Vacuum ultraviolet reflectivity of small gold clusters

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We report on the reflectivity spectra of continuous ($d = 1000$ Å) and discontinuous ($d = 12$, 25, 35, and 50 Å) gold films evaporated onto fused quartz substrates, measured in the photon energy range 15–35 eV using synchrotron radiation. The spectra of very thin films are attenuated and shifted predominantly towards higher energies relative to the bulk gold one. The shifts are explained in terms of a modification of the Au band structure induced by the contraction of the fcc nearest-neighbor distance.

I. INTRODUCTION

The optical properties of ultrathin films of noble metals have been studied by many authors almost exclusively in the visible[1,2] and near ultraviolet regions,[3] where they exhibit a strong absorption peak due to a collective electronic excitation in the cluster.[4] Instead, little effort has been dedicated to the investigation of their optical properties at higher energies, where, in the crystals, the contribution of interband transitions becomes dominant.[5,6] The purpose of this work was to study the evolution of the interband transitions for decreasing dimensions of the crystallites in the aggregated films.

We measured the reflectivities of both continuous ($d = 1000$ Å) and discontinuous ($d = 12$, 25, 35, and 50 Å) gold deposits in the range 15–35 eV using synchrotron radiation. The reflectivity spectra of the thinner films showed sizable shifts, predominantly towards higher energies, with respect to the bulk features. These shifts increase for smaller and smaller clusters and have been accounted for the modification of the band structure caused by the shortening of the nearest-neighbor distances.

II. EXPERIMENTAL DETAILS

The samples were prepared by evaporating pure gold (99.996%) from a tungsten boat onto 9×15 mm^2 highly polished fused quartz substrates at a pressure of about 10^{-7} Torr. Their thicknesses, as measured by a quartz balance, were 12, 25, 35, and 50 Å for the discontinuous films and 1000 Å for the continuous one. Equivalent films were characterized by electron microscopy with a Siemens EM 100. In Table I we report the thickness d, the mean diameter D, the standard deviation σ, and the filling factor (the fraction of the sample volume occupied by grains) f of the discontinuous films. The films were then annealed at 400 °C for 2 h before being transferred to a high-vacuum experimental chamber and ion pumped to a pressure of about 10^{-8} Torr for the reflectivity measurements. These were performed using the vacuum ultraviolet beam line of the synchrotron radiation facility Programma per l'Utilizzazione della Luce di Sincrotrone (PULS) at the Frascati Istituto Nazionale di Fisica Nucleare (INFN) National Laboratories.[7] The energy resolution $\Delta E/E$ was about 10^{-3} between 15 and 35 eV.

TABLE I. Data for the discontinuous gold films having mass thicknesses d, log-normal distribution of mean projected diameter D with a geometrical standard deviation σ, and filling factor f.

d (Å)	D (Å)	σ	f
12 ∓2	43	1.4	0.19
25 ∓2	90	1.3	0.28
35 ∓3	135	1.3	0.33
50 ∓3	210	1.3	0.46

III. RESULTS AND DISCUSSION

Figure 1 shows the reflectivity spectra of both continuous and discontinuous gold films, as well as of the fused quartz substrate from 15 to 35 eV. Our results for fused quartz are in excellent agreement with those reported by Platzoder and Steinmann[8] in the 500–1000-Å interval and furnish new data between 350 and 500 Å.

The reflectivity spectrum of the continuous gold film reproduces both in shape and in absolute values the spectrum obtained by Canfield, Hass, and Hunter[9] using a conventional source and that of Beaglehole, De Crescenzi, Theye, and Vuye[10] obtained with synchrotron radiation by a multiangle reflectance technique. The thick gold spectrum shows four features, labeled A, B, C, and D in Fig. 1. The reflectivity spectra of the discontinuous gold films show the same features as the thick film spectrum. The optical response of the 50-Å sample has not been reported in Fig. 1, since it reproduces exactly the structures of the thick film. In the case of the thinnest films, we note a reduction of the reflectivity and an energy shift of the mentioned structures except for peak A. In particular, the predominant peak B occurring at 22.1 eV for the bulk, shifts towards higher energies (arrows in Fig. 1) decreasing the thickness. Structure D seems to follow the trend of peak B with a larger shift towards higher energies.

In order to interpret the observed behavior, at first we have performed model calculations for both thin uniform

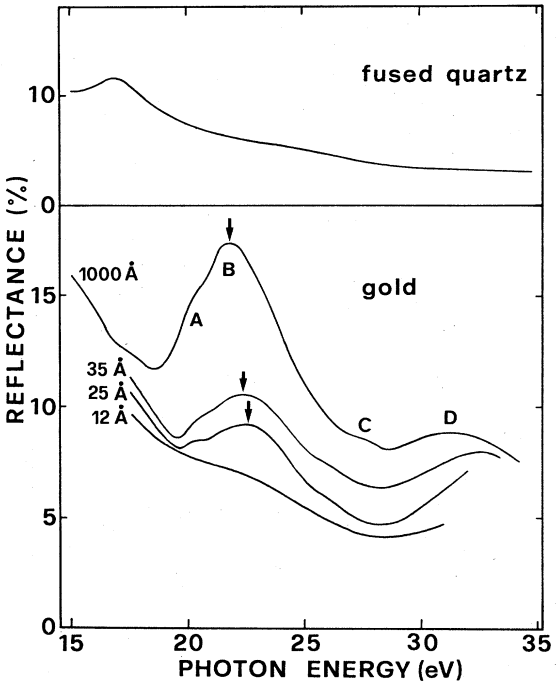

FIG. 1. Reflectivity spectra for discontinuous Au films with mass thicknesses of $d = 12$, 25, 35 Å and a 1000-Å continuous film between 15 and 35 eV. The upper curve shows the reflectivity spectrum of fused quartz.

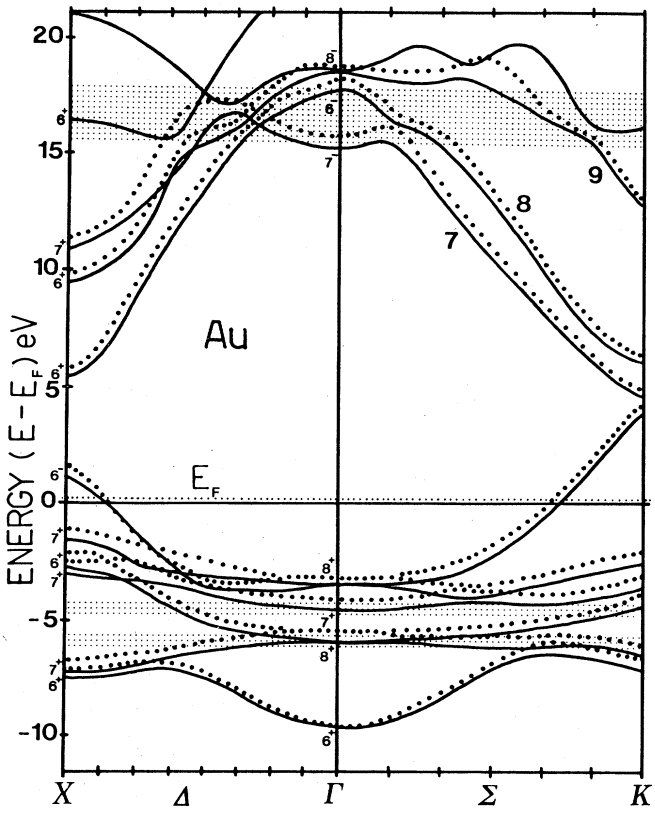

FIG. 2. Energy band structure computed by Christensen for gold along $\Gamma(\Delta)X$ and $\Gamma(\Sigma)K$ directions. The solid line corresponds to the normal lattice (Ref. 18) while the dotted line corresponds to a 0.8% compressed lattice (Ref. 15). The unoccupied 7–9 bands must be raised of about 1 eV (Ref. 16). The hatched zone above E_F shows the regions of high density of states (Ref. 17) coupled to two groups of d-band states at about 4.5 and 6.2 eV (hatched zones) below E_F. Their energy differences correspond to the experimental reflectivity features A and B of Fig. 1 at about 20.5 and 22.0 eV, respectively.

Au films on quartz substrates, and Maxwell-Garnett-type clusters,[11] which successfully reproduce the overall decrease in reflectance, but which do not reproduce the shift of structures to higher energy.

Since the structures in the 15–35-eV range are due to interband transitions, we have examined the energy shifts in terms of a modification of the band structure caused by the reduced crystallite dimensions. For very small clusters, the ratio of the surface to volume atoms becomes significant and may change the total density of states[12] and, consequently, the optical properties of the system.[13] In our case, the surface to volume ratio is smaller than 10% for the thinnest samples, and so we have excluded a surface effect as responsible for the shifts of the structures.

Recent extended x-ray absorption fine-structure (EXAFS) studies[14] on particulate Au samples showed a lattice parameter contraction (0.5% for particles of 90 Å diameter), without any change of the local structure as the particle size decreases. We ascribe the differences between the reflectivity spectra of thicker and very thin gold films as due to the variation of the gold fcc band structure induced by the shortening of the atomic distances.

Figure 2 reports the band structure of gold along the Γ–X and Γ–K directions calculated by Christensen[15] with the relativistic augmented plane-wave method for normal ($a = 7.6815$ a.u.) and compressed ($a = 7.6220$ a.u.) lattices. Portions of the bands 7–11 have energies above the Fermi level between 15 and 22 eV, covering the range of final states studied in our experiments.

Several authors have interpreted the rather broad peak observed in the reflectivity spectra of Au around 22 eV, embodying features A and B of Fig. 1, as due to interband transitions originating in the $5d$ bands and having final $5f$ or $6p$ states. The calculated joint density of states (JDOS) shows strong peaks around 20–22 eV for transitions originating in bands 2–4 and terminating in bands 9 and 10.[6] Similar results hold also for the equivalent peak of silver around 23 eV.[6] The calculated JDOS peaks lie approximately 1 eV below the experimental ϵ_2 features for both Au and Ag, in agreement with Christensen result.[16] According to the constant-initial-state photoemission experiment of Hermanson, Anderson, and Lapeyre,[17] the conduction bands of Au contain pronounced density of states peaks between 15 and 17 eV above E_F, which are strongly coupled to two groups of d-band states centered at about 4.5 and 6.2 eV below E_F. These regions of high density of states are shown as hatched areas in Fig. 2 and their average energy differences correspond nicely with the reflectivity structures A and B at 20.5 and 22.1 eV, respectively.

From Christensen's bands[18] we derived the energies of the direct transitions connecting the shaded areas in Fig. 2, namely, between the "$5d$" bands 2–5 and the "$5f$-$6p$" bands 7–9 for both the normal and the reduced lattice (E_{bulk} and $E_{\text{contracted}}$, respectively). Then we calculated their

differences $\Delta E = E_{\text{bulk}} - E_{\text{contracted}}$. Christensen's computed energy band[16] seems to be about 1 eV below the experimental determination. We expect the same to occur also for the reduced lattice calculations, so that the values of ΔE should not be affected by such discrepancies. From the comparison between our experimental results and the differences ΔE, we can justify the shifts of the reflectivity structures. According to Fig. 2, 22-eV transitions beginning 4.5 eV below E_F reach band 9 only in the middle of the $\Gamma-K$ direction, where we find the maximum negative difference $\Delta E = -1.5$ eV. It is noteworthy that the experimental ratio $\Delta E/\Delta a$ (where Δa is the lattice contraction) is -39 ± 5 eV/Å, in good agreement with the theoretical value of -48 eV/Å. Structure A at 20.5 eV may be associated to transitions involving final states along Δ, which show a negligible shift.

Before concluding this discussion, a further remark is mandatory. The broad features A and B at 20.5 and 22.1 eV in Au are composite structures that embody peaks of the JDOS originating from large volumes of the Brillouin zone, and different couples of bands, as well as critical point transitions. The evidence of critical point transitions have been collected with high-resolution spectroscopic techniques, made possible by the use of the continuum synchrotron radiation.[10,19-21] The interpretation of the experimental features associated with the critical-point transitions has been controversial. The two strongest structures observed in the thermomodulation experiments[19,20] at 19.9 and 21.2 eV have been assigned to spin-orbit-split transitions occurring at Γ,[10,18,19] at L (Ref. 6) and possibly at X.[6] Piacentini[22] excluded transitions of the M type at Γ from a detailed analysis of the thermomodulated line shape of the dielectric function. The 19.9-eV critical-point transition occurs close to peak A, which does not shift with the cluster dimension. The calculated energy differences ΔE indicate very small shifts for transitions at Γ, L, and X points. As a result, the present experiment suggests the assignment of the two thermomodulation features at 19.9 and 21.2 eV to a critical-point transition, probably at L [$L(3 \rightarrow 8)$ and $L(2 \rightarrow 8)$],[6] split by the spin-orbit interaction.

We did not attempt to interpret the behavior of feature C at 27 eV which moves to lower energies reducing the particle diameter, which occurs at energies higher than those available from the energy-band calculations of Fig. 2 for the compressed lattice. The apparent disappearance of peak D for thinner films seems to indicate a larger shift of this peak towards higher energies, decreasing the cluster size. An attempt to interpret the shift of structure D in terms of an EXAFS-type theory, where the reduction of the nearest-neighbor distance produces a widening of the period of the multiple scattering interference features, is in progress.[23]

In conclusion, we have investigated the electronic properties of small particles of Au evaporated on quartz substrates by measuring their vacuum ultraviolet reflectivity between 15 and 35 eV. We have found a systematic decrease of the reflectivity and an energy shift of the strongest structures as the cluster size decreases. The energy shifts are attributed to a variation of the electronic properties of bulk Au due to the reduction of the lattice parameter. From the calculated energy bands of Au for several values of the lattice constant we could assign the shift of peak B at 22.1 eV to the increased energy of interband transitions in the middle of the $\Gamma-X$ and $\Gamma-K$ directions.

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