Acoustic Plasmon on the Au(111) Surface

Sung Jin Park and Richard E. Palmer

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

(Received 5 March 2010; published 1 July 2010)

We report an acoustic surface plasmon mode on the Au(111) surface, which disperses into the visible region, as measured by high resolution electron energy loss spectroscopy. The new mode is assigned to an acoustic surface plasmon arising from the Shockley-type surface state electrons and coexists with the conventional surface plasmon. This low energy collective excitation disperses linearly up to ~2.2 eV, i.e., into the visible region. The divergence from theoretical prediction appears to emphasize the importance of band structure effects upon the dielectric function of the surface region.

DOI: 10.1103/PhysRevLett.105.016801 PACS numbers: 73.20.Mf, 68.35.B−, 73.20.At, 79.20.Uv

A large number of experimental and theoretical studies have explored the surface plasmon of three-dimensional (3D) metals [1,2]. The coupling between the surface plasmon and light is of significant interest because of its diverse potential applications [3,4]. In addition to this (hereafter ''conventional'') surface plasmon, another surface mode, due to a two-dimensional (2D) electron gas layer, has been predicted [5] and observed in quasi-2D systems prepared by the formation of monoatomic metal layers on semiconductors [6–9]. The experimental dispersion of this 2D plasmon follows theory. Recently it was predicted that a 2D surface plasmon could also exist on a 3D metal surface, when a partially occupied surface state is located in a projected 3D bulk band gap; this Shockley-type surface state can be thought of as a quasi-2D electron layer. For the (111) surfaces of the noble metals [10], theoretical calculations show that this 2D surface plasmon exhibits a linear dependence on the wave vector, like an acoustic wave, and is well defined up to several hundred millielectron volts. The new 2D (hereafter ''acoustic'') surface plasmon was reported experimentally on a Be(0001) surface in 2007 [11]. In this Letter we report the dispersion of an acoustic surface plasmon, alongside the conventional surface plasmon, of a Au(111) surface using angle-resolved high resolution electron energy loss spectroscopy (HREELS), which persists into the visible regime and diverges from theoretical calculations [10].

Au(111) films were prepared on cleaved mica substrates using thermal evaporation with the substrates kept at around 450 °C. The samples were slowly cooled down to room temperature before introduction into the ultrahigh vacuum (UHV) chamber (1×10^{-9} mbar) through a load-lock. Cleaning cycles (Ar^+ ion sputtering at 500 eV and annealing up to 300 °C using electron bombardment) were carried out several times. HREELS measurements (LK 3000) were performed at a detection angle of 70° from the surface normal for several different incident energies (from 10.0 to 20.0 eV). Plasmon dispersion curves were obtained as a function of $q_{\|}$, the momentum transfer parallel to the surface, by rotating the monochromator. The typical energy resolution employed was about 25–35 meV.

Figure 1(a) shows typical HREELS spectra of Au(111) at different angles and thus ranges of $q_{\|}$. Two peaks are clearly visible in the measured momentum space [12]. From our previous work [13], the higher energy peak at around 2.7 eV can be identified as the conventional surface plasmon of Au(111). The other peak in the lower energy region is attributed to the acoustic surface plasmon of Au(111). The momentum transfers, $q_{\|}$, corresponding to the acoustic and conventional modes are denoted as q_A and q_C, respectively. To analyze each peak position (plasmon energy), a combination of Gaussian and Lorentzian functions was employed. A typical fit is shown in Fig. 1(b).

The dispersion curves for the conventional and acoustic surface plasmon modes are plotted in Fig. 2 as a function of $q_{\|}$, the momentum transfer parallel to the surface. The conventional surface plasmon data obtained in this work are consistent with our previous results [13] for the bare Au(111) surface, denoted by the solid thick line [14]. Also shown on the graph for reference is the electron-hole pair excitation continuum for the surface state band of Au(111), whose upper edge is given by $\omega_u^{2D} = v_F^{2D} q + q^2/2$, where v_F^{2D} is the 2D Fermi velocity for Au, $v_F^{2D}/v_0 = 0.353$ and v_0 the Bohr velocity given by $e^2/\hbar$ [10].

It has been theoretically predicted that the proposed acoustic plasmon of the noble metal (111) surfaces can disperse up to a few hundred millielectron volts [10]. However, our results show that the acoustic plasmon of Au(111) survives to much higher energy (~2.2 eV), i.e., into the visible region. To explain this interesting and potentially technologically relevant behavior, we should consider the possible damping mechanisms of the acoustic plasmon. The three possible damping mechanisms are (i) intraband transitions within the 2D surface state band, (ii) intraband transitions within the 3D bulk bands, and (iii) interband transitions between the 2D and 3D manifolds. Regarding the intraband transitions within the 2D surface band, the dispersion curve in Fig. 2 lies just above

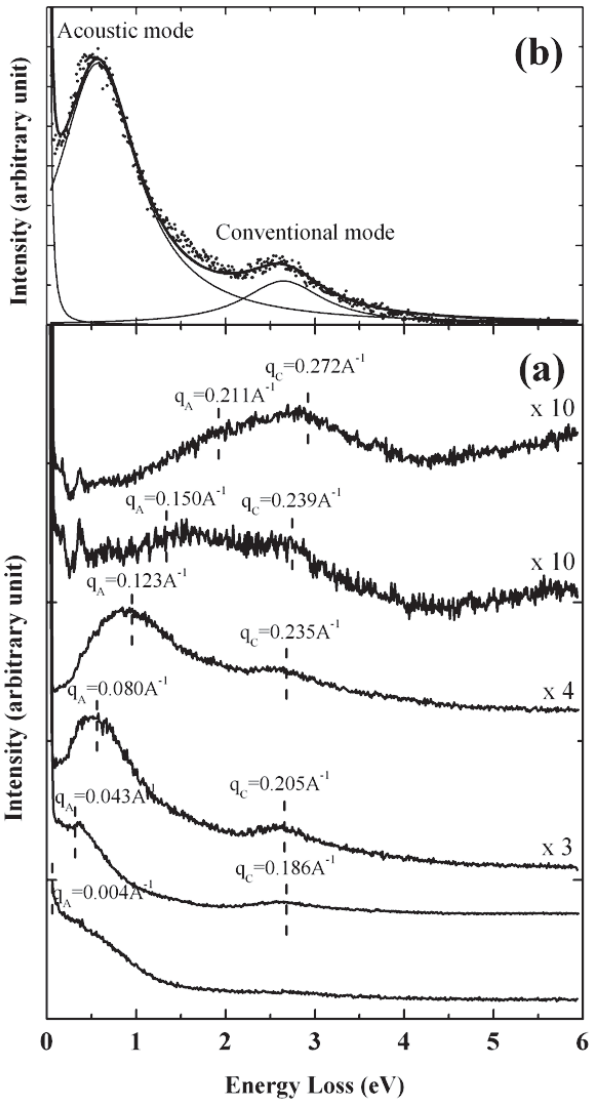

FIG. 1. (a) HREELS spectra of Au(111) at different incident angles; the values of the momentum transfer parallel to the surface, $q_{\|}$, corresponding to the acoustic and conventional modes, are denoted as q_A and q_C respectively. (b) Typical fit to the plasmon peaks.

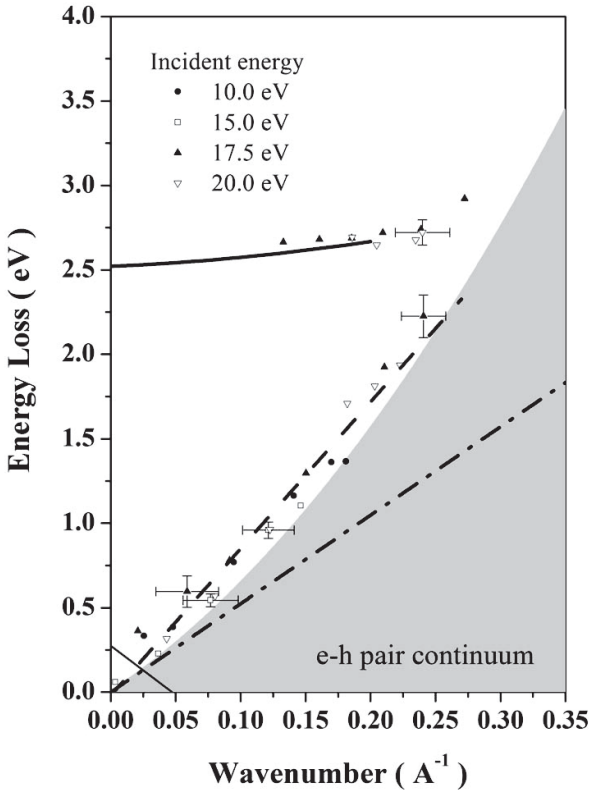

FIG. 2. Conventional and acoustic surface plasmon mode dispersion of Au(111) (electron beam energies from 10.0 to 20.0 eV) as a function of $q_{\|}$, momentum transfer parallel to the surface. The thick solid line is the conventional surface plasmon from Ref. [12] for comparison. The shaded area is the electron-hole pair continuum for surface states. The theoretical acoustic surface plasmon energy ω^{2D} of Au(111) is the dash-dotted line, $\omega^{2D} = \alpha v_F^{2D} q$, from Ref. [9] with $\alpha = 1.032$. The best linear fit to the experimental data is denoted by the dashed line, which gives $\alpha = 1.712$. The thin solid line represents the onset of the interband transitions between 2D and 3D bands at the minimum energy of 275 meV and minimum wave vector $\sim$0.047 Å^{-1}.

the expected electron-hole pair continuum, and does not enter the continuum till $\sim$2.2 eV, so these 2D intraband transitions should not damp the acoustic plasmon significantly until that energy is reached. Intraband transitions within bulk 3D bands can in principle cause damping of the acoustic plasmon because for Au the Fermi velocity of the 3D bands, $v_F^{3D}(v_F^{3D}/v_0 = 0.635)$, is higher than the 2D value, $v_F^{2D}(v_F^{2D}/v_0 = 0.353)$; thus all the measured data for the acoustic surface plasmon of Au(111) lie within the 3D intraband transition region. We conclude that this damping channel is weak. The interband transition onset between 2D and 3D bands in the Au(111) band structure is denoted by the thin solid line in Fig. 2, with minimum energy of 275 meV and minimum wave vector $\sim$0.047 Å^{-1} [10]. Thus the majority of the acoustic plasmon dispersion lies in this interband transition region (i.e., above the minimum energy and wave vector). The effect of interband transitions between 2D and 3D bands on the acoustic plasmon must then also be small, consistent with calculations [10]. In sum, the survival of the acoustic plasmon mode up to $\sim$2.2 eV in Fig. 2 implies all three damping effects are relatively small—that is, until the acoustic plasmon plunges into the 2D intraband continuum at this energy and is damped out, disappearing from the energy loss spectra. Note also that the continuum nature of each of the various single particle excitation channels shows that the discrete acoustic plasmon mode cannot instead be assigned to a single particle excitation.

The line width of the acoustic surface plasmon of Au(111) is shown in Fig. 3, for different incident energies,

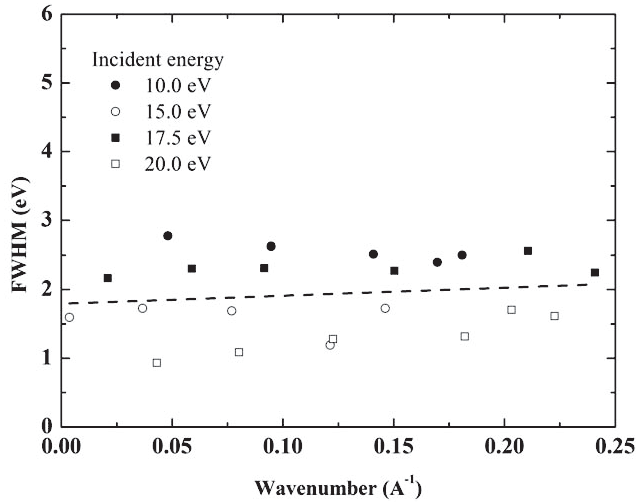

FIG. 3. Full width at half maximum (FWHM) of the acoustic surface plasmon mode of Au(111) as a function of $q_{\parallel}$, momentum transfer parallel to the surface, for various incident energies. The overall trend is denoted by the dashed line as a guide to the eye.

as a function of $q_{\parallel}$, and provides a further perspective on the plasmon damping. The full width at half maximum (FWHM) lies between ~1 to 3 eV, and depends in practice on the incident energy (for reasons that remain fully to be resolved, but may involve the sampling depth and beam size)—yet for each energy there is no strong dependence of the width (thus damping) on $q_{\parallel}$. The overall trend is denoted by the dashed line as a guide to the eye. The data seem to confirm that the contributions of the two relevant damping mechanisms in this regime, the intraband transitions within the 3D bands and the interband transitions between 2D and 3D bands, are small. As a result, the acoustic surface plasmon can survive up to ~2.2 eV as shown in Fig. 2, where the 2D intraband transitions kick in so that in effect the width blows up and the plasmon disappears from the spectrum (the peak is not observed in spectra at higher $q_{\parallel}$). This steplike behavior is analogous to that of the low energy graphite surface plasmon [15].

The theoretical dispersion of the frequency, ω^{2D}, of the Au(111) acoustic plasmon is given by $\omega^{2D} = \alpha v_F^{2D} q$ in Ref. [10], where the coefficient α depends on the 3D electron density and the distance between the 3D surface and 2D electron gas layer. This is reproduced as the dash-dot line in Fig. 2 for Au, $\alpha = 1.032$. The best linear fit for the experimental acoustic plasmon data of Au(111), denoted by the dashed line, gives $\alpha = 1.712 \pm 0.063$ [16]. Thus there is a large discrepancy in gradient between the experiment and theoretical calculations.

A likely cause of the discrepancy between the experimental and theoretical dispersion curves is the challenge of including a realistic band structure, as well as surface restructuring effects, in the plasmon calculations. The calculations in Ref. [10] for acoustic surface plasmon dispersion of Au(111) thus employ an ideal Au(111) surface and free-electron-like model. For Be(0001) [17], the acoustic plasmon dispersion is significantly changed due to the deviation from a free-electron-like behavior (i.e., from parabolic dispersion) of the surface states above the Fermi level, as well as the surface relaxation (the topmost interlayer expansion relative to the bulk layers is about 5.8%, corresponding to ~0.1 Å [18]). For the Au(111) surface, a deviation from parabolic dispersion of the unoccupied surface states has also been reported [19]; this scanning tunneling spectroscopy (STS) study shows a free-electron behavior near the zone center, but as the wave vector parallel to the surface increases, a significant deviation is found for the unoccupied surface state band.

Regarding the surface atomic structure, it is also well known that Au(111) exhibits a surface reconstruction with a $22 \times \sqrt{3}$ unit cell [20–22]. This so-called "herringbone" reconstruction acts as a superlattice along the compression direction, which induces a periodic surface electronic potential modulation. As a consequence, new band gaps within the occupied surface state band are formed. However, these gaps were estimated to be relatively small, less than 20 meV, by STS [23] and angle-resolved photoemission spectroscopy (ARPES) studies [24], so the surface state of Au(111) below the Fermi level (the occupied state) can still be thought of as a quasi-free-electron system.

On the question of surface relaxation, first principles calculations show that the topmost interlayer expansion of Au(111) for fcc (or hcp) sites and bridge sites are 1.5% and 3.7%, respectively, relative to the bulk interlayer separation (2.4 Å) [16]. This agrees well with the experimental result, 3.3%, corresponding to ~0.08 Å [25]. The surface atomic structure can, of course, influence in turn the electronic structure of the surface region [26,27]. It appears then that the deviation of the unoccupied surface state from free-electron behavior and the surface atomic restructuring should both be considered in the quest to reconcile theory with the experimental acoustic plasmon dispersion of the Au(111) surface reported here.

In summary, we have reported an acoustic surface plasmon of the noble metal Au(111) surface using angle-resolved HREELS. The conventional and acoustic modes were observed to coexist. The new acoustic mode plasmon disperses above the electron-hole pair continuum, and survives damping, up to ~2.2 eV, implying that the 3D intraband and interband damping channels are both relatively weak. Comparison with theoretical calculations shows that the acoustic plasmon of Au(111) disperses with a much steeper gradient than predicted, and hence reaches into the visible region of the spectrum. Probably this arises from the simplified surface electronic and geometric structure in the calculations. Our results should present a valuable test of quantitative theories of the acoustic surface plasmon of noble metal surfaces, and

demonstrate a new excitation channel in the visible region of the spectrum on the technologically important Au(111) surface.

We thank the EPSRC for financial support of this work.

[1] J. M. Pitarke, V. M. Silkin, E. V. Chulkov, and P. M. Echenique, Rep. Prog. Phys. **70**, 1 (2007).
[2] K.-D. Tsuei, E. W. Plummer, A. Liebsch, E. Pehlke, K. Kempa, and P. Bakshi, Surf. Sci. **247**, 302 (1991).
[3] S. Palomba and L. Novotny, Phys. Rev. Lett. **101**, 056802 (2008).
[4] B. Hecht, H. Bielefeldt, L. Novotny, Y. Inouye, and D. W. Pohl, Phys. Rev. Lett. **77**, 1889 (1996).
[5] F. Stern, Phys. Rev. Lett. **18**, 546 (1967).
[6] T. Nagao, T. Hildebrandt, M. Henzler, and S. Hasegawa, Phys. Rev. Lett. **86**, 5747 (2001).
[7] Y. Liu, R. F. Willis, K. V. Emtsev, and T. Seyller, Phys. Rev. B **78**, 201403(R) (2008).
[8] E. P. Rugeramigabo, T. Nagao, and H. Pfnür, Phys. Rev. B **78**, 155402 (2008).
[9] Y. Liu and R. F. Willis, Surf. Sci. **603**, 2115 (2009).
[10] V. M. Silkin, J. M. Pitarke, E. V. Chulkov, and P. M. Echenique, Phys. Rev. B **72**, 115435 (2005).
[11] B. Diaconescu, K. Pohl, L. Vattuone, L. Savio, P. Hofmann, V. M. Silkin, J. M. Pitarke, E. V. Chulkov, P. M. Echenique, D. Farias, and M. Rocca, Nature (London) **448**, 57 (2007).
[12] In some spectra small peaks around ~0.37 eV, which do not disperse in momentum space, were found. They can be attributed to CH stretching vibrations from trace surface contamination.
[13] S. J. Park and R. E. Palmer, Phys. Rev. Lett. **102**, 216805 (2009).
[14] Reproduction of the best fit result for the conventional surface plasmon of bare Au(111), $\omega_{sp} = 2.49 + 0.40q_{\|} + 1.70q_{\|}^2$, from Ref. [13].
[15] P. Laitenberger and R. E. Palmer, Phys. Rev. Lett. **76**, 1952 (1996).
[16] The intercept with the y axis gives -0.02 from the best fit of our experimental data. When the origin is included in the fitting, α is 1.687 ± 0.162.
[17] V. M. Silkin, J. M. Pitarke, E. V. Chulkov, B. Diaconescu, K. Pohl, L. Vattuone, L. Savio, Ph. Hofmann, D. Farias, M. Rocca, and P. M. Echenique, Phys. Status Solidi (a) **205**, 1307 (2008).
[18] H. L. Davis, J. B. Hannon, K. B. Ray, and E. W. Plummer, Phys. Rev. Lett. **68**, 2632 (1992).
[19] K. Schouteden, P. Lievens, and C. Van Haesendonck, Phys. Rev. B **79**, 195409 (2009).
[20] U. Harten, A. M. Lahee, J. P. Toennies, and Ch. Wöll, Phys. Rev. Lett. **54**, 2619 (1985).
[21] Ch. Wöll, S. Chiang, R. J. Wilson, and P. H. Lippel, Phys. Rev. B **39**, 7988 (1989).
[22] J. V. Barth, H. Brune, G. Ertl, and R. J. Behm, Phys. Rev. B **42**, 9307 (1990).
[23] W. Chen, V. Madhavan, T. Jamneala, and M. F. Crommie, Phys. Rev. Lett. **80**, 1469 (1998).
[24] F. Reinert and G. Nicolay, Appl. Phys. A **78**, 817 (2004).
[25] A. R. Sandy, S. G. J. Mochrie, D. M. Zehner, K. G. Huang, and D. Gibbs, Phys. Rev. B **43**, 4667 (1991).
[26] H.-G. Zimmer and A. Goldmann, Surf. Sci. **176**, 115 (1986).
[27] R. Paniago, R. Matzdorf, and A. Goldmann, Europhys. Lett. **26**, 63 (1994).