Quantum size effects in thermodynamic superconducting properties of ultra thin films

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By using multi-bands BCS theory, we have calculated the superconductivity energy gap and the critical temperature of a thin-film metallic superconductor. The thermodynamic superconducting characteristics such as critical magnetic field, specific heat, as well as the tunneling conductance are investigated for varying film thickness and temperature. We find the oscillation of thermodynamic superconducting properties with the film thickness, including the thermodynamic critical field $H_c$, the specific heat of normal, superconducting state, and position of the differential tunneling conductance peak. The two universal constants the nth sub-band energy gap $\Delta_n$ at temperature $T = 0K$ over $k_BT_c$, and the specific heat jump at $T_c$ over normal state specific heat at $T_c$ are independent of the film thickness. Their values are the same as in the bulk superconductor.

PACS numbers: 74.40.+k, 73.60.Dt, 74.10.+v

Quantum size effects (QSE) in superconductors have been a very attractive topic after some theoretical investigations of the superconducting transition temperature $T_c$ and energy gap for thin films. Some theoretical and experimental works have reported that several quantities were modulated by QSE, including electronic structure, electron-phonon interaction, resistivity, Hall conductivity, work function, surface energy and superconductivity critical temperature. In a metal film on a semiconductor substrate, the conduction electrons are confined by the vacuum on one side and the metal-semiconductor interface on the others. QSE and the simple stability of metal thin films on a supporting substrate have been discussed in several papers.

The report by Guo et al. is the first definitive and quantitative demonstration of $T_c$ oscillation with Pb film thickness as well as the normal state conductance. Using atomically uniform film of lead with exactly known numbers of atomic layers deposited on a silicon (111) surface, Guo et al. observed oscillations in $T_c$ that correlated well with the confined electronic structure and recently they demonstrated that film thickness can indeed affect superconductivity behaviors. It has been found that when the thickness of a film is reduced to the nanometer scale, the film’s surface and interface will confine the motion of the electrons, leading to the formation of discrete electronic states known as quantum well states (QWS). QWS have already been observed in thin metallic films. And they change the overall electronic structure of the thin film. At a tiny thickness, physical properties are thus expected to vary dramatically with the thickness. Very recently, Daejin et al. using a scanning tunneling spectroscopy study to show that both energy gap and transition temperature exhibit persistent oscillation without any suppression at ultra thin Pb films (5-18ML).

Quantum oscillations can be understood by considering QSE in these systems. The period is fixed for each system and equals one half of the bulk Fermi wavelength which is related to the average electron density and crystal structure. Although lots physical properties modulated by QSE in thin films have been revealed, the thermodynamic superconducting characteristics such as the specific heat, the thermodynamic critical field, tunneling conductance as the function of thickness and other parameters have not been reported. In this paper, by using the multi-band superconductivity theory which improves previous theory about QSE in superconductor film, we present the results of thermodynamic superconducting properties of ultra-thin metallic films.

From theoretical point of view, the resonance and the strong thickness dependence of $T_c$ are the characteristic features of a thin film superconductivity. The quantization of the transverse motion of the electron in the film leads to an increase of $T_c$ with decreasing film thickness, arising essentially from an enhanced effective BCS pairing interaction. In the previous calculations, the phonon modes were assumed to be the same as in bulk material and only the one dimensional quantum confinement effect of electrons were considered. Reference 16 considered the phonon dispersion in a thin film undergoing substantial modification compared with the bulk system with quantization of phonon spectrum. They found the resonant shape of superconductor transition temperature $T_c$ arises from both electronic and phonon confinements. Because of the quantization of both electron and phonon energies, the effective electron-electron interaction modified by the quantized phonon is different from the interaction arising from the bulk phonon. They found some fine structures in the energy gap and critical temperature by comparing with the bulk phonon model. However experimentally, no evidence of such fine structure from phonon confinement was
found.\textsuperscript{11,14} Thus, we will evaluate the thermodynamic characteristics by the same multi-band BCS theory, but neglect the phonon quantization effects.

We will start our model by taking into account of a realistic boundary condition. The thin film is confined in the x direction with geometric thickness N\textsubscript{t}. N is the thin film layer and t is the average inter-layer distance. Because of the finite potential barriers at the interface of thin film with Si substrates and vacuum, we will expand the film boundaries slightly to allow certain amount of charge spillage at two interfaces.\textsuperscript{15} For simplicity, we take charge spillage distances as the same at two interfaces. So the physical thickness is \(d = Nt + 2\Delta_0\).

The multi-band BCS Hamiltonian of the system is given by\textsuperscript{15}

\[
H = \sum_{\mathbf{k} \sigma} \xi_{\mathbf{n}}(\mathbf{k}) c_{\mathbf{n} \mathbf{k} \sigma}^\dagger c_{\mathbf{n} \mathbf{k} \sigma} + \sum_{\mathbf{k} \mathbf{k}'} \sum_{\mathbf{n} \mathbf{m} \mathbf{m}'} V_{\mathbf{k} \mathbf{k}'}^{\mathbf{m} \mathbf{m}'} c_{\mathbf{n} \mathbf{m} \mathbf{k} \sigma}^\dagger c_{\mathbf{m} \mathbf{m}^\prime \mathbf{k}^\prime \sigma} c_{\mathbf{n} \mathbf{m} \mathbf{k} \sigma} c_{\mathbf{n} \mathbf{m}^\prime \mathbf{k}^\prime \sigma},
\]

where \(c_{\mathbf{n} \mathbf{k} \sigma}^\dagger\) is the electron operator in the \(\mathbf{n}\)th sub-band with spin \(\sigma\), \(\xi_{\mathbf{n}}(\mathbf{k}) = \epsilon_{\mathbf{n}}(\mathbf{k}) - \mu\) the electron energy in the sub-band \(\mathbf{n}\) measured from the chemical potential \(\mu\), and \(V_{\mathbf{k} \mathbf{k}'}^{\mathbf{m} \mathbf{m}'}\) the attractive interaction between \(\mathbf{n}\)th sub-band and \(\mathbf{m}\)th sub-band is given by\textsuperscript{15}

\[
V_{\mathbf{k} \mathbf{k}'}^{\mathbf{m} \mathbf{m}'} = -\frac{J}{L^2} \frac{1}{d} \left[ \frac{\delta_{\mathbf{m} \mathbf{m}'} - \frac{b}{d}}{2} \right],
\]

Only if \(|\xi_{\mathbf{n}}(\mathbf{k})|\) and \(|\xi_{\mathbf{n}}(\mathbf{k}')| < \hbar \omega_D\). \(J\) is the interaction constant and \(L\) is the periodic distance in the y and z directions. \(\hbar \omega_D\) is the Debye energy. The constant \(b\) comes from the integral cutoff.

In the weak-coupling approximation, we have the superconducting energy gap for the \(\mathbf{n}\)th sub-band given by the gap function using the mean field method

\[
\Delta_{\mathbf{n} \mathbf{k}}(T) = -\sum_{\mathbf{m}, \mathbf{k}'} \frac{\Delta_{\mathbf{m} \mathbf{k}'}(T)}{2E_{\mathbf{m} \mathbf{k}'}} V_{\mathbf{k} \mathbf{k}'}^{\mathbf{m} \mathbf{m}'} \tanh\left(\frac{\beta E_{\mathbf{m} \mathbf{k}'}(T)}{2}\right),
\]

where \(E_{\mathbf{m} \mathbf{k}'} = (\epsilon_{\mathbf{m} \mathbf{k}'}^2 + \Delta_{\mathbf{m} \mathbf{k}'}^2)^{1/2}\).

The off-diagonal terms in the summation reflect the possibility of transition of the electron pair from one sub-band into another as the result of interaction with the confined phonons. Integration over \(\mathbf{k}\) gives the gap function of the \(\mathbf{n}\)th sub-band at \(T\). After some derivation, we arrive at the gap equation at zero temperature

\[
\Delta = \hbar \omega_D \sinh^{-1} \left( \frac{K a}{\gamma (1 - b/a) + \frac{t^2}{2}} \right),
\]

The critical transition temperature is

\[
kbTc = 1.14\hbar \omega_D \exp\left( - \frac{K a}{\gamma (1 - b/a) + \frac{t^2}{2}}\right),
\]

where we assume the integral range of \(k'\) in Eq. (3) are the same for each subband. \(K\) is a special interaction constant given by \(K = \pi \hbar^2 / m J\) and \(\gamma\) is the highest occupied sub-band, given by the integer part of \(dk_f / \pi\). The Fermi level only shifts slightly within 1\% of its bulk value at very thin thickness. So in our numerical calculation, we choose the Fermi wave vector as a constant, independent of film thickness. These results are similar as in Ref. 18. The bulk values of energy gap and transition temperature are given as:\textsuperscript{18}

\[
\Delta_{bulk} = \hbar \omega_D \sinh^{-1} \left( \frac{K \pi}{k_f} \right),
\]

\[
k_b T_{cbulk} = 1.14 \hbar \omega_D \exp\left( - \frac{K \pi}{k_f} \right).
\]

In Fig. 1, we compare the results of energy gap at \(T = 0\) and the superconducting transition temperature \(T_c\) with those of bulk values. We could see that the gap and \(T_c\) all oscillate with a period of 5 atomic layers. This can be understood by considering that the ratio of half Fermi wave length versus atomic layer distance is roughly 2/3. If the layer thickness changes continuously, the oscillation period is known to be \(\lambda_f / 2\). The modulating of these two quantities will lead the oscillation pattern differ by 5ML. We also notice that the oscillation amplitude will decay with increasing of the film thickness. But all these oscillation values are smaller than bulk values. This is in accord with several experimental results.\textsuperscript{11,12} And the most interesting thing is that the energy gap \(\Delta_n\) oscillate the same way as \(T_c\), which leads to the universal constant \(\Delta_n/k_B T_c = 1.76\). This constant is the same as
the bulk values. Similar conclusions have been reached by experiments in ultra thin Pb films, but a higher universal constant of 4.4 is obtained. Because Pb has a very strong electron phonon coupling, the weak coupling BCS theory used here is not quite applicable.

The Gibbs free energy, the thermodynamic critical field \( H_c \), the entropy and the specific heat per volume in a superconducting film are given, respectively by

\[
F = F_0 + \frac{k_B T}{V} \sum_{mk} \ln[f_{mk}(1 - f_{mk})],
\]

\[
-\frac{1}{8\pi} H_c^2 = \delta F(T) = -\frac{k_B T}{V} \sum_{mk} \ln[1 + \cosh(\beta E_{mk})],
\]

\[
S = -\frac{2}{V} \sum_{mk} [(1 - f_{mk}) \ln(1 - f_{mk}) + f_{mk} \ln f_{mk}],
\]

\[
C_v = \frac{2\beta^2 k_B}{V} \sum_{mk} f_{km}(1 - f_{km})(E_k^2 + \frac{1}{2} \frac{\partial \Delta_m}{\partial \beta}),
\]

where \( f_{km} = [\exp(\beta E_{km}) + 1]^{-1} \) and \( \beta = 1/k_B T \).

The thermodynamics critical field \( H_c \) is also shown in Fig. 2. We also find the similar oscillation of \( H_c \) with the film layers \( N \), although no experimental are available yet. The layer dependent \( H_c \) shows an oscillation amplitude of 22\% of the bulk situation at 5 to 8ML and decay to the amplitude of 5\% of the bulk \( H_c \) at thicker films. However, QSE on the perpendicular upper critical field

\[
H_{c2}\]
in the ultra-thin lead film has been reported whose oscillation is out of phase with the \( H_c \) oscillation.[20]

The specific heat is also calculated with Eq. (11) at both superconductor and normal state. In Fig. 3(a), we show the specific heat as a function of reduced temperature \( T/T_c \) at different films layers. We could see the jump of specific heat at critical temperature. Meanwhile, we also notice that although the specific heat both at normal and superconducting state oscillate with film thickness, the jump of specific heat at \( T_c \) divided by the normal state specific heat \((C_s - C_n)/C_n\)|\(T_c\) is another universal constant 1.42, and this constant is the same as in bulk situation. In Fig. 3(b) and 3(c), we can see that the specific heat at superconducting state varies in the same way as \( T_c \) does. But its value could be slightly higher than the bulk case. For the specific heat in a normal state, it oscillate unsymmetrically around its bulk value. This oscillation behavior is different from others. Hopefully, all these results could be verified in future experiments.

The ratio of superconductor-normal tunneling differential conductance \( G_{SN} \) to normal tunneling differential conductance \( G_{NN} \) is

\[
\frac{G_{SN}}{G_{NN}} = \int \frac{\text{sign}(\varepsilon)}{\sqrt{\varepsilon^2 - \Delta_n^2}} \frac{\partial f(\varepsilon + eV)}{\partial \varepsilon} d\varepsilon.
\]

The tunneling differential conductance versus bias voltage calculated at different film layers and different temperature from Eq. (12) are also shown in Fig. 4. The peak of the conductance is almost at \( eV = \Delta_n \). Because in our model all the energy gaps of each sub-band are assumed to be the same, we could only find one peak in the
different film thickness with $T$ of energy gap $\Delta$ for this kind of oscillation is due to the oscillation of conductance peak with thickness. The reason for this kind of oscillation is due to the oscillation of energy gap $\Delta$ at different thicknesses. In Fig. 4(b), we can see that the peak is depressed at high temperature, because energy gap decreases with increasing temperature. Recently, Daejin et al. have already extracted energy gap from the measured conductance spectra to determine the transition temperature. We hope that these interesting oscillations could all be observed experimentally in the future.

In this paper, we apply multi-band BCS theory to calculate thermodynamic quantities and find their oscillations with the film thickness, including the thermodynamic critical field $H_c$, the specific heat at normal and superconducting state and the position of differential conductance peak. These oscillations are the manifestations of the QSE. But two universal constants $\Delta_n/k_B T_c = 1.76$ and $[(C_n - C_n)/C_n]T_c = 1.42$ is independent of the film thickness, and their values are the same as in bulk situation. We hope that these interesting oscillations could all be observed experimentally in the future.

We greatly acknowledge financial support from US DOE under grant No. DE-FG02-04ER46124 and from NSF under grant No. CCF-0524673. B.C. is supported by NSF China under grants No. 10574035 and No. 10274070. Z.Z. also acknowledges support by a Grant-In-Aid of Research from Sigma Xi Society.

[1] J. M. Blatt and C. J. Thompson, Phys. Rev. Lett. 10, 332 (1963); C. J. Thompson and J. M. Blatt, Phys. Lett. 5, 6 (1963); V. Z. Kresin and B. A. Tavger, Sov. Phys. JETP 23, 1124 (1966); B. A. Tavger and W. S. Kresin, Phys. Lett. 20, 595 (1966).
[2] Z. Tesanovic, M. V. Jaric and S. Maekawa, Phys. Rev. Lett. 57, 2760 (1986); G. Govindaraj and V. Devanathan, Phys. Rev. B 34, 5004 (1986); N. Trivedi and N. W. Ashcroft, Phys. Rev. B 38, 12298 (1988); I. Vilfan and H. Pfnur, Eur. Phys. J. B 36, 281 (2003).
[3] D. Calecki, Phys. Rev. B 42, 6906 (1990).
[4] F. K. Schulte, Surf. Sci. 55, 427 (1976); P. J. Feibelman, Phys. Rev. B 27, 1991 (1983); P. Saalfrank, Surface Science 274, 449 (1992); Giuliana Materzanini, Peter Saalfrank and Philip J. D. Lindan, Phys. Rev. B 63, 235405 (2001); C. M. Wei and M. Y. Chou, Phys. Rev. B 66, 233408 (2002).
[5] B. G. Orr, H. M. Jaeger and A. M. Goldman, Phys. Rev. Lett. 53, 2046 (1984).
[6] M. Jalochowski, E. Bauer, H. Knappe and G. Lilienkamp, Phys. Rev. B 45, 13607 (1992); O. Pfennigstorf, A. Petkova, H. L. Guenter and M. Henzler, Phys. Rev. B 65, 045412 (2002); O. Pfennigstorf, A., Petkova, Z. Källassy and H. Henzler, Eur. Phys. J. B. 30, 111 (2002).
[7] T. Valla, M. Kralj, A. Siber, M. Milun, P. Pervan, P. D. Johnson and D. P. Woodruff, J. Phys. Condens. Matter 12, L477 (2000); D.-A. Luh, T. Miller, J. J. Paggel and T.-C. Chiang, Phys. Rev. Lett. 88, 256802 (2002); Yan-Feng Zhang, Jin-Feng Jia, Tie-Zhu Han, Zhe Tang, Quan-Tong Shen, Yang Guo, Z. Q. Qiu and Qi-Kun Xue, Phys. Rev. Lett. 95, 096802 (2005).
[8] Yu. F. Ogrin, V. N. Iutukii, M. V. Arifova, V. I. Kovalev, V. B. Sandomirskii, and M. I. Elinson, Sov. Phys. JETP, 26, 714 (1968); B. A. Tavger and V. Ya. Demikhovskii, Sov. Phys. Uspekhi, 11, 644 (1968).
[9] Z. Zhang, Q. Niu and C.-K Shih, Phys. Rev. Lett. 80, 5381 (1998) and references therein.
[10] T. Miller, A. Samsavar, G. E. Franklin and T. C. Chiang, Phys. Rev. Lett. 61, 1404 (1988).
[11] Yang Guo, Yan-Feng Zhang, Xin-Yu Bao, Tie-Zhu Han, Zhe Tang, Li-Xin Zhang, Wen-Guang Zhu, E. G. Wang, Qian Niu, Z. Q. Qiu, Jin-Feng Jia, Zhong-Xian Zhao and Qi-Kun Xue, Science 306, 1905 (2004).
[12] T.-C. Chiang, Science 306, 1900 (2004).
[13] T. C. Chiang, Surf. Sci. Rep. 39, 181 (2000).
[14] Daejin Eom, S. Qin, M.-Y. Chou and C. K. Shih, Phys. Rev. Lett. 96, 027005 (2006).
[15] V. Z. Kresin, Phys. Rev. B 25, 157 (1982).
[16] E. H. Hwang, S. Das Sarma and M. A. Stroscio, Phys. Rev. B 61, 8659 (2000).
[17] J. C. Nabyte and M. N. Wybourne, Phys. Rev. B 44, 8990 (1992); J. Seyler and M. N. Wybourne, Phys. Rev. Lett. 69, 1427 (1992).
[18] Ming Yu, Myron Strongin and A. Paskin, Phys. Rev. B 14, 996 (1976).
[19] P. Czoschke, H. Hong, L. Basile, T. C. Chiang, Phys. Rev. B 72, 075402 (2005); P. Czoschke, H. Hong, L. Basile, T. C. Chiang, Phys. Rev. B 72, 035305 (2005).
[20] Xin-Yu Bao, Yan-Feng Zhang, Yupeng Wang, Jin-Feng Jia, Qi-Kun Xue, X. C. Xie, and Zhong-Xian Zhao, Phys. Rev. Lett. 95, 247005 (2005).