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.

References and Notes
7. Materials and methods are available as supporting material on Science Online.
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Fig. S1
References
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**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-
mension (5). For conventional superconductors such as Pb, the coherence length \( \xi \) (83 nm for Pb) (6) is very large compared to atomic dimensions and the electron Fermi wavelength \( \lambda_F \sim 1.06 \text{ nm} \). 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 of all the films discussed in this paper. (Fig. 1), which typify the surface morphology of such 2D superconductors. There is an oscillatory behavior in \( T_c \) as due to QSEs in the discrete nature of the film thickness, the position of the highest occupied QWSs (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 \( T = 8 \text{ K} \), as indicated by the arrow in the inset of Fig. 3. We can see that 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

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

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 \( N(E_F) = (m^*\pi\hbar^2/2m^*) \), 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 \( 2m^*/\hbar^2 \) is the integer part of \( 2m^*/\hbar^2 \). In our case, the Fermi wavelength \( \lambda_F \) of Pb is
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 magneto-resistance measurements to estimate more accurately the density of states near the superconducting state. The photo-emission 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-Abrikosov-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)

$$N(E_F) \propto -\sigma(dH_{c2}/dT)_T,$$

where $\sigma$ 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 $-\sigma(dH_{c2}/dT)_T$, 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),

$$\lambda = 1 + \frac{\alpha}{2 \pi} \frac{\pi^2 k_B^2}{m^* c^2},$$

where $c$ is the phonon velocity, replaces $N(E_F)\nu$ in the BCS theory (Eq. 1) as the major parameter controlling $T_c$, where $\Delta E$ is the quasiparticle linewidth due to phonon broadening. We estimated $\Delta E$ 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 photomission spectroscopy measurements for all stable films with thickness smaller than 25 MLs (fig. S4), and obtained $\lambda$ (fig. S5) by the method described in (26). For thicknesses above 21 MLs, an oscillatory $\lambda$ 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 $N(E_F)$, and $T_c$ demonstrate that QWSs could greatly modulate the electron-phonon coupling as well. However, the relevance of the $\lambda$ 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.

References and Notes
18. Materials and methods are available as supporting material on Science Online.
21. For the ex situ transport measurements, ~4 MLs of Au was deposited on clean Pb thin films in a molecular beam epitaxy chamber to avoid air contamination. The Au film can also grow in layer-by-layer mode, and the surface morphology after Au deposition, which is shown by our STM data, is essentially the same as that of the Pb film shown in Fig. 1. The critical transition temperature $T_c$ at zero magnetic field extrapolated from the $H_{c2}$-$T$ curve shows the same oscillatory behavior as the $T_c$ value in the $R$-$T$ measurement. The results from the magnetic and resistance measurements are consistent, so that the effects from the Au cover layer are eliminated.
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