Visualization and classification of epitaxial alignment at hetero-phase boundaries

B. De Schutter *, K. De Keyser, C. Detavernier

Ghent University, Dept. of Solid State Sciences, Krijgslaan 281/S1, Ghent, Belgium

ARTICLE INFO

ABSTRACT

We use the concept of a Map of Interfacial Periodicity to visualize and classify the periodicity at hetero-phase boundaries. Periodicity in the plane of the interface is a necessary condition to achieve an optimized bonding arrangement across the interface. A periodic boundary plane may be achieved by plane matching, i.e., a 2D match of crystal planes within the plane of the interface, or plane alignment, i.e., matching of lattice planes that are aligned across the interface. The latter mechanism results in axiotaxy and aligned epitaxy and improves robustness for the 'matching' nature of the interface with respect to perturbations in grain orientation or interfacial roughness. Examples are presented for different types of epitaxial interfaces between tetragonal α-FeSi$_2$ or orthorhombic NiSi and Si(001), two systems that are known to exhibit both axiotaxial and epitaxial texture components.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Traditionally, epitaxy is considered within the context of (thin) film growth. Over the past decades, the majority of epitaxial growth experiments have been performed on inorganic films with a similar crystal structure and lattice spacing as the single crystal substrate, using techniques such as Molecular Beam Epitaxy (MBE) or Metalorganic Chemical Vapor Deposition (MOCVD) [1–3]. For example, there has been a lot of interest in the epitaxial growth of Ge and III–V films for (opto)electronic applications such as Ge or III–V based CMOS (Complementary Metal–Oxide–Semiconductor) devices [4–6] and III–V/Si photonics (on-chip lasers, optical interconnects,…) [7,8]. In view of this link with film growth, epitaxy is usually analyzed as a two-dimensional problem and epitaxial alignment is explained by a tendency for 'matching' within the plane of the interface.

However, the concept of matching interfaces is not restricted to film deposition. In the field of metallurgy, it is well-known that certain types of grain boundaries (homo-interfaces) or precipitate/matrix boundaries (hetero-interfaces) are preferred [9,10]. In thin film metallurgy, it is known that poly-crystalline thin films that are formed by a solid-state reaction are often strongly textured. Over the past decade, efforts in this field have been directed mostly towards the investigation of texture in silicides (or germanides) formed on single crystalline Si (or Ge) substrates due to their application as contacting material in CMOS devices [11–21]. A first major difference between these thin silicide films and most MBE-type epitaxially grown films is the different crystal structure between the silicide film (e.g., orthorhombic NiSi, tetragonal FeSi$_2$, cubic

CoSi$_2$,) and the Si substrate (cubic). This results in poly-crystalline films in which the grains can exhibit different types of texture: epitaxy (fixed orientation of the grain with respect to the substrate), random (no preferred grain orientation) and axiotaxy, a type of texture that was discovered by investigating the texture of NiSi on Si(001) [22], in which the grains exhibit a rotational degree of freedom around a specific crystal direction. A second difference is that in the case of these thin films formed through a solid-state reaction, the interface under consideration is usually not perfectly flat, as opposed to the case of film growth on single crystalline substrates. Therefore, it is important to evaluate the robustness of texture components found in these poly-crystalline films with respect to interfacial roughness.

Different crystallographic theories have been put forward that try to understand or predict texture components, such as the *coincidence site lattice* [23] and *O-lattice* [24] theories. While these theories have been successful at describing texture in systems for which the adjoining phases have a similar crystal structure, they have a harder time describing the aforementioned thin film hetero-phase silicide/germanide systems [25,26]. In the latter field, some material-specific theories have been put forward [27] that try to explain the observed texture through the 'matching' of atom lines or crystal planes at the interface, but none of them provides a truly general technique for texture prediction.

So far, attempts to explain the observation of certain epitaxial and axiotaxial texture components in silicide films have been made by looking at cross-sections of real-space ball-and-stick models of the film and substrate lattice near the interface region [28,29]. However, such visualizations have proven to be cluttered and often hard to interpret (especially for complex interfaces in the case of dissimilar crystal structures). In this paper, we propose an alternative method to visualize the degree of matching within the plane of the interface. We argue that

---

* Corresponding author.
E-mail address: bob.deschutter@ugent.be (B. De Schutter).

a matching periodicity between the film lattice and the substrate lattice within the plane of the interface is a necessary condition in order to achieve preferential grain growth in the film. Visualizing this match in periodicity allows one to interpret the quality and the geometrical nature of the matching periodicity for a certain grain orientation. Secondly, we argue that extending the traditional 2D approach of matching at the interface with the concept of plane alignment across the interface allows for an improved classification of low-energy interfaces. This is experimentally verified by comparing epitaxial texture components for α-FeSi$_2$ films and NiSi films on a Si(001) substrate.

2. Visualization of interfacial matching

The driving force for an epitaxial alignment of a silicide/germanide thin film on a single crystal silicon or germanium substrate consists of a minimization in interface energy which is achieved by optimizing the bonding across the interface, in the sense that all bonds are satisfied (which translates into dense packing for metallic bonding) and/or that the bonds are formed at 'natural' bond angles, resulting in a fully coherent interface. This reduction in interface energy usually occurs at the expense of a certain amount of strain energy. Optimization of the bonding may occur through interface reconstruction, whereby the atoms in the couple of atomic layers near the interface are re-arranged, analogous to surface reconstruction at the crystal/vacuum interface.

It is intuitively clear that in order for this interface optimization to occur, there must be some sort of 'match' between the crystal structures of the film and the substrate at the interface. This matching is easy to imagine if the crystal structure of the film is identical or very similar to that of the substrate (e.g., NiSi$_2$ on Si), but in the case of dissimilar crystal structures (which is the case for most silicide/germanide thin films on Si/Ge), determining which grain orientations give rise to a good match at the interface is a non-trivial problem. In order to assess this matching at the interface for a certain orientation of a film grain with respect to the substrate lattice, some sort of visualization of the interface is indispensable.

2.1. Disadvantages of atomistic interface models

The most straightforward way for visualizing the film–substrate interface is by constructing a 3D 'ball-and-stick' model of both crystal lattices and placing these on top of each other, taking into account a specific orientation of the film grain with respect to the surface. This has for example been used in the past to analyze the observed epitaxial alignments for a thin α-FeSi$_2$ film formed on Si(001) [29]. Fig. 1 shows some examples of 2D projections of such a 3D interface model along three different directions, covering a couple of unit cells along the horizontal and vertical directions, for an α-FeSi$_2$ grain on (001) oriented Si, belonging to an epitaxial texture component whereby a FeSi$_2${110} is parallel to a Si{110} plane and the FeSi$_2$(214) plane is parallel to the interface. Although the projection along Si(010) seems to nicely reveal a match between the two crystal structures, there are some important issues with this approach.

Firstly, texture studies are mostly performed using X-ray diffraction pole figures or electron backscattered diffraction. While these diffraction based techniques provide detailed information on the relative orientation between the film grain and substrate, they give no information on the relative translation between the two lattices. As such, creating such an atomistic model of the interface forces one to choose this relative translation based on intuition without direct experimental evidence. Secondly, complex local reconstruction will occur at the interface during nucleation and subsequent growth of a film grain [30], which is hard to measure and requires the use of additional techniques such as transmission electron microscopy.

Furthermore, even if a veracious model can be constructed that correctly accounts for the relative translation and the local reconstruction, it actually provides only limited information concerning the 'matching'
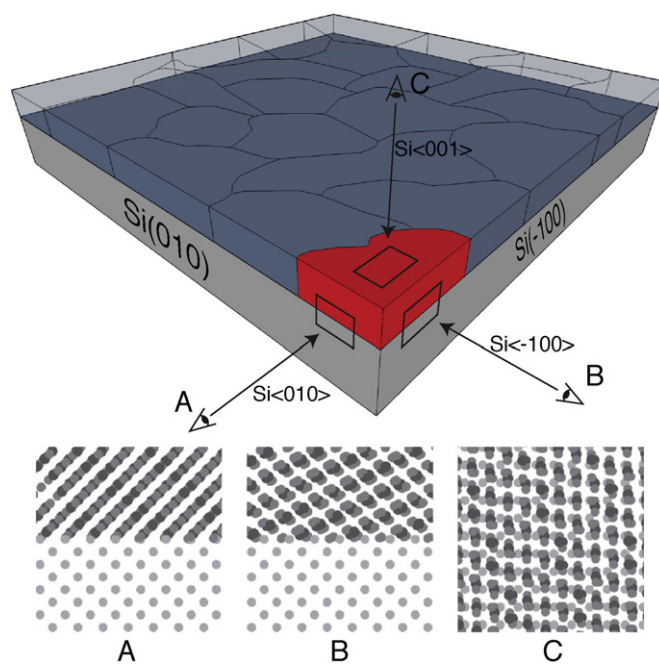
Fig. 1. *top* Schematic representation of a polycrystalline α-FeSi$_2$ film on a (001) oriented single crystal Si substrate. *bottom* Calculated atomistic interface models viewed along the Si<010> (A), <100> (B) and <001> (C, top view) directions for a FeSi$_2$ grain belonging to an epitaxial texture component where a FeSi$_2$110 plane is parallel to a Si110 plane and FeSi$_2$(214) is parallel to the interface. The viewing directions are indicated on the top schematic.

of the two lattices at the interface. A relatively small mismatch between the unit cells of film and substrate projected onto the interface plane might look good over the small distance displayed in the real-space atomistic model (usually only a few unit cells), while in reality this seemingly small mismatch might mean that a defect must be present e.g., every 20 cells for a 5% mismatch in order to maintain the matching.

Thus, constructing an atomistic interface model by simply stacking the two oriented crystal structures of film and substrate on top of each other results in an oversimplified visualization of the interface. Furthermore, while this technique might seem to result in 'good' visualizations of matching between 'simple' crystal structures (like tetragonal α-FeSi$_2$ on Si(001), see Fig. 1), for more complex interfaces (like e.g., orthorhombic NiSi on Si(001) or Si(111), see Fig. 2) such visualizations rapidly become cluttered and hard to interpret.

2.2. Map of Interfacial Periodicity (MIP)

As an alternative to the real-space atomistic representation of the interface discussed above, we propose a different method to visualize matching at the interface. As was mentioned before, the driving force for an epitaxial alignment is a reduction in interface energy through an optimization of the bonding across the interface. Since both the grain and the substrate have a periodic crystal structure, bonding can only be optimized in a systematic way along the entire length of the interface if the interface structure is periodic. Hence, periodicity in the plane of the interface may be considered as a hallmark of 'matching' interfaces.

To visualize interfacial periodicity, we use the concept of a Map of Interfacial Periodicity (MIP). For a certain orientation of a film grain with respect to the single crystal substrate (which can be defined by fixing the direction of two plane poles in both film and substrate), crystal planes from both the film and the substrate intersect the interface at angles ϕ and $90° - \chi$, with χ and ϕ the spherical coordinates (elevation and azimuth) of the pole for each plane (see Fig. 3a, $0 \leq \chi \leq 90°$; $0 \leq \phi < 360°$). The different planes in the crystal lattice of film and substrate each