

Surface Hydrogen Passivation and Sn distribution in $\text{Ge}_{1-x}\text{Sn}_x$ (001) materials: A DFT study

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Abstract

In this work, the effect of hydrogen passivation on Sn distribution in $\text{Ge}_{1-x}\text{Sn}_x$ (001) materials is investigated for p(2x2) reconstructed surfaces using density functional theory (DFT) calculations for $x=2.5\%, 5.0\%$ and 10% . For p(2x2) surface using a 2x2 unit cell, Sn has a lesser tendency to segregate to the surface when the clean surface becomes fully passivated with hydrogen. The distribution on the surface and into the bulk can be rationalised from consideration of Ge-H and Sn-H bond formation and decrease in surface energy by deactivation of reactive dangling bonds. Hydrogenation is therefore a feasible way for controlling the Sn population in a $\text{Ge}_{1-x}\text{Sn}_x$ system. Thus, during CVD growth using hydride precursors in the hydrogen limited growth regime, Sn segregation to the surface will be suppressed in a $\text{Ge}_{1-x}\text{Sn}_x$ epitaxial thin film.

1. Introduction

$\text{Ge}_{1-x}\text{Sn}_x$ alloys for device application are of great interests recently. The reasons stem from its potential application as a new channel material for p-channel metal-oxide semiconductor field-effect transistor (pMOSFET) as it can achieve a higher hole mobility compared to Si or Ge [1-4]. In addition, the indirect-to-direct band gap transition which is reported to occur for Sn composition $\sim 6\%$ – 11% also provides opportunity for it to be used as a direct gap material for optoelectronic applications [5-9]. However, the binary Ge-Sn system is more complicated than Si or Ge system and unlike the Si-Ge system where Si and Ge are completely miscible, the equilibrium solubilities of Sn in Ge is less than 1% [10]. During epitaxial growth using molecular beams or thermal annealing, segregation of Sn to the surface leading to formation of three dimensional islands have also been reported [11]. As Sn composition and hence its distribution within the active region of the device will be impacted by segregation of Sn, an understanding at the atomic level of Sn atoms in the $\text{Ge}_{1-x}\text{Sn}_x$ system is therefore of great interest. It will provide insights in the process of growing an abrupt interface which is essential for obtaining high-performance devices. For example, the presence of hydrogen adatoms at the growth front is known to have an

impact in achieving abrupt interfaces during epitaxial growth of SiGe/Si heterostructures. Ge segregation to the SiGe surface as well as into the Si overlayer is suppressed in the hydrogen limited growth regime via hydride precursors [12-18]. In this context, very little is known about the impact of hydrogen on the distribution of Sn in the GeSn material system. In this work, density functional theory (DFT) is used to investigate the effect of hydrogenation on the segregation and distribution of the Sn population for a $\text{Ge}_{1-x}\text{Sn}_x$ system containing $2.5\%, 5.0\%$ and 10% Sn.

2. Methodology

Spin-polarized calculations were carried out using the plane-wave density functional theory problem PWSCF (Quantum Espresso Version 5.0.1) [19]. For Ge, Sn and H, the Projector Augmented Wave [20] pseudopotential was used with Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) for the exchange-correlation functional [21]. A supercell with dimension $8.0\text{\AA} \times 8.0\text{\AA} \times 28.0\text{\AA}$ which consisted of 10 atomic layers of Ge or Sn was used in all calculations. The bottom layer of Ge was saturated with hydrogen atoms and this layer of hydrogen together with the bottom two layers of Ge were fixed in position to mimic a bulk-like structure. 30Ry and 120Ry were used as the energy and density cutoff respectively and the Monkhorst-Pack grid is $3 \times 3 \times 1$.

In this study, 3 different Sn compositions were studied. 2.5% where there is 1 Sn atom in the system, 5.0% where there are 2 Sn atoms and 10% where there are 4 Sn atoms. For a clean p(2x2) system, there are two dimers in the unit cell with 1 atom in the dimer being buckled up and the other being buckled down. The buckled up (down) atoms lie on the opposite side of each other as shown in Fig. 1a. For a fully hydrogenated system, the dangling bond for each of the Ge atoms in the dimers is now being passivated by a hydrogen atom as shown in Fig. 1b. The Sn atoms are placed in different configurations within the first three layers of the system and the energies compared within each composition.

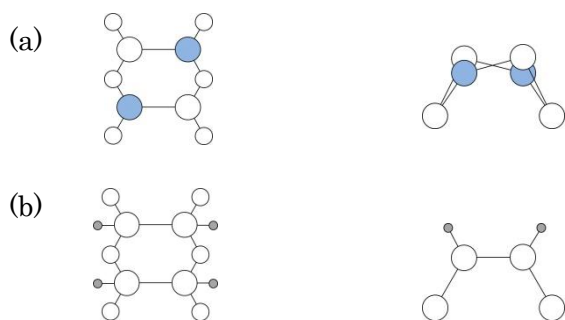


Fig. 1 Top view (left) and side view (right) of the first two layers of the clean (Fig 1a) and hydrogenated (Fig 1b) surfaces. Blue shaded circles represent atoms in the buckled down position and small grey circles represent H atoms.

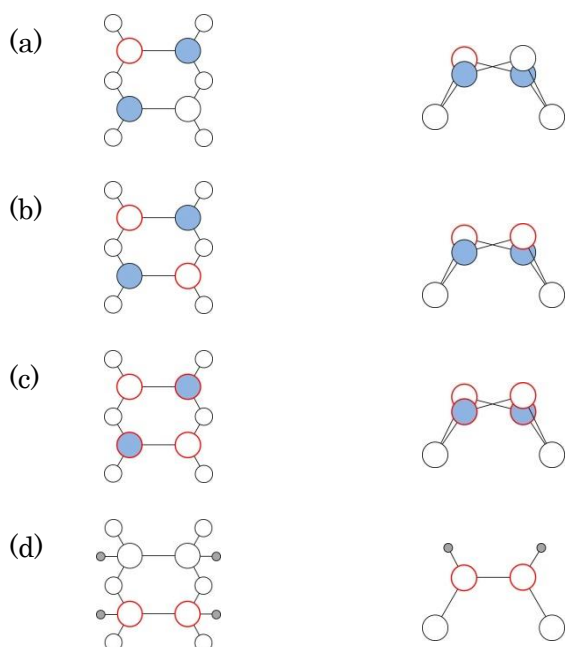


Fig. 2 Top view (left) and side view (right) of the most stable configurations for the clean 2.5%, 5.0% and 10% (Fig. 2a-2c) and hydrogenated (Fig. 2d) 10% Sn composition surfaces. Blue shaded circles represent atoms in the buckled down position and small grey circles represent H atoms. Red circles represent Sn atoms. For hydrogenated surfaces, the lowest energy configurations are where 1 Sn atom, 2 Sn atoms and 2 Sn atoms for 2.5%, 5.0% and 10% (Fig. 2d) Sn composition respectively are located in the 3rd layer.

3. Results and Discussion

The Sn atom is most stable in the buckled up position for 2.5% Sn composition. In the case of 2 Sn atoms (5.0% composition), the system is most stable when both Sn atoms are on separate dimers and both in the buckled up position. Sn atoms prefer to be in the surface layer for all the 3 different compositions of the clean surface as shown in Fig. 2a – 2c.

When the surface is passivated by hydrogen, Sn atoms tend to be in a sublayer level. For 2.5% composition, the single Sn atom went to the 3rd Ge layer of the system. For 5.0%, both Sn atoms are most stable in the 3rd layer. For the case of 10% (Fig. 2d), 2 Sn atoms remain in the first layer while another two Sn atoms are located in the 3rd layer.

This suggests that hydrogenation reduces the surface energy by deactivating the reactive surface dangling bonds and driving Sn interlayer migration to the subsurface layers. This can be seen from the energy differences in placing the Sn atoms in the 1st to 4th layer being lesser than 0.1eV in a fully hydrogenated system to larger than 0.2eV for a clean surface.

The presence of Sn atoms on the surface when the composition exceeds 10% implies that there is a critical total Sn concentration where the presence of Sn atoms in the surface layer will become energetically favorable.

4. Conclusions

The impact of hydrogen adsorption for Sn composition of 2.5%, 5.0% and 10% for a p(2x2)- Ge_{1-x}Sn_x(100) surface has been studied using plane-wave density functional theory. The results show that when the surface is fully hydrogenated, Sn prefers to be in the sub-surface layers. Thus during CVD growth using hydride precursors, Sn segregation to the surface will be suppressed in a Ge_{1-x}Sn_x epitaxial thin film in the hydrogen limited growth regime. Hydrogenation is therefore a feasible way for controlling the Sn population in a Ge_{1-x}Sn_x system.

Acknowledgements

E.S.T. acknowledges Grant Support from ARF: R-607-265-058-121.

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