Metal surfaces light up

Electromagnetic waves that exist on the surface of thin metal films are being used in novel optical components such as miniature waveguides and perfect lenses, as and explain

Many of us are not at our most alert when we examine our faces in the mirror first thing in the morning. It is therefore not too surprising that few people wonder how that thin metal film on the back of a glass sheet provides such a jaw-dropping image! Our jaws would perhaps drop even further if we were told that by drilling an array of microscopic holes in the metal film our mirror could suddenly become transparent; but this is precisely what recent experiments with metal films have shown.

In addition, researchers have confirmed the startling suggestion that such patterned metal films can act as a "perfect lens". Such a device overcomes the limitations due to diffraction, which prevents conventional lenses from resolving distances shorter than the wavelength of light being used. Although such a lens is an optician's dream, few opticians would believe that it could be manufactured from a seemingly opaque material.

The remarkable optical properties of patterned metal films, which have led to a wealth of research in the last few years, are due to the "free" electrons in such materials. These are the same electrons that allow metals to conduct electricity and to reflect radiation from microwaves to the ultraviolet almost perfectly. But free electrons also create surface waves, or surface "plasmons" as they are known in the visible domain.

As well as allowing seemingly opaque metal surfaces to become transparent, surface plasmons are providing new techniques for controlling light, detecting low levels of pathogens, imaging living cells and even probing the vibrations of single molecules.

A rich history

Surface plasmons are oscillations in the density of the free electrons that lie within about 20 nm of the surface of a thin metal film. The electromagnetic fields associated with these oscillations do not extend very far into or out of the surface of the film. The field also decays as it propagates across the surface as a wave due to interactions between the electrons and the vibrating atoms in the metal. These interactions are responsible for the usual electrical resistance of metals, and cause surface plasmons to lose power in the form of heat.

This power loss was first recorded unknowingly in 1902 by Robert Wood at Johns Hopkins University in Baltimore in the US while he was studying the spectra produced when visible light reflects off a ruled metal surface or grating. Wood was surprised to find sudden drops in intensity over very short ranges in wavelength, but it was 40 years before the young physicist Ugo Fano at the University of Rome came up with an explanation for these sharp spectral features.

Earlier attempts to explain Wood's anomalies failed because researchers had assumed that metals act as perfect conductors. But if this was the case, then there would be no mechanism other than diffraction by which the reflected light could drop in intensity. With substantial insight, however, Fano noted that a conducting surface could guide light in the form of a surface wave. These waves, which are trapped at the surface of the metal, absorb energy and therefore cause incoming light to be reflected at a lower intensity (see above).

In fact, a theory about the propagation of surface waves on 2D conductors already existed, albeit couched in the radio rather than the visible domain. Stimulated by Marconi's pioneering demonstration that radio waves could be sent across the Atlantic, Jonathan Zenneck had unknowingly described the behaviour of surface plasmons mathematically in 1907. Despite Fano's rederivation of this behaviour in the visible region, the field of surface-plasmon optics was to remain dormant

Wood's anomaly
Surface plasmons affect the way light reflects off a grating. If light is polarized in the same direction as the grooves, the spectrum is continuous (top). But perpendicularly polarized light can couple to surface plasmons and be absorbed at certain wavelengths (bottom).

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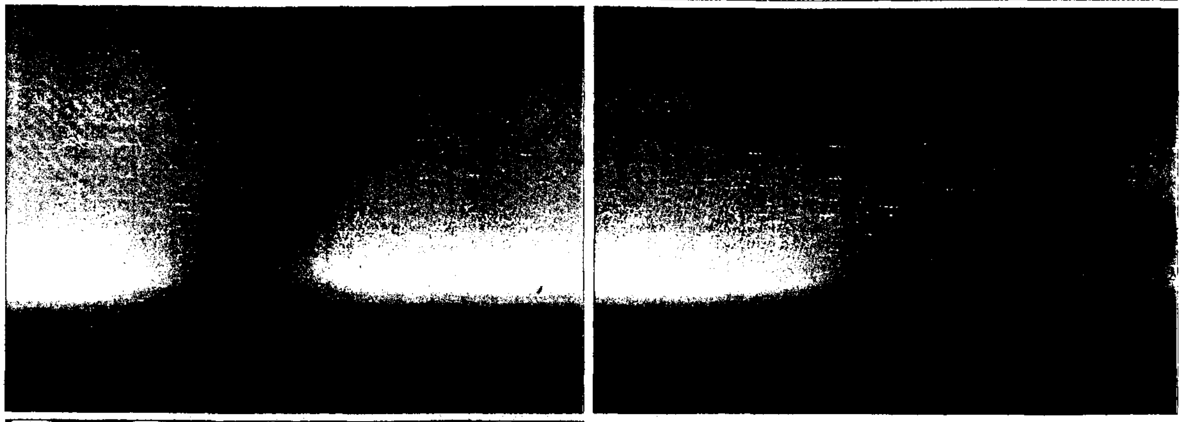
1 Surface band gaps



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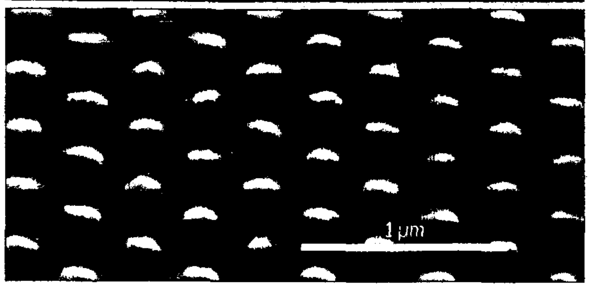


By shining light onto a metal surface using prism coupling and varying the angle of incidence, a black band corresponding to the surface plasmon (the Wood's anomaly) may be observed. This can be seen by plotting the inverse wavelength (vertical axis) versus the incident angle. On a flat surface (upper left), the existence of the black band across the whole spectrum shows that the surface plasmon can propagate at all visible frequencies. When the surface is textured periodically (left) there is a range of wavelengths for which there is a band gap and therefore no surface plasmon, as can be seen in the green region of the corresponding spectrum (upper right).

for the next 25 years.

Everything changed in 1968, when Andreas Otto at the University of Munich and Erwin Kretschmann and Hans Raether at the University of Hamburg used prisms less than a wavelength away from a metal surface to study how light couples to surface plasmons. The researchers – who had actually rediscovered an effect reported by Taher Turbador at Imperial College in 1959 – found that by shining light into the prism beyond the critical angle, the extra momentum imparted to the light along the base of the prism causes the light to couple strongly to surface plasmons. This is the same effect that Wood had observed for gratings, and the result led to a flurry of activity into optical excitation of surface plasmons in the early 1970s.

In the case of a prism, the surface plasmons travel on a flat surface. But the surface of a grating consists of a number of tiny grooves, which has important ramifications. For instance, if a metal surface with grooves in only one direction is rotated, the surface plasmons will no longer lie in the plane of incidence. The symmetry of the system is therefore broken and the grating can be used, for example, to change the polarization of a light beam.

At a Glance: Surface plasmons

- Surface plasmons are oscillations of electrons near the surface of a conductor plus their associated electromagnetic fields
- They were first observed unknowingly in 1902, although rediscovered several times since then
- Surface plasmons allow seemingly opaque metal surfaces to become transparent or to act as perfect lenses that overcome the diffraction limit
- The optical response of a metal surface can be precisely tailored by drilling a periodic array of sub-wavelength holes
- Surface plasmons could lead to miniature photonic components and have important applications in biological sensing

The situation becomes even more interesting when a metal surface contains more complex patterns. In 1996, for example, Steve Kitson and the present authors at Exeter University explored surface plasmons on a hexagonally patterned gold surface. This showed how the behaviour of surface plasmons can be manipulated by surface structure.

Designer surfaces

Nano-patterned surfaces are at the centre of current research into surface plasmons. For gratings with shallow grooves, the grooves merely cause the light to couple with the surface plasmons. A surface with very deep grooves, however, can alter the behaviour of a surface plasmon so dramatically that it becomes a highly localized standing wave. In fact, because the period of the standing wave matches the periodicity of the grating, two standing waves will form: one with its brightest spots at the top of the grooves and another with its brightest spots at the bottom of the grooves.

In 1996 the present authors, together with Kitson and Trevor Priest at Exeter, showed how these two standing-wave surface plasmons, while having the same period, have different energies. Furthermore, this difference in energy increases as the groves become deeper. As a result, there is a range of frequencies or band gap in which surface plasmons are forbidden to propagate (figure 1). Similar to the band gaps that prevent the movement of charge carriers in semiconductors, it allows physicists to control the optical response of a metal just by patterning it. Indeed, it is the response of a metal film containing a simple pattern – a regular array of holes – that awoke the optics community to the huge potential of metal films back in 1998.

The breakthrough came when Thomas Ebbesen at NEC in New Jersey and co-workers drilled a periodic array of holes some 150 nm in diameter and separated by a half wavelength in a silver film that was about 200 nm thick. Without any holes, such a film was expected to allow less than 0.3% of incident light through. In fact, Ebbesen's team found that the transmission of light through the "holey" film was dramatically enhanced. But since the holes are far too small to act as hollow waveguides, how did the light get through?

The answer is a subtle interplay of several processes. First, even though no wave can travel though the holes directly, some light can leak through because the optical power decays exponentially as a function of distance through the hole. For the films studied by Ebbesen and co-workers, however, this leakage cannot account for the degree of transmission observed. This is where surface plasmons enter the story.

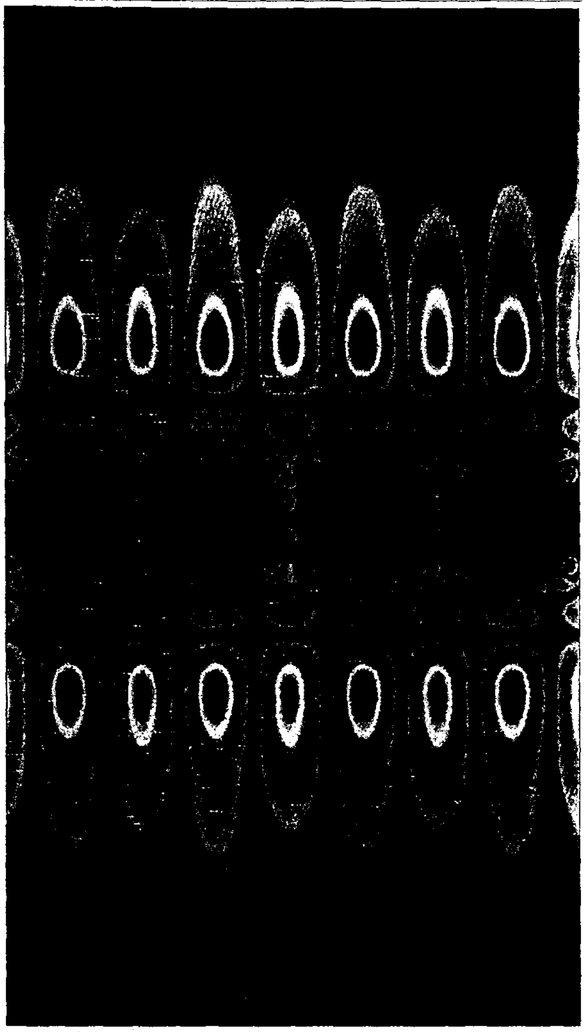
As the holes in the film are arranged periodically, the incident light couples to surface plasmons exactly as Wood observed in 1902. Under certain conditions, this may produce counter-propagating surface plasmons on the metal surface that combine constructively to produce an interference pattern (i.e. a surface-plasmon standing wave). If the maxima of this pattern coincide with the positions of the holes, the amplitude of the fields inside is boosted and lots of light is transmitted through the film.

Earlier last year, Esteban Moreno and colleagues at the University of Madrid and co-workers at the Max Planck Institute for Quantum Optics in Garching showed that a thin film containing an array of slits 50 nm wide and separated by 800 nm can provide a similar effect for *atoms*. Since the de Broglie wavelength of the atoms was about 800 nm, transmission through the slits should have been negligible. But the team showed that 100% of the atoms should be able to pass through the slits with the help of surface matter waves (figure 2). These waves are the atomic analogue of surface plasmons, and could open a new line of research in the field of atom optics.

Ebbesen's results stimulated a wealth of research into patterned thin-metal-film structures, and gave birth to the field of "plasmonics". Much of this work was carried out with gold and silver films, which have a large number of free electrons and therefore respond well to visible light. However, in 2004 John Pendry of Imperial College in the UK, Francisco Garcia-Vidal of the University of Madrid and Luis Martin-Moreno of the University of Zaragoza showed theoretically that even perfect conductors that do *not* ordinarily support surface plasmons can be made to do so by appropriate patterning. This might, for instance, involve drilling a large number of small holes to make a structure similar to that used by Ebbesen in 1998. In other words, Pendry and colleagues demonstrated that one can do more than just modify surface plasmons – we can create them too.

In 2005 this effect was verified by Alastair Hibbins and co-workers, including one of us (RS) at Exeter University and colleagues at QinetiQ in the UK. Using a "metamaterial" containing an array of deep square holes with a periodicity of 9.5 mm, we observed these new surface plasmons at microwave frequencies. Such structures may lead to new miniaturized aerials and electromagnetic shields. Moreover, the result showed that surface plasmons on structured metals can be found at wavelengths all the way from the ultraviolet right up to radio waves, uniting Wood's anomalies and Zenneck's theories at long last! But there is still much more to the remarkable story of surface plasmons.

2 Matter waves



Simulations of the matter wave corresponding to a collection of rubidium atoms (impinging from the top) show that there are no losses when the atoms are incident on a grating consisting of thin slits (red and black represent high and zero transmission, respectively). The de Broglie wavelength of the atoms is about 800 nm, whereas the slit is just 50 nm wide, which means that transmission is only possible due to the existence of surface waves.

The perfect lens

One of the most astounding developments in experimental physics in the last few years has been the development of materials with a negative index of refraction. In other words, they can bend light in the opposite direction to an ordinary material. In 2000, following on from the work of Viktor Veselago in 1968, Pendry predicted that a thin planar slab of such a material could act as a perfect lens. Such a lens could recover the optical components associated with sub-wavelength spatial information that are lost in conventional lenses, leading to perfect image reconstruction. But what have these exotic materials got to do with surface plasmons?

Metals support surface plasmons because they have a negative permittivity – which is a key step on the way to

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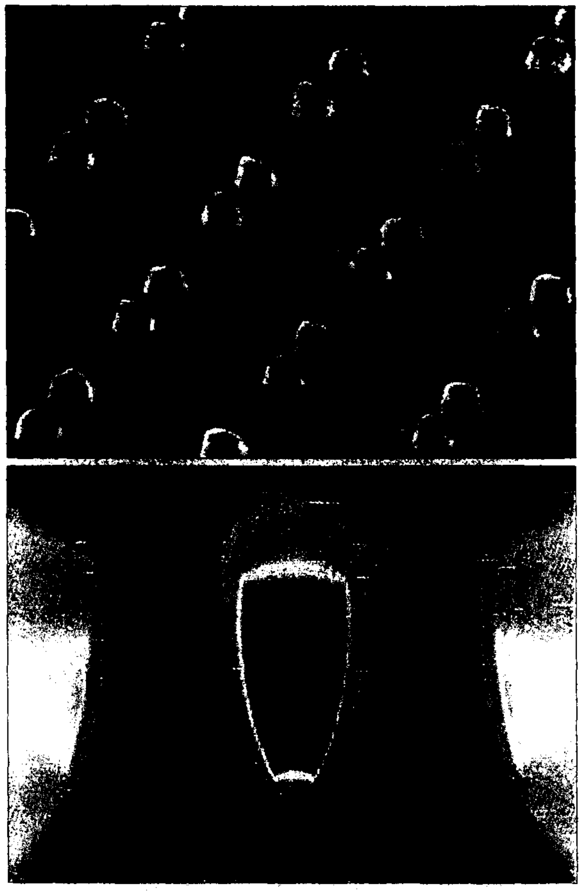
3 Negative-index materials



By patterning a gold surface periodically with pairs of gold posts (top), researchers have created a material with a negative index of refraction that operates in the visible region. When light shines on the surface, a current loop is set up between neighbouring posts to produce a magnetic field (bottom) that opposes the incident light field (red and blue regions represent high and low magnetic field intensity, respectively). This is precisely the property that is required to give the material a negative magnetic permeability, which, in turn, leads to a negative index of refraction.

A Grigorenko/Nature

a negative-index material. Such materials do not seem to occur naturally; they have, however, been developed for microwave radiation using specially engineered metamaterials that have sub-wavelength structure (see *Physics World* May 2004 pp23–24). Attempts to use the same approach in the visible regime are much more challenging because it is difficult to fabricate such structures at optical wavelengths, but substantial progress in this area has recently been made.

In November 2005, for example, Alexander Grigorenko and colleagues at the University of Manchester showed that gold films patterned with tiny metallic posts may have a negative permeability (figure 3). The permeability of a material, μ, essentially describes its response to a magnetic field, and is a complex number for materials that absorb radiation. Grigorenko's gold films were designed such that an incident light wave excites a magnetic dipole that, in turn, generates current loops that give rise to a negative permeability. This causes the refractive index of the material, which is defined as $n = \sqrt{(\varepsilon\mu)}$ where ε is its permittivity, to also have a negative value.

Plasmon pioneer
Robert Wood unknowingly discovered surface plasmons in 1902.

Such materials require periodic structures to be manufactured with a precision of at least 10 nm. Furthermore, the imaginary part of the permeability in Grigorenko's material, which dictates how "lossy" it is, is currently too large to enable a perfect lens to be built in the visible region. But the result is a major step in this direction, and other groups are already pursuing improved designs.

If, however, one is content to work with ultraviolet rather than visible light, then even a simple non-patterned metal film may be used to create what Pendry calls a "poor man's lens". In April 2005 Nicholas Fang and colleagues at the University of California at Berkeley showed that a silver film can work in just this way for ultraviolet light with a wavelength of 365 nm (see *Physics World* August 2005 pp23–24). The lens does not enable perfect image reconstruction, but it does mean that enhanced transmission of the evanescent waves can be achieved to form an image with a metal film as simple as the one in the back of your bathroom mirror.

Plasmon applications

So far we have focused attention on the rich physics of surface plasmons, but they also have enormous potential in photonics applications. In particular, the fact that surface plasmons do not penetrate very deeply into a metal surface means that they could offer "sub-wavelength" components for optical circuits. These might include miniature wavelength "multiplexing" devices that can send light with different frequencies simultaneously down telecommunications networks.

In the last few years, Pierre Berini and colleagues at the University of Ottawa in Canada have been making surface-plasmon waveguides by embedding metallic strips that are just a few nanometres thick in dielectric materials. These devices, which could form part of the infrastructure for all-optical circuits, have to be fabricated extremely carefully, but they have already been used to guide surface plasmons over distances of a few centimetres. Meanwhile, Jo Krenn and co-workers at the University of Graz in Austria have shown that patterned metal films can be used to make a range of 2D nonlinear optical components. These could enable us, for example, to change the direction of surface plasmons on a chip or to bring them to a controlled focus.

The most promising application of surface plasmons is as biosensors, because the plasmons are very sensitive to small changes in the vicinity of a metal surface. In 2004 Richard Van Duyne and colleagues at North Western University in Illinois used nanometre-sized metallic particles to detect the presence of molecules relevant to Alzheimer's disease. Such particles scatter light strongly at specific wavelengths due to standing-wave plasmon resonances that depend on the composition, shape and size of the particle as well as its surroundings. Van Duyne and co-workers showed that when the molecules were chemically bound to the metallic particles, the resonant wavelength changes, thereby offering a way to detect molecules or other pathogens.

The optical field associated with the plasmon resonances can be enhanced even further by bringing two metallic nanoparticles within a few nanometres of one another. Indeed, this enhancement is so big it can be

Surface plasmons at microwave frequencies may lead to miniaturized aerials and electromagnetic shields

used to detect light that has scattered elastically off molecules, which is normally very weak. This technique, which was first demonstrated by Katerina Kneipp and colleagues at Harvard and by Shuming Nei and Steve Emory at the Massachusetts Institute of Technology in 1997, can therefore provide information about vibrational modes at the single-molecule level.

Outlook

Surface plasmons have a rich and varied history, and there is no telling what we will see next in the magic metallic mirror. The perfect lens has already been fabricated at microwave frequencies using metamaterials, and we will no doubt soon see such a device at terahertz frequencies (10^{12} Hz), which will open up applications in surveillance imaging technology. However, while progress in the last 12 months has been substantial, making 3D metal metamaterials in the visible wavelength range is still a major practical challenge.

Further developments in the use of metallic nanostructures for sensing applications will also need to meet the stringent demands of researchers interested in pharmaceutical, chemical and biological sensing. For example, such devices will need to be able to detect and identify single molecules or pathogens at a rate of millions per second in order to compete with the fluorescence techniques already in use for drug screening.

We can also look forward to using surface plasmons in scanning probe imaging, such as combining arrays of holes or even perfect lenses with advances in CCD and CMOS technology. There are even suggestions of using holey metal films in colour displays, or for visible lasers based on surface plasmons. Thin metal structures that seem at first to act simply as mirrors are sure to have a major impact in several fields in the next few years.

More about: Surface plasmons

W Barnes *et al.* 2003 Surface plasmon subwavelength optics *Nature* **424** 824–830

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N Fang *et al.* 2005 Sub-diffraction limited optical imaging with a silver superlens *Science* **308** 534–537

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