Reduction of the Superconducting Gap of Ultrathin Pb Islands Grown on Si(111)

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The energy gap $\Delta$ of superconducting Pb islands grown on Si(111) was probed in situ between 5 and 60 monolayers by low-temperature scanning tunneling spectroscopy. $\Delta$ was found to decrease from its bulk value as a function of inverse island thickness. Corresponding $T_c$ values, estimated using bulk gap-to-$T_c$ ratio, are in quantitative agreement with ex situ magnetic susceptibility measurements, however, in strong contrast to previous scanning probe results. Layer-dependent ab initio density functional calculations for freestanding Pb films show that the electron-phonon coupling constant, determining $T_c$, decreases with diminishing film thickness.

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The fundamental question of how the superconducting properties of a material are modified when its thickness is reduced down to a few atomic monolayers has stimulated considerable theoretical and experimental interest since the 1960s [1–7]. Today, with the emergence of nanoscience and nanotechnology, this question is of special relevance for possible technological applications in superconducting nanodevices. The early model of Blatt and Thompson predicted an increase of the critical temperature ($T_c$) above the bulk value with decreasing film thickness, together with $T_c$ oscillations due to quantum size effects [1]. However, if proper boundary conditions allowing for spillout of the electronic wave functions in thin films are taken into account, a decreasing $T_c$ with decreasing film thickness is predicted [4,5,8–11]. Depending on the material, early experimental results showed either a decrease (Pb) or an increase (Al, Ga, Sn, In) in $T_c$ on film thickness reduction [12,13], mainly related to disorder in the films composed of small metallic grains [13]. In contrast, pioneering experiments on crystalline Al films reported no $T_c$ enhancement, allowing one to address intrinsic thickness-dependent properties of crystalline superconducting films [14].

Recently, Pb films grown on Si(111) attracted much attention in this context [15]. Ex situ resistivity [16] and magnetic susceptibility measurements [17] reported a decrease of $T_c$ with decreasing Pb film thickness. In contrast, recent in situ scanning tunneling spectroscopy (STS) investigations on Pb/Si(111) islands reported no significant change in $T_c$ upon thickness reduction [18,19], while the very small $T_c$ oscillations observed were attributed to quantum size effects [1,18]. These contradictory experimental results call for a clarification.

In this Letter, we report in situ layer-dependent STS measurements of the energy gap of ultrahigh-vacuum grown single-crystal Pb/Si(111)-(7 × 7) and Pb-$\sqrt{3} \times \sqrt{3}$/Si(111) islands in the thickness range of 5–60 monolayers (ML). In contrast to previous STS studies on this system [18,19], we show that the energy gap decreases with decreasing island thickness $d$ for both crystalline and disordered interfaces. Corresponding $T_c$ values, estimated using the bulk gap-to-$T_c$ ratio, decrease with a $-1/d$ dependence, in quantitative agreement with ex situ measurements of Ozer et al. [17]. Moreover, employing layer-dependent ab initio density functional theory (DFT) calculations for freestanding Pb films, we find for thin layers a similar behavior of $T_c$, caused by a thickness-dependent decrease of the electron-phonon coupling.

Pb was thermally evaporated on the Si(111)-(7 × 7) (hereafter 7 × 7) or on the Pb-$\sqrt{3} \times \sqrt{3}$/Si(111) (in short Pb-$\sqrt{3}$) substrate [20] kept at room temperature favoring the growth of Pb single crystals with their (111) axis perpendicular to the surface [15,20]. The samples were studied at a temperature of 4.6 K or, by pumping on the He dewar, at 3.0 K in a homebuilt STM [21]. Cut PtIr wires were used as STM tips. Differential conductance ($dI/dV$) measurements were performed with open feedback loop, using lock-in technique (modulation voltage of 0.2 to 0.5 mV$_{pp}$ at 277 Hz) at a typical tunneling resistance of 15 MΩ. Radio frequency (rf) noise has been carefully filtered [22–24].

Figure 1 shows a STM image of a flattop Pb island extending over two Si terraces separated by a single Si(111) step [25]. The island mainly consists of an 8 ML thick Pb area with respect to the Si surface, as determined...
from the apparent height in the STM topograph. The island thickness includes the \( \approx 1 \) ML wetting layer [26]. The inset shows a magnified view of the Pb surface lattice with atomic resolution. The observed superstructure reflects the buried \( 7 \times 7 \) interface [25]. Pb areas of constant thickness with a lateral extension larger than the \( T = 0 \) K Pb bulk coherence length (~80 nm) were selected for this study, excluding transition regions where the island thickness changes.

Figure 2 displays a selected set of measured \( dI/dV \) spectra for the indicated island thicknesses at \( T = 3.0 \) K. Measurements have also been performed at 4.6 K (not shown). Each curve is an average of more than 10 individual \( dI/dV \) spectra taken at various locations on one island. The background conductance was subtracted and the curves were normalized. The spectra display a clear superconducting energy gap \( \Delta \) decreasing with decreasing island thickness. The observed small spectral asymmetry between positive and negative bias reflects the limits of the background subtraction on the \( 7 \times 7 \) interface. Two phonon modes (indicated by arrows for the 60 ML curve) are clearly detected. Their energies (the difference between the local extrema in \( d^2I/dV^2 \) and \( \Delta \)) are 4.6 \pm 0.2 and 8.5 \pm 0.2 meV, in excellent agreement with the values reported for bulk Pb [27].

In order to quantify the observed \( \Delta \), a least squares analysis of the \( dI/dV \) spectra is performed based on the standard expression for the tunneling conductance between a normal metal and a superconductor:

\[
\frac{dI}{dV}(V) = -G_{no} \int_{-\infty}^{\infty} \frac{\rho_s(e)}{N(0)} f'(e - eV) de, \tag{1}
\]

where \( f'(e) \) is the derivative of the Fermi function, \( G_{no} \) is the Ohmic conductance of the junction, and

\[
\rho_s(e) = \frac{\rho_s|e|}{\sqrt{e^2 - \Delta^2}} \tag{2}
\]

is the ratio between the superconducting and the normal density of states (DOS) of the Pb sample. The broadening introduced by the voltage modulation is taken into account by a proper convolution and the remaining rf noise voltage present in the tunnel junction by an additional convolution, assuming a Gaussian distribution [not written in Eq. (1)] [22,23]. The fitted standard deviation of the voltage noise is 280 \( \mu \)V rms. The resulting \( dI/dV \) spectra, shown in Fig. 2 (thin red lines), describe convincingly the experimental data. For 60 ML, \( \Delta_{60 \text{ ML}}(3.0 \text{ K}) = 1.17 \) meV, which is very close to the bulk value \( \Delta_{\text{bulk}}(3.0 \text{ K}) = 1.23 \) meV [\( \Delta_{\text{bulk}}(0 \text{ K}) = 1.30 \) meV]. The observed relative reduction of the energy gap between 60 and 6 ML at 3.0 K is \( \approx 40\% \).

The extracted gap values are averaged and plotted in Fig. 3(a) as a function of inverse film thickness. The energy gaps for both interfaces show a comparable reduction upon decreasing thickness. To allow for a comparison with previous results, the critical temperature \( T_c \) was estimated from the measured gap values using the bulk \( \Delta/T_c \) ratio (see theory below) and assuming the BCS temperature dependence of \( \Delta(T) \). The results are displayed in Fig. 3(b). The continuous line represents a least squares analysis of the STS data, leading to the relation...
Pb are expected to vanish. Consequently, for

\[ T_c(d) = 7.08 \times (1 - d_0/d) \quad \text{with} \quad d_0 = 1.88 \, \text{ML}. \]

For these thicknesses, the superconducting properties of Pb are expected to vanish. Our estimated \( T_c \)'s are in quantitative agreement with the ones of Ozsr et al. [17], obtained \textit{ex situ} on Ge capped Pb/Pb/\( \sqrt{3} \times \sqrt{3} / \text{Si} \) and \textit{in situ} Pb/Si-(7 \times 7) interface. The trend observed in \textit{in situ} resistivity measurements [28] is consistent with the present findings, the quantitative differences with respect to our data being most likely caused by the inhomogeneity of the films. \textit{Ex situ} resistivity measurements [16] on Au capped Pb/Si(111)-(7 \times 7) films show a much faster decrease of \( T_c \) with decreasing film thickness than in our case, probably a consequence of the inverse proximity effect induced in the Pb film by the Au capping layer [29]. However, the previous \textit{in situ} STS results on Pb/Si(111)-(7 \times 7), which reported an essentially constant \( T_c \) in this thickness range [18,19], are at variance with our data. Furthermore, our observed energy gap reduction is much larger in amplitude than the very small oscillations of \( T_c \) as a function of thickness [18], the amplitude of which is of only 2% of the average \( T_c \).

In order to unravel the mechanisms responsible for the reduction of \( T_c \) with decreasing Pb film thickness, we have performed \textit{ab initio} calculations of the electronic structure (bands and density of states), phonon spectra, and electron-phonon \((e-ph)\) coupling properties. The gradient of the one-electron potential, the spectral Eliashberg function, and the mass-enhancement parameter \( \lambda \) were computed for freestanding Pb(111) films in the range of 4–10 ML and for bulk lead [30]. We have also calculated the gap \( \Delta \) and the critical temperature \( T_c \) by solving the full nonlinear Eliashberg equations, and for comparison, the linearized gap equation of the Eliashberg theory [35,36]. In both calculations the obtained \( T_c \) values agree within \( \pm 0.02 \, \text{K} \) for each Pb film thickness considered. These calculations take full account of quantum size effects on the electron and phonon band structures and on the electron-phonon coupling properties. The evaluated ratios \( 2\Delta(0 \, \text{K})/(k_B T_c) \) are within 2% of the 4.19 bulk ratio, except for the 4 ML film where the deviation is close to 5%. This gives theoretical support for the assumption used to relate the measured \( \Delta \) to \( T_c \) values for each thickness.

The results are summarized in Fig. 4. Between 4 and 10 ML the variations in \( \lambda \) closely follow the variations in the electronic DOS at \( E_F \) and the variations in the computed \( T_c \) (see Fig. 3). For the 5 ML film a quantum well state close to \( E_F \) results in a peak in the DOS, which causes the peak in \( \lambda \). A corresponding maximum is also found for \( \Delta \) and \( T_c \). The comparison of both the calculated DOS at \( E_F \) and \( \lambda \) for the 10 ML film and the bulk suggests that, also for thicknesses larger than 10 ML, variations in the DOS at \( E_F \) are the main reason for variations in \( \lambda \) and \( T_c \).

For all thicknesses studied theoretically, the largest contribution to the \( e-ph \) coupling originates from electronic states of \( p_z \) symmetry: both surfacelike and bulklike \( p_z \) states contribute to \( \lambda \). The states of in-plane symmetry, \( p_x \) and \( p_y \), play a minor role in the \( e-ph \) coupling. The \( e-ph \) coupling matrix elements do not affect qualitatively the

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Consequently, for \( d \leq 2 \, \text{ML} \) the superconducting properties of Pb are expected to vanish.

Our estimated \( T_c \)'s are in quantitative agreement with the ones of Ozsr et al. [17], obtained \textit{ex situ} on Ge capped Pb/Pb/\( \sqrt{3} \times \sqrt{3} / \text{Si} \) and \textit{in situ} Pb/Si-(7 \times 7) interface. The trend observed in \textit{in situ} resistivity measurements [28] is consistent with the present findings, the quantitative differences with respect to our data being most likely caused by the inhomogeneity of the films. \textit{Ex situ} resistivity measurements [16] on Au capped Pb/Si(111)-(7 \times 7) films show a much faster decrease of \( T_c \) with decreasing film thickness than in our case, probably a consequence of the inverse proximity effect induced in the Pb film by the Au capping layer [29]. However, the previous \textit{in situ} STS results on Pb/Si(111)-(7 \times 7), which reported an essentially constant \( T_c \) in this thickness range [18,19], are at variance with our data. Furthermore, our observed energy gap reduction is much larger in amplitude than the very small oscillations of \( T_c \) as a function of

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showing that both systems are in the diffusive limit [17,37].

similar experimental behavior, in agreement with results (Grant No. FIS 2004-06490-C03-01). The Department of Education of the Government of the Basque Country, and the University of the Basque Country, mediated by quantum size effects in Pb islands [39] were served reduction of the superconducting energy gap with the interaction parameter $\alpha^2 F$, from which the average $\epsilon$-ph coupling parameter $\lambda$ can be derived.

Note added in proof.---The recently reported pseudogaps mediated by quantum size effects in Pb islands [39] were also observed in our study and accounted for in the background correction of our conductance spectra.

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