

Temperature dependence of photoelectron scattering from a monolayer

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Monolayers of lead on Ge(111) were investigated using angle-resolved photoelectron spectroscopy with synchrotron radiation. A narrow state close to the valence-band maximum is found to have the characteristics of a lead-induced surface resonance. This surface resonance exhibits a strong intensity dependence on substrate temperature. The temperature dependence is found to be consistent with a Debye-Waller-factor model that incorporates atomic correlations only between overlayer atoms, and neglects multiple scattering. The effective surface Debye temperature is reduced from that of a Pb(111) surface.

Lead monolayers on Ge(111) provide a good medium in which to study quasi-two-dimensional behavior. At the temperatures used in monolayer film growth, the solid solubility of Pb in Ge is negligible,¹ so that compound formation or alloying due to interdiffusion of overlayer and bulk is not a problem. Accurate determination of the absolute lead coverage is also quite straightforward by monitoring the intensity of Pb Auger electron emission. Because of the short mean free path of low-energy electrons in the high- Z Pb overlayer, the slope of Auger yield versus coverage exhibits a change of about an order of magnitude at the monolayer coverage point. Additionally, the Ge(111) surface has been extensively studied by photoemission,²⁻⁶ so that modifications in electronic properties due to the lead overlayer can be readily identified.

Previous low-energy electron diffraction⁷ (LEED) and reflection high-energy electron diffraction^{8,9} (RHEED) studies of Pb/Ge(111) agree on some general characteristics of film growth. At coverages of one monolayer or less, the lead film grows epitaxially, forming two distinct structures with the same superlattice period, denoted $\sqrt{3} \times \sqrt{3} R 30^\circ$. As we have noted, the point at which the first monolayer is completed can be accurately determined from the Auger electron yield.⁷ This does not, however, determine the overlayer density, which can be expressed as the ratio, Θ , of Pb overlayer atoms to Ge atoms of an unreconstructed Ge(111) surface. With a Θ of $\frac{4}{3}$, it is possible to construct a hard-sphere monolayer of Pb corresponding to a Pb(111) surface with a 1% contraction of the bulk lead lattice constant. Our initial analysis of LEED I - V spectra from integral-order and $(\frac{2}{3}, \frac{2}{3})$ diffraction spots supports this assignment.¹⁰ This structure contains two atoms per unit cell, with Pb atoms occupying threefold hollow and asymmetric on-top sites on an unreconstructed Ge(111) surface.

Monolayers of Pb on Ge(111) undergo a phase transition at $T_c = 192^\circ\text{C}$,^{8,9} which can be identified from the LEED diffraction pattern by the disappearance of fractional-order spots due to the Pb superlattice. From the isotropy of RHEED diffraction intensities above T_c , Ichi-

kawa concluded that the monolayer Pb/Ge(111) film undergoes an order-disorder transition to a two-dimensional liquid state. For coverages of one monolayer or less, this transition was found to be completely reversible.

We have performed a series of photoelectron spectroscopy experiments on the $\Theta = \frac{4}{3}$ Pb/Ge(111) adsorbate system, focusing on the valence-band and shallow core-level features. These experiments utilized both conventional resonance lamp photon sources, and monochromatized synchrotron radiation from the Tantalus synchrotron light source. In addition to finding valence-band electronic states induced by the lead adsorbate, we find large changes in the valence-band photoemission spectra upon thermal cycling from room temperature to just above T_c . As discussed below, these temperature-dependent changes to the photoelectron spectra are fully reversible in the temperature range studied. Nonreversible changes at higher temperatures were found to simply be due to sublimation of the lead monolayer.

Sample substrates were mechanically polished 0.5-mm-thick wafers of 40- Ω cm resistivity. Clean surfaces of Ge(111) were obtained by repeated cycles of argon-ion sputtering and annealing. Substrate surface preparation was monitored by a combination of Auger electron spectroscopy, LEED, and photoemission. The clean Ge(111) surface produced a LEED pattern characteristic of a $c(2 \times 8)$ reconstruction,^{6,11,12} and exhibited a pair of surface states in the normal-emission geometry in accord with previous experimental results.³ The photoemission data taken for the clean surface with a photon energy of $h\nu = 21.2$ eV agree in detail with the prior results of Bringans and Höchst.⁶ Lead of 99.999% purity was evaporated from a resistively heated quartz oven. Relative amounts of lead deposition were monitored by a quartz-crystal microbalance; the absolute coverage was determined from the Pb Auger electron yield.

A set of characteristic spectra from clean and Pb-covered Ge(111) are shown in Fig. 1. All of the spectra shown in this paper are taken with an angle-resolving photoelectron spectrometer.¹³ Emitted photoelectrons are col-

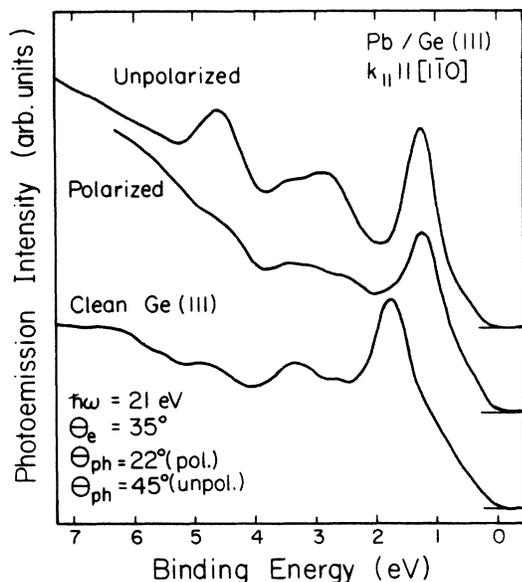


FIG. 1. Photoelectron energy distribution curves (EDC's) for clean Ge(111) and monolayer coverage Pb/Ge(111). The polarized spectrum is taken with 21 eV synchrotron radiation; the polarization vector lies in the plane containing the sample normal and emitted electron direction. The unpolarized spectrum used helium I ($\hbar\omega = 21.2$ eV) radiation. The zero of energy is taken at the valence-band maximum. The polar angle of collection of the photoelectron is θ_e ; the incident photon angle is θ_{ph} .

lected in a symmetry plane parallel to the bulk Ge $[0\bar{1}1]$ direction. The characteristic spectra show several new peaks in the valence-band, arising from lead adsorption, with binding energies within 5 eV of the valence-band maximum. There are four well-defined features in the Pb/Ge(111) valence band, at binding energies of 1.3, 2.7, 3.5, and 4.6 eV with respect to the valence-band maximum. As indicated, there is a strong dependence of the intensity of these features on the polarization of the incident photon beam. The spectrum in Fig. 1 labeled "polarized" was taken with p -polarized light, collecting electrons in the plane of incidence, so that only initial states with even symmetry with respect to the $[0\bar{1}1]$ plane are detected. For the unpolarized spectrum, the collection geometry is the same, but now states with both even and odd reflection symmetry are detected. The C_{3v} symmetry of the substrate-overlayer complex splits the $6s$ - $6p$ lead valence orbitals into a pair of orbitals with s - p_z symmetry (A_1) and a pair with s - $p_{x,y}$ symmetry (E).¹⁴ The electron emission intensity from orbitals with s - $p_{x,y}$ character will be sensitive to the component of the polarization vector perpendicular to the $[110]$ direction, which is present only in the unpolarized spectrum. The intensity from s - p_z -like orbitals will only contain contributions due to the in-plane polarization component. According to this argument and the data of Fig. 1, we identify the sharp peak at 1.3-eV binding energy with an orbital of s - p_z symmetry. The remainder of this discussion deals only with this low binding energy peak. Details of the energy bands for Pb/Ge(111) will appear elsewhere.¹⁵

The 1.3-eV state was studied in detail by measuring

photoemission energy distribution curves as a function of momentum parallel to the bulk $[0\bar{1}1]$ direction for several different incident photon energies. We find that the peak intensity is a strong function of the region of momentum space that is observed. Specifically, independent of photon energy, the peak is strong only for values of the momentum parallel to the surface (k_{\parallel}), in the range $0.75 < k_{\parallel} < 1.3 \text{ \AA}^{-1}$. Further, while there is a small (0.1 eV) dispersion with k_{\parallel} for this peak, there is no observable dispersion with perpendicular momentum, which varies as the photon energy is changed.

We have measured the dispersion of the bulk Ge bands from the same portion of k space, and compared these measurements to a projection of all bulk bands in the $[0\bar{1}1]$ plane, using a method which has become well known in photoemission band-structure studies.¹⁶ What we find is that for the region of k space in which the 1.3-eV feature from Pb/Ge(111) is strong, there are *no* bulk bands which can mix with the Pb-induced state. We conclude that the initial-state wave function corresponding to the 1.3-eV feature has little contribution from bulk states with long-range extent perpendicular to the surface, and is therefore quasi-two-dimensional. It is also apparent that the degree of orbital overlap from one Pb-atom site to the next is fairly small, given the size of the dispersion with k_{\parallel} .

This quasi-two-dimensional surface resonance was found to be extremely sensitive to the sample temperature. Examples of the temperature dependence of photoemission from the valence band of Pb/Ge(111) are shown in Fig. 2.

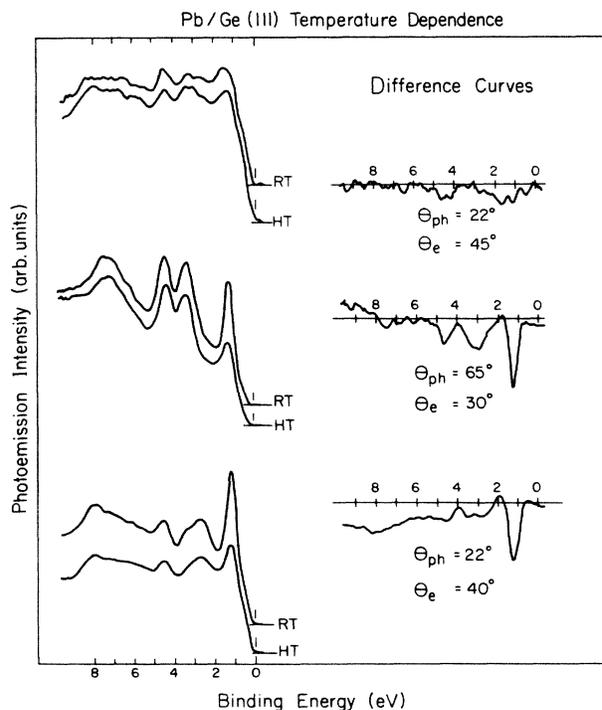


FIG. 2. In each pair of spectra, only temperature is varied. The difference curve shows the high-temperature spectrum (HT) minus the room-temperature (RT) spectrum, so that decreased intensity upon heating shows up as a negative peak. The photon energy is 21 eV.

Spectra in this figure were taken at room temperature (RT) $\approx 25^\circ\text{C}$ and an elevated temperature (HT) 240°C over the entire polar angular range of electron emission from normal emission to grazing. Heating was accomplished using a pulsed current in anticoincidence with photoelectron detection. Spectra at three polar angles are shown in Fig. 2, taken with a photon energy of $h\nu = 21\text{ eV}$. The difference curves represent the change in valence-band emission when only temperature is changed. Several important effects are illustrated by these difference curves. Notice that there is a large change in intensity with temperature in the region of the surface resonance peak, as shown in the bottom curves of the figure. There is also evidence for changes in the Pb-related features at high binding energy, as seen more clearly in the middle set of spectra. The angular dependence of the temperature effect is evident from the top spectra. In this case, spectral features in the valence band are primarily substrate derived; they do not change significantly upon Pb adsorption. The difference curves for this angular region show no change with temperature. This behavior was found to be characteristic of the entire angular distribution—only those peaks associated with the ordered overlayer are affected by the temperature change.

A model for the temperature dependence of valence-band photoemission can be constructed by viewing photoemission as a scattering process. As an example, consider an initial electron described by a Bloch wave $|\mathbf{k}_i\rangle$. In the scattering model, this wave scatters into a final state $|\mathbf{k}_f\rangle$ while absorbing a photon. Momentum conservation requires $\mathbf{k}_i = \mathbf{k}_f + \mathbf{G}$, where \mathbf{G} is a reciprocal-lattice vector, and the small momentum of the photon has been neglected. The temperature dependence of this photoelectron scattering event will be described by a static structure factor $S(\mathbf{G})$ which contains a Debye-Waller factor $e^{-|\mathbf{G}|^2\langle U_0^2\rangle}$.¹⁷ The $\langle U_0^2\rangle$ factor represents the mean-square fluctuations of atomic positions due to thermal disorder. This model has been discussed in detail for bulk photoemission by Schevchik,¹⁸ who used a more sophisticated initial- and final-state wave function. Application of a similar model to bulk photoemission has been experimentally tested for single-crystal tungsten¹⁹ and copper,²⁰ and for several alkali halides.²¹

The photoelectron scattering model needs to be modified slightly for application to the current data involving a quasi-two-dimensional overlayer system. The initial-state wave function should reflect the fact that long-range order is present only in the direction parallel to the surface. This can be done by simply replacing the three-dimensional reciprocal lattice vector with its surface analog, \mathbf{G}_\parallel . Then the temperature-dependent photoemission spectrum will have two contributions:

$$\sigma_{tot}(T) = W(T)\sigma_1 + [1 - W(T)]\sigma_2, \quad (1)$$

where σ_1 and σ_2 are, respectively, the direct (momentum-conserving) and indirect components of the photocurrent. The Debye-Waller factor becomes

$$W(T) = e^{-|\mathbf{G}_\parallel|^2\langle U_0^2\rangle}, \quad (2)$$

where now $\langle U_0^2\rangle$ corresponds to positional disorder only in the surface plane.

The measured temperature dependence of the Pb/Ge(111) surface resonance is shown in Fig. 3. To demonstrate reversibility, the experiments include data collected with temperature increased from room temperature to above T_c , and also with temperature decreasing from above T_c . Data for two different photon energies are also shown, taken for the same value of \mathbf{k}_\parallel . The various experimental runs are normalized to an arbitrary unit intensity at $T = 44^\circ\text{C}$.

In order to test the intensity variation predicted by (4), we need to determine the value of $\langle U_0^2\rangle$. In the Debye model, the mean-square fluctuations are given by^{17,18}

$$\langle U_0^2\rangle = \frac{3\hbar^2}{Mk_B\Theta_D^2}, \quad (3)$$

where M is the atomic mass of Pb and Θ_D is the Debye temperature. This expression represents a three-dimensional isotropic average. Strictly speaking, only the two-dimensional fluctuations should be used, which would multiply (3) by a constant factor. However, the form quoted has been used in analyzing experimental LEED temperature-dependent intensities,²² so we retain the expression as is. In effect, this defines an empirical Debye temperature, which is commonly denoted T_m .^{17,18}

In Fig. 3 we show calculations for the Debye-Waller intensity variation with temperature using (2) and (3) for two values of T_m . LEED measurements of surfaces of pure lead find that $T_m = 49\text{ K}$ for Pb(111), and $T_m = 37\text{ K}$ for Pb(110).^{22,23} The Debye-Waller factor for $T_m = 49\text{ K}$ and $T_m = 41\text{ K}$ are shown for comparison with the data in Fig. 3. The calculation uses a surface reciprocal lattice vector of magnitude $G_\parallel = 1.81\text{ \AA}^{-1}$, which is parallel to the direction of electron emission. From the very low values of T_m found in the Pb/Ge(111), it is in retrospect justified to use the high-temperature Debye approximation in (3) at the temperatures studied experimentally.

From this comparison, we find that the measured surface Debye temperature using photoelectron scattering is

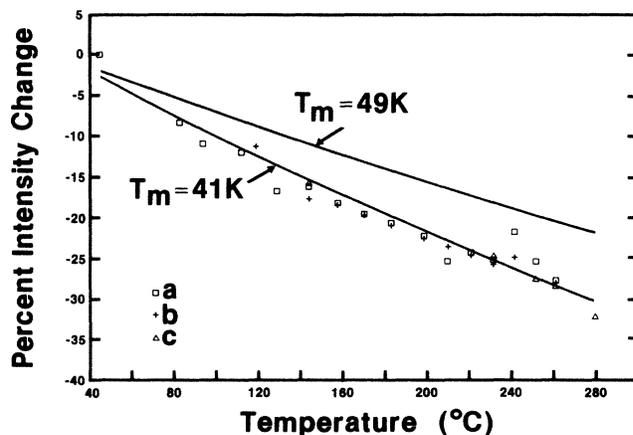


FIG. 3. Temperature-dependent intensity change of the -1.3-eV valence-band peak. (a) $h\nu = 21.2\text{ eV}$, $\mathbf{k}_\parallel = 1.2\text{ \AA}^{-1}$, heating. (b) $h\nu = 13\text{ eV}$, $\mathbf{k}_\parallel = 1.3\text{ \AA}^{-1}$, heating. (c) As for (a), but cooling. The solid curves are for a function of the form $[\exp(-aT) - 1]$, as discussed in the text.

somewhat lower than that measured for bulk Pb(111) using electron scattering. This result is consistent with the overall picture of Pb/Ge(111) bonding that arises when the data from RHEED, LEED, and photoemission are considered together. The observation from the Auger and LEED data that Pb monolayers grow epitaxially, layer by layer, indicates that the Pb-Ge interaction in the monolayer film is stronger than the Pb-Pb interaction. It is found, for example, that for thicker films the lead overlayer will form three-dimensional crystallites upon heating, rather than exhibiting a reversible phase transition.⁷ The stronger Pb-Ge bond might at first suggest that the melting temperature of the substrate-overlayer complex should be higher than that for pure lead. However, the transition temperature of Pb/Ge(111) as measured by RHEED and LEED is actually lower than that of bulk lead.⁷⁻⁹ As we have found, the photoelectron scattering measurement is consistent with this result, since we find a lower value of the surface Debye temperature for the monolayer.

As we have indicated above in (2), the photoelectron scattering from an initial state localized in the adsorbate measures fluctuations in the overlayer plane. From the Debye expression (3), a lower Debye temperature corresponds to larger in-plane fluctuations, which can further

be traced to a reduction in the Pb-Pb force constant. We can conclude that the increase in Pb-Ge bond strength over that of bulk Pb occurs at the expense of a weakening in the in-plane Pb-Pb interaction. This is despite the 1% contraction of Pb-Pb bond distance required for epitaxy.

The overall qualitative agreement between theory and experiment indicates that the basic features of the photoelectron scattering model from an overlayer are correct. In particular, the spatial character of quasi-two-dimensionality of the overlayer seems justified. These experiments suggest the possibility of using temperature-dependent valence-band photoemission to differentiate between electronic states having primarily bulk, overlayer, or perhaps mixed interfacial character.

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