UDC 669 . 14 : 539 . 24 : 681 . 3

Atomistic-scale Computational Materials Science on Surface and Interface Phenomena for Materials Development

Koji MORIGUCHI*

Yoichi MATSUZAKI

Abstract

Functionalities of materials usually originate from the spatial inhomogeneity in the associated systems. The phenomena on the surface are, therefore, expected to induce essentially different physical properties from ones in bulk systems. One of the most important missions of the recent computational materials science is to create universal concepts on the functionalities of practical materials based on the basic physical science. In this article, we review our recent theoretical research activities on some surface and interface phenomena associated in the technologies of "protection against metal dusting", "molecular design of organic corrosion inhibitors", "graphite anodes for lithium-ion secondary batteries", and "SiC single crystal growth", using the atomistic-scale computational materials science.

1. Introduction

In a material as a system, local inhomogeneity such as a defect in the parent phase, surface, interface, and nanostructure often assumes an important role in the development of the functionality of the material. The scientific phenomenon at a surface or interface without spatial homogeneity is utilized for engineering purposes in a broad range of fields including material engineering, corrosion protection engineering, semiconductor engineering, electrochemistry, and catalytic engineering. For this reason, the research on the areas of surfaces and interfaces is deemed as extremely interdisciplinary and one that is required to elicit as much of the functionality of a material as possible.¹⁾ The atomistic-scale computational materials science collectively refers to theoretical simulation technologies intended for nanoscale phenomena, which has become an indispensable tool for the research and development in a variety of engineering fields along with the remarkable recent progress in hardware/ software.2-4)

For transition metal alloys including steel materials in which the electronic d-band states around the Fermi level are strongly localized, the concept of chemical bond formation can be applied between constituent atoms. There are atoms that do not form bonds with other atoms even at the surfaces of materials having strong interatomic bonds in a bulk state (i.e. dangling bonds), which leads to a chemically activated state with locally high internal energy. For this reason, most phenomena of deep interest at surfaces and interfaces are influenced by the interactions between a few atomic layers and other actions that develop in the nanoscale regime. In addition, a surface or interface is a boundary at which the external phase comes into contact with the internal phase, serving as a place for particles and energy to be transferred and received. Therefore, the physical properties at surfaces and interfaces are expected to be essentially different from those in a homogeneous bulk system. This also opens up the possibilities for a material with new functionality added.

One of the most important missions of computational materials science is to reproduce realistic material phenomena in computers based on the basic laws of physics (fundamentals and principles), and to analyze the behavior under a particular set of conditions, thereby creating new universal laws and functionality development concepts. In this article, examples of Nippon Steel & Sumitomo Metal Corporation's research activities in which the atomistic-scale computational materials science rapidly progressed in recent years has been applied to the surface phenomena are outlined including practical materials, in the hope that this article will be of some help to readers taking a panoramic view of the ties going forward between a variety of material development and computational materials science.

2. Application of Computational Materials Science to Surface Phenomena of Metallic Structural Materials

This chapter starts with an overview of the Friedel model theory,

^{*} Chief Researcher, Ph.D. in Engineering, Mathematical Science & Technology Research Lab., Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511

which is useful for foreseeing intuitively the relations between the bulk cohesive properties and surface physical properties of a transition metal, which is followed by research examples on electronic state calculations that made a contribution primarily to the construction of a corrosion protection function for metallic structural materials.

2.1 Friedel model theory regarding the electronic states on the surface of transition metal

In most cases, physical properties related to the cohesive force and interatomic bonds in transition metals including alloys can be organized by the number of d electrons (n_d) per atom in the system. The Friedel model provides such behavior simply and clearly in terms of physics.⁵⁾ In the Friedel model, the rectangular electronic density of states (DOS) shown in **Fig. 1**(a) is boldly assumed for the d-band states of the transition metal, thereby examining the cohesion mechanism of the system. Using five d-orbital levels ($E_d^{atom} = W/2$) that are degenerated in an isolated atom state as the benchmark of the orbital energy, the total energy (E_{tot}^{bulk}) of the bulk system is expressed as equation (1) with simple calculation in between,⁵)

$$E_{tot}^{bulk} = -\frac{W}{20} n_d \left(10 - n_d\right) = -E_{coh}^{bulk} \tag{1}$$

where, W is the band width of the rectangular DOS, and E_{coh}^{bulk} is the cohesive energy of the bulk system.

The important conclusion derived from the Friedel model of the bulk system is that the physical properties of transition metal alloys related to the cohesive force and interatomic bonds are essentially determined by the number of electrons that occupy the d-band and the band width. The interatomic bonds in the system are strongest when the number of n_d is five, and the larger the band width W is, the larger the maximum value of the cohesive energy E_{coh}^{bulk} becomes. The d-band state of $n_d < 5$ corresponds to the bonding state. In this regime the interatomic bonding force increases along with the occu-



Fig. 1 Rectangular DOS in Friedel model for (a) the bulk and surface states. (b) Schematic illustration of coordination number reduction for the surface atoms on (001) in fcc structure. (c) Comparison of the surface energies for the 4d metals including Rb and Sr based on the first-principles⁷⁾ and Friedel model analyses.

pation of electrons. However, it is explained based on electronic theory that with $n_d > 5$, the bonding force decreases as electrons occupy the anti-bonding state.⁵

At the surface where the crystal periodicity is broken, there is a reduction in the number of coordinated atoms that constitute the surface as shown in Fig. 1(b). This weakens the interaction between atoms, resulting in reducing the band width W. When this band width reduction is ΔW as shown in Fig. 1(a), the total energy (E_{tot}^{surf}) of the surface system is expressed as follows analogically based on the process of derivation of equation (1).

$$E_{tot}^{surf} = -\frac{W - \Delta W}{20} n_d \left(10 - n_d\right) \tag{2}$$

As the surface energy is equal to the loss from the total energy due to the breaking of bonds, the surface energy per atom (E_{surf}) is expressed as follows.

$$E_{surf} \equiv E_{tot}^{surf} - E_{tot}^{bulk} = \frac{\Delta W}{20} n_d (10 - n_d)$$
(3)

In the framework of tight-binding approximation, when the number of coordinated atoms is N_c , the band width W is scaled in $\propto \sqrt{N_c}$.⁶⁾ Accordingly, the band width ratio between the bulk system and the surface system are expressed as follows, with the numbers of coordinated atoms of these systems respectively denoted as N_c^{bulk} and N_c^{surf} .

$$\frac{\frac{c}{W-\Delta W}}{W} = \sqrt{\frac{N_c^{surf}}{N_c^{bulk}}}$$
(4)

This derives the following equation for the band width reduction (ΔW) of the surface system.

$$\Delta W = \left(1 - \sqrt{\frac{N_c^{surf}}{N_c^{bulk}}}\right) W \tag{5}$$

This concept of associating the number of coordinated atoms N_c with the band width reduction ΔW is often called the bond-cutting model.⁶⁾

On the (001) surface of an fcc structure as shown in Fig. 1(b) as an example, the equality $N_c^{surf}/N_c^{bulk} = 8/12$ is true in terms of simple geometry, obtaining the value $1 - \sqrt{N_c^{surf}/N_c^{bulk}}$ to 0.2(=1/5) or so, and the surface energy of equation (3) can be approximately evaluated using the following equation.

$$E_{surf} = \frac{\Delta W}{20} n_d \left(10 - n_d \right) = \left(1 - \sqrt{\frac{N_c^{surf}}{N_c^{bulk}}} \right) E_{coh}^{bulk}$$
$$\approx \frac{1}{5} E_{coh}^{bulk} = \frac{W}{100} n_d \left(10 - n_d \right)$$
(6)

Equation (6) is a concept in terms of physics that associates the bulk cohesive physical properties with the surface physical properties, in which the surface energy of the transition metal is considered as approximately 1/5 or so of the bulk cohesive energy. In a system with strong interatomic bonds in the bulk state, the presence of dangling bonds at its surface, which are more highly activated than interatomic bonds in the bulk state, leads to an increase in surface energy.

To make a comparison between the Friedel model of the surface system described above and more precise first-principles computation analysis, we plotted relations between the theoretically calculated values⁷⁾ of the surface energy of 4d transition metals by Vitos et al. and the number of d electrons (n_d) as shown in Fig. 1(c). Although there are some exceptions such as 3d transition metal due to magnetism, the crystal structures in the ground state of the transition metal from the left side in the periodic table are changed as hcp \rightarrow bcc \rightarrow hcp \rightarrow fcc \rightarrow hcp.⁵⁾ For the plots with the vertical axis, the surface energy theoretical values⁷⁾ for the close-packed surface plane of the ground state crystal structure of each element are used.

For n_d on the horizontal axis, the number of occupying d electrons that were derived from an electron density analysis by Mulliken⁴) through our previous band structure calculations on the bulk system⁵) are used.

Figure 1 (c) also shows the transition of surface energy that was derived from the Friedel model (W=6.4 eV) after the fitting process for the above plots using the last term of equation (6). Even in transitions metal with different crystal structures, a wide range of transitions of surface energy in the periodic table can be reproduced almost quantitatively using the Friedel model. In the next section, we show that the Friedel model theory is effective for creating concepts for practical material development, taking for example a metal dusting corrosion-resistant technology, while the model ignores the precise view of associated microstructures and crystal structures.

2.2 Metal dusting corrosion-resistant technology

When using syngas production equipment in the production process of clean fuel, etc., materials are damaged by metal dusting (MD) corrosion attributable to gas with a carburization property as shown in **Fig. 2**(a).^{8, 9)} To deal with this corrosive phenomenon, Nishiyama et al. succeeded in developing an MD-resistant alloy called NSSMCTM696 using the hybrid corrosion-resistant method, a new corrosion-resistant concept as shown in Fig. 2(b).⁸⁾ The development concept of this corrosion-resistant technology is outlined

based on the Friedel model theory that was described in the previous section. In the elementary process of MD corrosion in the initial stage, atomic C is dissociated from CO molecules to enter metals (carburizing). As this process controls the MD corrosion rate more than other chemical reactions,⁹⁾ here we consider a means for controlling the dissociative adsorption reaction of CO molecules.

Figure 2(c) shows the change of DOS when CO molecules are put close to the iron surface.9) The lowest unoccupied molecular orbital (LUMO: CO- π) of CO is an anti-bonding orbital constituted mostly of C atoms. When electrons occupy the LUMO, the bonding force of the CO molecule is weakened. In the vicinity of the iron surface (r(Fe-CO)=0.57Å), the CO- 2π orbital hybridizes with the Fe-3d orbital as shown in Fig. 2(c), and the electron transfer (back-donation) from the Fe element of the surface to CO molecules is promoted, which is followed by the distribution of electrons to the hybrid CO- 2π anti-bonding orbitals, leading to CO molecules starting dissociation. The electron reaction described above is the catalytic mechanism that has long been known as the Blyholder mechanism.¹⁰⁾ On the other hand, this mechanism does not function in the case of a Cu surface from a similar computational analysis.9) Therefore, the MD corrosion control depends on successful inhibition of the Blyholder mechanism catalysis of CO molecules that originate in the parent phase metal surface.



Fig. 2 (a) Example of MD corrosion on the alloy containing 23%Cr-60%Ni-1.5%Al.⁸⁾ (b) Concept of preventing technique against metal dusting phenomena proposed for the alloy NSSMCTM696.⁸⁾ (c) Electronic density of states (DOS) for the cluster model which mimics the adsorption of CO on bcc-Fe(100) surface⁹⁾ as a function of distances between CO and metal surfaces, calculated using the DV-Xα method. (d) Calculated Fermi level as a function of valence electrons in the 3d transition metals within the rigid band model using the DOS of non-magnetic fcc-Fe.⁹⁾ Zero energy is set to the bottom of the s-state band, i.e. the Γ₁ eigenvalue.

Figure 2(d) shows the transition of the Fermi level across the periodic table of the 3d transition metals using the DOS of non-magnetic fcc-Fe (rigid band model).⁹⁾ As touched on in the previous section, the number of electrons that occupy the d-band of transition metal monotonically increases across the periodic table from the left side to right side, and the Fermi level rises upward. This extends the distance in terms of energy between the CO- 2π orbital and the surface d-band in the elements on the right side of the periodic table, making it difficult for the hybridization of both orbitals to take place; and thus, the catalysis according to the Blyholder mechanism is inhibited. Accordingly, in order to develop the MD anti-corrosion action in transition metal with $n_d > 5$, the addition of electron donor elements that allow for electrons donation to the surface d-band and for the Fermi level to be raised is likely to be effective.

Elements that show such donor behavior are not limited to Cu. The donor behavior can be seen by the addition of elements in groups III, IV, and V, which have confirmed the actual exercise of preferable MD-resistant anti-corrosive actions through our experimental and theoretical analyses.¹¹⁾ In addition, as alloys such as steel and Ni-base alloys are those with the number of parent phase d electrons being $n_d > 5$, an electron donor element (often referred to as a corrosion-resistant element in the field of steel materials) that increases the number of electrons that occupy the d-band generally works to reduce the surface energy as shown in Fig. 1 (c). This effect of reducing the surface energy serves as the local driving force, often causing significantly strong surface segregation to be observed regarding these electron donor elements.⁸⁾

Figure 2(b) shows the MD corrosion-resistant concept proposed by Nishiyama et al. for practical materials in view of the surface electron reaction mechanism described above. In the environment of high temperature syngas, protective scale is formed from an oxide of Cr or Si, blocking CO gas. Whereas the metal surface is exposed when the scale cracks or peels, Cu, which is an electron donor element, is strongly segregated at the surface concerned, inhibiting the dissociative adsorption catalytic action of CO gas. If the protective oxide scale is reproduced (restored) in the interim, it is possible to block CO gas. Using these cycle processes, it becomes possible to obtain an enduring MD-resistant property without concern about the cracks and peeling of the oxide scale. The concept of developing the MD corrosion-resistant property with the use of these two phenomena (formation of an oxide film and strong segregation of an electron donor element) is called a hybrid anti-corrosion method.⁸⁾

2.3 Corrosion inhibition effect of an organic compound

In this section, we describe the theoretical research that focuses on an interfacial phenomenon in the vicinity of the surface of a steel material. Here we present an overview of the theoretical analysis process for obtaining information on the atomic-level state of interface structures/coatings, illustrating some experiments of XPS (X-ray photoelectron spectroscopy), IR (infrared spectroscopy), and other methods that measure objects indirectly.

The addition of an inhibitor to the coating film is effective as a measure to combat the red rust on the end face of coated steel sheets/plates. Nippon Steel & Sumitomo Metal has ascertained through investigations that certain organic acids such as carboxylic acid are effective as inhibitors in addition to inorganic substances such as sodium tungstate.¹²⁾ However, the inhibition ability of organic inhibitors greatly varies depending on the molecular structures, and there is a very strong correlation in organic inhibitors between the structure and inhibition ability. For instance, comparing a tartaric acid with succinic acid in **Fig. 3**(a), tartaric acid, which has hy-



Fig. 3 (a) Molecular structures for succinic (left) and tartaric (right) acids. (b) Cluster models adopted for the molecular orbital calculations, which are used for the theoretical assignments in the experimental X-ray photoelectron (XPS) and infrared (IR) spectroscopies. (c) Final atomistic configuration theoretically predicted for the organic corrosion inhibitors based on the present quantum chemistry analyses.

droxy groups, largely excels in the anti-rusting effect. The following is an example of research that succeeded in identifying the mechanism in which tartaric acid exerts the anti-rusting effect through the surface analyses and quantum chemical calculations in combination. The findings have been used in the guidelines for the search for high-performance inhibitors.

In the XPS measurement conducted with the aim of clarifying the adsorbed state of tartaric acid in cold rolled steel sheets, the Ols signal originated from the tartaric acid was detected, and a chemical shift toward the energy level lower than the level of the tartaric acid standard reagent by about 1 eV was observed. Considering the bonding with iron and the dimerization between tartaric acid molecules as the change in the state of tartaric acid, the quantum chemical calculation of the Ols level was performed using models in Fig. 3(b). It was found that the average value of the Ols levels was raised by 0.10 eV in (i) and by 0.32 eV in (ii) in qualitative agreement with the experimentally observed features. This is attributable to the transfer of electrons from the Fe cluster to tartaric acid. There was almost no change in the Ols level in the dimer of (iii). Accordingly, it is concluded that the observed XPS spectra indicate the chemical bonding between the tartaric acid and iron surface.

As a result of the IR spectrum measurement using a tartaric acid standard reagent and tartaric acid-processed steel sheet, it was observed, compared with the tartaric acid standard reagent, that in the

IR spectra of the tartaric acid-processed steel sheet there was a shift toward a lower wavenumber by 71 cm⁻¹ in the carboxyl group C=O stretching vibration and also that there was an increase in the relative intensity by 2922 cm⁻¹. This measurement was followed by the theoretical IR spectra calculation for (i) to (iii) models in Fig. 3(b), which resulted in the favorable reproduction of the characteristics of the above-mentioned IR spectra using the dimer model of (iii). It is presumed from the experiment-theory combined analyses through the XPS and IR spectra described above that dimeric tartaric acid is adsorbed to the Fe surface. It has been observed through STM (scanning tunneling microscopy) and other methods that tartaric acid takes the form of an adsorption structure similar to the above also on the Cu(110) plane under the condition at room temperature and high coverage rate.¹³)

Tartaric acid and succinic acid molecules in water each have one carboxyl group from which the proton has dissociated. As such an anionic state forms a closed-shell structure of electrons, it is considered that the bonding force with iron is not strong. However, when electrons are injected to iron and a radical state is created, the strong bonding with iron is allowed. In light of this adsorption process, adsorption energy ($E_{ads} = -E_i + \phi + E_r$) is evaluated through first-principles calculations. E_i is the ionization energy of organic acid anions in water, and its evaluation is possible from quantum chemical calculations in a purely theoretical manner. In addition, an experimental value of 4.65 eV is used as a work function ϕ of iron. E_r is the bonding energy of organic acid radicals with the Fe surface, which is theoretically evaluated through the first-principle calculations.

In the evaluation of adsorption of monomolecular layers with a low coverage factor, the adsorption energy E_{ads} of tartaric acid is smaller than that of succinic acid by 5.7 kcal/mol, showing no superiority over succinic acid at the monomolecular level. This is attributable to hydroxyl groups of tartaric acid, which withdraw electrons and do not easily discharge electrons (large E_i). Next, the dimeric adsorption structure that was indicated by the surface analysis as described above was conducted, which led to the finding that the hydrogen bonds between dimers as well are possible, as a tartaric acid molecule has two hydroxyl groups. Figure 3(c) shows an example of the adsorption structure that was estimated from this theoretical analysis, in which the hydrogen bonds between dimers in which hydroxyl groups are involved is spread in the two directions parallel and perpendicular to the surface.

The above result led to a view that tartaric acid can form a fine and thick protective film on the surface of iron. In contrast, it is interpreted that succinic acid with no hydroxyl group is incapable of forming a structure similar to that of tartaric acid to provide sufficient protection over the iron surface, resulting in little anti-rusting effect. According to the semi-quantitative values obtained from the XPS measurement, it is indicated that the amount of adhesion to the surface of steel sheets is larger in tartaric acid than in succinic acid, which is consistent with the mechanism obtained from the calculation. As described above, while hydroxyl groups of tartaric acid with electron-withdrawing characteristics reduce the bonding force of the carboxyl group, the formation of hydrogen bonding allows for the protective film to be densified and to be increased in thickness, achieving the function as a corrosion inhibitor with favorable effect.

Introduced in this chapter was an example of application of the computational materials science to the surface phenomena of practical metallic structural materials. The significance of numerical simulation is not necessarily in the preparation of a dead copy of a real material in a computer, but in the provision of data and information sufficient for us to understand a phenomenon that has previously not been understandable. We would like to emphasize here that in the computational materials science, the extraction of events essential to a phenomenon from the analyses combined with experiments that start from simple physical/chemical pictures is the most precious research process.

3. Application of Computational Materials Science to Surface Phenomena of Electronic Functional Materials

One of the advantages of the computational materials science, which is based on the basic laws of physics (rules and principles), is that there is no limitation to the materials that can be examined. In this chapter, we illustrate the researches in which the computational materials science is applied to the study of phenomena at the surfaces of electronic functional materials of the group IV elements.

3.1 Carbon anode materials for lithium ion secondary batteries

Tar is a byproduct of steelmaking and is also a raw material for a variety of functional carbon materials. Here we outline a research that was started from the search for a use as graphite carbon materials for lithium ion secondary battery (LIB) anodes, and succeeded in developing a high-performance graphite anode material by controlling the nanoscale surface structures, which was finally commercialized.

Figure 4(a) and (b) show the electron micrographs of surface structures typically seen in graphite anode materials that have been developed by Nippon Steel & Sumitomo Metal.^{14, 15)} A surface network (nano-terminated surface structure: NTSS) in which the graphite end portions closed in the shape of a carbon nanotube is shown. From the analysis of the surface closed structure formation process shown in Fig. 4(c) through a molecular dynamics method utilizing the Tersoff potential¹⁶⁾, and the identification of the lithium ion penetration site using electronic structure calculations shown in Fig. 4(d), etc., the nanoscale structural control for this surface structure is expected to be enabled through appropriate surface processing. Furthermore, this expectation with an eye to the prospect of the ability of the control above to allow for a material to have an advantage was confirmed through electrochemical experiments.¹⁴

On chemically stable surfaces of graphite materials with NTSSs, the formation of SEI (solid electrolytic interface) films, which deteriorates the charge and discharge efficiencies, is inhibited. This promising property as that of a highly efficient anode material accorded with the user demand performance. This is a case example that took advantage of the information of atomic-level computational materials science in a skillful manner for the differentiation and functional improvement of a practical material. During this computational analysis, some interesting phenomena as an elementary process of carbon nanotube formation were observed as well, including the "takeover" phenomenon of a graphite plane by another layer.¹⁴⁾ It seems that the formation of a curved structure at the graphite surface observed in this anode material is a universal phenomenon; we would like to add that a structure similar to an NTSS was found afterward at the edge of a single-layer graphene by a research group led by Andre Geim who was awarded the Nobel Prize in Physics in 2010.17)

3.2 SiC single-crystal growth

For highly efficient utilization of electric energy, power electronics devices, which assume an important role for power conversion/ control in a wide variety of fields including information and telecommunications, electric power, automobiles, and household elec-



Fig. 4 Typical (a) SEM and (b) HRTEM images of the graphite powder prepared. (c) MD snap shots for the nano-terminated surface structure (NTSS) in graphite anodes for lithium-ion secondary batteries. (d) Typical atomistic configurations in the NTSS. Arrows show the 'open-interstices' between two adjacent laminar NTSSs.^{14, 15)}

trical appliances, are demanded to achieve higher performance. Against this backdrop, silicon carbide (SiC) is attracting attention as a material for highly efficient power devices in lieu of silicon (Si), whose limit in terms of material properties has started to be seen. Nippon Steel & Sumitomo Metal has advanced the development of SiC single crystal since the early 1990s. If a SiC power device is realized, the operating frequency can be 10 times, the power loss would be reduced to 1/100 times, and the operable temperature would be three times that of Si.¹⁸

Normally, a SiC single crystal is made to grow using a gas phase method (sublimation method). A solution method is a technique in which carbon is dissolved in a solution that consists mainly of Si so as to oversaturate the solution, which is followed by taking a SiC single crystal from the liquid phase in the dual phase region (SiC and liquid phase) in the phase equilibrium diagram. Solution methods allow for the crystal growth under low temperature and are potentially capable of producing a high-quality crystal under the condition close to thermal equilibrium. This ability of solution methods has recently attracted attention as single crystal growth technology that complements a sublimation method.^{19, 20)}

In a SiC crystal, one-dimensional polymorphous structures generally referred to as polytypes energetically degenerate with the energy of about $\Delta T=2K$ corrected for temperature,²¹⁾ which makes it difficult to control the phase stability during the growth of single crystal. In addition, the growth of SiC single crystal taking place under high temperature also makes it even more challenging to obtain a good quality single crystal with less dislocations and stacking faults.^{18, 19)} For this reason, many investigations are being carried out from a variety of physical perspectives in the pursuit of technology to grow single crystal, and on the SiC {0001} plane, there are two polar faces that consist of the (0001)Si and (000-1)C faces with chemically different properties. In this section, a study through experiments and calculations in combination is illustrated; in the study, correlations between the surface step bunching and crystal polarity in the course of crystal growth in a 4H-SiC solution were investigated on an off-angle substrate with the polar face inclined at a certain angle (cut-off angle) from a polar axis.²²⁾

In the study, SiC was made to grow in a solution using the TSSG (top seeded solution growth) method.²³⁾ Using a Si solvent and a graphite crucible, with the growth temperature set to 1650°C, the crystal growth was carried out while measuring the temperature gradients in a vertical direction in the solution on a real time basis using thermocouples installed on the substrate back face and the crucible bottom. Using 4°off-angle substrates of 4H-SiC(0001) as seed crystals, the surface morphology after the growth of about 80 μ m was observed both for the Si and C faces. When a (0001) off-angle substrate is used as a seed crystal, the step bunching and step bending are caused by the high density step structure, resulting in the degradation of crystalline.²³)

Figure 5(a) shows the change caused by the surface morphology during the growth of crystals influenced by surface polarities (Si and C faces) and temperature gradients. In addition, shown in Fig. 5(b) is a graph in which the average surface roughness values deduced from AFM (atomic force microscope) images are plotted. On the Si face, there is a tendency for the bunching to progress along with an increase in temperature gradients; however, there is not much influence of temperature gradients on the C face. Furthermore, it is visible on both polarity faces that the small temperature gradients worked to stabilize the surface morphology. In addition, there is a tendency for the steps to be linearized on the Si face. These observation results are assumed to indicate that the movement behaviors of steps and the surface diffusion behaviors of adsorbed species are different on the Si face and C face.

Shown in Fig. 5(c) is an example of analyses that were conducted for the diffusion barriers of the adsorbed species on the respective polar faces of the SiC $\{0001\}$ plane, when the Tersoff potential is used as with the previous section.¹⁶) The orange color seen in the vicinity of the steps in the energy contour line below the upper image is a kink site, which corresponds to the atom positions into



Fig. 5 (a) Surface morphologies on the 4°-off Si surface (upper) and on the 4°-off C surface (lower) as a function of temperature gradients. (b) Surface roughness (Ra, or average deviation) as a function of temperature gradients on each polar face of 4H-SiC (Si- and C-faces) deduced from the associated AFM images. (c) Computational analyses on the diffusion barriers for the adsorbed species of Si and C on each polar face based on the Tersoff's inter-atomic potential.

which the adsorbed species (Si and C) are taken during the growing of a crystal. Moreover, the purple and white indicate portions in which the diffusion barriers are higher. When comparing the Si faces (upper two) with C faces (lower two), the color gradation of the energy barrier is clearly deeper on the C face, meaning that the diffusion path is limited, and also showing the diffusion barrier is even higher. On the other hand, almost no such color gradation can be seen on the Si face, indicating that the diffusion at the surface terrace may be faster. As the diffusion of the adsorbed species (Si and C) on the Si face is faster than on the C face, the adsorbed species are quickly incorporated into the kink site, thus steps are linearized. For this reason, the findings in the observation based on this calculation/analysis were interpreted as the indication of a tendency for the bunching to more easily progress with the growth on the Si face than that on the C face.

4. Conclusion

In this article, we outlined some examples of researches on the surface phenomena of practical materials conducted at Nippon Steel & Sumitomo Metal for the application of the atomic-level computational materials science, which has made rapid progress in recent years. To allow readers to take a panoramic view of the prospects produced by the ties going forward between a variety of material development and computational materials science, here we described mainly examples of researches promoted by computation and experiments in combination.

The functionality of a material seems to be developed along with an important mechanism of local inhomogeneity in many cases. However, examination of such inhomogeneity from a universal viewpoint has just been started. Determining the guiding principle for achieving the reduction, omission, and substitution of an additive element, and enhancing the function exerted by an element as well have become the most important tasks in steel material development, as with the cases of other materials. While a wide variety of approaches in the present computational materials science are available, we would like to build elemental technologies that are capable of making a contribution to the development of various materials and processes, always focusing on the original purpose of the computer simulation to extract events essential to a phenomenon by means of selecting approaches in a manner that places the right one in the right place as much as possible. We conclude this article with the expectation for further progress in the basic investigation of surface and interface phenomena through the combination of state of the art experimental science and computational science.

References

- 1) Tsukada, M.: Introduction to Surface Physics. Tokyo, University of Tokyo Press, 1989
- Raabe, D.: Computational Materials Science: The Simulation of Materials, Microstructures and Properties. New York, Wiley-VCH, 1998
- Deák, P., Frauenheim, T., Pederson, M.R.: Computer Simulation of Materials at Atomic Level. Berlin, Wiley-VCH, 2000
- Satoko, C., Onishi, S.: Density Functional Method and Its Application— Electronic State of Molecules/Clusters. Tokyo, Kodansha, 1994
- 5) Moriguchi, K., Igarashi, M.: Journal of Smart Precessing. 2 (3), 102 (2013)
- 6) Groß, A.: Theoretical Surface Science: A Microscopic Perspective. Berlin, Springer-Verlag, 2007
- 7) Vitos, L., Ruban, A.V., Skriver, H.L., Kollár, J.: Surf. Sci. 411 (1), 186 (1998)
- Nishiyama, Y., Moriguchi, K., Okada, H., Osuki, T., Kurihara, S.: Shinnittetsu Sumikin Giho. (397), 65 (2013)
- 9) Nishiyama, Y., Moriguchi, K., Otsuka, N., Kudo, T.: Novel Approaches to Improving High Temperature Corrosion Resistance. Chapter 6. Edited by Schütze M., Quadakkers, W.J., Cambridge, Woodhead Pub. Lim., 2008
- 10) Blyholder, G.: J. Phys. Chem. 68, 2772 (1964)
- 11) Nishiyama, Y., Moriguchi, K., Otsuka, N.: J. Electrochem. Soc. 158 (12),

C403 (2011)

- 12) Furukawa, H., Ueda, K., Morishita, A.: Re-publication of WO2011/071171 in the Japanese national phase, 2011
- 13) Lorenzo, M.O., Haq, S., Bertrams, T., Murray, P., Raval, R., Baddeley, C.J.: J. Phys. Chem. B, 103, 10661 (1999)
- 14) Moriguchi, K., Munetoh, S., Abe, M., Yonemura, M., Kamei, K., Shintani, A., Maehara, Y., Omaru, A., Nagamine, M.: J. Appl. Phys. 88, 6369 (2000)
- 15) Moriguchi, K., Itoh, Y., Munetoh, S., Kamei, K., Abe, M., Omaru, A., Nagamine, M.: Physica B: Cond. Mat. 323 (1–4), 127 (2002)
- 16) Moriguchi, K., Shintani, A.: Jpn. J. Appl. Pys. 37, 414 (1998)
- 17) Gass, M.H., Bangert, U., Bleloch, A.L., Wang, P., Nair, R.R., Geim, A.K.: Nature Nanotechnology. 3, 676 (2008)
- 18) Ohashi W., Sakamoto, H., Tanaka, M., Fujimoto, T., Dohnomae, H., Morita, M.: Shinnittetsu Giho. (391), 175 (2011)
- 19) Danno, K.: Oyo-Butsuri. 83 (12), 993 (2014)
- 20) Kusunoki, K.: Study on 4H-SiC Bulk Crystal Growth Using a Solution Technique and Conduction Type Control. Doctoral Thesis (No. 10725), Nagoya University, 2014
- 21) Moriguchi, K., Kamei, K., Kusunoki, K., Yashiro, N., Okada, N.: J. Mater. Res. 28 (1), 7 (2013)
- 22) Endo, S., Kamei, K., Kishida, Y., Moriguchi, K.: The 61st JSAP Spring Meeting Proceedings. 17a-PG3-2, 2014
- 23) Kamei, K., Kusunoki, K., Yashiro, N., Okada, N., Tanaka, T., Yauchi, A.: Journal of Crystal Growth. 311 (3), 855 (2009)



Koji MORIGUCHI Chief Researcher, Ph.D. in Engineering Mathematical Science & Technology Research Lab. Advanced Technology Research Laboratories 20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Yoichi MATSUZAKI Senior Researcher, Ph.D. in Engineering Mathematical Science & Technology Research Lab. Advanced Technology Research Laboratories