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A twinned PbTe film induced by the 7 × 7 reconstruction of Si(1 1 1)

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Abstract

The PbTe films were grown on Si(1 1 1) substrate by hot wall epitaxy (HWE). X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the films. The results show that the PbTe films are twinned ones with preferred ⟨1 0 0⟩ orientation. The angles of normal direction of PbTe(1 0 0) facets which are perpendicular to the surface of Si substrate are 30° or 60°. The interface energy is calculated by CASTEP module of materials studio and the reason for this phenomenon is discussed.

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Keywords: A1. Reconstruction; A3. Hot wall epitaxy (HWE)

1. Introduction

PbTe is of interest due to its potential application as thermoelectric material and in infrared detectors and lasers within 3–30 μm range. The fabrication of hybrid sensors of IR focal plane arrays integrated with readout electronic circuits requires epitaxial growth of PbTe on Si wafers [1,2]. This is constrained by the large mismatch in lattice constants and thermal expansion coefficients between Si and PbTe. In order to reduce the constraints, buffer layer of CaF_2 and BaF_2 are used [3]. However, epitaxial growth of PbTe directly on Si wafer is desire for simplicity of the process. Vaga et al. [4]; Yang et al. [5]; Ugai et al.

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[6]; tried this by hot wall epitaxy (HWE), while Sahay and Guruswamy [7] did this by RF magneto sputtering. The PbTe films on Si(1 1 1) substrate are usually considered as texture ones with preferred ⟨1 0 0⟩ orientation. In the present work PbTe films were grown on Si(1 1 1) 7×7 substrate directly by HWE and studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that the PbTe films on Si(1 1 1) 7×7 substrate are actually twinned ones with preferred ⟨1 0 0⟩ orientation. The acute angles of normal directions of PbTe(1 0 0) facets which are perpendicular to the surface of Si substrate are only 30° or 60°. Companied with a calculation of interface energy by CASTEP module of materials studio, the reason of this phenomenon is discussed.

2. Experiment

A modified HWE apparatus [5] was used to grow PbTe films on Si(1 1 1) 7×7 substrate. *p*-type Si(1 1 1) wafers were first cleaned with methylbenzene, acetone and ethanol, and subsequently boiled in $1NH_3.H_2O{:}2H_2O_2{:}5H_2O$ and $1HCl{:}2H_2O_2{:}5H_2O$ mixture for 15 min. Then they were dipped into hydrofluoric acid solution and dried with nitrogen gas. Finally they were mounted on substrate holder and put into HWE oven under protection of nitrogen gas. The temperature of evaporation source and the oven wall was 793 K and the temperature of substrate was 653 K. The film growth proceeded for 1.5 h under the condition of vacuum of 1×10^{-6} Torr. The thickness of the film was 1.5 μm.

3. Results

XRD spectrum of the as-produced film was taken by a D/max-rA X-ray diffractometer, using CuKα radiation at a voltage of 50 kV and current of 150 mA. Fig. 1 is the XRD spectrum (20–100°) of PbTe/Si(1 1 1) 7×7. Only PbTe(2 0 0), (4 0 0) and (6 0 0) peaks can be observed on it, no other peaks appear. This means that the as-produced PbTe film has the preferred ⟨1 0 0⟩ orientation.

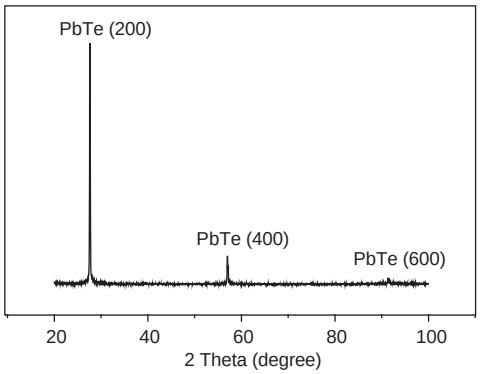

Fig. 1. XRD spectrum of PbTe/Si(1 1 1) film.

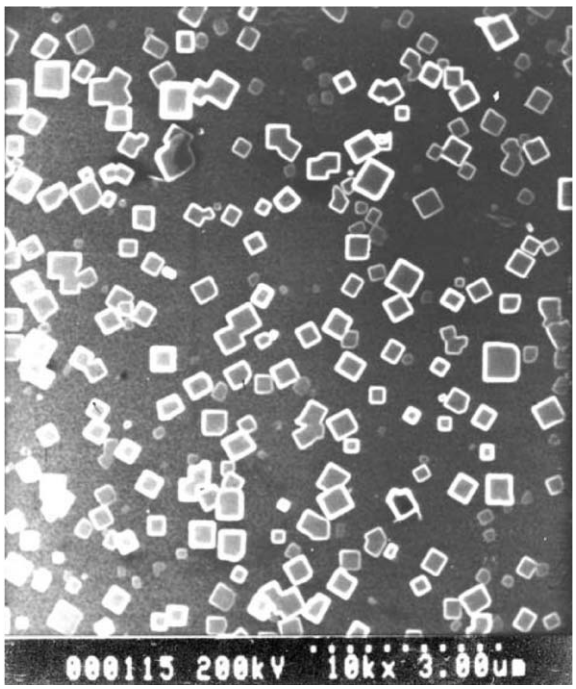

Fig. 2. The configuration of PbTe nuclei grown on Si(1 1 1) substrate.

SEM pictures were obtained on a HITACHI H-8100 IV transmission electron microscope with the function of SEM at 200 kV. In order to study the detailed structure of the films, configuration of PbTe nucleus on the Si surface was observed by SEM. As shown in Fig. 2, the shape of all PbTe nuclei are square, showing that the nuclei have the preferred ⟨1 0 0⟩ orientation, in accordance with

the result of XRD. Surprisingly, the angles between the lateral sides of these nuclei are either 30° or 60° according to the careful measuring results. So it is more reasonable to consider that the PbTe films on Si(1 1 1) 7×7 substrates are twinned ones.

4. Discussion

There are three kinds of reconstruction on Si(1 1 1) surface. When H-terminated Si(1 1 1) surface is heated to 823 K, termination will be lost and 7×7 reconstruction will be formed [8]. Boschetti et al. [9] had studied the growth of PbTe on Si(1 0 0) substrate with 2×1 reconstruction. Their results show that the growth of PbTe does not destroy the reconstruction. So we assume that the growth of PbTe do not destroy the reconstruction of Si(1 1 1) surface.

According to the dimer-adatom-stacking (DAS) fault model of Si(1 1 1) 7×7 reconstruction [10], there are 19 dangling bonds on one Si(1 1 1) 7×7 reconstruction. Seven of them are fully occupied. Another 12 dangling bonds belong to Si adatoms, they are partially occupied and can be bonded with adsorbed atoms or molecules.

In Si(1 1 1) 7×7 reconstruction, the nearest distance between two Si adatoms is $d = 6.66$ Å (see Fig. 3). It closes to the interplanar spacing of PbTe (1 0 0) $d_{\mathrm{PbTe}(1\,0\,0)} = 6.454$ Å. The mismatch is 3.1%. This constrains the $\langle 1\,0\,0 \rangle$ direction of square PbTe nuclei to be along the direction of d. In addition, in Si(1 1 1) 7×7 reconstruction, there are three d directions and the angle between them is 120° (see Fig. 3). So the angle of the lateral sides of square-shaped PbTe(1 0 0) nuclei will be 30° or 60°.

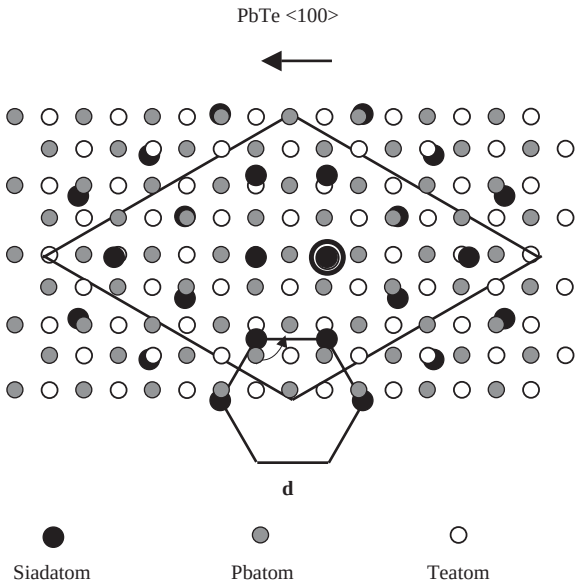

Fig. 3. DAS model of the Si(1 1 1)-(7×7) unit cell.

5. Theoretical calculations

In order to prove our assumption that the interface energy reaches the minimum when the direction of PbTe $\langle 1\,0\,0 \rangle$ facets is along d, the interface energy was calculated by CASTEP [11] module of materials studio software. CASTEP employs the density functional theory (DFT) plane-wave pseudopotential method which allows you to perform first-principles quantum mechanics calculations. We chose a local functional (CA-PZ: Ceperley and Alder data [12] as parameterized by Perdew and Zunger [13]) for calculating the energy.

For simpleness, only 12 adatoms in Si(1 1 1) 7×7 reconstruction are considered, and Si(1 1 1) 7×7 cell and PbTe(1 0 0) cell are both considered to be rigid. The position of Si adatom is described by (u_x, u_y, u_z), indicating the coordinate fractions along x, y and z axis. As shown in Fig. 4, the lattice is $a = 4.564$ Å, $b = 4.564$ Å, and $c = 10$ Å. H atoms were used to terminate three bonds of Si, and the fourth bond of Si was left to be perpendicular to the surface of PbTe(1 0 0). In all the cases, the bond length of H–Si and the bond angle of H–Si–H do not change. In our case, u_z is a constant of 0.25, this is the result of geometry optimization of Si(0.5,0.5, u_z). The total interface energy of one 7×7 cell is considered to be the sum of interface energies of 12 adatoms. When the direction of PbTe(1 0 0) is along the d, the rotation angle φ is set to be zero. The rotation axis is shown in Fig. 3 as an empty circle. The Si adatom which stands on the rotation axis is called axis adatom.

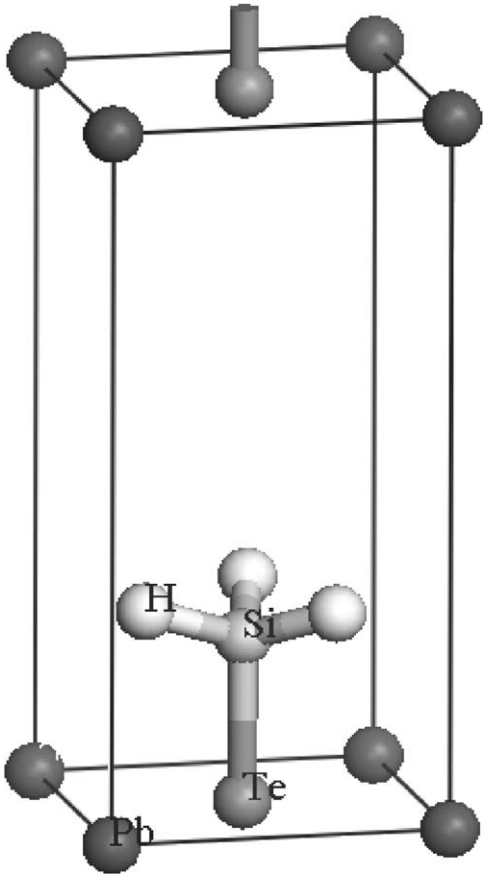

Fig. 4. The model for calculating interface energies.

The rotation angle changes with 0.1 step in the range of 0–90°. At each angle, the position of the axis adatom change over all places of a PbTe(1 0 0) plane cell (4.56 Å × 4.56 Å) with a 0.1 Å × 0.1 Å step. The positions of all 12 adatoms in whole 7 × 7 cell relative to PbTe(1 0 0) plane cell change accordingly, and total of 2025 interface energies of a 7 × 7 cell can be obtained. The minimal interface energy among them is considered as the interface energy of this angle.

Fig. 5 is the curve of interface energy vs. rotation angle φ, in which, the lowest energy occurs at the rotation angle of zero. This proves our assumption is true. And the second lowest energy is reached at the rotation angle of 30° or 60°. The difference between the two lowest energies is about 0.4 eV. Accordingly the difference

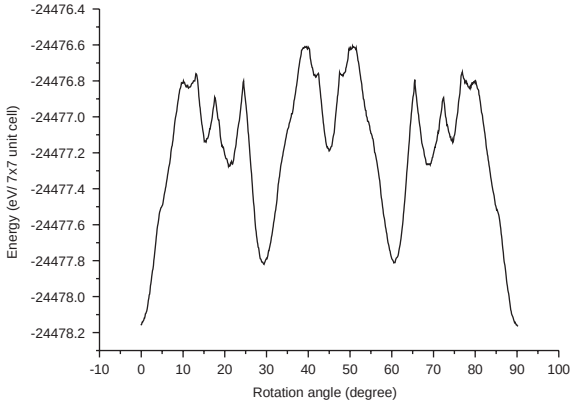

Fig. 5. The curve of interface energy vs. rotation angle φ.

of the two highest energies at the angle of 10° and 40° is about 0.2 eV, respectively. These differences will be eliminated if more 7 × 7 cells are considered. Obviously, there exists an energy barrier of large than 1 eV between the angle of 0° and 10°. So our assumption that the interface energy reaches the minimum when the direction of PbTe ⟨1 0 0⟩ facets is along d is true.

6. Conclusion

The present work shows that PbTe(1 0 0) film grown on Si(1 1 1) 7 × 7 substrate is actually twinned. The angles of normal direction of PbTe(1 0 0) facets which are perpendicular to the surface of Si substrate are 30° or 60° only. A calculation of interface energy shows that a minimum of energy is reached when the direction of PbTe(1 0 0) facets along the direction of d. So it is Si(1 1 1) 7 × 7 reconstruction that leads the PbTe(1 0 0) film to form a twinned structure.

Acknowledgements

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