Surface-plasmon excitation by electrons in microlithographically produced channels

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Energy-loss spectra have been measured for low-energy (900 eV) electrons transmitted through cylindrical microchannels in silver foils. Arrays of such channels were produced by a microlithographic process. Inelastic scattering of the electrons results in a peak in the energy-loss spectrum in the vicinity of the silver surface-plasmon energy. The probability of surface-plasmon excitation was measured as a function of incident-beam angle and compared with theory. The results indicate that inelastic scattering occurs principally in a narrow region close to the metal surface where roughness features are important. Calculations in which these roughness structures are modeled as small spheres give excellent agreement with the measured shape and position of the energy-loss peak.

INTRODUCTION

The interaction of fast electrons with collective oscillations in polarizable media has been an important area of both experimental and theoretical research.[1,2] The electrons may induce any of a number of collective surface and volume excitations[3–8] in the medium, the study of which has provided useful information about the electronic and optical properties of solids. In most experiments of this kind, the electron is either transmitted through a thin specimen or reflected from a surface. Resulting electron energy-loss spectra may be quite complex, containing contributions of both bulk and surface plasmons as well as other structures.[9–11] It is possible to isolate, to a large degree, effects of surface excitations from those of bulk oscillations using grazing-incidence reflection.[12,13] This can be particularly useful for such target materials as transition metals with complex bulk loss spectra.[14,15] The use of aloof scattering (nontouching trajectory) in order to completely remove the effect of bulk losses was first suggested by Gumhalter and Newns[16] and by Muscat.[17] The electrons in this case are inelastically scattered by the surface-plasmon field which determines the resulting energy-loss spectrum. A number of theoretical treatments of surface-plasmon excitation exists in the literature for both planar[18–22] and spherical[23–29] surfaces.

Measurements of aloof-scattered electrons were first reported by Lecante, Ballu and Newns,[30] who were thereby able to detect surface-plasmon excitation on the planar surface of a Mo crystal. Later aloof-scattering studies have employed the extraordinarily narrow electron beam of a scanning transmission electron microscope to excite surface plasmons on cubic microcrystals of MgO (Refs. 31 and 32) and on Al spheres (Ref. 33). Such experiments allow for detailed study of the loss probability as a function of beam location.

A recent paper by Warmack *et al.*,[34] described a novel aloof-electron-scattering experiment that was carried out at our laboratory. In that experiment, the targets were silver foils containing large numbers of microchannels. The foils were otherwise opaque to the electron beam so that the only detected electrons were those transmitted through the microchannels. The small diameter of the channels constrained the electrons to pass close to the metal surface. The probability of surface-plasmon excitation was therefore relatively high, which resulted in good signal-to-noise ratios in the energy-loss spectra of the scattered electrons. The maximum impact parameter for the incident electrons was given by the channel radii which could be found from electron micrographs.

In this paper we describe electron energy-loss experiments using silver-foil samples containing microchannel arrays prepared microlithographically. These experiments have provided significant new information, inaccessible in the study by Warmack *et al.*, about the nature of the interaction of aloof-scattered electrons with metal surfaces.

The microchannels in the experiment of Warmack *et al.* were formed by evaporating silver onto commercially available submicrometer filters and then dissolving away the filter material. In this way, channels less than 50 nm in diameter could be produced in $\approx$100-nm-thick foils. While such samples have well-controlled channel diameters, the orientation of the channel axes is found to vary randomly by angles of up to 30°. Moreover, there is occasional overlap between channels due to the random nature of the high-energy particle tracks which are used in producing the filters. Our new microlithographic method for producing microchannel arrays which have well-controlled channel density and orientation is described in the following section. Use of these new microchannel arrays has allowed us to measure the surface-plasmon excitation probability as a function of the angle between the incident-beam direction and the channel axes. These measurements provide a sensitive test of the model used to describe surface-plasmon excitation in the experiments of Warmack *et al.*

In the study of Warmack *et al.*, the inelastic scattering was treated in terms of a model in which the electrons move uniformly parallel to a plane surface. Although the probability for surface-plasmon production agreed well with calculations, the calculated position and width of the energy-loss peak disagreed with the experimental data. The results discussed below indicate that such a planar model is not entirely appropriate. Our experiments indicate that electron energy losses occur primarily near roughness structures close to the ends of the microchannels. These roughness features can sustain localized surface plasmons with a slightly lower energy than the planar geometry. We model these structures as spheres and calculate the surface-plasmon excitation probability for electrons passing near the spherical surface. When the experimental geometry is included, the discrepancies noted by Warmack *et al.* between the calculated and observed energy-loss spectra are removed.

EXPERIMENTAL

The energy-loss-measurement apparatus is exactly as described by Warmack *et al.* Our silver-foil samples were made using a microlithographic process. Arrays of microchannels were first produced in free-standing films of electron resist. This was done by exposing the films to the computer-controlled beam in a scanning electron microscope (SEM), and then dissolving away the exposed regions. The resulting films were then overcoated with silver.

The free-standing films were prepared as follows. A glass slide was flooded with a dilute solution of detergent to act as a parting layer and spun at 3000 rpm for 10 sec. An electron resist solution [4%, 950 K mol. wt. PMMA (Ref. 35) in methylethylketone] was microfiltered to 200 nm, flooded over this layer, and spun at 3000 rpm for 10 sec. The thickness of the electron resist determined the final channel length and could be varied by changing the concentration of the resist solution and the spin parameters. After 5 min at room temperature, the slide was baked at 70 °C for 15 min. Small squares were then scribed onto the slide so that separated pieces of resist could be floated off in water. Films were lifted from the water onto polished stainless-steel sample holders with 1.6-mm holes over which the films were free-standing. The films were then baked at 170 °C for 45 min and were found to be very resistant to mechanical shock even though their thickness was less than 300 nm.

The free-standing films of electron resist were exposed in a computer-controlled SEM. The digital scan generator of a Zeiss Novascan 30 SEM was interfaced with a computer which controlled the beam position, beam intensity, and stage position. A 15-keV electron beam was focused onto the plane of the film so that a spot of estimated diameter 20—60 nm was obtained. The computer then controlled the SEM for exposure as follows. The electron beam was first removed from the sample by applying a transverse electric field before the final aperture of the SEM. The sample stage was then moved by means of stepping motors to an area of the film. The electron beam was turned on and held stationary for approximately 150 μsec. It was then turned off and moved to a new position for another 150-μsec exposure. In this way, a linear position of spots was exposed. At the end of the line, the beam was turned off and the beam was set to expose another similar line. The process was repeated until a two-dimensional array of spots had been exposed in a close-packed or hexagonal pattern. The outside border terminating the exposure frame was chosen to be circular. This helped to prevent tearing during subsequent processing of the film. Such tears tended to originate primarily at the corners of square or rectangular arrays. The process was repeated by stepping the stage to new areas of the same film. There was no significant charge buildup on the PMMA since secondary emission was low and most of the primary beam passed through the film without appreciable loss. Thus the regions of damage to the polymer structure approximated right circular cylinders.

The channels were developed in isopropanol for 4 min to dissolve the damaged areas. The typical diameter of the developed channels was 200 nm. The films were then coated with silver in a high pressure rf sputter coater.[36] The diameter of the channels could be reduced by coating with increasing amounts of silver (typically 20—80 nm on each side of the foil). The pressure in the sputter coater helped to ensure that the wall of each channel was uniformly coated. By these techniques, 0.1-mm-diam arrays of microchannels of diameter 60—200 nm and center-to-center spacing $\gtrsim 3x$ diameter could be produced reliably. Figure 1 shows micrographs of such an array. These samples have a number of advantages over those used by Warmack *et al.* Channel densities are greater by a factor of 4 to 5; there are no overlapped channels and, very importantly for angular studies, all the channel axes are oriented normal to the surface of the foil.

RESULTS

Electron energy-loss spectra were measured using the same methods described by Warmack *et al.* A typical spectrum is shown in Fig. 2. An energy-loss peak is observed at 3.57 ± 0.07 eV. This is slightly displaced from the surface-plasmon energy (3.63 eV) for planar silver. The peak is very similar to that found by Warmack *et al.* The zero-loss, or elastic scattering, peak was recorded with each spectrum. The ratio of the area under the inelastic peak to that under the elastic peak (after the subtraction of a linear background) was taken as a measure of the total transition probability.

Measurements were made of the excitation probability as a function of the angle α between the channel axes and the direction of the incident electron beam. Figure 3 shows this angle dependence. According to the planar model described by Warmack *et al.*, the maximum transition probability should occur at $\alpha=0$, where the electrons pass parallel to the channel surfaces. Our measurements show that the transition probability is, in fact, a minimum at $\alpha=0$ and increases monotonically with increasing angle. This implies that the scattering can be treated using a model in which the dominant effect in the excitation of surface plasmons is the interaction of electrons with roughness structures near the ends of the channels.

At a particular angle α, the cross section of the channel presented to the electron beam has the form of the intersection of two identical ellipses displaced from one another along the (common) direction of their minor axes. For

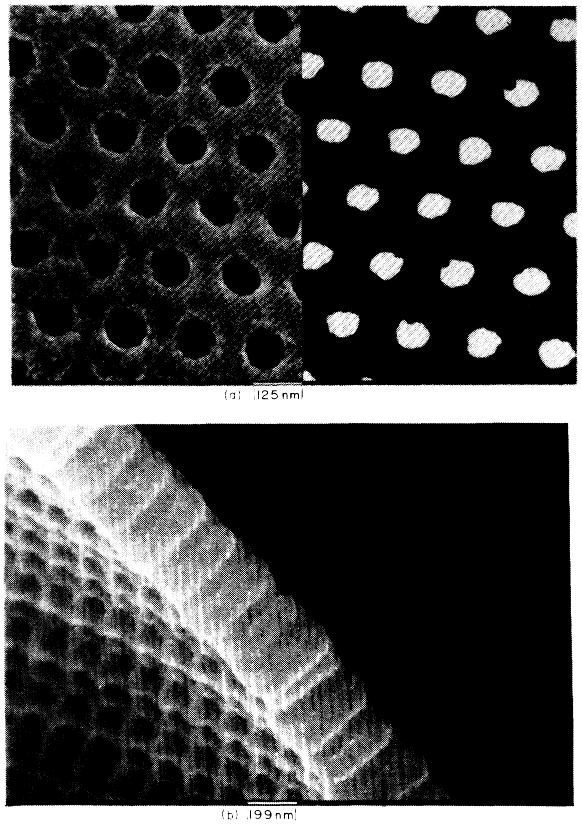

FIG. 1. Scanning electron micrographs of silver films containing microchannels. (a) A small section of a microchannel array. The frame on the right was taken in a scanning transmission electron microscope mode; the light areas are images of the transmission through the channels pictured on the left. The bar indicates a length of 125 nm. (b) A section of a torn foil sample showing part of a microchannel array as well as a number of channels in cross section. The bar indicates a length of 199 nm.

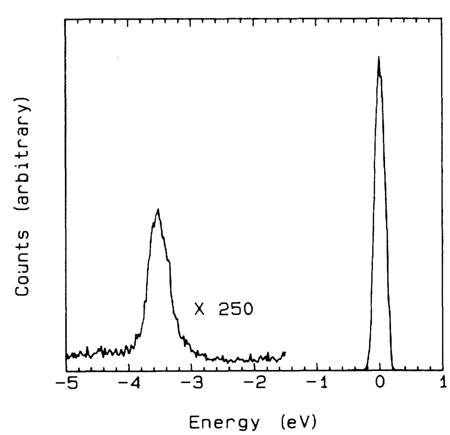

FIG. 2. Electron energy spectrum for 900-eV electrons transmitted through 100-nm-diam microchannels in a silver foil. (Beam parallel to channel axes.) The abscissa has been shifted so that the incident energy is at 0 eV.

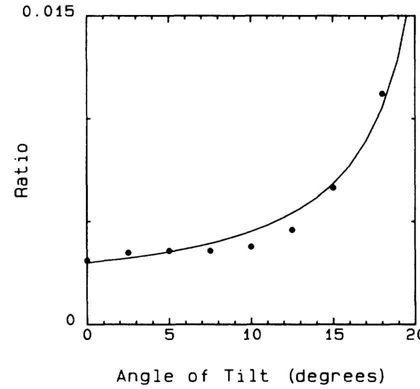

FIG. 3. Ratio of area under electron energy-loss peak to the incident flux as a function of angle between microchannel axes and direction of incident beam. Circles: experimental results; solid line: theoretical results.

$\alpha=0$, the eccentricity and the distance of separation are both equal to zero. They both increase with increasing α. As an electron traverses a channel, the closest distance of approach to the channel wall, and hence the highest probability of surface-plasmon excitation, occurs near the ends (except in the case of $\alpha=0$ when the impact parameter is nearly constant throughout). Suppose that this probability is appreciable only when the electron passes extremely close to the metal surface, i.e., within a distance much less than the channel radius. In that case, the measured transition probability should be proportional to the ratio of the circumference of the intersection of the two ellipses just described to the intersected area. The solid curve in Fig. 3 shows that ratio as a function of α for channels with a length-to-diameter ratio R of 3.5, the approximate aspect ratio for our microchannels. The signal-to-noise ratio in the data decreases with increasing angle since the total number of transmitted electrons diminishes, finally approaching zero as α approaches $\tan^{-1}R$. The good agreement shown in Fig. 3 implies that inelastic scattering occurs primarily at very small impact parameters where the nature of surface features plays a dominant role.

THEORY

Our measurements indicate that the dominant effect in the excitation of surface plasmons in the microchannels is the interaction of electrons with roughness features near the channel ends. We model these roughness structures as spheres on the channel walls.

The energy loss for a charged particle moving with uniform speed, v, past a sphere of radius a can be represented by a probability function $P_\omega(a,b,v)$. This function gives the probability of losing energy between $\hbar\omega$ and $\hbar(\omega+d\omega)$ when the distance of closest approach (from the center of the sphere) is b. This probability function has been obtained by Ferrell and Echenique,[23] whose treatment includes the interaction of the (classical) incident particle with all multipole excitations of the sphere. In Hartree atomic units ($e=\hbar=m=1$):

$$P_\omega(a,b,v)=\frac{4q^2}{\pi v^2 a}\sum_{l=0}^{\infty}\sum_{m=0}^{l}A_{lm}\left[\frac{\omega a}{v}\right]^{2l}K_m^2\left[\frac{\omega b}{v}\right]\times \mathrm{Im}[\alpha_l(\omega)]\ , \quad (1)$$

where

$$\alpha_l(\omega)=a^3\frac{\epsilon(\omega)-1}{\epsilon(\omega)+[(l+1)/l]} \quad (2)$$

and

$$A_{lm}=\frac{2-\delta_{0m}}{(l+m)!(l-m)!}\ . \quad (3)$$

Here K_m is the modified Bessel function of order m, δ_{0m} is the Kronecker delta, and q is the charge of an electron.

To obtain $P_\omega(a,v)$, we average Eq. (1) over a range of b determined by the experimental geometry. With the electron beam incident normally on the foil sample, the upper limit on b is equal to $r-a$, where r is the channel radius. The lower limit on b is determined by the detector geometry. We measured only forward-scattered electrons within an estimated acceptance angle of 1°. Values of b so small that they would result in absorption of the electron or in a deflection of more than 1° in the electron's path were excluded. The deflections were estimated by numerical calculation of the trajectories resulting from the classical electrostatic image potential.

DISCUSSION

Equation (1) is compared with experimental data in Fig. 4. The theoretical curve was broadened by convoluting with the experimentally measured instrument function. The best theoretical fit to the position and width of the measured peak was obtained by adjusting the sphere radius a. With increasing a, the energy-loss peak becomes narrower and shifts toward higher energy, gradually approaching the shape and position of the planar loss peak. The value of a which gives the best fit to the data is $a=13$ nm. This is not inconsistent with the size of the surface roughness features observed in electron micrographs (Fig. 1). Although more clearly resolved photographs could not be obtained, microprotrusions with radii of the order of 10 nm can be discerned.

Agreement between Eq. (1) and the measured energy-loss spectrum is sufficient so that theoretical refinements such as integration over a range of sphere sizes or inclusion of effects of nonsphericity of the surface structures (as, for example, modeling them as spheroids[37]) have not been included. It was found experimentally by Warmack *et al.* that the total transition probability increases monotonically with increasing energy E_0 over the range $60<E_0<1200$ eV. Total transition probabilities found by integration of Eq. (1) are in excellent agreement with those data.

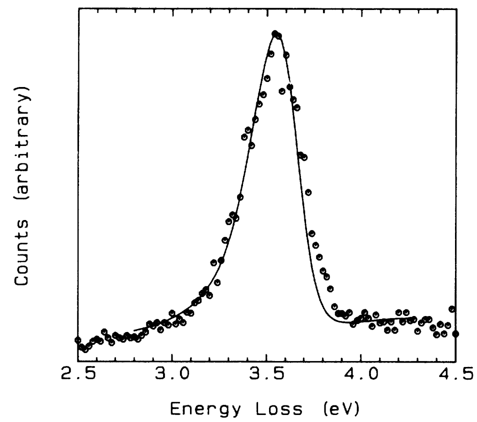

FIG. 4. Comparison of the theoretical energy-loss peak (as broadened by the energy distribution of the incident beam) with the measured peak for aloof-scattered 900-eV electrons. Circles: experimental results; solid line: theoretical results.

In conclusion, we have found that the dominant mechanism in the generation of surface plasmons by aloof scattering of electrons in microchannels in silver foils is the interaction of the electrons with small roughness structures near the ends of the channels. The data can be described satisfactorily by a model which treats these structures as spheres of a single radius.

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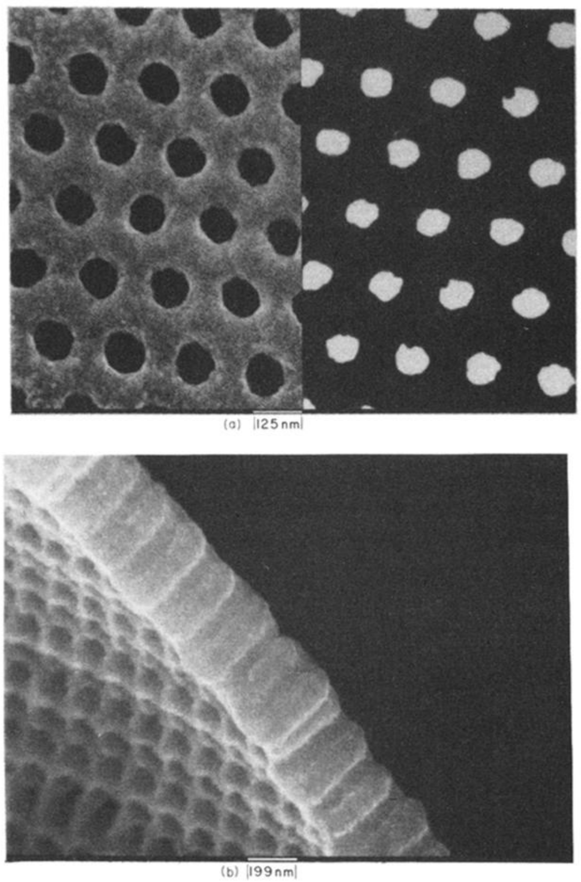

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