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Dewetting of Ni silicide thin film on Si substrate: In-situ experimental study and phase-field modelling

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Abstract

In this paper, the *in-situ* Scanning Electron Microscopy (*in-situ* SEM) technique and three-dimensional (3-D) phase-field simulation were combined to perform a comprehensive study on the kinetics and mechanisms of dewetting (or agglomeration) of a 30 nm NiSi films on Si(100) substrate at 600°C. The evolution of texture **during agglomeration of** the polycrystalline NiSi thin film was also studied by *ex-situ* Electron BackScattered Diffraction (EBSD). The phase-field simulation results showed that abnormal grain growth plays an important role in the dewetting process of polycrystalline films, while the misorientations between NiSi grains and the Si substrate are the main reason for the agglomeration of NiSi polycrystalline thin film on the monocrystal Si substrate. Moreover, 3-D phase-field simulations coupled with experimental information on misorientation distribution and initial grain size were also performed, and the simulated Ni silicide grain morphology is in good agreement with the *in-situ* SEM results during agglomeration. In order to slow down or to suppress the agglomeration, it **is** highly recommended to either increase the volume fraction of low angle grains, or decrease the misorientation of the NiSi grain/Si substrate or the NiSi grains.

Keywords: NiSi thin film, Dewetting, *in-situ* SEM, Phase-field simulation, Texture, Misorientation

1. Introduction

With the downscaling of microelectronic devices, the Ni monosilicide (NiSi) has been widely used as contacts for the source, drain, and gate in the complementary-metal-oxide-semiconductor (CMOS) transistors. Compared to the former contact materials (CoSi₂ and TiSi₂), NiSi has attractive advantages, including a lower resistivity, less Si consumption, and Ni diffusion-controlled growth [1]. However, a major disadvantage of the NiSi films is that they are not stable at high temperatures. Indeed NiSi films can quickly degrade during post-formation thermal treatment [2]. Two degradation mechanisms can be distinguished: *i*) in the morphological degradation, the agglomeration (or dewetting) of NiSi occurs upon annealing (when $T \geq 500^\circ\text{C}$ depending on the film thickness: the smaller the thickness, the lower the temperature). *ii*) in the phase degradation, NiSi transforms into the high resistivity NiSi₂ phase at a higher temperature (around 750~800°C) [3]. For thin NiSi films, such as the ones with a thickness smaller than 30 nm, it has been shown that agglomeration, i.e., that the thin NiSi film breaks up into small islands, occurs at much lower temperatures than the formation of the NiSi₂ phase [3]. The agglomerated film then consists of small islands of low resistive NiSi separated by the high-resistive silicon, destroying the low resistance of the contact [4]. In order to avoid this detrimental behavior, there is an urgent need to improve the morphology stability of NiSi films.

Over the last two decades, several experimental studies have been devoted to the factors affecting the agglomeration and phase stability of NiSi films, including heat treatment process [3, 5], thickness of film [3, 6], nature of substrates [3, 7], texture of NiSi grains [3, 4, 8-10], grain growth [11], and alloying elements or impurities [2, 6, 12-15]. Among the factors affecting the agglomeration of the NiSi film, the texture of NiSi grains has been found to play a crucial role in the morphological stability of a thin NiSi film [4].

As the NiSi phase is formed *via* solid-state reaction, the texture inheritance from a precursor phase may benefit the new phase and has been proposed to explain the preferred orientation of NiSi grains [4, 16]. Actually, the NiSi films on monocrystal Si substrates are strongly textured. There are four types of texture components identified in the NiSi film, i.e., *i*) random texture for which no preferential orientation is present in the film; *ii*) epitaxy or in-plane texture for which the orientation between the NiSi grains and the substrate is completely fixed, and there is a two-dimensional match between the film and the substrate at the interface, *iii*) fiber texture, where one of the (hkl) planes is oriented (nearly) parallel to the film/substrate interface, and the NiSi grains are randomly rotated around the axis perpendicular to the interface, i.e., the fiber

72 axis, that is normal to the surface. *iv*) axiotaxy [17], which can be understood as an off-normal
73 fiber texture (i.e., that the fiber axis is not perpendicular to the interface). The latter texture type,
74 axiotaxy, was revealed on the NiSi films and is due to the match between the spacings (or the
75 projected spacing) of a substrate plane and a film plane [17]. In this case, the interface between
76 the film and the substrate shows a one-dimensional (1-D) periodicity. The axiotaxy texture is
77 common in NiSi films [8-10].

78 De Schutter *et al.* [4] have reviewed the effect of texture on agglomeration: they emphasized
79 that the minimization of interface energy is the main driving force for agglomeration and
80 examined the contribution of the different textures. Epitaxial grains have an excellent interface
81 match with the substrate, and thus the lowest interfacial energy, unlike those with different
82 textures which have different interfacial energies. Axiotaxial grains still have a decent interface
83 match due to the 1-D periodicity, although slightly worse than epitaxy, and thus medium
84 interfacial energies, while the random grains have the highest interfacial energies. Therefore,
85 there is a driving force for axiotaxial and epitaxial grains to consume neighbor grains with
86 random orientation. However, for epitaxial grains, the interface with the lowest interfacial
87 energy corresponds to a plane-to-plane matching: it is thus difficult to curve the interface since
88 this destroys the matching interface and increases the interface energy. Therefore, the epitaxial
89 grains can only increase their size by lateral growth while keeping the flat interface [4]. For
90 axiotaxial grains, due to the 1-D periodicity interface with the substrate, the curving of the
91 interface does not cost much interface energy, and previous TEM results have shown that the
92 axiotaxial grains indeed have a curved interface in the agglomerated film [17].

93 For the axiotaxy textured NiSi film on monocrystal Si substrates, there are four common
94 types of NiSi planes parallel to the Si(220) plane: NiSi(211), NiSi(202), NiSi(103), NiSi(112)
95 [17]. De Keyser *et al.* [8] have measured the volume fraction for axiotaxy texture, and they
96 found that the volume fraction of grains for the four axiotaxial texture components is around
97 40% for two NiSi films with a thickness of 60 nm and 90 nm capped with a 2 nm Si film.

98 De Keyser *et al.* [9] have also studied the texture evolution during agglomeration by
99 annealing at 550°C for 72 hours of a 60 nm NiSi film obtained by reaction of a Ni film and Si
100 substrate without Si cap: the XRD pole figures show the increase of the axiotaxial and epitaxial
101 components and the decrease of random components after annealing [9]. More precisely, the
102 Electron BackScattered Diffraction (EBSD) results showed that the volume fraction of axiotaxy
103 components increased from 24% to 30% after annealing [9]. It was argued that the axiotaxial
104 grains promote agglomeration. Moreover, Deduytsche *et al.* [14] found that additional alloying
105 elements, such as Ti, W, and Ta, change the texture of thin film by suppressing the axiotaxial

106 grains and promoting the epitaxial ones. These changes in texture can increase the morphology
107 stability of NiSi film at high temperatures. More recently, Luo *et al.* [18] studied by atom probe
108 tomography the agglomeration of NiSi thin film using Si isotopes enriched multilayers. They
109 found that the diffusion of Si (the slow-diffusing species) along the NiSi/Si interface plays a
110 significant role in the agglomeration of NiSi thin films. Though there is noticeable progress in
111 understanding the agglomeration mechanism of NiSi film and more generally of polycrystalline
112 thin films [3, 4, 8, 9, 18], these mechanisms are still not fully understood. Moreover, the
113 morphological stability and the related effect of texture of NiSi film have been mainly studied
114 by the static experiments (*ex-situ*), such as X-Ray Diffraction (XRD) pole figure, EBSD,
115 Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM). A few *in-*
116 *situ* experiments were performed, such as *in-situ* XRD [3], and *in situ* sheet resistance
117 measurement [19]. However, with these experimental techniques, it is still difficult to study the
118 mechanisms, the complete dynamic evolution, and the kinetics of agglomeration to obtain a
119 good understanding of the agglomeration process. Accordingly, there is an urgent need to
120 develop an appropriate approach to remedy the situation.

121 Nowadays, the *in situ* experimental observation coupled with the phase-field simulation
122 may serve as an efficient way to bring insights into complex phenomena. *In situ* observations,
123 such as the ones done in an environmental SEM, can provide direct and reliable data to study
124 the mechanisms and the kinetics of agglomeration. With respect to the phase-field simulation
125 of agglomeration in NiSi films, Bouville *et al.* [20, 21] developed a phase-field method to study
126 grain boundary grooving and agglomeration of a NiSi polycrystalline thin film where each alloy
127 component has a unique diffusivity. They also examined the effect of introducing a slow-
128 diffusing species (Pt) into the film, and the effect of grain shape on the agglomeration of
129 polycrystalline thin films [21]. However, Bouville's work only considers two grains in a 2-D
130 simulation along the longitudinal section, and it cannot completely and quantitatively describe
131 the evolution of agglomeration. Moreover, such a simple model does not consider the effect of
132 texture. In order to perform a quantitative simulation of the agglomeration (or dewetting)
133 phenomenon and to study the effect of texture on NiSi thin films, the 3-D multi-phase-field
134 (MPF) model is required. This type of simulation has emerged as a powerful tool to simulate
135 the microstructural evolution in various materials processes during their lifetime [22-27]. It can
136 be utilized by coupling with reliable CALPHAD (calculation of phase diagram) thermodynamic
137 and atomic mobility databases [24].

138 Consequently, in this work, *in-situ* SEM observations and MPF simulations are combined
139 to investigate the mechanism of agglomeration in the polycrystalline NiSi thin film. The

140 agglomeration kinetics and the morphological evolution of the NiSi thin film are determined
141 by *in-situ* high-temperature SEM observations, while the evolution of texture for the
142 polycrystalline NiSi thin film during agglomeration is studied by *ex-situ* EBSD. The 3-D phase-
143 field simulation is performed by considering the orientation of both NiSi grains and Si substrate.
144 The effect of misorientation on the agglomeration is quantitatively investigated, to reproduce
145 the results of *in-situ* SEM. The role of the NiSi grain orientation is highlighted.

2. Experimental procedure

147 A 15 nm thick Ni film was deposited at room temperature by magnetron sputtering onto
148 (100) Si substrates. The Si(100) substrates were immersed into a 5% HF solution for 1 min to
149 remove the native oxide prior to the deposition. The deposition was performed in a sputtering
150 deposition system with a base pressure of 10^{-8} Torr using 99.99% pure Ar gas flow. The wafer
151 was mounted on a rotating sample holder to obtain a homogeneous deposit. The deposition rate
152 as a function of power was calibrated for the Ni target. The applied power on the Ni target is
153 50W and the corresponding deposition rate is 0.136 nm/s. According to the conservation of the
154 mass of Ni atoms, the full consumption of the 15nm Ni film by solid state reaction with the
155 silicon substrate will result in a NiSi film of about 30 nm.

156 *In situ* hot stage scanning electron microscopy has been done using an environmental SEM
157 FEG QUATTRO (Thermo Scientific). A 3mm×3mm sample consisting of a 15nm Ni film
158 deposited on Si substrate, was introduced into a MgO crucible mounted, in the SEM, on a
159 furnace capable of reaching 1000°C. Heating was done in vacuum mode, in order to avoid
160 oxidation of the Ni film. The sample was heated with the following ramp: 30 K·min⁻¹ up to
161 450°C, 10 K·min⁻¹ up to 550°C, and finally slowly (5 K·min⁻¹) till 600°C. Then the sample was
162 held at 600°C for almost 4 hours (238 min). Observations were done at 10 kV, in order to finely
163 see grains in the Ni layer with an Everhart-Thornley Detector. Pictures were taken every 1 or 2
164 minutes in order to build the detailed kinetic curves afterward. The evolution of phase area
165 fraction was deduced after treatment of image stack in ImageJ software.

166 Rapid thermal processing (RTP) was used for annealing sample at 600°C for 60 s under
167 vacuum ($\sim 10^{-6}$ mbar) with the ramp rate as nearly 50°C/s. A long-time annealing sample was
168 prepared by vacuum annealing furnace (the ramp rate is nearly 0.57°C/s) under vacuum (10^{-7}
169 mbar) at 600°C for 24 hours. The structure of the films was investigated using X-ray diffraction
170 (XRD) in the θ - θ geometry using a Cu K α source ($\lambda_{K\alpha} = 0.154$ nm). The NiSi grain orientation
171 maps were collected using the EBSD technique in a Zeiss Gemini 500 field-emission gun
172 scanning electron microscope (FEG-SEM) equipped with an EDAX Hikari Super acquisition

173 system. EBSD scans were performed at 12 kV accelerating voltage, using step sizes between
 174 20 and 50 nm. Post-processing analysis of the EBSD data was performed using the OIM
 175 Analysis™ software [28], combined with the MTEX Toolbox [29] for texture analysis and
 176 visualization. Low kV images were taken with this Zeiss FEG-SEM, using two secondary
 177 electrons (SE) detectors: an InLens SE detector (located inside the electron column) that
 178 provides high-resolution surface structure and an Everhart-Thornley SE detector, used for
 179 topography observation.

181 3. Multi-phase-field (MPF) modeling

182 3.1 MPF models

183 In this work, the contribution of the elastic field was not taken into account. Under this
 184 assumption, the total energy functional can be generally divided into the interfacial part f^{intf}
 185 and chemical part f^{chem} [30, 31]:

$$186 \quad F = \int_{\Omega} f^{\text{intf}} + f^{\text{chem}} \quad (1)$$

$$187 \quad f^{\text{intf}} = \sum_{\alpha, \beta=1, \dots, N} \frac{4\sigma_{\alpha\beta}}{\eta} \left\{ -\frac{\eta^2}{\pi^2} \nabla \phi_{\alpha} \cdot \nabla \phi_{\beta} + \phi_{\alpha} \cdot \phi_{\beta} \right\} \quad (2)$$

$$188 \quad f^{\text{chem}} = \sum_{\alpha=1, \dots, N} h(\phi_{\alpha}) f_{\alpha}(c_{\alpha}^i) + \tilde{\mu}^i \left(c^i - \sum_{\alpha=1, \dots, N} \phi_{\alpha} c_{\alpha}^i \right) \quad (3)$$

189 where $N = N(x)$ is the local number of phases, ϕ_i is the phase-field value of α phase/grain, **the**
 190 **condition** $0 \leq \phi_i \leq 1$ **and** the sum constraint $\sum_{\alpha=1, \dots, N} \phi_i = 1$ are always fulfilled, and $\sigma_{\alpha\beta}$ is the
 191 interface energy between phases/grains α and β . It can be anisotropic with respect to the relative
 192 orientation between the phases/grains. $\eta_{\alpha\beta}$ is the interface width and is treated to be equal for
 193 all interfaces. There are two terms in the brace of Eq.(2), i.e., $-\frac{\eta^2}{\pi^2} \nabla \phi_{\alpha} \cdot \nabla \phi_{\beta}$ **corresponding to**
 194 **the gradient term between two phases/grains α and β , while $\phi_{\alpha} \cdot \phi_{\beta}$ the double obstacle**
 195 **potential. In Eq.(3), $f_{\alpha}(c_{\alpha}^i)$ is the bulk free energy density of the individual phase, which**
 196 **depends on the phase concentrations c_{α}^i , and can be obtained from the reliable thermodynamic**
 197 **database. The interpolating function $h(\phi_{\alpha})$ is an arbitrary function which is defined changing**
 198 **monotonously from $h(0) = 0$ to $h(1) = 1$. Such a function is introduced to avoid the driving**
 199 **forces in the bulk region, but also to enhance numerical stability in applied computations. In**
 200 **most cases, the function is taken as: $h(\phi) = \phi$. $\tilde{\mu}^i$ is the diffusion potential of the component i**
 201 **introduced as a Lagrange multiplier to conserve the mass balance between the phases**

203 $c^i = \sum_{\alpha=1,\dots,N} \phi_i c_\alpha^i$. The chemical part f^{chem} depends on the sum of the bulk free energy density
 204 $f_\alpha(c_\alpha^i)$ of all phases and the contribution of diffusion potential $\tilde{\mu}^i$.

205 Based on the free energy functional shown in Eqs.(1) ~ (3), the MPF evolution equations
 206 can be then derived based on the above free energy functional [30-32]:

$$\dot{\phi}_i = \sum_{\beta=1,\dots,N} \mu_{\alpha\beta} \left\{ \sigma_{\alpha\beta} \left[\phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + \frac{\pi^2}{2\eta_{\alpha\beta}^2} (\phi_\alpha - \phi_\beta) \right] + \frac{\pi}{\eta_{\alpha\beta}} \sqrt{\phi_\alpha \phi_\beta} \Delta g_{\alpha\beta} \right\} \quad (4)$$

$$\dot{c}^i = \nabla \sum_{\alpha=1,\dots,N} \sum_{j=1,\dots,k} \phi_\alpha D_\alpha^{ij} \nabla c_\alpha^j \quad (5)$$

209 $\mu_{\alpha\beta}$ is interfacial mobility between the α and β phases. In Eq.(4), the evolution of the phase field

210 ϕ depends on two terms, i.e., the first curvature term $\left(\phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + \frac{\pi^2}{2\eta_{\alpha\beta}^2} (\phi_\alpha - \phi_\beta) \right)$, and

211 the second driving force term $\Delta g_{\alpha\beta}$. $\Delta g_{\alpha\beta}$ is the local deviation from thermodynamic
 212 equilibrium given as

$$\Delta g_{\alpha\beta} = -f_\alpha(c_\alpha^i) + f_\beta(c_\beta^i) + \tilde{\mu}^i (c_\alpha^i - c_\beta^i) \quad (6)$$

214 It should be noted that the chemical driving force $\Delta g_{\alpha\beta}$ can be obtained by linking to the real
 215 CALPHAD thermodynamic databases through the TQ-interface of Thermo-Calc software [33].

216 D_α^{ij} represents the multi-component diffusion matrix for all phase α and all solute interaction ij .

217 Actually, Eq.(4) cannot be directly derived from the free energy functional, but is a so-called
 218 antisymmetric approximation, which resigns from thermodynamic consistency at the multiple
 219 junctions [31, 32]. This is commonly done in most simulations using the MPF model [32], and
 220 has been incorporated in the MICRESS (MICROstructure Evolution Simulation Software) code
 221 [34], which will be utilized for the present phase-field simulation.

3.2 Materials parameters

224 The prerequisite for a quantitative phase-field simulation is to link the phase-field code to
 225 the CALPHAD thermodynamic and atomic mobility databases, in order to provide realistic
 226 chemical driving force, diffusion potentials, and chemical mobility/diffusivity at any
 227 composition and temperature. It should be noted that the chemical driving force $\Delta g_{\alpha\beta}$ can be
 228 obtained by linking to the real CALPHAD thermodynamic descriptions, while M_α is the
 229 chemical mobility in the α phase and can also be directly obtained from the CALPHAD atomic
 230 mobility descriptions.

231 For the Ni-Si system, the thermodynamic descriptions from *Du* and *Schuster* [35, 36] were
232 employed to provide the chemical driving force and diffusion potentials during the present
233 phase-field simulation. As we only study the agglomeration at low temperatures, there is no
234 phase transition from the NiSi phase to the NiSi₂ phase since the nucleation of NiSi₂ usually
235 occurs above 750°C [37]. Thus, only the NiSi and (Si) phases were considered in the simulation.
236 Each phase should obey the conservation of volume or mass during the agglomeration. In order
237 to respect the conservation of volume or mass for the NiSi and (Si) phases in the simulation, an
238 extremely tiny solid solubility of the (Si) phase was set manually in the thermodynamic
239 descriptions (see in Table S1), and then the initial composition of the (Si) phase was set as the
240 solid solubility limit at the corresponding temperature (see in Figures S1 and S2).

241 Concerning the atomic mobility, Luo *et al.* have shown that the diffusion along with the
242 interface of the slow diffusion Si species is crucial for the agglomeration process, and the
243 diffusion of Si at the NiSi/Si interface $D_{\text{NiSi/Si}}^{\text{Si}}$ was roughly estimated as 1×10^{-11} cm²/s at 600°C
244 [18]. This value is about 4 orders of magnitude larger than the self-diffusion of Si in NiSi [18,
245 38], and 14 orders of magnitude larger than the self-diffusion of Si in Si (i.e., 2×10^{-25} cm²/s)
246 [39]. Thus, only the value of Si diffusion along the NiSi/Si interface is considered in the
247 simulation.

248 Moreover, reliable thermophysical parameters are also critical for performing the
249 quantitative phase-field simulation. Two important interfacial energies are the NiSi/Si
250 interfacial energy ($\sigma_{\text{NiSi/Si}}$) and the NiSi grain boundary energy ($\sigma_{\text{NiSi/NiSi}}$). However, no reported
251 data are available for the two interfacial energies. Since the high-angle grain boundary energies
252 of metals are often found to be roughly 1/3 of their surface energies [40], the NiSi grain
253 boundary energy can be roughly estimated to 1/3 of its surface energy. Recently, Luo *et al.* have
254 observed the triple junction with NiSi-Si-vacuum by the APT (Atom Probe Tomography) under
255 the equilibrium state [18]. From this observation and the known Si surface energy, the NiSi
256 surface energy and the NiSi/Si interface energy can be thus calculated. As the Si surface energy
257 ranges from 0.84×10^{-4} J/cm² to 1.90×10^{-4} J/cm² for different cleavage-surfaces [41], the value
258 of 1.90×10^{-4} J/cm² for the Si surface energy corresponding to the (110) plane, has been used in
259 this work since it corresponds to the (110) plane, which is often observed in the axiotaxial
260 texture. Therefore, the NiSi surface energy and the NiSi/Si interface energy were evaluated to
261 be 1.8×10^{-4} J/cm² and 4.94×10^{-5} J/cm², respectively. Furthermore, the NiSi grain boundary
262 energy was taken as 6.0×10^{-5} J/cm² (i.e., 1/3 of the NiSi surface energy). The interfacial mobility
263 between different interaction pairs was evaluated according to Eq.(35) in Ref. 33 to achieve a

diffusion-control process. All the simulation parameters used in this work are listed in [Table S2](#).

In order to study the effect of texture on the agglomeration (or dewetting), the interfacial energy and interfacial mobility for cubic phase Si and the orthorhombic NiSi phase were considered to be dependent on the interface misorientation. The reduction of interfacial energy as a function of misorientation angle θ was taken to be governed by the Read-Shockley law [42] implemented in MICRESS:

$$\sigma(\theta) = \sigma_{HAB} \frac{\theta}{\theta_{HAB}} \left[1 - \ln \left(\frac{\theta}{\theta_{HAB}} \right) \right] \quad (7)$$

where σ_{HAB} and θ_{HAB} are the interfacial energy of a high angle grain boundary and the misorientation corresponding to the transition angle between low and high angle grain boundaries. The reduction of interfacial mobility as a function of the misorientation was taken to be described by the sigmoidal law suggested by Humphreys [43]:

$$\mu(\theta) = \mu_{HAB} \left(1 - \exp \left[-B \left(\frac{\theta}{\theta_{HAB}} \right)^n \right] \right) \quad (8)$$

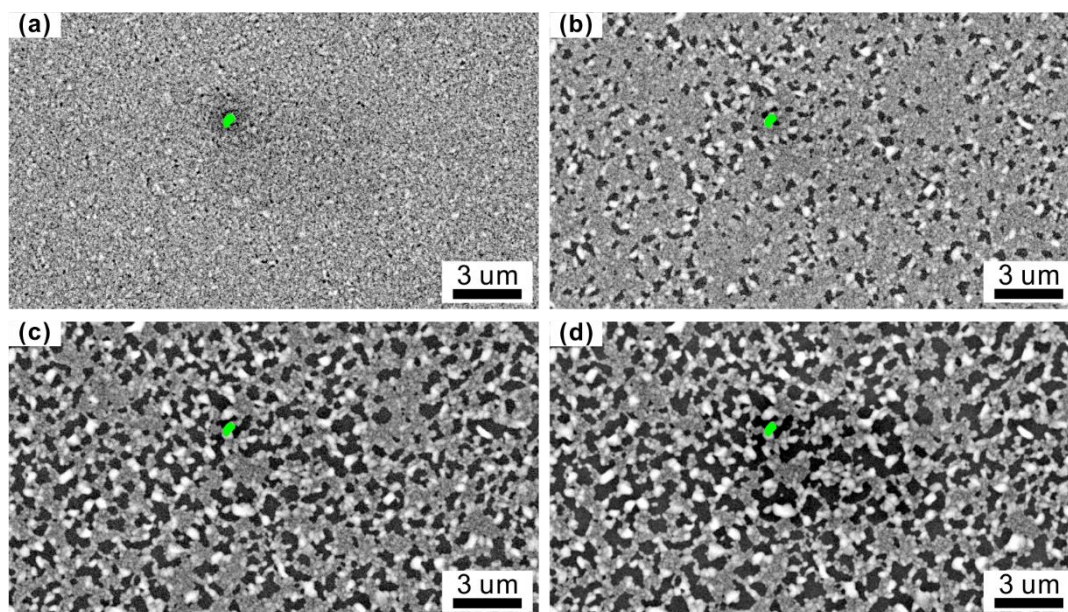
where μ_{HAB} is the interfacial mobility of a high angle grain boundary, B and n are two model parameters usually set to B=5 and n=4. Figure S3 shows the curve form of Eq.(7) and Eq.(8) with $\theta_{HAB}=15^\circ$. In the present phase field simulations, the orientation of each grain was defined by Euler angle, and the misorientation θ between NiSi grains and Si substrate, as well as that between neighbor NiSi grains, was calculated. Then, $\sigma(\theta)$ and $\mu(\theta)$ for each interface were calculated based on the Eq.(7) and Eq.(8) with the transition angle $\theta_{HAB}=15^\circ$, and used in the phase-field evolution equation (i.e., Eq.4) for describing the evolution of phase field. For the NiSi grain, different interfaces have different interfacial energies and mobilities, which depend on the misorientation between two grains or phases on both sides of the interface.

4. Experimental results

4.1 Microstructure evolution observed by the in-situ SEM

Figure 1 shows low magnification SEM images of a 30 nm NiSi film on Si(100) substrate *in-situ* heating at 600°C. Different phases could be distinguished from the contrast in the SEM images. The white and gray regions respectively correspond to the big NiSi grains and the smaller ones, while the black region is the exposed Si surface (the green region indicates dust on the sample surface). **Fig. 1a** shows the NiSi thin film morphology after 23 min annealing at

294 600°C. The agglomeration of NiSi thin film is at the beginning stages, as indicated by small
 1 295 black regions of Si. The initial NiSi grains are small and close to each other. With increasing
 2 296 the annealing time from 23 min to 32 min, most NiSi grains gradually shrink (small grains in
 3 297 grey), while some specific NiSi grains grow rapidly, appearing as large grains in white (**Fig.**
 4 298 **1b**). Meanwhile, the fraction of exposed Si increases. With the agglomeration process, the
 5 299 expansion direction of the exposed Si depends on the consumption of the small NiSi grains, as
 6 300 the large NiSi grains achieve a slow-growing stage and stop the expansion of the exposed Si
 7 301 (**Fig. 1(c-d)**). This shows that the agglomeration of the NiSi grains causes an increase in the
 8 302 exposed Si. Due to the large contrast between NiSi and Si (grey/white vs. black) and because
 9 303 of the difficulty to separate the grey level associated with the NiSi grains, the kinetic of the
 10 304 exposed Si would be used to study the agglomeration kinetics of the NiSi thin film on the Si(100)
 11 305 substrate.



306
 307 Fig. 1. SEM images showing microstructure evolution with time of the same area, during *in-*
 308 *situ* heating at 600°C, of a 15nm Ni thin film on Si(100) substrate: (a) 23 min (b) 32 min (c)
 309 194 min (d) 287 min. The white and gray regions are the NiSi phase, the black phase is the
 310 exposed Si surface. (the green region reveals dust on the surface's sample).
 311

4.2 Agglomeration kinetics

312
 313 **Figure 2** shows the kinetic of the exposed Si relative to a 15 nm Ni film deposited on Si(100)
 314 substrate annealing at 600°C determined from *in-situ* SEM results. As shown in **Fig. 2a**, the
 315 fraction of the exposed Si increases very slowly before 23 min, but then increases quickly
 316 following a power function (the details will be introduced later). **Fig. 2a** also shows that the
 317 number of exposed Si regions (blue curve, right axis) first increases fast to reach a maximum,

318 then decreases slowly and tends to a stable value. During the heating stage, it takes 40 min to
1 319 reach 600°C, as shown in Figure S4. However, the agglomeration of NiSi grains happens
2 320 already before the temperature reaches 600°C, i.e., before 40 min. Prior to the agglomeration
3 321 of NiSi, solid state reaction between Ni thin film and Si substrate to form NiSi as well as the
4 322 grooving at the grain boundaries of NiSi have also happened during the heating process. Thus,
5 323 it is difficult to know the accurate starting time of agglomeration and to compare agglomeration
6 324 kinetics with other experimental results from different holding temperatures or samples. In
7 325 addition, the exposed Si fraction is too small to be accurately determined at these initial stages.
8 326 Therefore, we prefer not to take into account the early stage and to start at a time corresponding
9 327 to a given $f_0(\text{e-Si})$ value, representing the initial fraction of the exposed Si that can be easily
10 328 measured. The value of $f_0(\text{e-Si})$ of 3 % was selected in our work and the time-shifted kinetics
11 329 (corresponding to a time shift of about 26 min) of the exposed Si are shown in **Fig. 2b**. When
12 330 the area fraction of exposed Si reaches 3 %, the temperature is around 550°C (26 min), which
13 331 is not so far from 600°C, the detail is shown in Figure S4.

25 332 The shifted kinetics of exposed Si for a 15 nm Ni thin film on Si(100) substrate for two
26 333 experiments with different magnifications (Exp-1: low-magnification with area=303 μm^2 and
27 334 Exp-2: high-magnification with area=20.3 μm^2 - see in Figure S5) are shown in **Fig. 2b**. In
28 335 order to assess the error of the area fraction of exposed Si, each image from the low-
29 336 magnification *in-situ* SEM experiment (Exp-1 with a total area of 303 μm^2 : 23 $\mu\text{m} \times 13 \mu\text{m}$) was
30 337 randomly divided into 120 regions, which size is the same as the high-magnification *in-situ*
31 338 SEM experiment (Exp-2 with a total area of 20.3 μm^2 : 5.4 $\mu\text{m} \times 3.8 \mu\text{m}$). The exposed Si area
32 339 fraction was determined for each of these regions to obtain the average, minimum, and
33 340 maximum of this value. In **Fig. 2b**, the orange line represents the average area fraction and the
34 341 orange region represents the measurement error from maximum and minimum. **Fig. 2b** shows
35 342 that the kinetics from the high-magnification *in-situ* experiment is within the error range of the
36 343 low-magnification *in-situ* experiment. Moreover, the average area fraction of exposed Si can
37 344 be well fitted by a power function ($y=a \cdot x^b$, where a is 7.7 and b is 0.28, and the fitting goodness,
38 345 R^2 , is 0.972). Therefore, the area fraction of exposed Si for larger $f_0(\text{e-Si})$ than 3 %, increases in
39 346 a power function.

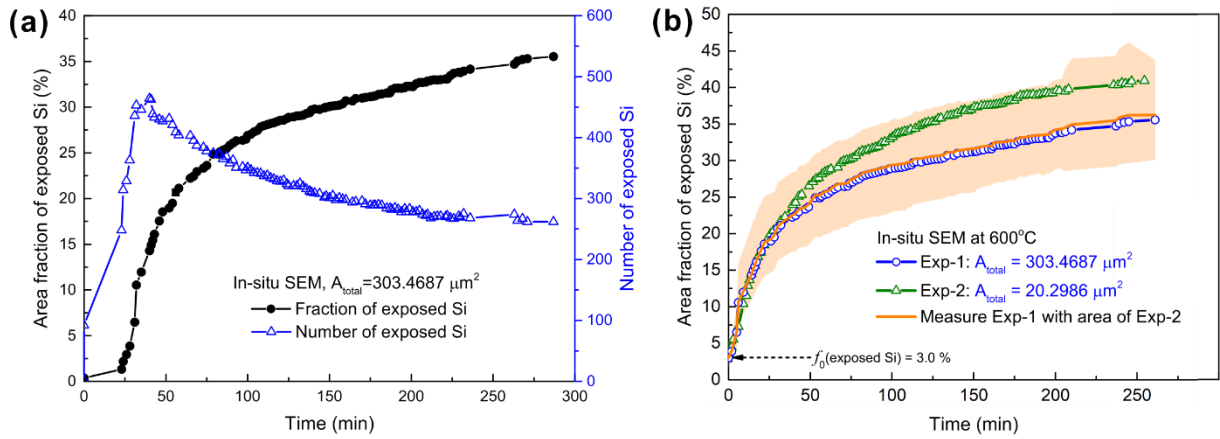


Fig. 2. Kinetic of exposed Si during *in-situ* SEM at 600°C of a 15 nm Ni film on Si(100) substrate: (a) Area fraction and the number of the regions for the surface-exposed Si with time, (b) Shifted kinetics of exposed Si from *in-situ* SEM results with different magnifications (Area=303 μm^2 and Area=20.3 μm^2): the orange region represents the measurement error of the low-magnification experiment (Exp-1 with a total area of 303.47 μm^2) using the same measured size with the high-magnification experiment (Exp-2 with the total area of 20.30 μm^2). This error range is from the maximum and the minimum.

4.3 Long-time annealing

In order to study the different states of NiSi agglomeration, long-time annealing of the 15 nm Ni film on Si(100) substrate was performed at 600°C for 24 hours, and a sample was also annealed at 600°C for 60 s by RTP for comparison.

XRD and low kV SEM images (**Fig. 3**) indicate that there is only the NiSi phase after long-time annealing at 600°C for 24 hours. Furthermore, XRD analysis (not shown) of a sample with vacuum annealing at 400°C for 1 hour was used to ensure that the Ni film is fully transformed to the NiSi well below 600°C. **Fig. 3a** shows the relative intensity of the XRD peak change with annealing time. In particular, there is an increase in the (013) peak intensity that indicates a change in texture. **Fig. 3b** shows the morphology of NiSi that is characteristic of a severe agglomeration with the formation of NiSi islands. The surface morphology and grain boundary of NiSi grains can be clearly observed in **Fig. 3b** zoom image.

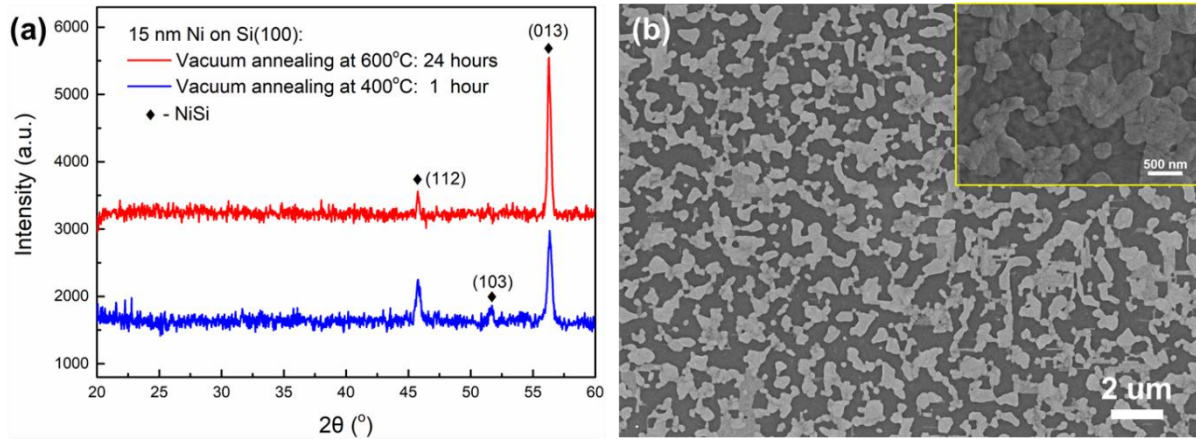


Fig. 3. (a) XRD scan at room temperature and (b) Low kV SEM images for a 15nm Ni film on Si(100) substrate with annealing 24 h at 600°C. The illustration in (b) shows the surface morphology of NiSi.

Figure 4 displays the EBSD orientation maps and pole figures for a 15nm Ni film on Si(100) substrate for 60 s and 24 hours at 600°C. In **Fig. 4a** and **Fig. 4b**, the black region is the Si substrate, and each color represents an orientation of the NiSi grains. After annealing at 600°C for 24 hours, some phenomena can be clearly observed: *i*) a number of small grains have disappeared, and there is a general grain growth with the average grain radius increasing from 137 nm to 193 nm, as shown in **Fig. 4c**, and *ii*) some grains with a particular orientation grow abnormally. Pole figures show that these special grains with particular orientations have similar fiber texture while grains with random orientation disappear, as shown in **Fig. 4d** and **Fig. 4e**. These results are in good agreement with De Keyser's work on 60 nm NiSi films with a dwell time of 72 h at 550°C [9]. These special grains (such as axiotaxy and epitaxy) have smaller interface energy than the random orientation grains due to matching with the Si substrate in one (axiotaxy) or two dimensions (epitaxy): this causes abnormal grain growth during the agglomeration of NiSi grains [4].

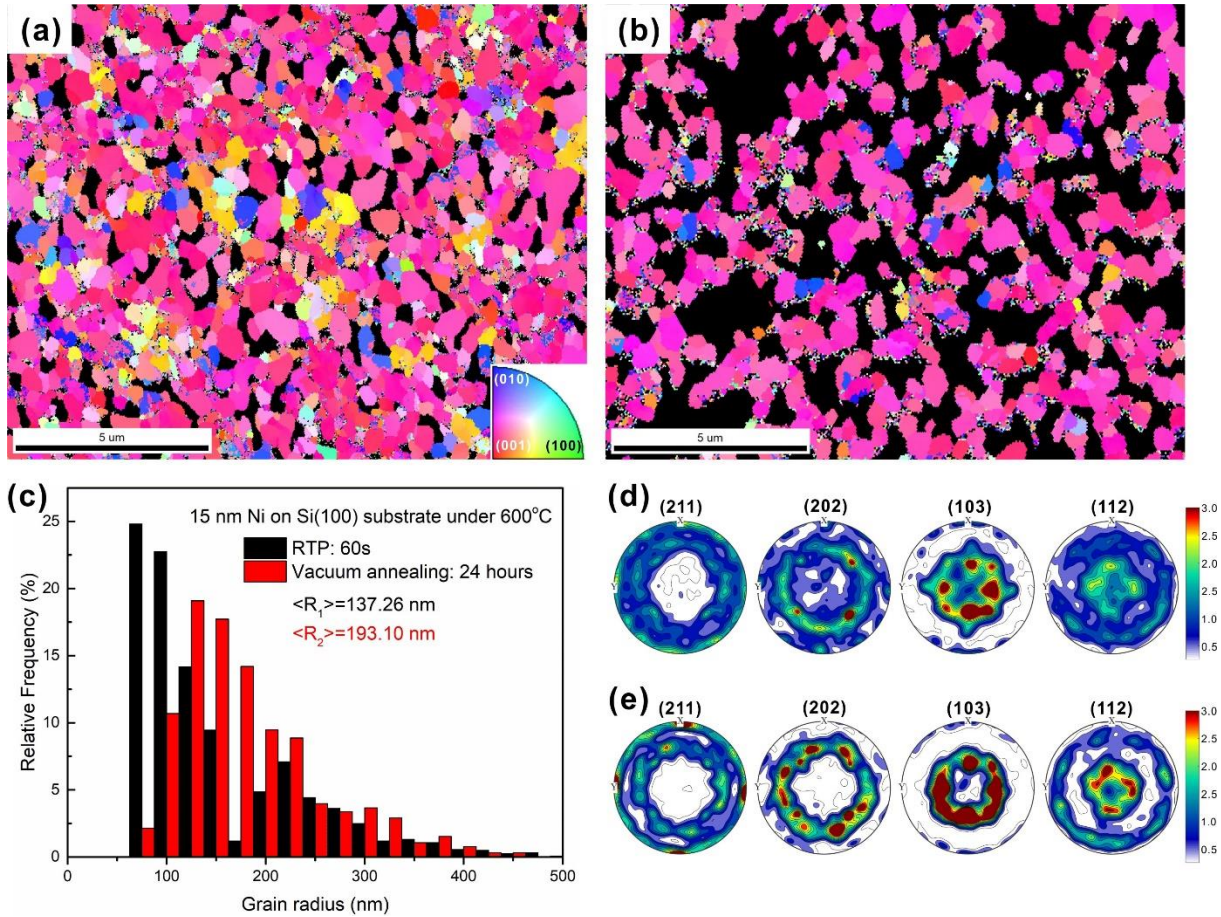


Fig. 4. EBSD orientation maps and pole figures for 15nm Ni film on Si(100) substrate after: (a) RTP at 600°C for 60 s and (b) vacuum annealing 24 hours at 600°C. (c) is the grain size distribution. Pole figures for 15nm Ni film on Si(100) substrate are shown in: (d) for RTP at 600°C for 60 s, and (e) for vacuum annealing 24 hours at 600°C.

5. MPF simulation results

In order to reveal the mechanism of NiSi agglomeration, the effect of NiSi grains orientation on the agglomeration has been studied by 3D phase-field simulations, focusing on different volume fractions and misorientation distributions of the NiSi grains.

5.1 Effect of NiSi orientation

The driving force for agglomeration is mainly the reduction of interfacial energy (including grain boundary energy) in the system. Misorientation affects the interfacial energy/grain boundary energy and the interfacial mobility between the NiSi grains and the Si substrate. The reduction factors are calculated by Eq.(7) and Eq.(8). **Table 1** lists the NiSi grains orientation types (1 to 4) used in the simulations (A to F groups). Orientation is not considered in type 1 NiSi grains. For the other types, the orientations are defined by the Euler angles. For type 2 NiSi grains, the Euler angles, $\varphi=270^\circ$, $\theta=20^\circ$, $\psi=90^\circ$, noted NiSi($\varphi=270^\circ$, $\theta=20^\circ$, $\psi=90^\circ$), are

407 **representative of the** Euler angles for the NiSi(103) axiotaxy. In order to conveniently study the
 408 effect of misorientation on agglomeration, the orientation of type 3 NiSi($\varphi=270^\circ$, $\theta=35^\circ$, $\psi=90^\circ$)
 409 and 4 NiSi($\varphi=270^\circ$, $\theta=30^\circ$, $\psi=90^\circ$) grains is set as high-angle **misorientation** grains (**HAMG**)
 410 compared to the type 2 NiSi($\varphi=270^\circ$, $\theta=20^\circ$, $\psi=90^\circ$) grains. The orientation of Si substrate is
 411 also set relative to the type 2 NiSi grains, as Si($\varphi=270^\circ$, $\theta=25^\circ$, $\psi=90^\circ$). It was chosen to always
 412 keep some misorientation between NiSi grains and Si substrate to allow the evolution of the
 413 system. Since only θ is changed for all the orientations, we will now use the following
 414 simplified notation: type 2 NiSi($\theta=20^\circ$), type 3 NiSi($\theta=35^\circ$), type 4 NiSi($\theta=30^\circ$), and Si($\theta=25^\circ$).
 415 The misorientation limit for high angle boundaries is set to 15° for NiSi/Si and NiSi/NiSi in the
 416 simulation. For simulations A to F, the simulated domain is $100 \times 100 \times 40$ grids, grid size Δx is
 417 5 nm, and the interface thickness is $4\Delta x$. The thickness of the NiSi film is set to 30 nm, and the
 418 initial average grain radius is 85 nm, closing to the *in-situ* SEM experiments at 600°C . Periodic
 419 boundary conditions are used along with the four horizontal directions (west, east, south, north),
 420 and isolation conditions are used for the top and bottom boundaries in all simulations. Only one
 421 set of thermophysical parameters was used in all simulations, which were obtained through
 422 reasonable evaluation, as described in *Section 3.2*. The volume fraction of the NiSi phase and
 423 the Si substrate are conserved in all simulations. The parameters (interfacial energy and
 424 interfacial mobility) used in the simulations A to F are listed in **Table S3**.

426 **Table 1** Volume fractions of different orientations in NiSi film in the simulations A to F.

Type of NiSi grains	Orientation [Euler angle, (φ, θ, ψ)]	Volume fraction					
		A	B	C	D	E	F
1	--	100	--	--	--	--	--
2*	$270^\circ, 20^\circ, 90^\circ$	--	22.65	43.21	69.23	77.25	--
3	$270^\circ, 35^\circ, 90^\circ$	--	77.25	56.69	30.67	22.65	69.23
4	$270^\circ, 30^\circ, 90^\circ$	--	--	--	--	--	30.67

427 * NiSi($270^\circ, 20^\circ, 90^\circ$) is one of Euler angle of the axiotaxy NiSi(103).

429 **Figure 5a** illustrates the effect of the misorientation on the agglomeration of NiSi film from
 430 the present phase-field simulations. Firstly, in simulation A, all NiSi grains are isotropic without
 431 orientation. The evolution of NiSi grains is then controlled by grain growth and interface
 432 diffusion, as shown in **Fig. 5a**. Indeed, **Fig. 5a** shows that grooving and agglomeration happen
 433 and lead to the isolated NiSi islands. Then some islands grow at the expense of the other and

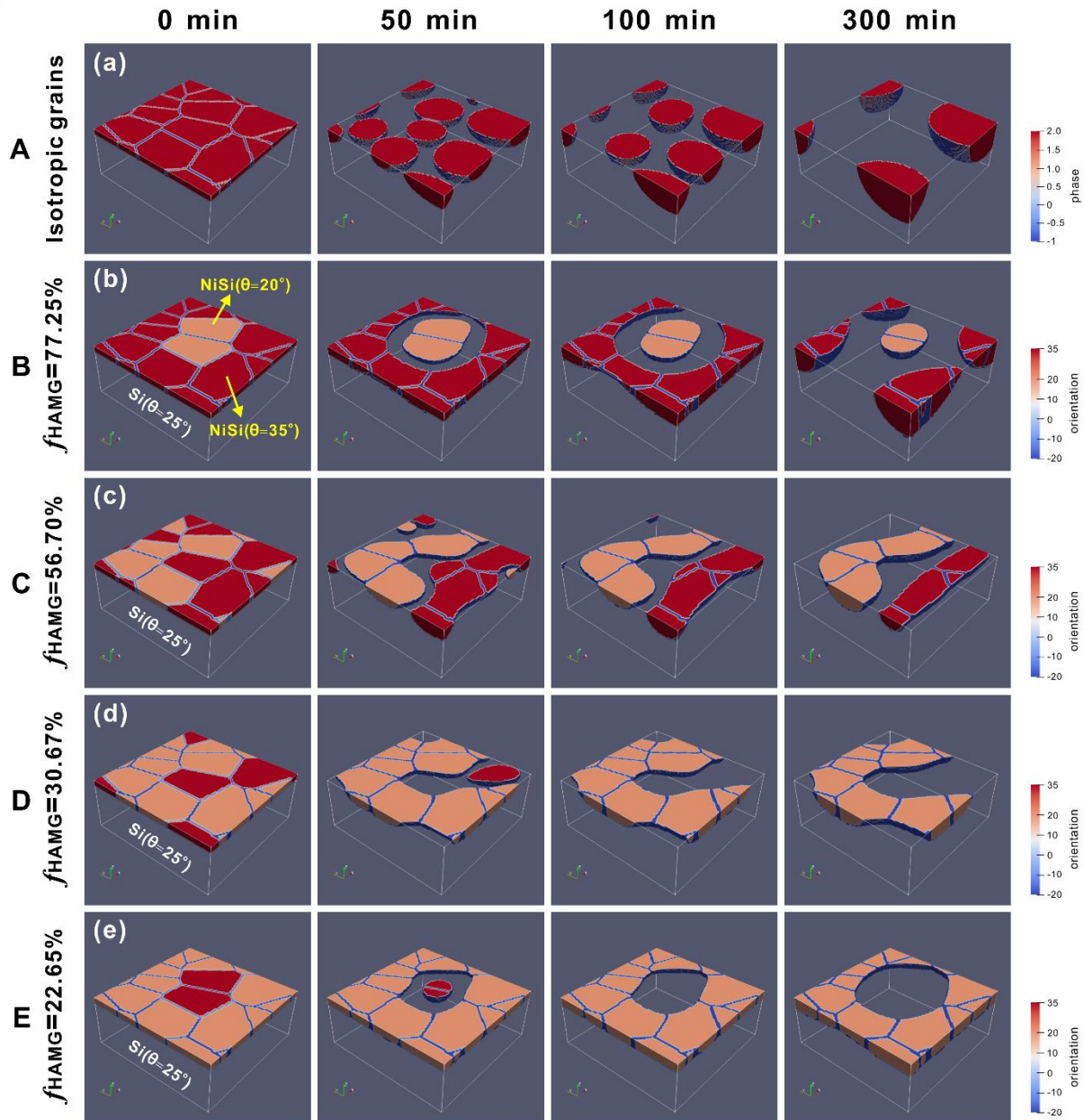
434 finally form a big isolated island. The kinetic of the exposed Si fraction for simulation A is
435 shown in **Fig. 6a**.

436 In order to check the effect of misorientation and texture on agglomeration, special
437 orientations between the NiSi grain and Si substrate were introduced in other simulations. In
438 simulation B, 77.25% of the NiSi grains are the type 3 with a 10° misorientation compared to
439 Si substrate (relatively high-angle misorientation-HAM that can be representative of the
440 random orientation grains), and 22.75% are type 2 grains with a 5° misorientation (low-angle
441 misorientation, LAM, representative of epitaxy or axiotaxy grains). It means that 77.25% of
442 NiSi grains (HAMG) have higher interfacial energy and mobility than the other grains (**low-
443 angle misorientation** grains-LAMG). Note that the interfacial energy and mobility between the
444 same type NiSi grains are close to 0 due to the 0° misorientation. **Figure 5b** shows the evolution
445 of the microstructure for simulation B (the HAMG are in red and the LAM ones in orange): the
446 abnormal grain growth of the LAM NiSi grains is clearly observed, and the evolution of HAMG
447 is faster than the LAMG. This phenomenon is very similar to the *in-situ* SEM results. Moreover,
448 the kinetics of the exposed Si fraction of simulation B with orientated grains is close to the *in-
449 situ* results, as shown in **Fig. 6a**. It is slower than simulation A with isotropic grains. By
450 comparing the results of simulations A and B, it is clearly found that the misorientation between
451 the NiSi grains and the Si substrate and the one between the NiSi grains strongly affect the
452 agglomeration of the NiSi film by affecting the interfacial energies and mobilities. Furthermore,
453 as the effect of misorientation on the agglomeration of NiSi is dependent on the volume fraction
454 and misorientation distribution, more phase-field simulations will now be presented to study
455 these factors.

5.2 Effect of the different volume fractions of different orientations

456
457 In order to study the effect of different volume fractions of NiSi orientations on
458 agglomeration, simulations (B to E) with different volume fractions of NiSi orientations but
459 with the same NiSi grain structure were performed (**Fig. 5b-e**). Two types of NiSi grains
460 (misorientations are 5° and 10° with Si substrate) with different fractions are set in the
461 simulations B to E, and the volume fraction of the HAM NiSi grains in the NiSi film varies
462 from 77.25% to 22.65%. These simulation results show that the lower fraction of the HAMG,
463 the lower fraction of exposure of Si substrate. **Figure 6a** shows the kinetics of the exposed Si
464 from the *in-situ* SEM and the simulation A to E with shifted time using $f_0(\text{e-Si}) = 3.0\%$ as the
465 initial time. The kinetics of simulations B to E confirms that a smaller fraction of HAMG slow

467 down the exposure rate of the Si substrate. It means that the LAMG are efficient in reducing
 468 agglomeration. Moreover, the simulations show that when the fraction of HAMG lies between
 469 30.67%~56.70%, the kinetics of the surface-exposed Si are in good agreement with the *in-situ*
 470 SEM results. In other words, when the fraction of LAMG is 43.30%~69.33%, the kinetic of the
 471 exposed Si obtained by the phase-field simulations reproduce the *in-situ* SEM results.



472 Fig. 5. Simulated microstructure evolution for different high-angle **misorientation** grains
 473 (HAMG) fraction of the agglomeration for a 30 nm NiSi film on Si substrate at 600°C: (a)
 474 isotropic grains, (b) $f_{\text{HAMG}}=77.25\%$, (c) $f_{\text{HAMG}}=56.70\%$, (d) $f_{\text{HAMG}}=30.67\%$, and (e)
 475 $f_{\text{HAMG}}=22.65\%$. Different colors represent the different NiSi orientations, while the Si substrate
 476 is transparent.

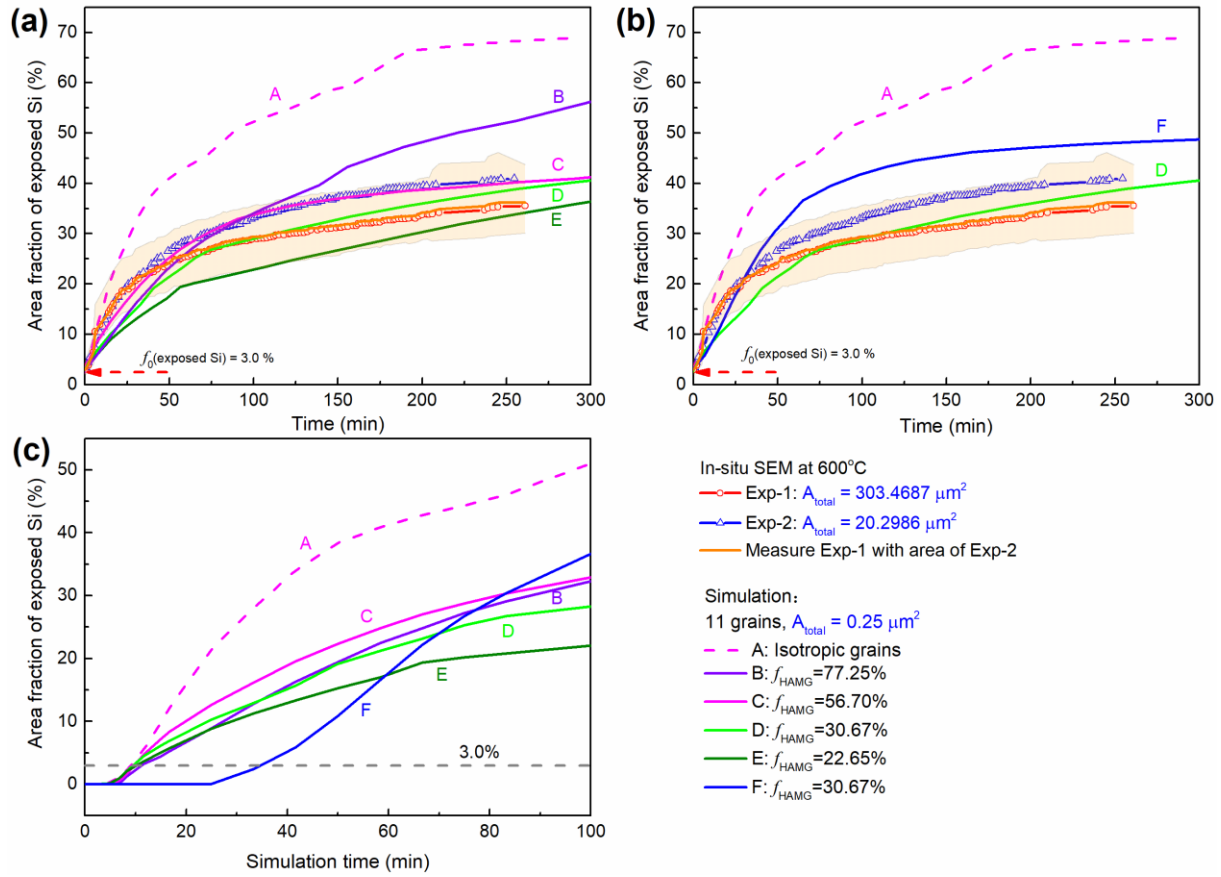


Fig. 6. Kinetics of the exposed Si area fraction with shifted time of *in-situ* SEM and simulated results for a 30 nm NiSi film on a monocrystal Si substrate at 600°C. The area fraction of exposed Si taken as initial time is equal to 3.0% in (a) and (b): (a) simulation A to E groups, (b) simulation A, D, and F groups, (c) simulation A to F during the early stage with a none shifted time.

5.3 Effect of different misorientation distributions

The simulations D and F were performed to study the effect of different misorientation distribution with the same volume fraction on the agglomeration of NiSi grains. In the two simulations, the volume fractions of HAM type 3 NiSi($\theta=35^\circ$) grains are equal to 30.67%. Type 2 NiSi($\theta=20^\circ$) grains are LAMG in simulation D with Si($\theta=25^\circ$) substrate, and type 4 NiSi($\theta=30^\circ$) are LAMG in simulation F with Si($\theta=20^\circ$) substrate, the misorientation between NiSi and Si substrate changes from 5° and 10° in simulation D to 10° and 15° in simulation F. Since the Si orientation is different for the two simulations (**Fig. 7**), the misorientation between the NiSi grains also changes from 10° to 5° from the simulations D to F. On the one hand, as the total interfacial energy of the NiSi/Si interface increases in simulation F compared to simulation D, the evolution of NiSi grains with the Si substrate should be enhanced. **Figure 6b** compares the kinetics of the exposed Si obtained by *in-situ* SEM with the results of time-shifted simulations A, D, and F: the kinetics of the exposed Si substrate is found to be faster for

simulation F than that for simulation D, as expected. On the other hand, the total energy of NiSi/NiSi grain boundary decreases in simulation F compared to simulation D, and the evolution between NiSi grains with different orientations should be weakened. **Fig. 7a** and **Fig. 7b** for a time of 50 min show that the evolution between NiSi grains with different orientations is indeed weakened in simulation F and slower than in simulation D.

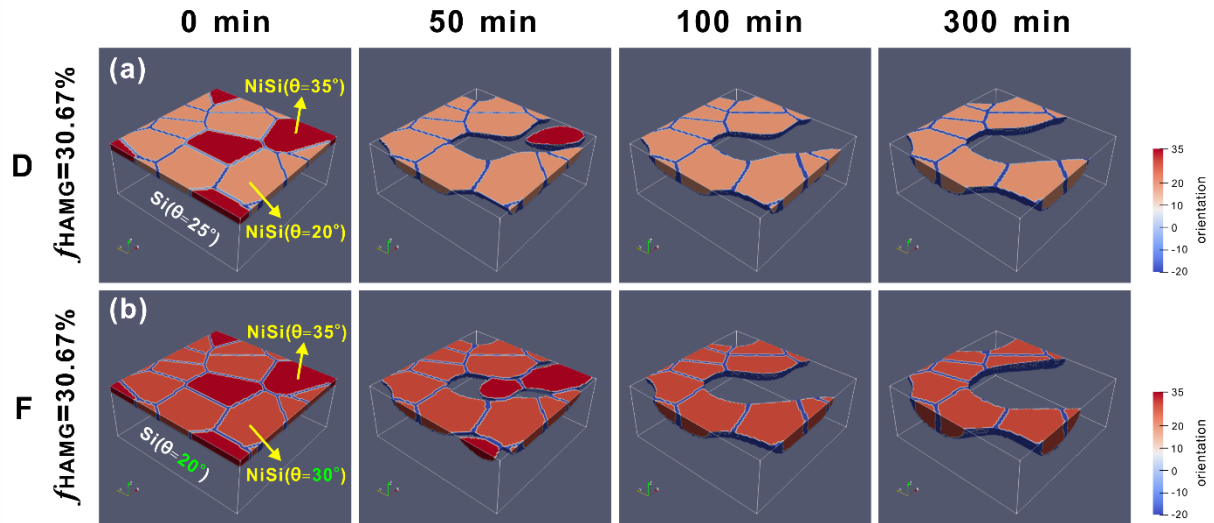
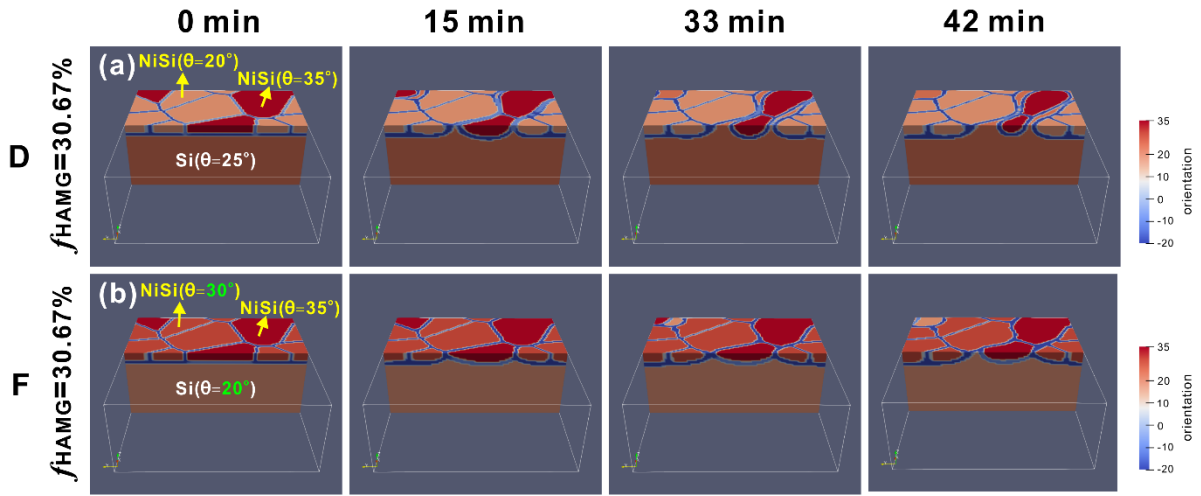


Fig. 7. Simulated microstructure evolution for different misorientation distributions with the same volume fraction on the agglomeration for a 30 nm NiSi film on Si substrate at 600°C: (a) $f_{\text{HAMG}}=30.67\%$, with $\theta_{\text{NiSi}^2/\text{Si}}$ is 5° , $\theta_{\text{NiSi}^3/\text{Si}} = 10^\circ$, $\theta_{\text{NiSi}^2/\text{NiSi}^3} = 15^\circ$, (b) $f_{\text{HAMG}} = 30.67\%$, with $\theta_{\text{NiSi}^3/\text{Si}} = 15^\circ$, $\theta_{\text{NiSi}^4/\text{Si}} = 10^\circ$, $\theta_{\text{NiSi}^3/\text{NiSi}^4} = 5^\circ$. The different colors represent the different NiSi orientations, while the Si substrate is transparent.

5.4 Grooving

Figure 8 shows the evolution of the longitudinal cross-section of the phase-field simulated microstructure with different misorientation distributions but the same volume fraction (simulation D and simulation F) during the early stage of the agglomeration for a 30 nm NiSi film on Si substrate at 600°C. Compared to the simulation D, the grooving process is weakened in simulation F due to the decrease in misorientation between NiSi grains, even if the increase in the NiSi/Si misorientation should accelerate agglomeration in simulation F. **This behavior was confirmed by using a bicrystal structure (Figure S6) and the phase-field simulation (Figure S7): the grooving phenomena was faster for high angle grain boundaries even if the misorientation with the substrate is lower.** **Figure 6c** shows the early stage of the exposed Si for simulation D and F: when the fraction of exposed Si is less than 3.0%, grooving is the primary microstructure evolution process in this case. The kinetics of the grooving process depends strongly on the misorientation between NiSi grains, but is less sensitive to the volume

526 fraction of the different misorientations. A small misorientation between the NiSi grains will
 527 be an advantage to delaying the grooving of the NiSi grains, and thus the agglomeration.



528
 529 Fig. 8. Longitudinal cross-section of the simulated microstructure evolution for different
 530 misorientation distributions with same volume fraction on the agglomeration for 30 nm NiSi
 531 film on Si substrate at 600°C: (a) $f_{\text{HAMG}}=30.67\%$, with $\theta_{\text{NiSi}^2/\text{Si}} = 5^\circ$, $\theta_{\text{NiSi}^3/\text{Si}} = 10^\circ$, $\theta_{\text{NiSi}^2/\text{NiSi}^3} =$
 532 15° , (b) $f_{\text{HAMG}}=30.67\%$, with $\theta_{\text{NiSi}^3/\text{Si}} = 15^\circ$, $\theta_{\text{NiSi}^4/\text{Si}} = 10^\circ$, $\theta_{\text{NiSi}^3/\text{NiSi}^4} = 5^\circ$. Different colors
 533 represent the different NiSi orientations, while the Si substrate is transparent.

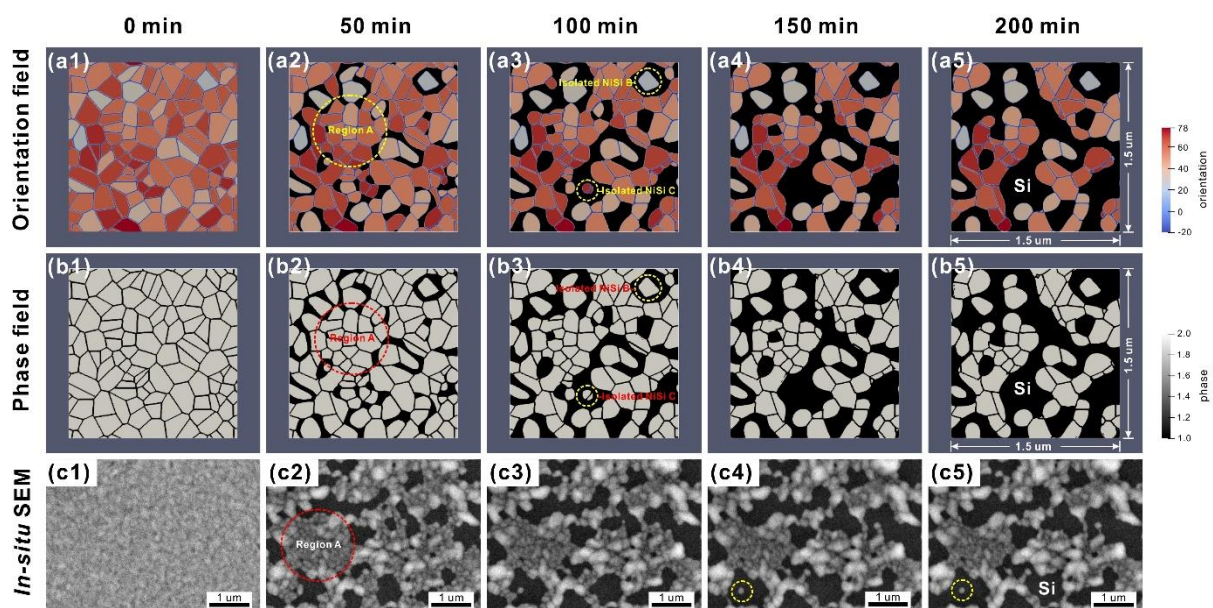
535 5.5 Application in real NiSi polycrystalline films

536 As discussed above, the misorientation distribution and the volume fraction of NiSi grains
 537 can strongly affect the agglomeration process in 30 nm NiSi films on a monocrystal Si substrate.
 538 In order to better account for the complexity of the NiSi polycrystalline film and compare it
 539 with the *in-situ* SEM results, a larger number of NiSi grains with an orientation distribution
 540 close to the experimental one was used in the following simulation. The initial microstructure
 541 with 107 grains was constructed based on the experimental orientation distribution in **Fig. 4a**
 542 and the average grain size in **Fig. 2a** (the details are given in **Figure S8**). The change of
 543 misorientation on the interfacial energies and mobility was calculated based on Eq.(7) and
 544 Eq.(8). The simulated domain is $300 \times 300 \times 40$ grids, grid size Δx is 5 nm, and the interface
 545 thickness is $4\Delta x$. The NiSi film thickness is 30 nm, and the initial average radius of NiSi grains
 546 was set to 81.8 nm, which is consistent with the *in-situ* SEM results (**Fig. 2a**). As for the other
 547 simulations, periodic boundary conditions were used in the four horizontal directions (west,
 548 east, south, north), and isolation conditions at the top and bottom.

549 **Figure 9** shows the microstructure evolution during agglomeration obtained by phase-field
 550 simulations and *in-situ* SEM for a 30 nm NiSi film on a monocrystal Si substrate at 600°C. As
 551 detailed above, the initial simulated structure was constructed based on the experimental

552 orientation distribution and the initial experimental grain size. As shown in **Fig. 9a**, the
 553 grooving always occurs first in the NiSi boundary with large misorientations between them
 554 (large difference in colors). A significant difference of misorientation between the NiSi grains,
 555 resulting in a significant difference in energy and mobility of NiSi/NiSi grain boundary, will
 556 accelerate the grooving, as discussed in *Section 5.4*. As time evolves, NiSi agglomeration
 557 occurs, and the number of exposed Si increases. The shape of the exposed Si first follows the
 558 initial NiSi grain boundary and then forms isolated ‘holes’ (Note: these ‘holes’ are not true ones
 559 since the exposed Si is at the same level as the NiSi [18]). This is in good agreement with the
 560 *in-situ* SEM results (**Fig. 9c**).

561 Meanwhile, some NiSi grains with a small misorientation with the neighboring grains
 562 evolve very slowly and give the slow evolution region as the *region A* in **Fig. 9 (a2) or (b2)**.
 563 This is also in good agreement with the *in-situ* SEM results as *region A* in **Fig. 9 (c2)**.
 564 Subsequently, two types of isolated NiSi grains are formed. An example of isolated B-type NiSi
 565 grains is marked in **Fig. 9 (a3) or (b3)**: these grains have LAM with the substrate but HAM
 566 with the neighboring NiSi grains, and they will remain in the whole agglomeration process due
 567 to the low misorientation with the Si substrate. That is in good agreement with the *in-situ* SEM
 568 results shown in **Fig. 9 (c3-c5)**. Isolated C-type grains are marked in **Fig. 9 (a3) or (b3)**: they
 569 are formed because of large misorientation with neighboring NiSi grains, similar to isolated B-
 570 type grains, but they will disappear by diffusion due to large misorientation with the Si substrate.
 571 Finally, most of the surface-exposed Si regions connect into a single region, and only a few
 572 isolated Si holes remain. To summarize, the phase-field simulation (**Fig. 9b**) can nicely
 573 reproduce the grooving and agglomeration behaviors observed in the *in-situ* SEM results.



575 Fig. 9. Microstructure evolution of agglomeration for a 30 nm NiSi film on a monocrystal Si
1 576 substrate annealing at 600°C: (a) simulation results with orientation field, where different colors
2 577 represent different orientations of NiSi, and black the Si substrate, (b) simulation results with
3 578 phase-field, where the gray represents the NiSi phase, and black the exposed Si substrate, (c)
4 579 *in-situ* SEM results. The initial microstructure for the simulation was constructed by coupling
5 580 the experimental misorientation distribution from the work of Luo *et al.* [18] and the initial
6 581 average grain size from *in-situ* SEM results.
7 582

11 583 6. Discussion

14 584 The phase-field simulations considering the effect of misorientation reproduce well the *in-*
15 585 *situ* SEM results. In order to better understand the effect of misorientation on the materials
16 586 parameter in the simulations and reveal the agglomeration mechanism, more details will be
17 587 discussed in the following.

21 588 In order to explore the agglomeration mechanism, the orientations of NiSi grains and Si
22 589 substrate were considered in the simulations. In order to simplify the simulations, the
23 590 NiSi($\varphi=270^\circ$, $\theta=20^\circ$, $\psi=90^\circ$), which is one of the possible Euler angles for NiSi(103) axiotaxy,
24 591 was set as the baseline, while the other orientations of the NiSi grains and the Si substrate were
25 592 set compared to this baseline. Therefore, the misorientation between the NiSi grains and the Si
26 593 substrate and between the NiSi grains can be easily calculated. The interfacial energies and
27 594 mobility in each interface depend on the misorientation through Eq.(7) (the Read-Shockley
28 595 law[42]) and Eq.(8) (the sigmoidal law [43]). For misorientation close to or larger than the high-
29 596 angle grain boundary θ_{HAB} , the interfacial energy and mobility will tend to the high-angle
30 597 misorientation value σ_{HAB} and μ_{HAB} . On the contrary, these parameters will tend to zero when the
31 598 misorientation is low, as shown in Figure S3. For a NiSi grain, the different interfaces will have
32 599 different interfacial energies and mobilities, which depend on the misorientation of the grains
33 600 or the phases on both sides of the interface. In simulation B, the NiSi film was constructed by
34 601 two types of NiSi grains: the LAM NiSi($\theta=20^\circ$) and the HAM NiSi($\theta=35^\circ$). The misorientation
35 602 between NiSi grains of different types is 15° and 0° for NiSi grains of the same type. The
36 603 orientation of the Si substrate was set as ($\theta=25^\circ$), the misorientation between NiSi($\theta=20^\circ$) and
37 604 the Si substrate is 5° , and 10° between NiSi($\theta=35^\circ$) and the Si substrate. The transition angle
38 605 misorientation θ_{HAB} was set to 15° for NiSi/NiSi grain boundary and NiSi/Si interface in the
39 606 simulations B to F. According to Eq.(7) and Eq.(8), the effect of misorientation on the interface
40 607 energy/grain boundary energy and mobility can be calculated. For the grain boundary with
41 608 different types of NiSi grains (misorientation is 15°), grain boundary energy and mobility value
42 609 are $\sigma_{NiSi/NiSi}$ and $\mu_{NiSi/NiSi}$, but are approximate to 0 for the grain boundary with the same type NiSi

610 grains (misorientation is 0°). The interface energy and mobility for the NiSi/Si interface with
611 HAM (10°) are $0.94 \cdot \sigma_{\text{NiSi/Si}}$ and $0.63 \cdot \mu_{\text{NiSi/Si}}$, respectively, but are $0.70 \cdot \sigma_{\text{NiSi/Si}}$ and $0.06 \cdot \mu_{\text{NiSi/Si}}$
612 for the NiSi/Si interface with LAM (5°). Therefore, the evolution is very slow between NiSi
613 grains with the same orientation. The grooving starts at the grain boundary of NiSi grains with
614 large misorientation, and the evolution of the NiSi/Si interface with HAM is faster than that of
615 the LAM interface, as shown in **Fig. 5b**. These are the main reasons for the agglomeration.

616 Subsequently, different simulations (simulations B to E) with the different volume fractions
617 of NiSi orientations were performed using the same NiSi grain structure. In simulation B to F,
618 the same NiSi grain structure and two types of NiSi grain orientations are found: the LAM
619 NiSi($\theta=20^\circ$) and the HAM NiSi($\theta=35^\circ$), but the volume fraction of HAM NiSi($\theta=35^\circ$)
620 decreased from 77.25% to 22.65%. The simulations show that the volume fraction of HAM
621 NiSi strongly affects the kinetics of NiSi agglomeration represented by the kinetics of the
622 exposed Si substrate. The simulations show that, for a fraction of HAM grain between
623 30.67%~56.70%, the kinetics of the surface-exposed Si is in good agreement with the *in-situ*
624 SEM results. In other words, when the fraction of LAMG is 43.30%~69.33%, the kinetics of
625 the exposed Si from the simulations reproduces the *in-situ* SEM results. The fraction of LAMG
626 could be in this range (43.30%~69.33%) for a 30 nm NiSi film on Si(100) substrate at 600°C
627 studied in this work. This is in good agreement with De Keyser *et al.* [8, 9], who measure a
628 total fraction of grains with axiotaxy and epitaxy texture (considered as low-angle grains with
629 low interfacial energy) of 45% and 41% for 60 nm and 90 nm NiSi film.

630 Moreover, simulations B to E show that the increase in the volume fraction of LAMG, which
631 have low interfacial energies and mobilities, will delay the agglomeration of the NiSi film.
632 These results may provide another good way to explain the reason for the stability improvement
633 of NiSi thin film when alloying Ni with some transition metals, such as W, Ti, Ta [14], and
634 increasing the phase stability of NiSi [12]. For instance, when alloying Ni with W, increasing
635 the W concentration changes the texture: the axiotaxial components decrease, and a particular
636 epitaxial component becomes prominent [14]. Due to the lower interfacial energy for the
637 epitaxial component than the axiotaxial component, the higher the volume fraction of epitaxial
638 NiSi grains, the less likely agglomeration is. The reason for a significant improvement of the
639 morphological stability of 20 nm NiSi on Si(001) by alloying the Ni film with 40% Si[19],
640 which increased the fraction of epitaxial NiSi grains formed by texture inheritance, can also be
641 explained in a similar way.

642 Furthermore, the effect of different misorientation distributions of NiSi grains on
643 agglomeration was investigated by simulations D and F. Both simulations D and F have the

644 same NiSi grain structure and volume fraction (30.67%) for the high angle NiSi($\theta=35^\circ$) grains,
645 but the orientation of low angle NiSi grains was set to NiSi($\theta=30^\circ$) and the Si substrate was set
646 to ($\theta=20^\circ$) in simulation F. Thus, the misorientation between the different types of NiSi grains
647 is 5° in simulation F. The misorientation between NiSi($\theta=30^\circ$) and Si($\theta=20^\circ$) is 10° , 15° between
648 NiSi($\theta=35^\circ$) and Si($\theta=20^\circ$). Comparing with simulation D, it is clear that the kinetics of
649 agglomeration in simulation F is faster than that in simulation D in **Fig. 6b**, due to the higher
650 misorientation distribution between NiSi/Si interface: the interface energy and mobility for the
651 NiSi/Si interface with LAM (10°) are $0.94 \cdot \sigma_{\text{NiSi/Si}}$ and $0.63 \cdot \mu_{\text{NiSi/Si}}$, and are $\sigma_{\text{NiSi/Si}}$ and $\mu_{\text{NiSi/Si}}$ for
652 the NiSi/Si interface with HAM (15°) in simulation F. However, for the early stage of
653 simulation, representing the grooving process, the kinetics of the exposed Si in simulation F is
654 slower than that in simulation D, especially for a fraction of exposed Si lower than 3.0%, as
655 shown in **Fig. 6c**. This is due to the decrease in the misorientation between the different types
656 of NiSi grains (from 10° in simulation D to 5° in simulation F). The energy and mobility of the
657 NiSi grain boundary are reduced to $0.70 \cdot \sigma_{\text{NiSi/NiSi}}$ and $0.06 \cdot \mu_{\text{NiSi/NiSi}}$. This slows down the
658 evolution between the NiSi grains with different orientations, mainly for the grooving process
659 during the early simulation stage, as shown in **Fig. 8**. Based on the simulation results from
660 simulation B to F in the early stage, it can be clearly found that the grain boundary grooving
661 mainly depends on the misorientation distribution between the NiSi grains. Therefore, reducing
662 the misorientation between individual NiSi grains will delay the grain boundary grooving.

663 In summary, some suggestions for suppressing or slowing down the agglomeration can be
664 given from texture based on the phase-field simulations: *i*) increase the volume fraction of low
665 angle grains; *ii*) decrease the misorientation between the NiSi grain and the Si substrate; and *iii*)
666 decrease the misorientation between the NiSi grains. The latter will also strongly act on the
667 grooving process. **These changes may be achieved using alloy elements.**

668 7. Conclusions

- 669 ● The microstructure evolution and kinetics of the agglomeration for a 30 nm NiSi film on
670 Si(100) substrate at 600°C were investigated by *in-situ* SEM. During the agglomeration
671 process, most small NiSi grains gradually shrink, except that some specific NiSi grains
672 grow rapidly. The agglomeration of the NiSi grains causes an increase in the exposed Si.
673 Moreover, the evolution of texture of a 30 nm NiSi polycrystalline thin film during
674 agglomeration was investigated by EBSD with *ex-situ* samples, and the results indicated
675 that some fiber texture components remain after long-time annealing while most of the
676 random orientations disappear, which is in good agreement with the previous reports.

- 677 ● 3-D phase-field simulations were used to reveal the mechanisms of grooving and
678 agglomeration of the NiSi polycrystalline thin film on the monocrystal Si substrate. The
679 simulation results showed that the grooving starts from the NiSi grain boundary with large
680 misorientation, and the kinetics of grooving mainly depends on the misorientation
681 distribution between the NiSi grains. The difference in misorientations of the NiSi/Si and
682 NiSi/NiSi interfaces leads to differences in the interfacial energies and grain boundary
683 energies, which are the main driving forces for agglomeration of the NiSi polycrystalline
684 thin film.
- 685 ● The 3-D phase-field simulation combined with experimental information (i.e., the
686 orientation distribution and the mean grain size of NiSi grains) well reproduced the
687 complex agglomeration process in 30 nm NiSi polycrystalline films observed by *in-situ*
688 SEM. According to the quantitative phase-field simulations, in order to suppress or to slow
689 down the agglomeration, either increasing the volume fraction of low angle grains, or
690 decreasing the misorientation between the NiSi grain and the Si substrate is recommended.
- 691 ● In this paper, the coupling of the *in-situ* SEM observations and MPF simulations was
692 successful to reveal the agglomeration mechanism in the NiSi polycrystalline thin film on
693 the monocrystal Si substrate, and can thus serve as an efficient way to bring insights into
694 dewetting phenomena of the polycrystalline thin film.

695

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