Extraordinary infrared transmission of Cu-coated arrays with subwavelength apertures: Hole size and the transition from surface plasmon to waveguide transmission

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The zero-order, infrared transmission spectra were recorded and studied at varying angles of incidence to study the dispersion of the resonances in both the $\Gamma-X$ and $\Gamma-M$ reciprocal lattice directions. Reduction of hole size shows dramatic effects on the intensity of transmission, the width of the resonances, the identity of the most prominent resonances, and the dispersion behavior of resonances. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1786664]

The surface-plasmon-mediated, extraordinary transmission[1,2] of commercial Ni microarrays has recently been examined[3] by zero-order Fourier transform infrared spectroscopy (FTIR). These meshes transmit more light than is incident upon their holes, so some light is transmitted when it does not strike a hole. This behavior is attributed to the excitation of surface plasmons (SPs) on the metal surface. Bandpass phenomena of meshes are well known in grating science,[4,5] however transmission above the fractional open area of the mesh (i.e., Ebbesen's extraordinary transmission[1]) is new and hard to explain without SPs. The infrared[3] (IR) and far-IR[6] represent an interesting regime between the new (SP-mediated) and classical transmission results. The hole sizes in this work are chosen such that the nominal waveguide transmission threshold tunes through the IR range with dramatic consequences for the SP-like dispersion. The remarkably high transmission of two-dimensional metal arrays[1] has been the subject of multiple studies.[2,3,6–14] There have been two-dimensional photonic band structure calculations on a square lattice of infinitely long metal cylinders[11,15] that are useful in interpreting the present results.

The base mesh (available commercially from Precision Eforming, Cortland, NY, formerly Buckbee-Mears, Inc.) for these studies is a Ni mesh with square holes of width 8.0 μm on one side tapering to 6.5 μm on the other side, a hole-to-hole spacing of 12.7 μm on a square lattice, and a thickness of 5 μm. We have developed an electrochemical way to uniformly reduce the square hole widths by electrodeposition of copper. The application of a -10 V over-voltage to the base nickel mesh in $CuSO_4$ solution drives a 10 s spike of deposition current (max of $\sim$0.2 A) producing an unexpectedly uniform coating. Further deposition proceeds at less than 1/5 of the peak current resulting in further closing of the holes and more typical growth of Cu crystallites. The final width of the holes can be varied from 6.5 to less than 1 μm by varying the deposition time. Hole widths were measured with scanning electron microscopy and optical microscopy. Statistical analysis of the images reveal an estimated standard deviation of 0.2 μm in the hole widths.

The zero-order FTIR transmission spectra of a sequence of Cu-coated meshes with successively smaller hole widths, but a common lattice parameter, are shown in Fig. 1. The locations of surface plasmon-mediated resonances are approximately given by[2]

$$\tilde{v} = \frac{\sqrt{i^2 + j^2}}{a_0 n_{\mathrm{eff}}}, \tag{1}$$

where i and j are reciprocal lattice vectors of the square array, a_0 is the lattice parameter (12.7 μm), and n_{eff} is the real part of the effective index of refraction of the perforated film. Early work in the visible suggested use of $(\epsilon_m/(\epsilon_m+1))^{1/2}$ for free standing mesh in air, where ϵ_m was the complex dielectric of the metal, but this quantity varies little compared to resonant shifts in the IR so a better theory is needed. The approximate locations of various resonances (labeled by i,j) are indicated in Fig. 1. This is an interesting size regime regarding hole widths in view of the nominal waveguide transmission cutoff wavelength (twice the hole thickness for individual rectangular waveguides[16]). This cutoff falls at $\sim$800 cm^{-1} for the largest hole widths (6.5 μm), is $\sim$1700 cm^{-1} for 3 μm-wide holes, and becomes $\sim$4500 cm^{-1} for the smallest holes in Fig. 1; so it tunes through the IR spectra in this study. For large holes, the $i,j=1,0$ resonance predominates and is the narrowest. This resonance gets narrower, shifts to higher wave number, and eventually disappears as the hole width gets smaller. The successive resonances undergo similar behavior—each being predominant at successively smaller hole sizes and eventually going away as they come to lay well below the waveguide cutoff (in wave numbers).

FTIR transmission spectra (Perkin Elmer GX Spectrum averaging 25 scan at 4 cm^{-1} resolution) are shown in Fig. 2 of the original Ni mesh (top, 6.5 μm holes) and a copper-deposited mesh (bottom, 3.7 μm holes) versus incident angle (θ, where perpendicular incidence corresponds to zero). The mesh was rotated in the spectrometer's polarized electric field which was aligned[17] with one of the grid axes (top of Fig. 2, $\Gamma-X$ direction, TM polarization) or at 45° to the grid axes (bottom of Fig. 2, $\Gamma-M$ direction). Data were recorded from θ=0, in steps of 5°, up to 75° for the Ni mesh and 50° for the Cu-deposited mesh.

We have previously shown that the original Ni mesh exibits SP-like dispersion as examined in terms of the angle-tuning version of Eq. (1).[3] The reduction of hole size from

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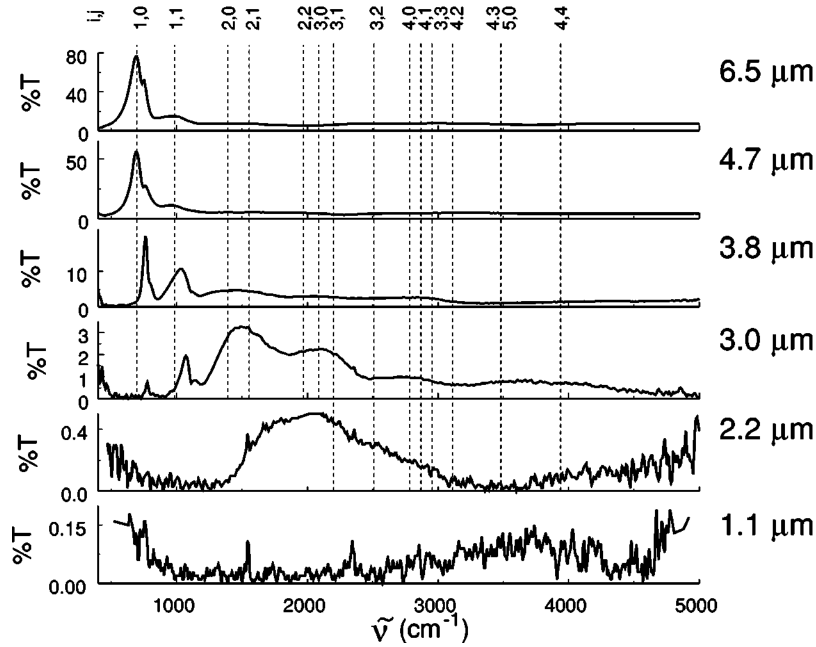

FIG. 1. Zero-order IR transmission spectra at $\perp$ incidence ($\theta=0$) of electrodeposited meshes with different hole widths. Nominal positions of resonances defined by Eq. (1) are labeled by the reciprocal lattice indices i,j (dashed vertical lines).

6.5 to 3.7 μm produces $i,j=1,0$ resonances (the lowest wave number peak in the $\Gamma-X$ direction) that track each other very closely throughout the first $\Gamma-X$ Brillouin zone. Both have a set of sharper peaks linearly redshifting and a set of peaks blueshifting nonlinearly and less quickly over the $\Gamma-X$ interval. Both show the two lowest frequency sets of peaks in the $\Gamma-M$ interval merging at point M. The general similarities suggest that this Cu-deposited mesh is also SP mediated.

There are also some differences in evidence. Cu-deposition produces resonances that are narrower, slightly blueshifted, and considerably different in intensity than the original Ni mesh (as also seen in Fig. 1 trends). In the $\Gamma-M$ direction, the Cu-deposited mesh shows peaks that are blueshifted from the Ni mesh by $\sim$50 cm^{-1}. There appear to be more peaks associated with the $i,j=1,0$ resonance with the original Ni mesh than with the Cu-deposited mesh. Equation (1) suggests four-fold degeneracy of the lowest energy resonance from different possible combinations of $i,j(0,\pm 1;\pm 1,0)$. In practice this degeneracy is lifted, producing the structure observed on the primary resonance at $\theta=0$. The splitting associated with this degeneracy gets smaller with the Cu-reduced hole size. The splittings at zero dispersion band gaps are reminiscent of those calculated[11] (H-polarization, Fig. 6) for a square lattice of infinitely long metal cylinders, particularly if allowance is made for the likelihood that some calculated bands may not couple directly with light.[13] The width and shape of individual resonances is of course affected by the surface metal, however dielectric differences of Cu/Air and Ni/Air interfaces are not so important at 700 cm^{-1}. Attention should be focused on surface roughness[18] (this Cu-deposited mesh has nanocrystallites of $\sim$160 nm width), hole thickness,[19] and the interplay of the waveguide cutoff.[16] All of this is complicated by the nearly degenerate resonances. Cleary, the deposition of Cu has dramatic effects on the extraordinary transmission of the mesh.

The dispersion behavior can change more dramatically when the holes get a bit smaller. A mesh was produced with 3 μm hole width which had a transmission spectrum similar to that shown in Fig. 1. The dispersion of this mesh is shown as a cross in Fig. 3. The dispersion is very flat in contrast to SP-mediated dispersion (like the air/metal interface[2,3,18]) as shown as an open circle and an open triangle in Fig. 3. At reduced hole widths where the resonance is very narrow and about to disappear, the dispersion is nearly flat until very high angles. This is just as seen in theoretical studies of one-dimensional waveguide modes.[20] Peaks with high dispersion for large hole/slit widths become less dispersing with smaller hole/slit widths in both the calculations and our data. In Fig. 1 the maximum transmission falls below the fractional open area (is no longer extraordinary) between the 3.8 and 3.0 μm hole sizes. The three lower traces in Fig. 1 do not show extraordinary transmission revealing a change in the transmission mechanism. Since the primary resonance in traces of the three smallest holes of Fig. 1 shows flat dispersions (like the cross in Fig. 3), we believe that this reveals a transition from SP-mediated behavior to waveguide-dominated behavior. The SP-mediated transmission of the three upper traces in Fig. 1 (as characterized by strong dispersion slopes) is associated with strong coupling between the front and back surfaces as occurs when the hole width is about the same size as the mesh thickness. As holes become smaller than the mesh thickness, the SP-mediated mechanism extinguishes as has been found in visible studies at perpendicular incidence of transmission versus mesh thickness by Degrion *et al.*[19] A similar conclusion is obtained in these studies versus hole width; however we add flat dispersion trends at low dispersions to the set of observations. Characterization of these regimes will be critical for the design of practical devices using extraordinary transmission.

The extraordinary transmission of these meshes in the IR region matches the fundamental vibrations of molecules. SPs will intrinsically have longer lifetimes in the IR than in the visible and therefore will propagate longer distances along

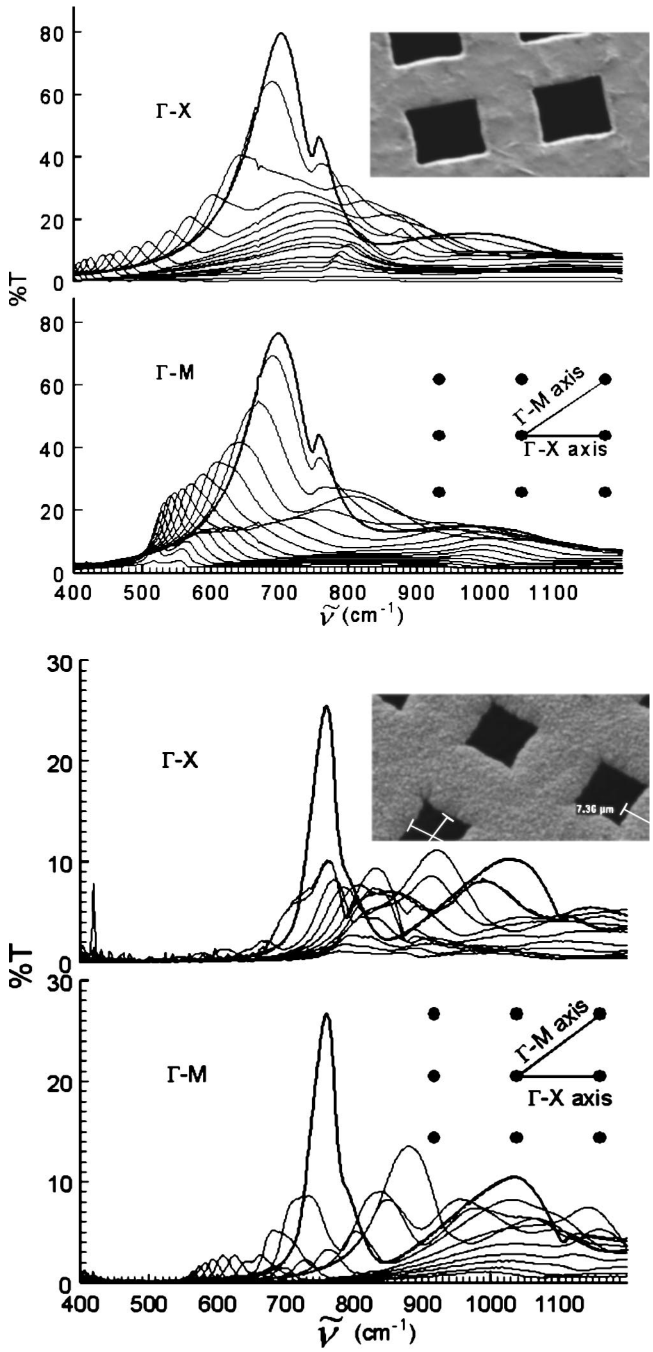

FIG. 2. Zero-order transmission spectra of the Ni base mesh (top) and Cu-deposited mesh (bottom) vs incidence angle, θ. The top insets show SEMs of the meshes and the bottom insets define the $\Gamma-X$ and $\Gamma-M$ directions in reciprocal lattice space.

the surface. This suggests the possibility of long path lengths for vibrational absorption by surface species. Preliminary work suggested that extraordinary IR transmission will make a good light source for enhanced absorption studies of surface molecular species.[3] We have already succeeded in recording very high quality IR absorption spectra of self-assembled monolayers with mesh of this sort.[21]

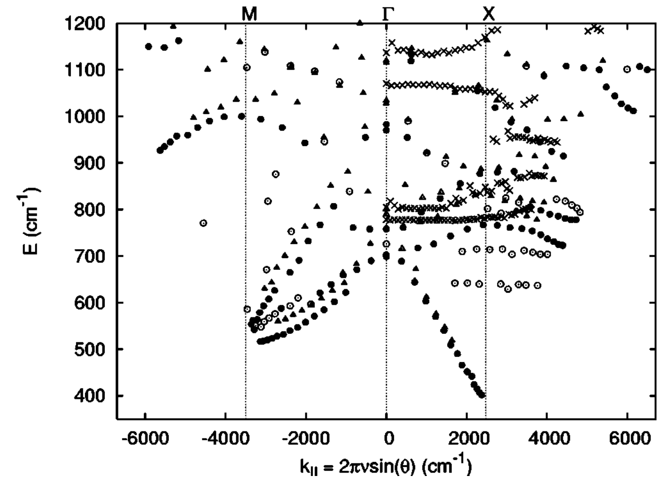

FIG. 3. The dispersion of the base Ni mesh (6.5 μm holes, ●) and the Cu-deposited mesh (3.7 μm holes, ▲). Closed symbols indicate peak positions, while the open symbols indicate shoulders (by second derivatives). Also shown is the $\Gamma-X$ dispersion behavior of a heavily deposited Cu mesh (3 μm holes, $\times$) which shows a transition to the waveguide behavior.

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