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Quantum effects in twinning boundary formation in Pb

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The stratification of Pb nanoislands on the vicinal Si(7 7 10) surface into layers 2 nm thick, due to the quantization of the electronic spectrum, implies the formation of two-dimensional defects separating the layers. Energy balance of energy gain due to the quantum confinement effect and energy consume for a twinning boundary formation was determined using DFT simulations. It was established that established that the twin boundary is formed at the stage of growth of the next layer after the formation of a layer 2 nm thick, in which a standing wave of Fermi electrons is formed. On the surface of a thinner layer, where there is no standing electron wave, a perfect crystal structure grows. The formation of a twin boundary between layers 2 nm thick Pb begins with the formation of a rarefied atomic monolayer of pairs of atoms.

Keywords: electronic growth, twinning boundary, vicinal surface, density functional theory.

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Introduction

Studies into thin Pb films on a vicinal Si(7 7 10) surface revealed that these films grow in the Stranski–Krastanov mode with the formation of a wetting layer on which Pb nanoislands grow [1–3]. It was found that nanoislands have a layered structure with 2-nm-thick layers (8 monoatomic layers (MLs) of Pb) [4]. This stratification is associated with the electronic growth (EG) mechanism [5–7]. Within the context of EG, the energy of a system of electrons in a 2-nm-thick Pb layer is lower than the energy of electrons of a layer of the same thickness in the bulk. This is attributable to quantization of the electronic spectrum and the formation of standing waves of Fermi electrons in the direction of the normal to the layer surface. In the quasi-classical approximation, interlayer boundaries should ensure cyclic motion of electrons reflecting off them in order to establish the conditions for quantization of the electronic spectrum. At the same time, the energy gain from stratification of an island into layers should be greater than the energy spent on boundary formation. Both twin boundaries and stacking faults may act as candidate interlayer boundaries, since these defects have the minimum formation energy in FCC metals [8]. The results of calculation of the energy of a twin boundary and a stacking fault in Pb in the density functional theory (DFT) approximation are reported below. A mechanism of growth of the next atomic layer upon the formation of a twin boundary as a two-dimensional defect between 2-nm-thick layers is proposed.

1. Results and discussion

The formation of interlayer boundaries in Pb nanoislands on a Si(7 7 10) surface may be related to the structure of the „Si(7 7 10) surface — Pb nanoisland“ boundary. However, it was demonstrated in [4] that 2-nm-thick layers form in the homoepitaxy mode with no contact to the silicon surface. Therefore, DFT calculations were performed for a freely suspended Pb layer. The Vienna Ab initio Simulation Package (VASP), which implements the projector augmented wave (PAW) method [9] and periodic boundary conditions, was used for the purpose. A cutoff energy of 400 eV, a $17 \times 17 \times 17$ k-mesh, and the PBEsol functional were used in calculations. The structure was relaxed first in model calculations.

An oscillating dependence of the energy of a Pb nanolayer on its thickness, which is attributable to quantization of the electronic spectrum, was observed in calculations at low thickness values (below 15 ML). In order to determine the formation energy of a two-dimensional detect, one needs to use a model of an island with a thickness of 15 ML above and below the defect and take the thickness of the defect itself (1 ML) into account. Thus, the minimum size of a computational cell is 31 ML. A computational cell with a thickness of 41 ML was chosen for calculations of the energy of formation of a two-dimensional defect, a twin boundary (Fig. 1, *a*), and a stacking fault. The energy of a two-dimensional defect was determined as the energy difference between a layer containing a two-dimensional defect and a layer with a perfect crystal structure. The calculated formation energy values for a twin boundary and a stacking fault were 15 and 32 meV, respectively. Further

calculations were performed for a defect with a lower formation energy (i.e., for a twin boundary).

Figure 1, *b* presents the calculated variation of the energy of a Pb layer containing a twin boundary with layer thickness. The results of similar calculations for unrelaxed structures have been reported earlier in [10]. Deviation E from the formation energy of a twin boundary is insignificant, and the layer energy gain from quantization of the electronic spectrum remains substantially smaller than the formation energy of a twin boundary at all layer thickness values. Therefore, a twin boundary forms at the stage of growth of the next atomic layer after the completion of growth of a 2-nm-thick layer.

The crystal structure of a twin boundary in the model of closely packed layers of solid spheres may be presented as the positioning of atoms of the top atomic layer at atomic sites of the hexagonal close-packed structure (hcp layer). Therefore, a computational cell 5×5 in size with a thickness of 8 ML (a standing wave of Fermi electrons forms in a layer) or 6 ML (a standing electron wave does not form) was used for calculation of the energy of structures emerging at the initial stage of formation of a twin boundary. A single adsorbed atom or an atomic cluster was positioned on the surface of such structures both at hcp layer sites and at fcc layer (face-centered cubic structure) sites.

Figure 2 presents the variation of the difference between the energies of crystal structures with a single atom at an hcp site and an atom at an fcc site on the surface of a layer with its thickness. It can be seen that structures with a thickness of 3, 4, and 8 ML are energetically favorable for a single atom at an hcp site.

Model calculations of the energy of clusters of 2, 3, and 4 atoms were performed for structures with a thickness of 6 and 8 ML. Atoms in clusters were positioned within the first coordination ring. The results of calculations are presented in the table. It was found that fcc sites of

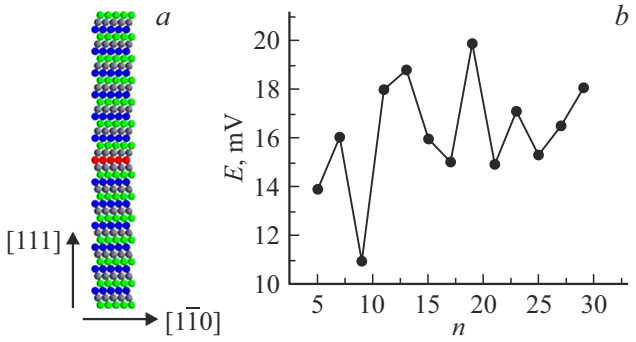

Figure 1. Sb41 structure model that was used to calculate the energy of formation of a twin boundary. The twin boundary is highlighted in red (in the online version) (*a*). Variation of the energy of a Pb layer containing a twin boundary with layer thickness n (*b*). Here, n is the number of atomic planes (111) in a computational cell and E is the energy difference between a layer containing a two-dimensional defect and a layer with a perfect crystal structure.

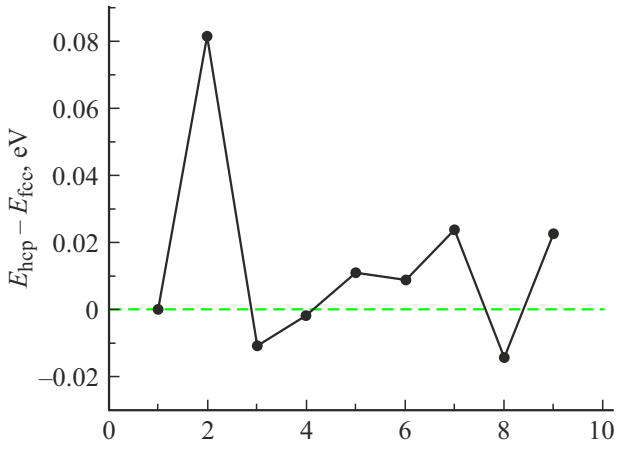

Figure 2. Variation of the difference between the energies of crystal structures with a single atom at an hcp site and an atom at an fcc site on the surface of a layer with its thickness.

Variation of the energy difference between clusters consisting of atoms occupying hcp sites and atoms occupying fcc sites with number of atoms in a cluster

Number of atoms in a cluster	Energy difference, eV	
	8 layers	6 layers
1	−0.0143	0.00898
2	0.05862	0.07496
3	0.19963	0.19863
4	0.18969	0.16651

cluster atoms are energetically favorable for both 6- and 8-monolayer structures. Modeling was performed for clusters with all atoms occupying FCC or HCP sites; mixed sites were not considered.

The presented data suggest that the growth of the next monolayer of atoms apparently starts with the formation of a rarefied structure on the surface of a finished layer. Therefore, calculations of the variation of the structure energy for a pair of atoms adsorbed on the surface of a Pb layer with distance between them were performed. The adsorption of a pair of atoms at hcp sites is energetically unfavorable at any distance between atoms on the surface of a layer with a thickness of 6 ML. Two atoms separated by a distance corresponding to the first ($R_1 = 3.5$ Å), the second ($R_2 = 6.06$ Å), the third ($R_3 = 7.0$ Å), and the fourth ($R_4 = 9.26$ Å) coordination rings have $E_{hcp} - E_{fcc} =$ 75, 11, 23, and 24 meV, respectively.

At a layer thickness of 8 ML, it is energetically favorable for a pair of atoms to occupy hcp sites at large distances between them. If atoms are positioned within the first coordination ring (the distance between them is R_1), the energy difference is positive. The interaction energy of a pair of atoms at large distances is specified by Friedel oscillations [11] and may be written as

$$E(R) \sim R^{-2} \sin(2k_F R).$$

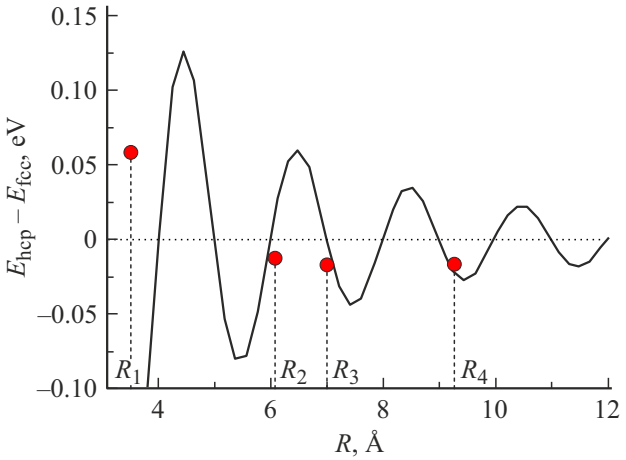

Figure 3. Difference between the energies of crystal structures with a pair of atoms at hcp sites and a pair of atoms at fcc sites on the surface of a layer with a thickness of 8 ML (red dots in the online version). The curve represents the dependence of the energy of interaction between atoms induced by Friedel oscillations with a Fermi wave vector for Pb in the model of free electrons $kF = 1.575$ Å-1.

The calculated values of interaction energy agree well with this dependence, which is represented by the black curve in Fig. 3.

Thus, the formation of a twin boundary between 2-nm-thick Pb layers starts with the formation of a rarefied atomic monolayer of pairs of atoms on the surface of a 2-nm-thick layer.

The application of current nanotechnology led to the development of fundamentally new hardware microelectronics components. Components with a characteristic size of 3 nm are already being fabricated on a commercial scale (e.g., gate-all-around transistors produced by Samsung Electronics). Quantum effects are of crucial importance in devices of this size. Such quantum effects in metals may affect significantly the transport characteristics of perfect single crystals and nanostructures. Twin boundaries exert a considerable influence on the superconducting properties of materials [12,13]. This is an important factor that should not be overlooked in the development of hardware components of quantum computers.

Conflict of interest

The authors declare that they have no conflict of interest.

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