

Pseudogap Mediated by Quantum-Size Effects in Lead Islands

Kedong Wang,^{1,2} Xieqiu Zhang,^{1,2} M. M. T. Loy,² T.-C. Chiang,^{3,*†} and Xudong Xiao^{1,2,*‡}

¹*Department of Physics, The Chinese University of Hong Kong, Hong Kong, China*

²*Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, China*

³*Department of Physics, University of Illinois, 1110 West Green Street, Urbana, Illinois 61801-3080, USA, and Frederick Seitz Materials Research Laboratory, University of Illinois, 104 South Goodwin Avenue, Urbana, Illinois 61801-2902, USA*

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Scanning tunneling spectroscopy measurements of Pb islands on Si(111) at high energy resolution reveal a novel pseudogap, or a pseudopeak in special cases, around the Fermi level in addition to the usual quantum well states. These gap or peak features persist to temperatures as high as ~ 80 K and are uniquely related to the quantum well nanostructure of the Pb islands. A systematic analysis indicates that electron-phonon scattering is responsible for the observed electronic structure.

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Quantum confinement effects in both metallic and semiconducting materials are subjects of intense prevailing interest [1–4]. For systems with sufficiently small physical dimensions, confinement of electrons can lead to the formation of discrete electronic states with important consequences. Specifically, the density of states at the Fermi level [5,6], charge distribution [7,8], and total energy [9,10] can differ substantially from their bulk counterparts, giving rise to property modulations as a function of systems dimensions. In particular, thin films and islands of Pb, which can now be routinely prepared with uniform thickness, have attracted great interest in recent years. Many works have demonstrated large bilayer oscillations, as a function of film or island thickness, in growth behavior [5,6,8,11], thermal stability [11,12], and superconducting transition temperature [13–15].

In this Letter, we report a surprising finding by scanning tunneling spectroscopy (STS) of a pseudogap near the Fermi level in Pb islands of many thicknesses. The observed pseudogap is ~ 10 – 30 meV wide, persists to a rather high temperature ~ 80 K, and bears a striking resemblance to the pseudogaps in high temperature superconductors (HTS) [16–19]. Through a systematic analysis of the STS spectra of various Pb island thicknesses, we found that electron-phonon scattering and quantum confinement conspire to give rise to the pseudogap features in this system. This novel manifestation of quantum-size effects has not been investigated before, and the induced change in the electronic structure near the Fermi level may result in important modifications in the physical and chemical properties of metal thin films.

In our experiment, Pb was deposited at a rate of ~ 0.003 monolayer (ML) per second onto a heavily As-doped Si(111)-(7 \times 7) substrate with a room temperature resistivity of $0.002 \Omega \cdot \text{cm}$. For substrate temperatures ranging from ~ 200 K to room temperature, the deposited Pb formed an atomic wetting layer first [20]; islands then grew on top of the wetting layer. The distribution in island

thickness and size could be controlled by the substrate temperature during deposition and the amount of deposition. The STS measurements were carried out with an Omicron low temperature scanning tunneling microscope in an ultrahigh vacuum chamber ($\sim 7 \times 10^{-11}$ torr). The scanning tunneling microscope tips used in the experiments were Pt/Ir tips, which were Ar^+ sputtered prior to use to ensure cleanliness. The dI/dV spectra were acquired using a lock-in amplifier with the bias voltage modulated at a frequency of 500–1000 Hz and a peak-to-peak amplitude of 0.5–1 mV.

Figure 1(a) shows a typical dI/dV tunneling spectrum as a function of electron energy E relative to the Fermi level E_F taken from a 19 ML thick island at 10 K at the

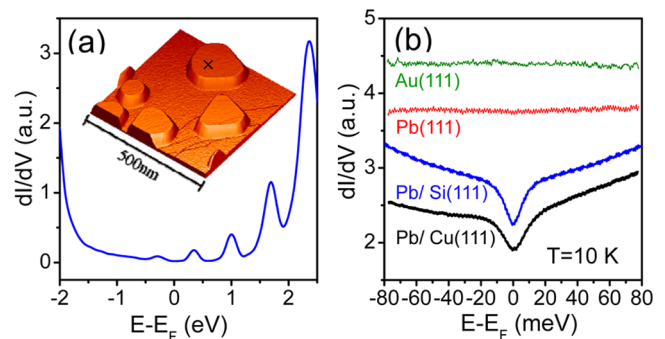


FIG. 1 (color online). (a) A dI/dV tunneling spectrum taken at 10 K on a 19 ML Pb island grown on Si(111) from the point marked \times in the included topographic image. $E-E_F$ is the electron energy relative to the Fermi level. The tip height is set by $V = -2$ V and $I = 1.0$ nA. (b) A detailed view of the tunneling spectrum near the Fermi level showing a pseudogap. The tip height is set by $V = -80$ mV and $I = 0.5$ nA. The convex background is caused by the overlapping tails of the two QWS peaks at -0.30 and $+0.35$ eV. For comparison, the dI/dV curves taken from a thick Au(111) film (~ 150 nm), a single crystal Pb(111), and a 19 ML Pb island on Cu(111) are also displayed; these curves are shifted vertically for clarity.

position marked “×” in the inset topographic image. Such spectra should be proportional to the electronic density of states (DOS). A number of approximately periodic peaks are observed; these correspond to electronic standing waves, or quantum well states (QWSs), formed by multiple electron reflections between the surface and the interface of the island [2,5,6,21]. A detailed view around the Fermi level reveals a narrow dip of ~ 14 meV wide and $\sim 18\%$ decrease of relative intensity [Fig. 1(b)]. This dip does not reduce the DOS to zero to open a true energy gap and is thus referred to as a pseudogap. Tunneling spectra taken from a thick Au(111) film and a single crystal Pb(111) at 10 K, using the same tip, display a constant DOS. Thus, the pseudogap is neither an instrument artifact nor a property of bulk Pb. The observation of a similar dip on a 19 ML thick Pb island grown on Cu(111), as shown in Fig. 1(b), further indicates that the pseudogap feature is intrinsic to the Pb island structure.

The pseudogap is observed for many different island thicknesses. Figure 2(a) shows a Pb island with a “crater” in the middle that consists of terraces with thicknesses ranging from 12 to 19 ML. The corresponding tunneling spectra [Fig. 2(b)] show QWS peaks; the zoomed-in spectra near the Fermi level [Fig. 2(c)] reveal a pseudogap for all thicknesses except 18 ML for which a pseudopeak is

observed instead. At 18 ML, a QWS is almost exactly centered at the Fermi level. The pseudopeak appears as a small bump atop the much broader QWS peak. For the other cases in the set, none of the QWS peaks overlaps the Fermi level, and the background slope of the spectra near E_F reflects the tail of the nearest QWS peak. Similar to the 18 ML case, the Fermi level coincides with a QWS peak at 27 ML, and again a pseudopeak is observed on a 27 ML island, as shown in Fig. 2(c).

To explain our findings, we have developed a simple but realistic model that well reproduces the overall structure of the QWS peaks [Fig. 2(b)]. Detailed calculations near the Fermi level [Fig. 2(d)] reveal a pseudogap or peak in good agreement with the experiment. The model involves a wave mechanical calculation, assuming a free-electron-like structure for both the Pb and the tip. Since the tunneling current is predominantly directed along the surface normal, a one-dimensional (1D) geometry is assumed. The vacuum barrier between the tip and the Pb is modeled by a square potential above the Pb Fermi level. The Pb-Si interface, being incommensurate, is modeled by a lossy reflective boundary with a certain phase shift and a reflectivity less than unity. Lifetime effects caused by scattering in the Pb are included using an optical potential [22,23]. With a bias applied between the tip and the Pb, the tunneling probability at the tip Fermi level is calculated, which is proportional to dI/dV as measured by STS.

Physically, the Pb film functions as an electron interferometer [24]; the calculation thus yields essentially a barrier tunneling function convoluted by a Fabry-Perot spectral function for the interferometer. The latter can be taken as a 1D DOS of the Pb film and is given by

$$\rho \propto \frac{1}{1 + \frac{4f^2}{\pi} \sin^2(kNt + \frac{\Phi}{2})}, \quad (1)$$

where f is the interferometer finesse, k is the electron wave vector, N is the number of Pb monolayers, t is the monolayer thickness, and Φ is the boundary phase shift. The finesse depends on the interferometer boundary reflectivities and the electron coherence length. For boundary reflectivities approaching unity and a long coherence length, f approaches infinity, and Eq. (1) yields a set of sharp, delta-function-like, QWS peaks. For Pb films, f is finite, and Eq. (1) yields a set of broadened QWS peaks. The regions in between the peaks have finite intensities as part of a coherent spectral function.

An increasing electron coherence length leads to an increasing f , which in turn, according to Eq. (1), causes the QWS peak heights to increase and the “coherent background” intensities in between peaks to decrease. However, for an energy dependent electron coherence length, the spectral function given by Eq. (1) can be modified locally, revealing features that are not expected for a constant or smooth f . The electron coherence length, related to the lifetime, is limited by impurity or defect

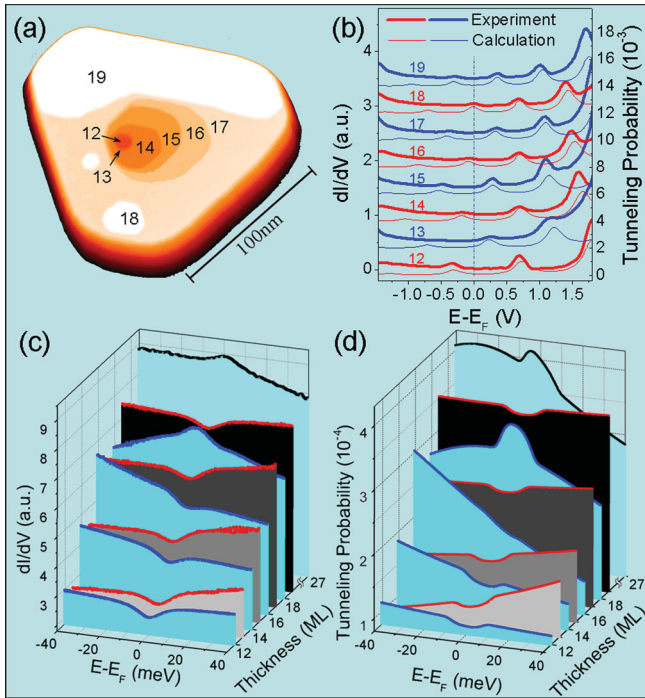


FIG. 2 (color). (a) A topographic image of an island with a crater in the middle, exposing multiple thicknesses ranging from 12 to 19 ML. (b) Experimental dI/dV tunneling spectra for various terrace thicknesses. The curves are shifted vertically for clarity. Also shown, for comparison, are theoretical tunneling probabilities. (c) Detailed view of the tunneling spectra near the Fermi level. (d) Calculated tunneling probabilities for comparison.

scattering, electron-electron scattering, and electron-phonon scattering [24,25]. Impurity or defect scattering is negligible for the present case. The electron-electron scattering contribution, proportional to E^2 , can be estimated from other similar metals [24,25]. The electron-phonon contribution, with a structure near the Fermi level, is solely responsible for the pseudogap or peak.

Within a Debye approximation, the electron-phonon scattering rate, as a function of electron energy E and temperature T , is given by [25,26]

$$\Gamma_{e\text{-ph}}(E, T) = 2\pi \int_0^{E_D} \lambda \left(\frac{E'}{E_D}\right)^2 \left(1 - \frac{1}{\exp\left(\frac{E-E'}{k_B T}\right) + 1} + \frac{1}{\exp\left(\frac{E+E'}{k_B T}\right) + 1} + \frac{2}{\exp\left(\frac{E'}{k_B T}\right) - 1}\right) dE', \quad (2)$$

where E' is the phonon energy, $E_D = 9.0$ meV is the Debye energy, and $\lambda = 1.55$ is the electron-phonon mass enhancement parameter of Pb [26]. At very low temperatures, electron-phonon scattering is largely suppressed within an energy window of $\pm E_D$ about the Fermi level because of a reduced phase space for scattering [25,26]; this corresponds to a longer electron lifetime and a higher finesse f . If the Fermi level is located in between QWS peaks, the Fabry-Perot spectral function within $\pm E_D$ is reduced, yielding a dip (pseudogap). However, if a quantum well peak is right at the Fermi level, the spectral function within $\pm E_D$ is enhanced, yielding a bump (pseudopeak). The agreement between the model prediction and our experimental observations, in particular, the pseudopeak structure at 18 and 27 ML, provides strong evidence supporting the model.

In the actual model calculation, we used three adjustable parameters: the electron reflectivity and the phase shift at the Pb-Si boundary, and the prefactor of the electron-electron scattering term. The vacuum barrier height is taken as the work function of Pb (4.0 eV), and the vacuum barrier width is taken from the experiment (4.5 Å). The adjustable parameters are determined by the positions, intensities, and widths of the quantum well state peaks. The known quantities E_D and λ in Eq. (2) determine the width and depth or height of the pseudogap or pseudopeak. Artificially setting the electron-phonon term to zero in the calculation yields essentially the same QWS spectra, but no pseudogaps or peaks. Augmenting the calculation with the crystal potential and Friedel charge oscillations in the Pb film [8,27] does not affect the pseudogap or peak but does yield a more accurate band dispersion of Pb, thus improving the QWS peak positions; however, these effects are not essential for the present discussion.

The temperature and island size dependence of the pseudogap is presented in Fig. 3(b). Three islands of thickness 19 ML but with different lateral sizes are compared [Fig. 3(a)]. Actually, island I-1 straddles across an atomic step on the Si surface, and its thickness is 19 ML

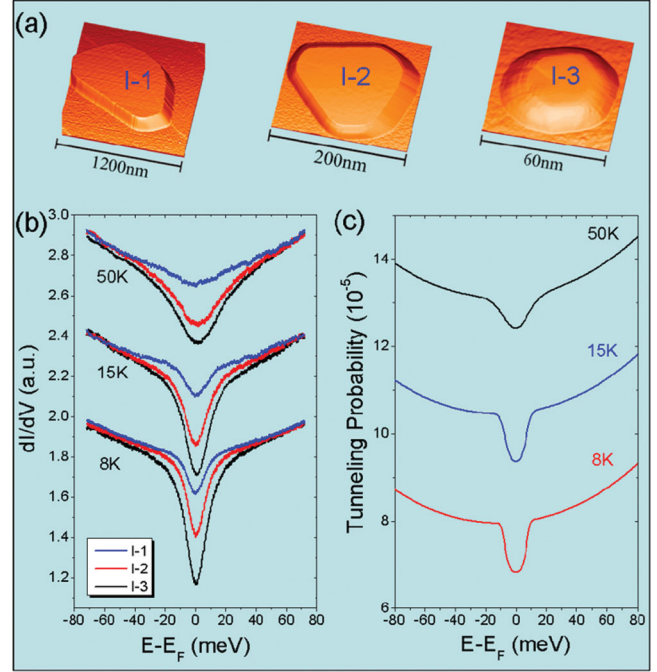


FIG. 3 (color). (a) Topographic images of three islands of different sizes. (b) Tunneling spectra at three temperatures from these islands at a thickness of 19 ML. (c) Calculated tunneling probabilities of a 19 ML film at the same three temperatures. The curves at 15 and 50 K are shifted vertically for clarity.

only on the left side. The experimentally observed dip at the Fermi level ranges from $\sim 10\%$ to 35% decrease in intensity and $\sim 10\text{--}16$ meV in width at 8 K for different size islands. Results from our 1D calculation [Fig. 3(c)] agree well with the data for the largest island I-1 at 8, 15, and 50 K. As the system temperature rises, the phonon population increases, and the phonon scattering window within $\pm E_D$ around the Fermi level becomes filled in according to Eq. (2). As a result, the pseudogap or peak structure fades away with a characteristic temperature given by the Debye temperature (105 K). The pseudogap effects are clearly enhanced for smaller islands (I-2 and I-3), with an increased pseudogap depth at the Fermi level. If the lateral confinement is assumed to enhance the electron-phonon coupling and to modify the phonon spectrum, our one-dimensional model with Eq. (2) may also provide a reasonable agreement with experiment.

It is interesting to note that the evolution of this pseudogap from the superconductivity gap for the Pb island is surprisingly similar to that for HTS, as demonstrated by a comparison of Figs. 4(a) and 4(b), where the spectra taken from a 19 ML Pb island and an underdoped Bi2212 [19,28] show similar temperature dependence both below and above the respective superconducting transition temperature. One might naturally speculate a certain connection, although the similarity could be entirely superficial or fortuitous. Specifically, the reduced scattering by phonons (or other collective excitations including spin fluctuations)

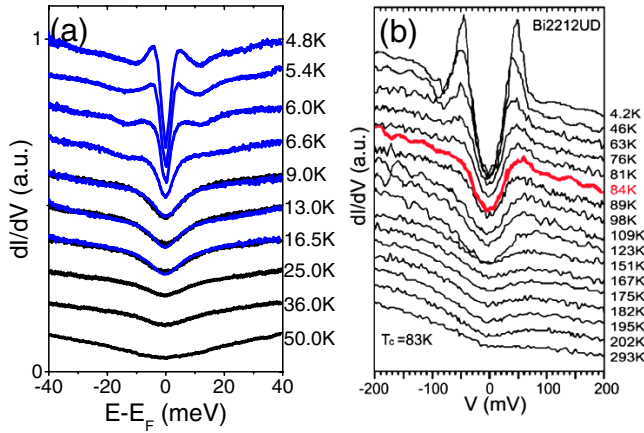


FIG. 4 (color online). (a) Temperature dependent dI/dV curves on two large 19 ML Pb islands with a size over $1 \mu\text{m}$. Bulk Pb has a superconducting transition temperature of 7.2 K. (b) Temperature dependent dI/dV curves taken from an underdoped Bi2212 with a superconducting transition temperature of 84 K (taken from [19,28]). There is a strong similarity between the two cases.

at low temperatures for energies near the Fermi level ($\pm E_D$) is a universal feature. The same mechanism leading to the pseudogap or peak in the Pb islands could potentially work for other materials with similar coherent spectral functions, provided the electron-phonon coupling is sufficiently strong. Further research is needed to determine if this speculation in connection with HTS has merit.

In summary, we have observed pseudogaps and pseudo-peaks from Pb islands with scanning tunneling spectroscopy. These electronic structures can further modify the DOS at the Fermi level in addition to the QWSs and can be well explained by an interplay between electron-phonon scattering and quantum confinement. While our simple model calculation accounts for the major experimental findings, the effects of finite island dimensions remain an interesting subject for future investigation.

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Note added.—A recent paper from the Hasegawa group [29] also revealed a pseudogap in the normal state of Pb islands obtained by applying a magnetic field to suppress the superconductivity, but they did not examine its temperature dependence or elaborate on its origin [30].

*To whom correspondence should be addressed.

†chiang@mrl.uiuc.edu

‡xdxiao@phy.cuhk.edu.hk

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