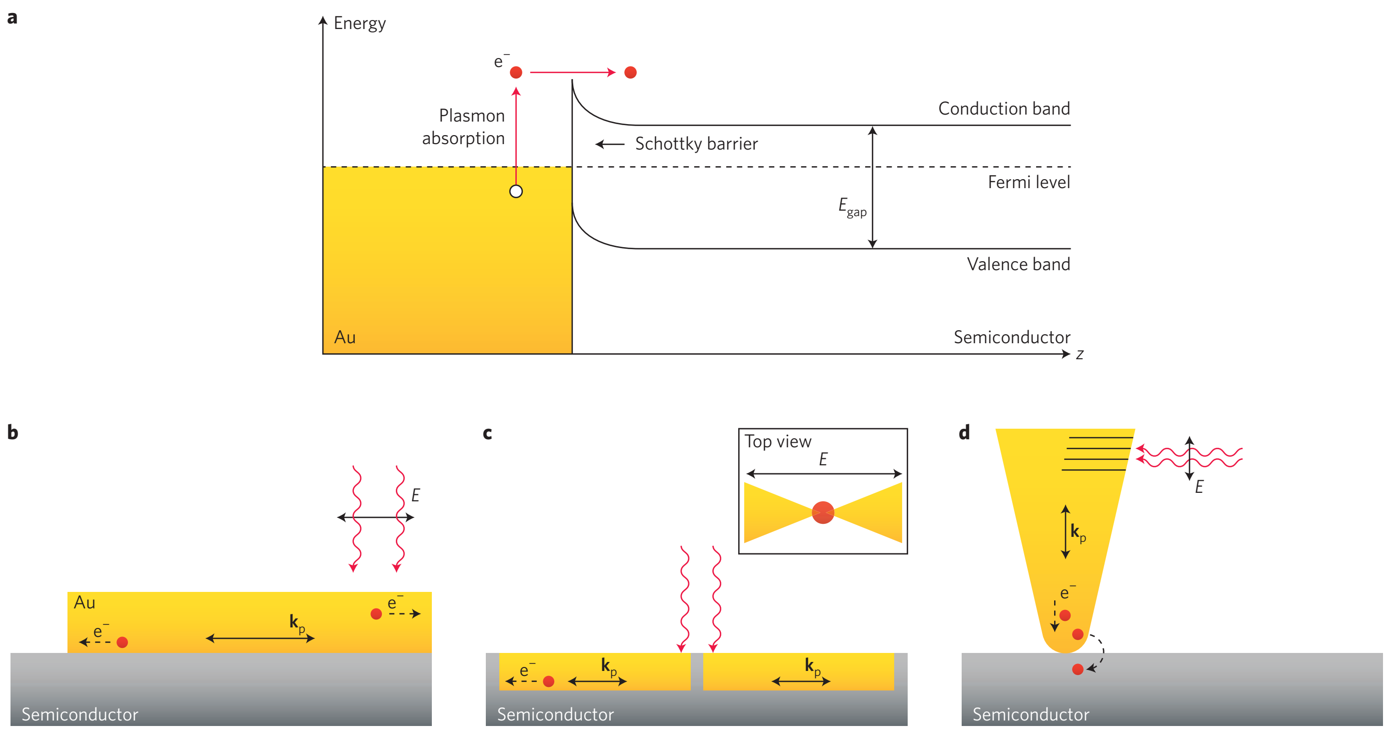

Figure 1 | Hot-electron transfer mechanism from a metal to a semiconductor. **a**, Plasmon absorption in the metal can lead to creation of a hot electron with sufficient energy to overcome the Schottky barrier at the metal/semiconductor interface. For transfer to occur, the hot electron's energy need only be greater than the Schottky barrier, not the bandgap energy (E_{gap}) of the semiconductor. **b**, A planar optical antenna excited by polarized light (red arrows) with an electric field *E* parallel to the interface can induce localized surface plasmon oscillations with an in-plane momentum k-vector $\mathbf{k}_p$. Hot electrons that result from absorption of these plasmons will also tend to have in-plane momentum directed at the antenna sides rather than the interface, making transfer less likely. **c**, Embedding plasmonic nanostructures (inset) directly into the semiconductor enhances hot-electron injection. Even though $\mathbf{k}_p$ is still parallel to the antenna's top and bottom surfaces, hot electrons can be transferred to the semiconductor at the antenna's sides. **d**, Plasmons created on a tapered metal tip in contact with a semiconductor sample are adiabatically compressed at the tip apex, creating hot electrons very near the interface with momentum directed at the interface, leading to highly efficient hot-electron transfer.

than the bandgap of the semiconductor. In such cases, an excited electron does not necessarily need to possess an energy greater than the semiconductor's bandgap to be extracted, as would be the case for normal semiconducting devices.

However, for efficient extraction of hot carriers from a metal, total energy is not the only condition. Once created, the hot carriers must also be moving towards the interface: that is, the hot carrier's momentum must be primarily in the direction perpendicular to the interface, so that the carrier's kinetic energy component in that direction is sufficient to overcome the Schottky barrier. The difficulty of achieving both the energetic and momentum requirements has been the main cause of the generally low quantum efficiency for extracting hot electrons in devices.

As an example, hot carriers generated in planar plasmonic devices often have their momentum oriented in the wrong direction (Fig. 1b). This is because the hot carrier's momentum follows that of the plasmon mode, and plasmons are typically excited by light with the electric field polarized in the plane of the interface[3]. Therefore, hot carriers initially propagate parallel to the interface and not towards it, resulting in a low probability of injection into the semiconductor[4,5]. This problem has recently been circumvented by embedding an optical antenna within the semiconductor, so that hot carriers can be extracted throughout the interfaces at the antenna side walls and not just through the bottom interface[4] (Fig. 1c).

Di Fabrizio and colleagues instead use a tapered conical metallic tip[6,7] that is in close proximity to a semiconductor surface. Far-field light is irradiated onto a nanofabricated grating that is milled into the side of the tip where the light is converted to surface plasmons. These plasmons then propagate towards the apex of the tip. As they travel to smaller and smaller volumes, they are adiabatically compressed and tightly focused at the apex relaxing the momentum conservation constraint[8,9]. The advantages of this approach are threefold: (1) it produces hot carriers with high efficiency and localization; (2) it can control the hot carrier momentum, which is primarily oriented along the tip apex, normal to the tip/semiconductor interface; and (3) it can confine energy in a tight space (~10 nm), making it more likely to extract the hot carriers before they have a chance to scatter[9,10] (Fig. 1d). Therefore, when this type of plasmonic tip is brought into contact with a semiconductor, the conditions are nearly ideal for the transfer of hot carriers. In this way, the researchers are able to achieve hot-electron extraction efficiencies of ~30%, a value comparable to the incident-photon-to-current conversion efficiencies previously seen only in photoelectrochemical reactions[11] and many times greater than what has been achieved in other solid-state devices.

Di Fabrizio and colleagues take advantage of this high efficiency to develop an intriguing imaging tool that tackles the critical and longstanding challenge of mapping chemical information and electronic structure with nanoscale resolution[12]. In their set-up, the optically excited tip is scanned over a sample while the hot-electron transfer current is measured. Because the Schottky barrier is intimately related to the electronic properties of the surface, the researchers managed to map out the local work function and surface charge density of the semiconductor. In particular, the researchers imaged nanoscale patterns of oxidation on GaAs, showing clear material contrast with a lateral resolution below 50 nm, as well as local differences in Ga-ion concentration in implanted GaAs. These experiments demonstrate that hot-electron imaging works well even when there is very little change in topography. It is conceivable that with further optimization, this technique can be pushed to the single-defect level, therefore providing key insights into the relationship between atomic structure and electronic properties, a previously inaccessible realm within nanostructured systems. ❐

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SPINTRONICS

Skyrmions singled out

Single magnetic skyrmions — topological whirls in the magnetization of certain ferromagnets — can be created and manipulated in nanostructures using electrical currents.

Rembert Duine

Spintronic devices based on the current-driven manipulation of magnetization in nanoscale ferromagnets could be used as future memory elements, which will combine low cost, high performance and non-volatility. Examples of such devices include magnetic random access memory[1,2], the magnetic racetrack memory[3], and those based on the manipulation of magnetic skyrmions. Magnetic skyrmions (Fig. 1) are textures of magnetization that cannot be continuously deformed into the uniform ferromagnetic state without causing a singularity, and are therefore topologically protected. They were recently observed in certain ferromagnetic materials[4,5], and their stability, together with their small size and the fact that they can be moved by currents of very small densities[6], makes them attractive as information carriers in memory technology. So far, experimental results on current-driven motion have concerned lattices of skyrmions. However, it is likely that any future technology will be based on the manipulation of individual skyrmions. Writing in *Nature Nanotechnology*, two

Correction

In the version of the News & Views article 'Nanoimaging: Hot electrons go through the barrier' originally published (*Nature Nanotech.* **8,** 799–800; 2013), in ref. 2, the volume number was incorrect. Corrected in the PDF and HTML versions after print 7 November 2013.