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The Hakoniwa method, an approach to predict material properties based on statistical thermodynamics and ab initio calculations

Eiji Kamiyama [a,b,*], Ryo Matsutani [a], Ryo Suwa [a], Jan Vanhellemont [c], Koji Sueoka [a]

[a] Department of Communication Engineering, Okayama Prefectural University, 111 Kuboki, Soja-shi, Okayama 719-1197, Japan
[b] Technology, GlobalWafers Japan Co., Ltd., 6-861-5 Higashiko, Seiro, Niigata 957-0197, Japan
[c] Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, Ghent B-9000, Belgium

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ABSTRACT

An approach based on statistical thermodynamics and ab initio calculations to predict properties of materials composed of different types of atoms is presented. The key point of what the authors called the "Hakoniwa" method, is to take into account all possible structural supercells constructed by the fixed number of atoms of each species according to the composition of the target material. The conservation of the total number of atoms enables calculating the average value of a material property for a given temperature by applying statistical thermodynamics to the material property values obtained for each of the possible supercells. The application of the Hakoniwa method is illustrated by calculating the average energy gain by mixing Sn and Si atoms in a Ge matrix, as function of the $Ge_{1-x-y}Sn_xSi_y$ composition. The relative stability of each composition is compared allowing predicting the impact of Si doping on the stability of $Ge_{1-x-y}Sn_xSi_y$ films epitaxially grown on a Ge substrate. In addition, the average bandgap is calculated for a given $Ge_{1-x-y}Sn_xSi_y$ composition as a function of the temperature.

1. Introduction

The stability of semiconductor alloys during hetero-epitaxial film growth at a given temperature is critical to be able to use bandgap engineering to obtain specific devices characteristics. The present paper discusses and demonstrates a statistical thermodynamics and ab initio calculation based method to predict composite material properties using all possible supercells with the given material composition, that the authors named the "Hakoniwa" method. The application of the Hakoniwa method is illustrated for the evaluation of the effect of Si doping on the stability of $Ge_{1-x}Sn_x$ films and on their bandgap. This type of films is studied intensively for their use in strained $Ge_{1-x}Sn_x$ quantum well channels on Ge substrates to take advantage of both carrier mobility enhancement [1] and bandgap reduction [2]. The Hakoniwa method allows calculating in a straightforward way the average value of material parameters that can be obtained by ab initio calculation. The method is based on the assumption that each value of a material parameter can be linked directly to a particular supercell using ab initio calculation which is not the case for the cluster expansion (CE) method [3].

Ab initio calculation can not only directly calculate bulk properties but also allows estimating various properties of impurities both in elemental crystals and in alloys by using the supercell method [4]. Applying the supercell method to semiconductor alloys, however, leads to a drastic increase of the number of possible configurations compared to the case where a single point defect in a supercell consisting of only one type of atoms is investigated. Some attempts have been made to estimate the properties of semiconductor alloys by calculating a specific model like a quasi-random configuration cell [5–8] for a given composition of atoms although not all possible configurations were examined. The quasi-random configuration approach is correct if the temperature of crystal growth is so high that the atoms can arrange themselves at random during growth. However, this is not possible when the crystal growth temperature is rather low as is the case for some epitaxial film growth processes like e.g. $Ge_{1-x}Sn_x$ on Ge [9]. The method that is described in the present paper considers all possible configurations for the supercell size that is chosen and, based on that, calculates the average material parameter for a given temperature. Using the proposed Hakoniwa method, the most likely configurations can be obtained without any parameter fitting or additional assumptions.

The application of the Hakoniwa method is illustrated for $Ge_{1-x-y}Sn_xSi_y$ epitaxial growth on Ge and is used to estimate the average formation energy and the bandgap based on all possible configurations in a supercell containing a given number of Ge, Sn

* Corresponding author at: Department of Communication Engineering, Okayama Prefectural University, 111 Kuboki, Soja-shi, Okayama 719-1197, Japan.
E-mail address: ejkamiyama@aol.com (E. Kamiyama).

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and Si atoms. This allows comparing the relative stabilities and bandgaps at various substrate temperatures which is useful for designing a $Ge_{1-x-y}Sn_xSi_y$ epitaxial film growth process. Furthermore, the Hakoniwa method is used to investigate also the effect of the level of Si doping and the growth temperature.

2. Principle of the Hakoniwa method

2.1. Overview

"Hakoniwa" is a Japanese traditional play creating "miniature gardens", by arranging a collection of beautiful objects in different ways in order to express something. The procedure proposed in the present paper is somewhat similar whereby the miniature garden is the supercell in which the different atoms, the "beautiful objects" are arranged in order to estimate a given material parameter. A set of supercells of all possible atom configurations for a given supercell size with the target composition is first prepared. In order to estimate the properties of the material at a given temperature, the probability of each of the possible configurations is calculated in a statistical way. By using this approach, one can also obtain an insight in the dominant configuration of atoms for the macroscopic phenomenon in the real material that is being investigated.

The main advantages of the "Hakoniwa" method are the following:

- Representation of the configuration of atoms is straightforward since they are located in a supercell as is commonly used for ab initio calculation. For each temperature, the dominant configurations are then determined by applying conventional statistical thermodynamics using the calculated formation energy and the weight of each irreducible configuration (= the total number of equivalent configurations). The formation energy and the weight obtained for each configuration allow determining the configurations which are dominant for the given composition and temperature.
- Pseudomorphic hetero-epitaxial film growth can be considered by treating an anisotropically shaped supercell as will be illustrated further for epitaxial $Ge_{1-x-y}Sn_xSi_y$ films on a Ge substrate.
- In case that experimental values of the calculated material parameter are available, the comparison between experiment and calculation based on a chosen set of supercells will increase the confidence of the assumed structural origin of a physical phenomenon at a specific temperature. If there is no good agreement between the experimental values and the calculated ones, it is probable that the chosen supercell (size, composition, perhaps also some of the atoms not on substitutional positions, …) was not suitable. The whole Hakoniwa procedure might then be repeated assuming a different supercell to start with.

The compositions and structures that are used are somewhat similar to atoms that are arranged in several ways inside a supercell in order to replicate a "macroscopic" crystal. The supercell used in the usual method can represent objects of all kinds in a crystal but is not always corresponding well to a macroscopic phenomenon that can be observed in actual material, and the obtained calculated result always depends on how the supercell was defined. There is therefore an uncertainty gap in the understanding and predicting of properties of actual materials using models based on the use of supercells with a limited number of atoms. The Hakoniwa method enables to overcome this problem to a large extent by evaluating the probability of each configuration of the objects in the supercells as a replica of the micro structure of the real material.

Table 1
Number of atom configurations of a 16 atom Ge supercell containing 1 Sn atom and up to 6 Si atoms.

Compositions	Irreducible Configurations	Total Configurations
$Ge_{15/16}Sn_{1/16}$	1	16 ($=_{16}C_1$)
$Ge_{14/16}Sn_{1/16}Si_{1/16}$	4	240 ($=_{16}C_2$)
$Ge_{13/16}Sn_{1/16}Si_{2/16}$	13	1680 ($=_{16}C_3$)
$Ge_{12/16}Sn_{1/16}Si_{3/16}$	39	7280 ($=_{16}C_4$)
$Ge_{11/16}Sn_{1/16}Si_{4/16}$	97	21840 ($=_{16}C_5$)
$Ge_{10/16}Sn_{1/16}Si_{5/16}$	187	48048 ($=_{16}C_6$)
$Ge_{9/16}Sn_{1/16}Si_{6/16}$	290	80080 ($=_{16}C_7$)

2.2. The Hakoniwa method procedure

The detailed procedure of the Hakoniwa method is as follows:

- [A] Determine the size of the supercells that will be used to approximate the real crystal by superposition of a limited set of them, similar with the number of atoms in the maximum size cluster to be selected in the CE method.
- [B] Choose the number of atoms of each species in the set of supercells according to the composition of the target material. The conservation of total number of atoms allows calculating the average material parameter values statistically in step I, using a microcanonical ensemble.
- [C] Determine all possible configurations of the atoms in the supercell.
- [D] Extract the set of base cells (= corresponding with the irreducible configurations of Table 1) from step C based on the symmetry and periodic conditions of the cell and calculate the weight of each irreducible configuration.
- [E] Optimize the geometry of all the base cells and obtain the total energy for each base cell.
- [F] Calculate the formation energy E_f^i of the ith supercell by the standard procedure using ab initio calculation, see e.g. [4] using the total energies and the chemical potential of atoms in the supercells.
- [G] Calculate the probability ^{pi} of each base cell from the formation energies of all the base cells taking their weight w^i into consideration.
- [H] Calculate the target material parameter M^i for all the base cells.
- [I] Calculate the average of the material parameter $\bar{M}$ by using the probabilities obtained in step G.

Similar to the expansion degrees in CE method, the size of the base supercell determines the accuracy of the calculated results and of the range of atom concentrations that can be studied in a composite material whereby the calculation costs increase very rapidly as the supercell size increases. Besides calculation of alloy properties, the Hakoniwa method can in principle also be used to calculate average properties related to impurity complexes or clusters. It is also possible to include a low concentration of intrinsic point defects by using a larger cell to examine their impact and behavior, although even in that case, the calculated properties may still show a base supercell size dependence similar to that obtained with the usual supercell method. Steps A to G are similar to the SOD (Site-Occupancy Disorder) method [10] while steps H and I are an application of statistical thermodynamics on the results obtained in steps A to G. Using statistical thermodynamics, the probability ^{pi} can be written as: