Quantitative Structural Determination of Metallic Film Growth on a Semiconductor Crystal: $(\sqrt{3}\times\sqrt{3})R30° \rightarrow (1\times1)$ Pb on Ge(111)

H. Huang, C. M. Wei, H. Li, and B. P. Tonner
Department of Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

S. Y. Tong[(a)]
National Science Foundation, 1800 G Street, N.W., Washington, D.C. 20550

(Received 21 October 1988)

Step-by-step structural information has been obtained for the growth of a metallic film on a semiconductor substrate: Pb/Ge(111). Complete three-dimensional atomic coordinates have been determined for each equilibrium phase formed in the growth process, from submonolayer to multilayer coverages. The quantitative structural model explains for the first time the observed 30° rotation in the overlayer basis vectors of the 1×1 multilayer epitaxial Pb film from those of the two low-coverage phases.

PACS numbers: 68.55.—a

Recently, there has been considerable attention focused on the study of structural properties of metallic film growth on semiconductor substrates. This interest is fueled in part by a number of interesting scientific questions, and in part by the overlap such systems have with the formation of Schottky barriers in electronic devices. However, studies of heterogeneous metal-semiconductor interfaces and metallic film growth on semiconductors have so far yielded little step-by-step information concerning the geometric structures that are formed during the different equilibrium phases of the growth process. In this Letter, we present the first detailed three-dimensional structural results for the growth of Pb films on Ge(111), from submonolayer to a 5-6 monolayer thick film. An extremely interesting and conceptually challenging observation is that at low coverages, i.e., < 1.3 monolayers (ML), two ordered structures have superlattice basis vectors rotated by 30° from those of the (111) Ge surface.[1-6] However, further growth of the Pb layers reorients the overlayer film parallel to the Ge(111) basis vectors.[6] In overlayer films 5 ML or thicker, one clearly observes that the Pb film grows in a close-packed fcc (111) structure, in an orientation that is rotated by 30° from that of the two low-coverage structures. Such a rotation is not a symmetry operation of the substrate, or of the substrate-overlayer complex. As we shall see from the following analysis, the quantitative structural information obtained at each equilibrium phase *requires* such a 30° rotation to take place for Pb coverages greater than 2 ML.

For coverages of less than 1 ML, the Pb overlayer induces a $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern. This structure, commonly known as the α phase, has been extensively studied in the literature.[1-6] However, the most detailed structural analysis was done by grazing-incidence x-ray scattering.[4,5] The x-ray studies of Feidenhans'l *et al.*[4,5] convincingly determined that a simple adatom model is valid and that the Pb atom adsorbs at the T_4 site, with a coverage of $\rho=\frac{1}{3}$ ML. The x-ray studies, however, cannot unambiguously distinguish between the two orientations (i.e., 180° rotation) of the Ge(111) substrate.[4,5]

We have carried out dynamical LEED *I-V* spectral analysis and confirmed the T_4 adsorption site. With LEED, there is no ambiguity in the substrate orientation, as the *I-V* spectra for the (01) and (10) beams are very different [see Figs. 1(a) and 1(b)], due to the threefold symmetry of the Ge(111) crystal and the rapid attenuation of the LEED wave field inside the crystal.[7] Figure 1 shows the comparison between theory and experiment for the (01), (10), (11), and (02) beams, to-

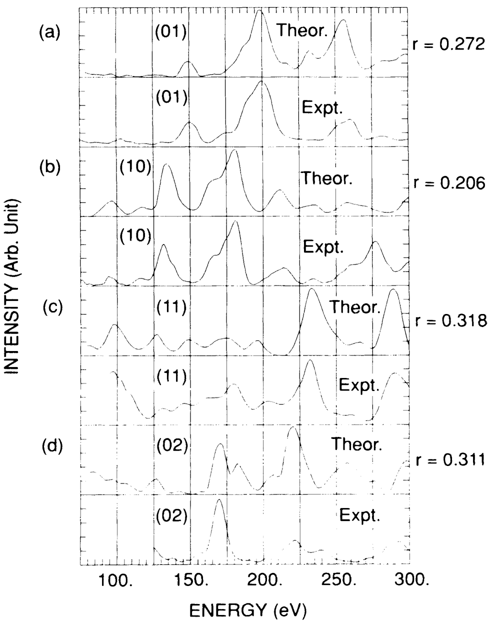

FIG. 1. Comparison of data with theory for the optimal α-phase structure. r: individual beam R factor; averaged R_T (five beams) = 0.280.

gether with the Van Hove–Tong R factor[8] for each beam. The calculated curves shown were for an optimized structure in which the Pb atoms occupy the T_4 site, and the substrate atoms relax in both perpendicular and parallel directions (the overall R factor improves by 10.4% from no substrate relaxation to full relaxation). The LEED dynamical calculations were done by a new vectorized code[9,10] which takes advantage of real[11] and reciprocal space[12] symmetries in the system. We show in Fig. 2(a) a top view of the α-phase structure, in which the Pb atoms (largest circles) are seen occupying the T_4 site. A side view of the α structure is shown in Fig. 2(b), together with substrate relaxation. Table I summarizes the atomic coordinates of the LEED structure.

TABLE I. Atomic coordinates of the α-phase structure; the Cartesian coordinates and atom numbers are according to Fig. 2(b).

Atom No.	$\hat{x}$ (Å)	$\hat{y}$ (Å)	$\hat{z}$ (Å)	Displacement from bulk position (Å)
1	0.000	2.310	5.785	
2	1.637	1.365	4.085	$-0.364\hat{x}+0.21\hat{y}-0.05\hat{z}$
3	0.000	4.201	4.085	$-0.42\hat{y}-0.05\hat{z}$
4	2.001	−1.155	3.368	$+0.10\hat{z}$
5	0.000	2.310	2.918	$-0.35\hat{z}$
6	2.001	−1.155	0.867	$+0.05\hat{z}$
7	0.000	2.310	0.617	$-0.20\hat{z}$
8	0.000	0.000	0.000	

At further deposition of Pb atoms, an equilibrium β-phase structure is reached. This structure also has a $(\sqrt{3}\times\sqrt{3})R30°$ superlattice. There is some uncertainty concerning the exact coverage of the β phase. Our analysis favors a structure with four Pb atoms per supercell (i.e., $\rho=\frac{4}{3}$ ML), and introduces for the first time an explanation of the 30° rotation of the overlayer unit cell starting from the $\frac{4}{3}$-ML coverage. Our model for the β phase involves two types of Pb overlayer atoms. They form a bilayer separated by 0.48 Å. In a $\sqrt{3}\times\sqrt{3}$ unit cell, one Pb atom is fitted down at a threefold hollow site (the H_3 site) at a vertical distance of 2.22 Å from the nearest Ge atoms. The remaining three Pb atoms occupy a site along the bond direction between the top (T_1) and hollow (T_4) sites. A top view of this structure is shown in Fig. 3(a).

Our picture of the growth of Pb overlayers on Ge(111) is, thus, as follows: At low coverages, the initial Pb

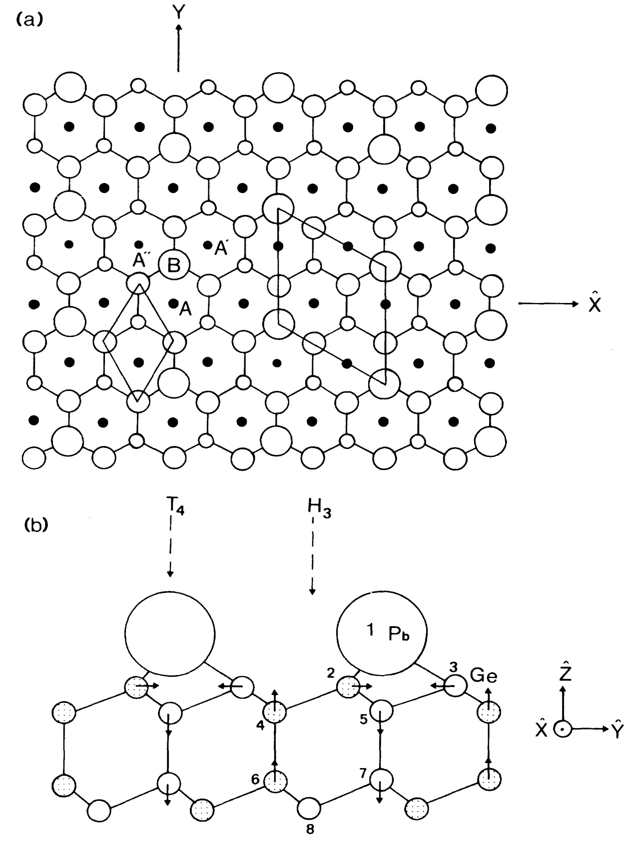

FIG. 2. (a) Top and (b) side views of the α-phase structure. In (b), distances between atoms and the Pb radius are to scale.

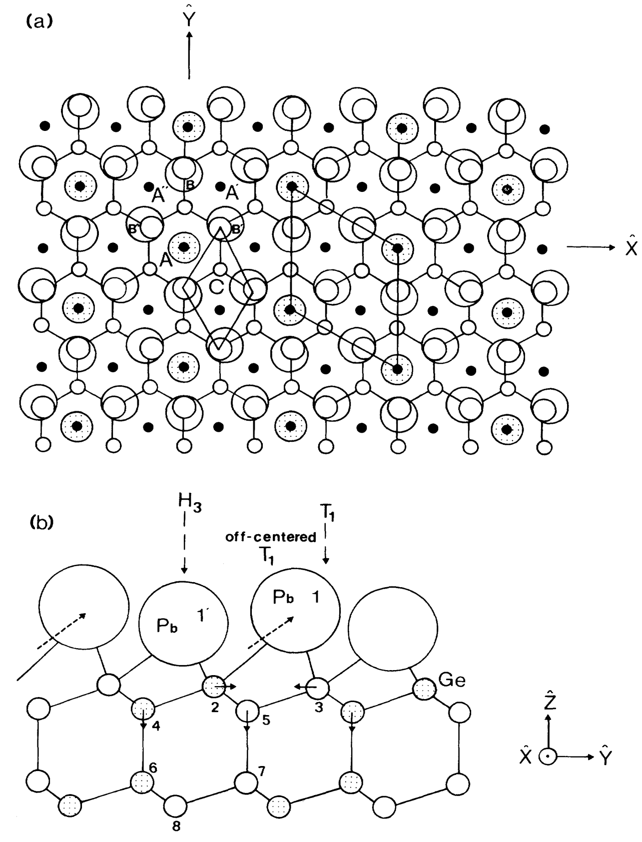

FIG. 3. (a) Top and (b) side views of the β-phase structure. In (b), distances between atoms and the Pb radius are to scale.

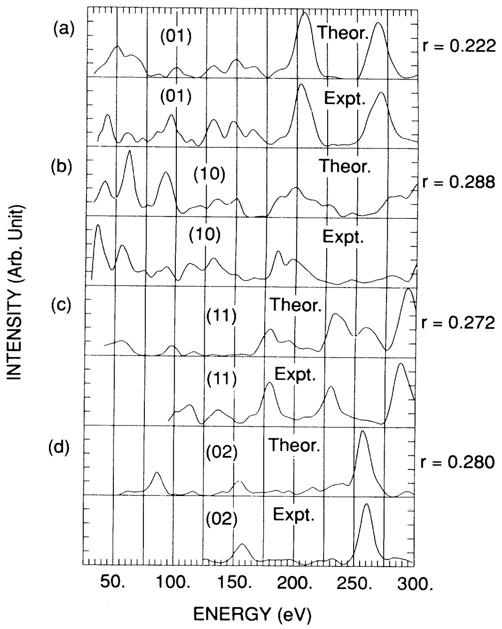

FIG. 4. Comparison of integral-order beams between data and theory for the optimal β-phase structure.

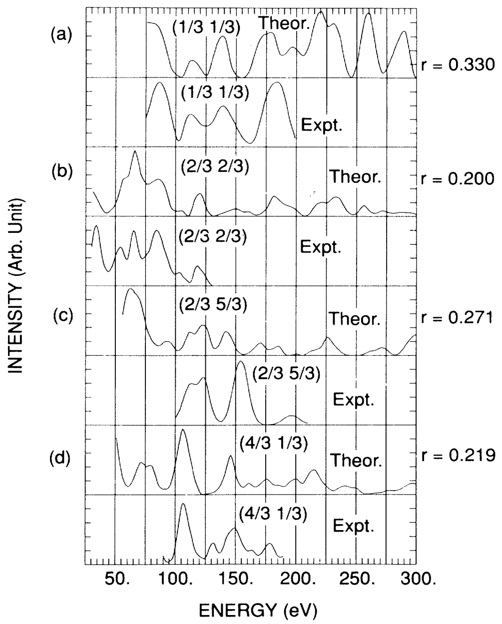

FIG. 5. Same as in Fig. 4, except for fractional-order beams. Averaged R_T (ten beams) = 0.276.

atoms are bonded to the T_4 site, in agreement with x-ray analysis[4,5] and theoretical predictions.[13,14] The lattice gas then coalesces to form an ordered $(\sqrt{3}\times\sqrt{3})R30°$ structure at $\rho=\frac{1}{3}$ ML [atoms B in Fig. 2(a)]. These Pb atoms induce surface relaxation in the Ge(111) crystal, resulting in Ge atoms moving away and opening up the other threefold site, i.e., the H_3 sites [see Fig. 2(b)]. We suggest that the Ge relaxation allows the subsequently arrived Pb atoms to drop into a H_3 site [A in Fig. 3(a)]. As a consequence of changes in the Pb-Ge bonding and Pb-Pb repulsion, the T_4 occupied Pb atoms move towards the T_1 site. At the same time, these Pb atoms increase their vertical distance from the substrate [dotted arrows in Fig. 3(b)]. The translation of the B-type Pb atoms to the off-centered sites also blocks the adjacent two H_3 sites from being occupied [A′ and A″ in Fig. 3(a)]. Further deposition of Pb atoms must then occupy the other two off-centered sites [B′ and B″ in Fig. 3(a)], thus forming the $\rho=\frac{4}{3}$-ML equilibrium structure shown in that figure.

The dynamical LEED study of the β phase is based on the comparison between theory and experiment of ten I-V spectra, five integral-order and five fractional-order beams. Figures 4 and 5 show the comparison for eight beams, the individual R factors, and the ten-beam–averaged R factor for the optimal structure. Table II summarizes the atomic coordinates of the LEED structure.

If we now consider the Pb double layer in Fig. 3(a), the outermost Pb layer contains three Pb atoms per substrate $\sqrt{3}\times\sqrt{3}$ unit cell (i.e., B-, B′-, B″-type atoms), which corresponds to an effective areal density of $\rho=1$ ML at the surface. Further deposited Pb atoms would occupy the T_4 hollow sites [i.e., C-type sites in Fig. 3(a)], forming a 1×1 structure. The next-layer Pb atoms would occupy the A-type hollow sites. Because of the larger lattice of the Ge(111) substrate (by 12.5%), these initial 1×1 Pb layers are probably made up of separate domains. Domains of fcc close-packed Pb layer are observed to form at 5–6 ML.[6] Thus, the 30° rotation from low to high coverages of the Pb film is a natural consequence of our model.

The structural model also explains the somewhat surprising result that for the β phase, the anchoring Pb

TABLE II. Atomic coordinates of the β-phase structure; the Cartesian coordinates and atom numbers are according to Fig. 3(b).

Atom No.	$\hat{x}$ (Å)	$\hat{y}$ (Å)	$\hat{z}$ (Å)	Displacement from bulk position (Å)
1	0.000	3.896	6.786	
1′	0.000	0.000	6.305	
2	1.949	1.185	4.085	$-0.052\hat{x}+0.03\hat{y}$
3	0.000	4.561	4.085	$-0.06\hat{y}$
4	2.001	−1.155	3.218	$-0.05\hat{z}$
5	0.000	2.310	3.218	$-0.05\hat{z}$
6	2.001	−1.155	0.817	
7	0.000	2.310	0.817	
8	0.000	0.000	0.000	

atoms occupy the H_3 site. This site has been shown to be stable by theory; however, its binding energy is higher than that of the T_4 site.[13,14] With Pb atoms already adsorbed at T_4 sites, substrate relaxation opens up the H_3 sites for bonding. Once a Pb atom settles into an H_3 site, symmetry and the smaller vertical distance it has from the substrate atoms suggest that this site is more stable. Indeed, it is the Pb atoms at the T_4 sites that are pushed up and towards the off-centered T_1 sites. There are experimental studies that support this model. A recent photoemission study revealed two sets of surface states that suggest inequivalent Pb atoms at different heights above the surface.[15] A grazing-angle x-ray scattering study by Feidenhans'l[16] has determined that Pb atoms are at H_3 and off-centered sites, although no quantitative determination of vertical spacings has been carried out.

In summary, we have presented results that revealed the quantitative structures of the different equilibrium states that are formed as Pb overlayers are grown on a Ge(111) substrate. The Pb/Ge(111) system is a good candidate for studying epitaxial growth because there is negligible alloying of lead with germanium. Also, the high atomic number of Pb makes it possible to determine very accurately the coverage corresponding to monolayer completion with electron spectroscopy.[15] The coadsorption of Pb at H_3 and off-centered T_1 sites in the β phase should present an interesting physical situation for theoretical calculations to explain the electronic and energetic properties.

This work was supported by NSF Grants No. DMR-84-15158 and No. 84-05049, and National Center for Supercomputing Applications, Illinois.

---

[a] Permanent address: Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, WI 53201.

[1] J. J. Metois and G. LeLay, Surf. Sci. **133**, 422 (1983).

[2] T. Ichikawa, Solid State Commun. **46**, 827 (1983).

[3] G. LeLay and Z. Imam, Surf. Sci. **154**, 90 (1985).

[4] R. Feidenhans'l, J. S. Pedersen, M. Nielsen, F. Grey, and R. L. Johnson, Surf. Sci. **178**, 927 (1986).

[5] J. S. Pedersen, R. Feidenhans'l, M. Nielsen, and K. Kjaer, Surf. Sci. **189**, 1047 (1987).

[6] H. Li and B. P. Tonner, Surf. Sci. **193**, 10 (1988).

[7] M. A. Van Hove and S. Y. Tong, *Surface Crystallography by LEED* (Springer-Verlag, Heidelberg, 1979).

[8] M. A. Van Hove, S. Y. Tong, and M. H. Elconin, Surf. Sci. **64**, 85 (1977).

[9] S. Y. Tong, H. Huang, C. M. Wei, W. E. Packard, F. K. Men, G. Glander, and M. B. Webb, J. Vac. Sci. Technol. A **6**, 615 (1988).

[10] H. Huang, S. Y. Tong, W. E. Packard, and M. B. Webb, Phys. Lett. A **130**, 166 (1988).

[11] M. Moritz, J. Phys. C **17**, 353 (1984).

[12] M. A. Van Hove and J. B. Pendry, J. Phys. C **8**, 1362 (1975).

[13] J. M. Nicholls, B. Reihl, and J. E. Northrup, Phys. Rev. B **35**, 4137 (1987).

[14] D. Vanderbilt, in *The Structure of Surfaces II,* edited by J. F. van der Veen and M. A. Van Hove (Springer-Verlag, Berlin, 1987).

[15] B. P. Tonner, H. Li, M. J. Robrecht, M. Onellion, and J. L. Erskine, Phys. Rev. B **36**, 989 (1987).

[16] R. Feidenhans'l, Ph.D. thesis, University of Aarhus, Denmark, 1987 (unpublished).