Quantum Size Effects on the Perpendicular Upper Critical Field in Ultrathin Lead Films

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We report the thickness-dependent (in terms of atomic layers) oscillation behavior of the perpendicular upper critical field $H_{c2\perp}$ in the ultrathin lead films at the reduced temperature ($t = T/T_c$). Distinct oscillations of the normal-state resistivity as a function of film thickness have also been observed. Compared with the T_c oscillation, the $H_{c2\perp}$ shows a considerable large oscillation amplitude and a π phase shift. The oscillatory mean free path caused by the quantum size effect plays a role in $H_{c2\perp}$ oscillation.

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There is a long history of scientific research on superconducting thin films. In particular, theoretical and experimental studies have been carried out to understand how the film thickness affects the superconducting properties. It seems that the reported experimental results of thin films can be explained by the existing theories of superconductivity [1–7]. However, most previously studied superconducting films were still relatively thick, normally over several tens of nanometers, and the film morphology was usually poor. If the film surface is atomically uniform and the thickness is further reduced to several nanometers so that the quantum size effects become apparent, a natural question arises: Will some unexpected new phenomena emerge? In particular, does the conventional theory still work?

Previous theoretical works have predicted many possible prominent physical properties modulated by quantum size effects: electronic structure, critical temperature, electron-phonon interaction, resistivity, Hall conductivity, and so on [8–13]. There are also some related important experimental results [14–21], such as the T_c oscillations in ultrathin Pb films, which are caused by the density of state oscillations in confined quantum well structures [22,23] and by the electron-electron interaction mediated by quantized confined phonons [11,24]. However, the properties of the upper critical field affected by the quantum size effect have not been reported in previous works. In this Letter, we report our experimental observation of the oscillatory $H_{c2\perp}$ through magnetotransport measurement of ultrathin Pb films. The oscillations are similar to those of T_c, but the motivations are more complex. Besides the factors for T_c oscillation, we interpret this unexpected phenomena by the oscillatory mean free path in ultrathin superconducting films caused by the quantum size effect.

The 3 mm × 10 mm sized Si(111) wafers were used as substrates and prepared by the standard cleaning procedure to obtain the clean Si(111)-7 × 7 surface. The base pressure of the UHV-MBE-STM-ARPES (MBE, molecular-beam epitaxy technique; ARPES, angle-resolved photoemission spectroscopy) combined system we used was about 5×10^{-11} Torr. The Si substrate was cooled down to 145 K during the MBE layer-by-layer growth of the Pb films. The growth rate was controlled at 0.2 ML/min (monolayer/minute), and a reflection high-energy electron diffraction was used for real time monitoring of the growth. After deposition, the sample was warmed up slowly to room temperature and transferred to the analysis chamber where the STM and ARPES were used to investigate the surface topography and the electronic structures, respectively [24]. For *ex situ* magnetotransport measurements, all the Pb films were covered with a Au protection layer of 4 ML before being taken out of the UHV system.

The $R - H$ measurements were carried out shortly after the samples were taken out of the vacuum. The applied field was perpendicular to the sample surface and the temperatures were set near and below T_c. To avoid trapping flux in, the magnet was discharged to zero in oscillate mode and the sample was warmed up to 8 K before the $R - H$ measurement for each temperature. Then the perpendicular upper critical field $H_{c2\perp}$ at different temperatures was obtained from the $R - H$ measurements at the field where the resistance reached half of the normal-state resistance R_N. The resistance approaches R_N very gradually because of the magnetoresistance effect. So we took R_N as the resistance where the resistance variation ratio is within 0.1%.

Figure 1 shows the $R - H$ curves of a 21 ML sample at different temperatures. The arrow points out the defined perpendicular upper critical field $H_{c2\perp}$ at 4.7 K. The inset of Fig. 1 shows $H_{c2\perp}$ vs temperature for the 21 ML film. It shows a perfect linear dependence on T near T_c, which is a typical property of a superconductor with a high value of the Ginzburg-Landau parameter κ. The inset of Fig. 1 can be used to determine the zero field critical temperature T_c by extrapolating the plot to $H_{c2\perp} = 0$. T_c determined in this way is shown as a function of thickness in Fig. 4(a). Normally, a direct way of determining critical temperature is through the $R - T$ measurement at zero field. We find

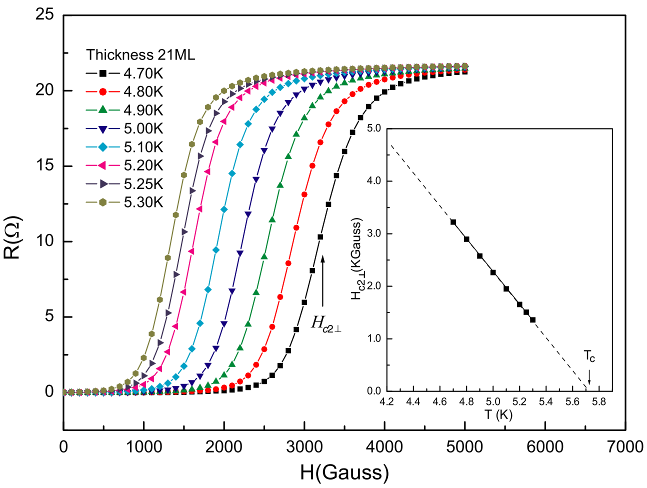

FIG. 1 (color online). $R - H$ curve of the 21 ML sample. The magnetic field is perpendicular to the sample surface. The black arrow indicates the determined upper critical field at 4.70 K. The inset shows the $H_{c2\perp}$ as a function of T for this sample. The plot is linearly extrapolated with dashed lines to both high and low temperature sides. The measurements were carried out with a quantum design magnetic property measurement system (MPMS-5).

that the critical temperatures determined by both methods show a consistent oscillation behavior and the values are quite close for every thickness.

The reduced $R - T$ curves of Pb films from 21 to 28 ML are shown in Fig. 2(a). The normal-state resistivity ρ_n oscillation with film thickness at $T = 8$ K is shown in Fig. 2(b). The rough oscillations of normal-state resistivity caused by the quantum size effect have been reported in single crystalline Pb and Pb-In thin films at $T = 110$ K [16]. But in polycrystalline films, oscillations of the normal-state resistivity have not been observed, although T_c has been found to oscillate with film thickness [15]. In our experiment, the distinct oscillations of both T_c and ρ_n have been observed with a clear period of 2 ML. It indicates that the quantum size effects show up in both the superconducting state and the normal state, but the intensities and mechanisms may vary in different ways depending on sample conditions.

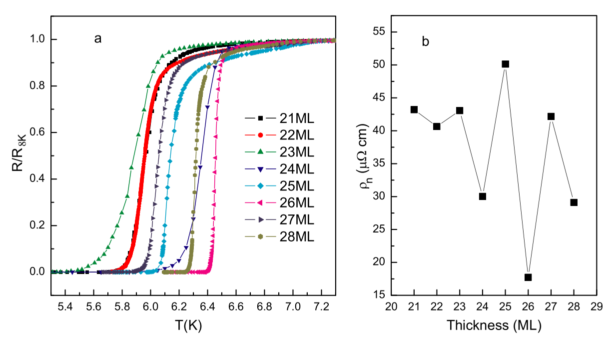

FIG. 2 (color online). The reduced resistances of Pb films as a function of temperature are shown in panel (a). The resistances are normalized by the normal-state resistance at $T = 8$ K. Panel (b) shows an oscillation of normal-state resistivity at 8 K as a function of film thickness.

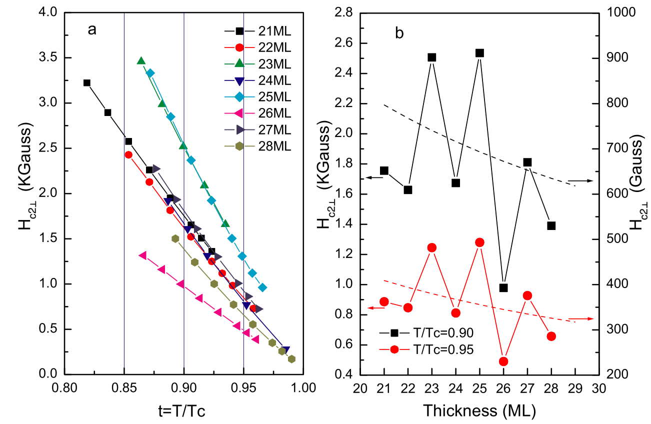

FIG. 3 (color online). Panel (a) shows the perpendicular upper critical field vs the reduced temperature t. The oscillation behavior at $t = 0.90$ and 0.95 are plotted in panel (b). The dashed lines correspond to the calculated results using Eq. (1).

Figure 3(a) shows $H_{c2\perp}$ as a function of the reduced temperature $t = T/T_c$. For every thickness, $H_{c2\perp}$ shows a good linear dependence on t near $t = 1$. $H_{c2\perp}$ vs film thickness for $t = 0.90$ and 0.95 are shown, respectively, in Fig. 3(b). It is shown that with the film thickness variation $H_{c2\perp}$ exhibits an oscillation behavior that is similar to the reported T_c oscillation [22]. However, the oscillations of $H_{c2\perp}$ are π out of phase to that of T_c; i.e., peaks appear in the odd-layer samples where dips appear in the even layer samples, which is opposite to the T_c oscillation shown in Fig. 4(a).

In the early theories proposed to understand the magnetic properties of thin film superconductors, the Tinkham-

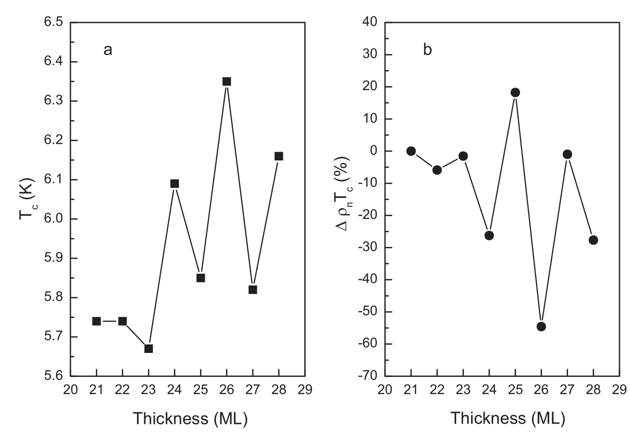

FIG. 4. Panel (a) shows the oscillation behavior of T_c with film thickness, which is defined by the way shown in the inset of Fig. 1. The rescaled $\rho_n T_c$ variation is shown in panel (b), which is defined in the following way: $\Delta\rho_n T_c = (\rho_n T_c - \rho_n' T_c')/\rho_n' T_c'$, where $\rho_n' T_c'$ is the value of $\rho_n T_c$ for the 21 ML film.

de Gennes-Saint James (TGS) theory [3,5] was validated as showing a good agreement with the former experimental results [6,7]. According to the TGS theory, the upper critical fields $H_{c2\perp}$ near T_c should monotonically increase when the film thickness decreases, which can be described in the following form [6]:

$$H_{c\perp}(T, d) = \sqrt{2}\kappa(T, \infty)H_c(T)(1 + b/d), \qquad (1)$$

where $\kappa(T, \infty) = 2\sqrt{2}\pi H_c(T)\lambda_\infty^2(T)/\Phi_0$ and $b = 3\lambda_L^2(T)\xi_0/8\lambda_\infty^2(T)$. Here $H_c(T)$ is the thermodynamic critical field, λ_L is the London penetration depth, λ_∞ is the bulk weak field penetration depth, Φ_0 is the flux quantum ($\Phi_0 = hc/2e = 2.07 \times 10^{-15}$ Wb), and d is the film thickness. In Fig. 3(b), the dashed lines, calculated using Eq. (1) and the related parameters in previous work [6] with film thicknesses appropriate to our samples, show the same tendency as the experimental curves if the oscillations are ignored. The measured $H_{c2\perp}$ values of our samples are about 3 times larger than the calculated values [note the different scales on the two sides of Fig. 3(b)], which may be caused by stronger interface or impurity scattering in our films that gives rise to a large resistivity, thus large $H_{c2\perp}$ (see discussion below). The linear dependence on t shown in Fig. 3(a) also gives information that for a given film thickness, the temperature dependence follows reasonably well with Eq. (1) whether that particular film is at the peak or valley of the $H_{c2\perp}$ oscillation.

The TGS theory above includes surface scattering effects but does not consider the quantum size effects that occurs in ultrathin films. The absent $H_{c2\perp}$ oscillation from the TGS theory means that the thickness-dependent quantum size effect is the original source of the $H_{c2\perp}$ oscillation. According to the Ginzburg-Landau (GL) theory, $H_{c2\perp}$ is determined by the in-plane coherence length $\xi_\parallel$. In a three-dimensional anisotropic superconductor, the perpendicular upper critical field near T_c is given by [4,7] $H_{c2\perp} = \frac{\Phi_0}{2\pi\xi_\parallel^2}$. Our ultrathin films are thinner than 10 nm, which is much smaller than the Pipard coherence length of a bulk Pb superconductor ($\xi_0^{\text{bulk}} = 83$ nm). We can use the quasi-two-dimensional formula [25]

$$\left(\frac{dH_{c2\perp}}{d(T/T_c)}\right)_{T_c} = -\frac{\Phi_0}{2\pi\xi_\parallel^2}. \qquad (2)$$

For the linear dependence on t near $t = 1$ shown in Fig. 3(a), $H_{c2\perp}$ has the same oscillation behavior with thickness as that of $-(\frac{dH_{c2\perp}}{dt})$ at a certain t. The system should be considered as a dirty-limit superconductor because of the strong scattering. For dirty superconductors near T_c, $\xi_\parallel^2 \approx \xi_0 l$, where ξ_0 is the Pipard coherence length and l is the mean free path for a film [2,4]. According to BCS theory, $\xi_0 \propto 1/T_c$; therefore we can get $H_{c2\perp} \propto T_c/l$ at a certain t. In Figs. 3(b) and 4(a), it is shown that the oscillation amplitude of $H_{c2\perp}$ and T_c are about 40% and 10%, respectively. On the other hand, the mean free path l and the normal-state resistivity ρ_n have the following relation: $l \propto 1/\rho_n$, from which we can derive $H_{c2\perp} \propto \rho_n T_c$. In Fig. 2(b), the ρ_n oscillation shows a big amplitude of about 60% and the same phase as $H_{c2\perp}$. The rescaled variation of $\rho_n T_c$ is shown as $\Delta\rho_n T_c$ in Fig. 4(b), which fits well with the oscillation behavior of $H_{c2\perp}$. It implies that the ρ_n oscillation dominates over the T_c oscillation in $H_{c2\perp}$ and gives rise to a π phase shift between T_c and $H_{c2\perp}$ oscillations. In earlier works, some of the effects of impurity and surface and interlayer roughness on quantum size effects in thin films were theoretically discussed [12,26]. Although at the moment we do not have a complete answer to the oscillations of ρ_n with thickness for our films with atomically uniform surfaces, the previous experiments on the layer-spacing oscillation [20] provides a strong indication that the modulation of the interface roughness with thickness may play an important role. In that experiment, they found that the interlayer spacings oscillate with a period of quasi-double-layer and even-monolayer samples have shorter interlayer spacings. This is also supported by the binding energy modulation observed [22,24]. It indicates that the lattice feels at home with the conduction electrons for the even-monolayer samples, while it is not so for the odd-monolayer samples. The unaccommodating lattice and conduction elections in the odd-layer samples could induce some lattice distortion and therefore enhance the interface roughness. This enhanced interface roughness must induce a higher resistivity.

We believe the experimental findings in our ultrathin films are due to a variety of combined quantum size effects from ultrathin film thickness. The quantum size effect can show up as either a modulation of the interface roughness induced by the interlayer spacings or a modulation of the phonon modes and the electron-phonon couplings, both of which affect the normal-state transport properties of the samples, of course, also causing the wave vector quantization along the thickness direction. Under the circumstance, only the components of electronic wave vector in the surface plane, i.e., the x-y plane, have a continuous distribution. Therefore, the electron density distribution is rather inhomogeneous along the z direction. The modulation of the electron densities may further feed back to the electron-interface and electron-phonon scattering processes and therefore to the mean free path. Another relevant issue is that the GL theory is only a mean-field theory, in which all the short-distance fluctuations are integrated out. For our ultrathin films, to give an adequate description of all the electronic states and the scattering processes, we must go back to the microscopic theory of BCS superconductivity within the subband framework and derive the multiband GL theory. The GL order parameter Ψ perpendicular to the film is limited to quantized values and may also show modulation with the interlayer-spacing modulation. Each subband may have a different value of coherence length ξ in the x-y plane, namely, $\xi_{n,d}$, where n is the subband index and d is the number of the monolayers. In general, $H_{c2\perp}$ is determined by a matrix equation with m being the size of the matrix in which m is the number of subbands below the Fermi energy. In the limit that one of the $\xi_{n,d}$ is much smaller than all the others, $H_{c2\perp}$ is predominantly determined by this minimum value, which could be much higher than that of the bulk. The story here is similar to that of the newly discovered superconductor MgB_2, where only two bands are involved [27]. If the film becomes thicker, the number of subbands will increase. The interaction of subbands will weaken the quantum size effects and the coherence length will be close to the average one. The oscillation behavior of $H_{c2\perp}$ will eventually disappear beyond a large thickness.

In conclusion, a large oscillation of $H_{c2\perp}$ in the ultrathin lead films are observed as a function of film thickness. The $H_{c2\perp}$ oscillation is opposite to that of T_c in phase and cannot simply be attributed to the modulation of the density of states and T_c. A large value of $H_{c2\perp}$ is also observed. Considering the interface and surface scattering and the modulation of coherence length and mean free path induced by the quantum size effect, a possible mechanism is proposed to explain both the anomalous oscillation of $H_{c2\perp}$ and its large value. We believe that a quantitative description for the findings in our experiments must be based on the combined quantum size induced modulation effects on the interlayer structures, electronic structures, phonons, and electron-phonon and electron-interface scattering processes. Further consideration about the flux dynamics is also necessary by including the interface and surface scattering effects and two-dimensional fluctuations in the multiband GL theory.

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