The role of lattice mismatch and kinetics in texture development: $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ thin films on Si(100)

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Mixed $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ films ($0 \leq x \leq 1$) were grown by solid phase reaction of homogeneous $\text{Co}_{1-x}\text{Ni}_x$ metal films, codeposited on Si(100). The texture of these films was contemplated using complementary experimental techniques: Rutherford backscattering and channeling spectrometry, x-ray pole figure measurements, and orientation imaging with electron backscattering diffraction. Based on the increasing $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ lattice parameter with increasing Ni concentration, a gradual, continuous improvement of the epitaxial quality of the film would be expected. The observed trend is significantly different. The epitaxial quality of the disilicide film indeed improves with increasing Ni concentration, but only up to 15% Ni. Moreover, the increasing epitaxial quality is due to a large volume fraction of (110)-oriented grains, instead of the anticipated (100) orientation. The most abundant texture component is not necessarily the one with the best *in-plane* match with the substrate, i.e., epitaxy, nor the one which assures the continuity of crystallographic planes *across* the plane of the interface, i.e., axiotaxy. Clearly, geometrical arguments alone cannot account for the observed large size and high volume fraction of (110)-oriented grains. On the other hand, we demonstrate that growth kinetics plays an important role in texture development and epitaxial growth during the solid phase reaction. Above 15% Ni, the epitaxial quality rapidly decreases and a polycrystalline film is formed for 40% Ni. This decrease is explained by a gradual shift of the disilicide nucleation site from the interface with the substrate to the surface of the thin film. For high Ni concentrations, i.e., $\geq 50\%$ Ni, the (100) orientation dominates the thin-film texture, due to the growth of a NiSi_2 -rich film at the substrate interface. The changing nucleation site, due to this phase separation, and the differing growth kinetics can significantly alter the texture of ternary films. These two factors should be taken into consideration when implementing ternary alloys in devices, since their physical properties, stability, roughness, resistance, etc., depend critically on the texture of the films. © 2008 American Institute of Physics. [DOI: 10.1063/1.2888554]

I. INTRODUCTION

For decades, metal silicides have been used in the microelectronic industry.¹ CoSi_2 has long been the material of choice to contact the source, drain, and gate areas of complementary metal-oxide-semiconductor (CMOS) devices. However, for very narrow linewidths the CoSi_2 contacts suffer from an increase in sheet resistance.² At the time, it was proposed to replace CoSi_2 by the ternary $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$.³ Kittl *et al.*⁴ showed, however, that $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ exhibits the same problems as CoSi_2 for linewidths below 40 nm. NiSi shows a much better scaling behavior and is now being used in state-of-the-art CMOS devices in the form of a Ni(Pt)Si alloy.² When problems with CoSi_2 arose, the use of epitaxial silicides was brought about to improve the quality of the contacts. Although the industry has reached the consensus that epitaxial silicides as such do not present particular advantages over polycrystalline films, recent studies have pointed out that the texture (preferred crystallographic orientation) of thin films has a drastic influence on their thermal stability,⁵ roughness,⁶ Schottky barrier characteristics,⁷ and resistance.⁸ A thorough understanding of the origin of the texture devel-

opment or epitaxial quality is therefore crucial for the fabrication of optimally performing and reliable devices.

CoSi_2 and NiSi_2 are prototypes in the field of epitaxy.^{9,10} Both compounds nucleate in the cubic CaF_2 structure, which is compatible with the Si diamond structure. Moreover, CoSi_2 has a lattice parameter of 5.364 Å, which is only 1.23% smaller than that of Si (5.431 Å). NiSi_2 has a slightly larger lattice parameter (5.406 Å) and therefore a smaller mismatch at room temperature (−0.46%). Sophisticated methods, e.g., reactive deposition epitaxy (RDE),^{11,12} ion beam synthesis, etc.,¹³ have been developed to grow high-quality epitaxial CoSi_2 and NiSi_2 thin films. In this work, however, we investigate the texture of films that are formed in a solid phase reaction (SPR). Despite the equal lattice structure of CoSi_2 and NiSi_2 and the small difference in their lattice parameters (<0.05 Å), there are large differences in the epitaxial quality of the CoSi_2 and NiSi_2 thin films on Si(100). CoSi_2 thin films formed in a SPR are polycrystalline. Bulle-Lieuwma *et al.*¹⁴ and van Ommen *et al.*¹⁵ identified several competing CoSi_2 orientations on Si(100), while Özcan *et al.*¹⁶ showed that the polycrystalline character of the CoSi_2 film is related to axiotaxy.¹⁷ The growth of NiSi_2

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FIG. 1. Different ways for a thin film to match on a substrate. (a) In-plane matching or epitaxy, resulting in a 2D periodic interface. (b) Edge-to-edge matching or axiotaxy, resulting in a 1D periodic interface, leaving a rotational degree of freedom for the orientation of the grain.

on Si(100) by SPR does not suffer from multicrystallinity.¹⁸ Single orientation, NiSi₂(100) epitaxial films with a reasonable quality can be formed in a SPR.

One of the methods to promote the epitaxial growth of silicide films is the use of alloying elements.^{16,19,20} Here, we report on the texture of the mixed Co_{1-x}Ni_xSi₂ compound that is the final phase after annealing a CoNi metal alloy on silicon. This compound is a solid solution of CoSi₂ and NiSi₂ with the same CaF₂ structure as the binary silicides.²¹⁻²³ By changing the Ni content in the metal alloy, we can gradually vary the lattice parameter of the mixed Co_{1-x}Ni_xSi₂ phase.¹⁹ As such, we have a system to investigate the role of the lattice match in the growth of epitaxial thin films. This geometrical match between the thin film and the substrate is generally considered the most important factor determining the epitaxial quality.²⁴⁻²⁷ Zur and McGill²⁸ argued that the lattice mismatch for epitaxial thin films should not just be regarded as the mismatch between two bulk crystal lattices. Instead, they define a lattice match as the presence of a periodic translational symmetry of the interface that is compatible with the crystal structures on both sides of the interface. Their treatment considers an *in-plane* matching at the interface as shown in Fig. 1(a).

Detavernier *et al.*¹⁷ discovered another type of alignment between a thin film and its substrate. Apart from epitaxially oriented grains, they found grain orientations that result in a 1D periodic interface instead of a 2D periodic interface typical for epitaxy (see Fig. 1). Such a periodicity is achieved by an *edge-to-edge* match of low index planes at the interface. Often this alignment is accompanied by the continuation of crystallographic planes with similar interplanar distances *across* the plane of the interface, as shown in Fig. 1(b). The texture component is then referred to as axiotaxy,¹⁷ although this term is also used for edge-to-edge matching where the matching planes are tilted with respect to each other.^{16,20} For the *epitaxial* orientation of a grain, all three crystallographic axes are fixed to the substrate, while for *axiotaxy* there remains a rotational degree of freedom around an axis perpendicular to the matching planes [see Fig. 1(b)]. In an investi-

FIG. 2. The location of low-index poles of the Si substrate for the sample alignment used in this paper. The Si(011)-type cleaving directions are at $\phi = 0^\circ$ and 90° .

gation of the importance of the geometrical match in texture development, as conducted in this work, both approaches to matching lattices; i.e., in plane and edge-to-edge matching, have to be considered.

In this paper we investigate the texture of Co_{1-x}Ni_xSi₂ thin films on Si(100) as grown during SPR. In view of the dependence of the silicide lattice parameter on the Ni concentration in the compound, the results are used to discuss the role of the geometrical lattice match in epitaxial growth, a parameter that is generally accepted as the main parameter in determining the epitaxial quality of a thin film. In addition to the evaluation of the importance of the geometrical match, we will argue that the alloying element has little influence on the interface chemistry. The silicide growth kinetics, on the other hand, is significantly modified by the Ni content in the ternary compound, and we will highlight the importance of the growth kinetics in texture development.

II. EXPERIMENT

Thin (12 nm) Co_{1-x}Ni_x metal films ($0 \leq x \leq 1$) were codeposited in a molecular beam epitaxy system equipped with two e-guns. Prior to metal deposition, the Si substrates were cleaned *ex situ* in a 2% HF solution and *in situ* using a two-step silicon-flux method. The last step of this procedure consists of the deposition of a homoepitaxial Si buffer layer of 60 nm, resulting in an atomically clean, reconstructed Si(100)- 2×1 surface. The metal films were annealed in a two-step rapid thermal processing annealing in a high-purity N₂ ambient ($O_2 < 1$ ppm). Following a first annealing step at 540 °C for 1 min, the unreacted metal was removed by a selective etch. To complete the silicidation process and form a disilicide film, subsequent annealings were performed at 800 °C (1 min).

To study the texture of the silicide films three complementary experimental techniques were used. Rutherford

FIG. 3. The RBS minimum yield for the MSi_2 films on Si(100) as a function of the nominal Ni concentration. The dotted line in the plot is a guide to the eye. The dashed line depicts an example of the expected continuous decrease of the minimum yield with increasing Ni concentration. The backscattering angle used is 168° .

backscattering and channeling spectrometry (RBS/C) using a 1.57 MeV He^+ beam allowed us to perform a depth-sensitive investigation of the epitaxial quality of the film. Therefore, the samples are mounted on a three-axis goniometer and the backscattered He^+ particles are detected with two solid-state detectors at scattering angles of 168° and 102° , respectively.

X-ray diffraction (XRD) measurements were performed with a Bruker D8 x-ray diffractometer with a Cu source ($\lambda = 1.54056 \text{ \AA}$) and at the X20A beamline of the National Synchrotron Light Source in Brookhaven National Laboratory, where a Si monochromator was used to select a wavelength of $1.54 \text{ \AA}$. This wavelength was chosen to simplify comparison with the lab-based measurements. For the pole figure measurements we used the same synchrotron radiation. The samples were mounted on a four-circle diffractometer (Schultz geometry). A scintillation counter was used to detect the diffracted intensity. The pole figures were acquired in steps of 0.5° in ϕ and χ . Sample alignment was achieved by setting ϕ and χ equal to 45° at the location of the Si(110) substrate peak. As a consequence, the directions ($\phi=0^\circ, \chi=0^\circ$), ($\phi=0^\circ, \chi=90^\circ$), and ($\phi=90^\circ, \chi=90^\circ$) correspond to the Si(100), Si(01-1), and Si(011) poles, respectively. The locations of other low-index substrate poles for this alignment are indicated in Fig. 2. We measured both the (220) and (111) pole figures of the disilicide films, although we only show the (220) pole figures in this paper. For further information on pole figures the reader is directed to Ref. 29 or 30.

With electron backscattering diffraction (EBSD), the spatial distribution of texture components, grain size and grain orientation, and the volume fraction of texture components are directly accessible.³¹ As such, this technique provides complementary information to the XRD and RBS data. The details of the setup used and the measurements performed can be found in Ref. 32. The analysis of the EBSD data was performed using the HKL CHANNEL 5 software, combined with the Gent University software for texture analysis and visualization (GUSTAV), a computer program developed to analyze texture using the combined information of XRD and EBSD measurements.

FIG. 4. (a) $\theta-2\theta$ XRD measurement for the disilicide films on Si(100). The diffraction peaks are indexed according to the CoSi_2 phase. (b) Normalized intensity for the different diffraction peaks observed in (a), plotted as a function of the Ni concentration in the metal film. The intensity for the (220) diffraction peak has been rescaled.

III. RESULTS

A. RBS channeling (RBS/C)

RBS is a technique which is based on the backscattering of monoenergetic He^+ particles.³³ The fraction of backscattered particles, i.e., the backscattering yield, depends on the number of close encounters between the energetic projectile and the lattice atoms in the specimen under investigation. In a so-called channeling experiment, the He^+ beam is incident

FIG. 5. (220) XRD pole figures for the films containing 0%, 15%, and 40% Ni. The data are plotted in a linear grayscale. Black is high intensity, white is low intensity.

along a low index direction of the investigated crystalline material. In this geometry, the probability for a close encounter collision will drastically decrease, resulting in a lower backscattering yield. We performed RBS channeling (RBS/C) experiments with the ion beam aligned along the Si(100) direction. The ratio of the backscattering yield in channeling geometry to the yield in random geometry is defined as the RBS minimum yield, $\chi_{\min}$, which depends on the volume fraction of aligned (i.e., epitaxial) silicide grains. Hence, it is a direct, quantitative measure for the epitaxial quality of the film. $\chi_{\min}$ ranges from a few percent for an ideal epitaxial film to 100% for a polycrystalline thin film.

The RBS minimum yield for the disilicide films is plotted in Fig. 3 as a function of the nominal Ni concentration. The value of 100% for the CoSi₂ film indicates the polycrystalline character of the film. With the addition of Ni, the epitaxial quality of the silicide film clearly improves, and a value of $\chi_{\min}=56\%$ is achieved for a film containing 10% Ni. Above that concentration, however, the epitaxial quality of the silicide film is deteriorating. A minimum yield of 100% is obtained for the film containing 40% Ni. If the disilicide is formed from a Ni-rich metal film, the epitaxial quality of the film is improving again with increasing Ni concentration. For the pure NiSi₂ film a minimum yield below 10% is achieved, showing that NiSi₂ films with a good epitaxial quality can be grown by SPR.

Based on pure geometrical considerations, i.e., the improving lattice match, we would expect a continuous decrease of the minimum yield with increasing Ni concentration, as indicated by the exemplary dashed line in Fig. 3. This trend is not observed, which is a first indication of the overestimation of the role played by the geometrical match in epitaxial growth.

B. XRD scans in Bragg-Brentano geometry

A direct quantitative value for the epitaxial quality of a thin film, like the RBS minimum yield, cannot be extracted from θ - 2θ XRD measurements. On the other hand, these measurements yield valuable information on the dominating grain orientations in the silicide film. In Fig. 4(a), the θ - 2θ measurements on the different silicide films are shown. All data are acquired using synchrotron radiation, except those for the pure NiSi₂ film and the MSi₂ (where M=Co, Ni, or Co_{1-x}Ni_x throughout this paper) film containing 75% Ni, where a Cu source was used. To obtain comparable statistics for both sets of measurements, the measure-

ment time for the latter experiments is significantly longer than those for the synchrotron measurements.

For all films, we find diffraction peaks corresponding to the CaF₂ structure, showing that the annealing has resulted in the formation of a disilicide thin film. When the relative intensities of the diffraction peaks as measured from the pure CoSi₂ film are compared to that of a CoSi₂ powder,³⁴ a slightly more intense (220) diffraction peak is observed. This indicates that there is a preferred orientation for the CoSi₂ grains. Nonetheless, the relatively strong (111) and (311) diffraction peaks reveal that the pure CoSi₂ film is essentially polycrystalline. By incorporating Ni in the Co_{1-x}Ni_xSi₂ solid solution, the intensity of the (220) MSi₂ diffraction peak increases with increasing Ni concentration. This is even clearer in Fig. 4(b), where the diffracted intensity is plotted as a function of the nominal Ni concentration. The intensity of the peaks was normalized to the background counts in the spectrum to minimize the effects of sample size and alignment on the plotted values. The strong (220) diffraction peak in the XRD spectra demonstrates that there is a large volume density of grains for which the (220) planes—or equivalently the (110) planes—are parallel to the specimen surface. We will refer to these grains as *(110)-oriented grains* or *(110) grains* and adapt the same terminology for other orientations. The decreasing minimum yield for Ni concentrations up to 10%–15% Ni is thus related to the strongly increased volume fraction of (110)-oriented grains rather than the increase in the volume fraction of grains with the “natural” (100) epitaxial orientation.

Further increasing the Ni content in the film results in a decreasing fraction of (110)-oriented grains without a significant increase in the volume fraction of grains with another orientation, a result that agrees with the degrading epitaxial quality in the region 15%–40% Ni, as inferred from the RBS/C measurements. For the films with 50 and 75% Ni, (100)-oriented grains are clearly the most prominent in the disilicide film; for the pure NiSi₂ film this is the only orientation observed. In contrast to the films with 15% Ni or less, the improving epitaxial quality for the films formed from a Ni-rich metal alloy is due to a larger volume fraction of the (100)-oriented grains.

C. Pole figures

For the high Ni concentrations it is clear that the grains adapt the same orientation as the substrate, similar to the pure NiSi₂ film. It is however not that obvious how the texture develops in the low and intermediate Ni concentrations.

TABLE I. The observed axiotaxy components for a MSi_2 film on Si(100).

Component	Simulation	Axiotaxy fiber axis
α	See Ref. 16	$\text{MSi}_2(110)$ fiber axis at $\chi=45^\circ$ and $\phi=45, 135, 225$, and 315°
β	See Ref. 16	$\text{MSi}_2(110)$ fiber axis at $\chi=90^\circ$ and $\phi=0, 90, 180$, and 270°
γ	See Ref. 16	$\text{MSi}_2(110)$ fiber axis at $\chi=29^\circ$ and $\phi=0, 90, 180$, and 270°
δ	See Ref. 23	Weak $\text{MSi}_2(110)$ fiber axis at $\chi=45^\circ$ and $\phi=0, 90, 180$, and 270°
η	See Ref. 23	Weak $\text{MSi}_2(110)$ fiber axis at $\chi=90^\circ$ and $\phi=45, 135, 225$, and 315°

Therefore, we further examined the texture of these films by XRD pole figure measurements. Figure 5 shows the (220) pole figures for the films containing 0, 15, and 40% Ni. Dark areas on these pole figures are areas of high diffracted intensity and represent a large density of grains with a specific orientation. The pole figure for the pure CoSi_2 film shows symmetrical line patterns as well as dark spots.

1. Axiotaxy

As explained in Ref. 16, the symmetrical patterns are evidence for axiotaxy, an off-normal fiberlike texture that originates from the alignment of low index lattice planes across the plane of the interface between the silicide and the substrate.¹⁷ For axiotaxy-related grains, only a set of planes is aligned with respect to the substrate, and there remains a rotational degree of freedom around the axis normal to the these planes, the fiber axis [see Fig. 1(b)]. This gives rise to the symmetrical line patterns in the pole figures. Three axiotaxy components were identified for CoSi_2 on Si(100). These are labeled α , β , and γ in Table I. The details can be found in Ref. 16.

For the film containing 5% Ni, we identified two additional, though very weak, axiotaxy components that are labeled δ and η .²³ The location of the fiber axes are given in Table I and the details of the texture components can be found in Ref. 23.

2. Epitaxy

For the film with 15% Ni the axiotaxy lines can still be envisioned, only now the intensity along the lines is redistributed. In fact, the pole figure consists of a collection of elongated spots. The grains that give rise to such a spot have a well-defined orientation relationship with respect to the substrate, i.e., these are epitaxial grains. The unequal intensity distribution along the axiotaxy lines is also observed for the CoSi_2 pole figure, but it is more pronounced for the film containing 15% Ni. The same epitaxial orientations are found in all films, though with clearly different volume fractions. The observed silicide-silicon crystallographic relationships for the different components are gathered in Table II, and Fig. 6 shows the corresponding pole positions on the (220) pole figure. For the $\text{MSi}_2(15\% \text{ Ni})$ film the spots corresponding to the (110)-oriented grains are much more intense than all other spots, supplying additional evidence for the strong (110) texture of this film.

TABLE II. The observed epitaxial components for a MSi_2 film on Si(100).

Component	Crystallographic relationship
(100)	$\text{MSi}_2(110)//\text{Si}(100)$ and $\text{MSi}_2(011)//\text{Si}(011)$
(110)	$\text{MSi}_2(110)//\text{Si}(100)$ and $\text{MSi}_2(1-10)//\text{Si}(011)$
(221)	$\text{MSi}_2(221)//\text{Si}(100)$ and $\text{MSi}_2(1-10)//\text{Si}(011)$
(335)	$\text{MSi}_2(335)//\text{Si}(100)$ and $\text{MSi}_2(1-10)//\text{Si}(011)$

The comparison in Fig. 5 shows that the pure CoSi_2 film is polycrystalline with an axiotaxy-related texture, while the addition of a small amount of Ni (15% Ni) results in a transition toward a nearly epitaxial thin film with a very strong (110) texture. The pole figure for the film containing 40% Ni is virtually featureless: only the Si(110) substrate poles are observed at $\chi=45^\circ$ and $\phi=45, 135, 225$, and 315° (compare with Fig. 2). Such a flat pole figure indicates a completely random (i.e., polycrystalline) texture.

Worth mentioning here is that the improved epitaxial quality of the films (0%–15% Ni) is not accompanied by a smaller surface roughness. Atomic force microscopy (not shown) shows that Ni-containing films are in fact rougher and exhibit a significantly different morphology from that of a pure CoSi_2 film. The CoSi_2 film consists of grains of the order of 100–200 nm, while the Ni-containing (15% Ni) MSi_2 films consist of large grains ($\sim \mu\text{m}$) with a smaller grain structure (100–200 nm) superimposed on that.

D. EBSD

The position of the Si(110) poles (Fig. 2) and the $\text{MSi}_2(220)$ poles corresponding to the (100)-oriented grains (Fig. 6) overlap. This is a consequence of the similar lattice parameter of the MSi_2 and Si lattice and the geometry of XRD pole figure measurements.³⁰ The contamination of the XRD pole figure with substrate peaks hinders the estimation of the volume fraction of $\text{MSi}_2(100)$ grains in the silicide films. In general, the presence of substrate peaks, the fact

FIG. 6. The (220) pole figure for the film formed from a CoNi alloy with 15% Ni. The position of the (220) poles for the different epitaxial orientations is indicated.

FIG. 7. (Color online) EBSD image of the CoSi_2 film. The different colors of the grains indicate different texture components, which are given in the legend. The same image is shown twice; image (a) is the image obtained after the EBSD analysis and image (b) is slightly manipulated (trace bitmap colors) to highlight the grain structure.

that several XRD pole figures are needed for a complete texture analysis, defocusing and absorption effects, etc., makes quantitative texture analysis from XRD pole figures of thin films a difficult task.^{30,32}

Recently, De Keyser *et al.*³² showed that EBSD on thin silicide films provides valuable local texture information that is complementary to the integrated, high statistics texture information achieved with XRD pole figure measurements. Additionally, EBSD allows direct quantification of different texture components.³² Figures 7 and 8 show EBSD images of the pure CoSi_2 film and the film containing 15% Ni, respectively. The Ni-containing film can be regarded as a prototype of a $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film with a significantly improved epitaxial quality with respect to CoSi_2 . Following the procedure described in Ref. 32, every grain with an orientation that can be assigned to a texture component within a 5° misorientation has been given the same color. The same color convention is used in both figures. Selection of the different texture components used in the analysis is based on the XRD pole figures. The colorful pallet for the pure CoSi_2 film (Fig. 7)

shows that there are many orientations in the film with comparable volume densities. The image for the Ni-containing film (Fig. 8) is more monotonous, which shows that one orientation is dominating the texture of this film. The black areas on the map correspond to grains that have an orientation that differs by more than 5° from any of the texture components used in the analysis. These grains can therefore be regarded as grains with a random orientation. The blue (light gray) areas consist of points for which the Kikuchi patterns could not be indexed.³⁵ Usually, these points are found in the grain boundaries.

The relative frequency for each of the texture components is given in the legend of the figures. For the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ thin film, only 18% of the grains is found in an axiotaxy component, while nearly all other grains (79%) have a (110) orientation. For the pure CoSi_2 thin film, the situation is opposite. A large volume fraction of grains is found in an axiotaxy component (50%), while the orientation of only a small volume fraction (12%) deviates less than 5°

FIG. 8. (Color online) EBSD image of the film with 15% Ni. The different colors of the grains indicate different texture components. These components are given in the legend. The top left part of the figure shows the image as obtained from the EBSD measurements. The rest of the microscopy image is slightly manipulated (trace bitmap colors) to highlight the grain structure.

from one of the identified epitaxy components. Moreover, it is obvious that the (110)-oriented grains in the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film are larger ($\sim \mu\text{m}$) than other grains in this film and any of the grains in the pure CoSi_2 film (100–200 nm). Furthermore, it is striking that a large fraction of grains (38%) has a random orientation (black) in the pure CoSi_2 film, while the orientation of nearly all grains (98%) in the Ni-containing MSi_2 film can be associated with one of the identified texture components.

IV. DISCUSSION

The evolution of the MSi_2 texture with increasing Ni concentration can be divided into three regions (see Fig. 3). (i) Low Ni concentration, 0%–15% Ni. The addition of a small amount of Ni to the metal film results in a gradual transition from a polycrystalline CoSi_2 film, with an axiotaxy-related texture, to a highly textured MSi_2 film, with a large volume density of (110)-oriented grains. (ii) Intermediate Ni concentration, 15%–40% Ni. Further increasing the Ni content renders the film polycrystalline again, without any trace of axiotaxy. (iii) High Ni concentration, 50%–100% Ni. If the silicide is formed from a Ni-rich metal alloy, the volume fraction of the (100)-oriented grains is increasing with increasing Ni concentration, resulting in a gradually improving epitaxial quality of the film. In this section the results for the different concentration regions will be discussed.

A. Low Ni concentration

From the pure CoSi_2 film to a film containing 10%–15% Ni, a large improvement of the epitaxial quality of the MSi_2 film with increasing Ni concentration has been demonstrated. Especially, the volume density of the (110)-oriented grains drastically increases with increasing Ni concentration. Not only does the number of (110)-oriented grains increase, but also the size of the grains with this specific orientation is larger than grains with another orientation.

1. Geometrical lattice match

To evaluate the role of geometrical lattice match in epitaxy, we first have to define a *good match*. Several methods have been proposed to predict the configuration of optimum matching between a layer and a substrate. In the O-lattice theory of Bollmann,³⁶ the two crystals are considered as two interpenetrating mathematical translation lattices. From the lattice calculated with the best fit, the possible boundaries between the two crystals are obtained. Zur and McGill²⁸ define two lattices as matching if the interface translation symmetry is compatible with the symmetry on both sides of the interface, to within a given precision.³⁷ This precision is a measure for the quality of the lattice match. Both these theories are purely geometric and do not consider strain or misfit dislocation energies. The treatment by van der Merwe does consider strain and misfit dislocation energy.²⁶ Calculations for the different epitaxial orientations, based on this theory, are beyond the scope of this paper. Instead, we adopt the concept of *areal mismatch* as defined by Bulle-Lieuwma *et al.*,¹⁴ which contains parts of the treatments of both Zur *et al.*³⁷ and van der Merwe.²⁶

et al.,¹⁴ which contains parts of the treatments of both Zur *et al.*³⁷ and van der Merwe.²⁶

To define the areal mismatch, matching vectors in the film and substrate have to be found for the epitaxial orientation under consideration. The difference between the areas determined by these vectors is the significant value in the evaluation of the epitaxial component. In their paper, Bulle-Lieuwma *et al.*¹⁴ show how the areal mismatch is related to the coincidence site density and the strain energy. The smaller the areal mismatch, the larger the coincidence site density and the smaller the strain energy. In this sense the areal mismatch is a measure for the probability for a certain orientation to occur, with a small mismatch corresponding to a large probability. The use of the concept of areal mismatch for $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ films is especially useful because it allows a direct comparison of our research with the work by Bulle-Lieuwma *et al.*¹⁴ on CoSi_2 thin films.

To calculate the areal mismatch for the (110)-oriented grains, we use the matching vectors for this texture component. A periodic interface between the (110)-oriented CoSi_2 grains and the $\text{Si}(100)$ substrate is achieved by matching the $\text{CoSi}_2\langle 011 \rangle$ and $\text{Si}\langle 011 \rangle$ lattice vector in one direction and $5\times$ the $\text{CoSi}_2\langle 100 \rangle$ lattice vector with $7\times$ the $\text{Si}\langle 0\bar{1}1 \rangle$ lattice vector in the other direction.¹⁴ Because of the large difference in thermal expansion coefficients between the silicide and the substrate,³⁸ this areal mismatch has to be evaluated at the nucleation temperature of the silicides. This is approximately 550 °C for CoSi_2 and about 50 °C lower for the MSi_2 (15% Ni) film.³⁹ The effect of incorporating Ni in the silicide can be taken into account by Vegard's law.⁴⁰ Incorporating Ni in the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ compound results in an increase in the lattice parameter of the mixed silicide proportional to the Co-Ni ratio in the compound. The last factor we have to consider is the inhomogeneous metal distribution in the monosilicide phase when the MSi_2 phase forms from a CoNi alloy.^{21,41} As verified by Auger electron spectroscopy (AES), segregation of Ni at the interface between the silicide and the substrate takes place during the formation of the monosilicide phase [see Fig. 9(a)]. This phase precedes the MSi_2 phase in the CoNi silicide phase sequence.^{23,42} Therefore, at the interface, the Ni concentration will be higher than the nominal concentration in the CoNi alloy [see Fig. 9(b)].

Figure 10 shows the areal mismatch for (110)-oriented MSi_2 grains as a function of temperature. The figure shows that the mismatch is increasing with increasing Ni content in the silicide film. This explains why a NiSi_2 film will not grow with this orientation on a $\text{Si}(100)$ substrate, but it cannot account for the large increase in (110)-oriented grains for $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ films. Based on Fig. 10, the volume fraction of (110)-oriented grains should decrease with increasing Ni concentration. Evaluation of the in plane match between film and substrate thus appears insufficient for the prediction of the epitaxial quality of a thin film.

However, the concept of areal mismatch does not take into account the periodicity across the plane of the interface. The observation of axiotaxy shows that such a periodicity can play an important role in texture development. With the increase in disilicide lattice parameter with increasing Ni content, the mismatch between the silicide and silicon inter-

FIG. 9. (Color online) AES depth profile from a silicide film formed from a CoNi(15% Ni) metal alloy on silicon by annealing up to (a) 500 °C and (b) 750 °C at 1 °C/min in N₂. The formation of the monosilicide (a) and the disilicide (b) phase after annealing up to 500 and 750 °C, respectively, was confirmed by RBS. The silicide-silicon interface is shown in a shaded box.

planar distances decreases as shown in Fig. 11. Based on these geometrical arguments, the probability for axiotaxy would increase with increasing Ni content. When two independent types of axiotaxy are combined within the same grain, this grain will have a two-dimensional periodic inter-

FIG. 10. The areal mismatch for (110)-oriented grains on a Si(100) substrate as a function of temperature. The mismatch is calculated based on the lattice parameters and thermal expansion coefficients for Si, CoSi₂, and NiSi₂ and using Vegard's law to calculate the lattice parameter for Co_{1-x}Ni_xSi₂ at a fixed temperature.

FIG. 11. The lattice mismatch for CoSi₂, NiSi₂, and Co_{1-x}Ni_xSi₂ with respect to Si, as a function of temperature. The mismatch is calculated based on the lattice parameters and thermal expansion coefficients for Si, CoSi₂, and NiSi₂ and using Vegard's law to calculate the lattice parameter for Co_{1-x}Ni_xSi₂ at a fixed temperature.

face with the substrate, which is typical for epitaxial alignment.²⁹ The MSi₂(110) epitaxial orientation results from such a combination of two axiotaxy components, as seen from Table III, where the possible double-axiotaxy combinations are gathered. One could therefore argue that the large density of epitaxially oriented grains for Ni-containing films is a consequence of the increased probability for *double axiotaxy*. However, one may wonder why the (110) grains are much more abundant than other epitaxial orientations that are a combination of two axiotaxy components, such as (100)-oriented grains (see Table III). Hence, axiotaxy or edge-to-edge matching cannot account for the observed texture evolution either.

Although geometrical arguments are typically used to predict or explain the epitaxial quality of a film, the discussion above clearly indicates that such arguments alone are insufficient, even for the simple CoSi₂-NiSi₂ system. Predictions about the epitaxial quality of a film will be deficient without the consideration of, at least, the interface chemistry and thin film growth kinetics.

TABLE III. Overview of the geometrically allowed cases of double axiotaxy, i.e., where two planes within the same MSi₂ grain are axiotaxially aligned with the substrate. The axiotaxy components are defined in Table I. If a given combination is geometrically possible, the MSi₂ plane which is parallel to the Si(100) surface is listed. The experimentally observed epitaxial orientations are underlined. The combinations that result in a (110) epitaxial orientation are in bold.

Component	α	β	γ	δ	η
α	(122)/(100)	(122)/(100)			(100)
β	(122)/(100)	(100)	(211)/(233)	(322)/(110)	(100)
γ		(211)/(233)			
δ		(322)/(110)		(110)	
η	(100)	(100)			(122)

FIG. 12. Diagram showing the position of the preferred nucleation site as a function of the Ni concentration in the metal alloy: (a) $\leq 15\%$ Ni; (b) $15\% - 40\%$ Ni; (c) $\geq 50\%$ Ni (see the text for a full explanation).

2. Interface chemistry

Interface chemistry might significantly influence the surface energy for specific orientations. For example, it is expected that the highly directional bonding in these silicides plays a role in the texture selection.²³ On the other hand, bonding in CoSi_2 and NiSi_2 is almost identical, and differences between the $\text{CoSi}_2(100)/\text{Si}(100)$ and $\text{NiSi}_2(100)/\text{Si}(100)$ interfaces are found to be small, both experimentally and from *ab initio* calculations.^{43–46} The modification of the interface chemistry with the incorporation of Ni in the silicide will therefore be minimal and is expected not to have a drastic influence on the texture of the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film. In other words, the trend in the epitaxial quality of the films is not related to changes in the interface chemistry.

3. Kinetics

Because geometrical considerations cannot account for the observed texture evolution, and because the differences in interface chemistry for CoSi_2 , NiSi_2 , and therefore $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ are expected to be minor, it can be argued that the kinetics of the phase formation plays a dominant role in the texture development.

With respect to the growth kinetics of these films, a decrease of the MSi_2 formation temperature with increasing Ni concentration has been observed, with a (relative) minimum at around 15% Ni.^{6,47} Additionally, our study of the growth kinetics shows that Ni-containing films grow significantly slower than pure CoSi_2 ; in particular, for films with 15% Ni the growth rate is low.⁴⁷ Based on the growth kinetics, two paths can be followed to explain the observed texture development. On the one hand, a fast lateral growth of (110)-oriented grains, followed by a slow vertical growth of the film, could account for the observed trend. On the other hand, the low temperature nucleation of this specific texture component and a reasonable lateral growth rate would result in a continuous (110)-oriented film before any other texture component could nucleate. Probably a combination of both phenomena is at the origin of the strong (110) texture: the (110)-oriented grains nucleate at a lower temperature and grow faster laterally than any other texture component.

These kinetic arguments would not only explain the predominance of the (110) orientation, but would also account for the abnormally large size of the (110) grains. *In situ* texture measurements⁴⁸ will be performed to reveal differences in growth kinetics for different texture components and exploit the relative importance of the lower formation temperature and faster growth kinetics (laterally) in texture development.

B. Intermediate and high Ni concentration

The texture of the films containing more than 15% Ni is determined by the phase separation during the growth of the monosilicide.^{21,41} d'Heurle *et al.*²¹ showed that the MSi_2 phase preferentially nucleates at the interface between the NiSi-rich and CoSi-rich regions in the film. The film nucleates at this interface because the nucleation barrier is the smallest where the inhomogeneity in the metal distribution is the largest.⁴⁹ For the grains that grow from this interface, the substrate can no longer play its role as a grid on which the silicide forms. A random orientation of the grain follows.

As shown in Fig. 9, the phase separation, which creates the NiSi/CoSi interface, takes place even for low Ni concentrations. Up to 15% Ni, the metal distribution at the silicide-silicon interface is Co-rich. The largest gain in free energy during the formation of the disilicide is achieved where the Ni concentration is the highest, i.e., at the interface with the substrate, as shown in diagram (a) of Fig. 12, and nucleation will take place there. With increasing Ni concentration ($\geq 15\%$ Ni), however, the phase separation is more pronounced, the metal distribution at the interface is Ni-rich, and the NiSi/CoSi interface is located further from the silicon substrate. At least part of the film will nucleate at a position different from the interface between the substrate and the layer and have a random orientation [diagram (b) in Fig. 12]. This explains the evolution toward a random orientation of MSi_2 grains for intermediate Ni concentrations. The presence of epitaxial grains, for example for the film containing 25% Ni, is due to grains that still nucleate at, or close to, the substrate interface (dashed grains in Fig. 12). Their number decreases with increasing Ni concentration (15%

–40% Ni), due to an increase in the width of the NiSi/CoSi interface (as deduced from AES measurements, not shown).

For the film with 50% Ni, the phase separation will be nearly complete and the (sharper) NiSi/CoSi interface is located far from the substrate. The NiSi₂ phase nucleates at the substrate interface, before the grains forming from the NiSi/CoSi interface have transformed the complete monosilicide film into the disilicide phase. The grains that form from the NiSi-rich interface layer will take the orientation of a pure NiSi₂ film, which is the (100) orientation. Further increasing the Ni content to 75% Ni results in an even smaller NiSi/CoSi interface region, located still further away from the substrate [diagram (c) in Fig. 12]. More NiSi₂-like, (100)-oriented grains can therefore form, and a better epitaxial quality is found.

V. CONCLUSION

Through the combination of independent and complementary experimental techniques—RBS and channeling, XRD Bragg-Brentano and pole figure measurements, and EBSD—we could contemplate the dependence of the Co_{1-x}Ni_xSi₂ texture on the Ni concentration in the compound. The observed trend in the epitaxial quality differs significantly from what can be expected on the basis of purely geometrical arguments. By alloying a Co metal film with Ni, it is possible to gradually change the lattice parameter of the Co_{1-x}Ni_xSi₂ phase from the value for CoSi₂ to the NiSi₂ lattice parameter. One would therefore expect a gradual evolution from a polycrystalline CoSi₂ film to an epitaxial NiSi₂ film. The epitaxial quality of the film indeed improves with increasing Ni content in the disilicide, but only up to 15% Ni. Moreover, the MSi₂ film does not adopt the expected (100) orientation. We rather observe the formation of large (~μm) (110)-oriented MSi₂ grains with a volume fraction of nearly 80%. Above 15% Ni, the epitaxial quality of the MSi₂ film is degrading—for 40% Ni a completely random grain orientation is found. Further increasing the Ni content in the metal alloy to Ni-rich values results in an improvement of the epitaxial quality again. For these high Ni contents, the MSi₂ film is dominated by (100)-oriented grains, the epitaxial orientation that is also found for pure NiSi₂ films.

Although in the literature geometrical arguments have often been suggested as the main parameter determining the epitaxial quality of a thin film, our investigation shows that *geometrical considerations* only are insufficient to predict the relative abundance of the epitaxial components in a thin film grown by solid phase reaction. In particular, the *growth kinetics* will play a significant role, as evidenced by the large grain size for the (110)-oriented grains. *In situ* texture measurements will be required to disentangle the exact role of the kinetics in texture development.

The texture of Co_{1-x}Ni_xSi₂ films that are formed from Ni-rich metal alloys on Si(100) is dominated by the position of the nucleation site for the disilicide with respect to the silicon substrate. This nucleation site changes with increasing Ni concentration, due to the spatial separation of the

immiscible NiSi and CoSi phases. Such phase separation is not uncommon for ternary systems, and might also influence the texture of other ternary thin films.

It has been thoroughly argued in the literature that the texture of thin films has a drastic influence on their physical properties. Nowadays, various ternary silicides are implemented in microelectronic devices. Often the incorporation of an alloying element results in a markedly different thin-film texture. This paper shows that the texture development is not simply related to a change in lattice mismatch. On the one hand, thin-film growth kinetics can be as important in texture development as the geometrical match between the film and the substrate. On the other hand, phase separation can significantly influence the texture of ternary films. These two factors should be considered when ternary alloys are evaluated for implementation in devices since they have a distinct influence on device performance and stability.

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- ¹L. J. Chen, *JOM* **57**, 24 (2005).
- ²C. Lavoie, F. M. d'Heurle, C. Detavernier, and C. Cabral, Jr., *Microelectron. Eng.* **70**, 144 (2003).
- ³A. Lauwers, M. de Potter, O. Chamirion, R. Lindsay, C. Demeurisse, C. Vrancken, and K. Maex, *Microelectron. Eng.* **64**, 131 (2002).
- ⁴J. A. Kittl, A. Lauwers, O. Chamirion, M. Van Dal, A. Akheyar, M. De Potter, R. Lindsay, and K. Maex, *Microelectron. Eng.* **70**, 158 (2003).
- ⁵C. Lavoie, C. Detavernier, C. Cabral, Jr., F. M. d'Heurle, A. J. Kellock, J. Jordan-Sweet, and J. Harper, *Microelectron. Eng.* **83**, 2042 (2006).
- ⁶C. Lavoie, C. Cabral, Jr., F. M. d'Heurle, J. L. Jordan-Sweet, and J. Harper, *J. Electron. Mater.* **31**, 597 (2002).
- ⁷R. T. Tung, *Mater. Sci. Eng., R.* **35**, 1 (2001).
- ⁸M. Cannaeerts, O. Chamirion, K. Maex, and C. V. Haesendonck, *Nanotechnology* **13**, 149 (2002).
- ⁹H. von Känel, *Mater. Sci. Rep.* **8**, 193 (1992).
- ¹⁰R. T. Tung, *Mater. Chem. Phys.* **32**, 107 (1992).
- ¹¹C. W. Lim, J. E. Greene, and I. Petrov, *J. Appl. Phys.* **100**, 013510 (2006).
- ¹²A. Vantomme, S. Degroote, J. Dekoster, G. Langouche, and R. Pretorius, *Appl. Phys. Lett.* **74**, 3137 (1999).
- ¹³R. Pretorius, C. C. Theron, A. Vantomme, and J. W. Mayer, *CRC Crit. Rev. Solid State Mater. Sci.* **24**, 1 (1999).
- ¹⁴C. Bulle-Lieuwma, A. H. van Ommen, J. Hornstra, and C. Aussems, *J. Appl. Phys.* **71**, 2211 (1992).
- ¹⁵A. H. van Ommen, C. Bulle-Lieuwma, and C. Langereis, *J. Appl. Phys.* **64**, 2706 (1988).
- ¹⁶A. S. Özcan, K. F. Ludwig, Jr., C. Detavernier, C. Lavoie, and J. L. Jordan-Sweet, *J. Appl. Phys.* **95**, 8376 (2004).
- ¹⁷C. Detavernier, A. S. Özcan, J. Jordan-Sweet, E. A. Stach, J. Tersoff, F. M. Ross, and C. Lavoie, *Nature (London)* **426**, 641 (2003a).
- ¹⁸J. P. Sullivan, R. T. Tung, and F. Schrey, *J. Appl. Phys.* **72**, 478 (1992).
- ¹⁹D. Mangelinck, P. Gas, J. M. Gay, B. Pichaud, and O. Thomas, *J. Appl. Phys.* **84**, 2583 (1998).
- ²⁰C. Detavernier and C. Lavoie, *Appl. Phys. Lett.* **84**, 3549 (2004).
- ²¹F. M. d'Heurle, D. D. Anfigateiro, V. R. Deline, and T. G. Finstad, *Thin Solid Films* **128**, 107 (1985).
- ²²J. A. van Beek, P. Oberndorff, A. A. Kodentsov, and F. van Loo, *J. Alloys*

- [Compd.](#) **297**, 137 (2000).
- ²³D. Smeets, Ph.D. thesis, Katholieke Universiteit Leuven (2007); Available online at <http://hdl.handle.net/1979/797>
- ²⁴D. J. Dunstan, *J. Math. Sci.* **8**, 337 (1997).
- ²⁵S. C. Jain, A. H. Harker, and R. A. Cowley, *Philos. Mag. A* **75**, 1461 (1997).
- ²⁶J. H. van der Merwe, *CRC Crit. Rev. Solid State Mater. Sci.* **7**, 209 (1978).
- ²⁷R. Hull and J. C. Bean, *CRC Crit. Rev. Solid State Mater. Sci.* **17**, 507 (1992).
- ²⁸A. Zur and T. C. McGill, *J. Appl. Phys.* **55**, 378 (1984).
- ²⁹C. Detavernier, C. Lavoie, J. Jordan-Sweet, and A. S. Özcan, *Phys. Rev. B* **69**, 174106 (2004).
- ³⁰U. F. Kocks, C. N. Tomé, and H.-R. Wenk, *Texture and Anisotropy: Preferred Orientations in Polycrystals and Their Effect on Materials Properties*, XII ed. (Cambridge University Press, Cambridge, 1998).
- ³¹F. J. Humphreys, *J. Math. Sci.* **36**, 3833 (2001).
- ³²K. De Keyser, C. Detavernier, and R. L. Van Meirhaeghe, *Appl. Phys. Lett.* **90**, 121920 (2007).
- ³³W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic Press, New York, 1978).
- ³⁴1996 JCPDS, International Centre for Diffraction Data (1996).
- ³⁵*Electron Backscattering Diffraction in Materials Science*, edited by A. J. Schwartz, M. Kumar, and B. L. Adams (Springer, Berlin, 2001).
- ³⁶W. Bollmann, *Crystal Defects and Crystalline Interfaces* (Springer, New York, 1970).
- ³⁷A. Zur, T. C. McGill, and M.-A. Nicolet, *J. Appl. Phys.* **57**, 600 (1985).
- ³⁸D. Smeets, G. Vanhoyland, J. d'Haen, and A. Vantomme (unpublished).
- ³⁹C. Detavernier, R. L. Van Meirhaeghe, F. Cardon, and K. Maex, *Phys. Rev. B* **62**, 12045 (2000).
- ⁴⁰L. Vegard, *Z. Phys.* **5**, 17 (1921).
- ⁴¹T. G. Finstad, D. D. Anfiteatro, V. R. Deline, F. M. d'Heurle, P. Gas, V. L. Moruzzi, K. Schwarz, and J. Tersoff, *Thin Solid Films* **135**, 229 (1986).
- ⁴²S. S. Guo and C. J. Tsai, *J. Vac. Sci. Technol. A* **21**, 628 (2003).
- ⁴³J. Tersoff and D. R. Hamann, *Phys. Rev. B* **28**, 1168 (1983).
- ⁴⁴M. Falke, U. Falke, A. Bleloch, S. Teichert, G. Beddies, and H.-J. Hinneberg, *Appl. Phys. Lett.* **86**, 203103 (2005).
- ⁴⁵U. Falke, A. Bleloch, M. Falke, and S. Teichert, *Phys. Rev. Lett.* **92**, 116103 (2004).
- ⁴⁶B. D. Yu, Y. Miyamoto, O. Sugino, A. Sakai, T. Sasaki, and T. Ohno, *J. Vac. Sci. Technol. B* **19**, 1180 (2001).
- ⁴⁷D. Smeets, C. Detavernier, C. M. Comrie, C. C. Theron, A. Vantomme, and C. Lavoie (unpublished).
- ⁴⁸A. S. Özcan, K. F. Ludwig, Jr., C. Cabral, Jr., C. Lavoie, and J. Harper, *J. Appl. Phys.* **92**, 7210 (2002).
- ⁴⁹C. Detavernier, X. P. Qu, R. Van Meirhaeghe, B. Z. Li, and K. Maex, *J. Mater. Res.* **18**, 1668 (2003b).