Prediction of interface and vacancy segregation energies at silver interfaces without determining interface structures

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Interfaces play a crucial role in determining the functional and mechanical properties of materials. However, predicting interface properties is not straightforward because the atomic arrangements at the interface are different from those in the bulk. Hence, in this study, we discovered a descriptor from the bulk that helps predict the interface properties without the need to determine the interface structure. The descriptors related to the angle of elevation effectively described the structure units on both the bulk surface and optimized interface. Our model successfully predicted the interface and vacancy segregation energies at silver interfaces without using the interface structure.

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An interface is formed by two misoriantated crystals or different materials and is known to strongly impact material properties.1) For instance, atomic migration, electronic conduction, and mechanical properties of polycrystalline materials are largely influenced by the interface characteristics; moreover, peculiar properties, such as the formation of a two-dimensional electron gas, giant thermopower, and superconductivity, have been observed at artificially constructed interfaces.2–5) These degrees of freedom are used for classifying the interfaces into three types; if the rotation axis is parallel to the interface plane, then it is called a tilt interface; if the rotation axis is perpendicular to the interface plane, it is called a twisted interface; otherwise, it is called a mixed interface. Furthermore, the rotational degrees of freedom define the coincidence site lattice (CSL), which describes the periodicity of the bicrystal and interface structure. For a specific parameter set of the relative rotation and interface orientation, we can consider the interface structure at the microscopic scale; here, there are four additional degrees of freedom: rigid body translation (x, y, and z directions) and position of the interface plane. For each of these degrees of freedom, the local atomic position is relaxed to obtain energetically stable structures. Thus, exhaustive computation is necessary to determine even one interface structure specified by a set of macroscopic degrees of freedom because several trials are needed to search the parameter space of the microscopic degrees of freedom.6–19)

To overcome this limitation, machine-learning-aided methods have been reported and these have achieved high efficiency in interface structure determination. High-throughput structure determination methods have been utilized for unveiling the structure–property relationships at interfaces.6–19) Till date, most investigations on interfaces have focused on symmetric tilt interfaces with relatively small CSLs owing to difficulties in experimental observations and theoretical calculations. However, in general, most of the interfaces in practical polycrystals are twisted and mixed interfaces and also ones with infinitely large CSLs, i.e., “general” interfaces.

Furthermore, existing studies on structure–property relationships of interfaces have a limitation; that is, determination of interface structures is mandatory to identify their properties. For instance, determining interface structures becomes critical when we need to identify the properties of “general” interfaces, which are the abundant structures in polycrystalline materials but do not have any structural periodicity. If one can construct a model that can predict these interface properties “without” the interface structures, then understanding interface properties and developing functional materials is considerably facilitated. Such a prediction model is extremely beneficial for determining the properties of complex interfaces, such as the general interfaces.

Therefore, in this letter, we report the prediction of the interface properties using geometrical descriptors, which can be constructed only using the macroscopic degrees of freedom. As described later, we obtained 14 descriptors from a bulk-surface model which can be determined after determining the macroscopic degrees of freedom. We constructed the interface structures of face-centered-cubic silver including both symmetric and asymmetric tilt interfaces. We constructed a prediction model using these descriptors and succeeded in predicting the interface energy as well as vacancy segregation energy of silver interfaces without determining the interface structures.

As a model material, simple face-centered-cubic silver was selected and the database of the tilt interface structures was constructed. For our study, we selected totally 105 interface structures, including 28 [001], 38 [011], and 16[111] symmetric tilt interfaces and 2 [001], 20 [011], and 1 [111] asymmetric tilt interfaces because of the following two reasons: (1) their Σ value is lower than 100 and (2) the number of atoms in the interface model is lower than 10 000.

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To determine the microscopic structures of these interfaces, we selected a fast simulation method using an empirical potential. Embedded atom modified potential values for silver were employed.\textsuperscript{20} The initial interface structures were constructed using the bicrystal model, which contains two crystalline regions and two equivalent interfaces. For each interface, a calculation cell was constructed as the supercell of the unit cell corresponding to the interface periodicity. Structural optimization and energy calculations of the interface supercells were performed using the LAMMPS code.\textsuperscript{21,22}

To efficiently determine the interface structures, a kriging method based on Bayesian optimization involving Gaussian process regression were used.\textsuperscript{6,22,23)

Figure 1 shows some calculated interface structures with \( [001] (320) \Sigma 13 \) symmetric tilt, \( [001](430)/(100) \Sigma 5 \) asymmetric tilt, and high-sigma \( [111](167) \Sigma 43 \) symmetric tilt. The first two interfaces of cubic crystals have been experimentally and theoretically studied and commonly show good correspondences.\textsuperscript{7,24,25) The interface energy, \( E_{\text{interface}} \), was estimated using the following formula:

\[
E_{\text{interface}} = \frac{TE_{\text{interface}} - TE_{\text{bulk}}}{2A},
\]

where \( TE_{\text{interface}} \) and \( TE_{\text{bulk}} \) are the total lattice energies of the supercells at the interface and in the bulk, and \( A \) is the area of the interface. Because the supercell contains two identical interfaces resulting from the periodic boundary condition, the energy is divided by two.

To identify the atomic site at the interface, local coordination numbers of all atomic sites were extracted, and all atomic sites were classified into bulk-like or nonbulk-like sites through common neighbor analysis (CNA).\textsuperscript{26} Bonds having lengths 5% longer or shorter than the original bond length were regarded as nonbulk-like bonds; others were classified based on their coordination numbers, and sites having a coordination number of 12 were considered bulk-like sites. The atomic sites classified as nonbulk-like sites around the interface through CNA are represented by orange in Fig. 1. Based on CNA results, totally 26,179 nonbulk-like atomic sites were selected.

We focused on the atomistic behavior affording interface properties and vacancy segregation energies because it influences interface functions, such as atomistic migrations and sliding. The vacancy formation energies of the sites near the interface (\( E_{\text{vacancy@interface}} \)), which were selected through CNA, and those inside the grain (\( E_{\text{vacancy@bulk}} \)) were separately calculated; the energy difference between them, \( E_V = E_{\text{vacancy@interface}} - E_{\text{vacancy@bulk}} \), was calculated as the vacancy segregation energy at the interface. Although each atomic site has its individual \( E_V \), we considered the minimum \( E_V \) values for the respective interfaces, \( E_{V_{\text{min}}} \), as the interface property to be predicted. This is because the target variable needed to be interface-specific for prediction using interface-specific descriptors.

To predict \( E_{V_{\text{min}}} \) at each interface, descriptors were obtained from “bulk surface models”, which were determined using only the parameters corresponding to macroscopic degrees of freedom. “Bulk surface models” refer to models in which the surface planes are identical to the interface planes, but the structures are not optimized. The selection of these descriptors is not straightforward because the commonly used site-specific geometrical features, such as the bond lengths and angles, are all identical even in the bulk surface models.

Figure 2 and Table I shows the 14 descriptors considered in the present study. Two sets of seven descriptors are defined for each surface structure forming the interface, i.e., the surface structures of the upper and lower crystals of an interface (Fig. 2 and Table I). The descriptors for the upper and lower crystals are identical in case of symmetric tilt interfaces, whereas they are generally different in asymmetric tilt interfaces. As discussed later, the descriptors include parameters related to the angles of elevation, which were found important for predicting the interface properties. For each of the two crystals forming an interface, we considered the right-handed coordinate system so that the \( z \)-axis corresponded to the rotation axis, \( y \)-axis was perpendicular to the interface, and \( x \)-axis was perpendicular to both the \( y \)- and \( z \)-axes. We considered the origin of the coordinate systems at the position of the atom on the interface, atom site 0. Then, two other atom sites, site 1 at position \( r_1 \) and site 2 at \( r_2 \), were chosen among the atom sites neighboring site 0 using the following procedure: Atom site 1 was chosen so that the elevation along the \( y \) direction, \( \Delta y_1 \equiv |r_1 \cdot \hat{y}| \), became the smallest, and site 2 was chosen so that the elevation along the \( x \) direction, \( \Delta x_2 \equiv |r_2 \cdot \hat{x}| \), became the smallest when \( (r_1 \cdot \hat{y})(r_2 \cdot \hat{y}) \geq 0 \) and \( (r_1 \cdot \hat{x})(r_2 \cdot \hat{x}) \leq 0 \), where \( \hat{x} \) and \( \hat{y} \) are the unit vectors along \( x \) and \( y \) directions, respectively.
neglected the $z$ components and omitted sites without finite components along both the $x$ and $y$ directions. This is because the set of $\Delta x_i$ and $\Delta y_i$ components uniquely determines $\Delta z_i$ because the shortest interatomic distance is constant in the face-centered-cubic structure. Then eight descriptors of the elevation along both the $x$ and $y$ axes at sites 1 and 2 in both the upper and the lower crystals were extracted, as shown in Fig. 2 and Table I.

Random forest regression was used for constructing the prediction model. In the random forest method, multiple decision trees were constructed, and overfitting was prevented by the number and depth of the decision trees. Through grid searching, the number and maximum depth of the decision trees were set to 50 and 8, respectively. The ratio of the number of data points used for training to that used for testing was 7:3.

**Table I.** List of descriptors used in this study. The upper and lower crystals are identical in case of symmetric tilt interface. The symbols are schematically shown in Fig. 2.

| Surface-specific descriptors | Upper crystal | Lower crystal |
|------------------------------|---------------|---------------|
| Interface plane index        | $hkl_{up} = h^i_{up} + k^i_{up} + l^i_{up}$ | $hkl_{low} = h^i_{low} + k^i_{low} + l^i_{low}$ |
| Number of atoms on interface plane | $n_{up}$ | $n_{low}$ |
| Interface plane distance | $d_{up}$ | $d_{low}$ |
| Elevation along $x$-direction | $\Delta x_{1,up} \equiv \|r_{1,up} \cdot \hat{x}\|$ | $\Delta x_{1,low} \equiv \|r_{1,low} \cdot \hat{x}\|$ |
|                             | $\Delta x_{2,up} \equiv \|r_{2,up} \cdot \hat{x}\|$ | $\Delta x_{2,low} \equiv \|r_{2,low} \cdot \hat{x}\|$ |
| Elevation along $y$-direction | $\Delta y_{1,up} \equiv \|r_{1,up} \cdot \hat{y}\|$ | $\Delta y_{1,low} \equiv \|r_{1,low} \cdot \hat{y}\|$ |
|                             | $\Delta y_{2,up} \equiv \|r_{2,up} \cdot \hat{y}\|$ | $\Delta y_{2,low} \equiv \|r_{2,low} \cdot \hat{y}\|$ |
First, we attempted to predict the interface energies, $E_{\text{interface}}$, of the respective interfaces using the descriptors. Figure 3(a) shows the calculated and predicted interface energies. In addition to the training data (red dots), the test data (blue dots) are also plotted on the orthogonal dashed line; the coefficient of determination $R^2$ was 0.91 for the test data, indicating that the predicted interface energies using the present descriptors show good agreement with the accurate values obtained through calculations. $R^2$ was 0.80 even when the ratio of the training data to the test data was set to 6:4. Therefore, we succeeded in predicting the interface energies using the descriptors obtained “without” optimized interface structures. This result indicates that the present descriptors include some “characteristic” features of the interface structures, even though the descriptors were obtained from structures without interfaces. To investigate the role of these descriptors, their importance in performing regression analysis was confirmed using the feature importance measures of the trained model. We found that the descriptors related to the angle of elevation, such as $\Delta y_{1,2,\text{up,low}}$ and $\Delta y_{1,2,\text{up,low}}^*$, were
all highly ranked, indicating that the components in parallel and normal directions to the interface plane play a crucial role in predicting the interface energy.

As the descriptors related to the angle of elevation were confirmed suitable to represent the interface energy, the model using the same set of descriptors was applied to predict the interface property, \( E_{V_{\text{min}}} \). Figure 3(b) shows the training and prediction results for \( E_{V_{\text{min}}} \). Similar to the interface energy, both training data (red dots) and test data (blue dots) are located near the orthogonal dashed line in the graph, and \( R^2 \) of the test data was confirmed to be 0.89. Though the descriptors were obtained from structures “without” interfaces, the interface property and interface energy were predicted very well. Based on the importance of the descriptors, we found that the important descriptors for predicting the vacancy segregation energies were those related to the angle of elevation.

Based on these results of the predictions, we can conclude that the proposed descriptors, i.e. variables related to the angle of elevation, are effective in predicting the interface energy and property. Further, we analyzed the reason why descriptors obtained from structures without the interfaces could be used for the predicting the interface property. Figure 4(a) shows the bulk surface models of [001](430) and [001](100), forming the [001](430)//[001](100) \( \Sigma 5 \) asymmetric interface shown in Figs. 1(b) and 4(b). The bulk surface structure of (430) has zigzag-edged structural units, shaded in gray, whereas that of (100) has a flat shape [Fig. 4(a)]. These structural units can be represented by two angles of elevation, 1 and 2, represented by the black arrows. For instance, the right sides of the edges have angled identical to angle of elevation 1, and those on left sides have angled identical to angle of elevation 2, and angle of elevation 1 is steeper than angle of elevation 2. Namely, the angles of elevation represent characteristic shapes of the structural units on the bulk surface.

These structural units on the bulk surface were distorted by optimizing the structure of the interface, as shown in Fig. 4(b). The original atomic positions of the structures on the bulk surface were overlaid on the interface structure, indicated using dashed circles. The original angles of elevation 1 and 2 of the bulk surface were also overlaid on the black dashed arrows. These are slightly deviated from the atomic positions of the interface; for instance, the zigzag structures on the upper crystal are slightly distorted, and small steps are formed on the lower crystal. However, the characteristic features of the bulk surface and zigzag edge structural units are present in the interface.

Figure 4(c) shows one of the non-stable interface structures generated in the kriging process. The interface energy of the stable [001](430)//[001](100)\( \Sigma 5 \) structure [Fig. 4(b)] was 0.73 J m\(^{-2}\), whereas that of the non-stable interface [Fig. 4(c)] was 1.35 J m\(^{-2}\). The atomic positions of the bulk surface models were again overlaid on the non-stable interface structure using dashed circles. Different from the structure shown in Fig. 4(b), the atomic positions largely deviated from those of the bulk surface models.
The atomic shifts during structure optimizations for the stable and non-stable interface models were quantified. Figure 4(d) shows the histogram of the atomic shift during structure optimizations. The stable structure resulted from very small atomic shift (blue), whereas the non-stable structure was formed because of relatively large atomic shifts (orange). We examined average atomic shifts during structure optimization for all interfaces that were calculated in the kriging process, and confirmed that the most stable structure was obtained after the minimum atomic shift during optimization.

Generally speaking, the interface energy is described by two components: interaction energy between two surface structures and elastic energy due to the atomic distortions in the crystal regions. The similarity between the bulk surface and optimized interface structures and the resultant small atomic distortions indicate that the increase in elastic energy tends to be minimized. Furthermore, this result implies that the surface structures alone can provide a good approximation of the optimized interface structure.

One of the advantages of the present prediction model is that it does not require finite and short periodicities of interfaces. Moreover, the interface energy as a function of the tilt angle shows some cusps but continuously changes, implying that the properties of general interfaces can be estimated by interpolating the properties of relatively small CSL interfaces. Therefore, the present prediction model can potentially predict the properties of general interfaces from the training data set including only interfaces with finite periodicity.

However, only tilt interfaces were considered in the present study. Thus, we could not predict the properties of twisted and mixed interfaces using the present prediction model because the twist-related descriptors were not considered in this study. Implementation of twist-related descriptors in this model would enable a property prediction for all types of interfaces.

In conclusion, we predicted the interface energy and property of silver “without” determining the microscopic interface structure. We found that the descriptors obtained from the bulk surface model, i.e. variables related to the angle of elevation, were suitable for predicting interface energies and properties for the present case. By comparing the optimized interface structures and bulk surface structures, we found that the descriptors related to the angle of elevation effectively described the structural units on both the bulk surface and the optimized interface.

Successful prediction of the interface and vacancy segregation energies using the descriptors obtained from the bulk surface model indicates that the present method can be applied to explore various tilt interfaces, irrespective to their periodicity. Therefore, this model may be useful in predicting those energies of general interfaces; these are the most abundant types of structures found in polycrystalline materials, but their properties cannot be determined owing to their long periodicity or non-periodicity.

Finally, we should mention that the present study achieved the only predictions of the interface and vacancy segregation energies of the tilt interfaces of silver. To generally predict the interface properties of complex materials, further investigations are mandatory.

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