Linear growth kinetics of nanometric silicides in Co/amorphous-Si and Co/CoSi/amorphous-Si thin films

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Evolution of the reaction zone on the nanoscale has been studied in bi- and multilayered Co/α-Si as well as in trilayered Co/CoSi/α-Si and Co/CoSi/α-Si thin film diffusion couples. The kinetics of the phase boundary movement during solid state reaction has been followed with special interest of the initial stage of the diffusion, i.e. effects happening on the nanoscale (short time, short distance). The interfacial reactions have been investigated in situ by synchrotron radiation. The formed phases were also characterized by transmission electron microscopy and resistance measurements. The effect of phase nucleation and shift of phase boundaries have been separated in order to determine the “pure” growth kinetics of the crystalline CoSi and Co₂Si product phases at the very early stages. Deviations have been found from the traditional diffusion controlled parabolic phase growth. Computer simulations based on a kinetic mean field model illustrated that the diffusion asymmetry (large difference in diffusion coefficients of the materials in contact) may offer a plausible explanations for this. © 2008 American Institute of Physics. [DOI: 10.1063/1.2957071]

I. INTRODUCTION

Interface reactions are widely used in metallurgical and microelectronic applications, and there is an increasing need to control them on the nanoscale. Because of the long standing interest in electronic applications the literature on reactive diffusion in transition metal/silicon systems on micrometer scale is well documented (see e.g. Refs. 1 and 2 for review). Cobalt silicides attract much attention because of their possible application in very large scale or in ultralarge scale technology as an interconnect material. Understanding and control of the silicide formation to obtain desirable metallization is therefore paramount.

Atomic movement through interfaces and growth of new phases are still in the focus of experts.3–4 Several papers have been published recently studying interface shift5–7 and/or interface sharpening8 in binary ideal solid solutions5 and in phase separating systems6,7 as well. These studies suggest that linear interface shift may occur due to large diffusion asymmetry (large difference in the diffusion coefficients of the materials in contact) even if there is no extra potential barrier present accounting for an interface reaction control. The earlier evidences show that such nonparabolic kinetics can occur on the nanoscale at the early stage of diffusion process, which later on, for longer diffusion distances turns back to the usual Fick type, parabolic growth law.5–7 Then it is a plausible question whether linear kinetics can similarly be observed during solid state reactions with growth of an ordered phase.

In this work we investigate phase boundary shift during the growth of crystalline CoSi intermetallic phases between Co and amorphous Si. According to literature data9,10 in this system the first appearing phase is always the monosilicide, which has the lowest formation energy.9 In order to avoid the difficulties which may originate from the nucleation of the new phase, we artificially built a thin layer of the CoSi phase among the initial constituents. Although there are indications in the literature10–12 that such a phase (amorphous or crystalline) can already be formed during the deposition at the Si/metal contacts, our main aim was to investigate samples having such a complete intermediate layer at the interface. Besides specimens produced in this trilayered geometry, bi- and multilayered specimens with usual preparation technique has also been studied for comparison. The isothermal growth kinetics of the amorphous and crystalline Co/Si was primarily studied by synchrotron x-ray diffraction (XRD). The obvious advantage of the x-ray diffraction is its directness, monitoring the evolution of all the crystalline phases. On the other hand, the possible amorphous phase(s) cannot be detected. The growth of a compound amorphous phase, however, requires material from the other crystalline constituents in the sample (pure materials and/or other phases) thus there is always indirect indication on reactions leading to amorphous product. As a complementary tool, we also used resistance measurement technique to follow the kinetics. The structure and the composition of the samples have been checked by transmission electron microscope (TEM) equipped with energy-dispersive x-ray spectrocope (EDX).

II. EXPERIMENTAL

Co, Si, as well as CoSi, films were deposited by magnetron sputtering onto (111) oriented Si wafers as well as sapphire sheets. The same structure was built on both substrates. The Si substrate used for synchrotron and TEM investigations was cut into 10 mm×10 mm squares, whereas the Al₂O₃(1012) substrate used for resistance measurements was
cut into 2 mm × 30 mm long stripes. The different substrates were cleaned and dried as usual just before placed into the preparation chamber. 10 nm of amorphous Si was sputtered onto the substrates, which was followed by 3 nm of amorphous or partly crystalline CoSi. The CoSi layer was prepared by codeposition of the Si and Co. The cover layer was 6 nm of crystalline Co. In order to produce at least partly amorphous or partly crystalline CoSi, the substrate was heated up to 423 K temperature during the deposition; in all other cases the substrates were kept at room temperature. Multilayered samples, in order to increase the amount of material to be detected, were also prepared producing ten bilayers of Co/Si, each of them having 5 nm (λ = 10 nm), or 10 nm thicknesses (λ = 20 nm). The parameters of sputtering were as follows: Ar purity: 99 999%, base vacuum: \( P_{\text{base}} = 5 \times 10^{-5} \) Pa, and sputtering Ar pressure: \( P_{\text{sput}} = 5 \times 10^{-1} \) Pa. The deposition rates were 0.14 nm/s as well as 0.24 nm/s, for Si and Co, respectively.

The XRD measurements were performed at the high flux hard x-ray BESSY MAGS beamline (7TMPW) (Ref. 13) at vacuum (\( \sim 10^{-6} \) Pa). The temperature was controlled with \( \pm 1 \) K accuracy during the heat treatments. Symmetrical scans between 25° and 36° of the scattering angle 2\( \Theta \) were performed at 12 keV.

There were two specific temperature regimes for the studied solid state reaction. In the lower regime (523 and 543 K) crystalline CoSi was formed while in the higher one (573 and 593 K) crystalline Co2Si appeared.

The structure and composition of the intermediate CoSi phase have been checked by TEM/EDX and electron diffraction by a JEOL 2000FX-II TEM at 200 keV. The CoSi film was also separately deposited onto a surface of a cleaved NaCl crystal from where it was transferred to Cu grid in order to check the microstructure and composition. Different annealing conditions were applied to delimit the temperature range, where crystalline seeds of the CoSi phase started to appear. Isothermal 4-wire resistance measurements were performed with specimens on sapphire substrate at 473, 508, and 511 K in vacuum (\( P \sim 10^{-5} \) Torr) and at 483, 493, and 503 K in oil bath. The resistance and the temperature were measured simultaneously during heat treatments. The temperature was controlled within the accuracy of \( \pm 1 \) K.

### III. RESULTS

Figure 1 displays TEM pictures of the as deposited and annealed (493 K for 30 min) multilayered samples. Thin reaction layers can be observed at the Co/a-Si interfaces already in the as-deposited sample. According to the literature, these are amorphous CoSi layers formed during the deposition. Bright-field TEM images, taken on a CoSi intermetallic layer deposited at 423 K onto NaCl, contained dark spots, indicating that the layer was partially amorphous. In Fig. 1(b) 4 nm thick crystalline layer can be seen between the remaining Co and Si, which is the developed crystalline CoSi layer. Note, that all these layers are continuous.

In situ synchrotron XRD measurements of multilayered Co/a-Si samples allowed one to follow the net intensity changes of Co (100), CoSi (210) peaks, as well as several Co2Si peaks [(112),(103),(020) and (113),(203)]. Figure 2 shows the time evolution of a typical XRD spectrum at around the Co (100) and CoSi (210) reflections. PowderCell 2.4 software package was used to fit the spectra and to separate the overlapping peaks of the Co, CoSi, and Co2Si phases. While for the CoSi phase, all the Co2Si peaks, with intensity ratios roughly equal to a random oriented powder, appeared on the spectra, for Co and CoSi only the Co (100) and CoSi (210) reflections were visible. The built-in Rietveld–Toraya type fitting has been used for this texture. The evaluation of the CoSi spectra had been performed in successive steps involving background fitting with a polynomial expression of the fifth order and peak fitting using Lorentzian forms for both Co and CoSi peaks. In case of Co2Si a somewhat different approach was adapted as it was impossible to resolve the three different peaks and the background in one step. Thus, first, the region where the main Co and CoSi peaks located was excluded from the evaluation and the rest of the spectra was fitted assuming random Co2Si orientation. The processing of the remaining part was very similar to the CoSi case. The relative error in the Co–CoSi fitting was less than 1%, while in case of the more complicated Co–CoSi–Co2Si fitting it was about 3%–5%.

The peak area for a given phase is proportional to the amount (in our case also to the thickness) of the diffracting material. Since we needed only the change of the thicknesses (\( \Delta x \approx \rho x \)) no other factor was required for the evaluation.

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**FIG. 1.** TEM images of (a) a room temperature deposited and (b) an annealed (at 493 K for 30 min) multilayered sample.

**FIG. 2.** XRD spectra measured at BESSY synchrotron source. The curves indicate increasing annealing times at 523 K. The Co (100) peak decreases, at the same time, the CoSi (210) peak appears and increases. (The symbols represent the measured data, whereas the lines display the fitted spectra.)
Plotting the change of the peak area versus time on a log-log scale, the kinetic exponent, $k_c$, could be determined.

In the lower temperature regime (523 and 543 K) the shrinkage of Co as well as the growth of the crystalline CoSi layer were determined. It is important to note that the Co peak area (the thickness) always decreased during the whole process. This is indirect evidence that the increase of the CoSi signal—at least partly—comes from the growth of the crystalline CoSi phase. The calculated kinetic exponents, as it is illustrated in Fig. 3, are different from 0.5 (diffusion control). For the growth of CoSi $k_c=0.65 \pm 0.1$, whereas for the shrinkage of Co $k_c=0.8 \pm 0.1$.

As was mentioned earlier, in the higher temperature regime (573 and 593 K) formation of the Co$_2$Si phase was observed. Thus, after the appearance of the Co$_2$Si phase the kinetics of three different processes can be measured simultaneously; the growth of the Co$_2$Si, the growth/shrinkage of the CoSi and the shrinkage of the Co (Fig. 4). In our measurements only the Co$_2$Si thickness increased and both the Co and CoSi layers shrunk. All five kinetic exponents measured were equal to 1 within the experimental error ($\pm 0.1$) ($k_c=1.1$, 0.9, and 1.0 for the shrinkage of Co, CoSi, and for the Co$_2$Si growth, respectively), i.e., pure linear kinetics has been observed in this case (Fig. 4).

As a complementary tool, we also used the 4-wire resistance measurement technique to follow the change of the thickness of the Co and CoSi layers in bi- and multilayered Co/a-Si as well as in trilayered Co/a-CoSi/a-Si and Co/CoSi/a-Si samples. Denoting by $x$ and $y$ the thickness of the CoSi phase growing in the expense of Co and a-Si, respectively, and taking into account that $\rho_{Co}=6.34 \ \mu\Omega \ cm$, $\rho_{CoSi}=142 \ \mu\Omega \ cm$, and $\rho_{aSi}=10^{11} \ \mu\Omega \ cm$, $^{15}$ ($\rho_{Co}/\rho_{CoSi}=0.02; \rho_{Co}/\rho_{aSi}=6.34 \times 10^{-11}$) one can write for the measured resistance, $R$, of parallel resistors

$$\frac{1}{R} = \frac{1}{R_0} - \frac{x}{l \rho_{Co}},$$

where $1/R_0=(d/l)(h_{Co}^0/\rho_{Co})$, $d$ and $l$ are the thickness and length of the sample, respectively. $h_{Co}^0$ denotes the initial

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**FIG. 3.** Change in the peak intensities for the growth of CoSi and shrinkage of Co at 523 (■) and at 543 K (□). (For shrinking the intensity change is negative, thus its absolute value is plotted due to the logarithmic scale.)

**FIG. 4.** Change in peak intensities for the growth of Co$_2$Si and shrinkage of CoSi at 573 (■) and at 593 K (□). (For shrinking the intensity change is negative, thus its absolute value is plotted due to the logarithmic scale.)
thickness of the Co layers. Thus, \((1/R_0 - 1/R)/(1/R_0) = x/h_{\text{Co}}\), therefore the kinetic exponent, \(k_c\), characterizing the shrinkage of the Co layer can be determined by plotting \((1/R_0 - 1/R)/(1/R_0)\) versus time. Note that Eq. (1) can also be applied even if the intermediate CoSi layer is amorphous \((P_{\text{Co-CoSi}} \gg P_{\text{CoSi}})\).

Figure 5 shows the logarithm of the normalized relative change of the reciprocal resistances versus the logarithm of the annealing time at 503 K. Drawing this figure the first part of the \(R(t)\) curve was omitted, since in this part a fast decrease in \(R\) was observed, indicating some structural relaxation of the sputtered layers and/or crystallization of the intermediate amorphous CoSi layer took place. The figure also clearly displays that, in accordance with Ref. 10, the process slows down at the very end. The middle parts, however, are parallel to each other, i.e., the slope is independent of the original layer thicknesses. The value of \(R_0\) (and the incubation time to the start of the “growth of the CoSi layer”) was determined by the criterion that the points in this middle part fall on a straight line. All kinetic exponents obtained were different from 0.5 (which would correspond to diffusion control), and fell between 0.8 and 1. There were no significant differences between the growth rates obtained for samples with and without artificially prepared intermediate layers. Neither of the kinetics was influenced by the fact whether the initial CoSi layer was fully amorphous or partly crystalline.

**IV. DISCUSSION**

In the lower temperature range (where only CoSi grows) the kinetic exponents, characterizing the growth rate of the CoSi phase and the shrinkage of the Co layer, were different from 0.5 which would correspond to a parabolic kinetics. Synchrotron measurements provided numerical values of \(k_c\) of about 0.8 for the shrinkage of the Co layer. For the growth of the crystalline CoSi phase they were 0.65 ± 0.1. Resistance kinetics provided \(k_c\) values of 0.8, . . . , 1 for the shrinkage of the Co layer, even if the applicability of the model of parallel connected thin film resistances with interface roughness in the range of 1 nm can be questionable. Nevertheless, the kinetic exponents obtained from synchrotron and resistance measurements are in good agreement, which indicates that the resistance method could provide reliable data in this case.

It is known from the literature\(^{11,12}\) that amorphous CoSi layers can be formed at the interfaces already during the deposition. Furthermore, it was also reported in Ref. 10 that up to 533 K this layer (of about 10 nm thick) remains amorphous and it does not grow under heat treatments. In contrast, we observed immediate crystallization of the \(a\)-CoSi layer (at a bit lower temperatures, which can also be attributed to the different morphology and thickness of our amorphous interlayer). Miura et al.\(^{10}\) also stated that the nucleated crystalline CoSi always stops growing at about 5 nm thickness, which is in accordance with our observations: the change in the resistance gradually diminished after sufficiently long time.

At higher temperatures both Co2Si and CoSi form and depending on the diffusion mechanism and experimental conditions, they can grow sequentially or simultaneously.\(^{16,17}\) In Ref. 10 it was concluded that “the Co2Si layer has grown to a significant thickness, while the CoSi layer appears to have remained at its original thickness.” Our observations refine the earlier picture because we observed simultaneous growth of the Co2Si layer and consumption of the Co and CoSi layers. Moreover, in all previous investigations\(^{10-12,16-21}\) the kinetic exponents for the growth of CoSi and Co2Si phases were found to be 0.5. In contrast, we observed a very definite deviation from the parabolic growth law. Our synchrotron measurements have shown that all the kinetic exponents—growth of the Co2Si, shrinkage of both the Co and CoSi layers—were equal to 1 within the experimental errors, which indicates the so called “interface reaction control.”

According to the literature, the most important factors of linear growth rate are the nucleation,\(^{22}\) the formation of nonequilibrium interfaces (e.g., with nonequilibrium interface concentrations)\(^{23}\) and the transformation of the crystalline structure.\(^{22,23}\) However, for example in Ref. 23 the authors excluded the first two possibilities and the only one which remained is the sluggish transformation of the crystalline structure. On the other hand, in Ref. 22 the author expressed the opinion that this alone should make a small effect. In order to clear up the role of the nucleation in solid state reaction kinetics, we also attempted to separate the nucleation and “pure” growth processes by depositing an intermediate CoSi layer between Co and amorphous Si. We found that the obtained kinetic exponents were practically the same, indicating that nucleation effects really could not have serious influence (at least in our case). Therefore, our results reflect the kinetics of the corresponding interface shifts.

Very recently nonparabolic growth rates were obtained, by sophisticated techniques and by careful analysis of experimental data on the very early stages of reactions, on the nanoscale even in systems (formation of Ni3Si between in crystalline Ni/Si couple\(^{24}\)) in which diffusion control was observed before. In Ref. 24, however, only a formal treat-
ment of the linear-parabolic law was performed and no physical reasons for the “interface reaction” or “nucleation” control were given. Moreover, as was mentioned in Sec. I, nonparabolic (even linear) kinetics can be observed if there is a large diffusion asymmetry present in the diffusion couple, without needing any other factors or extra potential barrier at the interface. Therefore, the large diffusion asymmetry between the two phases separated by the interface may explain nonparabolic kinetics alone. Furthermore, this linear kinetics is a typical noneffect: it is observable because of the finite permeability of the interface at the very beginning of the process, when the concentration gradient and thus the diffusion flux are very large. After a certain time/interfacenesshift, the kinetics returns to the usual parabolic one. Thus, similarly to the formal “unified” linear-parabolic growth expression used also in Ref. 24, this offers a plausible interpretation for the values of kinetic exponents falling between 0.5 and 1.

In order to prove that asymmetric diffusion can indeed lead to anomalous interface shift kinetics during ordered phase growth, we carried out computer simulations based on a kinetic mean field model (Fig. 6). Starting from a structure having about a 10 atomic layer thick ordered phase, we applied one, two, three, and four orders of magnitude differences in our calculations; this is quite common in nature, even larger asymmetry is realistic. We obtained that the interface between the AB ordered phase and matrix B shifted in an anomalous way. The shift was proportional to $t^{\nu}$ with $k_{c} > 0.5$. Typical values of $k_{c}$ were 0.7–1 at the beginning of the shift. During the shift the kinetic exponent $(k_{c})$ decreased continuously, however, its value was well above 0.5 for a long range of shift (hundreds of atomic planes). In contrast, the interface between A and the AB ordered phase shifts proportionally to $t^{1/2}$ regardless of the ordering and asymmetry parameters used. These simulation results prove that the experimentally obtained anomalous interface shift can be explained by diffusion asymmetry. Obviously the nucleation and growth of an AB ordered phase can be rather complex in an A/B diffusion couple and it is beyond the scope of this paper. Detailed investigations are in progress and the results will be published separately.

We must note here that there could be cases when the classical interpretation by interface reaction control can be rather plausible: for instance in oxidation reactions the extra activation barrier for oxidation gives a good explanation for the linear kinetics. Finally, we note that our calculations prove not only that diffusion asymmetry may lead to non-Fickian kinetics in growth process of ordered phases but also suggest that the effective diffusion is faster in the polycrystalline Co than in the amorphous Si, since, in the experiments we measured $k_{c} > 0.5$ for the Co/CoSi interface. This indication may contribute to the still unanswered questions in the literature, namely in which matrices and phases the effective diffusion (in thin film geometries and crystalline layers typically the grain boundary diffusion dominates) is faster in the Co–Si system (see e.g. Refs. 1, 2, and 27).

V. CONCLUSIONS

The effects of phase nucleation and shift of phase boundaries have been separated in our measurements in order to determine the pure growth kinetics of the crystalline CoSi and Co$_2$Si product phases at the very early stages of the solid state reaction. In contrast to earlier studies, typically carried out in the micrometer range, we observed a very definite deviation from the parabolic growth law. Our results for the kinetic exponent, $k_{c}$, were rather close to unity indicating the so called interface reaction control. Since it is difficult to find reasonable arguments why interface reaction control should operate in silicide formation reactions we suggest, based on our simulations as well, that diffusion asymmetry alone can offer quite a general and plausible explanation for a set of solid state reactions with nonparabolic growth kinetics.

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