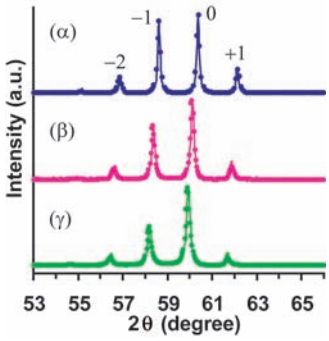

Fig. 3. Diffraction patterns measured (circles) during the heat treatments and their reconstructions by the modified Stearns model (solid line): (α) room temperature, (β) 903 K, and (γ) 953 K. a.u., arbitrary units.

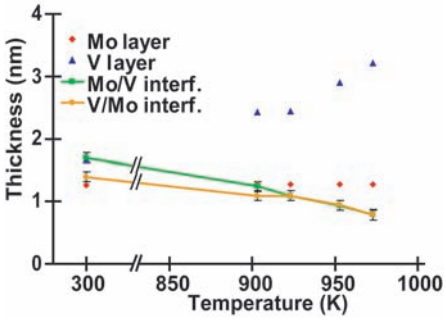

Fig. 4. Thickness of the interfaces as well as the pure Mo and V layers, as obtained from the fits. Error bars show the estimated errors of fitting. In case of the pure Mo and V layer, respectively, error bars are comparable to the symbol sizes. The solid curves are to guide the eye. interf., interface.

obtained in Si/Ge (*4*, *5*) and Au/Ni (*10*, *12*) multilayers. During deposition of one element (e.g., A) having a segregation tendency on the surface of the other (B), a segregation-assisted intermixing takes place and the B/A interface is more diffuse than the A/B interface.

Because the fits resulted in a decreasing interface thickness (i.e., the increase of I^0/I^i, with $i = -2, -1, +1$, and the decrease of I^{+1}/I^{-2}), we conclude that the interface sharpened during the heat treatment. The most notable feature of the reconstructions is the reproduction of changes of the intensity ratios with increasing temperature.

Finally, at a fixed temperature no more changes were observed after a certain time (i.e., a gradually increasing temperature was necessary), which also supports that the interfaces sharpen. Because the interface is sharper, the Mo atoms are bound more strongly in the interface (the interface is more and more Mo rich), and consequently their diffusion into the V is slower (Fig. 1). Thus, to counterbalance this effect, we had to increase the temperature slightly (the diffusivity has exponential dependence on both the temperature and the composition).

One may argue that other effects could produce a similar evolution. For example, stress development and relaxation during intermixing could be one of the most relevant effects. However, as was shown in (*2*), the composition profile develops similarly to that of a stress-free case, and only the time scale of the process is expected to be slightly different.

We successfully followed in situ interface sharpening in coherent Mo/V multilayers. As data in Fig. 4 show, the thickness of the Mo layers did not change, apart from a tiny increase caused by thermal expansion. In contrast, the V-rich layers became much thicker, which cannot be explained solely by thermal expansion. The interface thicknesses decreased by about a factor of 2 (from 1.7 and 1.4 nm, respectively, to 0.78 nm), confirming the sharpening effect.

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23 August 2004; accepted 10 November 2004
10.1126/science.1104400

Superconductivity Modulated by Quantum Size Effects

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We have fabricated ultrathin lead films on silicon substrates with atomic-scale control of the thickness over a macroscopic area. We observed oscillatory behavior of the superconducting transition temperature when the film thickness was increased by one atomic layer at a time. This oscillating behavior was shown to be a manifestation of the Fabry-Pérot interference modes of electron de Broglie waves (quantum well states) in the films, which modulate the electron density of states near the Fermi level and the electron-phonon coupling, which are the two factors that control superconductivity transitions. This result suggests the possibility of modifying superconductivity and other physical properties of a thin film by exploiting well-controlled and thickness-dependent quantum size effects.

Modern electronic and opto-electronic devices are often made of thin films. Ideally, following the textbook description for quantum particles in a box, electrons confined in a perfectly uniform thin film are quantized into discrete energy levels in the vertical direction, forming standing-wave–like eigenstates, or quantum well states (QWSs), similar to the Fabry-Pérot modes in an optical interferometer (*1*, *2*). Such electron interference is very sensitive to film thickness and smoothness because of the very short wavelength of electron waves (~1 nm) and has been shown to modulate the electronic distribution near the Fermi level (E_F), thus substantially affecting the physical and chemical properties of a thin film (*3*, *4*). We report on the effect of electron-wave interference on the superconductivity property of two-dimensional (2D) thin films.

Traditionally, 2D thin-film superconductors are defined as those whose material size is less than the coherence length in one di-

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mension (*5*). For conventional superconductors such as Pb, the coherence length ξ_0 (83 nm for Pb) (*6*) is very large compared to atomic dimensions and the electron Fermi wavelength (λ_F ~1.06 nm). Therefore, 2D superconductors are still made of 3D electrons; only the condensate wave function for the Cooper pairs may be regarded as 2D. A common trend of such 2D superconductors is that the superconducting transition temperature (T_c) is continuously reduced as the film thickness is decreased. This reduction of T_c is caused by enhanced quantum fluctuations of the phase of the condensate wave function for thinner films (*7*, *8*). Oscillatory behavior in T_c from the quantum size effect (QSE) was suggested in early theoretical works (*9*, *10*), and experimental observation of such an effect was claimed in a study of thin Sn films (*11*). However, the observed T_c oscillations differed quantitatively from the theoretical predictions, and there was no corresponding oscillation in the normal-state resistivity as expected. These results were explained later (*12*, *13*) as due to QSEs in the grain structures of the films, which were typically polycrystalline and granular in nature. Conductance measurement of ultrathin Pb films on Si(111) showed clear variations in T_c, but the data were insufficient to establish an oscillating period (*14*).

We were able to grow ultrathin crystalline Pb films on Si(111) substrates with atomic-scale uniformity in thickness over a macroscopic area. We were therefore able to make transport measurements on the films and identify T_c as a function of the number of atomic layers in a well-controlled manner (*18*).

Scanning tunneling microscope (STM) topographic images are shown of the Pb films with 23 and 24 atomic monolayers (MLs) (Fig. 1), which typify the surface morphology of all the films discussed in this paper. The steps seen in the images originate from the Si substrate, and there is exactly the same number of Pb atomic layers on each terrace. Such high-quality films are crucial for electron coherence, because the wavelength of electrons in Pb is only 1.06 nm. We found that when the thickness was smaller than 22 MLs, only stable odd-layered films were obtained; the intervening even-layered films and the films thinner than 12 MLs tended to be rough. Such "magic" thicknesses are due to QWSs, whose discrete energy levels are known to strongly regulate the relative stability of such films (*15*–*17*). Above 21 MLs, we were able to achieve layer-by-layer growth with the perfect uniformity mentioned above.

One expects that with films of almost perfectly uniform thickness (Fig. 1), the electronic motion in the vertical direction should be frozen into a small number of quantized levels (QWSs), and motion in the horizontal directions should remain free. This is indeed

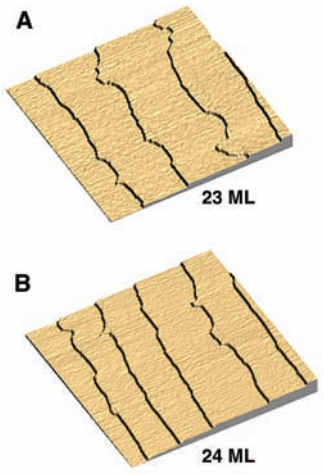

Fig. 1. Room temperature STM images (2000 × 2000 nm) of the Pb films at the completion of 23 (**A**) and 24 (**B**) MLs, grown at a deposition rate of 0.2 ML/min on Si(111) substrates held at 145 K. All the Pb films discussed in this paper exhibit essentially the same morphology.

observed. The thickness-dependent photoemission spectra measured in situ from these samples (Fig. 2) show clearly well-defined QWS peaks, which shift progressively in energy as the film thickness is increased by each atomic layer. In contrast, the spectrum for a film of 26.85 MLs, which deviates only slightly from the ideal case of 27 MLs, shows a considerable contribution from the spectrum of 26 MLs. The observation of the clean QWS peaks is therefore another good indication of the high quality of the films. Because the QWSs progress in energy as a function of film thickness, and because of the discrete nature of the film thickness, the position of the highest occupied QWS (marked by crosses) oscillates with respect to E_F (0.0 eV) between the odd and even layers. This is further confirmed by our first-principles calculations, which show the same oscillatory behavior with a higher density of states near E_F for the odd layers and lower ones for the even layers (*18*). According to our photoemission spectra, the total intensity (density of states) between neighboring even and odd layers changes by ~5, 10, and 20% within energy ranges of 10, 20, and 30 meV below the Fermi level, respectively (fig. S2). Because most physical properties such as transport and superconductivity depend strongly on the distribution of electrons near E_F, we expect that these properties will also be modulated as a function of film thickness.

Figure 3 shows T_c (black solid balls) as a function of film thickness. Here, T_c is defined as the temperature at which the film resistance becomes half of the normal-state resistance at T = 8 K, as indicated by the arrow in the inset of Fig. 3. We can see that

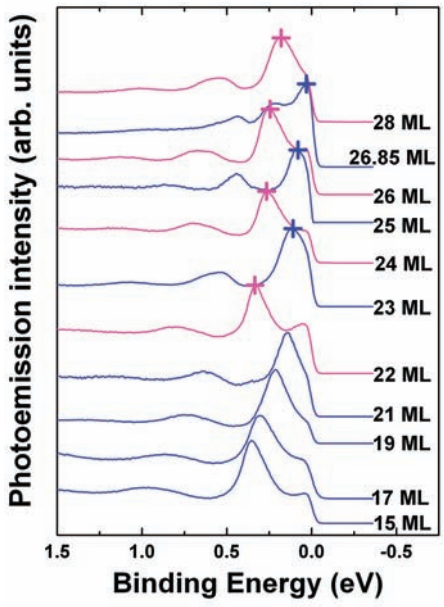

Fig. 2. Monolayer thickness–resolved normal-emission photoemission spectra of the Pb thin films measured in situ at 75 K. The crosses highlight the peaks of the highest occupied QWSs for the odd-layered (blue) and even-layered (pink) films, respectively, showing an oscillatory thickness dependence in the density of states near E_F (0.0 eV). The photoemission spectra were collected with a Gammadata Scienta SES-2002 analyzer with a HeI light source of 21.2 eV. arb., arbitrary.

there is an overall trend of increasing T_c with increasing film thickness, which is consistent with the behavior of conventional 2D superconductors. There is an oscillatory behavior in T_c above 21 MLs, with an oscillating period of 2 MLs, with a higher T_c for the even-numbered thicknesses and a lower T_c for the odd-numbered thicknesses. Monotonic behavior below 21 MLs is observed, but the intervening even layers are missing there.

According to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity (*19*), T_c depends exponentially on the electron density of states $N(E_F)$ at the Fermi energy and on the phonon-mediated attractive interaction V between the electrons in the form of

$$T_c = 1.14T_D\exp[-1/N(E_F)V] \qquad (1)$$

where T_D is the Debye temperature characterizing the energies of the phonons. From Fig. 2, we know that the presence of QWSs can strongly modulate the density of states $N(E_F)$, and thus the oscillatory T_c should be closely related to the formation of QWSs in the films. For a system in which the QSE is involved, $N(E_F)$ oscillates as $N(E_F) = (m^*/\pi\hbar^2 t)[2t/\lambda_F]$, as a function of the film thickness t, where m^* is the effective mass of electrons, $\hbar$ is $(h/2\pi)$(where h is Planck's constant), and $[2t/\lambda_F]$ is the integer part of $2t/\lambda_F$ (*11*). In our case, the Fermi wavelength λ_F of Pb is

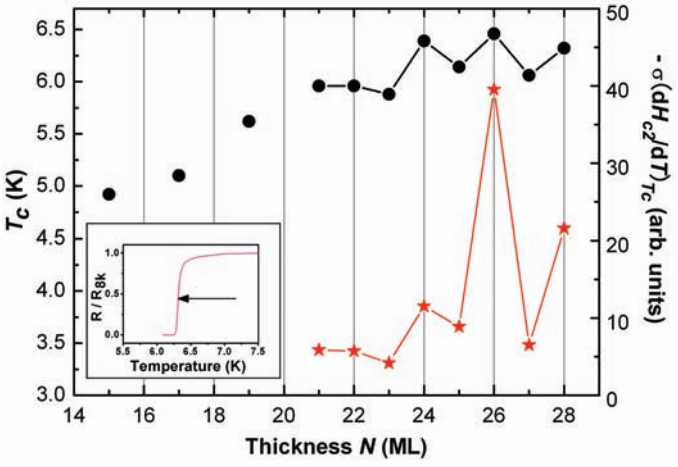

Fig. 3. T_c (black solid dots) and the density of states $N(E_F) \propto -\sigma(dHc_2/dT)_{T_c}$ (red stars) as a function of Pb film thickness, demonstrating a nonmonotonic oscillatory behavior in both T_c and $N(E_F)$. The inset shows the resistance as a function of temperature measured from the 28-ML film, which reveals a sharp transition to superconductivity at 6.32 K, as indicated by the arrow. The vertical scale is normalized with the resistance at 8 K. The measurements were carried out with a Quantum Design Magnetic Property Measurement System (MPMS-5).

about 4 MLs, which corresponds to an oscillating period of 2 MLs (*16*). When the film thickness fits to an integer multiple of half wavelength, resonance of QWSs occurs.

To further identify the role of the QWS-modulated density of states in T_c, we performed magnetoresistance measurements to estimate more accurately the density of states near the superconducting state. The photoemission data in Fig. 2 could not be directly used for this purpose for two reasons. First, those data were collected along the normal-emission direction (perpendicular to the sample surface), which is an incomplete measurement of the density of states. Second, those data were obtained in situ for the bare Pb films without Au coverage (T_c was obtained with an Au cap cover). Preliminary theoretical and experimental studies show that Au coverage can significantly shift the energy positions of the QWSs in the Pb films because of the change of boundary conditions. According to the Ginzburg-Landau-Abricosov-Gorkov theory, $N(E_F)$ of a Pb film is proportional to the slope of the upper critical field, H_{c2}, in its temperature dependence near T_c (*20*)

$$N(E_F) \propto -\sigma(dH_{c2}/dT)_{T_c} \qquad (2)$$

where σ is the normal-state conductivity. We measured the film resistance R as a function of applied magnetic field H along the surface-normal direction at different temperatures, and obtained H_{c2} as the magnetic field at which R reached half of the normal-state resistance at the onset point for the superconducting transition. In order to remove the influence from the Au cap layer, the normal-state relative conductivity of the Pb films was estimated from the resistance at T_c on the R-T curves. The measured value (red stars) of $-\sigma(dH_{c2}/dT)_{T_c}$, which is proportional to the density of states $N(E_F)$, is plotted in Fig. 2, and a one-to-one correspondence between the thickness dependence of $N(E_F)$ and T_c was observed (*21*).

The electron density of states is not the only factor affecting T_c. For a conventional superconductor such as Pb, electron-electron attraction, which is necessary for the binding of Cooper pairs, is ultimately due to electron-phonon interactions (*22*). As we mentioned earlier, QWSs strongly regulate the mechanical stability of films at different thicknesses, and they can cause expansion and shrinkage of interlayer spacing (*23*). Both of these facts indicate the possibility of modulating electron-phonon coupling by QSEs. Here we present more direct spectroscopic evidence of QSEs in electron-phonon coupling.

According to the more elaborate Eliashberg-McMillan theory (*24*), $\lambda = \frac{1}{2\pi k_B}\frac{d\Delta E}{dT}$ replaces $N(E_F)V$ in the BCS theory (Eq. 1) as the major parameter controlling T_c, where ΔE is the quasiparticle linewidth due to phonon broadening. We estimated ΔE from the QWS peak widths at high temperatures where phonon broadening dominates (*25*–*27*), and the QWS peaks were fitted by the Voigt profiles with the Lorentzian lineshape (fig. S3). We carried out variable temperature photoemission spectroscopy measurements for all stable films with thickness smaller than 25 MLs (fig. S4), and obtained λ (fig. S5) by the method described in (*26*). For thicknesses above 21 MLs, an oscillatory λ as a function of thickness was again seen. The overall similar oscillatory behavior and one-to-one correspondence in terms of the number of atomic layers in λ, $N(E_F)$, and T_c demonstrate that QWSs could greatly modulate the electron-phonon coupling as well. However, the relevance of the λ value, which is estimated from the QWSs at different binding energies, to T_c remains a question for further study.

Because the formation of QWSs greatly modulates electronic structure near the Fermi level of the films, we speculate that many other properties such as work function, friction force, thermal properties, electron mobility, Curie temperature (for magnetic materials), and catalytic properties can be modulated as well as superconductivity.

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28. The work at the Chinese Academy of Sciences was supported by the National Science Foundation and the Ministry of Science and Technology of China. Q.N. was supported by NSF through grant no. DMR-0306239 and by the Welch Foundation.

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10 September 2004; accepted 25 October 2004
10.1126/science.1105130