β Phase of Pb on Ge(111): The Competing Roles of Electronic Bonding and Thermal Fluctuations

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We have studied the low temperature phases of Pb/Ge(111) at Pb coverages $\Theta = 1/3$, 1, and 4/3 using *ab initio* molecular dynamics. Stable phases are found to occur at $\Theta = 1/3$ and 4/3. For the low-coverage phase, we confirm the model of Pb atoms adsorbed at T_4 sites of the Ge(111) substrate. For the high Θ phase and very low temperature, we determine a structure characterized by the presence of covalently bonded Pb chains parallel to $\langle 1\bar{1}0\rangle$ substrate directions. At room temperature, fluctuations are found to disrupt long-range Pb chains and restore the threefold symmetry of the ideal Ge(111). Our results agree well with x-ray diffraction and STM data.

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The suggestion that thin lead overlayers on Ge(111) surfaces may undergo two-dimensional melting at $T_c \sim$ 200–300 °C [1] has recently motivated numerous experimental investigations of the low ($T < T_c$) and high ($T > T_c$) temperature phases of these systems [2–7]. It has been found that Pb/Ge(111) has a rather complex phase diagram as function of Pb coverage (Θ) and temperature. However, no general consensus has yet been achieved on the nature and structure of these phases. Here we shall focus on the low T phases of Pb/Ge(111) in the monolayer and submonolayer regime. This part of the phase diagram is important for understanding not only the controversial high T behavior of this system [2,7,8], but also other interesting phenomena such as the growth properties of the lead overlayer or the metal-semiconductor interface formation.

At room temperature (RT) Pb/Ge(111) exhibits two ordered $(\sqrt{3}\times\sqrt{3})R30$ structures, a low-coverage phase, known as the α phase, and a high coverage β phase. While the α phase appears to be well characterized, the properties of the β phase are the subject of controversy. RHEED, x-ray, and LEED measurements [2,5,6] suggest that the β phase consists of a (111) fcc overlayer of Pb, rotated by 30° with respect to the Ge lattice, and with some distortions to accommodate the misfit with the substrate. The Pb coverage for such a model is $\Theta = 4/3$ (we define $\Theta = 1$ as corresponding to one Pb atom per one surface Ge atom). Recent STM measurements [7], on the other hand, appear to indicate the formation of a $\Theta = 1$ structure characterized by a periodic array of Pb trimers centered at the H_3 sites of the Ge substrate.

In this Letter we present first principles calculations of the low temperature properties of Pb/Ge(111) at Pb coverages $\Theta = 1/3$, 1, and 4/3. Our results for $\Theta = 1/3$ confirm the widely accepted model of the α phase, with Pb adatoms located at T_4 sites (above second layer Ge atoms) of Ge(111). The geometry at coverage $\Theta = 1$ was obtained by (locally) optimizing a recently proposed trimer model [7], while at $\Theta = 4/3$ the $T = 0$ structure has been determined via a simulated annealing (global) optimization procedure. This structure is characterized by covalently bonded Pb chains along a $[1\bar{1}0]$ direction of the substrate, which break the C_{3v} symmetry of the ideal Ge(111) surface. Both static total energy calculations and molecular dynamics simulations, however, indicate that near RT fluctuations disrupt these chains, and reestablish the ideal C_{3v} symmetry. From Pb-chemical potential dependent surface formation energies we find that stable phases occur at $\Theta = 1/3$ and 4/3, while the trimer geometry is unstable under equilibrium conditions. Calculated x-ray structure factors and STM images of our $\Theta = 4/3$ structure agree well with experiments.

Our calculations are based on local density functional theory, and have been performed using the *ab initio* molecular dynamics (MD) approach [9], that we have already applied in previous studies of Ge(111) [10]. The Ge(111) surface is modeled as a repeated slab consisting of 6 layers of 12 Ge atoms each, corresponding to four $(\sqrt{3}\times\sqrt{3})R30$ (in short $\sqrt{3}$) cells. The Pb adatoms are on the top surface, while the other surface is saturated by 12 hydrogen atoms. Consecutive slabs are separated by an empty space 10 Å wide. Norm conserving pseudopotentials with s and p nonlocality in a separable form are used. The wave functions are expanded in plane waves with kinetic energy up to 8 Ry. For structural optimizations and MD simulations, only the Γ point of our supercell was used, corresponding to 4 points in the Brillouin zone (BZ) of the primitive $\sqrt{3}$ cell. For the calculation of surface formation energies, a k-point sampling including 18 points in the BZ of the primitive cell was used. This extended k-point set was found to be necessary for comparing the formation energies of structures with different Θ values, while energy differences at a given Θ did not change significantly passing from 4 to 18 k points.

At each Pb coverage, we have optimized the surface structure starting from an ideal Ge substrate covered by a suitably chosen overlayer of Pb atoms. The four topmost layers of Ge plus the Pb overlayer were allowed to move, while all other layers were kept fixed. The structures were relaxed until the residual forces on atoms were less than 0.03 eV/Å. At $\Theta = 1/3$ we considered two $\sqrt{3}$ structures, one with Pb adatoms located at T_4 sites, and the other with the adatoms at H_3 sites (above fourth layer Ge atoms). In agreement with experiment, we found that the former is energetically favored (by $\sim$ 0.22 eV/adatom). The calculated structural parameters are close to those given in Ref. [6]. At $\Theta = 1$, a configuration with Pb trimers adsorbed above H_3 sites was optimized, resulting in a structure similar to that proposed in [7]. At $\Theta = 4/3$, our starting configuration was the model of Ref. [6] (hereafter referred to as the XED model), with Pb atoms forming a double layer, and the lower and upper Pb atoms at H_3 and off-centered (OC) T_1 (top) sites, respectively. After a local relaxation, we performed a long MD annealing cycle in which the temperature was first raised to $\sim$ 500 K and then reduced again to zero [11]. The resulting structure is shown in Fig. 1. Here all Pb atoms are approximately at the same height, $z \sim 2.7$ Å, above the Ge surface; three Pb atoms per $\sqrt{3}$ cell are in OC (by $\sim$ 0.8 Å) T_1 sites, whereas the fourth Pb atom is in an OC (by $\sim$ 0.5 Å) T_4 position. Although this geometry can be still described as a distorted (111) Pb overlayer, new features emerge. Particularly, Pb chains appear along a $[1\bar{1}0]$ direction of the substrate, as shown by the total valence charge density (see Fig. 1). The full C_{3v} symmetry of the ideal Ge(111) surface is lost, and only a mirror plane symmetry remains.

At low temperature, the relative stability of the various structures can be determined from the Pb-chemical potential dependent surface formation energies $\Omega = E_{\rm slab} - N_{\rm Ge}\mu_{\rm Ge,bulk} - N_{\rm Pb}\mu_{\rm Pb}$. Here $E_{\rm slab}$ is the total energy of the composite Pb-Ge system, $N_{\rm Ge}$ and $N_{\rm Pb}$ are the numbers of Ge and Pb atoms, respectively, $\mu_{\rm Ge,bulk}$ is the energy per atom in bulk Ge and $\mu_{\rm Pb}$ is the Pb-chemical potential referred to that of Pb atoms in the bulk phase. Under equilibrium conditions, only *negative* values of $\mu_{\rm Pb}$ are allowed, but values $\mu_{\rm Pb} > 0$ may be relevant in the case of Pb deposition from a gaseous phase. Our results are summarized in Fig. 2, which shows that the only stable phases are the $\Theta = 1/3$ T_4 adatom and the $\Theta = 4/3$ chain structures.

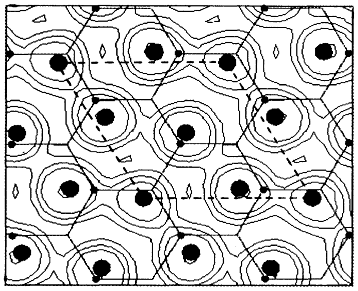

FIG. 1. Contour plots of the total valence charge density for the chain structure, in a plane $\sim$ 1.3 Å above the Pb overlayer. The underlying Ge lattice is outlined: dots represent surface Ge atoms. Bigger dots indicate Pb atoms. The $\sqrt{3}$ unit cell is also shown with black lines.

Since the chain structure breaks the C_{3v} symmetry of Ge(111), domains corresponding to the three possible chain orientations along the $\langle 1\bar{1}0\rangle$ substrate directions should occur. Orientational domains, however, are not experimentally observed at RT. Inspection of Fig. 1 shows that the three possible chain orientations can be obtained simply by rotating the Pb atoms at the OC T_4 sites by ±120° around their closest T_4 site. We have calculated the energy barrier $E_{b,r}$ for these Pb adatoms to jump between equivalent sites, and found an extremely small value, $E_{b,r} \sim 15$ meV. This suggests that near RT these Pb atoms should jump continuously between equivalent sites restoring the C_{3v} symmetry. This is confirmed by an MD simulation run spanning $\sim$ 4 ps at a temperature $T = 500 \pm 100$ K, during which our system remained in the $\sqrt{3}$ structure [11]. In this MD run we find very large in-plane rms displacements of the Pb atoms, corresponding to an effective Debye temperature $T_D \sim 36$ K, which compares favorably with the experimental value $T_D \sim 41$ K [13]. The rms displacements are particularly large for the Pb adatoms at the OC T_4, whose motion can be indeed approximately described as a rotation around the corresponding T_4 site. These fluctuations not only restore the C_{3v} symmetry of Ge(111), but also disrupt long-range Pb chains. Interestingly, the average structure resulting from our MD simulation is very close to

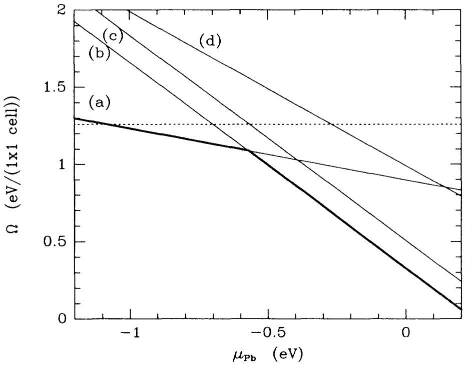

FIG. 2. Surface formation energies as functions of the Pb chemical potential. (a) α phase ($\Theta = 1/3$). (b) Chain structure ($\Theta = 4/3$). (c) XED model ($\Theta = 4/3$). (d) Trimer model ($\Theta = 1$). The zero of the Pb chemical potential is taken at its bulk value. The dashed horizontal line shows the formation energy of the clean Ge(111) surface. Its value, 1.26 eV, is rather close to that found in previous calculations [12]. Note that the formation energy of the XED model lies $\sim$ 0.5 eV per $\sqrt{3}$ cell higher than our chain structure.

that obtained by averaging the three $T = 0$ chain structures with different $[1\bar{1}0]$ orientations [14].

In Table I we compare the calculated x-ray diffracted intensities $I_{hk} = |\sum_i f_i(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{R})|^2$ for various structural models with the experimental data for the β phase of Ref. [5]. $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2$ is a surface reciprocal lattice vector, f_i are the atomic form factors of individual atoms [15], and $\mathbf{R}$ are the positions of the atoms inside the unit cell. For the chain model, I_{hk} is obtained by averaging the contributions of the three structures with different $[1\bar{1}0]$ orientations. This is meant to take approximately into account the effect of thermal fluctuations [16]. It appears from Table I that the calculated intensities for the chain structure and the XED model are in good agreement with experiments and of comparable quality. The unstable trimer structure fails completely to predict the observed intensities.

The $T = 0$ electronic properties of the chain surface are characterized by a small ($\sim$ 0.1 eV) energy gap, which should be related to the covalent chain formation, and is in fact absent in the disordered configurations generated in our finite T MD simulation, as well as in our MD-average structure or in the XED model. This suggests that the chain formation might originate from a Peierls instability. The small value of the gap indicates that Pb-Pb bonds along a chain are weak, consistently with the small difference between intrachain and interchain distances ($\sim$ 3.15 and $\sim$ 3.45 Å, respectively). By comparing the calculated DOS for Pb/Ge(111) and that of the clean (ideal) Ge(111) surface we find that a prominent Pb-induced peak is present at $\sim$ 1 eV below the top of the valence band E_V, with a shoulder at $\sim$ 0.7 eV, in agreement with photoemission results [17,18]. The 1 eV peak is mostly due to p_z-like states on the Pb atoms at OC T_1 sites coupled to dangling bond states on the Ge surface atoms, while the shoulder is related to states in which orbitals having a mixed $p_{x,y}$ character on the OC T_4 Pb atom are coupled to dangling bond states which are strong on both the three OC T_1 Pb atoms and on the Ge surface atoms.

TABLE I. Calculated and experimental structure factor intensities I_{hk}. (h,k) are the indices for the in-plane surface reflections. Calculated intensities have been normalized to yield the same value of the (2/3,2/3) intensity as found in the experiment [5].

(h,k)	Chain	XED	Trimer	Expt.
1/3,1/3	0.1	0.1	238.0	0.3
2/3,2/3	48.4	48.4	48.4	48.4
4/3,1/3	5.5	5.0	68.1	3.3
5/3,2/3	8.4	8.4	161.8	8.8
4/3,4/3	5.5	4.7	65.3	8.5
7/3,1/3	1.5	3.0	112.4	2.2
5/3,5/3	0.7	4.0	22.8	3.5
8/3,8/3	1.6	0.8	28.1	1.7
7/3,4/3	1.4	1.3	37.1	2.0
1,0	8.3	10.3	1304.6	6.9
2,0	11.0	10.3	36.7	6.5
2,1	3.1	1.9	60.9	4.3

In Fig. 3 we present theoretical STM images of our $\Theta = 4/3$ structure. The upper panels refer to a single chain ($T = 0$), whereas the images in the lower panels are obtained averaging the contributions of the three structures with different chain directions, to take approximately into account finite temperature effects. Left panels refer to filled states at $\sim$ 0.7 eV below E_V, and should be compared to the images of Ref. [7]. Remarkably, an array of trimerlike protrusions appears, similar to that imaged in the experiments. Despite the fact that *all* four Pb atoms in the $\sqrt{3}$ unit cell are at the same height, the one at the OC T_4 site does not show up in the charge density map, thus giving the impression that the coverage is $\Theta = 1$. The protrusions in our calculated image are due to the same states giving rise to the shoulder of the Pb-induced peak in the DOS. These states have a node at the OC T_4 Pb adatom site, and therefore this is not seen in the image. Another interesting point concerns the location of these trimers. For the single chain case our trimers appear to be centered on T_4, whereas once the average over the three chain orientations is performed, the trimers appear centered at H_3 sites and are rotated by 60° with respect to the trimers on T_4, as observed experimentally [7,19].

A quite different image is obtained from the empty states $\sim$ 0.1–0.2 eV above the Fermi level (right pan-

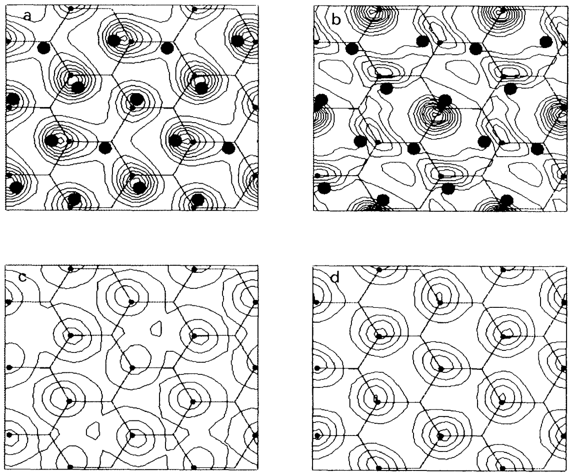

FIG. 3. Theoretical STM images of the high coverage phase of Pb/Ge(111) from topographic maps of constant local density of states (see text). The images in the upper (lower) panels are taken at $\sim$ 3 ($\sim$ 6) a.u. above the Pb layer. The underlying Ge lattice is always shown, while for better clarity Pb atoms (indicated by the big dots) are shown only in the upper panels. The slight deviation from threefold symmetry in the lower images is caused by small differences between the three chain structures used for averaging. A slight asymmetry might be present also in the experimental images [7].

els). These states, which are strongly localized on the Pb overlayer, give rise to an image which changes remarkably from the single chain (upper right) to the case where the average over the three chain orientations (lower right) is performed. In the latter case, which is the most relevant for comparison with available experiments, the image consists of three protrusions per $\sqrt{3}$ cell centered very close to the positions of the first layer Ge atoms again suggesting an apparent coverage $\Theta = 1$. This image can slightly change with varying, e.g., distance from the surface, possibly looking as an array of trimers. This appears consistent with recent observations [7,20].

In conclusion, we have presented a first principles study of Pb/Ge(111) at different coverages. A novel structure with $\Theta = 4/3$ has been found which well explains the observed properties of the β phase of this system. At $T = 0$ our structure shows covalent Pb-Pb bonds forming chains oriented along $\langle 1\bar{1}0 \rangle$ substrate directions. Close to room temperature, thermal fluctuations disrupt long-range chains and restore the symmetry of the ideal surface. According to these results a transition from ordered chains to the RT structure should be expected to occur at rather low T. Such a transition, which appears not to have been experimentally studied so far, seems a subject worth future investigations.

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[14] This structure—which has one Pb atom right at T_4 and the other three at OC T_1—is ~ 0.05 eV/(1×1) cell higher in energy than the optimized chain structure.

[15] The Pb atomic form factor is multiplied by a Debye-Waller factor $\exp(-G^2R_0^2/3)$. We use $R_0 \sim 0.6$ a.u., which at RT is consistent with the value of T_D from Ref. [13]. Since the Ge Debye temperature is more than 5 times larger than that of Pb, we have not included a similar correction in the Ge form factor.

[16] In Table I we have not included I_{hk} evaluated directly from our MD simulation, because the high temperature ($T \sim 500$ K) of that run causes a too strong attenuation of the intensities for the large G's, thus making the comparison with the RT experimental data not appropriate.

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[19] The image that we obtain by averaging over the three chain orientations shows trimers centered at T_4 close to the surface, while at distances $z > 3 - 4$ Å the trimers appear to be centered at H_3 (see Fig. 3).

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