APPLIED PHYSICS LETTERS **90**, 093120 (2007)

Oscillatory thermal expansion of Pb thin films modulated by quantum size effects

Yan-Feng Zhang, Zhe Tang, Tie-Zhu Han, and Xu-Cun Ma
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Jin-Feng Jia[a] and Qi-Kun Xue
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China and Department of Physics, Tsinghua University, Beijing 100084, China

Kun Xun and Si-Cheng Wu
Department of Physics, Peking University, Beijing 100871, China

(Received 8 November 2006; accepted 26 January 2007; published online 1 March 2007)

Varied temperature photoemission study is performed to investigate the quantum size effects on the thermal property of atomically flat Pb films grown on Si(111). The binding energies of the quantum well states for the films with thicknesses from 10 to 24 ML exhibit a linear increase with increasing temperature from 75 to 270 K. Under free electron approximation, thermal expansion coefficients of the thin films are determined, which manifest a large enhancement and oscillation behavior. The large enhancement is interpreted by a model based on the quantum confinement along the film normal direction. The oscillation is shown to be closely related to the structural instability and is a result of the formation of the quantized electronic states in thin films. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710223]

Quantum size effects (QSEs) originate from the electron confinement at reduced dimensionality could have dramatic effects on the physical property of a material. Early in 1970s, Schulte[1] calculated the thickness dependence of electron densities, potentials, and work functions of freestanding thin films in which QSE is expected to be observed when the film thickness is comparable with the Fermi electron wavelength (λ_F). Cyclic variations of the physical properties, such as the film stability, Hall mobility, and superconducting transition temperature,[2–5] have been proposed and verified. According to Feibelman and Batra,[6,7] structural relaxation can also be modulated by QSE, since structure variation can partially counteract the outcome of the electronic structure change. Later on, several techniques, for example, He atom scattering in Pb/Ge(100) system,[8] scanning tunneling microscopy (STM), and x-ray diffraction technique in Pb/Si(111) system,[9] were utilized to investigate the structure relaxation behavior in Pb islands.

Recently, atomically flat Pb films, characterized with distinct and well-defined quantum well states (QWSs), have been prepared on Si over a macroscopic scale, which enables precise determination of the QWS binding energy by an angle-resolved photoemission spectroscopy.[5] The binding energy of QWS can be a unique characteristic of the film thickness via a simple phase accumulation model,[10,11] and serves as an accurate footprint for absolute film thickness identification. In previous studies, temperature-dependent photoemission spectroscopy was successfully applied to investigate many-body effects with regard to the electron-phonon coupling of surface states of bulk materials or QWS of thin films, by using the temperature dependence of spectra width.[12–15] Thermal-dependent peak position, i.e., binding energy of the QWS, also became an interesting topic because of its close relation with the thermal expansion behavior of thin films.[13,14]

In this letter, we report on our study of the temperature-dependent quantum well spectroscopies of Pb films with a thickness range from 10 to 24 ML, prepared on Si(111) substrate. As reported before,[16] 10 ML is the smallest thickness for formation of complete and stable Pb films at room temperature, the growth manifests a QSE-driven bilayer mode from 10 to 21 ML and switches to a layer-by-layer mode above 21 ML. Contrary to the bulk material, with increasing substrate temperature from 75 to 270 K, we observed an exclusively linear increase of the QWS binding energies for all films studied. From this linear dependence, we deduce the thermal expansion coefficients of different Pb layers along the film normal direction, which oscillate between even and odd layers and present great enhancement for unstable layers.

The Pb films were prepared with a low temperature deposition method and the detail was described elsewhere.[5,16] An Omicron STM and a Gammadata Scienta SES-2002 electron energy analyzer were used for *in situ* surface morphology and electronic structure characterization. A sample manipulator, with a button heater attached to the head of an open-cycle He cryostat flowed with liquid nitrogen, was facilitated to control the sample temperature from 20 to 300 K. The analyzer with a 2 meV resolution ensures us to capture the delicate shift of the QWS binding energy.

Although various QSE-induced novel physical properties in Pb films were predicted theoretically before, there are only a few deterministic experimental proofs. This is because, for Pb, the oscillation period for electronic structure change is only 2 ML. 1 ML fluctuation in film thickness will smear out the expected oscillation in physical properties. Preparing a film with singular thickness in terms of atomic layers proves to be a great challenge, due to the lattice mismatch and different bonding nature between Pb overlayer and semiconductor substrates. In our experiment, we have successfully prepared atomically flat Pb films over a macroscopic scale and the perfect morphology can be characterized

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[a] Electronic mail: jjf@tsinghua.edu.cn

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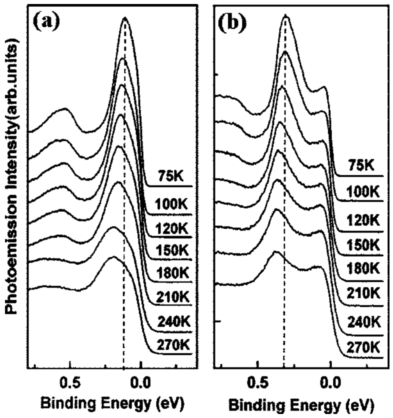

FIG. 1. (Color online) Temperature-dependent photoemission spectra of Pb films for (a) 23 ML and (b) 24 ML collected within a temperature range of 75–270 K. The vertical dashed lines are guides to the eye, for the variation of the QWS binding energy.

with perfect STM morphologies and singular set of QWS peaks.

In Fig. 1, we show two sets of temperature-dependent photoemission spectra of 23 ML [Fig. 1(a)] and 24 ML [Fig. 1(b)] Pb films, and their STM morphology assumes a flat surface over a macroscopic scale. The strongest peaks correspond to the highest occupied QWS. Note that for both films, the QWS peaks always shift towards higher binding energy with increasing substrate temperature from 75 to 270 K. For all the Pb films involved, the maximum shift of the QWS binding energy is less than 100 meV within the selected temperature range. However, a dramatic difference between even and odd Pb layers can be clearly detected, for example, the net shifts for the films of 23 and 24 ML are 84 and 65 meV, respectively. We also notice a thermal broadening of the QWS peaks with increasing temperature, and this was already discussed elsewhere.[16]

Such thermal-induced shift in QWS binding energy was observed in Ag/V(100) and Ag/Fe(100) systems previously,[13,14] but opposite results were obtained: the binding energy increases in Ag/V(100), and it decreases in Ag/Fe(100) as the film temperature is elevated. The reason is that the substrate [V(100) or Fe(100)] has a significantly lower or similar thermal expansion coefficient as compared with the overlayer materials. In this work, we report a similar behavior as that in Ag/V(100). Generally speaking, thermal expansion will increase the lattice constants of both the epitaxial film and the substrate, which will subsequently, in terms of the simple phase accumulation model,[10,11] increase the width of quantum well and lower the Fermi level, as well as change the phase shift at the interface between the film and the substrate. In a two-dimensional (2D) system, change of the phase shift at the interface was proven to play minor effects.[17] Therefore, the dominant factor in the observed binding energy shift should mainly arise from the first two factors.

To quantify our results, the temperature dependence of the QWS binding energy for some Pb films is fitted linearly and shown in Fig. 2. Because of very limited charge transfer between the overlayer and the substrate, the substrate Fermi level change cannot introduce a significant shift of the Fermi level of Pb films. Rather, we attribute the observed shift to the thermal broadening of the confinement well width, as well as the variation of the Fermi level of Pb films. Since for Pb film on Si(111) substrate, when temperature (T) increases, the Fermi energy E_F of Pb film drops more than the E_F of Si due to the dramatic difference of the thermal expansion coefficient, so there is a charge transfer from Si to Pb film. And these charges only stay at the Pb–Si interface (no charge in Pb film and the electric filed is zero in Pb film) and shift all energy levels (including QWS) in the Pb film up with the same amount until $E_F(\mathrm{Pb}) = E_F(\mathrm{Si})$. Therefore, the Fermi energy of Si and its change have minor effect on the relative shift of the QWS in Pb film. Within a simple free electron approximation, the temperature dependence of the Fermi energy of a bulk material is described as

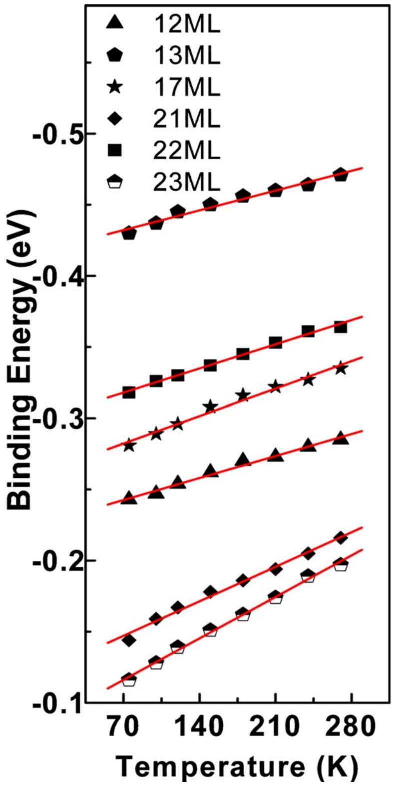

FIG. 2. (Color online) Binding energy of the QWS for various Pb films plotted as a function of temperature. The dots and lines indicate the experimental data and linear fits, respectively.

$$dE_F/dT = -2E_F\alpha_r, \tag{1}$$

where α_r is the linear thermal expansion coefficient of the material, and E_F is its Fermi energy relative to the bottom of valence band (for bulk Pb, $E_F = 9.47$ eV). Such approximation should be reasonable regarding to the fact that the QWS energies of the Pb films involved are within a small energy window of 0.6 eV below the Fermi level, and this energy regime has been successfully used to determine the Pb band structure.[16] For a 2D system, we can apply this formula to calculate the thermal shift of the QWS binding energy. The thermal shift of the QWS energy (E_{QW}) with respect to the bottom of valence band has a form of

$$dE_{\mathrm{QW}}/dT = -2E_{\mathrm{QW}}\alpha_Z, \tag{2}$$

where α_Z is the linear expansion coefficient along the confined direction.

Then, we calculated the linear thermal expansion coefficient of Pb films in the confined direction by the experimental thermal shift of QWS binding energy in terms of Eqs. (1) and (2), and the results are shown in Fig. 3. Several observations can be made: (1) the thermal expansion coefficients

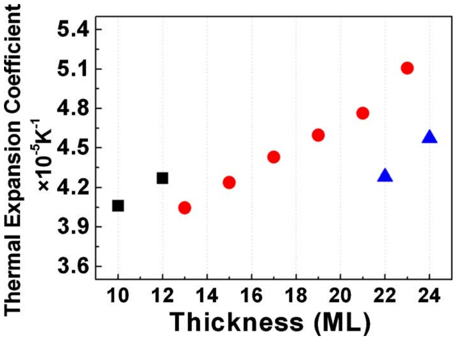

FIG. 3. (Color online) Thermal expansion coefficients of Pb films along the confined direction calculated with the proposed model.

in the film normal direction are greatly enhanced compared to the bulk Pb, (2) there is a 2 ML oscillation for the Pb films from 21 to 24 ML, and (3) the overall trend is that a lower expansion coefficient corresponds to a film with a higher QWS binding energy.

For Pb/Si(111), due to the Pb film being thin enough, its linear expansion coefficient in film plane (xy plane) should be very close to that of bulk Si, while in z direction, a great enhancement can be expected because of what is called Poisson effects and that the linear expansion coefficient of Si (2.8×10^{-6} K^{-1}) is one order of magnitude lower than that of Pb (2.89×10^{-5} K^{-1}). To understand the global enhancement of the linear thermal expansion coefficient along the confined direction, we use α_r, α_P, and α_Z to describe the linear expansion coefficient of the freestanding film, the confined film in the film plane, and the film normal (z) direction, respectively. α_Z can be expressed as

$$\alpha_Z = \alpha_r + \frac{2(\alpha_\gamma - \alpha_P)\eta}{1-\eta}, \tag{3}$$

where η is the Poisson ratio. For Pb/Si(111), substituting α_r and α_P by the linear expansion coefficients of bulk Pb and bulk Si, and taking η as Poisson ratio of bulk Pb (0.44), we obtain that α_Z equals $2.414\alpha_r$. That means, in an ideal case, the thermal expansion in z direction should be enhanced by 2.414 times of the bulk value, which is adequate to explain the global enhancement of our experimental data in Pb/Si(111). With increasing of the film thickness the substrate confinement in film plane plays a less dominate role, for example, expansion coefficient along the film normal of 28 ML Pb film was 3.80×10^{-5} K^{-1}, which is less enhanced and close to the bulk value. Therefore, we can anticipate a bulk thermal expansion of Pb films with thickness far beyond 30 ML.

Another important feature is the periodic oscillation of the thermal expansion coefficient. As is known that the λ_F of Pb is nearly four times of the atomic plane spacing (d_0) along the (111) crystallographic direction, namely, $\lambda_F \approx 4d_0$, thus, the periodicity for the Fermi level crossing of the QWS is about 2 ML. This has been used to account for the bilayer oscillation in Pb film stability.[18] A straightforward explanation of this oscillatory phenomenon comes from the so-called misfit function,[19]

$$\delta(n) = \left| nd_0 - m\frac{\lambda_F}{2} \right|, \tag{4}$$

where n is the number of atomic layers, and m is an integer and will be selected to make δ a minimum. Generally speaking, a dramatic mismatch, a large δ, can make the electron standing wave not to fit properly into the potential well (nd_0). For the Pb films of 21 or 23 ML with a lower QWS binding energy, δ is close to $\lambda_F/4$ (its maximum value). In this case, further change (either decrease or increase) of the confinement well width will always decrease the mismatch and thus the system energy; the expansion will become easier. Consequently, a large expansion coefficient can be expected for an unstable film with a large δ. On the other hand, for a stable layer (22 or 24 ML) with a higher binding energy and a small δ (close to 0), expansion will always increase the mismatch between nd_0 and $m\lambda_F/2$; thus the expansion are more energetically unfavorable from the point view of the system energy minimization. As shown before,[16] the oscillatory film stability with a period of 2 ML were explained to be due to the formation of the QWS, so is the expansion coefficient under the same mechanism.

In summary, temperature-dependent photoemission spectra of atomically uniform Pb films have been investigated over a wide thickness range (10–24 ML). From the observed linear dependence of the QWS binding energy versus temperature, we have obtained the thermal expansion coefficients of Pb films along the film normal direction. A clear oscillation of the expansion coefficients with a 2 ML period is identified and proven to be closely related to the electronic energy quantization.

The work is supported by the National Natural Science Foundation of China and the Ministry of Science and Technology of China.

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