Ordered structures in epitaxial nickel silicide films grown on (111) silicon substrates

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Abstract

The initial stages in the formation of epitaxial nickel silicide films resulting from the interdiffusion of nickel thin films (about 100 nm thick) into (111)-oriented silicon substrates have been studied using transmission electron microscopy. We report herein the formation of three ordered metastable epitaxial nickel silicide phases after short annealing treatments (about 10 min at 825 °C) that have been identified through selected-area electron diffraction, superlattice dark field imaging and X-ray microanalysis. It is argued that the observed metastable ordered phases are derivative structures of the CaF2 structure and that these structures serve as transition phases for the formation of the cubic NiSi2 phase.

1. Introduction

The epitaxial metal silicide NiSi2 has been studied extensively over the past 15 years, in particular, the structure of NiSi2–Si interfaces [1] and electrical properties of NiSi2 [2]. The cubic NiSi2 exhibits two orientations on Si(111) substrates: type A is epitaxial with the underlying substrate, whereas type B is twin related to the substrate through a 180° rotation around the surface normal. It has been demonstrated that the Schottky barrier height of NiSi2 on Si(111) substrates varies with the orientation of the silicide [3]. In spite of the fact that the silicide is scientifically very interesting, very little information is available on the stages of evolution of NiSi2 from the interaction between nickel and silicon. It has been generally accepted that NiSi2 forms from the reaction of a polycrystalline film of NiSi with silicon at temperatures of about 800 °C [4]. However, a metastable hexagonal phase, Ni2Si, has been shown to be a precursor for the growth of type A NiSi2 while type B forms spontaneously [5].

In the present paper, we report on the existence of a number of ordered epitaxial nickel silicide phases during annealing of Ni/Si(111) couples. Interestingly, two of the three ordered phases are based in part on the growth state structures derived from the f.c.c. structure uti-

lizing first- and second-neighbor interactions [6]. In addition, the implications on the existence of these epitaxially ordered nickel silicide structures to the formation of the equilibrium phase, NiSi2, will be addressed.

2. Experimental procedure

The Ni/Si(111) couples were prepared by sputter depositing nickel films (about 100 nm thick) onto Si(111) wafers. The couples were then annealed at 825 °C in either forming gas (90%N2–10%H2) or an ultrahigh purity argon (more than 99,999%–2%H2) mixture for 10 min and then slowly cooled to room temperature. Plan view transmission electron microscopy (TEM) specimens were prepared by first mechanically polishing and dimpling the silicon substrate followed by ion milling to perforation. Specimens were examined in a Phillips EM420 operating at 120 kV.

3. Results

Figure 1(a) is a bright field micrograph of an epitaxial nickel silicide grain formed on a Si(111) substrate after annealing for 10 min at 825 °C in a forming gas atmosphere. Figures 1(b)–1(d) are the corresponding [001]*, [110]*, [110]*,
and [111]* electron diffraction patterns taken from the above grain (* denotes a reciprocal section). The grain is delineated by straight boundaries which are oriented along the (110) directions lying in the (111) plane. From cross-sections of a similarly heat treated sample, interfaces parallel to the (111) growth plane and perpendicular to the growth plane {112} are often observed within the silicide films. These defects are commonly found in thin gold epitaxial films deposited upon {111} planes and are referred to as double positioning boundaries which delineate coherent {111} and incoherent {112} twin boundaries in the silicide film [7]. The boundaries observed in Fig. 1(a) are incoherent twin boundaries which separate epitaxial grains which are twin related.

In the [001]* diffraction pattern, intensities are observed at {100} and {110} positions which are allowed in neither the diamond cubic structure nor the CaF$_2$ structure ($a_{	ext{CaF}_2} = 0.541$ nm); these intensities are thus believed to arise from a super-lattice structure or ordered structure. In the [110]* diffraction pattern, superlattice intensities are observed at {001}, {110}, and (1/2){111} positions. In the [111]* diffraction pattern, superlattice reflections are evident at {110}, {112}, (1/6){422} and (1/3){422} positions. Of interest in the [111]* pattern is the fact that the (1/3){422} reflections are considerably brighter than the (1/6){422} reflections. Dark field images were obtained from several epitaxial nickel silicide grains which exhibited evidence of these superlattice reflections. Figures 2(a)−2(c) are dark field micrographs utilizing (1/2){111}, {110} and (1/3){422} superlattice reflections respectively. As was commonly observed in all the dark field images, the {110} and (1/2){111} superlattice reflections consistently image most of each grain, whereas the (1/3){422} reflections light up significantly smaller regions of the grains. Attempts at imaging with (1/6){422} reflections were largely unsuccessful due to the lack of intensity of these superlattice reflections.
4. Discussion

Each of the diffraction patterns contains a number of superlattice reflections all of which are found to be positioned at a fraction or multiple fractions of silicon "matrix" reflections (i.e. those reflections allowed for f.c.c. with the exception of diffracted spots in which $h + k + l = 4n + 2 = 0$ where $n = 0, 1, 2$ etc.). Thus the ordered structures have unit cells whose lattice parameters are nearly equal to that of silicon ($a_S = 0.543$ nm).

From the [001]" diffraction pattern, the superlattice reflections observed at [100] and [110] positions are reminiscent of diffracted intensities originating from several variants of the CuAu I L1$_0$-like structure. In this structure, [002] planes alternate with a particular atomic species (i.e. they are either pure nickel or pure silicon) [8-10]. We say that these superlattice reflections are "reminiscent" of reflections from a CuAu I-like structure; however, they do not appear to arise from a true tetragonal structure. A more critical look at the superlattice intensities reveals that these spots are elongated along one particular \{110\} direction (i.e. the \{110\} direction not contained in the \{111\} plane). Thus the rotational symmetry of the diffracted intensities along the [001] pole is not fourfold but twofold. This finding suggests that this structure, which is most likely based on the L1$_0$ structure, is not tetragonal and may possess symmetry elements of an orthorhombic structure.

From the [110]^* diffraction pattern, the \{110\} and \{001\} superlattice reflections can be accounted for by the presence of the L1$_0$-like structure. However, the \{1/2\}{111} reflections are not permitted in the L1$_0$-like structure; hence, a second ordered phase is evident from this diffraction pattern. These \{1/2\}{111} reflections are reminiscent of a CuPt L1$_1$-like structure with \{111\} planes alternating in a particular atomic species [11-13]. Because there are two different \{1/2\}{111} reflections evident in the pattern, this finding strongly indicates the presence of at least two of the crystallographic variants of the CuPt-
like structure. Indeed, by tilting to three (112) zone axes—[112]*, [121]*, [211]*—(1/2)[111] reflections are always present, thereby providing evidence for at least three variants of the L1₀-like structure.

In the [111]* diffraction pattern, some of the spots can be indexed to the L1₀-like structure (i.e. the {110} and {112} spots). However, the (1/6){422} intensities (which correspond to an interplanar spacing of 0.662 nm) are not allowed in either the L1₀ or L₁₁ ordered structure; thus a third ordered phase is present within these epitaxial grains. The origin of the (1/6){422} reflections can be best explained as arising from the scattering of a basal plane of an ordered hexagonal phase with the edges (a₁ and a₂) of the basal plane along two ⟨110⟩ directions which lie in the ⟨111⟩ plane. With this possible basis for the basal plane, it is observed that the prism planes are normal to the ⟨112⟩ directions which lie in the ⟨111⟩ plane and are spaced exactly 0.662 nm from the origin. (A more in-depth discussion of this ordered hexagonal phase is presented below.) This ordered hexagonal phase is also believed to contribute to the intensities of the (1/3){422} reflections (these correspond to {2200} interplanar spacings in the hexagonal structure). However, when superlattice dark field images were attempted using these brighter (1/3){422} spots, only small amounts of the hexagonal phase were evident within these grains. The primary origin of the bright (1/3){422} spots is most likely due to double diffraction from double position boundaries within the epitaxial grains. These “anomalous” (1/3){422} reflections have been found to be a common feature of thin films grown on ⟨111⟩ substrates[7].

Briefly summarizing, the diffraction patterns reveal that at least three ordered phases are present during the initial formation of an epitaxial nickel silicide film grown on Si(111). In each of the three patterns, we can assign a diffraeted intensity, referred to a silicon matrix reflection, which uniquely identifies an ordered structure: (1) {100}, {110}—CuAu I (L1₀) like; (2) (1/2){111}—CuPt(L₁₁) like; (3) (1/6){422}—ordered hexagonal structure.

Throughout the paper, the ordered structures have been described as “CuAu like” or “CuPt like” etc. The reasoning for this particular terminology is that the ordered structures are only partly based on the f.c.c. structure. Figure 3 is a schematic of the f.c.c.-based L1₀ unit cell with layering of nickel and silicon along the [001] direction (i.e. the variant with c axis layering) and which possesses the lattice constant of silicon. Note that we draw the unit cell as a cube with no tetragonal distortion and that the size of the atoms is drawn to scale in the figure. It is apparent that the lattice is much too large for bonding between nickel and silicon along the face diagonal. The length of the face diagonal is 0.768 nm and hence the nearest-neighbor bonding distance between nickel and silicon is about 0.384 nm which is much greater than the combined radii of nickel and silicon (about 0.241 nm)[14]. We must then alter the CuAu I structure by adding more atoms into the unit cell so as to make the structure become more compact, thereby “stabilizing” the structure. As the underlying substrate material is silicon, one might expect an L1₀-like structure to be based on a derivative of the silicon structure—the zinc blende structure (cubic, four tetrahedral sites filled). On the other hand, since the equilibrium structure of NiSi₂ is CaF₂, it is not unreasonable to speculate that an L₁₁-like structure may be based on the CaF₂ structure (cubic, eight tetrahedral sites filled). Thus the fundamental issue that needs to be resolved is the following: are the ordered structures based on the diamond cubic structure (silicon) or the CaF₂ structure?

From a bonding perspective, we can argue that these ordered structures should not be based on the diamond cubic structure. Diamond cubic as well as the zinc blende structures (e.g. GaAs) are typically covalently bonded structures charac-
terized by strong $sp^3$ hybridized bonds and show little evidence of metallic behavior [14]. Ordered structures that have been found in semiconducting epitaxial films such as AlGaAs [10], and Si$_2$Ge$_{1-x}$ alloys [13], and which are zinc blende or diamond cubic derivative structures, are bonded covalently by $sp^3$ bonds. On the other hand, for the case of all transition metal silicides such as the nickel silicides, these materials are metallic like, and hence bonding between nickel and silicon in these ordered structures should be inherently different from those found in the diamond cubic derivative structures. Previous investigations into the bonding properties of nickel silicides have argued that stability of NiSi$_2$ in the CaF$_2$ structure is largely promoted by strong hybridized silicon p–metal d bonding with silicon atoms perhaps exhibiting $sp^3$ hybridization [15, 16]. Bearing this in mind, it is proposed that these structures should not be, strictly speaking, diamond cubic derivative structures. We have not as of yet, however, provided any $a$ priori reason as to why these structures should be based on the CaF$_2$ structure. At this juncture, we do not fully understand the nature of the bonding in these ordered nickel silicides. Indeed, bonding of nickel and silicon appears to be considerably more complex than originally believed since a variety of structures are evident and with (most likely) different nearest- and perhaps second-nearest-neighbor environments. If, however, these structures are based on the equilibrium CaF$_2$ structure of NiSi$_2$, the same types of bonds present in the NiSi$_2$ structure most likely govern the stability of these ordered epitaxial phases. In order to verify that these structures are CaF$_2$-based structures, we have undertaken an in-depth analysis of comparing electron diffraction patterns that would be expected of ordered nickel silicide structures that can be derived from diamond cubic or zinc blende structures with those that can be created from the CaF$_2$ structure.

Martins and Zunger have calculated several "stable" ordered binary semiconductor structures, based on the zinc blende structure, by calculating the total energies (chemical and possible strain energies) through a first-principles quantum mechanical approach and minimizing the total energy with respect to the structural parameters [17]. It is interesting to note that these zinc-blende-based ordered structures can be created by ordering the two sublattices (f.c.c.) of the zinc blende unit cell. From their calculations, a CuPt-like structure with stoichiometry AB is proposed to be stable. This structure has stacking along [111] as $\{A-A-B-B-A-A-\ldots\}$. This doubling in the stacking of [111] planes doubles the zinc blende lattice parameter which describes the true lattice parameter of the ZnS-based CuPt-like structure. The ZnS-based I1$_2$-like structure consists of eight ZnS unit cells which are stacked in such a manner as to double the ZnS lattice parameter along all three axes. Figure 4(a) shows two of the eight unit cells of this particular CuPt-like structure. The complete unit cell of the CuPt-like structure consists of 64 atoms. Interestingly, a CuAu I-like structure is not found as a "stable" structure within their calculations. However, Martins and Zunger predict a Cu$_2$Au-like structure (trigonal, with eight atoms in the unit cell) with stoichiometry AB that can produce diffracted intensities which closely resemble those which originate from three variants of the CuAu I structure (Fig. 4(b)).

If we base the ordered structures on CaF$_2$, it is possible to construct a CuPt-like structure and a CuAu I-like structure again with stoichiometry AB. The CuPt-like structure based on CaF$_2$ becomes trigonal ($R_3m$) with layering along [111] as A–B–A–B–… Figure 4(c) shows two of the eight unit cells of the CaF$_2$-based CuPt-like structure. The overall CuPt-like unit cell consists of eight CaF$_2$ cells and contains 96 atoms. The CaF$_2$-based CuAu I-like structure becomes orthorhombic with mm$ar{m}$ symmetry and contains 12 atoms within the unit cell (see Fig. 4(d)). The layering of this orthorhombic structure is somewhat similar to that of the f.c.c.-based CuAu I structure, in that there exist planes of pure A and pure B along [001].

From our electron diffraction analysis, it is argued that the ordered structures are CaF$_2$ derivative structures. The key evidence in support for CaF$_2$ as the basis for the ordered phases is the presence of the $\{400\}$ reflections ($\{200\}$ reflections referred to silicon) in the CaF$_2$ derivative–CuPt structure. In the ZnS-based CuPt structure used to describe the $\{111\}$ ordering often observed in Si$_2$Ge$_{1-x}$, $\{400\}$ reflections are not allowed due to structure factor considerations [18]. However, in our ordered epitaxial nickel silicide grains which contain substantially greater amounts of the CuPt-like phase than the CuAu I-like phase, $\{400\}$ spots, e.g. present in a $\langle001\rangle$* diffraction pattern, are always observed (see Fig. 5). If we employ the CaF$_2$ structure as the basis
structure, the proposed CuPt-like structure does allow for \{400\} reflections (see Table 1).

The possible structure and stoichiometry of the ordered hexagonal phase are difficult to determine due in large part to the small quantity of the phase present within the nickel silicide grains and to the fact that only one diffraction pattern, the \{111\}*, yields the only evidence, thus far, for the hexagonal structure. We can only therefore determine a possible basal plane structure of the ordered hexagonal phase (see Fig. 6) [19]. The basal plane structure shown in Fig. 6 shows that the two axes of the plane lie along two \langle 110 \rangle directions which lie in the \{111\} plane—e.g. [110] and [101]—with \(a_1 = a_2 = 0.765\) nm. The prism planes lie normal to the \langle 112 \rangle directions which lie in the \{111\} plane. The stoichiometry of the proposed basal plane becomes 1:3. The
TABLE 1  
Calculated structure factor expressions of several reflections for ZnS-based and CaF$_2$-based CuPt-like NiSi

<table>
<thead>
<tr>
<th>Base</th>
<th>CuPt reflection</th>
<th>Reflection referred to Si</th>
<th>$F$ for m$\bar{3}$m sublattice</th>
<th>$F$ for 43m (tetrahedral sites) sublattices</th>
<th>$F^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>111</td>
<td>$\frac{1}{2}$3</td>
<td>$16(f_{\bar{3}}-f_{\bar{3}})$</td>
<td>$16[(2^{1/2}/2)[f_{\bar{3}}(i-1)+f_{\bar{3}}(1-i)]$</td>
<td>$2(2^{1/2})(16(f_{\bar{3}}-f_{\bar{3}}))^2$</td>
</tr>
<tr>
<td>ZnS</td>
<td>400</td>
<td>300</td>
<td>$16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$-16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>0</td>
</tr>
<tr>
<td>ZnS</td>
<td>800</td>
<td>300</td>
<td>$16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$[32(f_{\bar{3}}+f_{\bar{3}})]^2$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>111</td>
<td>$\frac{1}{2}$4</td>
<td>$16(f_{\bar{3}}-f_{\bar{3}})$</td>
<td>$-16(2^{1/2}/2)[f_{\bar{3}}(i-1)+f_{\bar{3}}(1-i)]$</td>
<td>$[16(1-2^{1/2})(f_{\bar{3}}-f_{\bar{3}})]^2$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>400</td>
<td>400</td>
<td>$16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$-32(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$[-16(f_{\bar{3}}+f_{\bar{3}})]^2$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>800</td>
<td>400</td>
<td>$16(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$32(f_{\bar{3}}+f_{\bar{3}})$</td>
<td>$[48(f_{\bar{3}}+f_{\bar{3}})]^2$</td>
</tr>
</tbody>
</table>

Fig. 6. Possible basal plane structure of the ordered hexagonal phase.

Stacking along the [111] direction, the c axis of the ordered hexagonal phase, is not completely understood at this time. If this particular phase is based on the CaF$_2$ structure, as we strongly suspect, the structure may actually possess rhombohedral stacking (i.e., A-B-C-A...).

It is important to emphasize that the above CaF$_2$ derivative CuAu I-like and CuPt-like structures are possible CaF$_2$-based structures that can account for the various superlattice intensities in the electron diffraction patterns in addition to the X-ray microanalysis data. In order to determine the exact structures of these ordered phases, one must first understand the structural ordering mechanisms which are possibly involved in the ordering of a CaF$_2$ unit cell.

The CaF$_2$ structure has the space group Fm$\bar{3}$m and the Pearson symbol cF12. It has Ca$^{2+}$ ions on the four face-centered Bravais lattice sites (of symmetry m$\bar{3}$m) and eight F$^-$ ions on the eight tetrahedral sites (43m) of the f.c.c. lattice which are arranged in a simple cubic lattice. The [111] planes of this structure are stacked: A$^{ba}$B$^{bc}$C$^{ca}$A... where the capital letter represents the planes that contain the m$\bar{3}$m sites and the lower case letters represent the planes passing through the tetrahedral sites. The underlined letters represent the Ca$^{2+}$ ions.

The equilibrium NiSi$_2$ phase has the CaF$_2$ structure. In order to create ordered structures based on CaF$_2$, ordering may occur on either or both of the sublattices. A CuPt-like structure, for example, may be constructed by ordering only the m$\bar{3}$m sublattice. The stacking of this structure becomes: A$^{ba}$B$^{bc}$C$^{ca}$A$^{ba}$B$^{bc}$C$^{ca}$A$^{ba}$... The underlined layer represents the nickel-enriched planes. Here the overall stoichiometry is NiSi$_5$ if the planes are pure nickel or silicon, and the space group is R3m. However, to obtain this symmetry all that is needed is that the composition of the underlined planes be different from that of those not underlined. A second CuPt-like structure can be constructed if ordering should occur on both the m$\bar{3}$m and 43m sublattices. Here the stacking would be: A$^{ba}$B$^{bc}$C$^{ca}$A$^{ba}$B$^{bc}$C$^{ca}$A$^{ba}$... This structure would also have the R3m space group and its stoichiometry is NiSi if all the planes are pure nickel or silicon. Both of these proposed structures would give rise to superlattice reflections at (1/2){111} positions; therefore it is not possible to differentiate between these two structures by selected-area diffraction patterns alone. However, our X-ray microanalysis data of similarly heat-treated cross-sectional TEM specimens reveal regions of the silicide film to consist of Ni:Si close to a 1:1 ratio. It is therefore argued that the CuPt-like structure present in our TEM foils is the latter of the two in which both sublattices are simultaneously ordered. The orthorhombic structure depicted in Fig. 4(d) is created by ordering the two sublattices of the CaF$_2$ structure. The structure resembles the CuAu I structure since the atoms on the m$\bar{3}$m sites contain pure planes of nickel and pure planes of silicon along the [001] axis.

From superlattice dark field microscopy of the epitaxial nickel silicide grains, the micrographs
consistently reveal extensive quantities of the L1₀-like and L₁₁-like ordered structures. Owing to the presence of the ordered phases, and undoubtedly to the number of variants of these ordered structures, the identification of the equilibrium NiSi₂ phase becomes greatly complicated. Indeed, there is at best sparse electron diffraction evidence for the NiSi₂ (CaF₂ structure) within these foils. Since we have evidence of “twinned” (type B) and “untwinned” (type A) NiSi₂ grains in specimens that have been annealed for much longer times (about 60 min at 825 °C), it is concluded that the formation of both types A and B NiSi₂ originates from one of these two epitaxial ordered phases. The most likely candidate is the CuPt-like structure since this structure and the CaF₂-like NiSi₂ have layering of pure nickel or pure silicon along the [111] direction. (The reader should be reminded that, like its f.c.c. L₁₁ counterpart, the CaF₂-based CuPt structure has this unique layering of pure A and pure B only along one of the four ⟨111⟩ directions.) As the (111) planes in the CaF₂-based CuPt structure are either pure nickel or pure silicon, the (111) planes in this structure may also be considered twin planes in this CuPt-like structure [20]. For the case of an L₁₁-like NiSi variant with layering along [111], displacements of successive (111) planes through a displacement vector of (a/6) (112) will effectively yield a “twinned” L₁₁-NiSi structure. It is argued that a “twinned” CuPt-like NiSi phase is the origin of the twinned variant of NiSi₂ (type B), whereas type A NiSi₂ derives its structure from a “non-twinned” variant of the CuPt-like structure.

We now comment on the apparent coexistence of the L₁₀-like and L₁₁-like NiSi phases. The two phases may be so close energetically that nucleation of the two phases appears to be simultaneous and that these phases are separate and distinct phases coexisting within the same grain. However, it has been known for about 25 years [21, 22] that the f.c.c. derivative L₁₀ and L₁₁ structures are intimately related through simple displacements of atoms. By displacing successive [111] planes of an L1₀ structure by a vector which places an atom above an unlike atom position, through either (1/2)(011) [21] or (1/6)(121) [22], the L₁₀ structure becomes the L₁₁ structure. A similar situation exists with the CaF₂-based L₁₀-like and L₁₁-like structures. From Fig. 4(d), one observes that the composition of successive [111] planes of the L₁₀ structure based on CaF₂ is exactly the same as that of the f.c.c. derivative L₁₀ structure. Displacing successive [111] planes of this L₁₀ structure would lead to the CaF₂-based L₁₁-like structure. Since there is additional evidence of epitaxial silicide grains which contain primarily the CuPt-like NiSi phase with little or no evidence of the CuAu I-like phase [23], it is concluded that the CuAu I-like phase is itself a precursor phase for the transformation of the CuPt-like NiSi phase.

5. Conclusions

In summary, we have presented TEM evidence (electron diffraction and superlattice dark field imaging) for the existence of at least three epitaxial ordered nickel silicide phases created after short annealing treatments (about 10 min at 825 °C): (1) CuAu I-like NiSi; (2) CuPt-like NiSi; (3) ordered hexagonal phase.

The structures of these ordered phases are believed to be derivative structures of CaF₂ which is the equilibrium structure of NiSi₂. The CuAu I-like and CuPt-like ordered phases appear to be the dominant phases in the epitaxial nickel silicide grains. It is argued that the ordered phases are transition phases which form during the transformation process of cubic NiSi₂. Specifically, it is proposed that the CuAu I-like phase is a transition phase of the CuPt-like phase while the CuPt-like phase is believed to be a precursor phase for NiSi₂.

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