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Plasmonic transparent conductors

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ABSTRACT

Many of today’s technological applications, such as solar cells, light-emitting diodes, displays, and touch screens, require materials that are simultaneously optically transparent and electrically conducting. Here we explore transparent conductors based on the excitation of surface plasmons in nanostructured metal films. We measure both the optical and electrical properties of films perforated with nanometer-scale features and optimize the design parameters in order to maximize optical transmission without sacrificing electrical conductivity. We demonstrate that plasmonic transparent conductors can out-perform indium tin oxide in terms of both their transparency and their conductivity.

Keywords: Plasmonic conductors, transparent conductors, sub-wavelength hole arrays, extraordinary optical transmission

1. INTRODUCTION

Material architectures that are simultaneously optically transparent and electrically conductive are highly sought-after for a variety of optoelectronic applications. However, the transmissivity and conductivity of materials are in direct competition with each other, as the electronic structure that gives rise to conductivity typically also leads to optical opacity. As a result, established solutions tend to favor one property over the other.¹ Transparent conducting oxides, such as indium tin oxide (ITO), which is the leading material choice for transparent electrodes, are generally not as conductive as metals. For example, commercial glass slides coated with 200 nm of ITO transmit 87% of incident radiation, averaged over the visible spectrum, but have a sheet resistance of 15 $\Omega/\square$. For comparison, a 30-nm-thick film of silver deposited on glass by electron-beam evaporation has a sheet resistance of 0.5 $\Omega/\square$, but transmits only 14% of visible light. The lack of materials that balance transmissivity and conductivity has driven the search for alternative transparent and conducting material architectures, such as carbon-based nanomaterials,^{2,3} networks of metal nanowires,⁴⁻⁶ and graphene-polymer composites.⁷

In this work, we will explore a nanotechnology approach to transparent conducting architectures that is based on the control of surface plasmons in nanostructured metal films. Such structures are already being employed as transparent electrical contacts in organic photovoltaic devices.⁸⁻¹⁰ We will demonstrate that nanostructured plasmonic architectures offer considerable flexibility in the design of their optical and electrical properties, allowing us to strike a balance between transmissivity and conductivity, and even out-perform ITO in certain situations.

1.1 A GENERALIZED FIGURE OF MERIT FOR TRANSPARENT CONDUCTORS

Different applications may place different requirements on the performance of transparent conductors. It is therefore useful to define a figure of merit that will allow us to assess the performance of transparent conducting architectures independently of the specific device structure in which they will be used. For the purposes of this work, we will adopt the ‘Haacke number’ as our device-independent figure of merit, which is defined as

$$\phi = T^{10}/R_s, \quad (1)$$

with R_s being the electrical sheet resistance of the material architecture, and T its optical transmissivity.¹ For example, the ITO coating discussed in the previous section has a Haacke number of $1.2 \cdot 10^{-2} \Omega^{-1}$.

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1.2 SUB-WAVELENGTH HOLE ARRAYS

Optically thick metal films perforated with periodic arrays of sub-wavelength holes exhibit transmission resonances above the cutoff wavelength of an individual hole of the same dimensions. On resonance, the optical transmission through such a nanostructured film normalized to the open area of the holes can exceed unity, which implies that each hole transmits more light than is impinging on it directly. This phenomenon is commonly referred to as ‘Extraordinary Optical Transmission’ (EOT) and has been the subject of a considerable amount of research.^{11–13} In this section we will briefly discuss the optical properties of such structures.

Figure 1. Numerical simulations of sub-wavelength hole arrays. (a) Schematic diagram of a perforated silver film on a glass substrate. α : lattice constant, r : hole radius, h : metal film height. (b) Simulated transmission spectra of a perforated silver film with $\alpha = 450$ nm, $r = 160$ nm, and $h = 100$ nm. The arrows denote the predicted locations for the maxima and minima associated with the excitation of surface plasmons at either the metal-air (dashed) or the metal-glass (solid) interfaces. (c), (d) On-resonance electric field profiles at $\lambda = 477$ and 683 nm, respectively.

The optical transmission spectrum of a 100-nm-thick silver film supported by a glass substrate and perforated with a hexagonal array of holes of radius $r = 160$ nm and with lattice constant $\alpha = 450$ nm [Figure 1(a)], calculated using fully-3D finite-difference time-domain methods (Lumerical FDTD solutions), is shown in Figure 1(b). The spectrum contains wavelength bands with transmission higher than the geometric film porosity $[2\pi r^2 / \sqrt{3} \alpha^2]$, Figure 1(b) right-hand axis]. It is understood that the transmission maxima in these structures are associated with the resonant excitation of surface plasmon modes.¹⁴ Freely-propagating light has insufficient momentum to excite these modes on a continuous metal film (i.e. $k_x < k_{\text{SPP}}$, where k_x and k_{SPP} are the in-plane components of the wave-vectors of the plane wave and surface plasmon mode, respectively.) The geometry of a periodically perforated metal film, however, changes the resonance condition to:

$$|\mathbf{k}_x| = |\mathbf{k}_{\text{SPP}}| + i|\mathbf{a}_1| + j|\mathbf{a}_2|, \quad (2)$$

where $i, j = 0, \pm 1, \pm 2, \dots$ are indices denoting the order of diffraction, and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the reciprocal basis vectors of the lattice – thus making the resonance accessible to incident light. In general, the optical properties of sub-wavelength hole arrays will depend strongly on the angle of incidence.¹⁵ However, in this work we will only consider normally-incident illumination ($k_x = 0$), as it is the relevant operating condition for most optoelectronic devices. For a sufficiently thick metal film, we can approximate the surface plasmon wave-vector by that of a single metal-dielectric interface:

$$k_{\text{SPP}} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}. \quad (3)$$

Here, ϵ_m and ϵ_d are the dielectric constants of the metal and the adjacent dielectric, respectively. For a hexagonal array of lattice constant α , and at normal incidence, Eq. (2) is satisfied when

$$\lambda_{\text{max}} = \frac{\alpha \sqrt{3}/2}{\sqrt{i^2 + ij + j^2}} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}. \quad (4)$$

The transmission minima correspond to Wood’s anomalies of diffraction, which occur when the diffracted wave-vector becomes tangent to the plane of the grating.¹⁶ The equivalent resonance condition for the minima, therefore, can be written as

$$\lambda_{\min} = \frac{\alpha\sqrt{3}/2}{\sqrt{i^2 + ij + j^2}}\sqrt{\varepsilon_d}. \quad (5)$$

The predicted locations of the maxima and minima obtained from Equations 4 and 5 by taking into account the full wavelength dependence of ε_m and ε_d are denoted by arrows in Figure 1(b). Note that since the structure is asymmetric, two sets of resonances are supported, each corresponding to the excitation of surface plasmons at either the metal-air or the metal-substrate interface. In Figure 1(b), solid arrows indicate the predicted maxima and minima for the metal-substrate interface, while dashed arrows correspond to plasmon resonances at the metal-air interface. We find that the simulated resonances appear consistently at longer wavelengths than those predicted using this formalism. For example, Equation 4 predicts the ($i = 1, j = 0$) silver-air and silver-glass resonances at 434 and 614 nm, respectively, whereas in the simulated transmission spectrum of this structure the transmission maxima are located at 477 and 683 nm. This is a result of interference between the two optical pathways that lead to transmission; the excitation of surface plasmons, which is a resonant process, and direct scattering, which is non-resonant.¹⁷

In order to adhere to typical fabrication constraints, our simulated structure includes a 5-nm-thick adhesion-promoting layer of chromium between the silver and the glass substrate. The presence of this layer affects the optical properties of the array by damping the surface plasmons excited at the metal-substrate interface, leading to reduced transmission for the corresponding resonances.

Figures 1(c),(d) show the electric field enhancement predicted by FDTD simulations at each of those resonances. “Hot spots” that are characteristic of the excitation of surface plasmons are seen.

The optical properties of perforated metal films can be easily tuned by controlling the nanostructure geometry. The resonance wavelengths of both the maxima and the minima are proportional to the lattice constant of the array (Equations 4, 5), while the separation of the metal-air and metal-substrate resonances depends on the difference in the dielectric constants ε_d of the two materials. The on-resonance optical transmission through a sub-wavelength hole array is maximized when the structure is symmetric.

2. RESULTS AND DISCUSSION

Nanostructured metal films can be designed to simultaneously have high transmission and low sheet resistance. Here, we choose our operating wavelength to be $\lambda = 805$ nm, which is a critical wavelength for light emitting diodes used in biomedical applications,¹⁸ and optimize the film’s design parameters in order to maximize its Haacke number at that wavelength.

Perforated metal films generally become more opaque with increasing film thickness.¹⁹ However, the use of ultra-thin films is not ideal as the increased influence of surface roughness and metal grain boundaries will adversely affect the electrical properties of the film. Increasing the radius of the perforations also results in higher overall transmission and broader resonances.²⁰ Unlike random arrangements of plasmonic nanoparticles, in which the metal fill fraction should be above the percolation threshold in order for a conducting pathway to exist,²¹ periodic structures can be made to be arbitrarily sparse while still maintaining electrical continuity, albeit with increased electrical resistance.⁶

To explore the limits of this strategy, we here consider the evolution of optical and electrical properties of a 94-nm-thick periodically-perforated silver film that is bound on both sides by glass [Figure 2(a)] as the hole radius is increased.

Silver films perforated with large-area (mm^2) hexagonal arrays of sub-wavelength holes are fabricated on 160- μm -thick glass coverslips using electron-beam lithography, metallization, and lift-off under ultrasonic agitation. As a consequence of our fabrication method, the structures are required to contain an adhesion-promoting layer between the metal film and the substrate (here using 5 nm of Cr). A scanning electron micrograph of a fabricated structure (with $\alpha = 450$ nm, $h = 94$ nm, and $r = 178$ nm) is shown in Figure 2(b). Finally, the structures are covered with index-matching fluid ($n = 1.518$) and a second glass coverslip.

Optical spectra are recorded using a broad-band CW laser-driven light source that is coupled to a commercial Fourier-transform spectrometer.⁹ The light is focused onto the sample using an upright optical microscope. A low numerical aperture $4\times$ objective (N.A. = 0.10) is used in order to accurately reproduce the normal-incidence transmission spectra. We find that the optical transmission through perforated metal films increases with increasing hole radius [Figure 2(c)], with our most sparse structures transmitting 91% of the incident radiation at $\lambda = 805$ nm.

Figure 2. (a) Schematic of the symmetric structure. IMF = index matching fluid, MHA = metal hole array. (b) Scanning Electron Micrograph of a fabricated perforated metal film prior to the addition of the index-matching fluid and the second glass slide. (c) Transmission spectra of symmetric structures of varying hole radius r with $\alpha = 450$ nm, and $h = 94$ nm. (d) Measured sheet resistance of perforated silver films as a function of hole radius.

The sheet resistance of such perforated silver films, measured in a 4-point geometry, is found to scale with increasing hole radius r as

$$R_s = R_{s,0}/(1 - \beta r), \quad (6)$$

where $R_{s,0}$ is the sheet resistance of an unpatterned silver film of the same thickness, and β is a scaling factor associated with the array geometry [Figure 2(d)].

Figure 3 summarizes our experimental results. As the hole radius increases, both the film's resistivity and its transmissivity at the target wavelength increase. For porosities larger than 35%, the performance of nanostructured silver films exceeds the Haacke number of ITO (shown in Figure 3 as a dashed red curve), with our most porous films having a Haacke number of $9.3 \cdot 10^{-2} \Omega^{-1}$.

3. CONCLUSION

We have demonstrated that plasmonic transparent conductors offer considerable flexibility in the design of their optical and electrical properties, allowing us to strike a balance between transparency and conductivity. These nanostructured material architectures can be used as electrical contacts for light emitting diodes, thin-film photovoltaic devices, liquid-crystal displays and other optoelectronic devices. In the limit of large hole size, perforated metal films out-perform indium tin oxide as transparent electrodes by being simultaneously more transparent and more conducting.

Figure 3. Evaluation of the performance of perforated metal films of varying hole radius as transparent conductors. The figure of merit (Haacke number, with units of Ω^{-1}) increases with increasing hole radius. For comparison, the locus of points with a Haacke number equal to that of ITO is also shown (dashed).

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