

Surface plasmon dispersion of a cluster-assembled silver nanoparticle film

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We report an investigation with high-resolution electron-energy-loss spectroscopy of a thin Ag film grown by deposition and aggregation of Ag_3^- clusters on graphite. We find the plasmon mode of the nanostructured film (particle size ~ 10 nm) at about 3.85 eV near the Brillouin-zone center, representing a blueshift of 0.15 eV with respect to the surface of a bulk Ag crystal. With increasing momentum parallel to the surface, the plasmon shows a very shallow positive dispersion and a distinct broadening. The results suggest a decrease in the s - d coupling in our nanoparticle film compared with the bulk. [S0163-1829(99)15215-9]

Collective electronic excitations at surfaces have been the subject of considerable interest.¹⁻⁴ In particular, surface plasmons not only represent a topic of fundamental interest in surface physics,⁴⁻¹³ but are also the basis of the probe surface plasmon resonance technique (see, for example, Ref. 14). The surface plasmon of silver has an energy of ~ 3.7 eV, which is easily accessible to optical and electron spectroscopies. The coupling of the plasmon to optical radiation allows one to monitor changes in the surface and its environment, and can be exploited¹⁵ in biosensing,^{5,14,16} gas sensing,¹⁷ characterization of thin films,^{6,7,18} and electrodeposition.¹⁹ Now that our understanding of the behavior of the surface plasmons of single crystal surfaces (e.g., of silver) has greatly improved as a result of recent experiments,^{8,20} there is an opportunity to characterize the plasmon modes of interesting surfaces, such as the nanostructured film explored here.

We have used high-resolution electron-energy-loss spectroscopy (HREELS) to characterize the surface plasmon excitation of a thin, nanostructured silver film made by deposition and aggregation of Ag_3^- clusters, produced with a cluster beam source, on the basal plane of graphite. Graphite is a relatively inert substrate, and has been well characterized by HREELS.^{21,22} The measured surface plasmon dispersion (as a function of the component of momentum parallel to the graphite surface) is compared with that of single-crystal silver surfaces,^{8,20} and to the Mie resonance in free Ag clusters.²³

Silver clusters were produced with a home built cluster source based on the principle of sputtering by positive cesium ions.^{24,25} The source produces a beam of small cluster anions which is extracted at 1.5 kV and mass-selected by a Wien filter. In these experiments silver trimers were produced with a typical intensity of 20 nA and decelerated to 30 eV for deposition onto a substrate of highly oriented pyrolytic graphite at room temperature in an ultrahigh-vacuum chamber (pressure during deposition: 1×10^{-9} mbar). Prior to deposition, the graphite substrate was cleaved in air and then cleaned in ultrahigh vacuum by electron bombardment heating up to ~ 900 °C. The amount of silver on the surface corresponds to 6×10^{16} atoms per cm^2 , and forms a visible film on the substrate. HREELS measurements were performed *in situ* at a pressure of $\sim 5 \times 10^{-10}$ mbar using a spectrometer

(L.K. 2000) operated with an energy resolution of 25 meV. The incident electron-beam energy was 32 eV, the angle of incidence 60° with respect to the surface normal, and the sample current typically 800 pA. HREELS spectra were recorded at different detection angles; each spectrum took several hours, and the whole experiment extended over several weeks. In order to avoid thermally driven changes of the silver film morphology, the sample was not heated after deposition. The position and width of the surface plasmon peak were checked at regular time intervals, and did not present any significant changes during the whole period of measurement. However, some residual adsorption (water/hydrocarbons) was inevitably observed. After completion of the HREELS experiments the sample was removed from the UHV chamber and imaged with a benchtop scanning tunneling microscope (DME Rasterscope 4000) which revealed; as expected,²⁶ that the trimers coalesce on the surface to form rafts of Ag particles of average size ~ 10 nm together with areas of bare graphite.

Figure 1 displays energy-loss spectra from the sample recorded in the specular geometry before and after deposition of the clusters. The spectrum of clean graphite (taken in the specular direction) is shown in Fig. 1(a), and shows the characteristic energy-loss tail due to π - π^* electron-hole pair excitations²¹ and a broad peak near 6.6 eV. The latter has been attributed to a π plasmon mode of graphite.²² No energy loss feature is visible in the energy range of special interest here (3–4 eV). Deposition of the silver clusters leads to the spectrum of Fig. 1(b). Three distinct features are present: (i) a sharp, well-defined energy-loss peak at about 3.85 eV; (ii) a rather constant signal level above this peak, creating a plateau; and (iii) a second, broader energy-loss peak at ~ 7.5 eV. A slowly sloping background, presumably coming from the graphite substrate, is still present, although strongly damped.

Optical-absorption and energy-loss spectra of silver films and silver crystal surfaces^{8,10-12,20,27,28} present features similar to those evident in Fig. 1(b). The main loss peak at 3.85 eV in Fig. 1(b) can be attributed to the well-known surface plasmon of silver, which has an energy close to 3.7 eV at the Brillouin-zone center on crystal surfaces.²⁹ The plateau in Fig. 1(b) results from intraband and interband transitions; electron-hole pair excitations within the sp band of bulk sil-

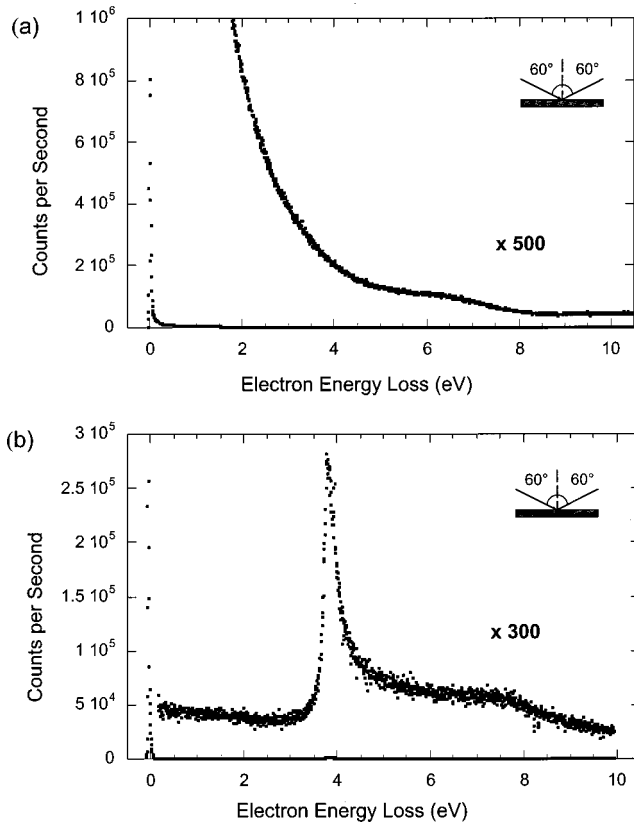


FIG. 1. HREELS spectra taken in the specular direction (a) before and (b) after deposition of Ag_3^- clusters (dose, 3.75×10^{11} atoms per cm^2 ; time, 420 min) on the graphite substrate at room temperature. Incident electron-beam energy, 32 eV; impact angle, 60° .

ver occur above 3.86 eV, while excitations between the d and sp bands appear above 3.98 eV.²⁷ The apparent asymmetry of the surface plasmon peak is a result of these electron-hole pair excitations just above the plasmon peak energy. We associate the broad, weak second peak which we observe at ~ 7.5 eV with the feature previously predicted and observed in the case of $\text{Ag}(001)$,³⁰ possibly also of plasmon character.

We will now focus on the silver surface plasmon peak observed at 3.85 eV in Fig. 1(b). In this case, the specular angle of collection of the scattered electrons corresponds to a parallel momentum transfer q_{\parallel} of 0.16 \AA^{-1} . By varying the collection angle we can investigate the dispersion of the surface plasmon. Note that for a particle diameter of ~ 10 nm, q_{\parallel} should be conserved to within $\sim 2\pi/100 \text{ \AA}^{-1} = 0.06 \text{ \AA}^{-1}$, which is a small fraction ($\sim 4.5\%$) of the width of the Brillouin zone.³¹ Figure 2 shows the surface plasmon peak for three values of q_{\parallel} . The change in plasmon frequency is small, whereas a clear broadening of the peak is visible. These spectra are part of a set of measurements which covers the range $0.09\text{--}0.31 \text{ \AA}^{-1}$ in q_{\parallel} . The frequencies and widths (full width at half maximum) obtained without subtraction of the electron-hole pair excitations are displayed as a function of parallel momentum in Fig. 3. These graphs confirm the trends observed in Fig. 2, i.e., we find (at most) a very weak positive dispersion of the plasmon energy while the increase of the peak width with increasing q_{\parallel} is more marked.

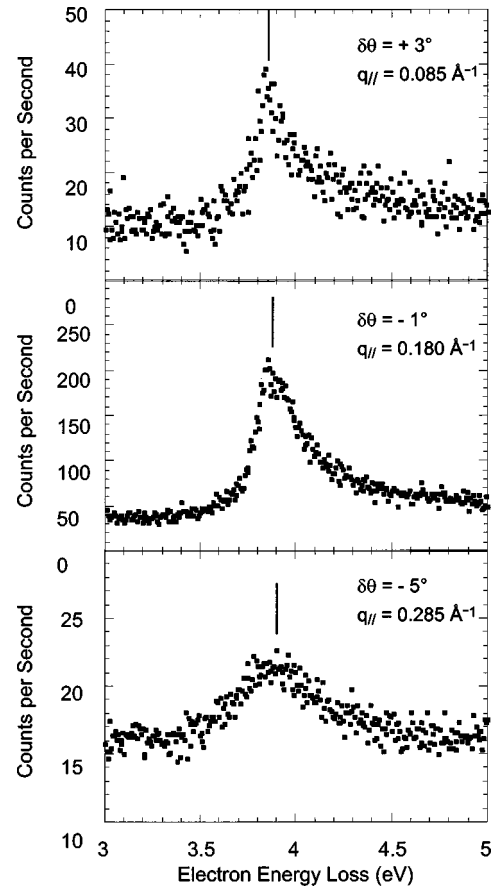


FIG. 2. HREELS spectra obtained at different collection angles showing how the surface plasmon broadens in frequency with increasing parallel momentum q_{\parallel} . $\delta\theta$ is the collection angle measured from the specular direction towards the surface ($\delta\theta < 0$) and the normal to the surface ($\delta\theta > 0$).

As a basis for the discussion of these results, we shall briefly review the plasmon excitation behavior of free Ag clusters and single-crystal Ag surfaces. The plasmon excitation (Mie resonance) in positively charged silver clusters in the gas phase has a limiting value of 3.5 eV for a large Ag particle, and shows an increase of frequency with decreasing size.²³ Similar behavior is observed in large Ag clusters embedded in a rare-gas film.³² Electrons in the sp band at the surface of the cluster are less strongly screened by the d band than are sp electrons in the cluster core; since the d -band screening lowers the plasma frequency, the frequency rises as the cluster becomes smaller and the surface effect more important. Intriguingly, the same basic physics²⁸ explains the positive dispersion of the Ag surface plasmon as a function of q_{\parallel} for all crystal surfaces reported;^{8,20} for larger q_{\parallel} the electric field penetrates less deeply into the Ag surface.

In our case [Fig. 3(a)], the value of the plasmon frequency as q_{\parallel} tends to zero, 3.85 eV, is blueshifted with respect to the plasma frequency (at $q_{\parallel} = 0$) for the single-crystal surfaces of Ag (3.7 eV). Moreover, the plasmon energy of our film increases much more slowly with q_{\parallel} than for all reported single-crystal surfaces of Ag (for a review, see Ref. 8). Note also that the widths which we obtain for the plasmon of the Ag cluster film [see Fig. 3(b)] are somewhat (typically ~ 100 meV) larger than for the single-crystal surfaces, perhaps because we have not attempted to remove the peak asymmetry

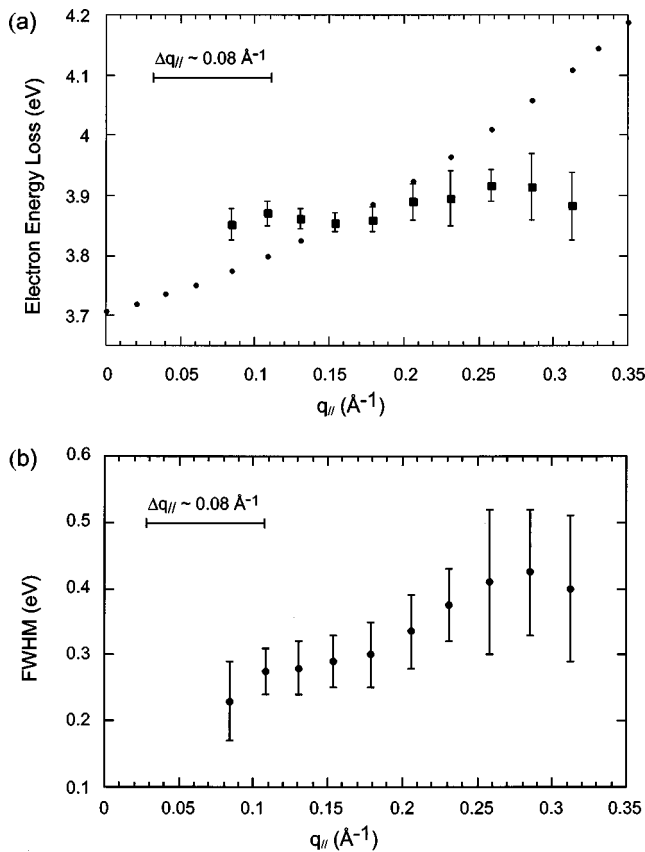


FIG. 3. Plot of (a) the surface plasmon energy of the cluster-assembled film of Ag (squares), compared with the Ag(111) surface (circles), and (b) the surface plasmon peak width of the cluster-assembled film, as a function of parallel momentum transfer. The experimental error bar (0.08 \AA^{-1}) on the measure of $q_{||}$ arises from the finite angular width ($\sim 3^\circ$) of the reflected electron beam.

in the analysis, or because of inhomogeneous broadening (due to varying film thickness and roughness²⁰) or “chemical interface damping.”^{18,33} However, our primary aim here is to explain (a) the (small) blueshift of the plasma frequency at low $q_{||}$, and (b) the flatter dispersion of the plasma frequency in the case of our cluster-assembled film.

Particularly helpful in the analysis of the experimental dispersion results are studies of the plasmon behavior in thin Ag films on Cu, Al, and Si substrates.^{9–11} In each of these cases a shift of the plasma resonance to higher frequencies was observed in optical reflectivity measurements. HREELS measurements of a 5-nm Ag film on Si(111) show a blueshift of ~ 50 meV at all $q_{||}$ with respect to Ag(111).¹² Calculations by Liebsch for a few layers of Ag on Al predict a blueshift (at *small* values of $q_{||}$) arising from reduced *s-d* coupling in the thin Ag film and from coupling to the higher frequency plasmon of the substrate.¹³ Both these effects should apply in the case of our thin nanostructured film of Ag on graphite, and provide an appealing qualitative explanation of the measured blueshift (~ 0.15 eV) at small $q_{||}$. Interestingly, the calculations for thin layers of Ag on Al also predict a much flatter dispersion than for Ag crystal surfaces, consistent with Fig. 3(a). Finally, we note that, in addition to the blueshift expected of a thin Ag film, dielectric screening by a slab or layer of material with $\epsilon > 1$ (e.g., $\epsilon \approx 3$ for graphite³⁴) should lower the plasma frequency across the *whole width* of the Brillouin zone.¹³ This effect would compete with the blueshift expected at small $q_{||}$, while it would drag down the plasmon frequency of the Ag nanoparticle film below that for the Ag(111) surface for high values of $q_{||}$, as observed in Fig. 3(a).

We have shown that high-resolution electron-energy-loss spectroscopy can be used to characterize the plasmon mode of a nanostructured film of Ag produced by deposition and coalescence of Ag_3^- clusters on the graphite surface. The observation of plasmon dispersion confirms that $q_{||}$ is approximately a good quantum number for particle sizes on the scale of 10 nm. The measured blueshift of the plasma frequency at small $q_{||}$ and the flatter dispersion as a function of $q_{||}$ mirror calculations for thin Ag films, and suggest a decrease in the *s-d* electron coupling in the nanoparticle film. As HREELS measurements of the plasmon modes of nanostructured films and deposited clusters become more common, an extension of the theory dealing with the coupling between the plasmon modes of clusters or nanoparticles and the substrate³⁵ will be most valuable.

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¹S. R. Barman, K. Horn, P. Häberle, H. Ishida, and A. Liebsch, Phys. Rev. B **57**, 6662 (1998).

²F. Moresco, M. Rocca, V. Zielasek, T. Hildebrandt, and M. Henzler, Phys. Rev. B **54**, R14 333 (1996).

³M. B. Sobnack, W. C. Tan, N. P. Wanstall, T. W. Preist, and J. R. Sambles, Phys. Rev. Lett. **25**, 5667 (1998).

⁴B. Hecht, H. Bielefeldt, L. Novotny, Y. Inouye, and D. W. Pohl, Phys. Rev. Lett. **77**, 1889 (1996).

⁵D. Pan and D. L. Phillips, Chem. Phys. Lett. **275**, 227 (1997).

⁶T. Yamaguchi, M. Ogawa, H. Takahashi, and N. Saito, Surf. Sci. **129**, 232 (1983).

⁷T. Götzw, W. Hoheisel, M. Vollmer, and F. Träger, Z. Phys. D **33**, 133 (1995).

⁸M. Rocca, Surf. Sci. Rep. **22**, 1 (1995).

⁹R. Kötz and D. M. Kolb, Surf. Sci. **97**, 575 (1980).

¹⁰T. Lopez-Rios, M. De Crescenzi, and Y. Borenstein, Solid State Commun. **30**, 755 (1979).

¹¹Y. Borenstein, M. Roy, and R. Alameh, Europhys. Lett. **31**, 311 (1995).

¹²J. M. Layet, R. Contini, J. Derrien, and H. Lüth, Surf. Sci. **168**, 142 (1986).

¹³A. Liebsch, *Electronic Excitations at Metal Surfaces* (Plenum, New York, 1997).

¹⁴R. A. Frazier, M. C. Davies, G. Matthijs, C. J. Roberts, E. Schacht, S. J. B. Tendler, and P. M. Williams, Langmuir **13**, 7115 (1997).

¹⁵J. R. Sambles, G. W. Bradbery, and Fuzi Yang, Contemp. Phys. **32**, 173 (1991).

¹⁶T. H. Koschmieder and J. C. Thompson, Phys. Rev. B **50**, 7845 (1994).

- ¹⁷G. J. Kovacs, *Surf. Sci.* **78**, L245 (1978).
- ¹⁸H. Hövel, S. Fritz, A. Hilger, U. Kreibig, and M. Vollmer, *Phys. Rev. B* **48**, 18 178 (1993).
- ¹⁹R. Kötz, H. J. Lewerenz, and E. Kretschmann, *Phys. Lett.* **70A**, 452 (1979).
- ²⁰M. Rocca and U. Valbusa, *Phys. Rev. Lett.* **64**, 2398 (1990); M. Rocca, F. Biggio, and U. Valbusa, *Phys. Rev. B* **42**, 2835 (1990); M. Rocca, M. Lazzarino, and U. Valbusa, *Phys. Rev. Lett.* **69**, 2122 (1992); M. Rocca, Li Yibing, F. Buatier de Mongeot, and U. Valbusa, *Phys. Rev. B* **339**, 291 (1995); M. Rocca, F. Moresco, and U. Valbusa, *ibid.* **45**, 1399 (1992); F. Moresco, M. Rocca, V. Zielasek, T. Hildebrandt, and M. Henzler, *ibid.* **54**, R14 333 (1996); F. Moresco, M. Rocca, V. Zielasek, T. Hildebrandt, and M. Henzler, *Surf. Sci.* **388**, 1 (1997); **388**, 24 (1997).
- ²¹R. E. Palmer, J. F. Annett, and R. F. Willis, *Phys. Rev. Lett.* **58**, 2490 (1987); J. F. Annett, R. E. Palmer, and R. F. Willis, *Phys. Rev. B* **37**, 2408 (1988); P. Laitenberger and R. E. Palmer, *Phys. Rev. Lett.* **76**, 1952 (1996).
- ²²U. Diebold, A. Preisinger, P. Schattschneider, and P. Varga, *Surf. Sci.* **197**, 430 (1988).
- ²³J. Tiggesbäumker, L. Köller, H. O. Lutz, K. H. Meiwes-Broer, and A. Liebsch, *Chem. Phys. Lett.* **190**, 42 (1992); J. Tiggesbäumker, L. Köller, K. H. Meiwes-Broer, and A. Liebsch, *Phys. Rev. A* **48**, R1749 (1993).
- ²⁴S. G. Hall, M. B. Nielsen, A. W. Robinson, and R. E. Palmer, *Rev. Sci. Instrum.* **68**, 3327 (1997).
- ²⁵G. D. Alton, *Nucl. Instrum. Methods Phys. Res. A* **244**, 133 (1986).
- ²⁶G. M. Francis, L. Kuipers, J. R. A. Cleaver, and R. E. Palmer, *J. Appl. Phys.* **79**, 2942 (1996).
- ²⁷P. Winsemius, F. F. Kampen, H. P. Lengbeek, and G. G. Van Went, *J. Phys. F* **6**, 1583 (1976).
- ²⁸A. Liebsch, *Phys. Rev. B* **48**, 11 317 (1993).
- ²⁹Note that this shift is rather small compared with the plasmon frequency shifts observed for Ag particles embedded in matrices, where changes in frequency greater than 0.5 eV are common. See, for example, Ref. 18.
- ³⁰J. A. D. Matthew, F. P. Netzer, and G. Astl, *Surf. Sci.* **259**, L757 (1991).
- ³¹Note also that the angular width (full width at half maximum) of the reflected elastic electron beam was only $\sim 3^\circ$, which corresponds to an integration interval of $\sim 0.08 \text{ \AA}^{-1}$ in momentum space.
- ³²K. P. Charlé, W. Schulze, and B. Winter, *Z. Phys. D* **12**, 471 (1989); H. Abe, W. Schulze, and B. Tesche, *Chem. Phys.* **47**, 95 (1980).
- ³³B. N. J. Persson, *Surf. Sci.* **281**, 153 (1993).
- ³⁴B. T. Kelly, *The Physics of Graphite* (Applied Science Publishers, London, 1981).
- ³⁵U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).