Theoretical Studies on the Role of Strain in Interfaces and Defects in Materials( )

	SORNTHEP VANNARAT
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論 文 内 容 要 旨

1. Introduction

First-principle methods allow theoretical prediction and study of material properties and phenomena in materials, without relying on experimental data or adjustable parameters. However, application of these methods to study strain related phenomena has been limited because the large distances involved are beyond their practical applicability. A number of strain related phenomena has been successfully treated by continuum models. Using a hierarchy of approximations, the models can be simplified and analytical solutions can be obtained. However, the models rely on material dependent parameters. In this work, the multiple scale simulation, which combines first-principle calculations and continuum modeling, is used to study the role of strain in interfaces and defects in materials. Using this approach, theoretical study of large systems can be performed without relying on experimental data.

2. Objectives

An objective of this work was to connect first-principle calculations with continuum modeling of strain related phenomena including the effect of strain on the growth of heterostructures and

the interaction between the strain and the solute atoms. The connection can be in a simple form that an *ab-initio* method is used to compute material dependent parameters, which are then used in a continuum model of a particular phenomenon. In this work, as an additional step, a continuum model of the interaction between the solute and the strain was reformulated so that the required parameters are well defined and conveniently computed. Three problems have been considered, namely, the interaction between self-assembled islands, the effect of strain on alloying in heterostructures and the interaction between a solute atom and a dislocation.

3. Background

The self-assembled coherent islands are formed during the growth of some lattice mismatched semiconductor heterostructures, e.g. InAs/GaAs, $In_xGa_{1-x}P/GaP$ and Ge_xSi_{1-x}/Si, where growth progresses in the so-called Stranski-Krastanov mode. The island formation has received much attention because of an important potential application of the islands as quantum dots for quantum devices. The islands interact with each other through the strain fields in the substrate. The interaction affects the island formation process, for example, by increasing the island nucleation barrier. It has been shown that the interaction affects the island shape transition. The interaction also affects the arrangement of the islands on the surface of the substrate, which is an important property for the application of the islands in quantum devices. In this work, an analytical expression of the inter-island interaction was derived, and the effect of the interaction on the spatial arrangement of islands was predicted. In particular, the phase diagram of the island arrangement was derived as a function of island size and island coverage for the InAs islands on GaAs substrate.

Also concerning the growth of lattice mismatch heterostructures, in the second problem the effect of strain on alloying in such heterostructures is considered. The alloying or intermixing between the deposited material and the substrate is important for the growth and the application of the heterostructure. It is known that surface segregation causes intermixing when a material is deposited on a substrate that has a stronger tendency to segregate at the surface. However, if the growth order is reversed, the segregating species is already on the surface, therefore segregation does not occur and intermixing, if it occurs, is caused by other factors. In this work, the strain

dependence of the solution energy was derived and calculated for InAs/GaAs heterostructures. The effect of strain on intermixing was discussed based on the strain dependent solution energy.

The interaction between a solute atom and a dislocation was considered because it is a fundamental mechanism of interesting phenomena such as the Cottrell's atmosphere and solid-solution hardening. The enhancement of solute concentration also leads to the enhancement of the probability of precipitation near the dislocation line. The origin of the solute-dislocation interaction was classified into three effects, namely, the size misfit effect, the modulus effect and the electrostatic interaction. However, in metallic alloys, strong screening effectively eliminates the electrostatic solute-dislocation interaction. In the available continuum models of the size misfit effect and the modulus misfit effect, the dislocation acts as a source of the strain field and the interaction results from the strain dependence of the energy of the solute atom. Physically, these two effects can be understood as an attraction of a smaller species towards a region with compressive strain and an attraction of a softer species towards areas of high strain, respectively. These continuum models of the interaction rely on the size misfit and the elastic modulus misfit, both of which are not well defined for single solute atoms. In the present work, the interaction between the strain field and the solute atom was derived from an expansion of the binary alloy energy.

4. Calculation methods

The *ab-initio* calculations were performed in the framework of the density functional theory within the local density approximation (LDA) using the pseudo-potential method with planewave basis set. The finite element method (FEM) was used to numerically calculate the strain energy of the self-assembled island array and the cluster variation method (CVM) was used to determine the phase diagram of the pseudo-binary alloy.

5. Results and discussion

An analytical expression for the interaction between self-assembled islands was derived from a simple model, in which the islands were assumed to be cylindrically symmetric and the materials were assumed to be isotropic. An isotropic repulsive interaction was obtained. The interaction was found to be proportional to the product of the volumes of the two islands, and is

inversely proportional to the third power of the distance between the islands, as has been previously shown by Shchukin *et. al.* (1995). However, unlike Shchukin's expression, the present result shows the island-shape dependence of the interaction such that the interaction is relatively stronger for islands with a steeper tilt angle between the island facets and the substrate. The distance dependence of the interaction is identical to the interaction between parallel dipoles. The dipole-like characteristic of the interaction arises from the fact that the force between the island and the substrate localizes near the island edge. The interaction increases the energy of the island, therefore the island nucleation barrier increases with the density and the average size of the existing islands. The nucleation barrier depends on the ratio of the average island size to the average inter-island distance. The nucleation barrier becomes infinite when the volume strain relaxation is completely cancelled by the interaction. Due to the dipole-like interaction between islands, the arrangement of islands on a substrate can be in two phases, namely the liquid and the crystalline phases. The relationship between the average island size and the island coverage, at the boundary between the two phases was derived from the result of a molecular dynamics study of two dimensional parallel dipole systems. When islands are small and the island density is low the island system is the liquid phase. As the islands grow larger and the island density increases, the interaction increases and the islands form a regular array in the crystal phase. Using FEM, the energy of pyramidal InAs islands on the GaAs substrate was calculated using the anisotropic elastic moduli. The transformation from the uniform deposited layer to pyramidal islands allows relaxation of the strain energy by as much as 56%. The dependence of the inter-island interaction agrees with the expression derived from the isotropic model, but the interaction is strongly anisotropic, and is twice as strong in the <110> directions as the interaction in the <100> directions. Even though the interaction between islands is small compared to the strain energy of the island, when the average island size is larger than a critical value, the interactions can lead to the formation of a regular array of islands. The phase diagram of the island arrangement was calculated. The critical island size is a function of temperature and is calculated to be between 50 to 70 Å for the temperature range of 0 to 500°C. The prediction of the phases of the island arrangement qualitatively agrees with the experimental observation that

the coherence length of an island array increases with the island coverage.

To study the interaction between the solute atom and the strain, the energy of binary alloy was expanded in terms of the strain and the concentration. For the homogeneous case, the complete set of coefficients for the second order expansion can be determined from LDA calculations. The coefficient of the cross term between the strain and the concentration was interpreted as the stress induced by the solute atom. This interpretation allows a new method that can determine the coefficient conveniently and accurately. For the inhomogeneous case, the coefficients of strain gradients were shown to relate to the force constants. Interactions between the strain and the solute can be derived from the alloy energy expansion.

A well-known expression for the solution energy was extended to the case where strains are present. The strain dependence of the solution energy was obtained from the second order expansion of the homogeneous binary alloy energy. The strain dependence arises from the strain energy of the solute and the matrix and from the cross term in the alloy expansion. The bulk solution energies of the $In_xGa_{1-x}As$ alloy were determined from LDA calculations, and from the solution energies, the phase diagram of the alloy was determined using the CVM. The solution energies and the maximum temperature of the miscibility gap were in good agreement with the results of a thermodynamic assessment. The solution energy as a function of the in-plane strain in the coherent heterostructure was calculated for both dissolving InAs into GaAs and vice versa. When strain is large the dissolving of a harder material (GaAs) into the softer one (InAs) is energetically favorable. The solution energy has an extremum close to the point where the matrix is strained to match with the solute lattice. Intermixing is not energetically favorable for the case of a thin layer of InAs on GaAs substrate. However, due to the significant reduction in the solution energy, the effect of entropy is expected to make intermixing thermodynamically favorable at room temperature and above. The calculations indicate that the coherency strain provides enough thermodynamic driving force for the intermixing at the growth temperature of 400 to 600°C as observed during the deposition of InAs on GaAs. For the case of a thin GaAs layer on InAs substrate, intermixing is energetically favorable at all temperatures.

The strain dependence of the solute atom energy was derived from the second order

expansion of the binary alloy energy. The result is equivalent to the size misfit model effect, but the present form relates the solute energy change to the solute induced stress, which is well-defined and can be calculated directly within standard electronic structure methods. Using LDA, the solute induced stress was calculated for Ag, Cu, Fe, Li, Mg, Mn, Si, and Zn atoms in aluminum-rich alloys. The order of the solute atoms according the magnitude of the solute induced stress is Ag, Li, Zn, Si, Mg, Cu, Mn and Fe, with a negative sign for Ag and Mg and a positive sign for the others. The solute-dislocation interaction strength obtained from the calculated solute induced stress is in good agreement with experimental data for Cu, Mg and Zn, suggesting that the size misfit effect is the dominant part of the solute-dislocation interaction for these solutes in aluminum. For elements that have almost no lattice mismatch with aluminum, the modulus change effect may be important. This appears to be the case for Ag where the calculation differs significantly from the experimental result. Near an edge dislocation, the concentrations of Fe, Mn, Cu and Mg are expected to be significantly enhanced from the values in the bulk. The effect is moderate for Si and Zn and very small for Li and Ag. The sign of the solute induced stress suggests that Ag and Mg prefer to be on the expansive side of the dislocation slip plane, while other solutes prefer to be on the compressive side. The local enhancement of solute concentrations might assist in the nucleation of precipitates. It was shown that precipitation of Fe, co-precipitation of Fe and Mn with various other alloying elements, and of Fe and Si should be most enhanced by segregation due to the presence of strain fields from lattice defects, while precipitation of Ag, Li, and Mg based compounds should be least affected.

6. Conclusion

In conclusion, the multiple scale simulation was used to study three phenomena relating to the role of strain in interfaces and defects in materials. It allows a wider class of problems to be studied theoretically than the application of first-principle methods or the continuum model, alone, does. The simulation can be done without adjustable parameters while at the same time interpretation of the result in the continuum model gives better understanding of the underlying mechanisms.

審査結果の要旨

　ひずみが物性に対して如何なる影響を及ぼすかと言う、材料研究の極めて基本的な問題を第一原理及びモデル計算を駆使して、各種構造に対して詳細に解析した。合金化に対する溶質とひずみの関係、溶質と転位の相互作用、量子ドット間相互作用による自己組織化、等の問題を系統的に研究した。全編7章より構成されている。

　第1章は序であり、本研究の背景と目的を述べている。

　第2章では、本研究で活用する密度汎関数理論に基づく平面は展開擬ポテンシャル法第一原理計算、線形弾性理論、有限要素法、及びクラスター変分法に関して述べている。特に、純元素系及び合金系に対するエネルギーや弾性定数算定は、本研究で独自に開発した研究手法に基づくものであり、各種物質に関して格子定数、体積弾性率、希薄合金エネルギー等を求めている。

　第3章では、量子ドットのような表面の構造に関する各種の検討を行った。具体的には、島状構造同士の相互作用と基板との相互作用との競合によって各種の構造が形成されるのであるが、第一原理計算によって原子レベルでの界面安定性を議論すると共に、有限要素法を適用して島状構造同士が形作る自己組織化に関して詳細な議論を行った。島間相互作用は島間距離の3乗に逆比例すること、及び島が安定化して存在するためのエネルギー関係を示すことが出来た。

　第4章では、2元合金を対象として、エネルギー展開を適用し、ひずみと溶質の相互作用に関する定量的研究を行った。合金の非均一性を取り込む方法を独自に開発し、複雑な系をも研究対象とすることを可能とした。

　第5章では、InAs/GaAs半導体ヘテロ構造を例に採り、合金化に対するひずみの影響の詳細を検討した。これらの複雑な構造体の溶解エネルギー算定を行い、実験値との比較検討により、本理論の有効性を確認した。

　第6章では、アルミニウム合金に対して、溶質と転位の相互作用に関する種々の物性計算を行った。特に、濃度分布の最適値に関する詳細な検討と、溶解エネルギーのひずみ依存性に関する計算を行った。

　第7章は、総括である。

　以上要するに、本研究では、各種物質中の界面と欠陥に対してひずみが如何なる影響を及ぼすかという古典的な問題に現代的な理論である第一原理計算及びモデル計算を適用して、具体的な系に対する本質的で定量的な物性理解を深めることに成功し、材料工学の発展に大きく寄与をなした。

　よって、本論文は博士(工学)の学位論文として合格と認める。