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PART I

Silicide Formation and Properties

COMPETING INITIAL REACTIONS AT TRANSITION-METAL/SILICON INTERFACES

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ABSTRACT

The process of silicide formation by contact reaction at metal/Si interfaces normally involves rather uniform motion of the growth fronts which separate metal, silicide, and Si regions, as has been observed for silicide growth in many transition-metal/Si systems. At lower temperatures, however, the reaction behavior can be complicated significantly by the presence of other material reactions which may compete with interfacial silicide formation. For refractory metals, strong interfacial mixing over considerable depth (~ 100 Å or more) is observed at temperatures too low for the normal interfacial silicide formation process to contribute; the highly nonuniform character of this reaction, as shown by ion scattering and TEM studies, suggests that other material reactions (e.g., grain boundary diffusion) must dominate the interfacial chemistry at low temperature. In a similar way, anomalous and nonuniform reaction behavior during the low temperature deposition of initial transition metal layers on Si apparently involves surface diffusion processes which are faster than interfacial silicide formation.

INTRODUCTION

Interfacial silicide compound formation is a well documented process that dominates the reactive chemistry of many transition and refractory metal/Si interfaces. [1] A simple picture of interfacial silicide formation has emerged as the result of systematic studies of Si-metal couples performed both on thicker metal films on Si (~ 1000 Å) under non-UHV (i.e. not atomically clean) conditions and on very thin films (≤ 100 Å) prepared under UHV conditions and characterized with a wide variety of surface analytical tools. Interfacial silicide growth is normally activated by annealing of the metal/Si contact, with temperatures required for silicide growth being relatively low (≤ 400°C) for near-noble transition metals and considerably higher (≥ 500°C) for refractory transition metals. Growth of silicide compounds to thicknesses of hundreds or thousands of Å involves consumption of both metal and Si species by a growing silicide interlayer, such that the moving silicide/Si interface remains relatively uniform and approximately planar.

However, prominent aspects of transition-metal/Si interfacial reactivity have been found to deviate considerably [2,3] from the simple picture of interfacial silicide compound formation, particularly at relatively low reaction temperatures. [4,5] In these situations, other competing material reaction paths dominate kinetically over the process of simple interfacial silicide compound formation. These material reactions *other than interfacial silicide formation* have been observed in two situations. First, such material reaction at low temperature dominates the behavior of a variety of buried metal/Si interfaces, particularly for refractory metals (e.g., Ti/Si [2,3,6] and V/Si [7]). Second, important material reaction is observed during low temperature deposition of transition metals on Si (e.g., Ni/Si [8], Ti/Si [9], Pt/Si [10], and Cr/Si [11]). These material reactions likely involve grain boundary and surface diffusion processes respectively, which lead to reaction along a complex network of boundaries and surfaces.

In this paper we review the different regimes of chemical reaction at transition-metal/Si interfaces, with emphasis on the reaction behavior at low temperatures where other competing material reaction paths often dominate over interfacial silicide compound formation. These aspects are particularly important in that the low temperature reactions are initiated first in any annealing treatment.

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INTERFACIAL SILICIDE GROWTH

The stages of interfacial silicide growth, resulting in formation of silicide compounds by contact reaction, are depicted schematically in Fig. 1. First, unreacted metal is deposited on the Si surface, as shown in Fig. 1a. With sufficient thermal energy, typically generated by annealing processes, a thin interlayer of silicide compound is produced, as seen in Fig. 1b. This initial interlayer then grows thicker as metal and/or Si is consumed (Fig. 1c). Finally, one of the reactant species (the metal for most silicide applications of interest) is fully consumed and the reaction is complete (Fig. 1d).

The process of silicide growth, as represented by Figs. 1a, 1c, and 1d, has been extensively studied by thin film deposition and analysis techniques [1], including especially x-ray diffraction, transmission electron microscopy (flat-on mode), and Rutherford backscattering spectroscopy. Since these methods usually involve limited depth sensitivity (~ 100 Å), the initial stage of the reaction (Fig. 1b) was not observed until more sensitive techniques were available. In recent years surface science techniques (XPS, UPS, AES, ion scattering) [12,5,13,14, 15,16,11,17,18,19,20,8, 9,21] as well as cross-sectional TEM [22,23,24,25] have contributed considerably more to the understanding of the initial stage of silicide formation. Furthermore, some of these surface analysis techniques have proven valuable in observing the sharp transition in surface composition which accompanies the completion of the reaction as a fairly uniform metal/silicide interface reaches the surface of the overlayer, as indicated by the transition from Fig. 1c to 1d.

INITIAL STAGE OF SILICIDE GROWTH

The most extensively studied transition-metal/Si system is that of Pd/Si [12], which turns out also to be the simplest. Usual silicide compound growth for this system requires ~ 200°C annealing for forming hundreds of Å of Pd_2Si reaction product at the interface. However, surface science techniques (UPS, AES, XPS, ion scattering, SEXAFS, etc.) and TEM techniques have shown that at room temperature (or even below) the composition, chemical bonding, and atomic structure of the first and/or first few monolayers of Pd on Si is essentially identical to that in Pd silicide. For the purposes of the present discussion, the crucial points of the Pd/Si behavior are: (1) that room temperature deposition produces uniform growth, leading to complete coverage of the surface within a few monolayers; and (2) that at room temperature (low cf. usual Pd_2Si growth temperatures) the initial reaction proceeds only to ~ 10-15Å thickness

This modest extent (in depth) of low temperature, initial interface reaction is fully understandable in the scheme of Fig. 1, in that such thicknesses of reacted material are necessary to define a silicide interlayer. At larger thicknesses of silicide, it is reasonably clear that two interface steps and a mass transport step are required for one or both atomic species to yield further silicide growth. At smaller silicide interlayer thicknesses, the chemical/physical distinction between these three steps would be lost, so that the system would be undergoing a microscopically different single reaction step at the interface between unreacted metal and the Si substrate.

LOW TEMPERATURE MATERIAL REACTION AT THE BURIED INTERFACE

In contrast to the pattern of interfacial silicide compound formation depicted in Fig. 1, several studies of refractory metal/Si interfaces (e.g., Ti/Si [6] and V/Si [7]) have shown extensive atomic mixing (~ 100 Å or more from the initial interface) at temperatures (~ 250-300°C) well below usual silicide growth temperatures (500-650°C). Surface analysis revealed that these low temperature reactions are extensive not only in depth but in composition, attaining ~ TiSi and VSi composition. Finally, TEM showed that the low temperature reaction leads to microcrystalline, if not amorphous,

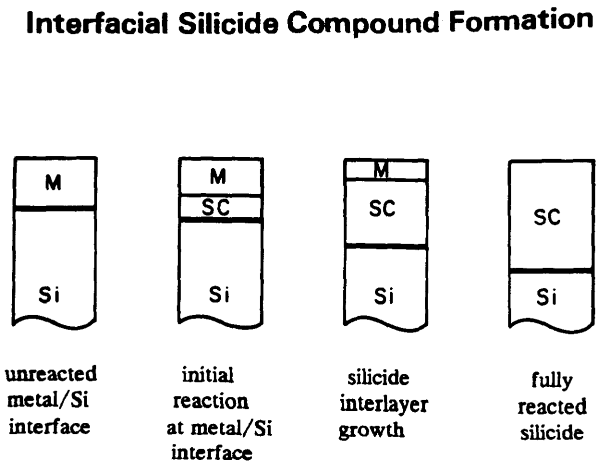

Fig. 1 The normal stages of simple interfacial silicide compound formation. Starting with the unreacted metal/Si interface in (a), an initial interfacial silicide layer a few unit cells thick (~ 3-10Å) is formed at the metal/Si interface. With further progress of the reaction (usually involving thermal processing to several hundred °C), further silicide is grown (c) until the reaction is completed and all the deposited metal overlayer is fully reacted (d).

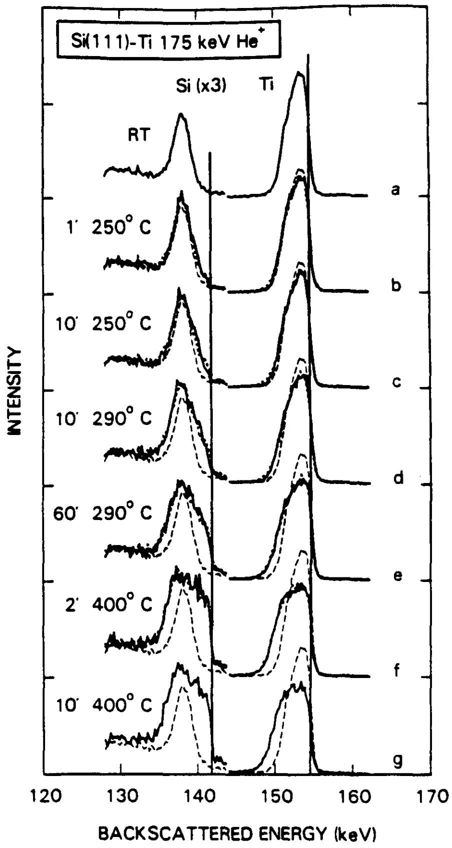

Fig. 2 Ti and Si ion scattering depth profiles (175 keV He$^+$ ions) for a 30 Å Ti overlayer on atomically clean Si(111), as-deposited and after annealing at temperatures and times noted. Vertical lines show the positions of Si and Ti surface peaks. The initial as-deposited (25°C) spectra are reproduced in each case as dashed curves for reference. The spectra were recorded at a scattering angle of 74.5°. Results of the fitting procedure (see Figs. 2 and 3) are represented by the dotted curves.

microstructure of the reacted layer, in contrast to much large silicide grains (~ 1000Å size) from normal silicide growth at higher temperatures, and the microcrystalline character - once formed - persisted to very high temperatures (approaching 800°C).

These observations suggest that the low temperature reaction in such systems may differ qualitatively from the normal pattern of interfacial silicide compound formation. [4,5,12] However, distinguishing truly different reaction paths appears to require more in-depth information as well as surface probes.

Such fundamental in-depth information about the low temperature reaction has recently been provided for the case of Ti/Si using high resolution ion scattering spectroscopy. [2,3] Figure 2 shows energy spectra (essentially high resolution depth profiles) for ions scattered from a Si(111) surface on which ~ 25 Å of Ti had been deposited at room temperature. The spectrum just below 154 keV (surface Ti position) is that of Ti concentration versus depth (to the left), while that for Si lies just below the Si surface position at 142 keV. Thus the spectra provide Ti and Si concentration versus depth (to the left), with ~ 5 Å depth resolution; the width of the Ti peak, corresponding to 25 Å Ti thickness, gives an indication of the depth scale and resolution. The Si signal is shifted down in energy from the position of the Si surface peak, because the Si substrate is covered by the Ti overlayer and Si is not present at the surface. The other spectra in Fig. 1 were recorded after annealing at the conditions indicated for each spectrum. All spectra were recorded at room temperature. Spectrum (a) is shown as a dashed line in spectra (b) - (g) so that changes can be seen more easily.

Two things are immediately obvious from these spectra. First, the leading edge of the Si peak moves to higher energy upon annealing, indicating the migration of Si to the surface. In fact, Si is observed at the surface already after the first annealing step at 250°C. Second, the area under the Si peak increases upon annealing, signifying displacement of Si atoms from ordered substrate lattice positions into the overlayer as a result of some interfacial reaction. A brief annealing at 400°C appears to saturate the changes in composition profile, as indicated by the similarity of the 2 and 10 min. spectra for 400°C.

The spectra have been successfully reconstructed by linear combinations of the initial (a) and final (g) spectra, as shown by the dotted lines in Fig. 2. The high quality of this fitting procedure demonstrates that the reaction of the overlayer has been **highly nonuniform in the lateral direction**: at each annealing step a fraction of the surface is unreacted, while a complementary fraction is fully reacted. Recognizing the saturation phase as (g) and evaluating its composition quantitatively (as TiSi), it is possible to estimate the average overlayer composition for the annealing treatments of Fig. 2. This analysis concludes that in all stages of reaction (Fig. 2) the overlayer consists of two phases, the 400°C fully reacted phase in Fig. 2a and the unreacted phase in Fig. 2g.

Another measure of this inhomogeneity is how rapidly Si reaches the surface of the film: after only 1 min. of annealing at 250°C, (1) Si is present at the surface (finite intensity increase at Si surface peak position in Fig. 1b), and (2) 18% of the surface has been reacted over the complete thickness of the overlayer film (see Fig. 2).

Such strong inhomogeneity is **incompatible** [2] with the simple picture [1] of interfacial silicide compound formation. As shown in Fig. 3a and 3b, interfacial silicide formation which is uniform (a) or even rather nonuniform (b) in the lateral direction should not lead to such rapid enrichment of the overlayer surface by Si as compared to the average composition of the overlayer film.

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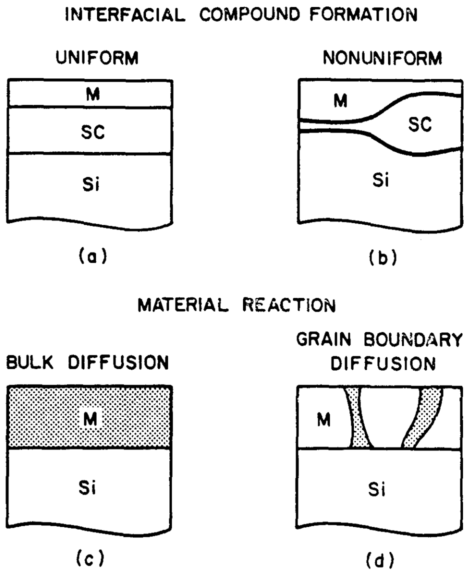

Fig. 3 Schematic description of interfacial compound formation and material reaction at the buried interface. For uniform compound formation (a), the silicide/Si and metal/silicide interfaces move through the unreacted metal and/or Si substrate while maintaining rather abrupt interface profiles. In spite of lateral nonuniformity (b), similar behavior would still be expected locally. In contrast, other types of material reaction like bulk diffusion (c) or grain boundary diffusion (d) would produce graded interface profiles and the appearance of Si at the surface early in the course of the reaction.

Strong additional evidence for a qualitative and quantitative difference between the low temperature buried interface reaction and the usual process of interfacial silicide compound formation arises from comparison of the kinetics of these processes. Thin film studies have yielded kinetics information on interfacial silicide compound formation [1], including typical activation energies for the reaction. As shown in Fig. 4 for reasonable values of activation energies, reaction rates drop by at least 10^4X between 600°C and 250°C. The rate of extensive (i.e., $>$ 20 Å in depth) reaction observed here is much too fast to be consistent with the higher temperature reaction process. For example, formation of $TiSi_2$ proceeds at a rate of ~ 10^3 Å/hr. (~ 10 Å/min.) at 600°C, suggesting $\leq 10^{-3}$ Å/min. at 250°C. Yet we observe significant reaction over a thickness of 30 Å in just 1 min., i.e. **reaction $>$ 10^4X faster than expected** from typical kinetics for interfacial silicide compound formation. This is a clear indication that the reaction which dominates at low temperature must be qualitatively as well as quantitatively different from the simple interfacial silicide reaction known to dominate at higher temperatures.

These results for the low temperature Ti/Si buried interface reaction demonstrate clearly that some material reaction other than normal silicide formation must dominate at temperatures well below the usual silicide growth temperature. Cross-sectional TEM studies have shown that the low temperature reacted films have extremely small grain size (microcrystalline or even amorphous). [7,6] Therefore grain boundaries might be expected to play an important role in the low temperature reaction, supplying a significant number of atom transport paths into the Ti overlayer with relatively low activation energies.

Therefore it seems reasonable to speculate [2,3] that the low temperature reaction which dominates over the range 200-400°C might involve grain boundary diffusion of Si inhomogeneously into the Ti overlayer, followed by silicide formation at the grain surfaces, as indicated in Fig. 3d. Grain boundary diffusion appears more plausible than a bulk diffusion process (Fig. 3c) due to the lower temperatures normally required to promote it. If grain boundary diffusion of Si into the Ti overlayer predominates and a composition ~ TiSi is attained, it appears that short-range silicides have been formed at a complex network of interfaces - namely in the grain boundaries. With microcrystalline silicide material having been formed in this way, it may not be surprising that very high temperatures are required to grow much larger silicide grains [6], since the activation energy for silicide grain growth is likely unrelated to that for silicide formation itself.

LOW TEMPERATURE MATERIAL REACTION DURING DEPOSITION

If other material reactions such as grain boundary diffusion can dominate the low temperature reactivity of buried transition-metal/Si interfaces, it would not be surprising if additional material reaction channels such as surface diffusion were open to dominate during the deposition of metal on the Si surface. Evidence for an important role of surface diffusion has been provided in studies of the room temperature deposition of Ni [8], Ti [9], and Pt [10], and Cr [11].

High resolution ion scattering studies of the Ni/Si [8] and Ti/Si [9] interfaces upon room temperature deposition of metal provide high surface-sensitivity which demonstrates that excess Si segregates on top of 3-dimensional islands of reacted material (Ni_2Si and TiSi). A schematic representation of this morphology is given in Fig. 5a for the case of Ni/Si. The Si surface diffusion changes the overall composition distribution of the overlayer in the initial stages of deposition. However, once the islands of reacted material coalesce and completely cover the surface, the channels for Si surface diffusion are blocked and both the Si surface segregation and the formation of reacted material stop. At this point it is not clear whether the Si which undergoes surface diffusion aids somehow in reacted the deposited metal.

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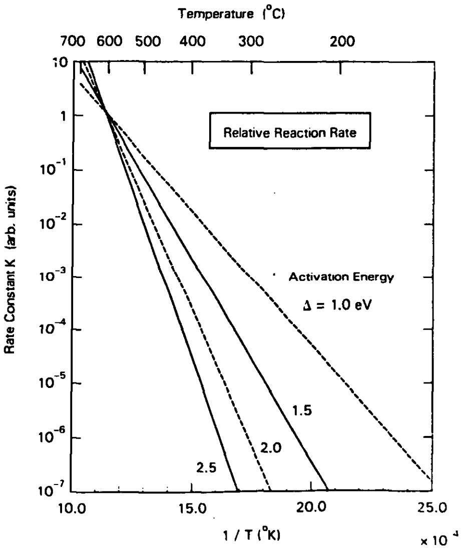
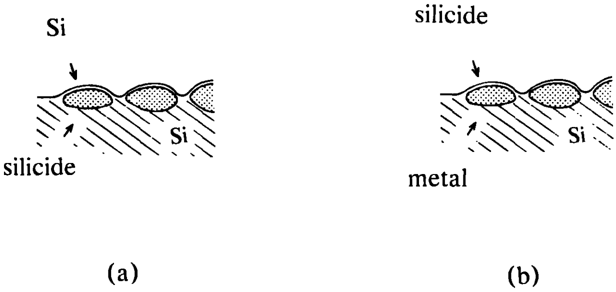


Fig. 4 Relative reaction rates at different temperatures (normalized to 1.0 at 600°C) for several activation energies of a kinetic process such as interfacial silicide formation.



(a)

(b)

Fig. 5 Schematic description of the results of surface diffusion and material reaction during low temperature deposition. In case (a), surface diffusion of Si has occurred at a rate at least comparable with the deposition rate, so that a Si layer covers the reacted silicide islands. In case (b), surface diffusion of Si has led to reaction of the Si with the surface of the metal islands, forming a silicide layer over unreacted metal islands. In both cases, competion of the island layer closes the paths for Si surface diffusion and stops the process. (From Ref. 8).