PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Quantum size effects in the surface-plasmon excitation of small metallic particles by electron-energy-loss spectroscopy

F. Ouyang*
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853

P. E. Batson
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

M. Isaacson
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853

(Received 4 June 1992)

Electron-energy-loss spectroscopy was used to study the quantum size effect in surface-plasmon excitations of small metallic particles, with diameters ranging from 4 to 20 nm. Scanning transmission electron microscopy was used, which provided the capability of observing electron-energy-loss spectra from individual, well-characterized silver particles. The measured relation between the surface-plasmon energy and the particle size shows a definite deviation from that predicted by macroscopic theories, and cannot be well explained by existing microscopic theories.

I. INTRODUCTION

The study of small particles or microclusters has been very active in recent years.[1,2] When a particle decreases in size, its properties deviate from those of bulk material and become size dependent. This phenomenon is referred to as the quantum size effect. By now, experimental and theoretical studies have been carried out for a large variety of clusters consisting of metals, insulators, and semiconductors. Properties studied include binding energy, magnetic moment, electric polarizability, ionization potential, electron affinity, chemical reactivity, fragmentation cross section, photon absorption cross section, plasmon resonance energy, etc.

Studies of the electronic structure of small metallic particles can be traced back to the 1970s.[3–6] Experimental and theoretical results in this area are helpful in understanding the electronic and lattice properties of a finite-size electronic system. The knowledge about electronic structure is also indispensable in understanding practical properties of small particles, such as reactivity of powder catalysts, conductance of very thin wires and electronic or optical properties of very small semiconductor structures.

Surface-plasmon excitation, a nonlocal response of material to time-varying external electromagnetic fields, was chosen as a probe of the electronic properties of small particles in our study. In electron-energy-loss-spectroscopy (EELS) measurements, surface-plasmon excitation results in specific peaks in the energy-loss spectra. These peaks occur even when the electron beam passes near the particle under study, but does not penetrate it. In comparison with other spectroscopy techniques, surface-plasmon EELS studies of the quantum size effect have certain advantages. The surface plasmon is a collective excitation which is characteristic of solids, therefore its quantum size effect is expected to occur at larger scales than those of atomic-based properties such as ionization energies or binding energies. Since the surface plasmon is a surface localized excitation, its intensity is roughly proportional to the surface area, rather than the volume, of the particles. Therefore, surface-plasmon excitation is relatively easy to observe from small particles.

Early studies of surface-plasmon excitation of small particles used optical-absorption spectroscopy[3,6–8] and broad beam EELS.[3,9–11] Optical measurements are very useful tools in this area because of their high-energy resolution. Not only the excitation energy, but also the resonance width, can be studied in detail. However, its power is limited in the sense that it is a broad beam probe. The observed effect is an average of contributions from particles with a finite size distribution. Optical methods cannot be used to study the effects of impact parameters, nor excitations with finite momentum transfer. With the development of molecular-beam techniques, it becomes possible to form a mass selected cluster beam of particles of very narrow size distribution from which the optical spectra can be studied.[12–15] To date, most of the studies using cluster beam have dealt with very small particles (less than 5 nm in diameter). Broad beam EELS shares the high-energy resolution and low spatial resolution characteristics of optical spectroscopy, but angular-resolved measurements are possible to study excitations with finite momentum transfers.[9]

The scanning transmission electron microscope (STEM) developed in the last decade provides us with a powerful tool to observe characteristics of materials at a local subnanometer scale. With a high brightness field emission gun, EELS can be performed with a probe size of 0.2–0.5 nm in diameter, and still achieve an adequate counting rate.[16] Particle selected EELS for surface-plasmon observation has been demonstrated to be possible. Work in this area has been concentrated on multimode characteristics and interaction between the particle and its surroundings (oxide coating or substrate).[17–19] These effects can be explained and modeled by macroscopic theories.

In this paper, we report the study of the quantum size effect using EELS and a subnanometer-diameter electron probe in the STEM. Specimens of silver particles deposited on very thin carbon film substrates were chosen to simplify considerations of the multimode effects or surface coating. Our measurement shows a distinct change in the excitation energies of the surface plasmons, which deviates from the predictions of macroscopic theory. The experiments will be described in the next section.

In order to exclude possibilities that the observed deviation is due to imperfection of the experimental system such as coupling between the particle and the substrate, accurate modeling of the surface-plasmon excitation in the framework of the macroscopic theory is necessary. The theory is reported elsewhere,[20] and will be outlined in Sec. III. A review and discussion of the microscopic theories on the quantum size effect will be presented in Sec. IV, where our conjecture on the interpretation of our experimental results will be put forward.

II. EXPERIMENT

We chose silver as the metal to study for a number of reasons. First, silver is very stable against surface contamination. Therefore, the preparation and transport of the specimens are much easier for silver than those for alkali metals, or even for aluminum. Second, the excitation energies of the surface plasmons corresponding to various modes are very closely separated. The energy shift due to the quantum size effect is therefore likely to exceed the range covered by multimode energies. It is thus easier to distinguish quantum size effects from multimode effects. In addition, the excitation energy of the silver surface plasmon is about 3.5 eV, which is higher than that of gold and platinum. The resonant peak is therefore easier to detect using EELS, since it is not as much obscured by the tail of the electron source energy distribution.

The small-particle specimens were prepared by two methods. Some were made by evaporating Ag onto 2-nm-thick carbon films through a shadowing mesh, and annealing the resulting film at 600 °C in the preparation chamber attached to the STEM. Other specimens were prepared by deposition from cluster beams generated by the gas aggregation technique[21] or electrohydrodynamic atomization technique.[22] The surface condition of the silver particles was examined by the energy-dispersive x-ray spectroscopy in the STEM, and no contamination other than a submonolayer of chlorine was evident. The thickness profile of the particles were measured by bulk EELS (Ref. 23) and annular dark-field imaging. The particles, diameters ranging from 25 to 3 nm, appear to be uniform in shape, and close to hemispherical.

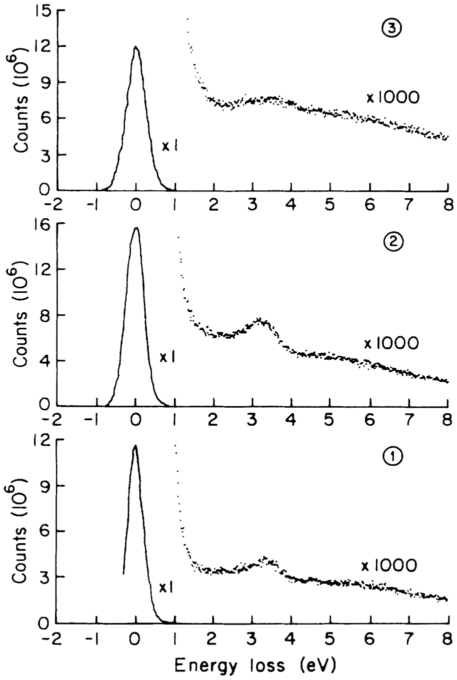

FIG. 1. Typical raw data of electron-energy-loss spectra from small silver particles. The particle diameters for the spectra 1, 2, and 3 are 18, 10, and 4 nm, respectively. The spectra were taken from the HB5 STEM at Cornell University. Electron-beam voltage was 100 kV. The illumination half angle was 6.5 mrad and the collection half-angle was 10 mrad.

The EELS measurements were performed on two different dedicated STEM's. One was the HB-501 UHV system at Cornell University, which has a vacuum generator electron-energy-loss magnetic sector spectrometer with full width at half maximum (FWHM) resolution of 0.3 eV. Because the stability of the EELS system is subject to long-term fluctuations of the microscope beam voltage, a multiscanning technique was employed to obtain sufficient counting statistics.[24] The other microscope used was the HB-5 STEM at the IBM T. J. Watson Research Center. It is equipped with a parallel detection Wien filter EELS system, on which the effect of beam voltage fluctuation is removed.[25] Both STEM's were operated at 100-kV incident electron energy. Figure 1 shows typical raw spectra from three particles of various sizes (with experimental conditions indicated in the figure caption). In Fig. 2, the contributions from the background and the underlying carbon substrate were removed from the measured spectra by subtracting from, after proper scaling, the EELS data taken from the carbon film alone. Processed spectra were further smoothed by Gaussian convolution, spline, or polynomial fitting, in order to determine the position of the surface-plasmon peaks. For a given spectrum, the spread in the peak posi-

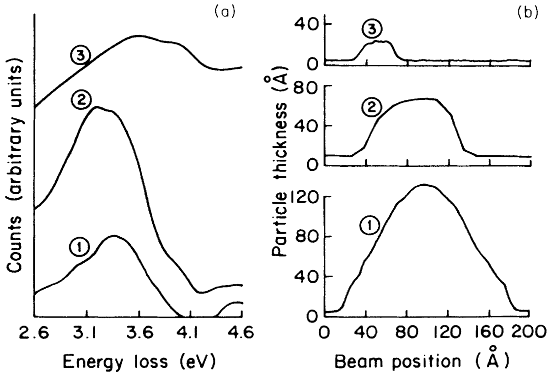

FIG. 2. (a) Same spectra as in Fig. 1, with background removed. (b) Thickness profiles of the corresponding particles (from Ref. 44).

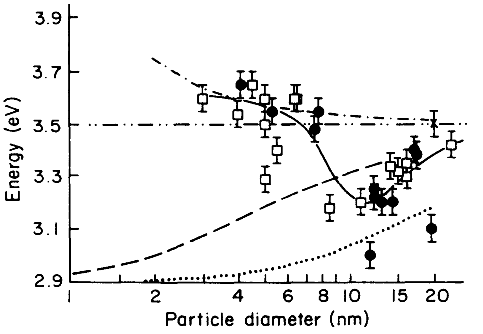

FIG. 3. Surface-plasmon excitation energies of silver particles with various sizes. Open squares (group 1) and crosses (group 2): data taken at Cornell HB-501, with different specimens. Closed circle (group 3): data taken at IBM HB-5, with another specimen. The solid line indicates a smoothed spline fit of the experimental data. Other plotted lines indicate computed results from theoretical models. Dashed-dotted line: prediction from hydrodynamic model. Dashed–double-dotted line: prediction from macroscopic theory. Dashed line and dotted line: prediction from macroscopic theory, for silver particles with 1 and 4 nm of carbon coating, respectively.

tions determined using different smoothing methods fell within the range of 0.1 eV, which was then taken as our measurement error. Thickness profiles of the particles from which the spectra were taken are also shown in Fig. 2.

Figure 3 shows the measured relation of the sizes (diameters) of the Ag particles and their surface-plasmon energies, in comparison with some theoretical calculations. The data in groups 1 and 2 were measured using the HB-501 system, with specimens made in different ways. The data in group 3 were measured using the HB-5 system, with another specimen. A smoothed spline fit of the data is also included in Fig. 3. As shown in the figure, the results from the various groups of data are rather consistent. It is evident from these measurements that as the particle size gets smaller, the surface-plasmon energy first decreases (at about 10-nm diam), then rises to a value higher than that of the large particles.

III. THEORY: MACROSCOPIC

Based on macroscopic properties of the material, theoretical efforts have been made by many authors to predict the surface-plasmon excitation energy-loss spectrum. In theoretical calculations related to STEM measurements, a fast electron is considered as a classical particle moving with a known path and a constant velocity.[18,19,26–31] The interactions between the fast electron and the dielectric object can be described either in a classical way or in a quantum-mechanical way. In the classical picture, the response from the object is generated by the induced charge distribution as characterized by the dielectric constant. In the quantum-mechanical picture, a harmonic-oscillator model is used to describe free-electron metals.[29–31] Or, more generally, the excitation states of the dielectric system are assumed to result in the same charge distribution as dictated by the dielectric constants.[20] Classical and quantum-mechanical pictures predict the same energy-loss spectra results if the scattered electrons are collected over all angles, as in the case of our experiment. The quantum-mechanical picture is further able to predict results from angular-resolved spectra.[20,32]

The energy-loss spectrum due to surface-plasmon excitations from spherical particles has been calculated by previous authors.[26] Other solvable geometric systems have also been studied.[18,28] A general physical picture and an algorithm were developed to deal with particle with arbitrary shapes and dielectric properties.[20] According to these papers, the electron-energy-loss spectrum due to surface-plasmon excitation is the sum of contributions from individual excitation modes. The energy and line shape of the contribution of each mode are determined by the dielectric constant of the material and the shape of the object. They are, however, independent of the size of the object. The weights of the various modes in the resultant spectrum depend upon the size of the object, as well as the trajectory and the energy of the incident electron.

For particles with the same shape but different sizes, the macroscopic theories predict spectral peaks at fixed energies, for individual surface-plasmon modes. However, the total spectrum from the particle can still change with size in the following ways. The weight of various surface-plasmon modes can change with the particle size and the impact parameters. If the difference in peak energies among the various modes is big, the shape and peak positions of their sum may change. The coupling between the particle and the supporting substrate could be important when the particle size is comparable with the substrate thickness. Such coupling would change with the particle size. If the particle is covered with oxide or other contaminants with constant thickness, the resulting excitation may also change with particle size.

In order to exclude these factors from our measured energy shifts, calculations and modeling were performed in the frame of macroscopic theory. Utilizing the result for a general system,[20] an accurate modeling of the system of silver particles on carbon film was established.[33] The result shows that the coupling between the carbon film and the silver particle affects the intensity but not the position of the EELS surface-plasmon peak. Figures 4

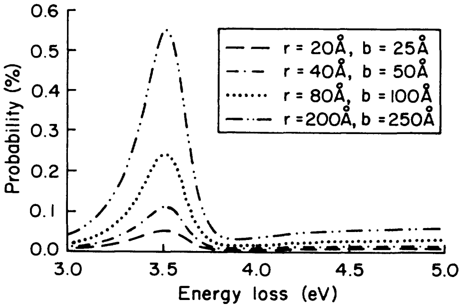

FIG. 4. Electron-energy-loss spectra from silver spheres on a 5-nm carbon film substrate, as calculated from macroscopic theories. The film contribution is subtracted. The particle radii (r) and impact parameters (b) are indicated in the inset (from Ref. 45).

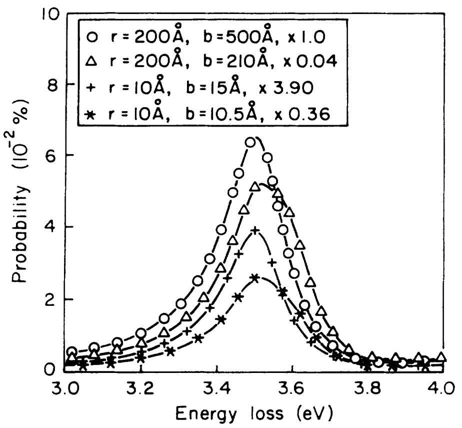

FIG. 5. Electron-energy-loss spectra from silver spheres as predicted by the macroscopic theories. Particle radii (r) and impact parameters (b) are listed in the inset. The spectra are scaled as indicated to make the comparison easier (from Ref. 45).

and 5 show the calculated spectra under various conditions. These results show that the macroscopic theory predicts no more than 0.01-eV change in EELS peak position due to the particle size change with this particular system, when one considers the substrate and multimode contributions. This statement is not general to all dielectric systems.[19] For the system we studied, the energy difference of various surface-plasmon modes is small, and the carbon film is not active to excitations in the energy range of interest. Therefore, the above-discussed complexities can be avoided.

As for surface contamination, x-ray analysis shows no evidence of more than one monolayer of contamination. However, it is possible that the silver particles are wrapped with a layer of hydrocarbon contaminant, whose x-ray signal would not be distinguishable from the carbon substrate. The macroscopic prediction of the behavior from carbon-wrapped silver particles, as shown in Fig. 3, deviates significantly from our observation. It thus appears that the observed energy shift cannot be explained by the macroscopic theories, even with the assumption of contamination.

IV. THEORY: MICROSCOPIC

There have been many theoretical studies of the electronic properties of small metallic particles based on microscopic models. For those related to surface-plasmon excitations, most studies use either the random-phase approximation or approximations somewhat equivalent, or hydrodynamic models.[6,34–43] Although there are some contradictions among the authors, it seems to be the consensus that when the particle becomes smaller, the energy of the surface-plasmon peak increases, in the order of tenths of an eV.

Some work further considered the surface condition of the particle.[39,42] The electron density was considered to be gradually decreasing to zero near the surface. For particles with such a diffuse surface, the surface-plasmon energy is lower than that for particles with a sharply bounded electronic surface. This result is actually understandable in the macroscopic picture. In a particle with a diffuse surface, the surface plasmon, which is localized near surface, "sees" a lower electron density than that in the bulk. A lower density results in a lower plasmon energy.

Although no predictions have been made so far for a nonmonotonic relation between the particle size and the surface-plasmon energy, the above-mentioned results can provide a qualitative explanation of our measurements. When the particle is relatively large, it behaves according to the macroscopic theories. The particle also has a surface layer, in which the electron density gradually decreases to zero. The thickness of the surface layer is determined by the local potential profile, and is thus a constant as the particle size changes. Under this condition, as the particle becomes smaller, the importance of the surface layer increases. Therefore, the energy of the surface-plasmon peak decreases as the particle size decreases. As the particle size becomes smaller, a surface layer with constant thickness eventually results in changes in the bulk electron density, as required by the conservation of electron number. The bulk density change disturbs the balance between the electron and the positive-ion background. The resulting net bulk charge distribution consequently suppresses such a density change. Under this condition, the thickness of the "effective" surface layer can no longer be considered constant as the particle size decreases. The importance of the surface layer is thus limited and yields to other quantum effects that result in the increase of the surface-plasmon energy. In this region, the net result is that the surface-plasmon energy increases as the particle size decreases.

It is difficult to be more quantitative in this picture without going through material-specific modeling and computations. However, one implication from the above discussion is that the transition between the two size regions happens when the effective surface layer thickness is comparable to the radius of the particle. In our measurement, the change of the energy-shifting direction happens at about 10-nm diam. This suggests that the diffuse surface layer of the silver particle is about ten times larger than the lattice spacing. Further experiments using angular-resolved EELS may be able to provide information about the electron distribution near the surface.

V. CONCLUSION

It is feasible to use EELS in the STEM as a tool to study the quantum size effect of individual metallic particles. Our measurement of the relation between surface-plasmon excitation energy and the particle size in silver shows a nonmonotonic behavior, which has neither been reported nor predicted previously. This is a definite deviation from the macroscopic picture of surface-plasmon excitation. An explanation based on microscopic theories seems to be necessary.

ACKNOWLEDGMENTS

The authors wish to acknowledge help at various stages of specimen preparation from Professor Dr. J. Urban (Fritz Haber Institute, Berlin), Professor T. Kelly (University of Wisconsin at Madison), and Professor M. Lamvik (Duke University), and technical assistance from Dr. E. Kirkland, M. Thomas, and Dr. P. Xu (Cornell University). Discussions with Dr. H. Kohl (Institut für Angewandte Physics, Technische Hochschule Darmstadt), Professor M. Scheinfein (Arizona State University), Professor Dr. E. Zeitler (Fritz Haber Institute, Berlin), and Professor J. Silcox (Cornell University) have been very helpful in this work. This work was supported in part by the U.S. NSF, AFOSR, and H. F. Johnson.

---

*Present address: Gatan Research and Development, 6678 Owens Dr., Pleasanton, CA 94588.

[1] T. Halicioglu and C.W. Bauschlicher, Jr., Rep. Prog. Phys. **51**, 883 (1988).
[2] *Microclusters,* edited by S. Sugano, Y. Nishina, and S. Ohnishi (Springer-Verlag, Berlin, 1987).
[3] U. Kreibig and P. Zacharias, Z. Phys. **231**, 128 (1970).
[4] A. A. Lushnikov and A. J. Simonov, Z. Phys. **270**, 17 (1974).
[5] M. Cini and P. Ascarelli, J. Phys. F **4**, 1998 (1974).
[6] L. Genzel, T. P. Martin, and U. Krebig, Z. Phys. **270**, 17 (1974).
[7] M. A. Smithard and M. Q. Tran, Helv. Phys. Acta **46**, 870 (1974).
[8] S. F. Chernov, Opt. Spektrosk. **59**, 235 (1985) [Opt. Spectrosc. (USSR) **59**, 141 (1985)].
[9] A. vom Felde, J. Fink, and W. Ekardt, Phys. Rev. Lett. **61**, 2249 (1988).
[10] W. J. Kaiser, E. M. Logothetis, and L. E. Wenger, Solid State Commun. **58**, 83 (1986).
[11] K. Breuer, Phys. Status Solidi B **91**, K69 (1979).
[12] W. A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Chatelain, and W. D. Knight, Phys. Rev. Lett. **59**, 1805 (1987).
[13] J. M. Pacheco and R. A. Broglia, Phys. Rev. Lett. **62**, 1400 (1989).
[14] K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. deHeer, and W. D. Knight, Phys. Rev. B **40**, 5417 (1989).
[15] J. Stapelfeldt, J. Wörmer, and T. Möller, Phys. Rev. Lett. **62**, 98 (1989).
[16] M. S. Scheinfein and M. Isaacson, J. Vac. Sci. Technol. B **4**, 326 (1986).
[17] P. E. Batson, Surf. Sci. **156**, 720 (1985).
[18] M. Acheche, C. Colliex, H. Kohl, A. Nourtier, and P. Trebbia, Ultramicrosc. **20**, 99 (1986).
[19] Z. L. Wang and J. M. Cowley, Ultramicrosc. **23**, 97 (1987).
[20] F. Ouyang and M. Isaacson, Philos. Mag. B **60**, 481 (1989).
[21] F. Frank, W. Schulze, B. Tesche, J. Urban, and B. Winter, Surf. Sci. **156**, 90 (1985).
[22] J. F. Majohoney, S. Taylor, and J. Perel (private communication).
[23] R. F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope* (Plenum, New York, 1986).
[24] F. Ouyang, M. Isaacson, and E. J. Kirkland, in *Proceedings of the XIIth International Congress for Electron Microscopy,* edited by A. W. Bailey (San Francisco Press, San Francisco, 1990), p. 40.
[25] P. E. Batson, Rev. Sci. Instrum. **37**, 43 (1986).
[26] T. L. Ferrell and P. M. Echenique, Phys. Rev. Lett. **55**, 1526 (1985).
[27] R. Garcia-Molina and R. H. Ritchie, Phys. Rev. B **31**, 121 (1985).
[28] B. L. Illman, V. E. Anderson, R. J. Warmack, and T. L. Ferrell, Phys. Rev. B **38**, 3045 (1988).
[29] J. C. Ashley and T. L. Ferrell, Phys. Rev. B **14**, 3277 (1976).
[30] M. Schmeits, J. Phys. C **14**, 1203 (1981).
[31] S. Munnix and M. Schmeits, Phys. Rev. B **32**, 4192 (1985).
[32] H. Kohl, Ultramicrosc. **11**, 53 (1987).
[33] F. Ouyang and M. Isaacson, Ultramicrosc. **31**, 345 (1989).
[34] W. Edkardt, Phys. Rev. B **31**, 6360 (1985).
[35] D. E. Beck, Phys. Rev. B **35**, 7325 (1987).
[36] A. Kawabata and R. J. Kubo, J. Phys. Soc. Jpn. **21**, 1765 (1966).
[37] A. A. Lushnikov and A. J. Simonov, Z. Phys. **270**, 17 (1974).
[38] E. Zarembe and B. N. J. Persson, Phys. Rev. B **35**, 596 (1987).
[39] P. Ascaralli and M. Cini, Solid State Commun. **18**, 385 (1976).
[40] R. Ruppin, J. Phys. Chem. Solids **39**, 233 (1978).
[41] D. B. Tran Thoai and E. Zeitler, Appl. Phys. A **45**, 249 (1988).
[42] R. J. Ruppin, Opt. Soc. Am. **66**, 449 (1976).
[43] R. J. Saniz, J. Phys. Condens. Matter **2**, 7925 (1990).
[44] F. Ouyang and M. Isaacson, in *Proceedings of the 47th Annual Meeting of the Electron Microscopy Society of America,* edited by A. W. Bailey (San Francisco Press, San Francisco, 1989), p. 230.
[45] F. Ouyang, Ph.D. dissertation, Cornell University, 1990.